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TETRAAZAMACROCYCLIC LIGANDS AND THEIR COPPER COMPLEXES

BY P. M. JUDD

A thesis submitted to the C.N.A.A. in partial fulfillment of
the requirements for the degree of Doctor of Philosophy
by P. M. Judd

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The work described in this thesis was carried out in the
Department of Chemistry, The Polytechnic of North London,
and with collaboration from I.C.I. (Ltd) (Pharmaceuticals).

Preface

While registered as a candidate for this degree for which submission is made, the author has not been a registered candidate for another award of the CNAA or of a University during the research programme. The results and conclusions represent original work by the author unless special reference is made.

In partial fulfillment of requirements of the degree the author completed courses in a) Electronic properties of transition metal complexes; b) Separation methods; c) Advanced structural methods.

TETRAAZAMACROCYCLIC LIGANDS AND THEIR COPPER COMPLEXES by

PATRICIA M. JUDD.

Abstract

The preparation and characterisation of several new types of tetraazamacrocycles and their copper(II) complexes are described. Condensations of 4,8-diaza-2,3:9,10-dibenzoundecane-1,11-dione with a range of aliphatic and aromatic diamines has allowed the isolation of metal-free diimine macrocycles without recourse to 'metal template' or 'high dilution' techniques. In several cases these diimines were successfully reduced to yield the related tetraamine macrocycles.

For the 15-membered macrocycle, 18,19,20,21-tetrahydro-17-*H*-tribenzo(*f*,*j*,*n*)(1,5,9,12)tetraazacyclopentadecine, derivatives bearing different substituents in one of the benzene rings were prepared. For the diimine ligands of this type both cationic and neutral copper(II) complexes were isolated and characterised; (the latter type result from loss of anilino protons on complex formation.)

Compounds which are structurally related to the above tetraazamacrocycles are described. C-alkylation of the diimines using organolithium reagents appears to proceed regioselectively. An X-ray structure determination of the copper complex of 5,12-dimethyl-5,6,11,12,18,19,20,21-octahydro-17-*H*-tribenzo(*f*,*j*,*n*)(1,5,9,12)tetraazacyclopentadecine shows this to be *meso*-dimethyl isomer. Condensation of 2,2'-(oxalyldiimino)bisbenzophenone with diamines in the presence of copper(II) acetate yields macrocyclic neutral copper(II) complexes which contain a dioxo linkage between the anilino nitrogen atoms. An X-ray structure determination of [5,12-diphenyl-18,19-dioxo-9,10,17,18,19,20-hexahydrodibenzo(*e*,*m*)(1,4,8,11)tetraazacyclotetradecinato(2-)]-dimethylformamidocopper II dihydrate indicates steric crowding for the phenyl substituents on the imine carbon atoms. Polycyclic tetraza compounds result from the condensation of the cyclic tetraamines with glyoxal.

A group of 20,21 and 22-membered sexadentate ligands having N_4O_2 donor sets, and 20-membered ligands with N_4S_2 and N_6 donor sets have also been studied; e.g.: 12,13,25,26,27,28-Hexahydrotetrabenzo(*e*,*i*,*o*,*s*)(11,14,1,4,8,17)dithiatetraazacycloeicosine. Reduction of the azomethine linkages was achieved for all these ligands and cationic copper(II) complexes have been prepared and characterised. An X-ray structure determination showed that one of the N_4O_2 tetraamine ligands uses only three of its nitrogen atoms in forming a complex with copper(II).

Acknowledgements

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Finally, I wish to express gratitude to the Science Research Council for the Studentship.

General experimental techniques

The infra-red spectra were recorded on a Pye Unicam SP 2000 spectrometer, in the region 4000-626 cm^{-1}. Nujol and hexachlorobutadiene mulls were made of compounds and were supported between KBr discs, or incorporated as a powder into a KBr disc. The spectra were calibrated against the 1603 cm^{-1} band of polystyrene. Mass spectra were obtained from MS9 and MS4 spectrometers, and at PCMU, Harwell.

Field desorption mass spectra were obtained on a Kratos MS50 spectrometer operated at 8-kV accelerating voltage with a potential difference of 10-kV between the emitter and extractor plate.

^{1}H nmr spectra were recorded on a Perkin Elmer R12B and a Brücker WP80 and at P.C.M.U., Harwell. ^{13}C spectra were recorded on a Brücker WP80 and at P.C.M.U.

U.v/visible spectra were recorded using a Pye Unicam SP 1800 spectrometer.

X-ray crystallographic data were collected on a Phillips PW 1100 diffractometer with Mo-K_{α} radiation.

Contents

Published work to date included at the back of the thesis.

Abbreviations

Å	Angstrom 10^{-10} metres
^{13}C nmr	^{13}C nuclear magnetic resonance
cm	centimetre
DMF	dimethylformamide
DMSO	dimethylsulphoxide
EtOH	ethanol
Fc	observed structure factor
Fdms	field desorption mass spectrometry
Fo	calculated structure factor
g	grams
'H nmr	proton nuclear magnetic resonance
M	moles
Me	methyl
MeOH	methanol
mmol	millimoles
nm	nanometres 10^{-9}metres
o-	ortho
OAc	acetate
p-	para
Ph	phenyl
R	residual index
Rw	weighted residual index
THF	tetrahydrofuran

Infra-red abbreviations

b	broad
s	strong
sh	shoulder
w	weak

'H nmr abbreviations

b	broad
b.s	broad singlet
c	complex
d	doublet
m	multiplet
t	triplet
quad	quadruplet
quin	quintuplet
sext	sextuplet

List of diagrams on facing pages.

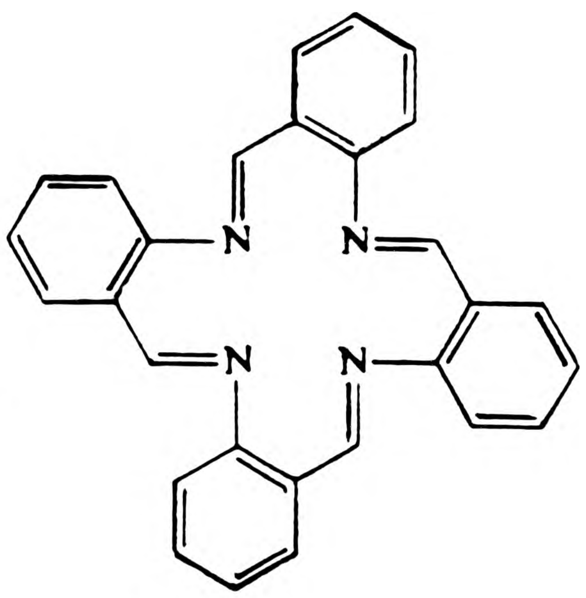
Chapter 1 Introduction

1. Introduction

1.1 General background

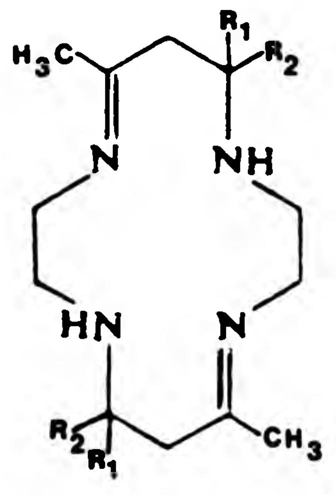
The first work on tetraaza macrocycles was begun before the Second World War[1] when research began on the synthesis and structure of the phthalocyanines. This work was continued in the immediate post-war period, and the first tetraazamacrocycle - tetraazaporphin (sic) - was obtained by the removal of the metal from the magnesium complex[2]. It is interesting to note that at the time methods of characterisation of these compounds were limited to degradative procedures and chromatography.

Subsequent work on macrocyclic complexes was carried out under the impetus of the search for relatively simple 'biological models' for metalloproteins containing an N_4 donor set, and the investigation into the special properties of macrocycles. Many detailed reviews of macrocyclic development have been published over the last 18 years.[3,4,5] However, some important landmarks in the development of macrocyclic chemistry are worthy of mention. Of particular interest in relation to the present work are those concerning metal-free macrocycles. A mixture of cyclic tetraaza compounds was obtained from the self-condensation of o-aminobenzaldehyde in the absence of metal ions.[6,7,8] In the presence of certain divalent metal ions, cationic complexes of the ligand I I. were obtained and these highly conjugated compounds excited interest as potential 'porphyrin model' compounds. However, limitations were imposed by the necessity for a 'controlling' metal ion and the fact that with certain ions mixtures of tri- and tetradentate ligand complexes were obtained.[9]



I I.

The aliphatic diimine macrocycles of type I II(a –d) were isolated initially as their metal complexes, but later in metal-free protonated forms as perchlorate salts[10] (or as bromides[11]) via the reaction of the monohydrogen-perchlorate salt of diaminoethane and mesityl oxide or acetone. More recently general reactions



a $R_1=R_2=CH_3$

b $R_1=R_2=H$

c $R_1=H$, $R_2=C_2H_5$

d $R_1=H$, $R_2=i\text{-}C_3H_7$

I II

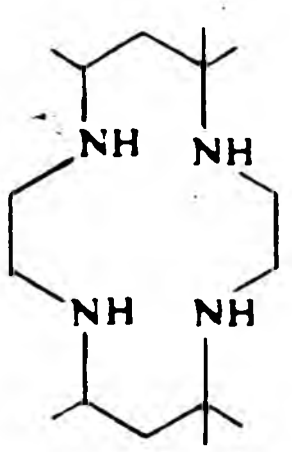
between the hydrogenperchlorate salt of diaminoethane and unsaturated ketones have been studied.[12,13,14] The preparation of cyclic polyethers, first reported fifteen years ago,[15] opened up an area of study into a new type of free macrocyclic ligand. These ligands are unusual in their ability to coordinat [illegible] Group IA and Group IIA metals, and these compounds constitute an extensive field of research. These ligands display the special properties, described as the macrocyclic effect, which is a feature of macrocyclic complexes including natural systems. However, they are outside the mainstream of research into compounds which have features approximating to the macrocycles found in transition metal-containing metalloproteins in which at least some of the donor groups contain nitrogen atoms.

1.2 Special features of macrocyclic ligands with N_4 donor sets, and their preparation

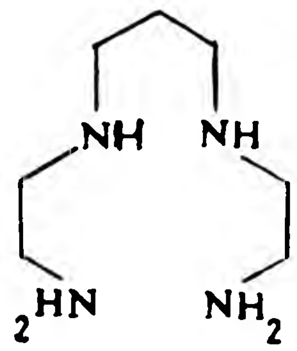
Interest in macrocycles containing four coordinating nitrogen atoms originally stemmed from the possibility that these compounds could be studied as simple models of the large ring systems which occur in nature, as mentioned above. The key biological roles of these appear to be dependent on special features which provide advantageous properties to coordinated metal ions. The ways in which macrocyclic ligands can influence coordinated metal ions are as follows:

(i) The stabilisation of particular oxidation states so as to allow considerable variations in the redox potential of a standard metal-ion couple.[16] This adjustment of electronic properties in metalloproteins, for example, will allow the metal to act as an oxygen carrier without being oxidised.[17] Recently a copper(I) complex of 1,10-phenanthroline has been found to act as an oxygen carrier in certain reactions.[18]

(ii) Compared to related linear ligands, macrocyclic quadridentate ligands usually give metal complexes which have greater kinetic stability. For example; rates of dissociation of complexes consisting of Cu^{2+} complexed to a tetraazamacrocycle of the type I III . have been shown to be reduced by a factor of 10^7 [19] compared with those of Cu^{2+} complexed to an analogous quadridentate ligand I IV



I III



I IV

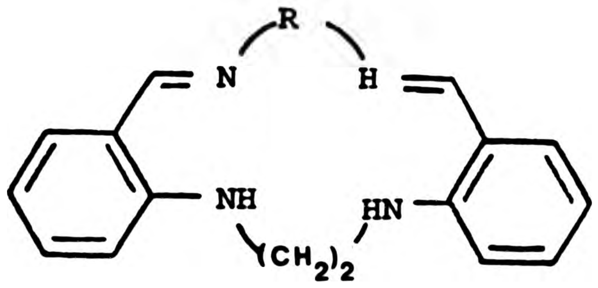
Later studies have shown that this stability is dependent on the relative size of the metal ion, and the inner great ring of the macrocycle[13,22].

(iii) Transport and storage of biometals depends on the thermodynamic stability of the metal complexes; the particular stability of macrocyclic complexes referred to above is termed the 'macro cyclic effect'.[19] Variations in solubility characteristics and membrane permeabilities of the metal are also selectively controlled by complexation to a macrocyclic ligand.[20]

(iv) Coordination to a macrocycle may modify the electronic properties of a metal to the extent of affecting its 'hardness' or 'softness' with respect to additional ligands.[21] Ring size has been shown to influence Dq^{xy} for given axial ligands in some metal complexes.[22]

Effects which influence the affinity of a metal for a binding site, as exemplified by observations of the metal-macrocycle systems, must be crucial in catalytic biological reactions which are often stereospecific, such as those at enzyme sites. Recently a series of binuclear copper complexes have been prepared, with variable intermetal distances, as model compounds for the study of substrate interaction with bimetallic metalloproteins.[23]

Research has centred on 'in-situ' preparation of macrocyclic metal complexes because of the ease of synthesis which results from the template role considered to be exerted by the metal ion during the course of the reaction. This is thought to occur in either or both of two ways. The metal may act as a 'kinetic template' by controlling steric factors which influence the reaction. It may also exert a thermodynamic template effect by forming a coordination compound which is both the thermodynamically-favoured compound and the desired product. To obtain a good yield of metal complexes, one or both of these effects was considered to be necessary. Before the publication of recent work few workers had developed methods for the preparation of free ligands.[24-29] In these methods, a high-dilution technique was often used to improve the yield of macrocycle by minimising the opportunity for side reactions, involving polymer formation or compounds of other stoichiometric combinations. In recent work[30] a series of free macrocycles of the type I IV have been prepared without resorting to 'metal template' or high dilution methods.



I V

As the preparation of these compounds provided the basis for some of the present work it is interesting to consider the thermodynamic aspects of the formation of free ligands, as opposed to the formation of metal complexes. In the latter case it is considered that a favourable free energy for the reaction results from the entropy factor. A positive overall entropy term results from desolvation of the metal ion on complexation.[31,32] No such effect can apply in the formation of the free ligand; here the resultant entropy term derived from both the condensation reaction and internal hydrogen bonding in the resultant ligand may not appear to be favourable. In addition it has been shown from results on the formation of copper complexes of tetraamine ligands, that the enthalpy term is less favourable for the cyclic ligand than for the open-chain product.[33] In the recent work[30] on free ligands the interesting point is made that in all successful syntheses of free ligands with approximately planar N_4 donor sets, intra-molecular hydrogen bonding can take place in the product which minimises nitrogen lone-pair-lone-pair repulsions.

1.3 Background to the present work

The initial impetus for the present work arose from the interest of the sponsoring company in anti-inflammatory agents as treatment for arthritic conditions. In this connection the special ligating properties attributed to polydentate macrocycles may be associated with physiological activity as antiinflammatory agents, when administered as free ligands or their copper complexes.

It now seems clear that not only copper complexes but also free ligands, which are capable of chelating copper, are useful in relieving arthritic conditions.[34] Their activity may be due to a number of effects.

Superoxide dismutases are metalloproteins containing copper and zinc (in mammals) which destroy superoxide radicals occurring in plasma, by the interaction of oxygen with free radicals.[35]

$$R^{\cdot} + O_2 \longrightarrow R^{+} + O_2^{-}$$

$$2O_2^{-} \xrightarrow[\text{dismutase}]{\text{superoxide}} O_2^{2-} \ (H_2O_2) + O_2$$

The reaction is followed by removal of the hydrogen peroxide by peroxidases;

$$2H_2O_2 \xrightarrow{\text{peroxidase}} 2H_2O + O_2$$

$$(\text{ie } O_2^{2-} \xrightarrow{+ \ 2e} 2O^{2-})$$

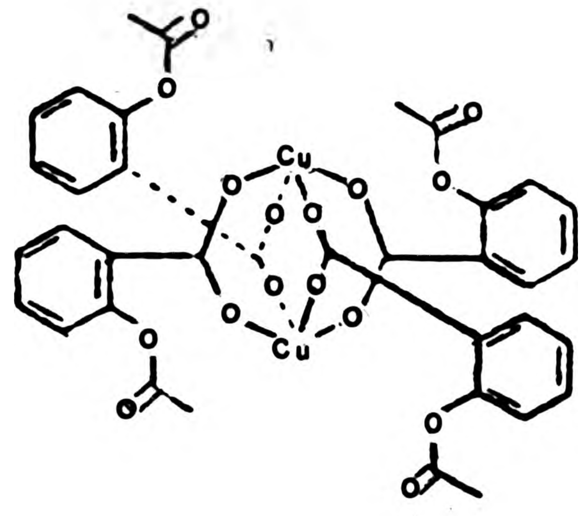
This sequence is important because superoxide radicals show toxicity which results from the generation of hydroxyl radicals by reaction with hydrogen peroxide.

$$O_2^- + H_2O_2 \longrightarrow OH^\bullet + O_2 + H_2O$$

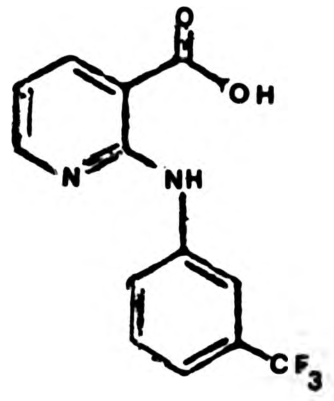
(as HO_2)

Hydroxyl radicals are known to depolymerise hyaluronic acid in synovial fluid, thereby thinning it and giving rise to inflammation of the surrounding tissues.[34] Hence copper availability for enzyme production is important in preserving this natural protective mechanism. Recently, certain binuclear copper complexes have been found to have similar properties to bovine erythrocyte superoxide dismutase.[36] Some free ligands which chelate copper have been shown to have pronounced anti-inflammatory activity.[34] Notable examples are acetylsalicyclic acid (aspirin) which coordinates to copper to give a binuclear complex;[37] (I VI), 2(3-trifluoromethylphenyl)aminonicotinic acid (niflumic acid, I VII), and 1-phenyl-5-aminotetrazole (Fenamole, I VIII) which gives analogous binuclear copper complexes.[37] The activity of these compounds suggest that they are able to chelate the copper present in all tissues, and thereby make available the protein-bound copper which is present at high levels in patients with rheumatoid arthritis.[38] Once formed, these therapeutically-active copper chelates may themselves exercise a superoxide dismutase-like function;[38,39] or expedite the formation of superoxide dismutase itself.[38] It might be expected that free tetraazamacrocyclic ligands capable of forming neutral copper complexes in vivo could be of therapeutic use in the ways outlined above. Recent investigation of the antiulcer drug 'Tagamet' has shown that it exists as a copper complex in the body, and it is suggested that the tendency to bind to copper may be important for biological activity.[40]

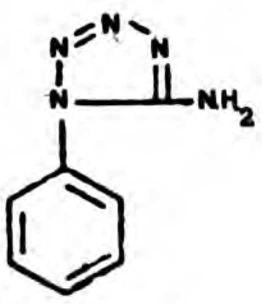
The copper complexes of the clinically-used ligands mentioned above have been claimed to be more active than the free ligands as anti-



I VI



I VII



I VIII

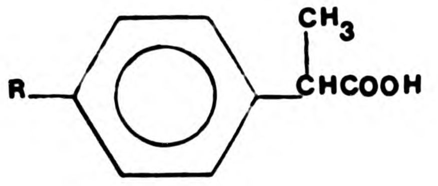
inflammatory agents.[39] In addition, unlike the free ligands, they show antiulcer activity.[39] This is not surprising as the cross-linking of protein, needed for repair at the site of ulcerated or inflamed tissue, is carried out by a copper-dependent enzyme;[39] thus introducing another aspect of the role of copper metabolism in inflammatory conditions.

On the basis of the results presented above it appears logical to examine polyazamacrocycles and their copper complexes for activity because (i) polyamines are known to exhibit a range of physiological activities in addition to those already described;[41] and (ii), nitrogen ligands form particularly stable copper(II) complexes[42] especially with macrocyclic ligands, and therefore such ligands may facilitate the labilising of protein-bound copper.

The design of free ligands having anti-inflammatory activity has another important basis in the structure of many of the prostaglandin synthetase inhibitors. These depress synthesis of the vasodilator prostaglandin, PGE2, and increase production of the anti-inflammatory prostaglandin PGF2[43]. These compounds include the substituted aryl acids,[44] of which acetylsalicyclic acid is one, indicating a dual reason for the effectiveness of this compound which is a widely-used antiarthritic.

One group of these compounds is of methylphenylacetic acid derivatives, substituted with hydrophobic alkyl or aryl groups.

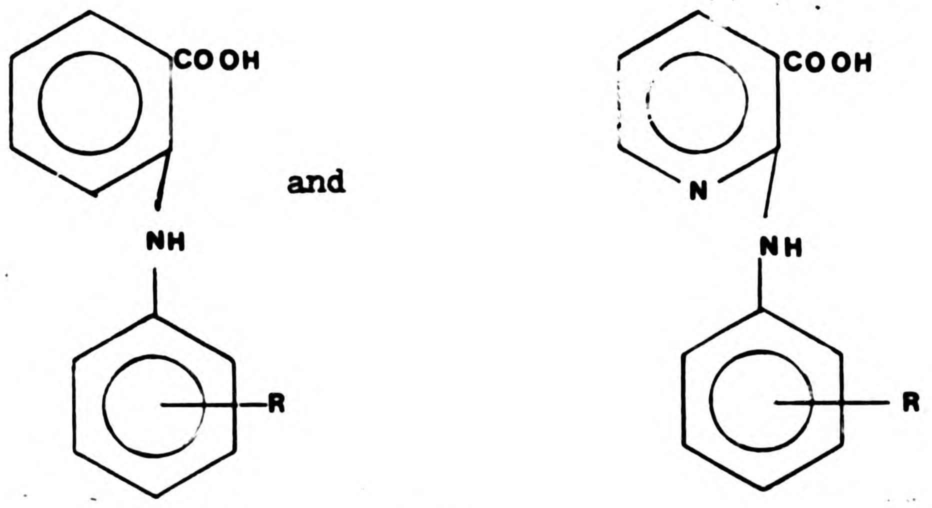
R = aryl or branched alkyl group



I IX

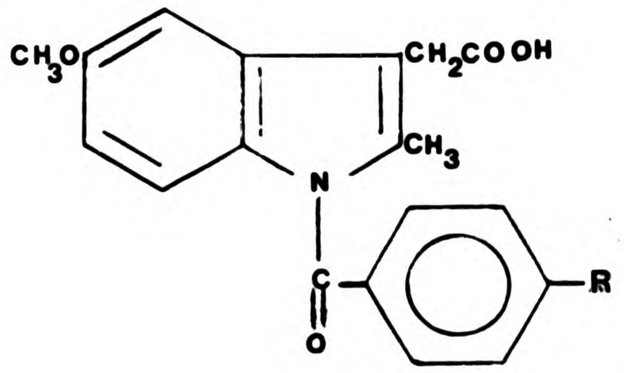
Another group consists of the anthranilic acid series; of which niflumic acid (R = CF_3 I VII)

R = CF_3, CCl_3



I X

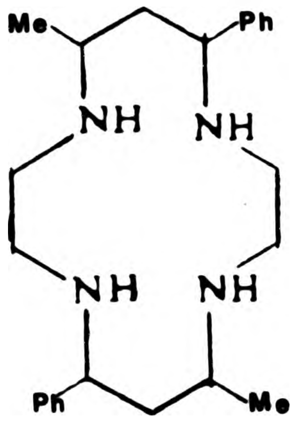
is one. The indomethacin analogues form another group; in which the presence of the 5-methoxy group is necessary to maintain anti-inflammatory activity. (R= Cl or F).



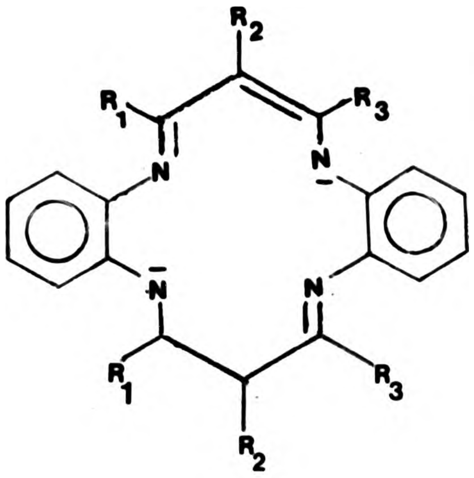
I XI

These compounds provide pointers to the kind of functional groups which may be useful.

Compounds of the type I XII had been investigated by the sponsoring company[45] and a modification; in which the macrocycle comprised fused benzene rings, was envisaged. Metal complexes of the ligand type I.XIII have been prepared.[46-48]



I XII.



$R_1, R_3 = H, CH_3, C_6H_5$

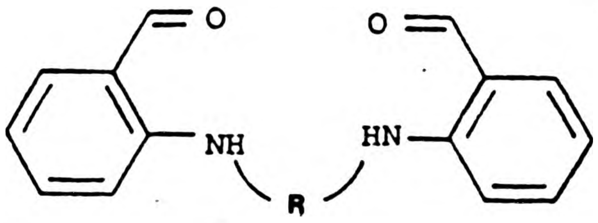
$R_2 = COOC_2H_5$

I XIII

It has been found possible to remove the metal ions (Cu or Ni) from these complexes to produce the free ligand. In addition, the free ligand in which $R_1 = R_2 = R_3 = H$ has been prepared.[48] However, these compounds are restricted in ring size, and to some extent in the choice of substitutents R_1, R_2, R_3.[49]

The system used for producing free ligands of the type I XV[44,50,51] is a versatile route to a large number of macrocycles because a number of diamines can be reacted with dialdehydes of the type I XIV

$R = (CH_2)_2, (CH_2)_3$

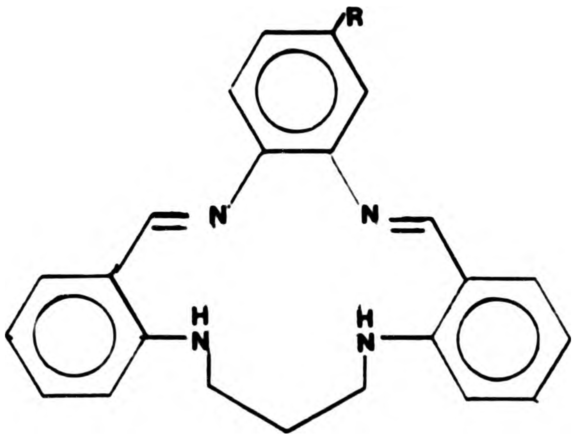


I XIV

This condensation allows a variation of ring size apart from the 14-membered systems used by other workers,[45,46,47] and permits the introduction of substituents by the use of substituted amines.

1.4 Systems chosen for study

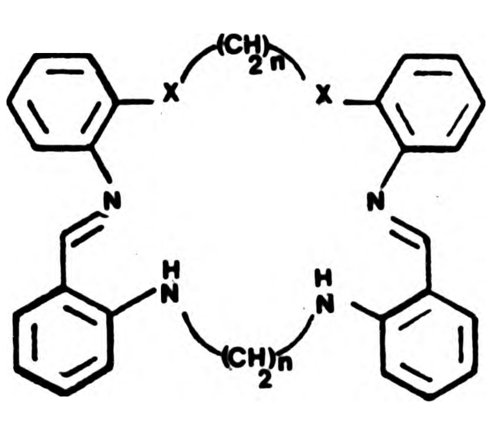
The interest of the sponsoring company prompted the selection of substituent groups in the quadridentate tetraaza macrocycles of the type I XV, on the basis of the types of structure, which have been found in therapeutically active anti-inflammatory agents, outlined in Section 1.3. These macrocycles are considered in Chapter 2.



I XV

More extensive ring modification of the quadridentate N_4 ligand systems, including reduction and alkylation of the basic quadridentate diimine (IXV, R = H) and reduction of some of the substituted ligands is considered in Chapters 2 and 3.

The incorporation of oxygen, nitrogen and sulphur atoms into the donor set to give free sexadentate ligands of the type I XVI is described in Chapter 4.



X = S, NH, O

I XVI

In-situ ('template') preparations of metal complexes[52] of certain examples of this type of ligand have been published previously. Previous work[53] has described a series of complexes with a dioxo bridge. In this project the work is extended to produce copper complexes of benzyl C-alkylated ligands with the dioxo bridge. As a modification of the inner ring, a bridging reaction was attempted. This was analogous to some work on aliphatic macrocycles, carried out by the sponsoring company.[45] Both the above types of work are described in Chapter 3.

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Chapter 2 The quadridentate tetraazamacrocycles

2.1 Methods of preparation of the quadridentate macrocycles

The diimine ligands with the substituent groups selected for study were prepared by the general method shown below.

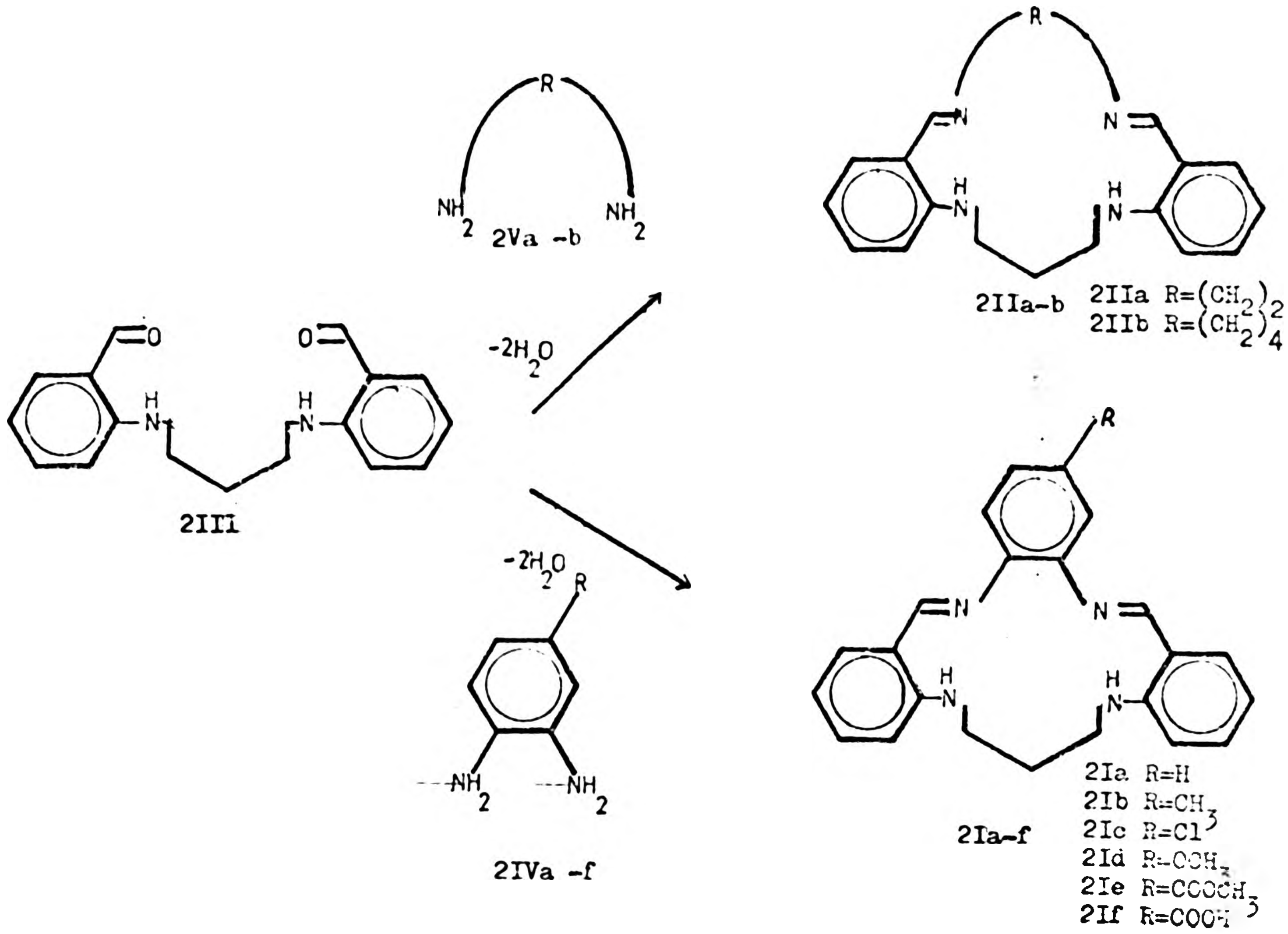
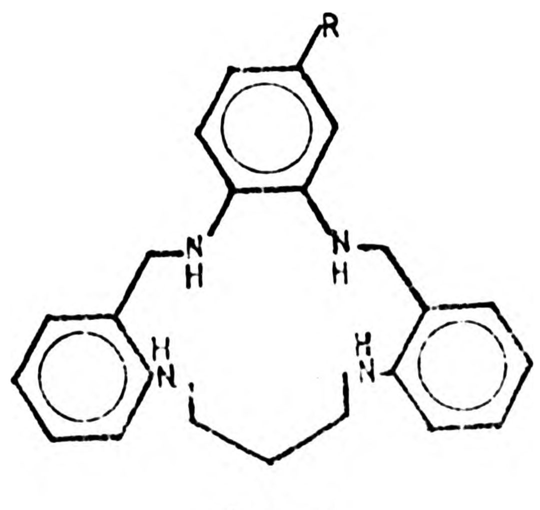


Fig 2.1 Preparative scheme for the quadridentate diimines.

The hydrogenated derivatives which were prepared had the general formula:



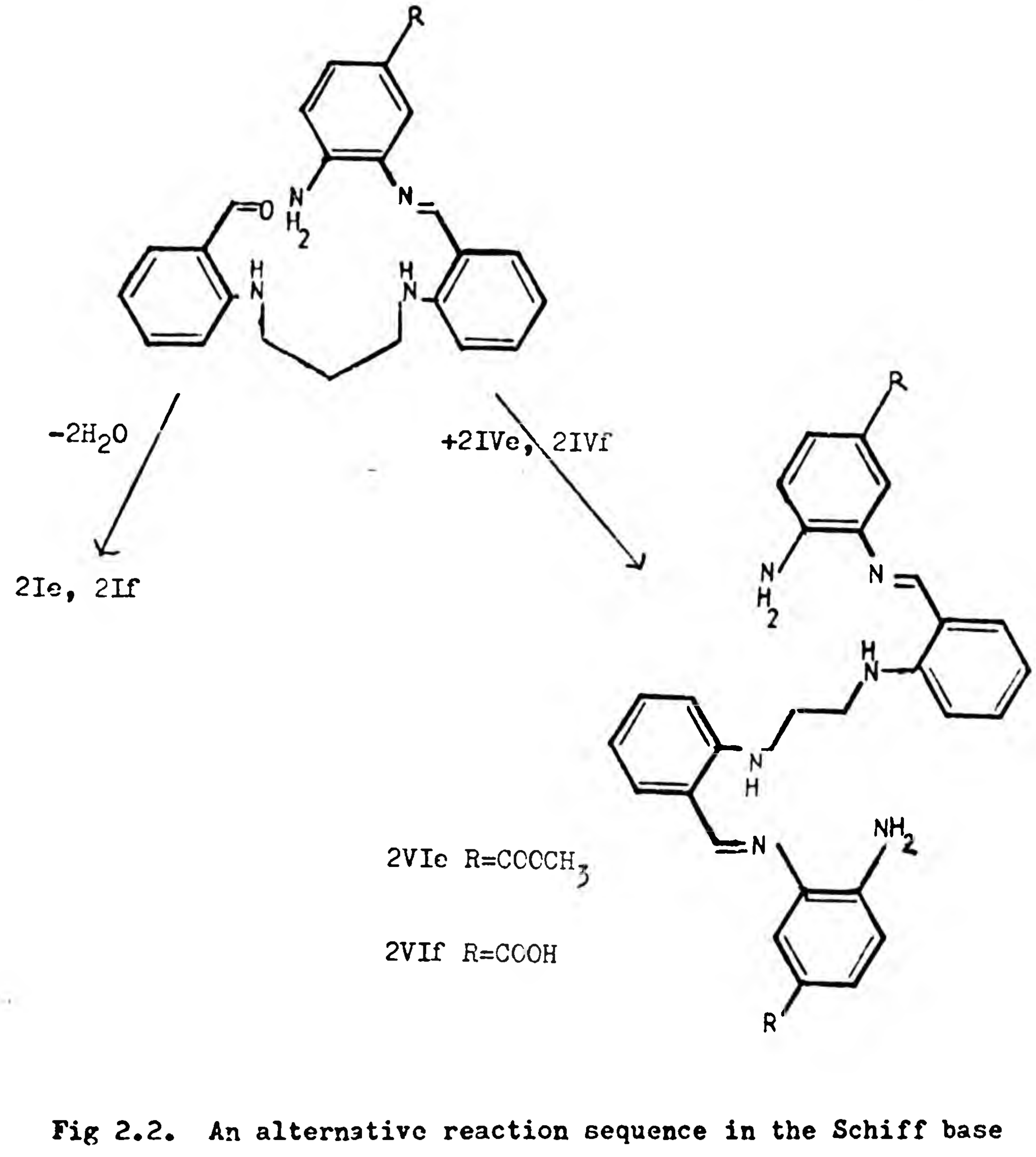
2IHa-f

2.1.1 Isolation and characterisation of the diimine systems

The diimines were formed by the Schiff base condensation[1] between the dialdehyde (2III) and the series of amines 2IVa-f and 2V, as shown in the reaction sequence above in Figure 2.1.

The condensations require the nucleophilic attack of the amine nitrogen atoms upon the carbon atom of the carbonyl group. The rate of reaction is dependent upon the electron density at the site of the amine nitrogen atoms, and the extent of polarisation of the carbonyl groups. The σ-donor characteristics of the amino group would be expected to be dependent on the nature of the substituent group, R. This can be seen by examining a series of pK_b values for substituted amines[2]. The methoxy, and to a lesser extent, the methyl group, are electron-releasing and the diamines (2Vb and 2IVd) gave faster reactions with the dialdehyde (2III) than the unsubstituted diamine (2IVa) e.g. the methoxy compound (2Id) was obtained in 72% yield after 2 hours at room temperature, whereas 2Ia required a 2-hour reflux in methanol to give a comparable (78%) yield. The chlorosubstituent seemed to have little effect on the rate of reaction. The diamines containing the electron-withdrawing groups R=COOH and R=COOCH$_3$, required longer reaction times, and gave a lower yield of the macrocycles 2Ie and 2If.

Here the cyclisation reaction is possibly only slightly more kinetically favourable than other reaction sequences, e.g. combinations of the diamine and dialdehyde in other stoichiometries. For reactions of 2IVe or 2IVf the amino group para to the carboxylate substituent will be significantly less nucleophilic. After 1:1 reaction between, presumably, the more basic amino group which is meta to the electron-withdrawing substituent, reaction with a second molecule could compete successfully with ring closure to give 2VIe and 2VIf as shown in Figure 2.2 . The unreacted amine group in the 1:1 derivative (2Ve, 2Vf) will be rendered more inactive by the incorporation of the lone pair electrons into the now extensively conjugated system.



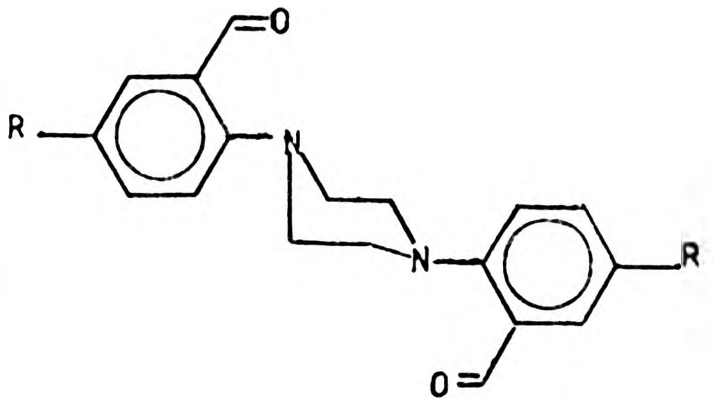
2Ie, 2If

2VIe R=$COOCH_3$

2VIf R=COOH

Fig 2.2. An alternative reaction sequence in the Schiff base condensation.

Open-chain condensation products of this type have been observed in reactions of the piperazino-bridged dialdehydes 2VIIa and 2VIIb.



2VIIa ($R=NO_2$)[3]
2VIIb (R=H)[4]

When R is a powerful electron-withdrawing group such as the NO_2 group, a p-amino group is much less basic[2] ($pK_b=13.0$) than an m-amino group ($pK_b=11.4$) and it was therefore not surprising that all attempts to prepare the macrocycle with the potentially very useful NO_2 subsituent on the o-phenylene ring resulted in compounds having residual amino groups. These were very insoluble products and work was not continued on these lines.

In all reactions involving the aromatic amines it was found that the presence of a Lewis acid catalyst increased the rate and yield of the reaction. Co-ordination to the carbonyl oxygen atom of protons (introduced in the form of p-toluenesulphonic acid) or metal ions (Zn^{2+} or Cd^{2+}, introduced as acetate salts), would increase the polarity of the carbonyl bond and facilitate the formation of a carbinolamine intermediate[5].

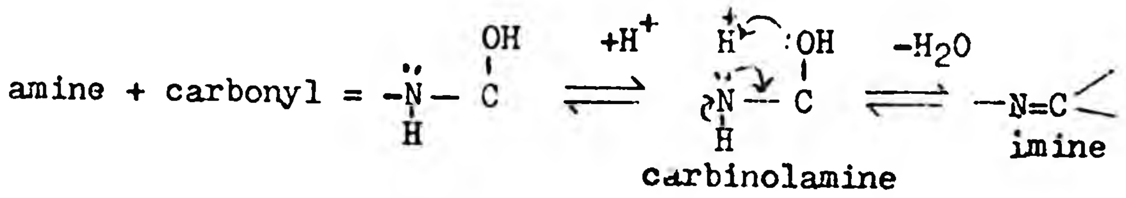


Fig 2.3. Formation of a carbinolamine intermediate.

In addition it has been found that further protonation of the intermediate, as above, results in rapid elimination of water to give the imine. However, electron-withdrawing groups on the amine inhibit the protonation of -OH and expulsion of water[6]. Thus amines with electron-withdrawing substituents (2IVe, 2IVf) would again be less likely to give good yields of diimine. However the presence of an excess of Lewis acid will have a deleterious effect on the reaction rate because co-ordination to the amino groups will remove their nucleophilic activity.

The action of metal ions as Lewis acid catalysts might be seen to have advantages in this type of reaction. Inhibition of amine nucleophilic activity does not take place, and in addition, the 'metal template' effect[7] may operate, even when the reaction product is not a metal complex. In this case the metal is thought to have a 'kinetic' role in which metal complexes of reaction intermediates are formed which promote a shift in reaction toward the desired macrocycle. However the 'thermodynamic' template effect operates under conditions of thermodynamic control in which the equilibrium is displaced by formation of a stable co-ordination compound which is more stable, and probably less soluble, than alternative products. The latter effect was obviously undesirable for this work because metal-free ligands were required for the screening programme. Many classes of imino-ligands have not been successfully isolated in metal-free forms[8], however the compounds described in this chapter were comparatively easy to isolate in their metal-free forms. A reason for this may be that compounds 2Ia-f were conjugated diimines, which were thermodynamically favourable products. Difficulties arose with aliphatic diamines, as described below where no such highly conjugated systems were formed. In addition, unfavourable lone-pair intra-annular interactions can be reduced by intra-molecular hydrogen bonding which is thought to provide a favourable thermodynamic condition for the formation of the free macrocycle[3]. Crystallographic evidence for this type of hydrogen bonding is available[3], and n.m.r. and infra-red data provide further evidence for the occurrence of intramolecular hydrogen bonding in the compounds described here. See Figure 2.4.

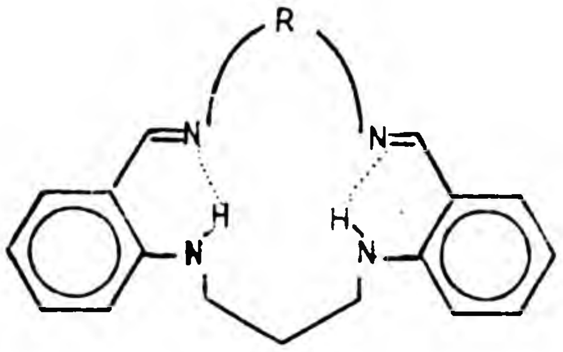
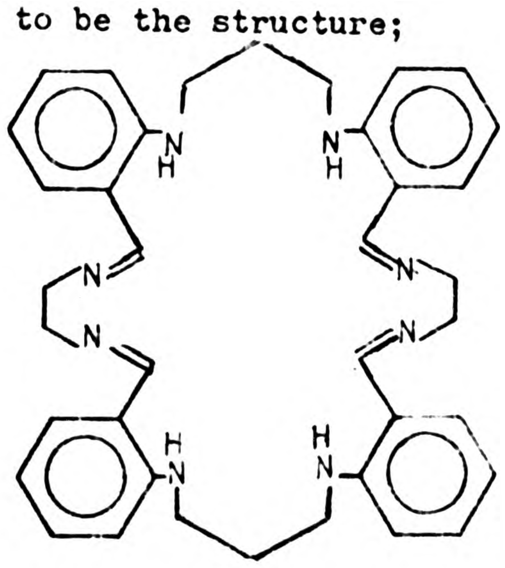


Fig 2.4. Intra-molecular hydrogen bonding.

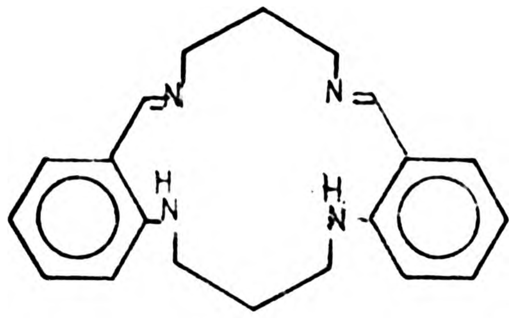
Although employing a similar general method, it was not trivial to establish optimum conditions for preparation of the diimines 2Ia-f. Most of the diamines were commercially available, some were very impure and it was found best to carry out special purification processes on the products as described in Section 2.5. 1,2-diamino methoxybenzene was prepared by reduction of the corresponding dinitro compound using palladium/carbon and hydrazine. Since this diamine was air-sensitive it was isolated and stored as the dihydrochloride salt. This was neutralised in situ during the reaction with the dialdehyde 2III by adding triethylamine in small successive portions. This method was found to give the best yields in a short time at room temperature. An attempt was made to prepare a limited series of metal-free diimines 2.IIa,b using aliphatic diamines 2 Va,b. The preparation of 2IIa had been reported previously by a high-dilution method[9]. All attempts to prepare this ligand in similar conditions to those used for the aromatic bridged species gave a mixture of products. In addition experiments were carried out using Zn^{2+} or Cd^{2+} ions under a variety of reaction conditions to try and utilise a template process for producing the monomeric ligand. These experiments gave materials with i.r. spectra which closely resembled that described for the monomeric macrocycle 2 II a, but which contained a mixture of products. Field desorption analysis showed that these products contained a variable proportion of the monomeric ligand 2IIa m/e 307 $(M+1)^+$ and a presumably dimeric product, m/e 613 $(M+1)^+$. This was likely to be the structure;



2VIII

It was possible to separate the monomer, which was soluble in $CHCl_3$, from the dimer but the recrystallised material was subsequently found to be partly insoluble. This indicated the possibility of an equilibrium in solution, between the monomer and the dimer. Attention was focussed on a method of obtaining pure dimer from the reaction mixture. It was found that by refluxing the mixture with D.M.F. for several hours an insoluble solid was formed. This was confirmed as the dimer 2VIII by a field desorption mass spectrum which showed a single peak at M=612. There was complete absence of peaks due to the monomer or to higher relative molecular mass species.

The preparation of the next higher homologue, (2IX), as the metal-free

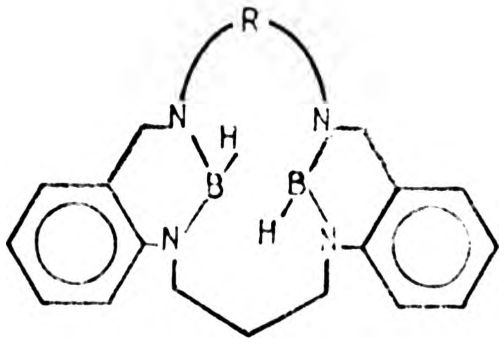


2IX

diimine had been attempted, with little evidence for preparation of the monomer[10]. Attempts to prepare the Cu^{2+} complex by an in situ reaction gave a uncrystallisable oil. Further work was done on the preparation of the four-carbon bridged ligand 2IIb. This could be obtained as the monomer, but there were indications that this ligand decomposed at room temperature, the characteristic smell of the free diamine being discernable a few hours after vacuum-drying and sealing the product. Attempts at recrystallisation usually resulted in deterioration of the product. Some spectroscopic data was obtained and is discussed below (Section 2.2). Treatment of the monomer 2IIb with D.M.F. in an attempt to produce a dimeric product as described above resulted in an exothermic decomposition reaction. It appeared that the aliphatic-bridged diimines were unstable compared to the conjugated diimines. It is not clear why those prepared from the dialdehyde 2III are less stable than those made with the ethane-bridged dialdehyde[11]. However the equilibrium that seems to exist between the monomeric and dimeric forms of the macrocycle in solution can be used to produce an interesting class of dinucleating octodentate ligands[12]. The isolation of these dimeric products is dependent on thermodynamic control, and their low solubility is an important factor.

2.1.2 Isolation and characterisation of the tetraamine systems

The diimines 2Ia-d were successfully reduced using a solution of diborane in T.H.F. Such reactions probably proceed via a boron intermediate of the type, shown below;



2X

A stable boron complex of this type has been isolated when $R=(CH_2)_2$ and the structure determined[13]. Presumably the stability of the complex depends on the cyclic nature of the N-B-N adduct, many stable heterocycles containing the B-N unit are known[14]. In this work the boron complexes were transient, or were decomposed by hydrolysis. No attempt was made to isolate the boron adducts. Attempted hydrolysis of the reduction product of 2Ic with aqueous reagents resulted in a very poor yield. An alternative method, using methanol, was used as described in Section 2.5.2.

In attempting the selective reduction of the imine groups in 2Ie $(R{=}CO\underset{2}{O}\underset{3}{H})$ it was probable that reduction of the carboxyl group would occur, particularly in 2If ($R=COOH$). In addition the presence of the electron-withdrawing substituents would be expected to make the imine bond less susceptible to reduction. The reduction product obtained from 2Ie was an off-white material of higher mass (426) than would be accounted for by reduction of the carboxylate substituent and/or the imine bonds. It was possible that a boron complex had been formed, although the material was intractable and attempts at further hydrolysis were unsuccessful. Reduction of 2If ($R=COOH$) gave a yellow solid of mass peak 382, with the next highest m/e value = 372. As a compound of lower mass than the parent diimine ($M_r=398$) was produced it was likely that the carboxyl group had been reduced. The yellow colour of the product was some indication that the imine bonds remained. However the infra-red spectrum was poorly resolved, suggesting that a mixture was present, and attempts at recrystallisation produced no significant improvement. Previous work had shown that lithium aluminium hydride was ineffective in reducing the imine bonds in these macrocycles[11]. However it should be possible to reduce the carboxyl group to an alcohol group, using this reagent. Treatment of 21f with lithium aluminium hydride gave a bright yellow intractable solid which was insoluble in all the usual solvents including hot D.M.F. The poorly-resolved infrared spectrum showed a very broad band at 3400 cm^{-1} indicating the presence of -OH groups, although the insolubility of the product suggested a polymeric structure. Further attempts at these reductions were not pursued.

2.2. Physical properties of the quadridendate diimines and tetraamines

2.2.1. Infra-red spectra of the quadridendate diimines and tetraamines

The spectra of the diimines (2Ia-f) and the related tetraamines (2IIa-d) are complex, but the similarities between the basic structures allow a number of common features to be identified. Characteristic bands associated with the functional group R could also be recognised. A table of the main absorption bands in the diimines is given below. Table 2.1. Assignments of bands below 1600 cm^{-1} are tentative and are based on work on similar compounds[11,16,17,18,19] as well as the range of literature values for specific groups[20].

A common feature of all the ligands was a band at 750 cm^{-1} due to C-H deformation in 1,2-substituted benzene[21]. A band at 1170 cm^{-1}, due to secondary aliphatic C-N stretch was common to all the ligands. All the diimines showed a distinctive strong group of 3 peaks between 1570 and 1630 cm^{-1} - these were also found in the sexadentate diimines (Section 4.2.1). The most likely assignment for these absorptions were NH bend (ca. 1580 cm^{-1}) aromatic C=C stretch (1590-1630 cm^{-1}) and C=N stretch (ca. 1620 cm^{-1}). The latter band did not appear in the spectra of the tetraamines, although the former two were still present. The N-H stretch absorption was usually seen as a broad, weak band at 3300 cm^{-1}. The broadening of this band may have been due to hydrogen bonding between the anilino hydrogen atoms and the imine nitrogen atoms (see Fig. 2.4). Further evidence for this type of bonding is given by the ^{1}H n.m.r. data (Section 2.2.2) and by X-ray analysis of similar structures[3]. When the compounds were obtained as hydrates (2If, R=COOH and 2IId R=OCH_3) another broad band was seen at slightly higher wavenumber, due to -OH stretch. Peaks due to specific functional groups (C=O, C-O-C) were a major feature of ligands 2Id (R=OCH_3), 2Ie (R=$COOCH_3$) and 2If (R=COOH).

In the aliphatic-bridged diimine 2IIb (R=$(CH_2)_4$) the main absorption bands were similar to those in the spectra of the phenyl-bridged ligands. A significant difference was the presence of several bands ca. 1050 cm^{-1}; these were possibly due to C-N stretch in secondary aliphatic amines. There was also an additional band at 730 cm^{-1}, attributable to the 'rocking' motion of the sequence of CH_2 groups in the four-carbon methylene bridge, and not present in the aromatic-bridged diimines.

In the preparation of 2IIa (R=$(CH_2)_2$) mixtures of the monomer and dimer were obtained as described in Section 2.1.1. The infra-red spectra of the mixtures showed[9] additional bands to those described for the monomer. The bands were at 820, 840, 860, 870, 890, 915, 960, 970 and 1250 cm^{-1}, and were present in the spectrum of the pure dimer 2VIII and might therefore be used to identify the presence of the dimer. There were also some small peaks ca. 3150 cm^{-1} in the spectrum of the dimer, which were not reported in the monomer spectrum, which were probably due to differences in C-H stretching and rocking modes because of conformational differences between the monomer and dimer.

The spectra of the tetraamines showed two significant differences from those of the diimines. The absorption due to NH stretch (ca 3300 cm^{-1}) was more intense and complex. In the unsubstituted ligand 2IHa, (R =H) there were two distinct peaks and in the spectra of 2IHb (R=CH_3) and 2IH (R=Cl), three peaks. In the monohydrate 2IHd (R=OCH_3) there was one broad peak, probably broadened by

Table 2.1 Absorption Maxima (cm^{-1}) in the Infra-red Spectra of the Quadridentate Diimines (nujol)

2Ia (R=H)	2Ib ($R=CH_3$)	2Ic (R=Cl)	2Id ($R=OCH_3$)	2Ie ($R=COOCH_3$)	2If (R=COOH)	Assignment
			3400		3400-3350	OH deformation
3240	3220	3260	3200	3220	3200-300	NH stretch
				1720	1680	C=O stretch
1625	1630	1630	1620	1630	1620	C=N stretch
1600	1600	1595	1610	1600	1590	Benzene derivatives C=C stretch (1590-1630)
1580	1570	1570	1585	1575	1570	NH bend
1495	1470	1480	1470	1470	1520	CH_2 deformation
	1340-1330			1345-1330		Symmetrical deformation in $C-CH_3$ unit
				1260	1270	C=O stretch + OH deformation
						C-O-C stretch in ester
			1280			C-O-C stretch in alkylaryl ethers (1240-1290)
1170	1170	1170	1170	1170		Secondary aliphatic 1191-1171
1130	1140-1130	1130	1130	1130	1200	C-N stretch 1146-11322
760-740	750	750	750	770-740	770-750	C-H deformation in 1,2 substituted benzene
		700				C-Cl stretch

Table 2.2 Absorption Maxima (cm^{-1}) in the Infra-red Spectra of the Quadridentate Tetraamines (nujol)

2IIIa R=H	2IIIb R=CH_3	2IIIc R=Cl	2IIId R=OCH_3	Assignment
			3400-3200	OH Deformation
3420 3380	3420 Triple 3380 Peak 3340	3420 3360 3315	3200	NH stretch
1610	1620	1610	1610	Aromatic C=C stretch in benzene derivatives
1585	1590	1590	1590	N-H bond
1520	1520-1510	1490	1510-1520	CH_2 deformation, secondary NH deformation
	1390		1470(adjacent to O)	Symmetrical deformation of CH_3 group
			1260	1290-1[illegible]0 C-O-C stretch
1150	1165	1160	1160	C-N stretch in aliphatic secondary amines
1130	1140	1125-1130	1140	1146-1132 1191-1171
740 755 Triple 760 Peak	800	740	750	C-H deformation in 1,2 disubstituted benzene
		700		C-Cl stretch

hydrogen bonding and merging into the band due to -OH stretch. The other major difference was in the double peak at 1590-1610 cm^{-1} - absorption in this region appearing as a characteristic triple peak in the diimines as mentioned above. The band at ca. 1590 cm^{-1}, attributed to -NH bending vibrations was more intense in the tetra amines, as would be expected.

2.2.2 N.m.r. Spectra of the quadridentate ligands

The ^1H n.m.r. spectra were obtained for the series of quadridentate ligands 2Ia-f and 2IIb (see key), and ^{13}C spectra were obtained for the ligands 2Ia-c which gave solutions of sufficient concentration to allow strong signals to be recorded. Ligands 2Id-f were not sufficiently soluble in $CDCl_3$ to allow a clear comparison of the ^{13}C spectra. DMSO was found to be unsuitable as a solvent because of the overlap of ^{13}C signals at high field and the tendency of the diimine ligands to decompose in this solvent.

The effect of substituents in ^1H n.m.r. is usually confined to the nearest atom[22], whereas ^{13}C signals occurring over a range of chemical shifts 20 times that of ^1H signals are much more sensitive to steric effects over several bond lengths[23]. Thus the ^{13}C spectra showed interesting evidence of the asymmetry of the substituted macrocycles.

The details of both types of spectra; including the methods of assignment of the signals, especially in the ^{13}C spectra, are given below.

2.2.2.1 'H n.m.r. spectra of the quadridentate diimines

The 'H signals of this group of compounds were assigned according to their chemical shifts and coupling characteristics.

The protons are labelled as in Fig. 2.5 and the chemical shifts tabulated in Table 2.3.

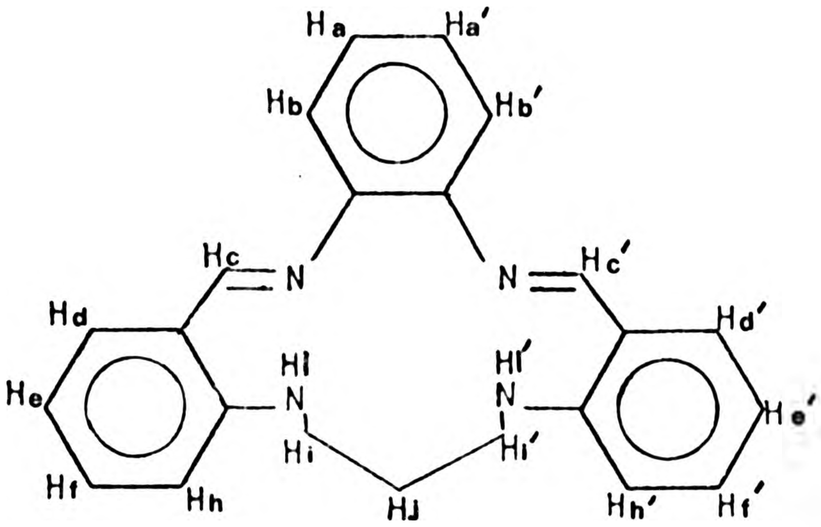


Fig. 2.5. Hydrogen labelling in the quadridentate diimine ligands.

A feature of interest was the coupling of the methylene hydrogen atoms (Hi,Hi') with the anilino protons Hl, Hl'. The Hi,Hi' signal gave what appeared to be a quadruplet but which was probably an overlapping sextuplet due to secondary coupling with the anilino protons. Amine hydrogen atoms are usually too rapidly exchanged to couple[24] except where internal hydrogen bonding occurs or where non-polar solvent systems are used[25]. The position of the anilino protons, occurring at the lowest field throughout the series, indicated that they were hydrogen-bonded to the electronegative nitrogen atoms of the azomethine group, causing deshielding of the hydrogen-bonded proton by the imine bond[26]. This hydrogen bonding was sufficiently strong to allow coupling of the anilino proton with the adjacent methylene group, as mentioned above. The anilino hydrogen signal appeared as a broad singlet except in one particularly well-resolved spectrum, that of 21b, where the signal was a triplet. The signals were assigned on the basis of their disappearance after shaking the solution with D_2O. The rate of exchange of anilino protons with deuterium ions was slow; probably because the exchange involved a conformational change as indicated in Fig. 2.6.

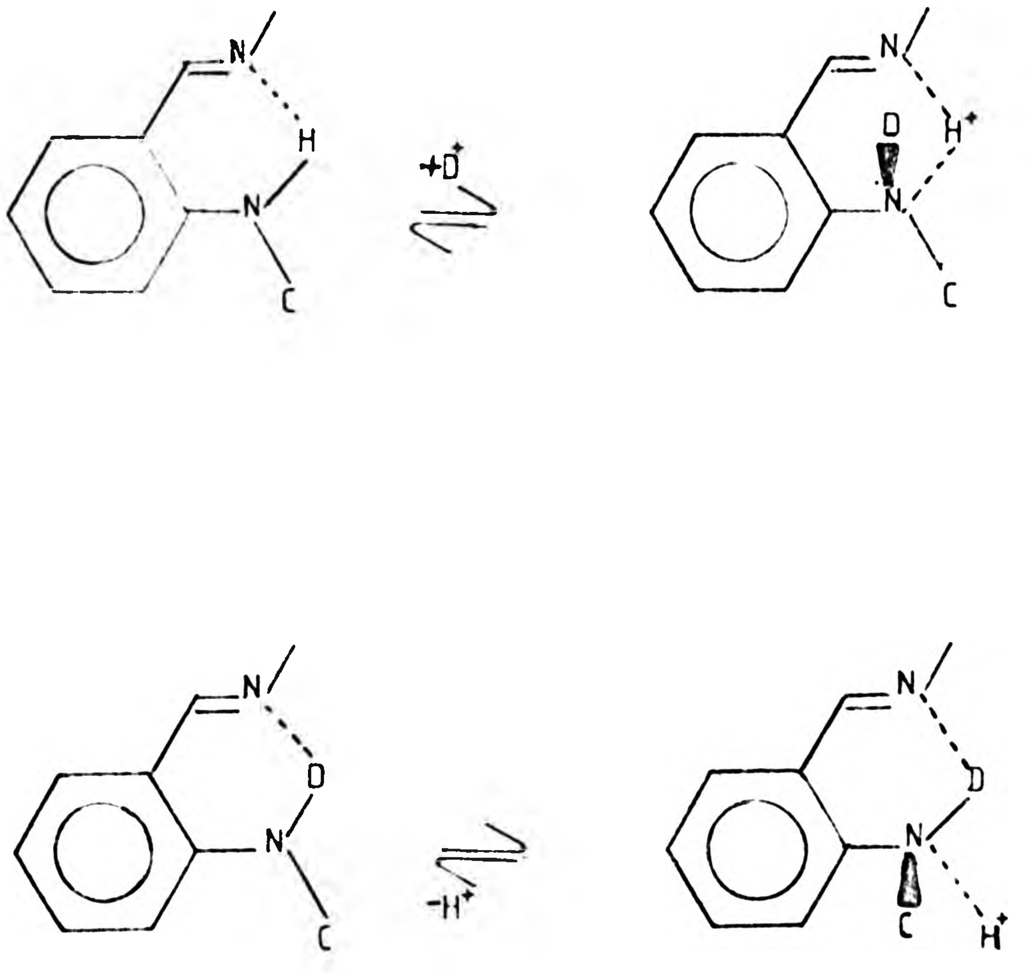
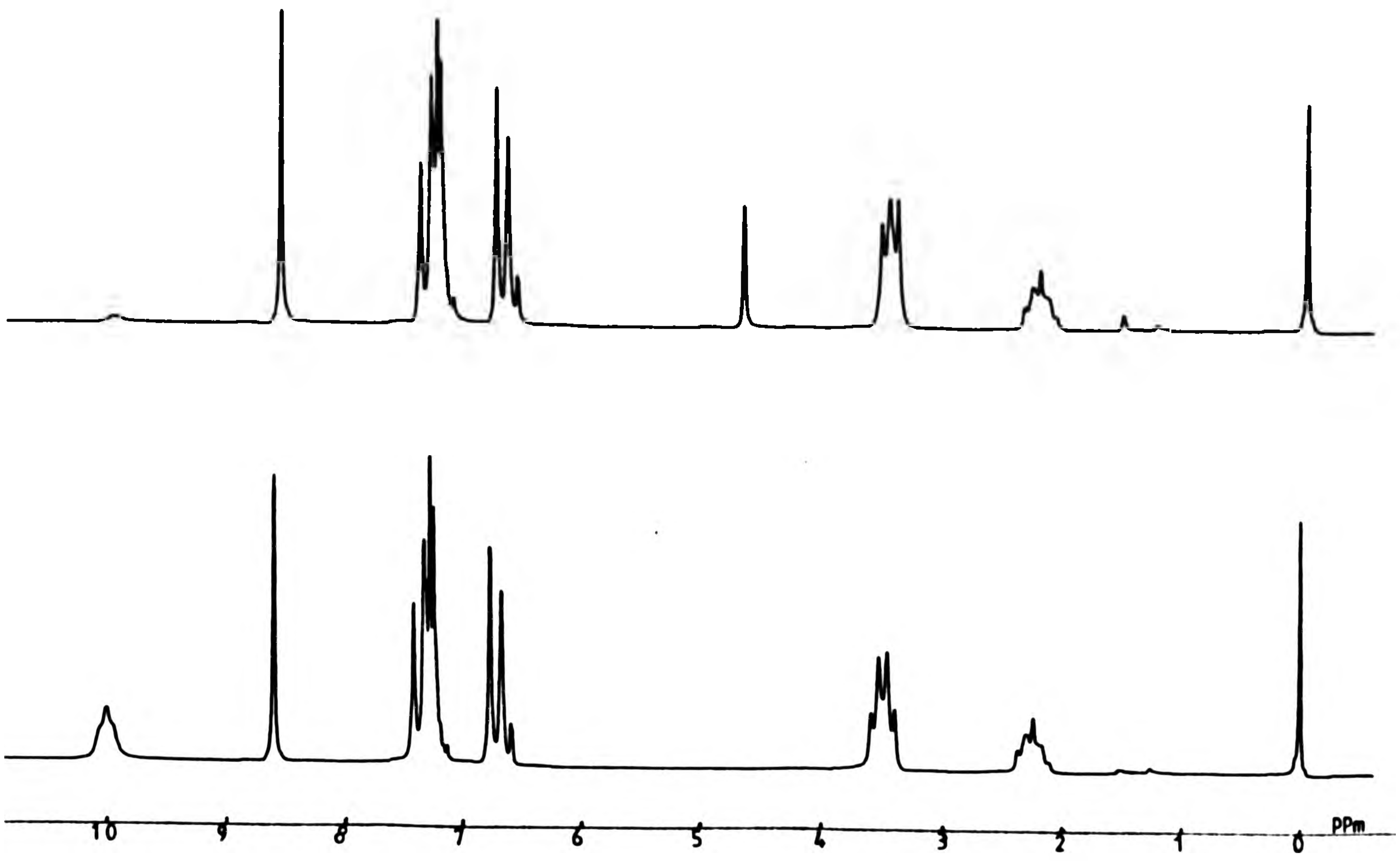


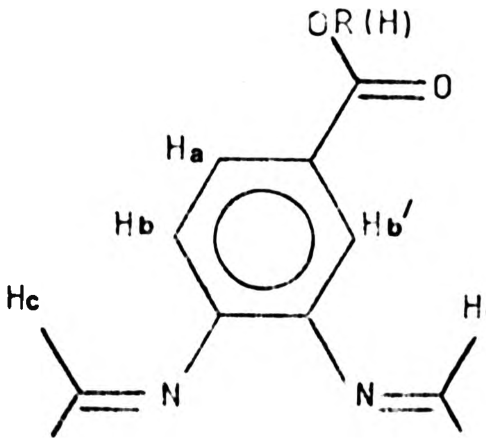
Fig. 2.6 Mechanism of deuteriation of anilino nitrogen atoms.



^{1}H spectra of the diimine 2Ia ($CDCl_3$) showing the effect of shaking with D_2O (top).

In this suggested mechanism the anilino nitrogen, is first deuterated to give an sp^3-hybridised nitrogen atom (step (1)). The slow, and probably rate-determining step (2) involves a conformational change in which the imino-nitrogen to hydrogen bond is cleaved and an imino-nitrogen to deuterium bond is formed.

The signals of all the protons in the aliphatic-bridged compound 2IIb (Table 2.4) were further upfield ($\geqslant$0.2 ppm) than their counterparts in the spectra of ligands 2I(a-f). In particular, the azomethine proton signal was further upfield ($\leqslant$0.4 ppm) than the azomethine proton signals in 2I(a-f). This indicates that the downfield chemical shift due to the imine bond is enhanced by the adjacent aromatic bridge. As the ligands 2I(a-f) are highly conjugated, additional deshielding effects appear to influence the other proton signals in these ligands as mentioned above. The azomethine signals were singlets except in the spectra of 2Ie ($R=COOCH_3$) and 2If ($R=COOH$) where two separate signals were seen. This could arise because of substantial differences in the environment of Hc and Hc' in the planar conjugated system. (2XI)



2XI

These electron-withdrawing groups (R=$COOCH_3$,COOH) appear to augment the aromatic ring-current induced chemical shifts of the azomethine proton signals. These are 0.02-0.08 ppm greater (Table 2.3) than that of the unsubstituted ligand 2Ia. In contrast, the azomethine proton signal in 2Id (R=OCH_3) was at a higher field(0.13 ppm) than in the unsubstituted ligand, perhaps due to the electron-releasing effect of the methoxy group. The effect of the methoxy group was also seen in the pattern of aromatic splitting.

The aromatic signals appeared either as a complex array of signals or as multiplets. There were two series of signals. In the spectrum of 2Id (R=OCH_3) a multiplet corresponding to seven hydrogen atoms was upfield of a multiplet signal produced by four hydrogen atoms. Perhaps this was due to the strong electron-releasing effect of the methoxy group, which provided extra shielding for the hydrogen atoms within the conjugated area of the molecule.

In the spectra of 2Ie (R=$COOCH_3$) and 2If (R=COOH) the pattern of aromatic splitting was more complex. A signal from one hydrogen atom appeared separately, further downfield. It is tempting to attribute this to Hb' (2XI), this being the hydrogen atom especially isolated (as opposed to Ha) and downfield by being adjacent to the large electron-withdrawing substituent groups. In general, however, it was not possible to make individual assignments of the aromatic proton signals. A further interesting feature of the spectra of 2Ie (R=$COOCH_3$) and 2If (R=COOH) was the presence of two azomethine proton signals (Table 2.3). This reflects the different chemical

2Ia R=H(a')
2Ib R=CH3
2Ic R=Cl
2Id R=OCH3
2Ie R=COOCH$_3$
2If R=COOH

Table 2.3 'H n.m.r. of the Quadridentate Diimines

Compound	2Ia	2Ib	2Ic	2Id	2Ie	2If
Hj	2.22 (quin, 2H, J=2.4)	2.16 (quin, 2H, J=2.1)	2.17 (quin, 2H, J=4.0)	2.1 (quin, 2H, J=8.0)	2.29 (quin, 2H, J=2.4)	2.67 (quin, 2H, J=8.8)
Hm		2.39(s,3H)		3.7(s,3H)	3.94 (s, 3H)	
Hi,Hi'	3.48 (quad, 4H, J=2.4)	3.42 (quad, 4H, J=2.1)	3.45 (quad, 4H, J=4.0)	3.3 (quad, 4H, J=8.0)	3.47 (quad, 4H, J=2.4)	3.4 quad,4H J=8.0)
He,He',Hf,Hf')	6.6-6.76(m,4H)	6.5-6.7(m,4H)	6.5-6.8(m,4H)	6.3-6.8(m,7H)	6.56-6.73(m,3H)	6.64-6.74(m5H)
Hd,Hd',Hh,Hh') Ha,Ha',Hb,Hb')	7.1-7.4(m,8H)	7.05-7.34(m,7H)	7.1-7.5(m,7H)	6.9-7.3(m4H)	7.12-7.38(m,7H) 7.85-7.89(d of d 1H)	7.26-7.38(m,5H) 7.6-7.9(m,1H)
Hc,Hc'	8.55(s,2H)	8.52(s,2H)	8.48(s,2H)	8.42(s,2H)	8.54(s,1H) 8.61(s,1H)	8.57(s,1H) 8.63(s,1H)
Hl,Hl'	9.93 (bs,2H)	9.9 (t. 2H, J=2.1)	9.75 (bs, 2H)	9.85 (bs,2H)	9.87 (bs,2H)	9.8 (bs 2H)
Hp						9.82-9.9(bs,1H)

environments of the azomethine protons. This difference is not manifest in the 'H spectra of the ligands with smaller substituent groups. It is, however, shown by the ^{13}C spectra in which the number of signals reveal the asymmetry of the ligands. (See section 2.2.3).

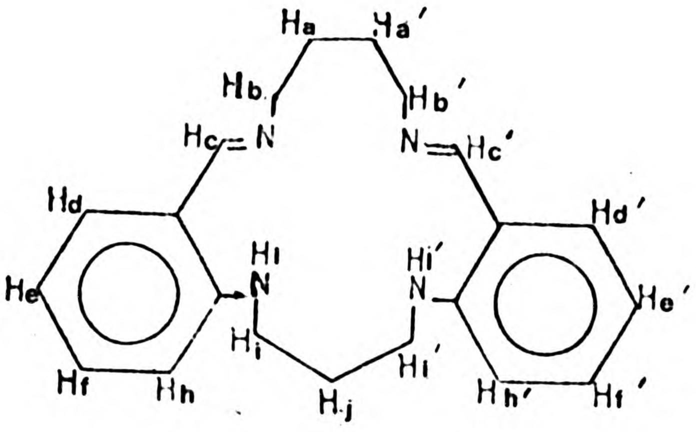
The methyl groups present as, or part of a substituent, (2Ib, $R=CH_3$; 2Id, $R=OCH_3$; 2Ie, $R=COOCH_3$) gave singlet signals which had chemical shifts which were probably dependent on the electronegativity of the adjacent oxygen atom or carbonyl group. Hence, in 2Ib the signal was a 2.39 ppm and in 2Id and 2Ie the signals were downfield, at 3.7 ppm and 3.94 ppm respectively.

In the aliphatic-bridged ligand 2IIb ($R=(CH_2)_4$) - (see Table 2.4) the azomethine protons were at low field (Section 2.5.1), although the chemical shifts were not as large as in the aromatic-bridged ligands. The methylene groups in the centre of the bridge (Ha, Ha') were at high field, and the methylene groups adjacent to the nitrogen atoms (Hb,Hb' ,Hi,Hi') showed as overlapping signals. The Hi,Hi' atoms gave rather poorly-resolved multiplets, suggesting that splitting by adjacent NH groups was occurring. As described above, this was made possible by internal hydrogen bonding of these groups with the nitrogen atoms of the imine bonds.

The dimer, (2VIII), was only slightly soluble in hot D.M.F. and it was not possible to obtain any n.m.r. spectral data.

Table 2.4

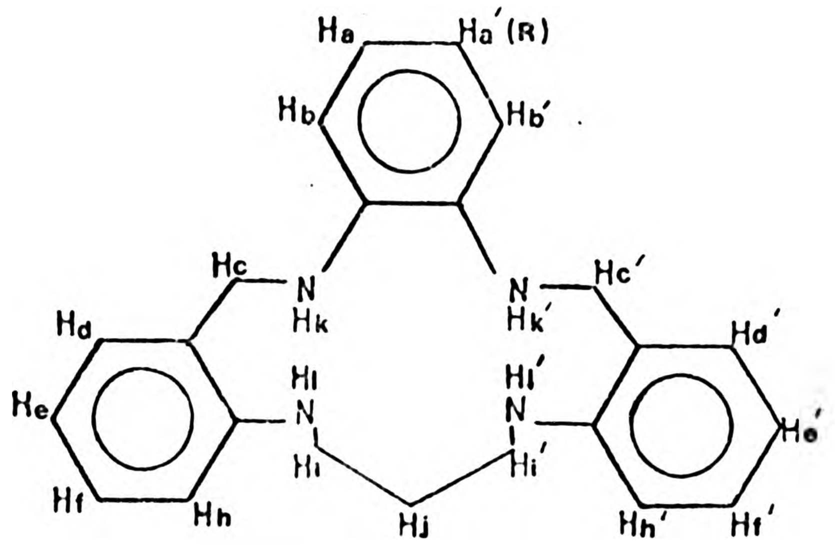
Proton signals in the spectrum of 2IIb



Ha,Ha'	1.5-1.7 (m, 4H)
Hj	1.9-2.1 (m,2H)
Hb,Hb'	3.0-3.3 (m,4H)
Hi,Hi	3.3-3.6 (m,4H)
He,He', Hf, Hf'	6.2-6.7 (m, 4H)
Hd,Hh,Hd',Hh'	6.75-7.25(m, 4H)
Hc,Hc'	8.15 (s, 2H)
Hl,Hl'	9.05 (b,s 2H)

2.2.2.2 ^{1}H n.m.r. Spectra of the quadridentate tetraamines

The ^{1}H signals in the spectra of the tetraamines could be assigned on the lines described above for the diimines. The protons are labelled as in 2XII and the chemical shifts tabulated in Table 2.5.



2 XII

The main general difference from the diimine spectra was the absence of the azomethine proton signal, and the presence of a signal from the methylene group resulting from hydrogenation of the azomethine bond. The presence of this signal was a useful confirmation of the predicted tetraamine, resulting from diborane reduction of the diimine.

Internal hydrogen bonding was a feature of the tetraamines; this was demonstrated, as in the diimines, by the coupling of the methylene protons (Hi,Hi') not only to Hj but to the anilino protons, Hl, Hl'. The quadruplet of signals that was seen was probably the result of an overlapping sextuplet. As there were two 'sets' of amino protons in the inner ring of the tetraamines, the hydrogen bonding might be expected to be more complex. In the unsubstituted tetraamine 2IHa, the signal from Hi,Hi' (the new benzylic methylene protons) was a singlet. This showed that, in contrast to Hl, the protons Hk,Hk' were exchanging too rapidly to couple with the benzylic methylene protons.

In the tetraamine 2IHb ($R=CH_3$) the benzylic methylene signal appeared as two very close singlets (220 MHz). That this signal was not in fact showing coupling to the adjacent amino proton was evident after shaking the solution with D_2O, after which no change was observed. The same effect was seen in the chlorosubstituted tetraamine (2IHc). This was evidence (confirmed by ^{13}C spectra measurements) that the asymmetry of the molecule was effecting the environment of the benzylic methylene groups on each side of the molecule and causing slight differences in their chemical shifts. (The asymmetry had a much more profound effect on the ^{13}C spectra as expected; (see below, section 2.2.3.2).) In the methoxy-substituted tetraamine (2IHd), the benzylic methylene groups gave two well-separated peaks, showing that the effect of asymmetry was more marked in this molecule; perhaps due to the size and electron-releasing effect of the methoxy group. Two effects were seen in the pattern of aromatic splitting of the tetraamines compared to the diimines. In the unsubstituted tetraamine, 2IHa, three multiplets each representing four proton signals were seen.

2IHa R=H(a')
2IHb R=CH_3(Hm)
2IHc R=Cl
2IHd R=OCH_3(Hm)

Table 2.5 ^1H n.m.r. of Quadridentate tetraamines

Compound	2IHa	2IHb	2IHc	2IMd
Hj	1.94 (quin, 2H, J=1.6)	2.0 (quin, 2H, J=2.4)	2.0 (quin, 2H, J=2.4)	2.0 (quin, 2H, J=2.2)
Hm		2.36 (s,3H)		3.8 (s,3H)
Hi,Hi'	3.35 (quad, 4H, J=1.6)	3.35 (quad, 4H, J=2.4)	3.46 (quad, 4H, J=2.4)	3.38 (quad, 4H, J=2.2)
Hc,Hc'	4.23 (s,4H)	4.15 (s, 2H)	4.15 (s, 2H)	4.15 (s, 2H)
		4.3 (s, 2H)	4.3 (s, 2H)	4.25 (s, 2H)
Hl,Hl' ,Hk,Hk'	4.2 (v. broad s, 4H)	4.67 v. broad s, 4H)	3.9 (b. s,2H) 4.5 (b. s,2H)	2.6-3.2 (b,c,4H)
He,He'Hf,Hf'	6.66-6.78(m,4H)	6.65-6.85(m, 7H)	6.7-6.9(m, 7H)	6.3-7.25 (m,11H)
Ha,Ha' ,Hb,Hb'	6.82-6.98 (m,4H)			
Hd,Hd' ,Hh,Hh'	7.16-7.28(m,4H)	7.15-7.3(m,4H)	7.15-7.3(m, 4H)	

Proton signals He,He' ,Hf,Hf' and Hd,Hd' ,Hh,Hh' were assigned by analogy with the corresponding diimine spectrum. The remaining multiplet was assigned to the protons of the phenyl bridge; no longer extensively conjugated and no longer experiencing the deshielding of the imine bonds. In the substituted tetraamines, 2IIIb($R=CH_3$) and 2IHc ($R=Cl$), two multiplets were present in which the ratio of proton signals was in reverse to that seen in the aromatic signals in the spectra of the diimines. This was again probably due to the absence of the deshielding effect of the imine bonds. A more complex pattern of aromatic signals was seen in the methoxy-substituted tetraamine, presumably because of the electron-releasing effect of the methoxy group. This effect was shown by the upfield shift of the low field aromatic signals. The amino proton signals were also considerably further upfield in the methoxy-substituted tetraamine, perhaps indicating higher electron density at the nitrogen atoms in the ligand.

2.2.3 ^{13}C Spectra of the quadridentate macrocycles

2.2.3.1 The assignment of ^{13}C signals in the quadridentate macrocycles

^{13}C spectra were obtained for the unsubstituted aromatic-bridged diimines, ie ; 2Ia (R=H); 2Ib (R=CH_3) and 2Ic (R=Cl) and the aliphatic-bridged ligand 2IIb (R=$(CH_2)_4$). ^{13}C spectra from the tetraamines derived from some of the above diimines were also obtained; 2IHa, 2IHb, 2IHc. The other tetradentate macrocycles were insufficiently soluble to give good spectra.

As a first approach to a complete assignment, the ^{13}C signals which were most likely to be from quaternary carbon atoms were selected. These were signals having some, but not necessarily all, the following characteristics;

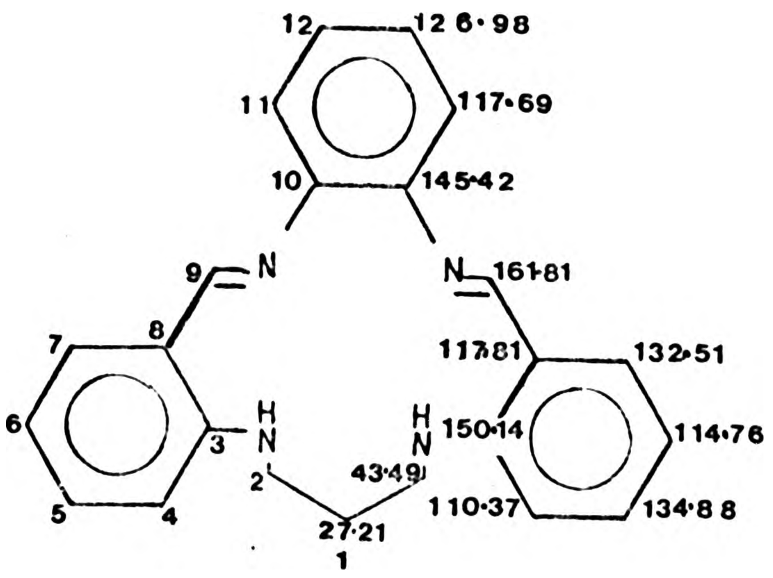
1. They were at low field[27].
2. They were at lower intensity than the other signals, due to the longer relaxation time experienced by quaternary carbon atoms.
3. The signals showed as singlets in the off-resonance spectra.

On this basis, the number of quaternary ^{13}C signals was one 'short' of the number expected for the unsubstituted macrocycle, 2Ia (R=H). This problem was resolved on 'inspection' of the off-resonance spectrum; where the coincidence of signals at ca. 117 ppm was revealed. In this spectrum, the relatively more intense signal at ca. 117 ppm was resolved into a doublet and a small singlet. It was rather unexpected to find a quaternary carbon signal at such high field, but this signal was also seen in the ^{13}C spectrum of the aliphatic-bridged macrocycles 2IIb ($R=(CH_2)_4$) and the spectra of the sexadentate diimines. This quaternary signal was eventually assigned to C8 (see 2.XIII), where the carbon atom probably experienced an upfield shift due to shielding by the imine bond. (A similar effect is seen when C=N is introduced as a substituent in benzene[27]). There is a considerable upfield shift of the C8 signal in the spectra of the tetraamines (Table 2.7).

Examination of the spectra of the aliphatic-bridged macrocycles made it possible to distinguish between the signals derived from the dialdehyde component (C1-C9), and the o-phenylene bridge part of the molecule (C10-C12, 2XIII) since the latter did not appear in the spectra of the aliphatic-bridged macrocycles. Hence the signal coincident with the quaternary carbon signal at 117 ppm observed in 2Ia could be assiged to the o-phenylene bridge.

It has been suggested that carbon shifts in aromatic rings depend on π-electron density[28,29]. In monosubstituted benzenes electron-donating substituents increase shielding at the *o*- and *p*- positions, and vice-versa[30]. In di- and tri- substituted benzenes the effects are additive,[31,23,33] although o-disubstituted benzenes show variations due to steric interactions between the substituents[30]. Although the aromatic rings forming the macrocycles were obviously subject to more complex steric effects than independent disubstituted rings, and so would not show exactly similar chemical shifts, the same general influences were held to be valid when assigning the ^{13}C signals. Hence C_4 and C_6, o- and p- to the electron-releasing fragment $-NH(CH_2)_3-$, were expected to show an upfield shift. Although some π-electron shielding of C8 might occur from the substituent imino fragment, this group was considered to be electron-withdrawing overall and C7 and C5, o and p to it, would show a downfield shift. These positions would be expected to be deshielded on the basis of resonance forms promoted by the presence of the $-NH(CH_2)_3-$ substituent as mentioned above.

Similar considerations were applied to the o-phenylene ring ^{13}C signals (C10-C12) where the carbon atoms least affected by the substituent (i.e. those meta to it) would have a chemical shift very near to that for benzene itself (128.7)[27].



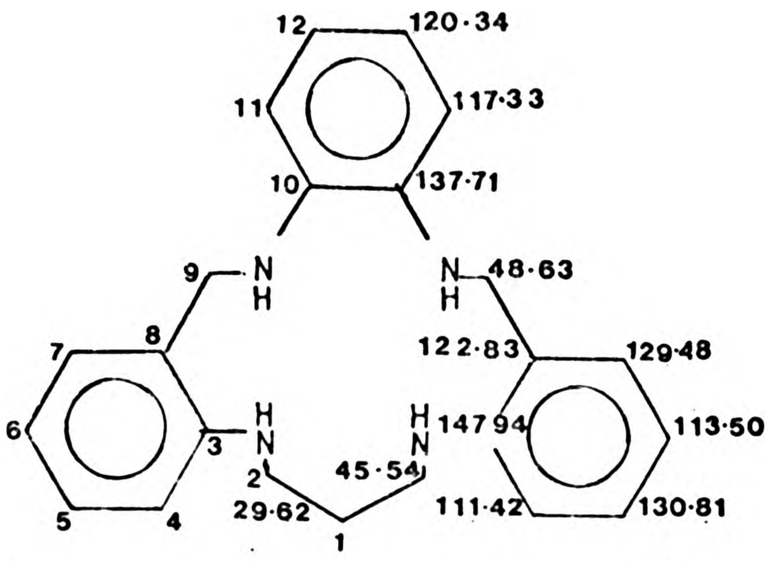
*

2 XIII (see note on 2XIV)

The signals at high field were assigned to the sp^3-hybridised carbon atoms in accordance with their chemical shift values[26] (2XIII).

Where the phenyl ring was substituted, the resulting molecular asymmetry resulted in a non-equivalence of the C10 signals and the C9 (azomethine carbon) signals, and a less marked non-equivalence of the ring carbons C5 and C7, o and p to the azomethine substituent. Of the pairs of signals, the higher-field signal was assigned to the carbon atom in the same 'half' of the molecule as the substituent (see Fig. 2.7). It was found that the chloro and methyl substituents produced similar chemical shifts, as predicted,[28] upon the carbon atom of attachment (C12), the quaternary carbon (C10), and the azomethine carbon atoms (C9,9'). As both chloro and methyl groups increase the π-electron density within the extensively-conjugated portion of the diimines, the higher field signal was assigned to the carbons nearest to the substituent, as mentioned above.

A similar approach was used to assign the ^{13}C signals of the tetraamines. When assigning the quaternary carbon atoms, the greatest differences in shift from those seen in the diimine ligands were attributed to C10 and C8, no longer part of an extensively-conjugated part of the molecule. The assignments for 2IIIa are as shown in 2XIV.



2XIV *

*where figures are not shown, values are the same as in the corresponding half of the molecule. This applies to subsequent diagrams showing chemical shift values.

Primes used in Tables 2.6,2.7 represent carbon atoms in the corresponding half of the molecule.

The assignments for the diimines and tetraamines are given in Tables 2.6 and 2.7, and the differences in chemical shifts are discussed below.

2.2.3.2. Molecular information from ^{13}C spectra

The chemical shift assignments made as above on the macrocycles 2Ia and 2Ib were compared with those reported in work on similar, dioxo-bridged ligands[34]. As shown in Fig. 2.7, the shifts were of the same order, but there was less overall upfield shift in the dioxo-bridged ligand probably because of

Table 2.6 Chemical shift values /ppm for the diimine ligands ($CDCl_3$)

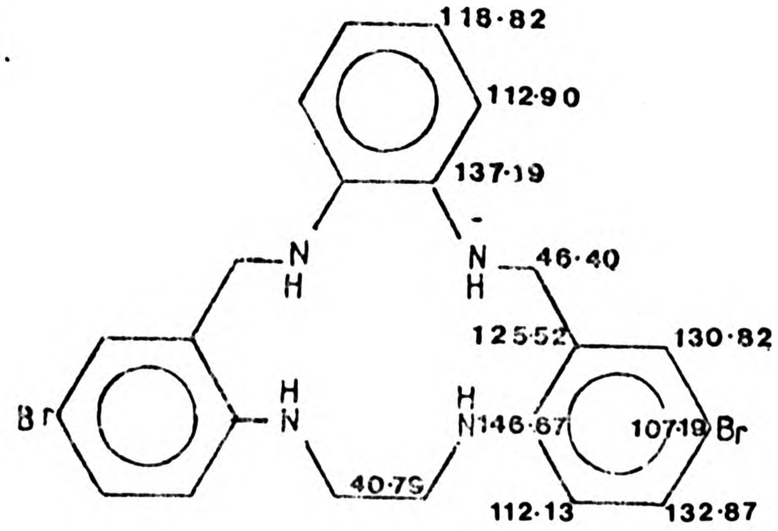
C atom	2Ia (R=H)	2Ib (R=CH_3)	2Ic (R=Cl)	2IIb (R=$(CH_2)_4$
1	27.21	27.21	27.11	28.79
2	43.49	43.39	43.42	40.28
3	150.14	150.03	150.15	150.15
4	110.37	110.26	110.47	110.59
5 5'	134.88	134.7, 134.78	134.15, 134.97	134.01
6	114.76	114.65	114.90	114.43
7,7'	132.51	132.25, 132.36	132.09, 132.78	131.41
8	117.69	117.26	117.57	117.43
9,9'	161.81	161.08, 161.56	161.42, 161.97	164.37
10,10'	145.42	142.82, 145.17	143.99, 146.24	61.24
11,11'	117.69	117.76, 118.28	117.97, 118.60	29.30
12,12'	126.98	136.86, 127.53	136.16, 126.59	Not present
13(CH_3)	Not present	21.18	Not present	Not present

Table 2.7 Chemical shift values (/ppm) for the tetraamine ligands ($CDCl_3$)

C atom	2IHa (R=H)	2IHb ($R=CH_3$)	2IHc (R=Cl)
1	29.62	29.59	29.66
2	45.54	45.54	45.60
3,3'	147.94	147.84, 148.13	147.69, 148.0
4,4'	111.42	111.36, 111.43	111.53, 112.83
5	130.81	130.49	131.96
6	113.50	113.88, 114.54	114.87
7	129.48	129.36, 129.43	129.54, 129.66
8	122.83	122.85, 123.03	122.25, 122.49
9	48.63	48.54, 49.06	48.31, 48.73
10	137.71	134.52, 138.58	135,34, 139.53
11,11'	117.33	117.18, 117.36	117.33, 117.57
12,12'	120.34	130.75, 119.99	126.10, 119.09
13(CH_3)	Not present	21.18	Not present

the reduction in electron density over the macrocycle due to the electron-withdrawing effect of the carbonyl groups. It is interesting to note that in the t-butyl-substituted dioxo-bridged macrocycle significant chemical shift differences between the two 'sides' of the molecule were noted only in the o-phenylene bridge. In the present work, small differences were observable, however, as noted in Fig. 2.7. In comparing the tetraamines with the diimines, an upfield shift of the signal of C8, the carbon of attachment to the 'new' benzylic methylene group, was noted. This was probably due to an electron-releasing effect of the adjacent methylene group. An additional difference was the greater degree of molecular asymmetry in the substituted tetraamines in which many of the ring carbons showed pairs of signals. (See Table 2.7). The greater flexibility of the tetraamines could allow greater steric differences between the 'halves' of the molecules; this is indicated by the ^1H n.m.r. data, but shown clearly here where the ^{13}C shifts are much more sensitive to steric effects.

In an attempt to confirm the assignment of the aromatic ring carbons, the ^{13}C spectrum of the brominated ligand[11] was obtained (2XV).



2XV

2Ia

2Ib

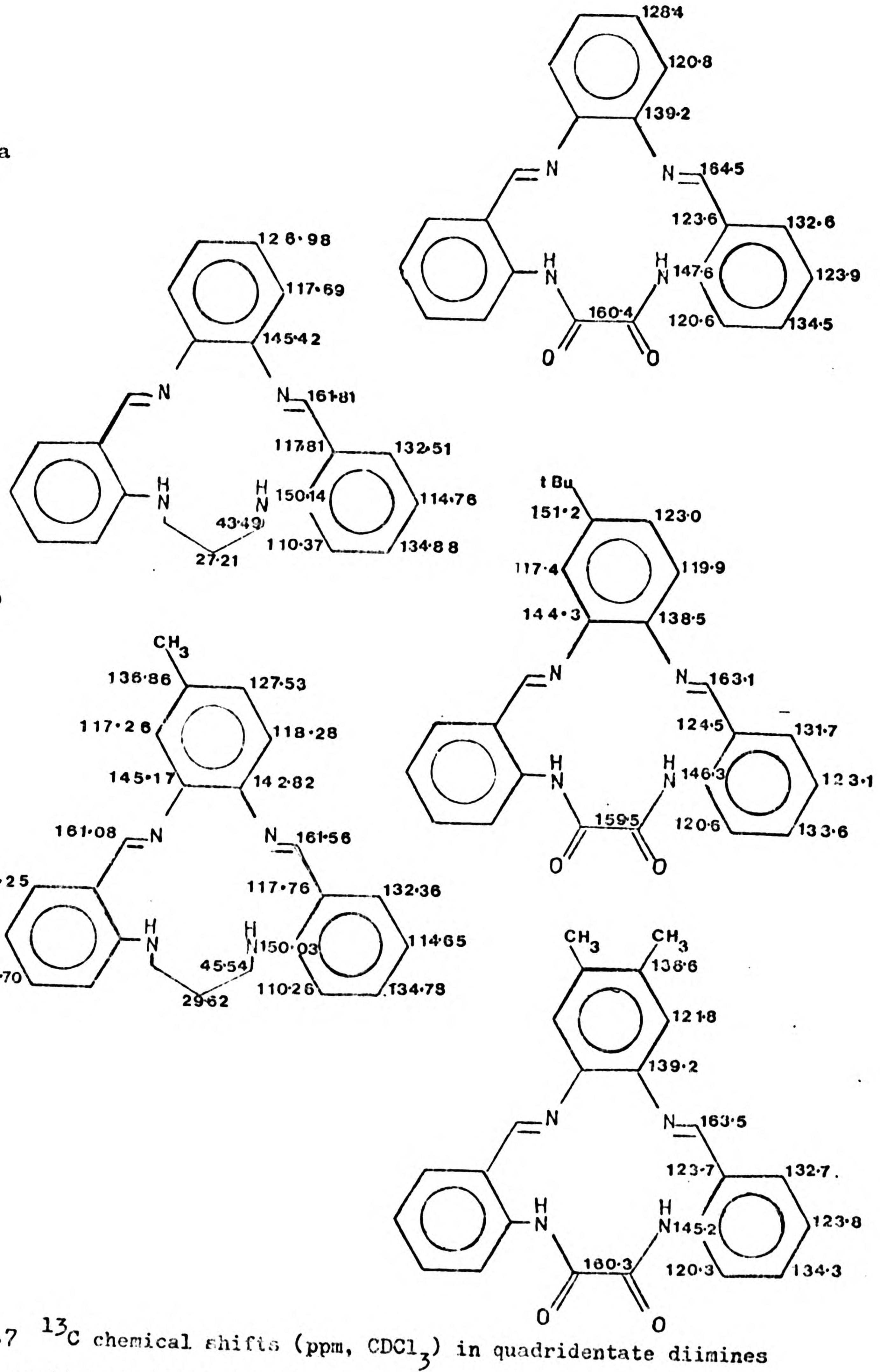


Fig 2.7 ^{13}C chemical shifts (ppm, $CDCl_3$) in quadridentate diimines (Data on dioxo-bridged ligands from reference 34).

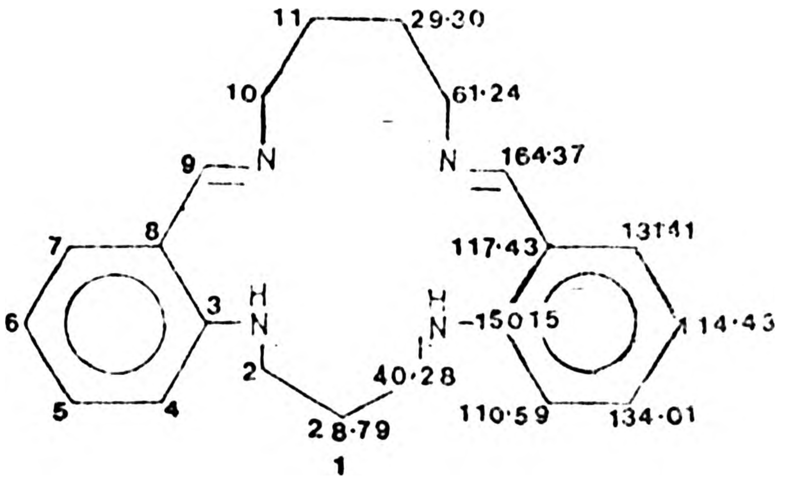
Small shift differences were to be expected, arising from solvent interactions, and the difference in the length of the methylene bridge between 2IHa and the brominated ligand, 2XV, shown above. The most striking difference was the disappearance in the brominated ligand, of the signal at 113 ppm seen in the unsubstituted analogue, thus confirming the position of the assignment at C6. (2XIV)

In monobrominated benzene the upfield shift experienced by the carbon attached to bromine was reported as ca. 5.5 ppm[28], with the signals of the carbon atoms ortho to the bromine-substituted carbon shifted downfield ca. 3 ppm[28]. In this compound, 2XV, the upfield shift is of the same order (ca. 8 ppm) for the carbon of attachment. The carbons atoms ortho to the bromine showed a downfield shift of ca. 1.5 - 2 ppm.

Another interesting feature of the spectrum of the brominated ligand was the almost equal intensity of the signals, including those of the quaternary carbon atoms. In the case of the ^{13}C nuclei bonded to ^{79}Br, spin-lattice relaxation can occur by means of scalar interaction[35]. In addition, ^{13}C - ^{79}Br and ^{13}C - ^{81}Br dipole-dipole relaxation dominates over ^{13}C - ortho - ^{1}H relaxation for the carbon of attachment, so that an efficient relaxation mechanism exists for this carbon atom. However it is interesting that in this compound shorter relaxation times caused all the quaternary ^{13}C signals to be intensified. This could not be due to the inductive effect of the heavy halogen atom, since the chemical shifts remain largely unchanged. Therefore some other relaxation mechanism must be looked for. This could perhaps be found in the shorter T_1 values for monosubstituted benzenes[36], reflecting longer molecular correlation times due to larger size, solvent interactions and other effects. The slower molecular tumbling of larger molecules leads to a decrease in spin-lattice relaxation time. The bromine atom is bulky, and may also contribute to hydrogen bonding with the solvent DMSO - both factors which may further slow molecular tumbling.

The -NH groups would hydrogen-bond in DMSO and there is evidence that hydrogen-bonded protons cause a decrease in ring carbon T_1 values. For example, T_1 values for the ring carbons in aniline decrease markedly in d-DMSO[37].

A ^{13}C nmr spectrum of the tetramethylene-bridged ligand 2IIb was obtained; **below.** (Table 2.6).



On standing in $CDCl_3$ solution, the ligand showed signs of decomposition, as shown by the appearance of extra signals in the region of the aliphatic carbon peaks. The freshly-prepared solution, however, gave an interpretable spectrum with values comparable to those obtained for 21a, in the dialdehyde moiety. There was an interesting feature of this spectrum - this was the very short relaxation times shown by the quaternary carbon atom signals, compared to the o-phenylene bridged ligands. Without further investigation it was not possible to say whether this was a general feature of the aliphatic-bridged ligands, or whether, in this case, it was due to small amounts of decomposition products in solution. These might provide a polar medium in which spin-matrix relaxation could be facilitated.

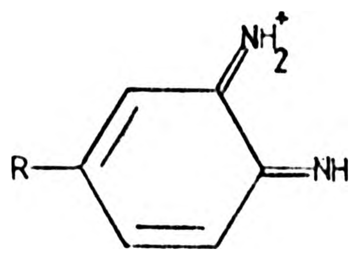
2.2.4. Mass spectra of the quadridentate ligands

2.2.4.1 Mass spectra of the diimines

The mass spectra of the quadridentate diimines gave mass peaks with m/e values in good agreement with the calculated values, thus giving further confirmation of their characterisation (Table 2.8). In the case of ligands 2Ia (R=H), 2Ib (R=CH_3) and 2Id (R=CH_3O) the mass peaks were the base peaks, an indication of the greater stability of these ligands.

On careful comparison of the spectra of the diimines it was noted that certain fragmentation patterns were common to the series of diimines. These common cleavage routes are shown in Table 2.9.

In route I, the smaller groups, containing the substituent R could have the possible structure;



2XVI

It was interesting that 2XVI, where R=COOH, was present at a comparatively high percentage (59%) although decarboxylation

2.2.4. Mass spectra of the quadridentate ligands

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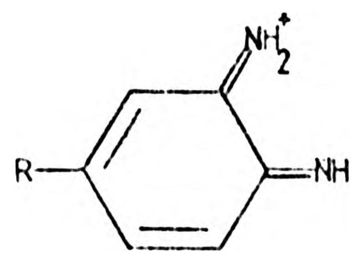
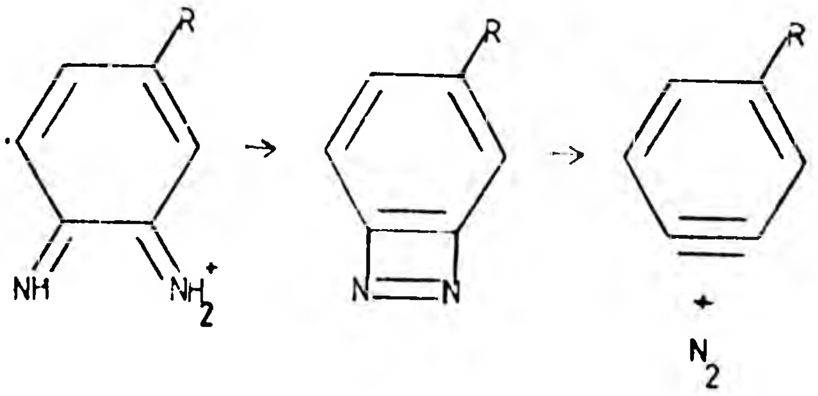


2XVI

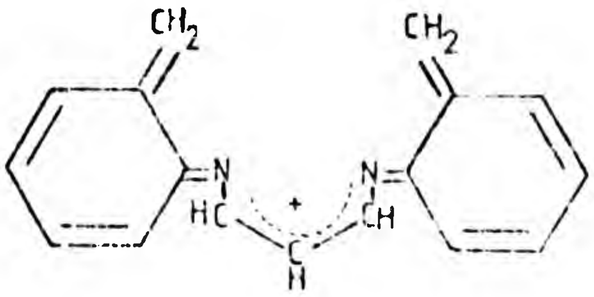
It was interesting that 2XVI, where R=COOH, was present at a comparatively high percentage (59%) although decarboxylation would be a likely reaction. The unexpected stability of the carboxy-substituted compound was also shown by the high percentage of the mass peak (Table 2.8) and the absence of a peak corresponding to loss of CO_2 from the molecular ion.

In addition to structure 2XVI there is the interesting possibility of a rearrangement involving loss of hydrogen and nitrogen, to give benzyne.



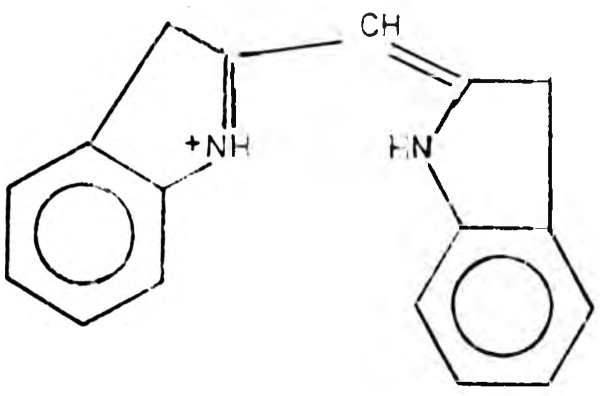
2XVII

In the spectra of the ligands 2 I a (R=H) and 2 I b (R=CH_3) this fragment was present at 4% intensity. Benzyne was not seen in the spectra of the ligands 2 I c. (R=Cl) and 2 I f (R=CO_2H). In the spectra of 2 I d (R=OCH_3) and 2 I e (R=$COOCH_3$) the accurate mass values for the substituted benzynes (106.04186 and 134.03677 respectively) did not correspond well with the observed values. The large fragment $C_{17}H_{15}N_2$ resulting from cleavage route I was present in the spectra of all the diimines. A possible structure is as shown.



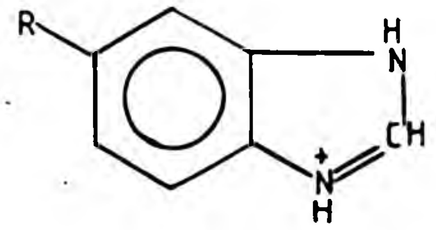
2XVIII

An alternative structure, involving more rearrangement but giving a more stable ring system, is as follows;



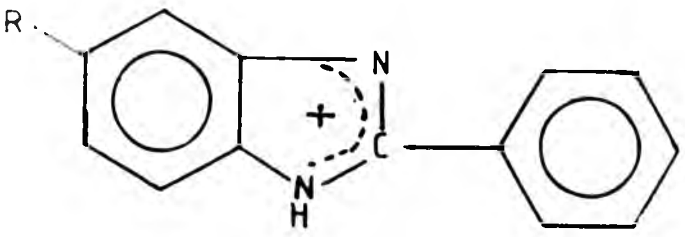
2XIX

This structure could cleave across the linear single bond to give the fragment of m/e ca. 118 (2.XXIV). For the proposed cleavage route II the large fragment at m/e 236 ($C_{16}H_{16}N_2$) was not seen in the ligand spectra; however, it was very probable that this would cleave immediately into the common unit C_8H_8N. In the spectrum of 2If (R=COOH) this route did not seem to be applicable as neither the small fragment $C_7H_6N_2R$, or the decarboxylated unit $C_7H_7N_2$ were seen. In the case of ligand 2Ic (R=Cl) the validity of this route was also doubtful, because although the structure $C_7H_6N_2{}^{35}Cl$ was present at rather low intensity, the fragment containing ^{37}Cl was not seen. However, for the other ligands this seemed to be an important route since the mass fragments $C_7H_6N_2R$ were present in the spectra, and the accurate masses were in good agreement with the calculated masses (See Table 3, for R=H). A possible structure is as shown;



2XX

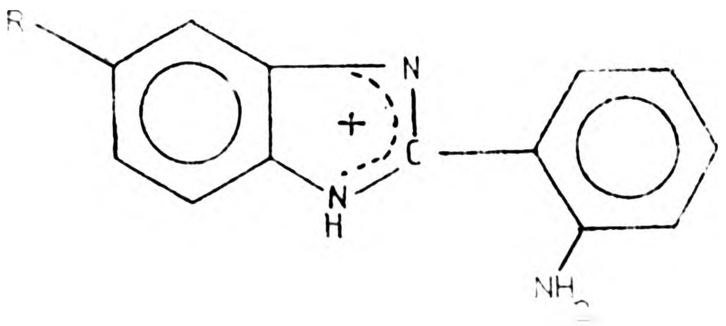
The cleavage illustrated as route III appeared to be important for all the diimines, since the fragments $C_{13}H_9N_2R$ were seen in all the spectra, in good agreement with the calculated accurate masses. (Table 3, for R=H). A possible structure is as shown;



2XXI

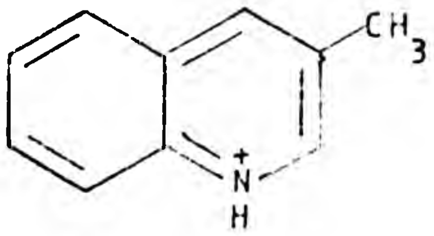
The smaller complementary fragment $C_{10}H_{12}N_2$ was not seen in any of the diimine spectra, but this would be expected to break down further to form the stable C_8H_8N unit.

All the diimine spectra showed both fragments resulting from cleavage route IV, and these were in good agreement with the calculated accurate masses. The structure of $C_{13}H_{10}N_3R$ could be as shown (2XXII)



2XXII

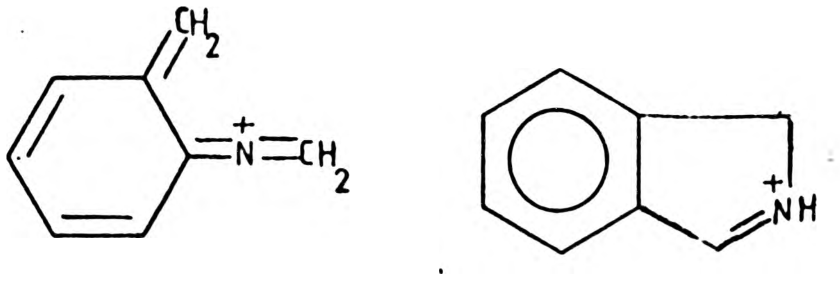
A suggested structure for $C_{10}H_{10}N$ is as follows



2XXIII

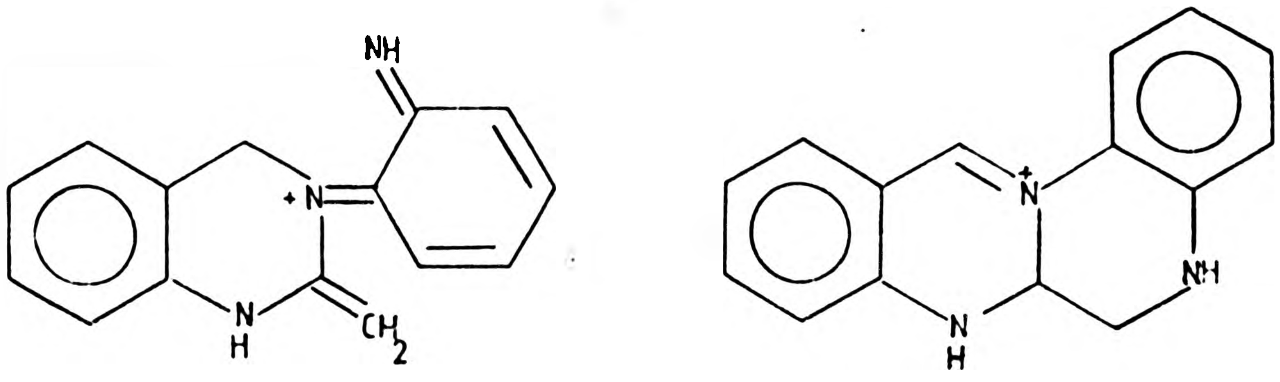
A fifth cleavage route, route V, gives rise to the characteristic, apparently very stable fragment C_8H_8N. The complementary fragments were also seen in all the spectra (Table 2.10) and the m/e values seen were in good agreement with the calculated accurate masses.

Suggested structures for C_8H_8N are as follows;



2XXIV

Possible structures for $C_{15}H_{14}N_3$ include;



2XXV

Ligands 2Ib (R=CH_3), 2Id (R=OCH_3) and 2If (R=COOH) only, had another fragmentation pattern in which the small unit C_7H_8N was seen (ca. 20%) leaving the complete remaining fragment ($C_{15}H_{14}N_3R$) ca. 15% intensity). This indicated that the substituent group might stabilise the larger fragment in these cases, and was a further example of the surprising stability of the carboxy group to decarboxylation.

Suggested structures for the units mentioned above are given.(Fig 2.8)

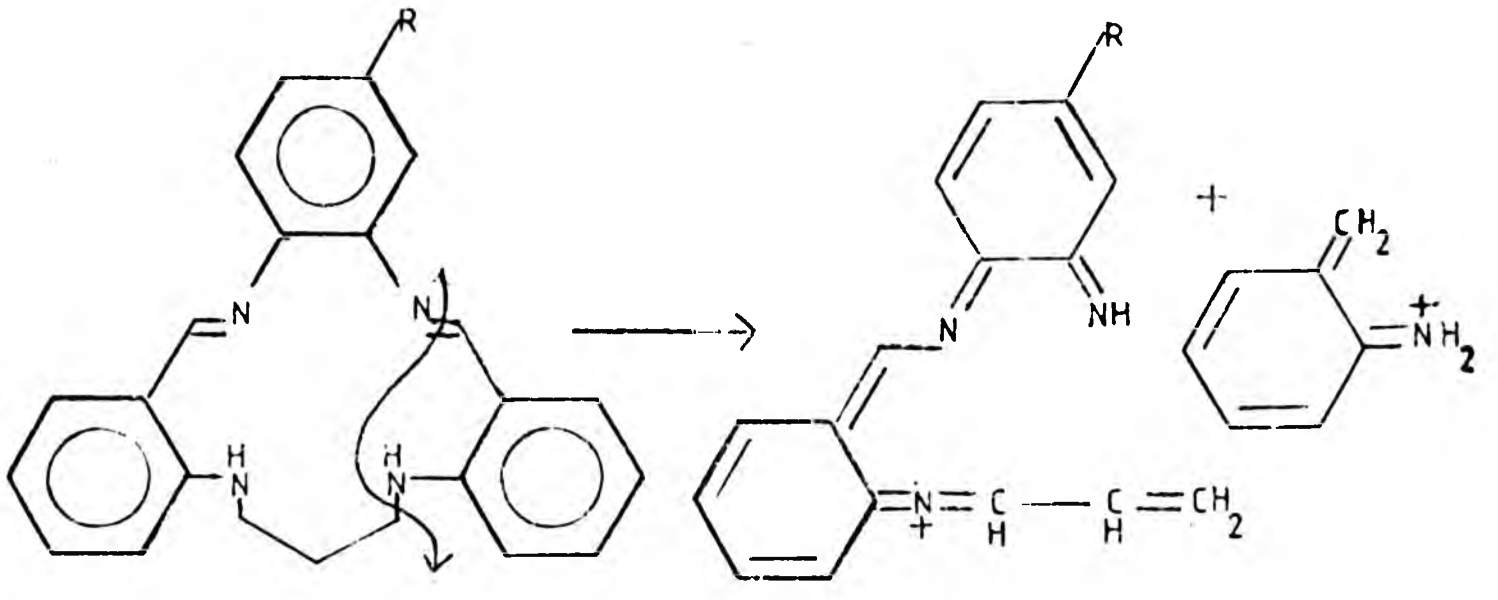
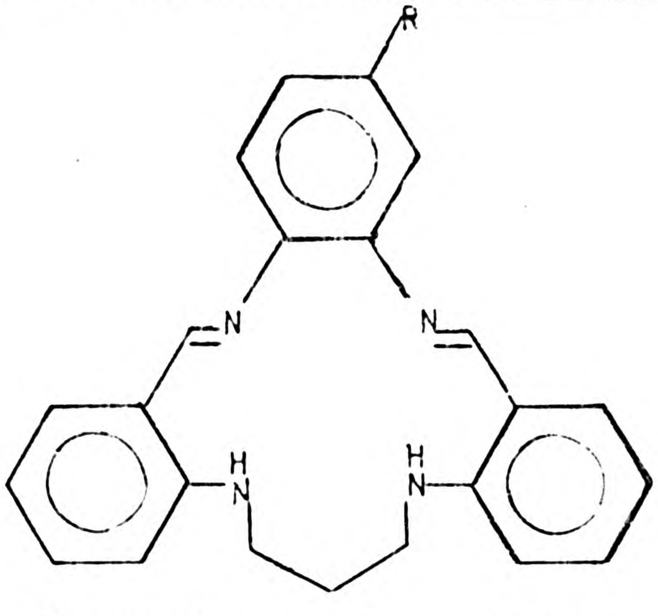


Fig. 2.8 Additional splitting route observed for R=CH_3, OCH_3 and COOH

Table 2.8

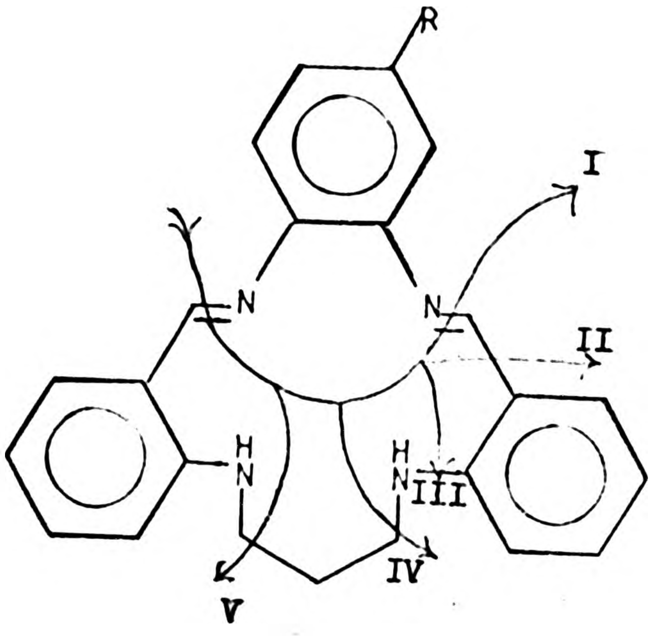
Molecular ions in the spectra of the diimine ligands



Ligand	Measured mass	Intensity %	Calculated mass
2Ia (R=H)	354.1844	100	354.1844
2Ib (R=CH_3)	368.2002	100	368.2001
2Ic (R=^{35}Cl)	388.1451	88.5	388.1454
(R=^{37}Cl)	390.1423	28	390.1452
2Id (R=OCH_3)	384.1949	100	384.1949
2Ie (R=CO_2CH_3)	412.1898	80	412.1898
2If (R=CO_2H)	398.1739	74	398.1741

Table 2.9

Common cleavage routes in the spectra of the diimine ligands.



I	II	III	IV	V
$C_6H_6N_2R$ (m/e 107,R=H)	$C_7H_6N_2R$ (m/e 119,R=H)	$C_{13}H_9N_2R$ (m/e 194,R=H)	$C_{13}H_{10}N_3R$ (m/e 209,R=H)	$C_{15}H_{13}N_3R$ (m/e 236,R=H)
$C_{17}H_{15}N_2$ (m/e 247)	$C_{16}H_{16}N_2$ (m/e 236)	$C_{10}H_{12}N_2$ (m/e 160)	$C_{10}H_{10}N$ (m/e 158)	C_8H_8N (m/e 116)

Table 2.10.

M/e values and abundances for fragments containing the 4-substituted benzene rings from the diimine macrocycles 2Ia-f

Compound	I $C_6H_6N_2R$	II $C_7H_6N_2R$	III $C_{13}H_9N_3R$	IV $C_{13}H_{10}N_3R$	V $C_{15}H_{13}N_3R$
2Ia (R=H)	107 (6%)	119 (25%)	194 (24%)	209 (63%)	236 (32%)
2Ib (R=CH_3)	121 (10%)	133 (19%)	208 (18%	223 (65%)	250 (27%)
2Ic (R=^{35}Cl	141 (4%)	-	228 (16%)	243 (40%)	270 (21%)
R=^{37}Cl)			230 (4%)	245 (10%)	272 (7%)
2Id (R=OCH_3)	137 (19%)	149 (30%)	224 (16%)	239 (68%)	266 (27%)
2Ie (R=CO_2CH_3)	165 (6%)	177 (18%)	252 (8%)	267 (50%)	294 (29%)
2If (R=CO_2H)	152 (59%)	-	238 (16%)	253 (52%)	280 (29%)

Table 2.11

Measured and calculated accurate mass values for fragments from routes I-V for 2Ia (R=H)

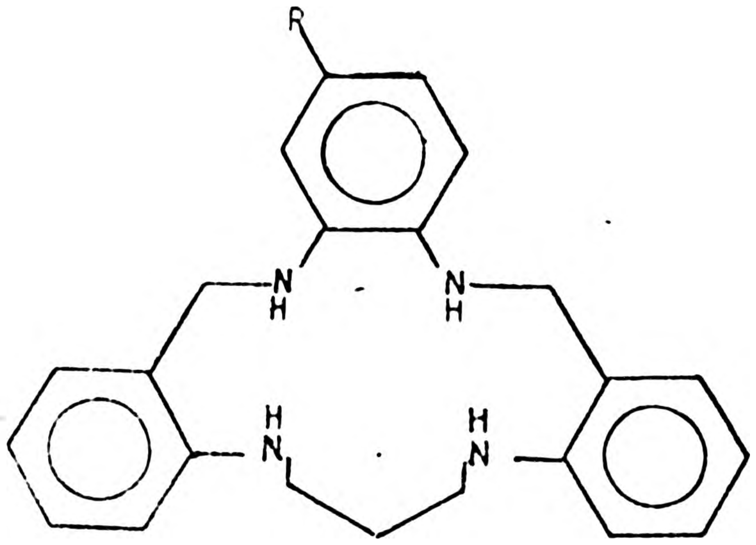
Route	Fragment	Measured mass	%	Accurate mass
I	$C_6H_7N_2$	107.0632	6%	107.0609
	$C_{17}H_{15}N_2$	247.1232	76%	247.1235
II	$C_7H_7N_2$	119.0624	25%	119.0609
	$C_{16}H_{16}N_2$	Not present		
III	$C_{13}H_{10}N_2$	194.0839	24%	194.0843
	$C_{10}H_{12}N_2$	Not present		
IV	$C_{13}H_{11}N_3$	209.0952	63%	209.0952
	$C_{10}H_{10}N$	144.0806	12%	144.0813
V	$C_{15}H_{14}N_3$	236.1172	32%	236.1187
	C_8H_8N	118.0647	47%	118.0657

2.2.4.2. Mass spectra of the tetraamines

The m/e values of the mass peaks obtained for the quadridentate tetraamines were in good agreement with the calculated values (Table 2.12). This provided evidence for the characterisation of these new compounds. In general, the mass spectra of the tetraamines were characterised by more extensive fragmentation of the molecules into small units. This was in contrast to the diimines, where initial fragmentation seemed to occur preferentially through the imine bonds. In addition, the dehydrogenated ligand fragment was observed only in the spectra of 2IHb ($R=CH_3$) and 2IHd ($R=OCH_3$). The base peak in the spectra of the tetraamines 2IHa (R=H), 2IHb ($R=CH_3$), 2IHc (R=Cl) was the fragment C_8H_8N (2.XXIV). In the spectrum of 2IHd ($R=OCH_3$), the base peak corresponded to the diamine, $C_7H_{10}N_2O$ (observed m/e = 138.0795, calculated value=138.0793). Only one splitting route was found to be common to all the ligands. The resulting fragments, and their observed and calculated values are compared in Table 2.13.

Table 2.12.

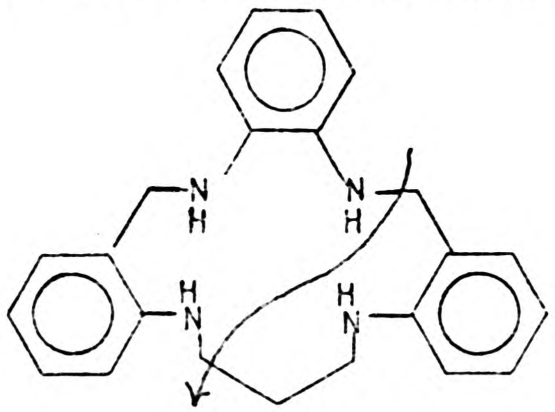
Molecular ions in the spectra of the tetraamine ligands.



Ligand	Measured mass	Intensity %	Calculated mass
R=H	358.2155	60.4	358.2157
R=CH_3	372.2312	60.4	372.2313
R=^{35}Cl	392.1769	53.7	392.1767
R=^{37}Cl	394.1719	17.1	394.1731
R=OCH_3	388.2262	98.2	388.2262

Table 2.13

The common cleavage route in the spectra of the tetraamine ligands

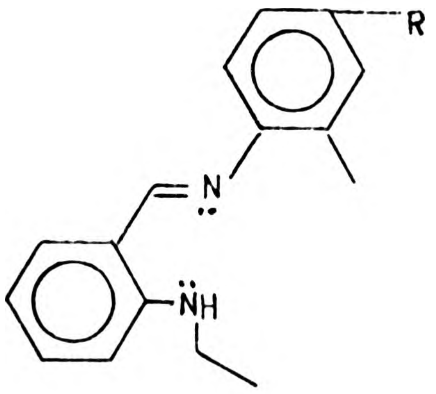


Fragment	R	Observed value	Intensity %	Calculated value	Fragment	R	Observed value	Intensity %	Calculated value
$C_{14}H_{13}N_3R$	H	224.1162	3.0	224.1187	$C_9H_{10}N$	H	132.0793	46.2	132.0813
	CH_3	238.1360	11.0	238.1344		CH_3	132.0806	68.8	
	^{35}Cl	258.0770	4.9	258.0797		^{35}Cl	132.0793	56.7	
	OCH_3	254.1280	8.4	254.1290		OCH_3	132.0802	56.5	

2.2.5. Electronic spectra of the quadridentate ligands

The λ_{max} and ε_{max} values obtained for the diimines 2Ia-f and 2IIb and the fully reduced free ligands 2IHa-2IHd are tabulated in Table 2.14.

The yellow diimines contained the benzaldehydeanil chromophore, as below; (2XXVI)



2XXVI

The absorption maxima in these compounds extend over a range from the near u.v. into the visible region. Since large portions of the molecule are conjugated the strong absorption bands are expected to arise from $\pi - \pi^*$ transitions which give intense bands, (ε_{max} ca. 63,000 in conjugated polyenes).[38] Transitions of the $\pi - \pi^*$ type occur in the u.v. region for isolated bonds, but would be expected to occur at longer wavelengths in conjugated systems.

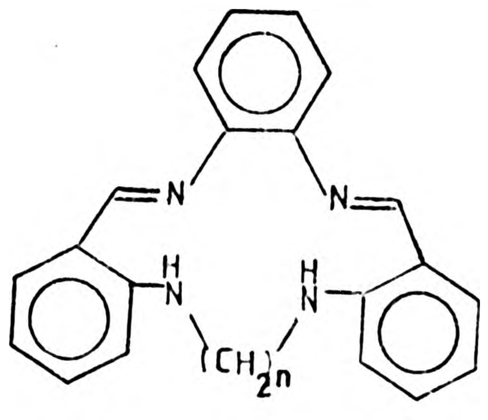
Table 2.14

U.v/visible spectra of the quadridentate diimines and tetraamines in methanol (ε = litre mol.$^{-1}$cm.$^{-1}$, λ = nm)

Diimine	λ_{max}	ε	Tetraamine	λ_{max}	ε
2Ia	242	33,800	2IHa	297	12,900
(R=H)	380	15,000	(R=H)		
2Ib	255	54,800	2IHb	255	44,800
(R=CH_3)	280	31,900	(R=CH_3)	308	9,900
	395	19,200			
2Ic	255	68,900	2IHc	305	13,000
(R=Cl)	395	23,700	(R=Cl)		
2Id	239	37,250	2IHd	364	21,800
(R=OCH_3)	256	36,100	(R=OCH_3)		
	300	13,400			
	418	14,200			
2Ie	240	57,700			
(R=$COOCH_3$)	395	17,300			
2If	240	36,300			
(R=COOH)	395	13,400			
2IIb*	270	17,800			
	360	9,500			

*measured in CH_2Cl_2

The n -π^* transitions which are possible with double bonds containing nitrogen having a lone pair, such as the imine bond, and with anilino nitrogen atoms linked to an aromatic π-system are symmetry forbidden so that the band is weak ($\varepsilon_{max} < 100$)[21]. In these compounds and in analogous compounds (2XXVII) the values of λ_{max} and ε_{max} are of the same order. The high values of ε_{max} are probably due to the 'end absorption' of π-π^* transitions overlapping the less intense n-π^* absorption band which occurs in the near u.v/visible region. In complex molecules of this type, it is not possible to distinguish precisely between the types of electronic transition occurring. Substitution of the bridging o-phenylene bridge lowers the molecular symmetry and the degeneracy of the molecular orbitals, allowing more possibilities for electronic transitions. When R was an electron-donating group, in 2Ia ($R=CH_3$) and 2Id ($R=OCH_3$) the spectra were more complex. When $R=OCH_3$, other n - π^* transitions between the oxygen atoms and the aromatic π-system were possible. The spectrum of this diimine (2Id) showed the lowest-energy transitions, bringing an absorption band fully within the visible region (Table 2.14). However, the net effect of the



2XXVII

n = 2, λ_{max} = 378 (nm)

ε_{max} = 13,500(litre mol^{-1}cm^{-1})

n = 3, λ_{max} = 380 (nm)

ε_{max} = 15,000(litre mol^{-1}cm^{-1})

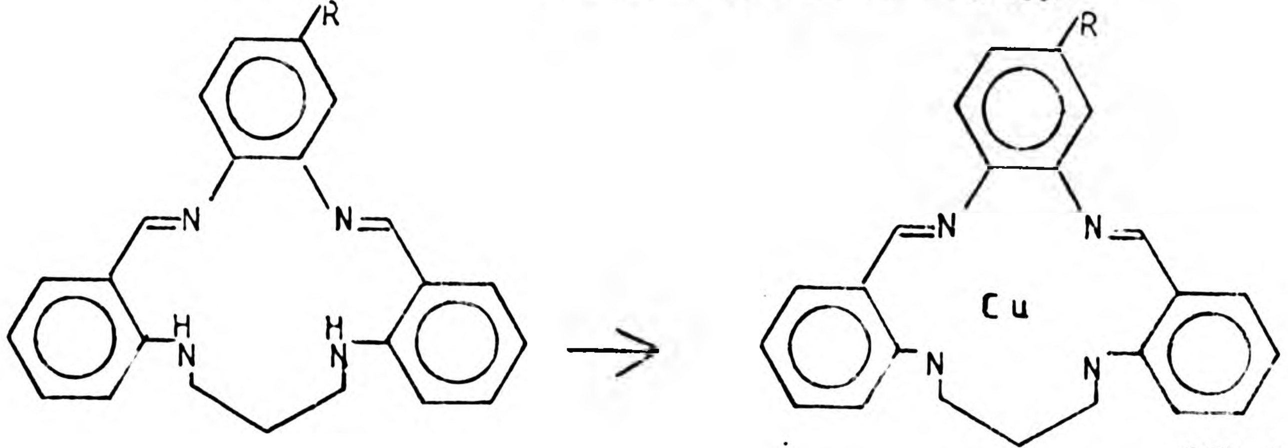
transition occurring in the chromophore was to make the diimine ligands bright yellow.

The aliphatic-bridged macrocycle, 2IIb, was white and gave two bands in the ultra-violet region. These were much less intense than those for the other ligands (Table 2.14) since the contribution of $\pi - \pi^*$ transitions would be considerably less.

The dimer of 2IIa, was too insoluble for u.v/ visible absorption measurements to be made.

2.3 Preparation of the copper complexes of the quadridentate ligands

Neutral copper(II) complexes of the diimines were made by refluxing the methanol solution or suspension of the diimine with copper(II) acetate for a short time as in Fig.2.9



$+2CH_3COOH$

$+ Cu(CH_3COO)_2$

$Cu[2I(a—e)-2H]$

2Ia R=H

2Ib $R=CH_3$

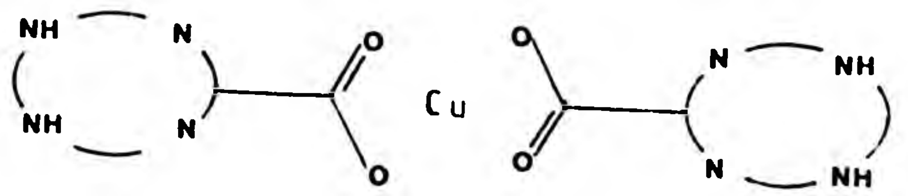
2IC R=Cl

2Id $R=OCH_3$

2Ie $R=COOCH_3$

Fig. 2.9 Preparation of copper complexes of the quadridentate diimines

In each case the solution changed colour immediately and the brown or red-brown complex separated. Better results were obtained for Cu(2c-2H) (R=Cl) when the ligand was dissolved in dichloromethane, as described in the Experimental section, 2.5.3. The preparation of the copper complex of **2If** (R=COOH) gave a product for which the analysis indicated a stoichiometry of one mole of copper to two moles of ligand. The infra-red spectrum of this compound suggested the coordination of the carboxyl group (see 2.4.1). It was not possible to obtain an electron-impact mass spectrum. The infra-red spectrum had a peak attributable to NH stretch. The only formulation which is consistent with the stoichiometry and the data appears to be as shown. (2XXVIII)

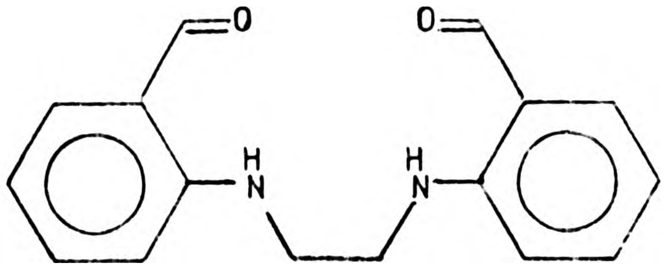


2XXVIII

Several copper carboxylate complexes of anilino bases have been reported[40]; however 2XXVIII is an unexpected formulation because the macrocyclic complex (with Cu^{II} in the N_4 ring) would be expected to have a very high stability constant - this is a feature of the 'macrocyclic effect'[41]. However dinuclear complexes of arylacetic acids show a low solubility in methanol and ethanol,[42] and 2XXVIII may separate from solution before the CuN_4 complex can be formed.

Subsequent work[43] has described a 'metal template' preparation of the copper complexes Cu(2a-2H) (R=H) and Cu(2c-2H) (R=Cl) as the hemihydrate and hydrate respectively. The preparation of the complex Cu(2b-2H) (R=CH_3) was attempted in this work but was reported as unsuccessful.

The aliphatic-bridged ligand, 2IIb did not form a stable neutral complex; this property had been observed in a range of similar compounds, in which the dialdehyde, 2XXIX , was used[44].

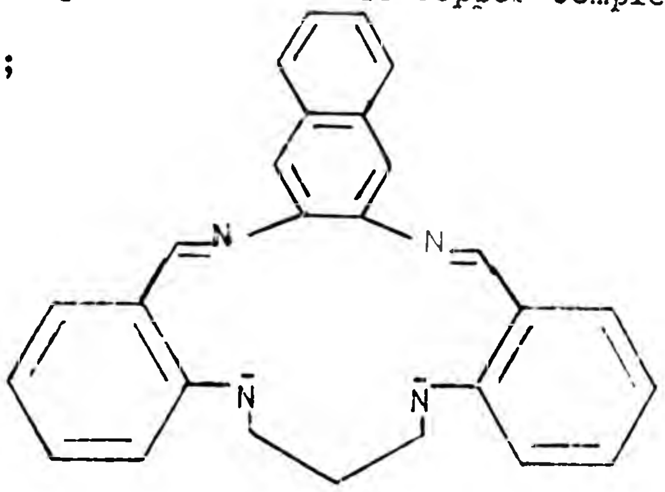


2XXIX

Earlier work, in which metal complexes of a number of aliphatic-bridged ligands were formed by a template method,[1,9] reported stable neutral copper complexes from the reaction between 2XXIX and diaminoethane and diaminopropane in the presence of copper acetate, while a similar complex was **not** reported from a reaction of 2III with diaminopropane. It is difficult to explain the apparent instability of these particular complexes. As a stable cationic complex was formed as a diperchlorate, it seems that the tetramethylene bridge destabilised the anilide anion;

Presumably the electron-releasing effect of the aliphatic bridge is unfavourable to the canonical form 'b' as above.

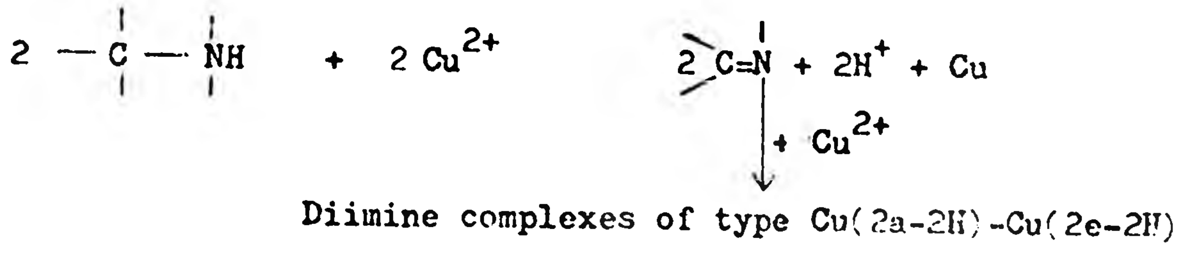
Recent work[43] has produced a stable copper complex with a **napthalene bridge** ;



2XXX

Such a system will enhance the stability of the anilide anion by providing an extensive conjugated area.

It is interesting that when the tetraamines (2IIIa-d) were treated with alcoholic solutions of copper(II) acetate, dehydrogenation of the benzyl-amino bonds occurred, and copper complexes were formed with infra-red spectra which were identical to those of the neutral diimine complexes (Cu(2a-2H)-Cu(2e-2H)). Copper metal was deposited in these reactions;

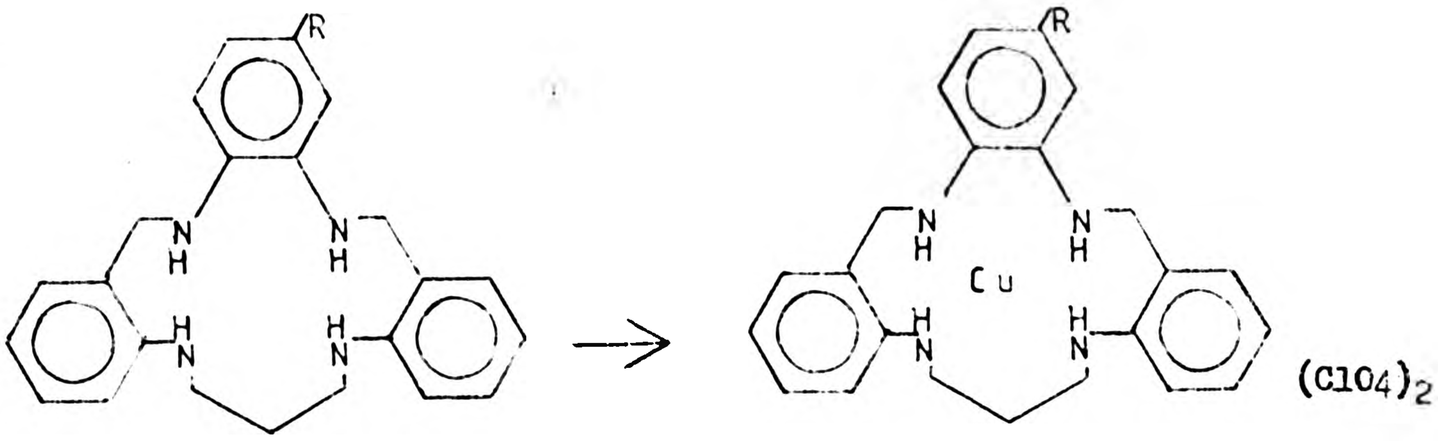


$$2\ -\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{N}}H \quad + \quad 2\,Cu^{2+} \qquad 2\ {>}C{=}\overset{|}{N} + 2H^{+} + Cu \;\Big\downarrow{+\,Cu^{2+}}$$

Diimine complexes of type Cu(2a-2H)-Cu(2e-2H)

Presumably in the presence of excess copper ions, the diimine complexes would be formed as shown above. In an attempt to isolate stable Cu^{II} complexes of the tetraamine ligands it was decided to make the copper(II) salts of a strong acid (perchloric acid), on the basis that the dehydrogenation reactions referred to above are favoured by conditions which facilitate the removal of protons from the ligand; i.e. the presence of a weak acid anion.

The general reaction for the formation of the tetraamine copper complexes was as shown in Fig. 2.10



\+ $Cu(ClO_4)_2$

2IH (a,b,c,d)

$[Cu(2IHa\text{-}d)](ClO_4)_2$

2IHa R=H

2IHb $R=CH_3$

2IHc R=Cl

2IHd $R=OCH_3$

Fig 2.10 Preparative scheme for copper perchlorate complexes of tetraamines

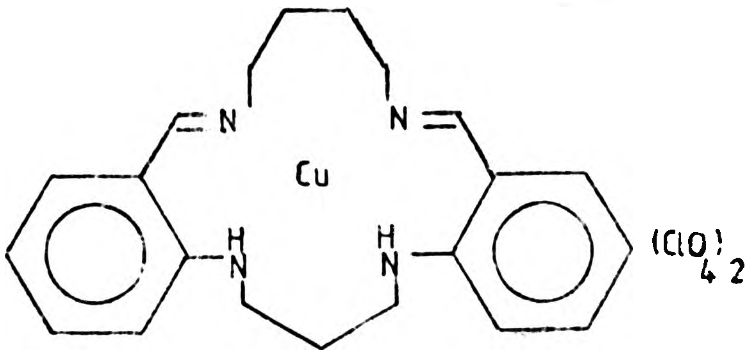
2.4 Physical properties of the copper complexes

2.4.1. Infra-red spectra of the copper(II)complexes of the quadridentate diimines and tetraamines

The spectra of the copper complexes showed the same major peaks as those of the diimines and tetraamines. The infra-red spectra of the range of neutral copper complexes are compared in Table 2.15. The infra-red spectra of the copper perchlorate complexes are compared in Table 2.16.

The spectra of the copper complexes showed the same major peaks as those of the ligands, with slight alteration in wavenumber. A comparison of the ligand spectra (2Ia, R=H and 2IHa, R=H) with the copper complexes is made in Table 2.17. In general the peaks in the spectra of the copper complexes were broader than those in the spectra of the corresponding ligands, and there were differences in the fingerprint region of the spectrum. As expected, the band due to NH stretch at ca. 3300 cm^{-1} was not seen in the spectra of the neutral copper complexes, except in the spectrum of Cu(2If-2H) (R=COOH). Analytical results showed the stoichiometry of this complex to be one mole of copper to two moles of ligand. On the basis of the infra-red evidence it was possible that the copper was complexed by the carbonyl groups (2XXVIII). Copper dicarboxylates do not give a band corresponding to C=O stretch; complexes of this type have been shown to exhibit strong bands at 1370-1400 cm^{-1}, and at ca. 1600[18]. The spectrum of Cu(2If-2H) showed a unique strong band in the former region (Table 2.15), and no peak at 1700 cm^{-1}, where absorption due to free -C=O stretch would occur. The spectra of the copper perchlorate complexes of the tetraamines show a very strong continuous broad band due to symmetrical ClO_4^- stretch; this indicates that the perchlorate anion is not complexed. -NH groups were present in the complexes, and the peaks at ca. 3200 cm^{-1} were due to -NH stretch as expected.

The copper diperchlorate complex of the ligand 2IIb (2XXXI)



2XXXI

also showed the characteristic band due to uncoordinated ClO_4^- stretch, at 1150-1050 cm^{-1}. The triple peak between 1630 and 1580 cm^{-1} was characteristic of the diimine. In addition, peaks attributable to NH stretch were present at 3250 cm^{-1}, and to o-substituted benzene at 760 cm^{-1}, which corresponded with values for the other copper perchlorate complexes [Cu(2IIa-d)]$(ClO_4)_2$).

Table 2.15 Absorption maxima in the infra-red spectra of copper complexes of quadridentate diimines (Nujol mull)

Cu(2Ia-2H) (R=H)	Cu(2Ib-2H) ($R=CH_3$)	Cu(2Ic-2H) (R=Cl)	Cu(2Id-2H) ($R=OCH_3$)	Cu(2Ie-2H) ($R=COOCH_3$)	Cu(2If-2H) (R=COOH)*	Assignment
				3500-3400	3500	OH deformation
					3300	NH stretch
				1730		C=O stretch
1620-1615	1620	1620	1620	1625	1625	C=N stretch
1600	1590	1600	1585	1585	1590	C=C stretch in benzene derivatives
1525-1500	1480-1460	1480-1460	1470-1460	1455	1490	CH_2 deformation
					1410-1380	Symmetrical stretch of co-ordinated C-O
	1345			1360		Deformation of CH_3 group
				1260-1240		C-O-C stretch in esters
			1270			C-O-C stretch in ethers
1200 1180	1190 1165	1200 1180	1200 1165	1200	1185	Secondary aliphatic C-N stretch
750	750	735	750	750	760	CH deformation in 1,2-substituted benzene
		710				C-Cl stretch

*Recorded as KBr disc

Table 2.16 Absorption maxima in the infra-red spectra of copper perchlorate complexes of quadridentate tetraamines (Nujol mull)

$Cu(2IHa)(ClO_4)_2$ R=H	$Cu(2IHb)(ClO_4)_2$ $R=CH_3$	$Cu(2IHc)(ClO_4)_2$ R=Cl	$Cu(2IHd)(ClO_4)_2$ $R = OCH_3$	Assignment
	3450	3450		OH deformation
3200	3230	3230	3230	NH stretch
1610	1625	1625	1610	C-C stretch in benzene derivatives.
1580	1590-1580	1590-1580	1590	NH bend
1500	1520	1520	1520	CH_2 deformation and/or
1470	1470	1470	1470	deformation CH_3 group
			1280	C-O-C
1270	1270	1255	1200	Secondary aliphatic C-N stretch
1150-1050	1150-1050	1150-1050	1150-1050	uncoord. Cl-O stretch in ClO_4
760	760	770-750	755	CH deformation in 1,2 disubstituted benzene
		725		C-Cl stretch

Table 2.17 Comparison of the main peaks in the infra-red spectra of the quadridentate ligands and copper complexes, (R=H). (Nujol mull)

2Ia(R=H)	Cu(2Ia-2H)	Cu(2Ia-2H)$\frac{1}{2}H_2O$[43]	2IHa	Cu(2IHa)$(ClO_4)_2$	Assignment
740-760	750	753	740 755 760	760	C-H deformation in 1,2 disubstituted benzene
				1050-1150	Symmetrical Cl-O stretch
1130 1170	1180 1200	1183	1130 1170	1200	Secondary aliphatic C-N stretch
1495	1500-1525	1511	1520	1470 1500	CH_2 deformation
1580			1585	1580	NH bend
1600	1593	1600	1610	1610	C=C stretch in benzene derivatives
1625					C=N stretch
3240			3380 3420	3230	NH stretch
		3260			OH deformation

2.4.2 Electronic spectra of the copper complexes of the quadridentate diimines and tetraamines

The u.v./visible spectra of the copper complexes were recorded in DMF. Because of absorption by this solvent at high energies, wavelengths below 300 nm were not recorded. All the diimine complexes were red-brown in colour, and absorption bands were found at the high energy end of the visible spectrum. The absorption bands are recorded in Table 2.18. Values obtained for complexes Cu(2Ia-2H) (R=H) and Cu(2Ic-2H)(R=Cl) obtained as the hydrates by an in situ method in subsequent work, as mentioned above, are also added for comparison[43]. These spectra were recorded in dichloromethane, and show additional high energy bands which have very high extinction coefficients, as noted previously in the spectra of the free ligands (Table 2.14). In general, the values of the extinction coefficients of the absorption bands, except for the lowest energy band of the copper perchlorate complex of the methoxy-substituted ligand, were too high for d-d transitions, which usually have values of up to 10^3 for six-coordinate and square complexes[21]. The bands were probably charge-transfer absorptions; the values are consistent with those obtained for Cu(II) complexes of unsaturated aliphatic macrocycles[16]. Values for Cu(2IIb)(2XXXI) are also included in Table 2.18.

It is not possible to deduce facts about the mode of coordination of the copper in these four donor-atom systems. Firstly, no clear-cut d-d bands were present and secondly, the Jahn-Teller effect will give rise to distortion of the geometry of coordination. In any case the coordination geometry of copper is variable; square planar, square pyramidal, 5-coordinate and distorted octahedral coordination all being possibilities.

In general, the ε values for the neutral Cu(II) complexes are significantly greater than for the copper perchlorate complexes of the reduced ligands; indicating stronger charge-transfer absorptions. As the intensity of charge-transfer bands is a function of the overlap of the orbitals between which the transfer occurs[46], the larger size of the electron-containing ligand orbitals in the neutral complexes may give rise to more intense charge-transfer bands in these complexes.

It would be expected that electron-releasing substituents ($R=CH_3$, $R=OCH_3$) would result in bands at relatively lower energies due to increased electron density within the ligand. This effect is seen (Table 2.18) within the narrow range 470-480 n.m. for both the neutral and perchlorate copper complexes.

Table 2.18 Electronic spectra of the copper II complexes λ_{max} (nm) (ε) of the quadridentate diimines and tetraamines (Recorded in dimethylformamide) (ε=litre mol^{-1}cm^{-1})

Cu(2Ia-2H)	R=H	335(14823), 440(10,450), 476(11,454)
Cu(2Ia-2H)$\frac{1}{2}H_2O$*		267(43000), 328(15,000), 436(11,000), 470(12000)
Cu(2Ib-2H)	R=CH_3	333(14297), 387(13330), 480(7632)
Cu(2Ic-2H)	R=Cl	440(8459, 480(8263)
Cu(2Ic-2H)H_2O*		250(25000), 269(28000), 334(9000), 436(8000), 470(7500)
Cu(2Id-2H)	R=OCH_3	440(9676), 480(9228)
Cu(2Ie-2H)	R=$COOCH_3$	400(13387)
Cu(2If-2H)	R=COOH	430(7854), 500(5222)
Cu(2Ia)$(ClO_4)_2$	R=H	470(3821)
Cu(2Ib)$(ClO_4)_2$	R=CH_3	333(13335), 430(9797), 480(10885)
Cu(2Ic)$(ClO_4)_2$	R=Cl	440(3146), 485(4767)
Cu(2Id)$(ClO_4)_2$	R=OCH_3	308(2775), 370(1356), 430(855), 514(678)
Cu(2IIb)$(ClO_4)_2$ (2XXX)		300(6138), 370(5129), 465(5089), 570(924)

* Recorded in CH_2Cl_2. Data obtained from reference 43

2.5.1 Experimental Data on Quadridentate Diimines

The abbreviations used in this section are as follows;

Infra-red spectra

s = strong
w = weak
b = broad
sh = shoulder

^{1}H.n.m.r. spectra

s = singlet
d = doublet
c = complex
t = triplet
m = multiplet
quad. = quadruplet
quin. = quintuplet
b = broad
b.s. = broad singlet

18, 19, 20, 21-Tetrahydro-17-H-tribenzo(f,j,n)(1,5,9,12)tetraazacyclopentadecine(2Ia)

The dialdehyde(2III) (2.9g, 10 mmol), was dissolved in MeOH(25cm^3) with p-toluenesulphonic acid (0.095g, 5 mmol). 1,2-Diaminobenzene (2IVa) (1.26g, 11 mmol), was added and the mixture refluxed at ca. 80°C for 2 hours; a yellow solid started to form after 20 minutes. The precipitate was filtered and recrystallised from CH_2Cl_2/MeOH to give 18,19,20,21-tetrahydro-17-H-tribenzo(f,j,n)(1,5,9,12) tetraazacyclopentadecine (2.7g, 78%) as fine yellow crystals, m.pt 218-220°C. (Found: C, 77.9; H, 6.3; N, 15.5%. $C_{23}H_{22}N_4$ requires C, 77.96; H, 6.21; N, 15.81%). λ_{max} (MeOH) 242 nm (ε = 33800), 380 nm (ε = 15000); ν_{max} (nujol) 3420 (b,NH), 1625 (s, C=N), 1600 (s,C=C), 1580 (s,NH bend), 1535-1525(s), 1495(s), 1385, 1330, 1250, 1200(s), 1170(s), 1130(w), 1100(s), 1050(s), 1025(w), 985(s), 940(s), 910(s), 860(w), 850(s), 760-740(s,o-substituted benzene); (^1H)($CDCl_3$)2.22 (quin. 2H. J=2.4 $CH_2\underline{CH_2}CH_2$), 3.48(quad. 4H. J=2.4 $\underline{CH_2}CH_2\underline{CH_2}$), 6.6-6.76(m.4H.aromatics), 7.1-7.4 (m.8H aromatics), 8.55 (s.2H.N=C$\underline{H}$), 9.93 (bs. 2H. N$\underline{H}$); (^{13}C)($CDCl_3$) see Table 2.6, Section 2.2.3; found: m/e 354.1844. $C_{23}H_{22}N_4$ requires M, 354.1844; m/e 354.1844 (M^+,100), 248.1222(26.32), 247.1232(75.91), 236.1172 (31.77), 234.1030(20.81), 224.1207(66.7), 222.1033(79.13), 221.0961(14.01), 220.0900(19.28), 219.0914(19.40), 210.1014(32.3), 209.0952(62.84), 195.0908(12.43), 194.0839(23.92), 144.0806(12.19), 130.0664(48.59), 119.0624(24.93), 118.0647(46.89), 117.0574(16.76), 108.0696(11.9), 106.0663(18.05).

8-Methyl-18,19,20,21-tetrahydro-17-H-tribenzo(f,j,n)(1,5,9,12) tetraazecyclopentadecine(2Ib)

The dialdehyde(2III)(1.45g, 5mmol) was dissolved in methanol (25cm^3), and p-toluenesulphonic acid (0.043g, 0.25mmol) was added. 1-Methyl-3,4-diaminobenzene(2IV.b)(0.61g, 5 mmol) was dissolved in methanol (10 cm^3) and added to the hot solution. The mixture was refluxed under N_2 and after 30 minutes a yellow solid, with yellow supernatant solution, was formed. The solid product was filtered and recrystallised from hot methanol to give 8-methyl-18,19,20,21-tetrahydro-17-$\underline{H}$-tribenzo($\underline{f}$,$\underline{j}$,$\underline{n}$)(1,5,9,12) tetraazacyclopentadecine (1.2g, 66%) as bright yellow needle crystals, m.pt 165-167°C. (Found: C, 78.2; H, 6.6; N, 15.2%. $C_{24}H_{24}N_4$ requires C, 78.26; H, 6.52; N, 15.21%); λ_{max}(MeOH); 255 nm (ε = 54800), 280 nm (ε = 31900) 395 nm (ε = 19200); ν_{max} (nujol) 3220(s,NH), 3100(w.CH), 1630 (s,C=N), 1600(s,C=C), 1570(s,NH bend), 1530(w), 1520(w), 1500(s), 1470(s), 1340-1330 (s,C-H), 1280(w), 1250(w), 1220, 1210, 1190(s), 1170(s), 1150(s), 1120, 1110(s), 1050(s), 1020(s) 980(s), 950(s), 900(s), 870(s), 850(s), 830(w), 820(s), 750 (s,b,o-substituted benzene); (^{1}H)($CDCl_3$ 2.16 (quin. 2H, J=2.1 $CH_2C\underline{H}_2CH_2$),2.39(s,$C\underline{H}_3$) 3.42 (quad, 4H, J=2.1 $C\underline{H}_2CH_2C\underline{H}_2$) 6.5-6.7(m.3H. aromatics), 7.05-7.35 (m.8H. aromatics), 8.52(s,2H.N=C$\underline{H}$), 9.9 (t,2$\underline{H}$.NH); (^{13}C)($CDCl_3$). See Table 2.6, Section 2.2.3; found: m/e 368.002 $C_{24}H_{24}N_4$ requires M, 368.2001; m/e 368.002(M^+,100), 262.134(15.38) 250.1331(26.74), 247.1234(69.38), 238.1326(57.57), 236.1177(68.93), 235.11(13.94), 234.1021(19.84), 223.1112(65.31), 219.0924(15.74), 208.099(17.71), 184.0988(15.58), 133.0760(19.3), 130.0647(44.48), 122.0837(22.51), 118.0640(39.1), 106.0653(20.64).

8-Chloro-18,19,20,21-tetrahydro-17-H-tribenzo(f,j,n)(1,5,9,12) tetraazacyclopentadecine(2Ic)

The dialdehyde(2III) (2.9g, 10 mmol) was dissolved in ethanol ($25\ cm^3$) and zinc acetate (0.7g, 0.3 mmol) was added followed by a solution of 1-chloro-3,4-diaminobenzene(2IVc) (1.42g, 10 mmol) in ethanol. The solution became brown. After refluxing overnight the liquid was filtered and evaporated to small volume to give a dark yellow solid. This was filtered and the solid dissolved in CH_2Cl_2, and warmed with activated charcoal and filtered. A little MeOH was added to the clear bright solution and small fluffy yellow needle crystals separated on standing. These were recrystallised from CH_2Cl_2/petroleum ether (80-90) to give 18,19,20,21-tetrahydro-17-*H*-tribenzo(*f*,*j*,*n*)-9-chloro(1,5,9,12)tetra-azacyclopentadecine as small yellow crystals (2.5g, 64.5%), m.pt 130-132°C. (Found C, 70.8; H, 5.4; N, 14.6%. $C_{23}H_{21}N_4Cl$ requires C, 71.04; H, 5.41; N, 14.43%; λ_{max} (MeOH) 255 nm ($\varepsilon = 68900$), 395 nm ($\varepsilon = 23700$); ν_{max} (nujol) 3260 (b,NH), 1630 (s,C=N) 1595(s,C=C), 1570(s,NH bend) 1515-1535(s), 1480(s), 1340(s), 1270(w), 1240(s), 1200(s), 1170(s), 1130(s), 1100(s), 1050(s), 980(s), 970(s), 960(s), 870(s), 845-850(s), 815-830(s), 750(s)(o-substituted benzene), 700(s,C-Cl) 655(s), 600(s), 565(w), 535(s), 510(w). (^1H)$CDCl_3$ 2.17 (quin. 2H, J=4.0, $CH_2C\underline{H}_2CH_2$), 3.45 (quad.4H, J=4.0,($C\underline{H}_2CH_2C\underline{H}_2$)6.5-6.8(m.3H. aromatics), 7.1-7.5 (m.8H.aromatics), 8.48(s.2H.N=C$\underline{H}$), 9.75 (3.2H.N$\underline{H}$); (^{13}C) ($CDCl_3$). See Table 2.6, Section 2.2.3; found: m/e 388.1451. $C_{23}H_{21}N_4\ {}^{35}Cl$ requires 388.1454; found: m/e 390.1423. $C_{23}H_{21}N_4\ {}^{37}Cl$ requires 390.1425; m/e 390.1423(M^+, 6.25), m/e 388.1451 (M^+, 88.46), 270.0786(13.91), 256.0645(11.61), 260.0759(18.63), 258.0756(65.6) 257.0662(13.91), 256.0626(54.92), 254.0485(10.89), 248.1268(17.32), 247.1344(100), 245.0577(10.99), 244.0616(18.33), 243.0554(40.0), 228.0448(16.46), 219.0918(19.51), 194.0762(11.15), 153.0210(11.95), 144.0813(12.51), 132.0797(17.84), 131.0657(11.54), 130.0658(64.05), 118.0657(72.5), 117.0602(18.42).

Preparation of 1-Methoxy-3,4-diaminobenzene

1-Methoxy-3,4-dinitrobenzene (10g, 0.5 mmol) was suspended in EtOH(50cm^3). Portions of hydrazine hydrate (99-100%) were added in the presence of 10% Pd on charcoal catalyst until all the colour had gone. (About 30cm^3 were required in all). On filtration through Celite the colourless solution darkened rapidly, so concentrated HCl was added to give the diamine dihydrochloride as a purple powder (9g, 75%).

8-Methoxy-18,19,20,21-tetrahydro-17-*H*-tribenzo(*f*,*j*,*n*) (1,5,9,12)tetraazacyclopentadecine(2Id)

The dialdehyde (2III) (1.45g, 5mmol) was dissolved in MeOH(25cm^3) and a few drops of triethylamine were added. The diamine (2IVd) was added as the dihydrochloride (1.5g, 5 mmol), giving a red solution. This was allowed to stir under N_2 at room temperature until a few particles of yellow solid began to adhere to the sides of the flask. A few more drops of triethylamine were added, when more yellow solid precipitated from solution. Addition of triethylamine was continued until a total of 1.0 cm^3 (10 mmols) had been added over 2 hours. The yellow solid was filtered and was recrystallised from hot MeOH and vacuum-dried to give 8-methoxy 18,19,20,21-tetrahydro-17-*H*-tribenzo(*f*,*j*,*n*) (1,5,9,12)-tetraazacyclopentadecine monohydrate as yellow crystals (1.3g 67%), m.pt 106-110°C. (Found: C, 71.5; H, 6.7; N, 13.9%. $C_{24}H_{26}N_4O_2$ requires C, 71.64; H, 6.46; N, 13.93%); λ_{max} (MeOH) 239 nm (ε = 37250), 256 nm (ε = 36100), 300 nm (ε = 13440) 418 nm (ε = 14200); ν_{max} (nujol) 3400-3200 (b,NH and CH), 1620 (s,C=N), 1610(s,C=C), 1585(s,NH bend), 1510-1495(s), 1470(s), 1330, 1300, 1280, 1210(s), 1130(w), 1170-1160(s), 1120(w), 1050(s), 970(b,s), 930(w), 900, 850, 800, 750(s,o-substituted benzene). (^1H)($CDCl_3$) 2.1 (quin. 2H, J=8.0, $CH_2\underline{H}_2CH_2$), 3.3 (quad. 4H, J=8.0, $C\underline{H}_2CH_2C\underline{H}_2$), 3.7, (s,3H.$C\underline{H}_3$), 6.3-6.8(m.7H.aromatics), 6.9-7.3(m.4H.aromatics), 8.42 (s.2H.N-C$\underline{H}$), 9.85 (bs.2H.N$\underline{H}$); found m/e 384.1948 $C_{24}H_{24}N_4O$ requires M, 384.1949; m/e 384.1948(M,$^+$100), 278.1289 (13.52), 266.1 289(26.64), 264.1143(14.73), 254.1277(54.08), 253.1184(20.35), 252.1132(83.0), 251.1050(14.73), 250.1001(25.03), 248.1282(14.86), 247.1244(66.4), 240.1141(33.73), 239.1058(68.27), 224.0878(16.47), 219.0918(14.86), 209.0725(13.39), 167.0734(12.58), 149.0704(29.59), 144.0802(11.78), 138.0796(33.07), 137.0715(19.14), 132.08(19.41), 130.0658(69.08), 118.0658(55.96), 117.0576(34.81), 106.0656(19.81).

8-Methoxycarbonyl-18,19,20,21-tetrahydro-17-H-tribenzo(f,j,n)(1,5,9,12)tetraazacyclopentadecine(2Ie)

The dialdehyde (2III) (1.16g, 4 mmol) was dissolved in MeOH (25cm^3) and p-toluenesulphonic acid (0.038g, 0.2 mmol) was added, followed by methyl-3,4-diaminobenzoate, (2IVe), (the crude commercial product, 0.73g, 4.4 mmol). The solution was refluxed under N_2 for 5-6 hours, when a dark orange, rather tarry suspension had formed. The reaction mixture was evaporated to dryness under vacuum, and the dark residue refluxed in toluene with activated charcoal. The mixture was filtered through Celite while hot. The clear dark yellow solution was evaporated to dryness under vacuum to give a red oil. This was recrystallised from hot methanol to give 8-methoxycarbonyl-18,19,20,21-tetrahydro-17-H-tribenzo(f,j.n)(1,5,9,12)tetraazacyclopentadecine (0.9g, 53%) as fine yellow needles, m.pt 110-112°C. (Found: C, 72.0; H, 5.9; N, 13.5%. $C_{25}H_{24}N_4O_2$ requires C, 72.81; H, 5.82; N, 13.59%); λ_{max} (MeOH) 240 nm (ε = 57700), 395 nm (ε = 17300); ν_{max} (nujol) 3220 (b,NH), 1720(s,C=O), 1630(s,C=N), 1600(s,C=C), 1575(s,NH bend), 1530-1520(w), 1500(w), 1470(s), 1420(w), 1345(w), 1330(w), 1300(s), 1260(s), 1230(s), 1200(s), 1170(s), 1130(s), 1100(s), 1050(w), 1000, 920, 900, 850(w), 770-740 (b.s. o-substituted benzene), (^{1}H)($CDCl_3$) 2.29 (quin. 2H. J=2.4. $CH_2C\underline{H}_2CH_2$), 3.47 (quad. 4H, J=2.4, $C\underline{H}_2CH_2C\underline{H}_2$) 3.94(s.3H.$C\underline{H}_3$), 6.56-6.73(t.3H.aromatics), 7.12-7.38(m.7H.aromatics), 7.85-7.89(d. of d. 1H aromatic), 8.61 (d.2H N=C$\underline{H}$), 9.87 (b.s. 2H N$\underline{H}$); Found: m/e 412.1898. $C_{25}H_{24}N_4O_2$ requires M, 412.1898; m/e 412.1898 (M,$^+$ 80.40), 306.1241 (15.73), 294.1239(29.11), 292.1080(15.61), 282.1249(80.75), 280.1090(69.6), 279.1022(11.85), 278.0931(11.62), 268.1082(33.80), 267.1003(50.12), 248.1273(19.84), 247.1235(100), 246.1144(14.2), 221.070((10.68), 219.0922(23.83), 206.0944(25.7), 177.0652(18.31), 145.088(12.09), 134.0601(23.59), 132.0801(36.5), 130.0652(75.35), 118.0652(80.16), 117.0572(24.41), 106.0657(38.97).

8-Carboxy-18,19,20,21-tetrahydro-17-H-tribenzo(f,j,n)(1,5,9,12) tetraazacyclopentadecine(2If)

The dialdehyde (2III) (1.16g, 4 mmol) was dissolved in absolute ethanol (25cm^3) and p-toluenesulphonic acid (0.038g 0.2 mmol) added, and then 3,4-diaminobenzoic acid (2IVf) (0.608g, 4 mmol) as the solid. After refluxing for 1 hour under nitrogen a yellow solid began to form, and after 2 hours the suspension was evaporated to small volume under vacuum. The yellow product was filtered and recrystallised from CH_2Cl_2/MeOH and dried under vacuum to give 8-carboxy-18,19,20,21-tetrahydro-17-H-tribenzo(f,j,n)(1,5,9,12)-tetraazacyclopentadecine monohydrate (0.8g, 50%) as fine yellow needles, m.pt. 178-180°C. (Found: C, 70.2; H, 5.7; N, 13.4%. $C_{24}H_{24}N_4O_3$ requires C, 69.23; H, 5.76; N, 13.46%). λ_{max}(MeOH) 240 nm (ε = 36300), 395 nm (ε = 134000, ν_{max} (nujol) 3400-3350 (b, OH), 3200-3000 (b,NH) 1680 (s,C=O), 1620 (s,C=N), 1590 (s,C=C), 1570 (s,NH bend), 1520 (s,b), 1340-1330 (s,b), 1270(w), 1200 (s,b), 110(s), 980(w), 950(s), 900-800(s,b), 850(s,b), 770-750(s,b o-substituted benzene). (^{1}H)($CDCl_3$) 2.67 (quin, 2H, J=8.8, $CH_2\underline{CH_2}CH_2$),
3.4 (quad, 4H, J=8.0, $\underline{CH_2}CH_2\underline{CH_2}$)6.64-6.74 (m.5H.aromatics), 7.26-7.38 (c.5H.aromatics), 7.6-7.9(c.1H.aromatics) 8.57(s, 1H) 8.6(s, 1H) C$\underline{H}$=N
9.8 (d.2H.N$\underline{H}$), 9.82-9.9 (b.s. 1H.O$\underline{H}$): found m/e 398.1739 $C_{24}H_{22}N_4O_2$ requires M,$^+$ 398.1741: m/e 398.1739 (M, 74.1), 292.1074(11.57), 280.1063(28.53), 278.0928(11.39), 268.1053(65.65), 266.0930(63.23), 264.0752(13.25), 254.0950(27.97), 253.0850(52.27), 248.1273(10.06), 247.1250(96.81), 238.0734(15.80), 199.0884(14.59), 152.0601(58.48), 144.0813(10.57), 135.0586(13.98), 134.0602(29.91), 130.0647(90.12), 129.0566(18.00), 118.0655(100), 117.0571(15.06), 106.0654(62.49), 104.0497(13.51), 93.0586(10.75), 91.0549 (25.68).

Reduction product of 8-methoxycarbonyl-18,19,20,21-tetrahydro--17-H-tribenzo(f,j,n,)(1,5,9,12)tetraazacyclopentadecine(2Ie)

8-methoxycarbonyl-18,19,20,21-tetrahydro-17-H-tribenzo(f,j,n) (1,5,9,12)tetraazacyclopentadecine (2.0g, 0.5 mmol) was refluxed with a solution of diborane in T.H.F. (40 cm^3, 40 mmol B_2H_6) until the solution became colourless. On addition of water (10 cm^3) the solution became yellow 2MHCl (10 cm^3) and 2MNaOH (10 cm^3) were added. As separation of the T.H.F. layer was difficult, it was extracted with CH_2Cl_2 and this extract was evaporated to give a yellow residue. Recrystallisation from $CHCl_3$/petroleum ether 60-80° gave a yellow friable solid, m.pt (decomposition) 140°-150°C (Found: C, 66.7; H, 6.2; N, 12.2%); ν_{max} (nujol) 3420-3400(s,b), 1695(s,b), 1610(s), 1590(s) 1520(s,b), 1480(s,b), 1350(w), 1300(s), 1260(w), 1250(s), 1200(w), 1150(w), 1130(w), 1100(s), 1050(w), 1010(s), 960(w), 950(w), 900(w), 860(w), 770(s), 750(s): found m/e 426.2241(9.0), 425.2155(33.58), 424.2086(100), 423.1991(43.09), 422.1928(12.29), 318.1425(13.65), 305.1299(11.9), 304.1235(37.94), 292.1215(33.48), 291.1163(70.88), 290.1197(19.15), 278.1095(33.98), 277.1052(16.36), 212.1038(10.15), 132.0802(16.93), 120.0792(13.83), 119.0729(12.36), 118.0671(54.31), 106.0663(11.22).

Reduction product of 8-carboxy-18,19,20,21-tetrahydro-17-H-tribenzo (f,j,n)(1,5,9,12)tetraazacyclopentadecine(2If)

8-carboxy-18,19,20,21-tetrahydro-17-H-tribenzo(f,j,n)(1,5,9,12) tetraazacyclopentadecine (1.95g, 5 mmol) was refluxed with a solution of diborane in T.H.F. (40 cm^3, 40 mmol B_2H_6). A grey solid was formed which decomposed on addition of water (10 cm^3) and dissolved to give a yellow T.H.F. layer. The solution was treated with 2MHCl(10 cm^3) and 2MNaOH(10 cm^3). The T.H.F. layer was separated and evaporated to dryness to give a yellow friable solid which was recrystallised from CH_2Cl_2/MeOH to give a paler yellow solid, m.pt (decomposition) 110-130°C. (Found: C, 66.7; H, 6.3; N, 12.8%). λ_{max} (nujol) 3400-3350(s,b), 2400(w), 1730(w), 1610(s), 1590(s), 1470(s), 1300(w), 1280(w), 1170(w), 1150(w), 1050(s), 860(w), 810(s), 750(s): Found m/e 382.2098(9.79), 380.2083(14.83), 260.1350(10.69), 248.1272(14.00), 234.1222(46.62), 220.1707(15.10), 205.1517(53.31), 159.0934(14.90), 149.0223(100), 133.0776(11.45), 132.0715(24.90), 131.0625(27.38), 122.0830(78.97), 121.0717(43.86), 120.0797(21.38), 118.0643(34.55), 107.0724(27.17), 106.0664(53.10).

7,8,9,10,18,19,20,21-Octahydro-17-H-dibenzo(*f*,*n*)(1,5,9,14) tetraazacycloseptadecine(2IIb)

The dialdehyde(2III) (2.9g, 10 mmol) was dissolved in MeOH (25 cm^3), and 3,4-diaminobutane (2Vb) (0.97 cm^3, 10 mmol) was added and the mixture refluxed under nitrogen for two hours, after which no more white product was formed. This was filtered and recrystallised from hot chloroform and vacuum-dried for several hours to give 10,11,12,13,18,19,20,21-octahydro-17-*H*-dibenzo(*f*,*o*)(1,5,9,14)tetraazacyclospetradecine (2.9g, 74%) as white needles, m.pt. 64°C. (Found: C, 74.8; H, 8.2; N, 16.7% $C_{21}H_{26}N_4$ requires C, 75.44; H, 7.78; N, 16.76%). λ_{max} (CH_2Cl_2) 270 nm (ε = 17800), 360 nm (ε = 9,500); ν_{max} (nujol) ewtO (S,B,NH), 1635(s,C=N), 1610(s,C=C), 1590(s,NH bend), 1530(s), 1470(s), 1345(s), 1335(s,sh), 1210(s), 1160(s), 1100, 1060, 1040, 1020(w), 980(s), 940(w), 890, 840, 750 (s, o-substituted benzene), 730; (^1H)($CDCl_3$) 1. 5-1.7 (m . 4H $CH_2C\underline{H}_2C\underline{H}_2CH_2$), 1.7-2.0 (m .2H.$CH_2C\underline{H}_2CH_2$), 3.0-3.35 (m.4H.$C\underline{H}_2CH_2CH_2C\underline{H}_2$), 3.35-3.5 (m.4H.$C\underline{H}_2CH_2C\underline{H}_2$), 6.2-6.7 (m.4H.aromatics), 6.75-7.25 (m.4H.aromatics), 8.13(s.2H.N=C$\underline{H}$) 9.05(b.s.2H.N$\underline{H}$). (^{13}C)($CDCl_3$). See table 2.6, Section 2.2.3; found (low resolution; *m*/e 334(M+), 118(100); field desorption showed 334(M) only.

7,8,15,16,17,18,19,26,27,34,35,36,37,38-Tetradecahydrotetrabenzo (*f*,*m*,*u*,b') (1,5,8,12,16,,19,23,27)octa-azacyclotreicosane

The dialdehyde (2III) (2.9 g, 10 mmol) was dissolved in MeOH (25 cm^3) and 1,2-diaminoethane (2Va) (10.7 cm^3, 11 mmol) was added. The mixture was refluxed under nitrogen for an hour, and the off-white solid filtered. This was then refluxed with D.M.F. for four hours, giving an insoluble white product which was filtered, washed with methanol, and vacuum-dried. M.pt (with decomposition) 190-195°C. (Found: C, 73.7; H, 6.5; N, 17.5%. $C_{38}H_{44}N_8$ requires C, 74.5; H, 7.18; N, 18.30%). λ_{max} (nujol) 3240(w, broad, NH) 3100(w), 1630(s), 1620(w), 1580(s), 1530(s), 1470(s), 1340(s) 1310(w), 1300(s), 1250(w), 1220(s), 1200(s), 1155(s), 1130, 1100, 1090(w), 1070, 1060, 1050, 1040(s), 980(w), 960(w), 915, 900, 870(w), 860, 750-740 (s, triple peak, o-substituted benzene). Found (low resolution); *m*/e 612(M$^+$), 118(100).

2.5.2 Experimental Data for the Quadridentate Tetraamines

The abbreviations used in this section are as follows:

Infra-red spectra

s = strong
w = weak
b = broad
sh = shoulder

^1H n.m.r. spectra

s = singlet
d = doublet
c = complex
t = triplet
m = multiplet
quad. = quadruplet
quin. = quintuplet
b = broad
b.s. = broad singlet

5,6,11,12,18,19,20,21-Octahydro-17-*H*-tribenzo(*f*,*j*,*n*) (1,5,9,12) tetraazacyclopentadecine (2IHa)

18,19,20,21-tetrahydro-17-*H*-tribenzo(*f*,*j*,*n*)(1,5,9,12) tetraazacyclopentadecine (2Ia, 1.77 g, 5 mmol), was refluxed under nitrogen with a solution of diborane in T.H.F. This was added in portions until the yellow colour of the solution had been discharged; (40 cm^3, 40 mmol B_2H_6). The mixture was treated with water (10 cm^3) to decompose any remaining diborane, and then with 2M NaOH (10 cm^3). The T.H.F. layer was separated from the aqueous layer, and evaporated to dryness. The yellow-brown residue was extracted with methanol, and an off-white solid was precipitated by the addition of a few drops of water. The solid was recrystallised from $CHCl_3$/petroleum ether (60-80°) to give 5,6,11,12,18,19,20,21-octahydro-17-*H*-tribenzo(*f*,*j*,*n*)(1,5,9,12) tetraazacyclopentadecine (1.2 g, 67%) as small white needle crystals, m.pt 162-164°C. (Found C, 76.8; H, 7.1; N, 15.5%. $C_{23}H_{26}N_4$ requires C, 77.09; H, 7.26; N, 15.64%); λ_{max} (MeOH) 297 nm (ε= 12900); ν_{max}(nujol) 3420, 3380 (w, sh, NH), 1610(s,C=C), 1585(s,NH bend), 1520(s,b), 1470(s), 1380(w), 1360(w), 1340(w), 1310(s), 1280(s), 1260(s), 1230(w), 1150(w), 1130(s), 1080(s), 1050(s), 980(w), 940(w), 930(w), 900(w), 880(w), 855(w), 840(w), 820(w), 760, 755, 740 (s, triple peak, o-substituted benzene); (^1H)($CDCl_3$) 1.94 (quin, 2H, J=1.6 $CH_2C\underline{H}_2CH_2$), 3.35 (quad, 4H, J=1.6 4H.$C\underline{H}_2CH_2C\underline{H}_2$), 4.25 (s.4H.NH-$C\underline{H}_2$) 4.2 (very broad s 4H N$\underline{H}$), 6.66-6.78 (m.4H.aromatics), 6.82-6.98 (m.4H.aromatics), 7.16-7.28(m.4H.aromatics), (^{13}C)($CDCl_3$). See Table 2.7, Section 2.2.3; Found: 358.2155 $C_{23}H_{26}N_4$ requires M, 358.2157; m/e 358.2155 ($M,^+$ 60.44), 210.1022(16.48), 146.0963(12.09), 144.08(12.09), 132.0791(46.15), 130.0649(21.98), 120.0796(49.45), 118.0469(100), 117.0597(13.19), 106.0579(29.67), 91.0545(52.75).

8-Methyl-5,6,11,12,18,19,20,21-octahydro-17-H-tribenzo (f,j,n,)(1,5,9,12)tetraazacyclopentadecine(2IHb)

8-methyl-18,19,20,21-tetrahydro-17-H-tribenzo(f,j,n)(1,5,9,12) tetraazacyclopentadecine (2Ib, 1.84 g, 5 mmol) was refluxed under nitrogen with a solution of diborane in T.H.F. This was added in portions until the yellow colour of the solution had been discharged; (40 cm^3, 40 mmol B_2H_6). The mixture was treated with water (10 cm^3), 2M HCl (10 cm^3) and, after stirring for 10 minutes, with 2M NaOH (10 cm^3). The T.H.F. layer was separated and evaporated to dryness to give an oily residue. On refluxing this with MeOH (10 cm^3) a white powder was formed. This was filtered, recrystallised from hot MeOH and dried under vacuum to give 8-methyl-5,6,11,12,18,19,20,21-octahydro-17-H-tribenzo(f,j,n)(1,5,9,12)tetraazacyclopentadecine (1.2 g, 64.5%) as small white needles, m.pt 149-150°C. (Found C, 77.6; H, 7.6; N, 15.0%. $C_{24}H_{28}N_4$ requires C, 77.41; H, 7.79; N, 15.05%) λ_{max} (MeOH) 255 nm (ε= 44800), 308 nm (ε= 9900); ν_{max} (nujol) 3420, 3380, 3340(s,sh,NH), 1620(s,C=C), 1590(s,NH bend), 1540-1510(s,b), 1490(w), 1470(s), 1390(s), 1330(w), 1310(s), 1280-1270(s), 1260(s), 1230(w), 1210(w), 1165(s), 1140(s), 1125(s), 1085(s), 1050(s), 1020(w), 985(w), 955(w), 930(s) 910(w), 855(s), 840(s), 800(s) 750(s, o-substituted benzene). (^{1}H)($CDCl_3$)2.0 (quin, 2H, J=2.4, $CH_2\underline{CH_2}CH_2$) 2.36 (s.3H.$\underline{CH_3}$), 3.35 (quad, 4H, $\underline{CH_2}CH_2\underline{CH_2}$), 4.15 4.3 (2 x s 2H. $\underline{CH_2}$NH), 4.67 (very broad 4H.N$\underline{H}$), 6.65-6.85 (c.7H.aromatics), 7.15-7.3 (m.4H.aromatics); (^{13}C). See Table 2.7, Section 2.2.3;

Found: 372.2312. $C_{24}H_{28}N_4$ requires M,372.2313; m/e 372.2312 (M^+,60.4), 238.1360(11.11), 224.1183(19.53), 208.1003(14.33), 164.1302(10.45), 146.0955(18.43), 144.0801(18.48), 132.0806(68.78), 120.0808(59.68), 118.0655(100), 106.0654(42.9), 91.0547(46.98).

8-Chloro-5,6,11,12,18,19,20,21-octahydro-17-H-tribenzo (*f*,*j*,*n*) (1,5,9,12)tetraazacyclopentadecine(2IHc)

8-chloro-18,19,20,21-tetrahydro-17-*H*-tribenzo(*f*,*j*,*n*)(1,5,9,12) tetrazacyclopentadecine (2Ic, 1.95 g, 5 mmol) was refluxed under nitrogen with a solution of diborane in T.H.F. (40 cm^3, 40 mmol B_2H_6). The yellow solution changed to very pale green but did not become completely colourless. Chloroform was added directly to the solution, and stirred for several hours to allow gradual evolution of hydrogen. The chloroform extract was evaporated under vacuum to give a brown solid. This was dissolved in hot methanol, and heated with activated charcoal. The solution was filtered hot, and on cooling gave a white powder. Recrystallisation from hot methanol gave 8-chloro-5,6,11,12,18,19,20,21-octahydro-17-*H*-tribenzo(*f*,*j*,*n*)(1,5,9,12)tetraazacyclopentadecine (1.2g, 61%) as white needles, m.pt 151°C. (Found C, 69.6; H, 6.5; N, 13.8%. $C_{23}H_{25}N_4Cl$ requires C, 70.31; H, 6.36; N, 14.26%); λ_{max} (MeOH) 305 nm (ε= 1300); ν_{max} (nujol) 3420, 3360, 3315(s,sh,NH), 1610(s,C=C), 1590(s,NH bend), 1520-1510(s,b), 1490(s), 1470(s), 1430(w), 1350(w), 1330(s), 1320(s), 1280(s), 1260(s), 1220(s), 1210(w), 1190(w), 1160(s), 1130-1125(s), 1100(w), 1090(s), 1060(s), 1050(s), 980(s), 940(s), 920(w), 865(w), 850(s), 830(s), 790(s), 790(s), 760,740(s, double peak, o-substituted benzene), 720(w), 700(s), 655(s); (^{1}H)($CDCl_3$)2.0 (quin, 2H, J=2.4 $CH_2\underline{CH_2}CH_2$) 3.46 (quad, 4H, J=2.4, $\underline{CH_2}CH_2\underline{CH_2}$), 3.9 (b.s 2H.N$\underline{H}$), 4.15-4.3(2xs. 4H.$\underline{CH_2}$NH), 4.5 (b.s. 2H.N$\underline{H}$)

6.7-6.9(m.7H aromatics), 7.15-7.3(m.4H aromatics); (^{13}C)($CDCl_3$). See Table 2.7, Section 2.2.3; Found m/e 394.1719. $C_{23}H_{25}N_4{}^{37}Cl$ requires M, 394.1731; m/e 392.1769. $C_{23}H_{25}N_4{}^{35}Cl$ requires 392.1767; m/e 394.1719(M,$^+$ 17.07), 393.1791(12.80), 392.1769 (M$^+$, 53.66), 146.0948(14.02), 142.0258(17.68), 130.0649(21.34), 120.0802(48.17), 118.0663(100), 117.0599(12.2), 106.0591(31.1), 91.0555(39.02).

8-Methoxy-5,6,11-12,18,19,20,21-octahydro-17-*H*-tribenzo (*f*,*j*,*n*)(1,5,9,12)tetraazacyclopentadecine(2IHd)

8-methoxy-18,19,20,21-tetrahydro-17-*H*-tribenzo(*f*,*j*,*n*)(1,5,9,12) tetraazacyclopentadecine (2Id, 1.9g, 5 mmol) was refluxed under nitrogen with a solution of diborane in T.H.F. The solution was initially dark red after the first addition of diborane; the latter was added in portions until the solution was yellow, and no further colour change occurred on addition (40 cm^3, 40 mmol B_2H_6). The solution was treated with 2M HCl (10 cm^3), stirred, and then 2M NaOH (10 cm^3) was added. The mixture was extracted with $CHCl_3$, and the extract filtered through Celite. Nitrogen was bubbled into the filtrate to evaporate the chloroform slowly, giving a white precipitate. Recrystallisation of this solid from $CHCl_3$/MeOH and drying under vacuum gave 8-methoxy-5,6,11,12,18,19, 20,21-octahydro-17-*H*-tribenzo(*f*,*j*,*n*)(1,5,9,12)tetraazacyclopentadecine monohydrate (0.8g, 50%), as small white needles, m.pt 97-100°C. (Found C, 71.1; H, 7.2; N, 13.0%. $C_{24}H_{30}N_4O_2$ requires C, 70.93; H, 7.38; N, 13.79%); λ_{max} (MeOH) 364 nm (ε = 21800), ν_{max} (nujol) 3400-3200(b,NH and OH), 1610(s,C=C), 1590(s,NH bend) 1530-1510(s,b), 1470(s), 1330(s), 1300(s), 1260(s), 1210(w), 1190(w), 1160(s), 1140(s), 1100(w), 1050(s), 1000(s), 980(w), 930(w), 910(w), 850(w), 800(w), 750(s, o-substituted benzene), 720(w); (^{1}H)($CDCl_3$) 2.0 (quin, 2H, J=2.2 ,$CH_2C\underline{H}_2CH_2$), 2.6-3.2 (b.c.4H.N$\underline{H}$), 3.38 (quad, 4H, J=2.2, $C\underline{H}_2CH_2C\underline{H}_2$), 3.8(s.3H.C$\underline{H}_3$), 4.15-4.25(2xs 2H.CH -NH), 6.3-7.25(c.11H. aromatics); found m/e 388.2262. $C_{24}H_{28}N_4O$ requires M, 388.2262; m/e 388.2262

(M^+, 98.22), 251.1556(10.46), 240.1125(17.28), 149.0718(12.98), 146.0972(19.54), 144.0820(14.8), 138.0795(100), 137.0721(14.26), 132.0802(56.5), 130.0649(18.76), 120.0806(47.34), 118.0658(15.28), 117.0576(10.86), 106.0671(27.87), 91.0551(35.95).

2.5.3 Experimental data on the copper complexes of the quadridentate diimines

18,19,20,21-tetrahydro-17-*H*-tribenzo[*f*,*j*,*n*][1,5,9,12]tetraaza cyclopentadecinato(2-)copper(II) Cu(2Ia-2H

Copper(II)acetate (0.1g, 0.5 mmol) was added to a methanol suspension of the diimine ligand 18,19,20,21-tetrahydro-17-*H*-tribenzo[*f*,*j*,*n*][1,5,9,12]tetraazacyclopentadecine (0.177g, 0.5 mmol) under nitrogen, and the mixture refluxed gently to give dark red crystals. These were recrystallised from dichloromethane/methanol to give 18,19,20,21-tetrahydro-17-*H*-tribenzo[*f*,*j*,*n*][1,5,9,12] tetraazacyclopentadecinato(2-)copper(II). (0.12g, 60%). (Found C, 66.6; H, 5.1; N, 13.6; Cu, 14.6%. $C_{23}H_{20}N_4Cu$ requires C, 66.34; H, 4.80; N, 13.46; Cu 15.26%); λ_{max} (CH_2Cl_2) 268 nm (ε = 40190), 335 nm (ε = 8800), 440 nm (ε = 10450), 476 nm (ε = 11450); ν_{max} (nujol) 1620-1615(s), 1600(s), 1575(s), 1525-1500(s), 1350(s), 1270(w), 1250(s), 1200(s), 1180(s), 1150(w), 1090(w), 1050(s), 960(s), 930(w), 920(s), 820(w), 750(s,o-substituted benzene). Found m/e 416. $C_{23}H_{20}N_4{}^{65}Cu$ requires 416; m/e 415. $C_{23}H_{20}N_4{}^{63}Cu$ requires 415; m/e 416(M^+), 415(M^+), 413(100), 356, 355, 248, 223, 210, 195, 130, 118.

8-Methyl-18,19,20,21-tetrahydro-17-*H*-tribenzo[*f*,*j*,*n*][1,5,9,12]tetraazacyclopentadecinato(2-)copper(II) Cu(2Ib-2H)

Copper(II)acetate (0.1g, 0.5 mmol) was added to a methanol suspension of the diimine ligand 8-methyl-18,19,20,21-tetrahydro-17-*H*-tribenzo[*f*,*j*,*n*][1,5,9,12]tetraazacyclopentadecine (0.184g, 0.5 mmol) under nitrogen, and the mixture refluxed gently for two hours to give a red copper complex. This was recrystallised from dichloromethane/methanol to give 8-methyl-18,19,20,21-tetrahydro-17-*H*-tribenzo[*f*,*j*,*n*][1,5,9,12]tetraazacyclopentadecinato-(2-)copper(II) (0.137, 63.5%). (Found C, 67.5; H, 5.9; N, 13.6; Cu 15.2%. $C_{24}H_{22}N_4Cu$ requires C, 66.97; H, 5.11; N, 13.02; Cu 14.81%); λ_{max} (DMF) 333 nm (ε = 14290) 387 nm (ε = 13330), 480 nm (ε = 7630); ν_{max} (nujol) 1620(s), 1590(s), 1520(s), 1500(s), 1480-1460(s, broad), 1360(s), 1345(s), 1330(s), 1290(w), 1255(s), 1205(s), 1190(s), 1180(s), 1165(s), 1140(w), 1125(w) 1100(w), 1080(w), 1040(s), 985(w), 900(s), 875(s), 810(s), 750(s, o-substituted benzene).

8-Chloro-18,19,20,21-tetrahydro-17-*H*-tribenzo[*f*,*j*,*n*][1,5,9,12]tetraazacyclopentadecinato(2-)copper(II) Cu(2Ic-2H)

Copper(II)acetate (0.1g, 0.5 mmol) was added to a dichloromethane solution of the diimine ligand 8-chloro-18,19,20,21-tetrahydro-17-*H*-tribenzo[*f*,*j*,*n*][1,5,9,12]tetraazacyclopentadecinato(2-)copper(II) (0.194g, 0.5 mmol). The red solution was refluxed under nitrogen, and evaporated under vacuum to small volume to give a red-brown solid. This was recrystallised from dichloromethane to give 8-chloro-18,19,20,21-tetrahydro-17-*H*-tribenzo[*f*,*j*,*n*][1,5,9,12]tetraazacyclopentadecinato(2-)copper(II) (0.14g, 62%). (Found C, 61.1; H, 4.5; N, 12.5; Cu, 13.3%. $C_{23}H_{19}N_4ClCu$ requires C, 60.99; H, 4.19; N, 12.37; Cu 14.03%); λ_{max}(DMF) 440 nm(ε=8460), 480 nm(ε=8260); ν_{max} (nujol) 1620(s), 1600(s), 1580(s), 1520(s), 1480-1460(s, broad), 1350(s), 1250(s), 1200(s), 1180(s), 1140(s) 1100(w), 1080(s), 1040(s), 1000(w), 955(s), 940(s), 900(s), 875(s), 850(s), 830(s), 805(s), 750(s, o-substituted benzene), 735(s), 710(s, C-Cl)

8-Methoxy-18,19,20,21-tetrahydro-17-*H*-tribenzo[*f*,*j*,*n*][1,5,9,12]tetraazacyclopentadecinato(2-)copper(II)trihydrate Cu(2Id-2H)

Copper(II)acetate (0.1g, 0.5 mmol) was added to a methanol solution of the diimine ligand 8-methoxy-18,19,20,21-tetrahydro-17-*H*-tribenzo[*f*,*j*,*n*][1,5,9,12]tetraazacyclopentadecine, (0.19g, 0.5 mmol), and the solution refluxed under nitrogen to give a red solution which was evaporated to small volume to give a red-brown solid. This was recrystallised from hot methanol to give 8-methoxy-18,19,20,21-tetrahydro-17-*H*-tribenzo[*f*,*j*,*n*][1,5,9,12]tetraazacyclopentadecinato(2-)copper(II) as the trihydrate (0.145, 65%). Found C, 58.2; H, 5.2; N, 10.8; Cu, 12.2%. $C_{24}H_{28}N_4O_4Cu$ requires C, 57.83; H, 5.62; N, 11.24; Cu 12.85%); λ_{max} (DMF) 440 nm (ε = 9980), 480 nm (ε = 9230); ν_{max} (nujol) 3450-3300 (v.broad, OH,) 1620(s), 1585(s), 1520(s), 1510(s), 1470-1460(s,d), 1350(w), 1310(w), 1270(s), 1250(w), 1220(w), 1200(s), 1165(s), 1120(s), 970(s), 835(s), 750(s, o-substituted benzene)

8-Methoxycarbonyl-18,19,20,21-tetrahydro-17-*H*-tribenzo[*f*,*j*,*n*][1,5,9,12]tetraazacyclopentadecinato(2-)copper(II)monohydrate Cu(2Ie-2H)

Copper(II)acetate (0.1g, 0.5 mmol) was added to a methanol solution of the diimine ligand 8-methoxycarbonyl-18,19,20,21-tetrahydro-17-*H*-tribenzo[*f*,*j*,*n*][1,5,9,12]tetraazacyclopentadecine (0.21g, 0.5 mmol) and the solution was refluxed gently. On cooling, dark brown crystals were formed. These were recrystallised to give 8-methoxycarbonyl-18,19,20,21-tetrahydro-17-*H*-tribenzo[*f*,*j*,*n*][1,5,9,12]tetracyclopentadecinato(2-)copperII as the monohydrate (0.155g, 63%). (Found C, 61.1; H, 4.8; N, 11.7; Cu 12.8%. $C_{25}H_{24}N_4O_3Cu$ requires C, 60.97; H, 4.97; N, 11.6; Cu, 12.95%); λ_{max}(DMF) 400 nm (ε = 13390); ν_{max}(kBr disc) 3500-3400(broad, OH), 2950(s,C-H stretch), 1730(s, C=O stretch), 1625(s), 1585(s), 1530(s), 1510(w), 1435(s), 1455(s), 1455(s), 1390(s), 1360(s), 1300(s), 1260-1240(s), 1200(s), 1180(w), 1150(w), 11.25(w), 1100(w), 1050(w), 1015(w), 965(w), 900(w), 750(s,t, o-substituted benzene). Found m/e 474. $C_{25}H_{22}N_4O_2{}^{65}Cu$ requires 474; m/e 473; $C_{25}H_{22}N_4O_2{}^{63}Cu$ requires 473; m/e 474(M^+), 413, 307, 292, 278, 268, 247(100), 222, 177, 166, 144, 132, 118.

Di[8-carboxy-18,19,20,21-tetrahydro-17-*H*-tribenzo[*f*,*j*,*n*][1,5,9,12]tetraazacyclopentadecinato](2-)copper(II) dihydrate Cu(2If-2H)

Copper(II)acetate (0.1g, 0.5 mmol) was added to a methanol suspension of the diimine ligand 8-carboxy-18,19,20,21-tetrahydro-17-*H*-tribenzo[*f*,*j*,*n*][1,5,9,12]tetraazacyclopentadecine (0.2g, 0.5 mmol) under nitrogen and the mixture refluxed gently and allowed to cool; when a red-brown copper complex was precipitated. This was recrystallised from hot methanol, and vacuum-dried to give the dimer as the dihydrate (0.138g, 60%). (See Section 2.3) (Found C, 63.8; H, 4.5; N, 12.1; Cu 7.1%. $C_{48}H_{44}N_8Cu$ requires C, 64.57; H, 4.93; N, 12.55; Cu, 7.17%). λ_{max}(DMF) 430 nm (ε = 7850), 500 nm (ε = 5220); ν_{max}(KBr disc). 3500(s,broad, OH), 3300(w,broad,NH), 2950(s, CH stretch), 1625(s), 1590(s), 1530(s), 1490(s), 1460(w), 1440(w), 1410-1380(s, broad), 1310(w), 1280(w), 1255(w), 1210(s), 1185(w), 1150(w), 1110(w), 1090(w), 1050(w), 975(w), 790(s), 760(s, o-substituted benzene).

2.5.4. Experimental data on the copper complexes of the quadridentate tetraamines

(10,11,12,13,18,19,20,21-Octahydro-17-*H*-dibenzo[*f* *o*,][1,5,9,14] tetraazacycloseptadecine)copper(II)diperchlorate $Cu(2IIb)(ClO_4)_2$

Copper(II) perchloratehexahydrate (0.132g, 0.5 mmol) was dissolved in methanol, and the diimine 10,11,12,13,18,19,20,21-octahydro-17-*H*-dibenzo[*f*, *o*][1,5,9,14]tetraazacycloseptadecine (0.166g, 0.5 mmol) was added. The mixture was stirred at room temperature for several hours. On standing, very dark brown crystals of (10,11,12,13,18,19,20,21-octahydro-17-*H*-dibenzo[*f*, *o*,][1,5,9,14]tetraaza-cycloseptadecine)copper(II)diperchlorate formed. (0.2g, 68%) (Found C, 42.5; H, 4.7; N, 9.6%. $C_{21}H_{24}N_4CuCl_2O_8$ requires C, 42.20; H, 4.35; N, 9.38%); λ_{max}(DMF) 300 nm (ε = 6140), 370 nm (ε = 5130), 465 nm (5090), 570 nm (920); ν_{max} (nujol) 3250(w,b,NH), 1630(s), 1600(s), 1570(s), 1500(s), 1310(w), 1300(w), 1270(w), 1230(w), 1210, 1200, 1150-1050(s, broad, ClO_4), 980(w), 930(w), 870(w), 825(w), 750(o-substituted benzene.)

(5,6,11,12,18,19,20,21-Octahydro-17-*H*-tribenzo[*f*,*j*,*n*][1,5,9,12]tetraazocyclopentadecine)copper(II)diperchlorate $Cu(2Ia)(ClO_4)_2$

Copper(II)perchlorate hexahydrate (0.132g, 0.5 mmol) was dissolved in methanol (15 cm^3) and the tetraamine ligand 5,6,11,12,18,19,20,21-octahydro-17-*H*[*f*,*j*,*n*][1,5,9,12]tetraazacyclopentadecine (0.179g, 0.5 mmol) was added, giving a brown solution. After refluxing for a few minutes and reducing the volume of the solution under vacuum, a dark brown precipitate was formed. This was recrystallised from dichloromethane/methanol to give (5,6,11,12,18,19,20,21-octahydro-17-*H*-tribenzo[*f*,*j*,*n*][1,5,9,12]tetraazacyclopentadecine) copper(II)diperchlorate as dark brown crystals (0.21g, 67.5%). (Found, C, 44.1; H, 4.3; N, 9.0; Cu, 9.9%. $C_{23}H_{26}N_4CuCl_2O_8$ requires C, 44.48; H, 4.19; N, 9.02; Cu, 10.30%); λ_{max}(DMF) 470 nm (ε = 3820); ν_{max}(nujol) 3200(broad,NH), 1610(s), 1580(s,sh), 1500(s), 1470(s), 1315(s), 1290(w), 1270(w), 1150-1050(s,broad,ClO_4), 930(s), 880(w), 835(s), 760(s, broad, o-substituted benzene).

(8-Methyl-5,6,11,12,18,19.20,21-octahydro-17-*H*-tribenzo[*f*,*j*,*n*][1,5,9,12]tetraazacyclopentadecine)copper(II)diperchlorate $Cu(2Ib)(ClO_4)_2$

Copper(II)perchlorate hexahydrate (0.132g, 0.5 mmol) was dissolved in methanol (15cm^3) and the tetraamine ligand 8-methyl-5,6,11,12,18,19,20,21-octahydro-17-*H*-tribenzo[*f*,*j*,*n*][1,5,9,12]tetraazacyclopentadecine (0.186g, 0.5 mmol) was added. A brown suspension was formed. This was refluxed for a few minutes, filtered and recrystallised from dichloromethane/methanol to give (8-methyl-5,6,11,12,18,19,20,21-octahydro-17-*H*-tribenzo[*f*,*j*,*n*][1,5,9,12]tetraazacyclopentadecine) copper(II)perchlorate as brown crystals (0.21g, 66%). (Found C, 45.9; H, 4.7; N, 8.8; Cu, 11.7%. $C_{24}H_{28}N_4CuCl_2O_8$ requires C, 45.49; H, 4.09; N, 8.84; Cu, 10.14%); λ_{max}(DMF) 333 nm (ε = 13330), 430 nm(sh)(ε =9800), 480 nm (ε = 10890); ν_{max}(nujol) 3250(w, broad NH) 1610(s, broad), 1590-1570(s,sh), 1520(s, broad), 1470(s), 1315(s), 1300(s), 1270(w), 1150-1050(s, broad, ClO_4), 950(w), 930(s), 870(w), 815(s), 760(s, o-substituted benzene).

(8-Chloro-5,6,11,12,18,19,20,21-octahydro-17-*H*-tribenzo[*f*,*j*,*n*][1,5,9,12]tetraazacyclopentadecine)copper(II)diperchloratedihydrate Cu(2Ic)(ClO$_4$)$_2$

Copper(II)perchlorate hexahydrate (0.132g, 0.5 mmol) was dissolved in methanol (15 cm^3) and the tetraamine 8-chloro-5,6,11,12,18,19,20,21-octahydro-17-*H*-tribenzo[*f*,*j*,*n*][1,5,9,12]tetraazacyclopentadecine (0.196g, 0.5 mmol) was added, and the mixture refluxed to give a brown product. This was filtered and recrystallised from dichloromethane/methanol to give (8-chloro-5,6,11,12,18,19,20,21-octahydro-17-*H*-tribenzo[*f*,*j*,*n*][1,5,9,12]tetraazacyclopentadecine)copper(II)-diperchlorate as brown crystals of the dihydrate (0.25g, 76%). (Found C, 40.2; H, 3.5; N, 7.1; Cu, 9.76%. $C_{23}H_{29}N_4Cu\,Cl_3O_{10}$ requires C, 39.91; H, 3.90; N, 8.08; Cu, 9.80%). λ_{max}(DMF) 440 nm ($\mathcal{E}$ = 3150), 485 nm ($\mathcal{E}$ = 4770); ν_{max}(nujol) 3450(s, broad, OH), 3230(w, broad, NH), 1625(s), 1605(s), 1590?1580(s,sh), 1520(s), 1470(s), 1315(s), 1255(s, broad), 1150-1050(s, broad, ClO$_4$), 935(s), 820(s), 770-750(s, broad, o-substituted benzene).

(8-Methoxy-5,6,11,12,18,19,20,21-octahydro-17-*H*-tribenzo[*f*,*j*,*n*][1,5,9,12]tetraazacyclopentadecine)copper(II)diperchlorate Cu(2Id)$(ClO_4)_2$

Copper(II)perchlorate hexahydrate (0.132g, 0.5 mmol) was dissolved in methanol (15 cm^3) and the tetraamine 8-methoxy-5,6,11,12,18,19,20,21-octahydro-17-*H*-tribenzo[*f*,*j*,*n*][1,5,9,12]tetraazacyclopentadecine (0.194g, 0.5 mmol) was added. A very dark brown precipitate was formed. After refluxing the mixture for a few minutes the solid was filtered and recrystallised from dichloromethane/methanol to give (8-methoxy-5,6,11,12,18,19,20,21-octahydro-17-*H*-tribenzo[*f*,*j*,*n*][1,5,9,12]tetraazacyclopentadecine)copperIIdiperchlorate (0.25g, 76%). (Found C, 43.5; H, 4.4; N, 9.3; Cu, 8.75%. $C_{24}H_{28}N_4CuCl_2O_8$ requires C, 44.23; H, 4.30; N, 8.60; Cu, 9.83%). λ_{max}(DMF) 308 nm (ε = 2780), 370 nm (ε = 1360), 430 nm (sh) (ε = 860), 514 nm (ε = 680), ν_{max}(nujol) 3230 (w, broad, NH), 1610(s), 1590(s), 1520(s, broad), 1470(s), 1280(s, broad), 1200(w), 1150-1050(s, broad, ClO_4), 950(w), 850(w), 755 (s, broad, o-substituted benzene)

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Chapter 3 Derivatives of the quadridentate ligands

3.1 Introduction

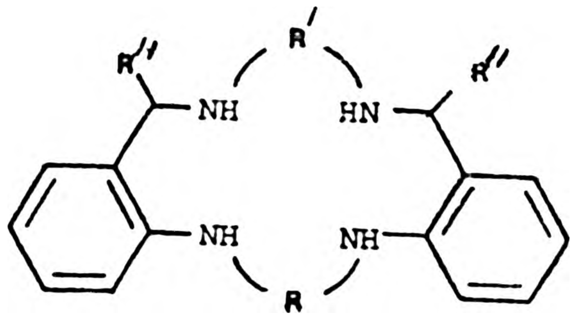
This chapter is concerned with derivatives of the N_4 donor-set systems described in Chapter 2. Modification of the N_4 donor-set ligands was considered to be of interest to see how incorporation of new types of functionalities influenced the pharmaceutical activity. The types of functionalities introduced were of three kinds, as follows;

a) Incorporation of alkyl groups, R'', at the benzyl carbon atoms (Structure 3I)

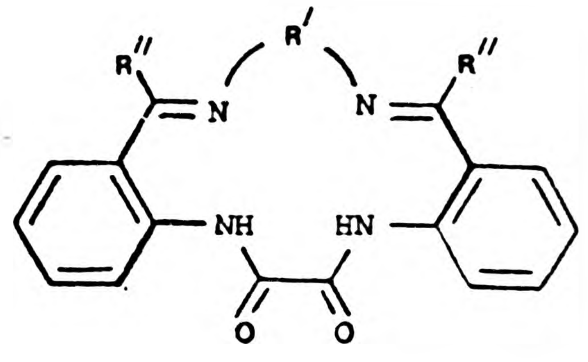
b) Incorporation of oxo groups in the ethane linkage between the anilino nitrogen atoms, as in the oxanilide unit (Structure 3II).

c) Incorporation of a polycyclic unit, via N-alkylation, to give the possible structures 3III and 3IV.

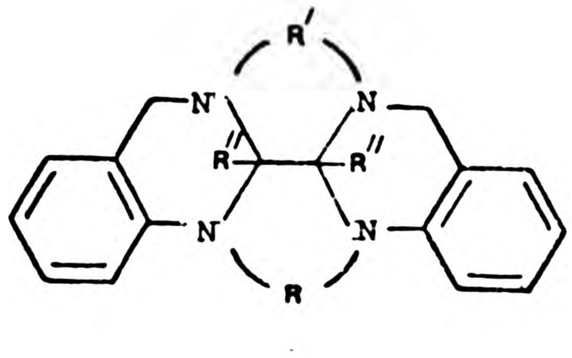
Free ligands of the type 3I were prepared and characterised, where $R=(CH_2)_2, (CH_2)_3$, $R'=C_6H_4$, $R''=CH_3$, C_4H_9, and the copper complexes were also investigated. A bridged compound of the type 3III was isolated where $R=(CH_2)_3$, $R'=C_6H_4$, $R''=H$. It was not found possible to isolate a free ligand of type 3II, when $R'=(CH_2)_2$, $R''=C_6H_5$; $R'=C_6H_4$, $R''=C_6H_5$ although copper complexes of these ligands were obtained and studied.



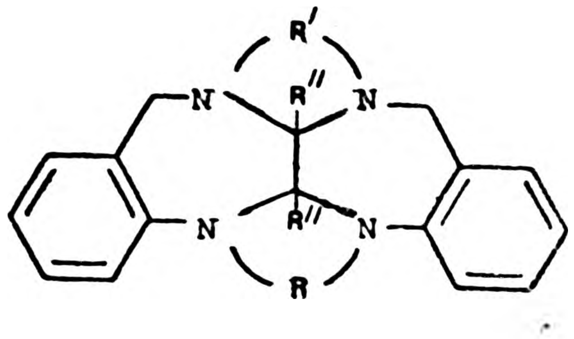
3I



3II



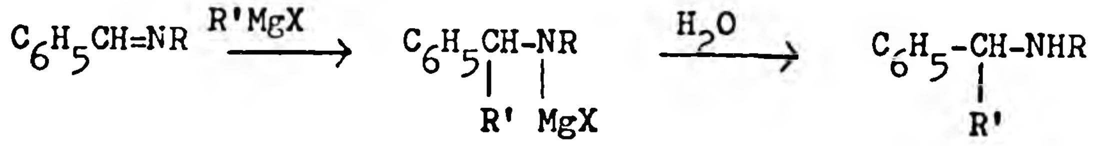
3III



3IV

3.1.1 Preparation of benzyl C-alkylated derivatives and their copper complexes

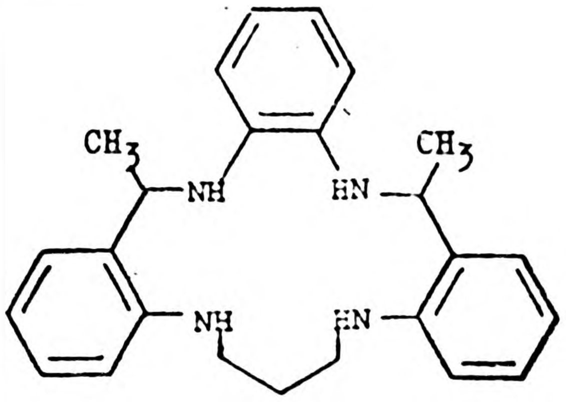
Successful reduction of the imine bonds in the free N_4 donor-set ligands was carried out using diborane as described in Section 2.1.2. The boron atom in diborane is a strong Lewis acid and reduction involves hydrogen replacement followed by electrophilic attack on the centres of highest electron density.[1] In the case of the diimines the initial electrophilic reaction takes place on the imine nitrogen atom, followed by hydride transfer to the benzyl carbon atom. There is evidence that an intermediate boron complex may be formed with boron atoms incorporated into the o-amino-anilino chelating part of the molecule[2], as described in Chapter 2, Section 2.1.2. This reduction reaction indicates that the polarisation of the imine bond might be sufficient to allow alkylation with metal alkyls and aryls. In this case the alkylation would be by the reaction of a carbanion with the carbon atom of the azomethine bond. Sources of carbanions include Grignard reagents which will react[3] with azomethine bonds including those in Schiff bases formed from aryl aldehydes, and in this reaction the alkyl group of the Grignard reagent is attached to the carbon atom of the azomethine bond; subsequent hydrolysis resulting in a secondary amine;



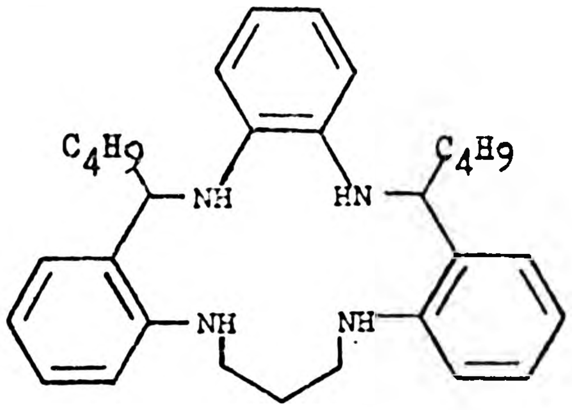
$$C_6H_5CH{=}NR \xrightarrow{R'MgX} C_6H_5\underset{R'}{CH}-\underset{MgX}{N}R \xrightarrow{H_2O} C_6H_5-\underset{R'}{CH}-NHR$$

Since the present work successful alkylations have been carried out to give macrocycles of the type 3I where $R=R'=(CH_2)_2$, $R''=CH_{2n+1}$[4]. In the present work it was thought that alkylation of the benzyl carbon atom could be carried out using metal alkyls and aryls. Methyl lithium and phenyllithium have been found to be more specific than Grignard reagents in alkylating the azomethine bond[3]. Experiments were carried out treating the diimine 2Ia (Fig. 2.1) with methyl lithium and butyl lithium as described in Experimental Section 3.4.

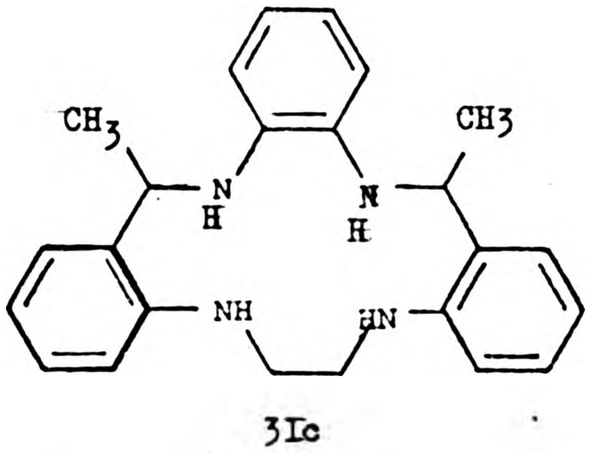
The off-white alkylated ligands formed were as follows:



3Ia

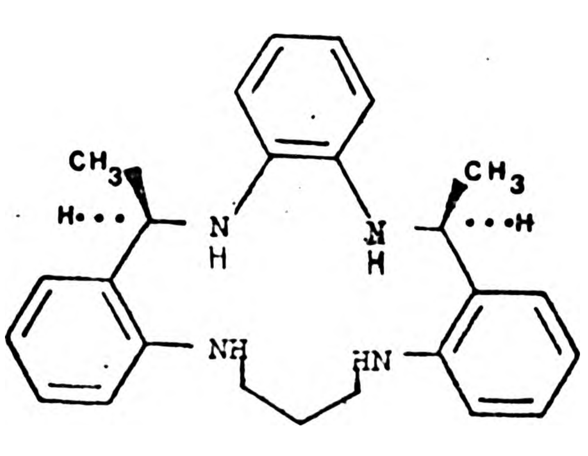


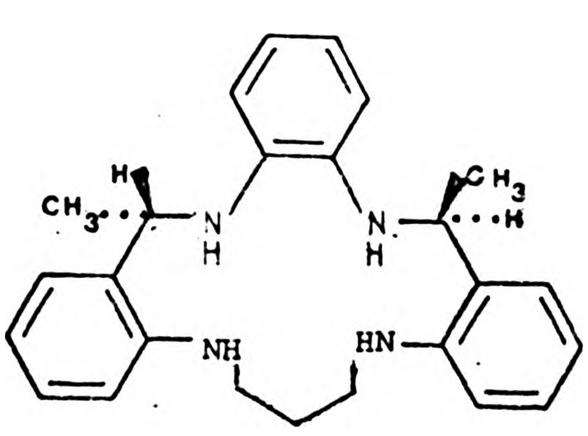
3Ib



3Ic

Additional interest in these ligands lay in the fact that structural isomers are possible, since addition of the alkyl groups creates chiral centres thus giving rise to the possibility of the meso- or racemic forms;





3V (meso)

3VI (racemic)

The type of product obtained would depend on the stereochemistry of an intermediate and the most favourable mode of approach by the second alkyl carbanion. In practice the number of 'H and ^{13}C signals in the spectra of the ligands showed that the two halves of the alkylated ligand were symmetry related, and indicated, but did not confirm, the presence of one or other isomer only. To distinguish between the meso- and rac- isomers, X-ray analysis was required and, although crystalline, the ligands did not provide suitable crystals for analysis.

The copper perchlorate complexes of the alkylated ligands [Cu(3Ia-c)] $(ClO_4)_2$ were prepared as described previously (Section 2.3). Crystals of the copper perchlorate complex of 3Ia which were suitable for X-ray analysis were prepared by recrystallisation from DMF. The crystal structure of one of these crystals is described fully in Section 3.1.7. The copper complex of 3Ia was found to have the meso- structure (3V). A recent crystal structure[5] determination of a ligand of type 3I where $R=(CH_2)_2$, $R'=(CH_2)_3$, $R''=C_2H_5$ which was prepared by reaction with a Grignard reagent, was found to be the meso- form.

3.1.2. ^1H spectra of the benzyl C-alkylated derivatives

The ^1H spectra of the alkyl-substituted ligands showed more complex coupling than the unsubstituted ligands. This was an indication that the alkyl groups, even the methyl groups, exerted sufficient steric hindrance to make the hydrogen atoms on the methylene groups attached to the 'anilino' nitrogen atoms (Hi,Hi') non-equivalent. However, the two halves of the molecule were symmetry related as confirmed by the ^{13}C spectra. The details of the spectra are set out in Table 3.1 and compared to that of the non-alkylated tetra-amine where R=H. The signals due to the protons of the ligand 3Ia are designated according to the diagram below.

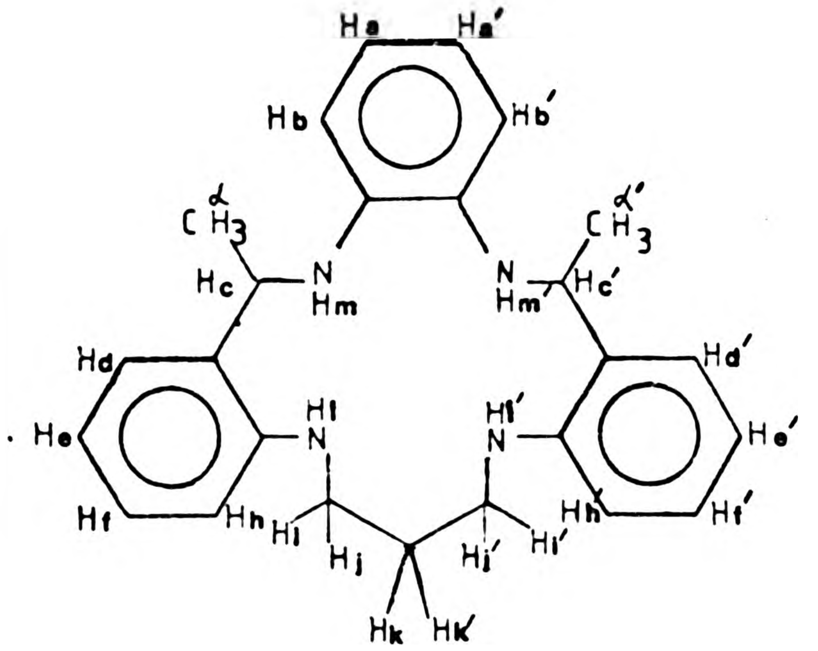


Fig. 3.1 Hydrogen labelling in the ligand 3Ia

The methyl protons ($H\alpha$, α') showed the expected doublet due to coupling with Hc, at high field. Signals from Hk(k') appeared as a just-discernible septuplet, and this indicated the non-equivalence of the methylene protons Hi,Hj. The septuplet was probably the result of overlapping signals.

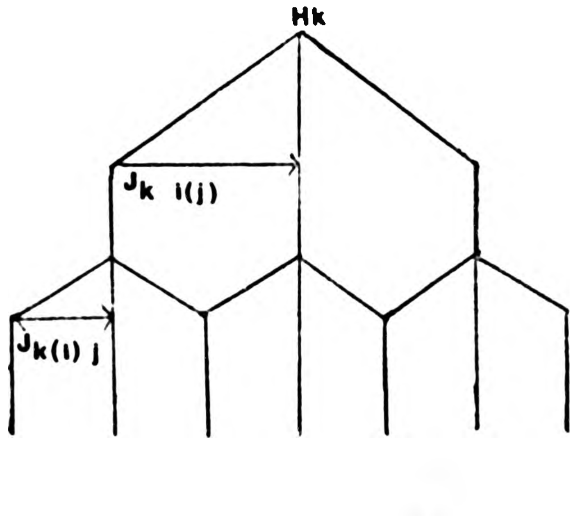


Fig. 3.2 Splitting patterns in ^{1}H spectra of 3Ia

The signals from the methylene protons Hi(i'), Hj, H(j') appeared as a complex multiplet, again showing the non-equivalence of Hi and Hj, and indicating reduction in flexibility of the macrocycle caused by benzyl C-alkylation. The benzylic protons Hc,c' were coupled to the adjacent NH protons, as eight peaks were seen. After shaking with D_2O, this signal was resolved into four clear peaks. The coupling was seen in 3Ia ($R''=CH_3$) in the doublet signal given by the amino protons (Hm,m'). Reduced flexibility of these rings may enhance the intramolecular hydrogen bonding, thus reducing the rate of exchange of the benzylic NH protons. It is unusual to see any clear coupling on these amino proton signals[6]. The observed coupling of the benzylic methylene protons in the spectrum of 3Ia is in contrast to the ^{1}H n.m.r. spectrum of the non-alkylated tetraamine 2IHa in which no such coupling is observed (see also Section 2.2.2.2).

The spectrum of the butyl-substituted ligand, 3Ib, was more complex and indicated further steric restriction of the methylene groups in the methylene bridge. The protons were designated as below;

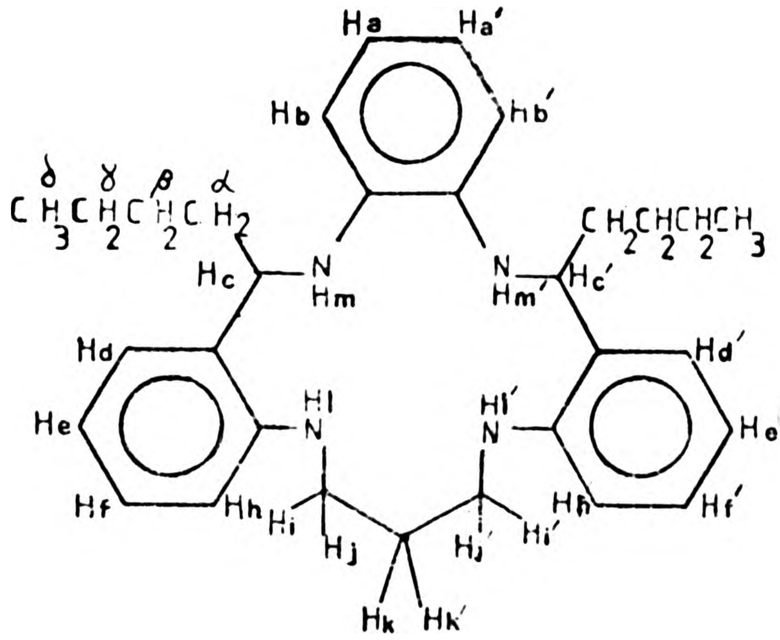


Fig. 3.3 Hydrogen labelling in the ligand 3Ib

The 'α' methylene protons of the butyl group showed as a quadruplet and the 'β' and 'γ' methylene protons gave signals which appeared as a combined septuplet. At very high field, the terminal methyl groups appeared as a triplet. It was evident from this spectrum, and from the ^{13}C spectrum, (see below) that the butyl groups were sterically equivalent and that the molecule had two symmetrical 'halves' in spite of the restricted rotation of the methylene groups. In this molecule, the methylene protons, Hk,Hk' seemed to be non-equivalent as the signal appeared as two multiplets; in contrast to the spectrum of 3Ia. The benzylic protons Hc,Hc' showed as a triplet due to coupling with the adjacent methylene group of the butyl group, and additional coupling of this signal to the adjacent amino proton was not apparent.

The spectrum of 3Ic was less complex than the above spectra as would be expected; however the signal from the methylene groups (Hi,Hj,Hi',Hj') showed as a sextuplet again indicating non-equivalence of the protons due to restricted interconversion of ring conformations, and showing clearly the coupling with adjacent amino protons. Overall, the chemical shifts were very similar for all the tetraamines (3Ia-c) and for the unsubstituted ligand 2IHa (See Table 3.1)

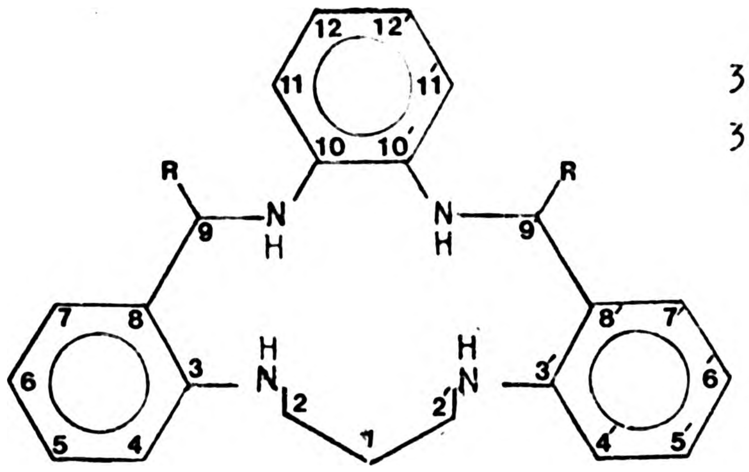
3.1.3 ^{13}C spectra of the benzyl C-alkylated derivatives

The ^{13}C spectra of the alkyl-substituted ligands 3Ia and 3Ib were of interest because the number of signals indicated that only one isomer was present, probably the meso isomer since ^{13}C spectra are very sensitive to small steric differences. The carbon atoms

Table 3.1. Comparison of ^{1}H spectra of benzyl C-alkylated tetraamines of type 3Ia where $R'=C_6H_5$.(ppm, $CDCl_3$)

Assignment	3Ia $R=(CH_2)_3$ $R''=CH_3$	3Ib $R=(CH_2)_3$ $R''=CH_2CH_2CH_2CH_3$	3Ic $R=(CH_2)_2$ $R''=CH_3$	2IHa $R=(CH_2)_3$ $R''=H$
$H\alpha$, $H\alpha'$	1.7(d,6H,J=4.4)	1.8(quad,4H,J=10.0)	1.6(d,6H,J=6.0)	Not present
$H\beta$ $H\beta'$	Not present	1.2(sept.8H,J=5.0)	Not present	Not present
$H\gamma$ $H\gamma'$	Not present		Not present	Not present
$H\delta$ $H\delta'$	Not present	0.92(t.6H,J=10.0)	Not present	Not present
Hk, Hk'	1.55(sept,2H,J=2.0)	1.8-2.0,2.0-2.2 (2 x m, 2H)	Not present	1.95(quin,2H,J=4.4)
Hi,Hi',Hj,Hj'	3.5(m, 4H)	3.18-3.3, 3.3-3.47 (2 x m, 4H)	3.35(sext,4H,J=6.0)	3.35(quad,4H,J=4.4)
Hc, Hc'	4.5(oct.2H,J=2.2)	4.1(t,2H,J=10.0)	4.4(quad,2H,J=6.0)	4.24 (s.4H)
Hl,Hl',Hm,Hm'	3.2(b.s, 2H) 5.15(d,2H,J=2.2)	3.58(s,2H),4.9(s,2H)	4.90-5.2(m,4H)	3.9-4.4(b.s,4H)
Ha-Hb,Ha'-Hb'	6.61-6.85(m.6H)	6.66-6.89(m.8H)	6.62-6.92(m.8H)	6.66-6.78(m.6H)
Hd-Hh,Hd'-Hh'	7.1-7.39(m.6H)	7.15-7.38(m.4H)	7.12-7.32(m.4H)	6.82-6.98(m.6H)

were labelled as shown in Fig. 3.4;



3Ia, $R=CH_3$, Fig 3.5

3Ib, $R=C_4H_9$, See text.

Fig. 3.4 Carbon labelling in the ligands 3Ia, 3Ib.

In the methyl-substituted ligand 3Ia, two signals coincided at ~~ca. 128 ppm; these~~ were resolved in the off-resonance spectrum into a quaternary ^{13}C signal (singlet) and a C-H signal (doublet) which were assigned to C_8 and C_7 respectively by analogy with the values of these signals seen in the unsubstituted ligand (Fig 3.5). Thus there were nine aromatic ^{13}C signals, and four sp^3 ^{13}C signals (C_1, C_2) in the spectrum of this ligand, indicating that the 'halves' of the molecule were symmetrical.

In the spectrum of the butyl-substituted ligand, 9 aromatic signals were observed. Two ^{13}C signals in the butyl side chain were coincident; this was to be expected from the calculated values obtained by using the formula;

$\delta(C_i) = -2.6 + 9.1\, n\alpha + 9.4\, n\beta - 2.5\, n\gamma + 0.3\, n\delta$ (ppm) where $\delta(C_i)$ is the chemical shift in ppm for a carbon atom in a saturated hydrocarbon chain, n is the number of adjacent carbon atoms.

i.e.. $C_{\gamma} - C_{\beta} - C_{\alpha} - C_{i} - C_{\alpha} - C_{\beta} - C_{\gamma}$ etc. [7]

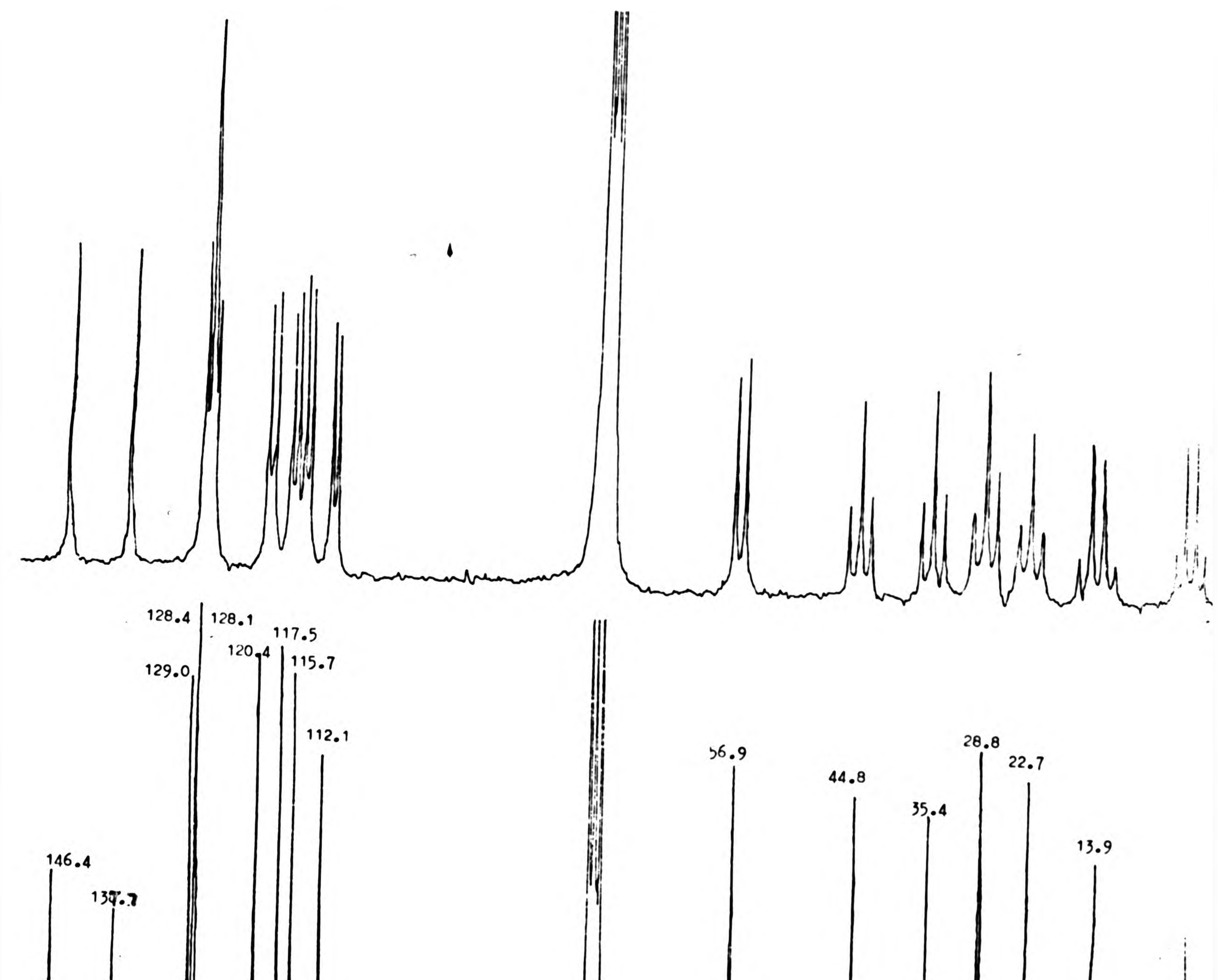
Thus for the substituent butyl side-chains which were apparently sterically and chemically equivalent, the observed and calculated values are as follows;

$CH_3 - CH_2 - CH_2 - CH_2 - C - H$
d(d') c(c') b(b') a(a')

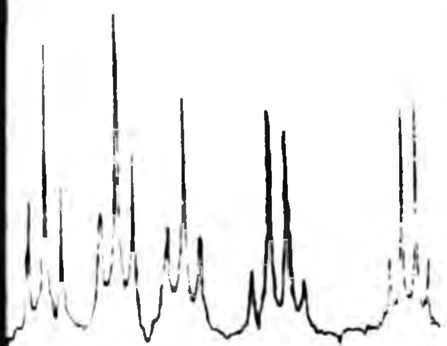
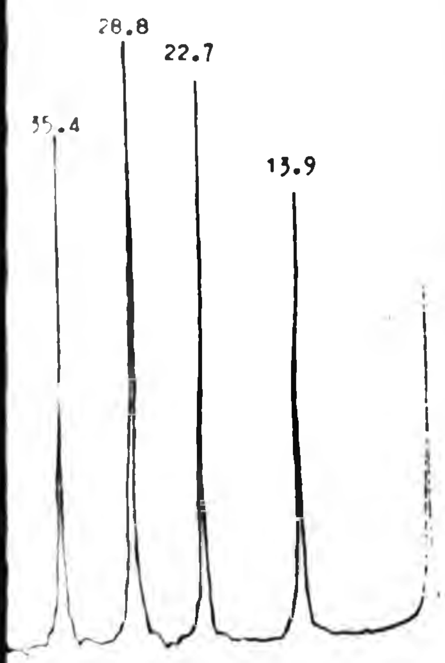
C atom	Observed value	Calculated value
Ca, Ca'	22.7	22.5
Cb, Cb'	35.4	34.4
Cc, Cc'	22.7	22.5
Cd, Cd'	13.9	13.7

Allowing for the coincidence of the Ca and Cc signals, an expected total of seven sp^3-type ^{13}C signals were seen, and this showed that the two halves of the molecule were symmetrical. The assignment of the signals in the unsubstituted tetraamine (2IHa) and the methyl- and butyl- substituted tetraamines (3Ia and 3Ib) are given in Fig. 3.5.

The signals were generally slightly further upfield in the alkyl-substituted ligands than in the tetraamines (previously discussed in Section 2.2.3). This might be considered to be due to the electron-releasing effects of the alkyl groups, and is particularly marked at C_8, the alkyl-substituted benzyl carbon atom, where there was a comparative upfield shift of 6 ppm in both alkylated ligands.



^{13}C spectra of the butyl-substituted tetraamine 31b,showing decoupled and off-resonance signals.

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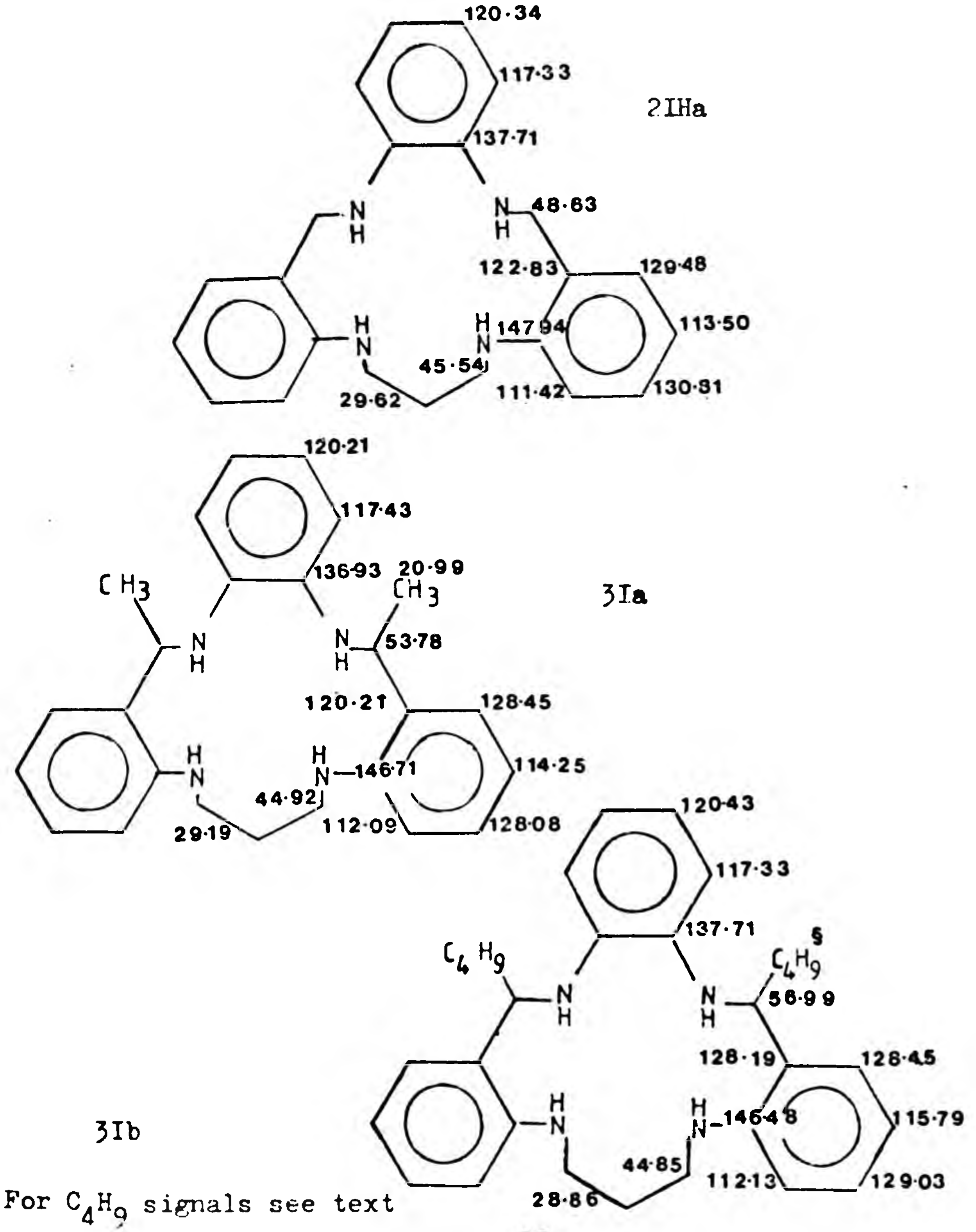


2IHa

3Ia

3Ib

§For C_4H_9 signals see text

Fig. 3.5 Chemical shifts in the ^{13}C nmr spectra of 3Ia,b compared to the non-alkylated tetraamine (2IHa).

The ^{13}C spectra confirmed the evidence of the 'H spectra being consistent with only a single isomer being present, and an element of symmetry relating the two halves of the macrocycles. Whether this is a mirror plane, indicating the meso form, or a two-fold axis, indicating the racemic form, cannot be definitely concluded on the basis of the spectra.

3.1.4. Infra-red spectra of the benzyl C-alkylated ligands and their copper complexes

The infra-red spectra of the alkyl-substituted ligands were similar to those of the tetraamines described previously. The bands due to the amino groups showed greater complexity and sharpness in these alkylated ligands. As expected, there were additional peaks due to the methyl groups. Three peaks, characteristic of C-H stretch in the methyl group[8] were clearly shown in the range 2850-2970 (spectrum recorded in H.C.B). In particular, a band at 2960 cm^{-1}, where methylene groups do not absorb, was especially characteristic of the C-H bond. Absorption due to NH stretch in both 3Ia and 3Ic were seen as strong individual bands between 3420-3295 cm^{-1}. In contrast, the NH stretch absorption in the butyl-substituted tetraamine (3Ib) showed as a single strong band at 3400 cm^{-1}. In addition to the peaks characteristic of CH stretch in the methyl group, additional bands were seen in the spectrum (recorded in H.C.B) between 3000-3100 cm^{-1}. Presumably these were due to the sequence of methylene groups in the butyl groups. The main peaks in the spectra (recorded in nujol) are given in Table 3.2 The spectra of the copper perchlorate complexes of the tetraamines 3Ia-c showed the features previously encountered in copper complexes of this type; namely broadening of the bands in the fingerprint region, particularly at ca. 750 cm^{-1}. In all the spectra the very broad band at 1150-1050 cm^{-1} was characteristic of uncoordinated ClO_4^- groups.[9]

Table 3.2 Main peaks in the infra-red spectra of the tetraamines 3Ia-c (nujol)

3Ia	3Ib	3Ic	Assignment
3410	3400	3420, 3400	NH stretch
3295, 3230, 3220		3310, 32900	
1600	1610	1605	C=C in benzene derivatives
1590	1590	1585	NH bend
1530-1510	1530-1520	1520	CH_2 deformation
1470	1470	1470	CH_2 in-plane deformation
1350-1330	1320	1330	Symmetrical deformation of the CH_3 group
1310	1320		
1250	1270	1260	CH_2 vibration
	1250		
1220			
1140	1130	1140	C-N stretch in aliphatic secondary amines
1100	1050	1090	
		1065	Additional C-N stretch
		1050	

3.1.5. U.v/visible spectra of the alkyl-substituted tetraamines

The alkyl-substituted tetraamines were white compounds, and the absorption maxima were in the u.v. region, as would be expected. In the saturated macrocycles absorption was due to $n-\sigma^*$ transitions. The values of the extinction coefficients were comparable with those shown by the tetraamines described previously (See Section 2.2.5).

The copper perchlorate complexes of the methyl-substituted ligands were purple, and gave a range of absorption maxima ranging from absorption in the u.v to absorption in the far visible region (at ca. 450 nm and 710 nm) which were of the same order in both complexes. The latter was probably due to d - d transitions. These were not normally seen in the more usual red-brown complexes obtained from the quadridentate ligands where charge transfer bands were very intense (See 2.2.5). The brown copper perchlorate complex of the butyl-substituted tetraamine, in addition to the charge transfer band, showed absorption within the visible region. The absorption data is summarised in Table 3.3.

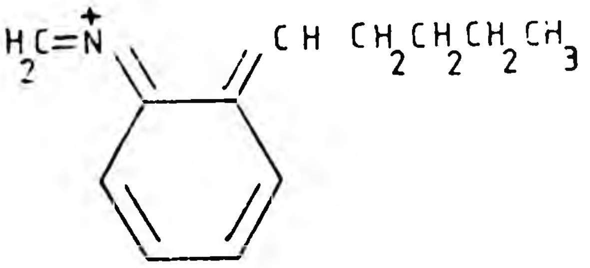
3.1.6 Mass spectra of the benzyl C-alkylated ligands

The mass peaks obtained in the spectra of the ligands 3Ia-c were in good agreement with the calculated values (Table 3.4). There was no common fragmentation pattern seen in the spectra of these tetraamines, although a peak corresponding to $C_9H_{10}N$ was seen in all three spectra. This had been seen in many of the previous

Table 3.3. U.v/visible data of the benzyl C-alkylated tetraamines, and their copper complexes (ε=litre $mol^{-1}cm^{-1}$, λ= nm)

3Ia	λ_{max}	235	295		
	ε	10580	6690		
3Ib	λ_{max}	254	302		
	ε	19050	6800		
3Ic	λ_{max}	235	300		
	ε	8900	7260		
$[Cu(3Ia)](ClO_4)_2$	λ_{max}	310	380	450	710
	ε	6490	2800	1050	1890
$[Cu(3Ib)](ClO_4)_2$	λ_{max}	267	375	440	-
	ε	10770	6600	1470	-
$[Cu(3Ic)](ClO_4)_2$	λ_{max}	310	385	440	712
	ε	9810	3020	1750	1910

spectra described (Section 2.2.4), but it was unlikely to have arisen from a common fragmentation route in the benzyl C-alkylated ligands because of the basic differences in their inner great rings. There was also considerable difference in the base peaks (Table 3.4), that of the ligand 3Ib probably corresponding to a unit in which the butyl group was retained; a possible structure is as shown (3VII).



3VII

It was interesting that in these spectra the characteristic peak at ca. 118 was less intense than in the spectra of the non-alkylated tetraamines - this was some indication of the o-substituted structures proposed for this unit (2XXIV) since formation of these would require greater breakdown and/or rearrangement of the benzyl C-alkylated ligands.

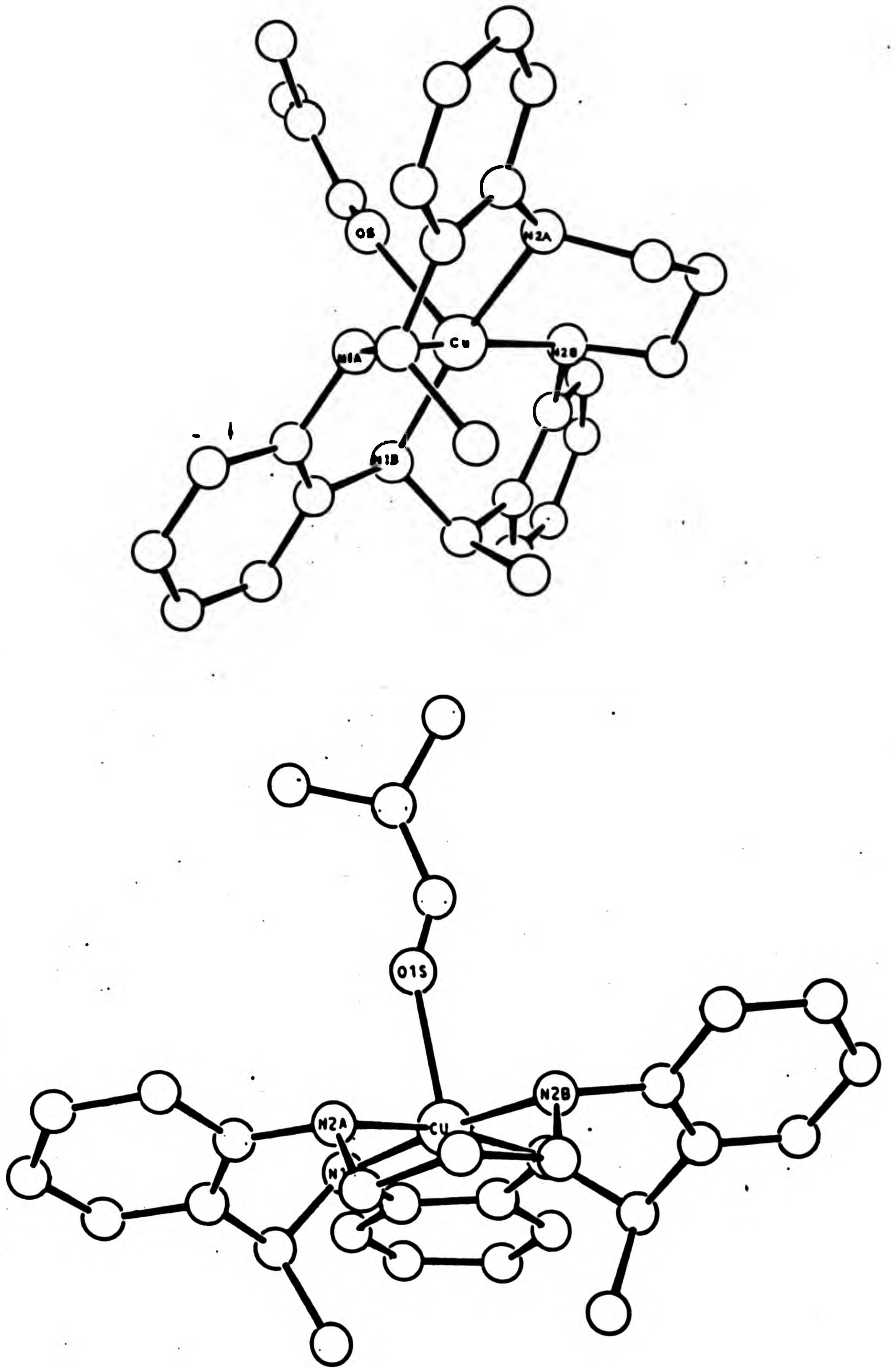
Table 3.4 Measured and calculated values of the mass peaks and base peaks in the spectra of the tetraamines 3Ia-c

Ligand	Formula	%	Measured value	Calculated value
3Ia	$C_{25}H_{30}N_4$	22.0	386.2475	386.2470
	$C_6H_8N_2$	100.0	108.0697	108.0687
3Ib	$C_{31}H_{42}N_4$	47.0	470.3405	470.3470
	$C_{12}H_{16}N$	100.0	174.1291	174.1282
3Ic	$C_{24}H_{28}N_4$	74.0	372.2308	372.2318
	$C_9H_{10}N$	100.0	132.0824	132.0813

3.1.7 The crystal structure of /5,12-dimethyl-18,19,20,21-tetrahydro-17-H-tribenzo(f,j,n)(1,5,9,12)tetraazacyclopentadecine7 /dimethylformamide7copper(II)diperchlorate. DMF

Crystals of the copper complex were obtained by the interaction of the ligand 3Ia in solution in DMF, with a methanol solution of copper(II)perchlorate, as described in Section 3.4.1.
Crystal data and details of reflection intensity and data reduction are given in Appendix A, tables 1A-4A.

The space group $P2_1/C$ was assumed and confirmed by satisfactory solution and refinements of the structure. The position of the copper atom was identified from a Patterson synthesis, and inclusion of this atom in a Fourier synthesis revealed the positions of all the remaining non-hydrogen atoms. Six cycles of full-matrix least-squares refinement with these atoms assigned isotropic thermal parameters resulted in a conventional R factor of 0.083. In the final six cycles the copper atom, both chlorine atoms and the oxygen atoms of the non-disordered perchlorate anion /O(21)-O(24)7, and the carbon atoms of the coordinated solvent molecule were assigned anisotropic thermal parameters. The hydrogen atoms were included in calculated positions with C-H lengths of 1.08Å. Final R factors were R = 0.0716, R' = 0.0671 (Appendix A, Table 1A). Tables of position parameters, anisotropic thermal parameters, bond lengths and angles in the ligands are given in Appendix A, Tables 2A-4A. Structure factors are listed in Appendix D, Table 1D. The unit cell contains four discrete molecules of the complex



Ortep diagrams of the copper complex of 3Ia $[Cu(C_{25}H_{30}N_4).DMF](ClO_4)_2.DMF$.

$[\mathrm{Cu}(C_{25}H_{30}N_4)\mathrm{DMF}]^{2+}$, eight perchlorate anions and four disordered DMF molecules. Atom labelling is shown below;

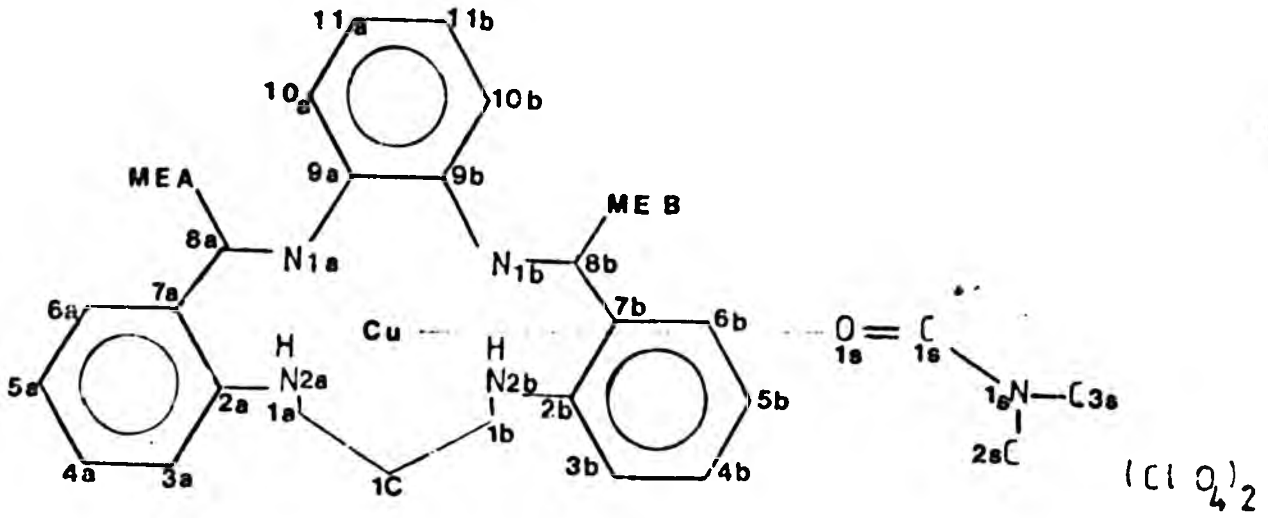


Fig 3.6 Atom labelling in $[\mathrm{Cu}(3\mathrm{Ia})\mathrm{DMF}](\mathrm{ClO}_4)_2$

Coordination to the copper atom was approximately square pyramidal; the oxygen atom of the dimethylformamide molecule being the apical donor atom. The oxygen atom was at a greater bonding distance than the nitrogen atoms (Table 3.5)

Chemically equivalent bond lengths and angles in the two halves of the molecule are compared in Appendix A, Table 4A. The values can be seen to be very close, and can be considered to be equal within experimental error.

In interesting contrast to the conformation adopted by the sterically-crowded complex 3IIc (Section 3.2.5) the chelate rings were found to form a roughly dome-shaped structure, in which the copper formed the 'top' of the dome.

The benzene rings (C(2)-C(7)), in contrast, are bent upwards away from the dome of chelate rings, and tilted with respect to the plane of the N_4 donor set. The torsion angles are given in Table 3.6.

The methyl groups are both found on the same side of the molecule, showing that the crystal and probably the whole of the crystalline sample was the 'meso' form, as opposed to the racemic form of the structure. Alkylated macrocycles have been obtained using Grignard reagents[4], and a crystal structure determination of one of these[12] has shown that it is the 'meso' form. This is some evidence for the 'meso' structure of a bulk sample. Other evidence is discussed in Section 3.1.3.

In this structure the methyl groups are located on the inside of the dome and are bent away from the copper, and are positioned pointing slightly inwards towards the copper atom. The torsion angles, and the angles round these groups are, within limits of experimental error, equivalent on each side of the molecule (Tables 3.6 and 3.7.)

In this complex, one of the perchlorate anions centred on Cl(1) was found to be disordered. The site occupation factors of the oxygen atoms in the disordered model of this molecule were refined as detailed in Footnote* to Table 2A, Appendix A. The total of the site occupation factors amounted to 3.97 which is close to the theoretical value of 4.0. A solvated DMF molecule was also present in the unit cell. This was disordered along a pseudo 2-fold rotation axis passing through the N(2s) and O(2s) atoms, as detailed in Footnote mentioned above.

Table 3.5 Bond lengths and angles in the coordination sphere of $[Cu(C_{25}H_{30}N_4)DMF](ClO_4)_2$ DMF

Bond lengths/Å

Cu-N(1a)	2.028(9)	Cu-N(1b)	2.007(9)
Cu-N(2a)	2.069(9)	Cu-N(2b)	2.052(10)
Cu-O(1s)	2.205(12)		

Bond angles/°

N(1a)-Cu-N(2a)	91.6(4)	N(1b)-Cu-N(2b)	92.7(4)
N(1a)-Cu-N(2b)	175.3(4)	N(1b)-Cu-N(2a)	170.5(4)
N(1a)-Cu-O(1s)	89.9(4)	N(1b)-Cu-O(1s)	96.9(4)
N(2a)-Cu-O(1s)	92.1(4)	N(2b)-Cu-O(1s)	94.7(4)
N(1a)-Cu-N(1b)	85.6(4)		
N(2a)-Cu-N(2b)	89.5(4)		

Table 3.6 . Torsion angles /° in the inner great ring of $[Cu(C_{25}H_{30}N_4)DMF](ClO_4)_2$ DMF

	part a	part b
N(2)-C(1)'-C(1C)-C(1)'*	63.36	-64.67
C(1C)-C(1)-N(2)-C(2)	-161.56	163.16
C(1)-N(2)-C(2)-C(7)	-98.13	96.42
N(2)-C(2)-C(7)-C(8)	-10.51	10.26
C(2)-C(7)-C(8)-N(1)	-43.72	46.3
C(7)-C(8)-N(1)-C(9)	-167.72	162.18
C(8)-N(1)-C(9)-C(9')	-127.01	135.91
N(1)-C(9)-C(9')-N(1)'	- 4.7	-

Footnote; * Primes denote atoms in the alternative part (a or b) of the molecule.

Table 3.7 Torsion angles /° round the methyl substituent groups in the inner and outer great ring; and angles round the methyl-substituted bond in $[\mathrm{Cu(C_{25}H_{30}N_4)DMF}](\mathrm{ClO_4})_2\mathrm{DMF}$

	part a	part b
C(2)-C(7)-C(8)-C(ME)	81.14	-78.17
C(6)-C(7)-C(8)-C(ME)	-102.61	104.81
C(ME)-C(8)-N(1)-C(9)	64.75	-69.48
C(7)-C(8)-C(ME)	115.2(10)	116.4(11)
C(7)-C(8)-N(1)	109.0(9)	108.7(10)
C(ME)-C(8)-N(1)	110.5(10)	109.7(11)

Table 3.8 Least-squares planes and atom deviations in $[Cu(C_{25}H_{30}N_4)DMF](ClO_4)_2DMF$

Plane 1	atoms	
	N(1a)	0.04
	N(2a)	-0.04
	N(1b)	-0.04
	N(2b)	0.04
	Cu*	0.12
	C(MEA)*	-2.38
	C(MEB)*	-2.38

equation (-15.0188)X + (4.5623)Y + (9.5536)Z = -4.6744

Plane 2	atoms	
	N(2a)	-0.156
	C(2a)	0.224
	C(7a)	0.035
	C(8a)	-0.388
	N(1a)	0.375
	Cu	-0.091

equation (-11.0194)X + (6.3393)Y + (10.9354)Z = 0.4909

Plane 3	atoms	
	N(2b)	-0.192
	C(2b)	0.241
	C(7b)	0.051

	C(8b)	-0.415
	N(1b)	0.376
	Cu	-0.061

equation (-13.8037)X + (1.9271)Y + (12.4303)Z = -4.1269

Footnote;* This atom not used in calculation of the plane.

Plane 4	atoms	
	N(2a)	-0.326
	C(1a)	0.286
	C(1c)	-0.183
	C(1b)	0.251
	N(2b)	-0.295
	Cu	0.266

equation (17.4860)X + (-5.3305)Y + (-21831)Z = 8.8421

Plane 5	atoms	
	N(1a)	0.130
	C(9a)	0.0077
	C(9b)	-0.0323
	N(1b)	0.0329
	Cu	-0.0213

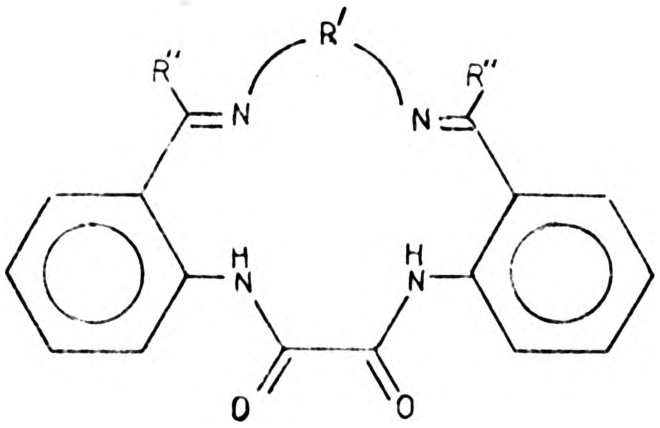
equation (-14.1546)X + (3.9143)Y + (11.0323)Z = -3.6690

Table 3.9 Angles between planes /°

Plane	1	2	3	4	5
1	0	15.8	17.3	28.0	6.8
2	15.8	0	24.2	38.5	15.2
3	17.3	24.2	0	43.0	11.2
4	28.0	38.5	43.0	0	34.6
5	6.8	15.2	11.2	34.6	0

3.2 The copper complexes of the oxalo-bridged ligands

This section is concerned with the background to, and preparation of, the neutral copper complexes of the oxalo-bridged ligands of the type 3II as shown;



3IIa R''=H, R'=C_6H_4

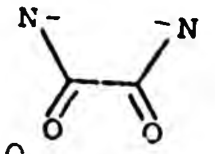
3IIb R''=CH_3, R'=C_6H_4

3IIc R''=C_6H_5, R'=C_6H_4

3IId R''=CH_3, R'=$(CH_2)_2$

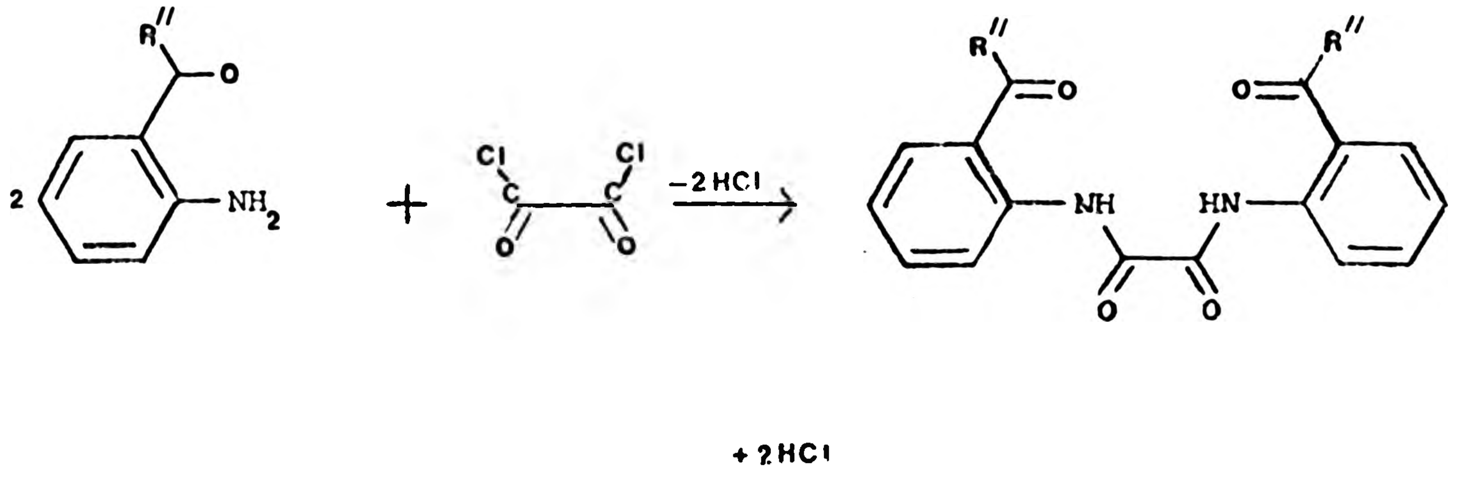
3IIe R''=C_6H_5, R'=$(CH_2)_2$

3.2.1. Previous studies on the oxalo-bridged ligands

Several systems involving metal coordination to the oxalo-bridged unit  have been prepared. The free ligand 3IIa, where R=H[10], has been synthesised following previous work in which the Ni(II), Cu(II) and Co(II) complexes of that ligand were prepared by an in situ method[11]. Subsequent work has shown that the Fe(III) complex of the ethane-bridged ligand of the type 3I, where

$R=(CH_2)_2$, $R'=C_6H_4$, $R''=H$, could be oxidised to give a (dimeric) Fe(III) complex of the oxalo-bridged ligand of the type 3IIa ($R'=C_6H_4$, $R''=H$, Section 3.2).[12] Preliminary results indicated that the Cu(II) and Co(III) complexes of this ligand were also susceptible to this type of oxidation. (Scheme I).

In this work it was decided to extend this work to involve ligands where R'' = alkyl or aryl groups. In order to attempt synthesis of the ligands 3IIb and 3IIc, the precursors 2,2'-(oxalyldiimino)bis-acetophenone (3VIII) and 2,2'-(oxalyldiimino)bisbenzophenone (3IX) were prepared by condensation of the appropriate o-amino-substituted diketones with oxalyl chloride as described in previous work.[13]

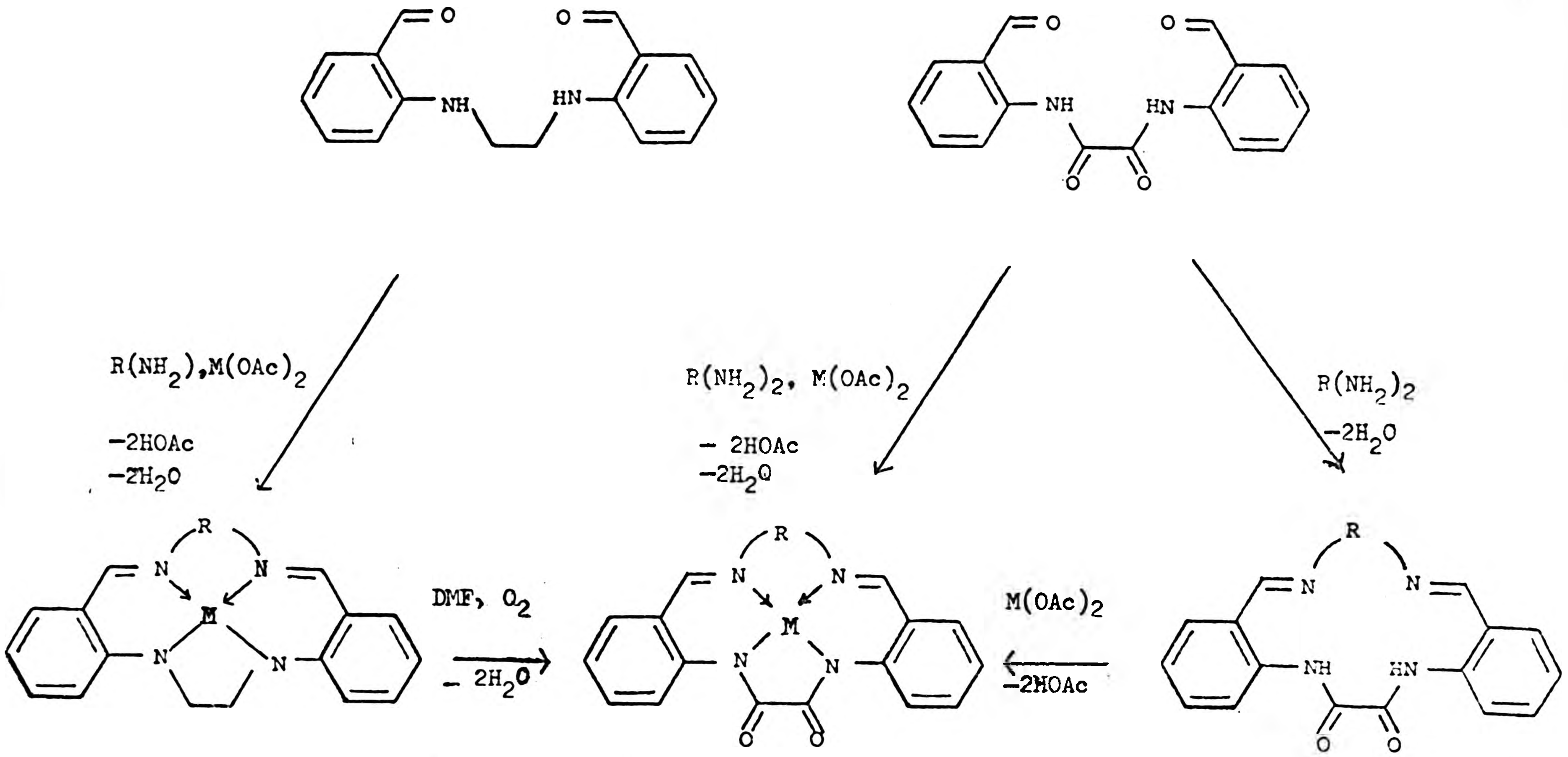


3 VIII $R''=CH_3$

3 IX $R''=C_6H_5$

Scheme I

A summary of the interrelationships between the oxalo- and ethane-bridged ligands



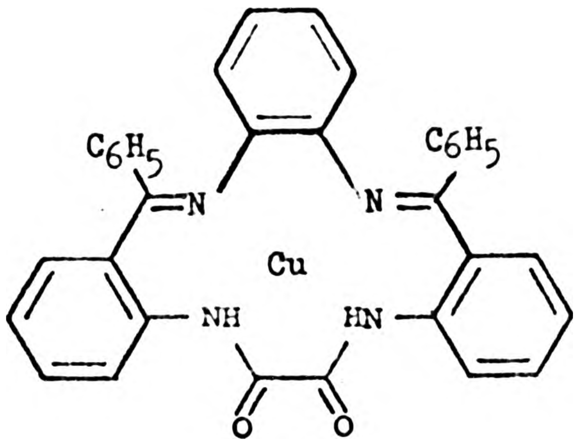
3.2.2. The attempted synthesis of the methyl- and phenyl-substituted ligands (3IIb-e)

In a series of experiments 2,2'-(oxalyldiimino)bisacetophenone, 3VIII, was refluxed with a slight excess of diaminoethane (Scheme II) to try to obtain the ligand 3IId. Although heating in DMF was continued for up to five days, the solid which separated on cooling the solution always proved to be the starting material. The experiments were repeated with the addition of copper acetate in an attempt to make the copper(II)complex in conditions where the copper ions might provide a thermodynamic template. In some of these experiments excess diamine or triethylamine was used to promote the removal of amido protons[14]. The copper complexes were not obtained by these means. Similar experiments were carried out using 1,2-diaminobenzene, both with and without the addition of p-toluenesulphonic acid as Lewis acid catalyst. None of the free ligand 3IIb was obtained, and the dark materials obtained when copper acetate was included in the reaction mixture, under reaction conditions as above, proved to be the copper complexes of the diketone.

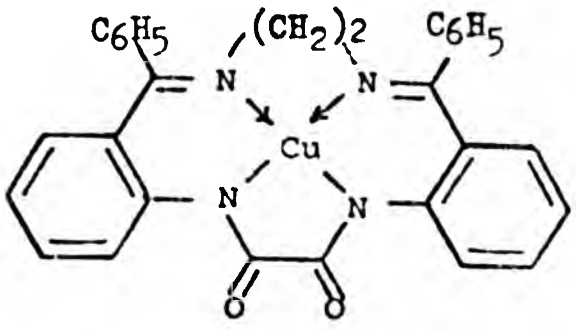
Failure of the reactants to cyclise was probably due to the increased electron density at the carbonyl carbon atoms, due to the electron-releasing methyl groups to which they were attached. An alternative approach to obtain the copper complex of this ligand is described in Section 3.2.5. Where R"=phenyl (3IX), however, the carbonyl carbon would not be expected to be the site of greatly increased electron density, and the probability of cyclisation seemed to be greater although steric restrictions will be imposed by the phenyl rings. Experiments to obtain the free ligands 3IIc and 3IIe treating 2,2'-(oxalyldiimino)bisbenzophenone with 1,2-diaminobenzene and with 1,2-diaminoethane were unsuccessful. However, the copper complexes of the phenyl-substituted ligands (3IIc, 3IIe) were readily prepared as described below.

3.2.3 The copper complexes of the phenyl-substituted ligands (3IIc and 3IIe)

Although preparation of the free ligands 3IIc and 3IIe was unsuccessful, addition of copper acetate to the reaction mixture resulted in crystalline samples of the desired copper complexes (See Experimental Section 3.4) as below.



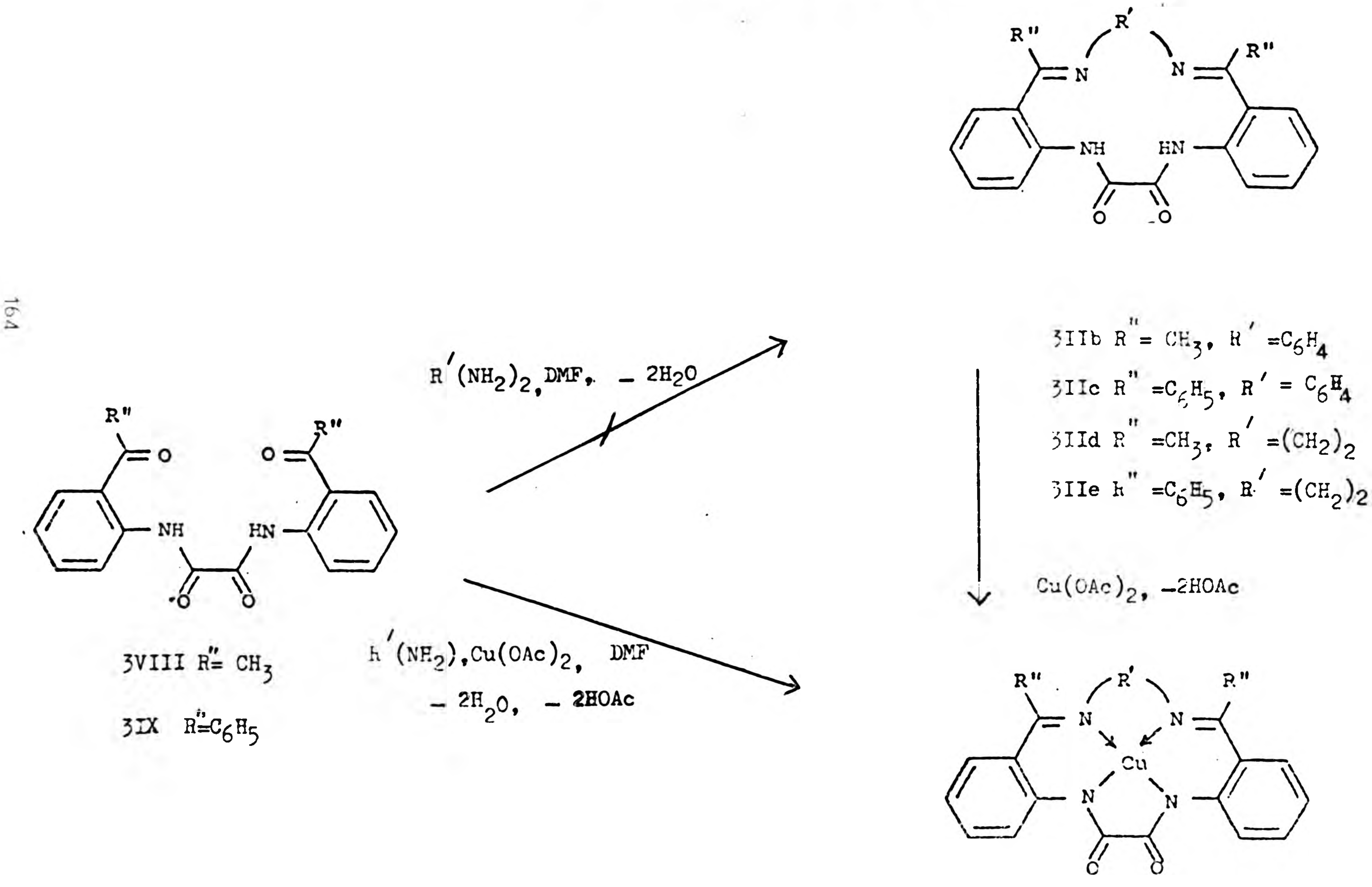
[Cu(3IIc-2H)]



[Cu(3IIe-2H)]

Scheme II

Preparation of copper complexes of oxalo-bridged ligands



An X-ray crystallographic study of the copper complex [Cu(3IIc-2H)] showed that the complex, as would be expected from the proximity of the phenyl rings was sterically crowded, resulting in a 'saddle-shaped' molecule, as described in Section 3.2.6.
The complex [Cu(3IIc-2H)] crystallised as large dark green crystals containing solvated DMF. The infra-red spectrum showed the presence of a carbonyl group from uncoordinated DMF. The presence of the imine bond was shown by a strongband at ca. 1650 cm^{-1}. No NH stretch absorptions were seen. There were many sharp bands in the fingerprint region. The complex [Cu(3IIc-2H)] crystallised in a red, needle-like form. The infra-red spectrum showed clearly that this was a hydrate. The imine bond gave rise to a very strong band, and there were strong bands in the region 1250 cm^{-1}, probably due to methylene group absorptions.

The u.v/visible spectra of these two complexes did not show an identifiable d - d band. The absorption maxima and extinction coefficients were of the same order as those of the copper complexes of the quadridentate diimines described previously (Section 2.2.5), and are summarised below.

U.v/visible data of the copper complexes

[Cu(3IIc-2H)] and [Cu(3IIe-2H)] (DMF)

[Cu(3IIc-2H)]	λ_{max}	375	420	(nm)
	ε	14070	4270	(litre $mol^{-1}cm$)
[Cu(3IIc-2H)]	λ_{max}	365	395	460
	ε	21950	19790	6180

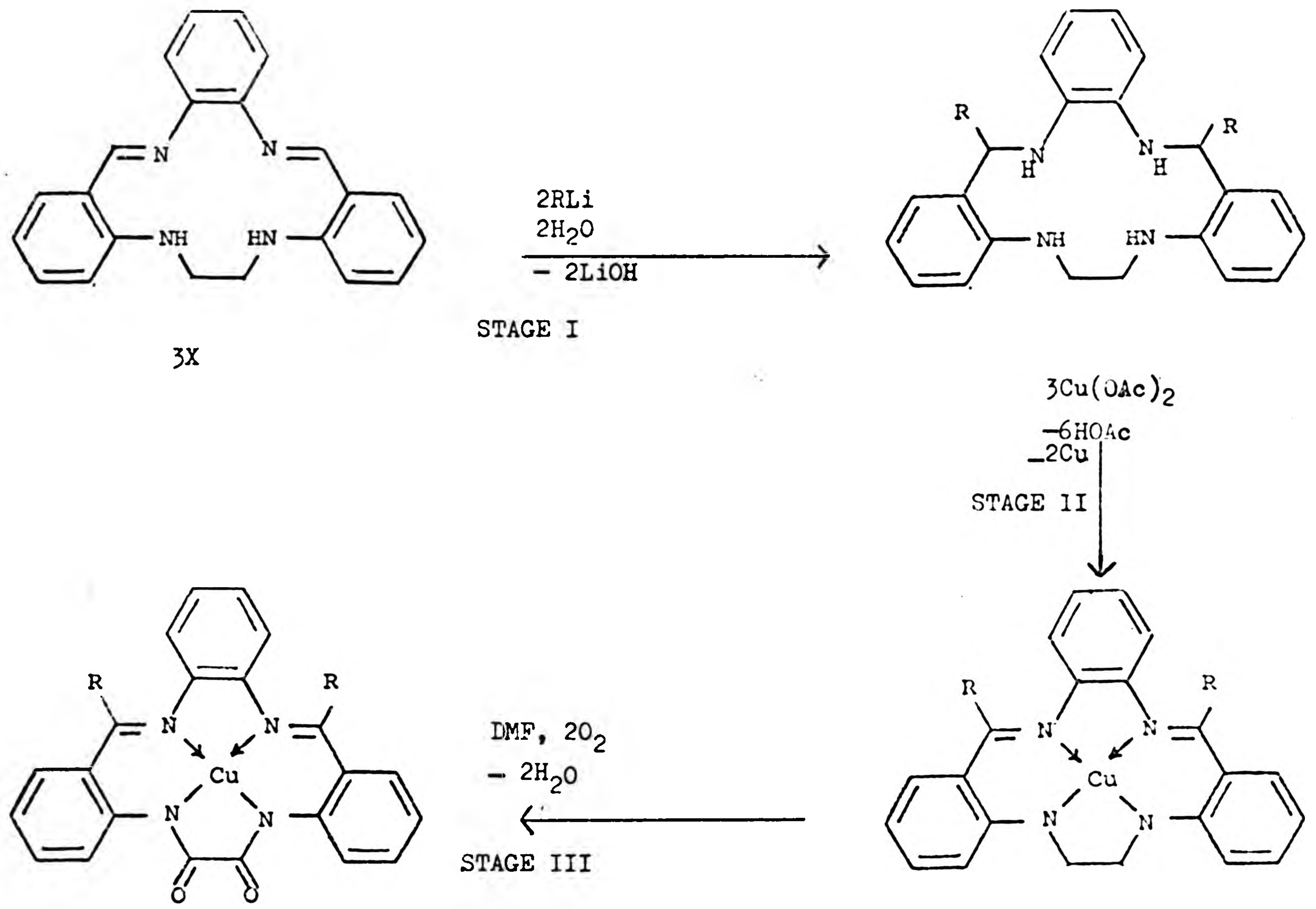
3.2.4. An alternative route to (5,12-dimethyl-18,19-dioxo-17,18,19,20-tetrahydrotribenzo[c,i,m][1,4,8,11]tetraazacyclotetradecinato (2-)) copperII

The following procedure, illustrated for a general case in Scheme III, was considered. The dimethylated ligand, 3IIb, can be prepared readily by methylation of the diimine precursor (2Ia, see Section 3.1.1). It had been found previously (Section 2.3) that the tetra-amine ligands (2IIIa-d) were dehydrogenated to give the neutral copper(II) complex of the diimine [Cu(2I[a-d]-2H)] when treated with copper(II) acetate in methanol. It has also been found that the ethane bridge in metal complexes of the ligand 3X (Scheme III) could be oxygenated to give oxanilide derivatives[12]. The best documented example of a reaction of this type was for the iron(III) complexes, although preliminary work has also shown that the analagous reaction can be observed with the copper(II) analogue as mentioned above.

The sequence of reactions shown in Scheme III could, in theory, yield the methyl-substituted oxanilide complex via the intermediate neutral copper complex of the diimine [Cu(3II-2H)] obtained by stage II of the reaction sequence. If copper complexes of the ketimines were not obtained, it would be interesting to observe how far the predicted reaction sequence proceeded and the nature of the resulting product.

Scheme III

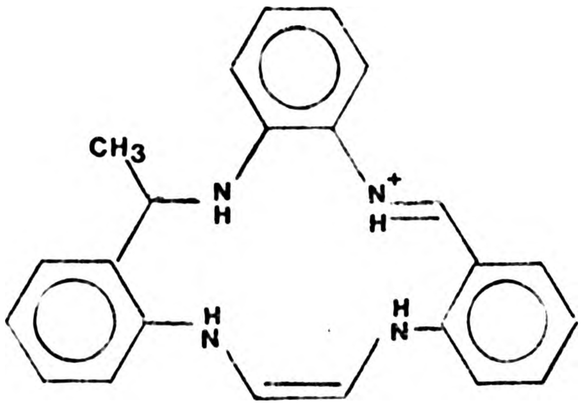
An alternative route to copper complexes of the oxanilide ligands



The ligand 3Ic($R=(CH_2)_2$, $R'=C_6H_4$, $R''=CH_3$) was obtained by treatment of 3X with CH_3Li, Scheme III, Stage I. It was reacted with copper acetate in methanol, giving a dark brown solid (Stage II). The infra-red spectrum contained very broad bands, indicating that this was a mixture. However, the main peaks were found in similar positions to those in the spectrum of the copper complex of the diimine [Cu(2Ia)] and it was clear that a copper complex was present, although there did not seem to be any evidence of dehydrogenation.

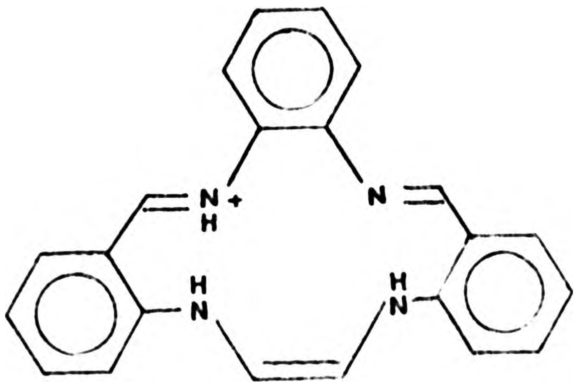
The dark solid was heated in DMF for several days and the solution allowed to stand at room temperature. The dark solid which was deposited had an infra-red spectrum with broad bands, including one at ca. 1700 cm^{-1} which was probably due to a carbonyl group. This may have been on the ligand as a result of oxidation of the ethane bridge, or possibly oxidation of the methyl groups. Compounds having carbonyl groups in this position have been described[15]. Alternatively the carbonyl group could arise from the presence of DMF as solvate.

The mass spectrum of this product did not have a mass peak corresponding to a copper complex; the highest peak being m/e = 384, although involatile copper complexes could be present. This was an addition of 12 mass units to the mass of the ligand 3Ic, ($C_{24}H_{28}N_4$), which might indicate dehydrogenation combined with partial oxidation of the ethane bridge to give a compound of formula $C_{24}H_{24}N_4O$. More intense peaks, of lower m/e values could represent products of dehydrogenation of the original methyl-substituted ligand (3Ic). A peak at m/e = 355 might be attributed to a product 'half-way' to the original diimine ($C_{23}H_{23}N_4$). One possible structure is as below.



3XI

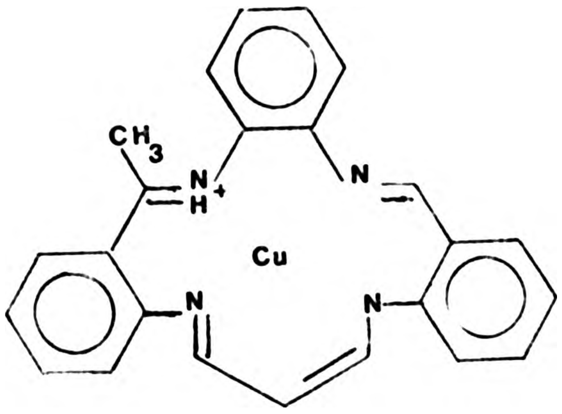
This seemed likely, since the next more intense peak was at m/e = 341 ($C_{22}H_{21}N_4$) which could represent a protonated diimino compound;



3XII

It seemed, therefore, that any neutral copper complex formed was involatile and that the reaction sequence in Scheme III resulted in a mixture of products. The extent of formation of a mono- or dioxo- bridge was uncertain.

At the same time, a similar experiment was carried out using the tetraamine 3Ia, with a propane bridge, to see what the extent of dehydrogenation would be under these conditions. Again, a black solid of mixed composition was formed, of which the mass spectrum indicated the presence of some copper complex at m/e = 428. This could be tentatively assigned as the dehydrogenated complex ($C_{24}H_{20}N_4{}^{64}Cu$) as shown;



3XIII

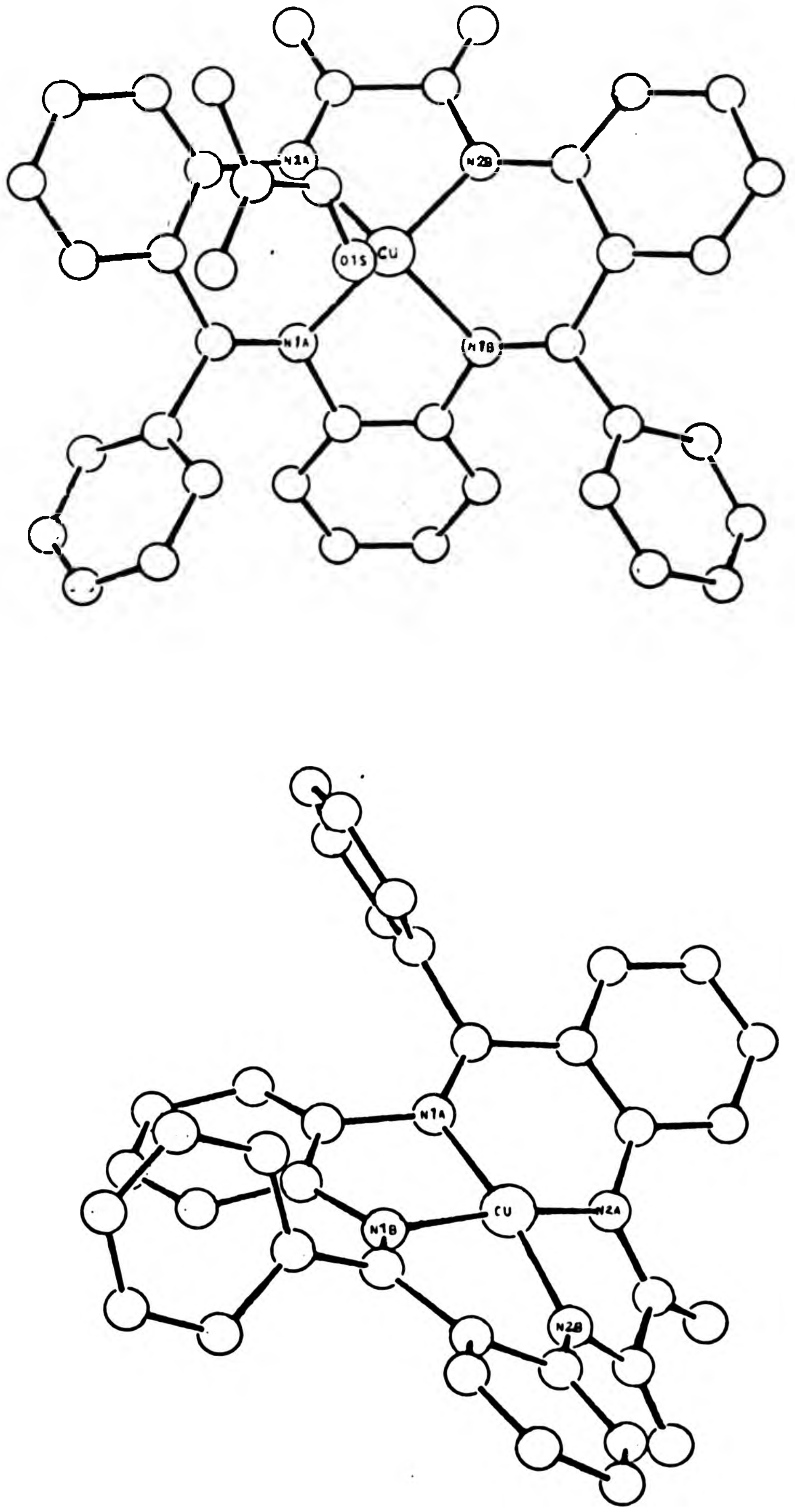
It seemed therefore that, in both attempts, the reaction sequence resulted in a mixture which probably included copper complexes. More work is required to optimise reaction conditions, and to separate the products. Further investigation was not carried out at this stage.

3.2.5. The crystal structure of [5,12-diphenyl-18,19-dioxo-17,18,19,20-tetrahydrotribenzo[e,l,m][1,4,8,11]tetraazacyclotetradecinato(2-)]dimethylformamidocopper(II)

Crystals of the complex were obtained from a condensation reaction between N,N'-di(o-benzoylphenyl) oxalodiamide and 1,2-diaminobenzene in the presence of copper acetate as described in Section 3.4.2. Crystal data and details of reflection intensity measurements and data reduction are given in Appendix B, tables 1B-3B. The space group P 1 was assumed and confirmed by satisfactory solution and refinements of the structure.

The position of the copper atom was identified from a Patterson synthesis Inclusion of this atom in a Fourier synthesis revealed the positions of all the remaining non-hydrogen atoms. Six cycles of full-matrix least-squares refinement with these atoms assigned isotropic thermal parameters resulted in a conventional R factor of 0.085. In the final six cycles the copper atom, and the nitrogen and oxygen atoms for the complex and the coordinated solvent molecule were assigned anisotropic thermal parameters. The hydrogen atoms were included in calculated positions with C-H lengths of 1.08Å. A conventional R factor of 0.081 resulted (Appendix B, Table 1B).

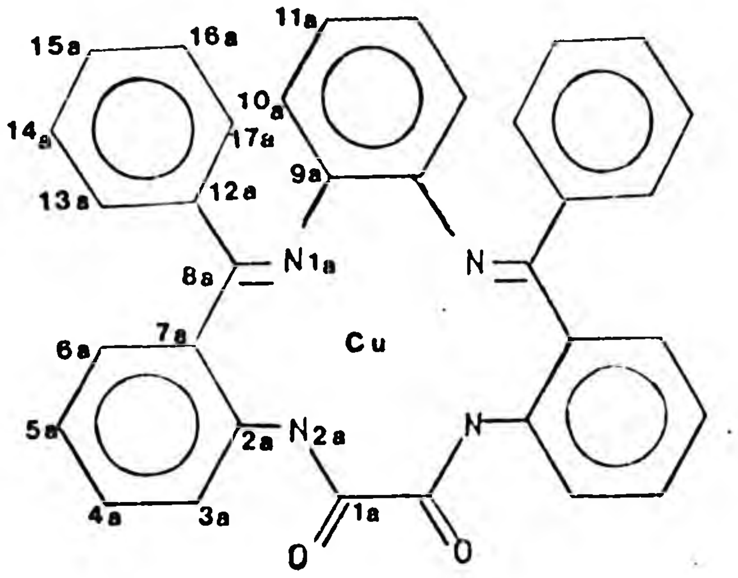
Tables of position parameters, anisotropic thermal parameters, bond lengths and angles in the ligands are given in Appendix B, (Tables 2B-4B). Structure factors are listed in Appendix D, Table 2D. The unit cell contained two discrete molecules of the complex,



Ortep diagrams of the copper complex of 3IIc

Cu($C_{34}H_{22}N_4O_2$).DMF.

related by a centre of symmetry, and two molecules of DMF. Atom labelling is shown below.



(labelling the same in the 'b' half of the molecule.)

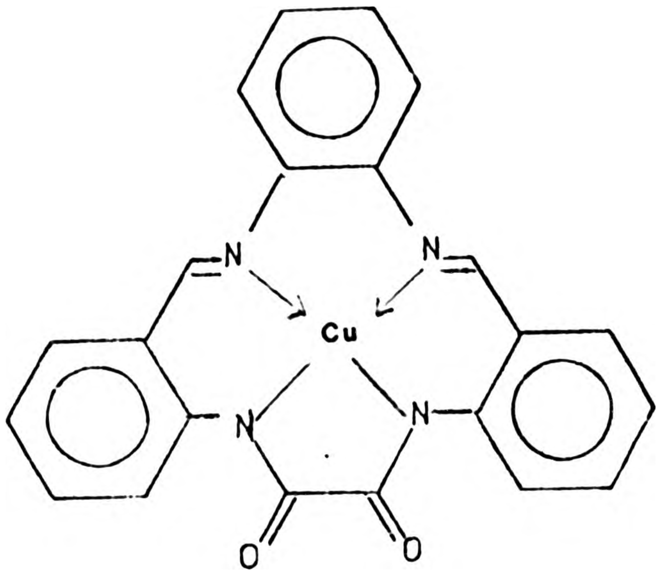
3XIV

Coordination to the copper atom in this complex was approximately square pyramidal, the apical donor atom being the dimethylformamide oxygen atom, which was at a greater bonding distance than the nitrogen atoms. (Table 3.10)

Chemically equivalent bond lengths and angles in the two halves of the molecule (denoted by the suffix a or b) were found to be equal within experimental error. (See Appendix B, Table 4B).

To facilitate the coordination of the N_4 donor-set in the sterically-crowded conditions created by the substituent phenyl rings, the macrocycle was found to have assumed a 'saddle-shaped' conformation in which the 5-membered chelate rings, containing the ortho-phenylene nitrogen atoms N(1a) and N(1b) and the oxanilide nitrogen atoms N(2a) and N(2b) were bent away from the coordinated DMF at angles of approximately 17° and 18° respectively from the N_4 plane. The six-membered chelate rings were bent 'towards' the DMF at angles of 9° and 13° to the 'N_4' plane. (Table 6B). Intramolecular contacts between the phenylamine substituents and adjacent ortho-hydrogen atoms are apparently minimised by this conformation of the chelate rings as discussed below.

A comparison can be made between the characteristics of this phenyl-substituted complex, and those of the unsubstituted analogue[12]. (3XV)



3XV

In contrast to the square pyramidal coordination of the phenyl-substituted complex, the coordination of the unsubstituted complex is square planar and there is no coordinated solvent molecule.

A comparison of the bond lengths in both complexes (Table 3.10) shows similar Cu-N bond distances. The Cu-O (DMF) bond in 3XIV is considerably longer than the Cu-N bond, the oxygen atom forming the apex of the square pyramid. In the unsubstituted complex 3XV the angles between diagonally opposite donor nitrogen atoms were very close to 180°, as would be expected in a square planar configuration. In contrast, in 3XIV the copper atom lies above the plane of the nitrogen atoms, contracting the angle between diagonal nitrogen atoms to ca. 168°. Further evidence for the planarity of the inner great ring of the unsubstituted complex is shown by the torsion angles (Table 3.11) about the bonds, which were almost zero or very close to 180°; the bonds in the oxanilide ring showing the greatest deviation. In the phenyl-substituted complex the torsion angles about N(2)-C(2) were comparable with those above; the angles about the N(2)-C(1) bonds in the oxanilide ring showing greater deviation than those in the unsubstituted ligand. In both complexes the oxalyl bridge was planar with the adjoining chelate ring, since the carbon atoms (C(1a) and C(1b) were sp^2-hybridised. The phenyl-substituted ligand shows considerable twisting about the bonds from the phenyl substituted carbon atom C(8). The deviations of the torsion angles from the theoretical values of 0° or 180° for a planar inner great ring are compared for both complexes in Table 3.11.

The presence of the substituted phenyl rings imposes considerable constraints on the molecule (Fig. 3.7). In the unsubstituted complex intramolecular contacts involving the o-hydrogen atoms (Table 3.13) are short enough to indicate that the presence of a substituent phenyl ring in a planar system would produce extremely short C(12)-H(6) and C(12)-H(10) contacts, and unfeasibly large interatomic repulsive forces. The stability of the molecule is probably dependent upon the assumption of the saddle-shaped configuration, in which the interatomic distances are kept to a maximum; they are in fact comparable to those in the unsubstituted complex (Table 3.13). The twisting of the phenyl substituents about the C(8)-C(12) bonds also minimises the contacts in this part of the molecule.

Atom deviations from the least-squares planes in the substituted and unsubstituted complexes are compared in Table 3.14
In both complexes the four nitrogen donor atoms are planar within experimental error.

Atom deviations from the planes of the six-membered chelated rings in the substituted ligand complex demonstrate that both rings are puckered in a very similar manner. In this complex the atoms in the chelate ring containing the oxalyl bridge (Plane 6) do not deviate from planarity. In contrast, in the unsubstituted complex the oxygen atoms are tilted slightly above and below the plane of the ring. In this case the planarity of the molecule as a whole results in close O(1)-H(3) interactions (Table 3.13), whereas in the substituted complex the saddle-shaped distortion reduces this type of interatomic contact.

Intramolecular contacts involving the substituent phenyl rings (Fig 3 .7) are also important in promoting the saddle-shaped conformation. This allows the H(6),H(10)-C(12),C(13) contact distances to be of the same order as the H(8)-H(10) distances in the unsubstituted complex, by taking the ortho-hydrogens H(6) and H(10) to opposite sides of the phenyl carbon atoms C(12) and C(13). The twisting of the phenyl substituents about the C(8)-C(12) bonds also minimises contacts in this region. The intramolecular contacts are compared in Table 3.13

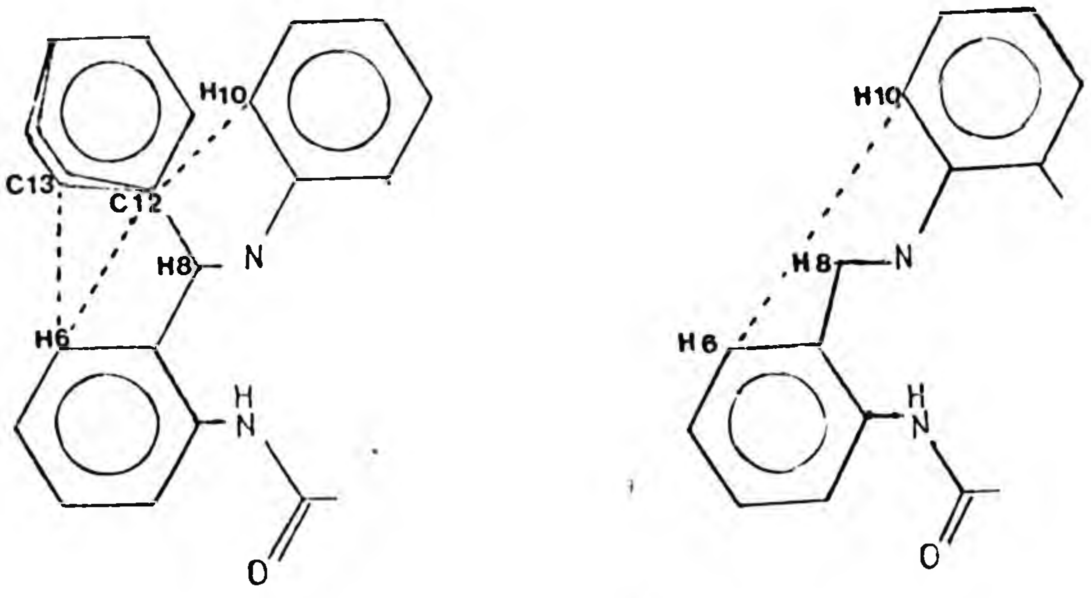


Fig 3.7 . Intramolecular contacts in the substituted complex (3 XIV) and the unsubstituted complex (3XV)

Table 3.10 Bondlengths and angles in the coordination spheres of the phenyl-substituted and unsubstituted complexes 3XIV and 3 XV

Bond lengths/Å	3 XIV	3 XV
Cu-N(1a)	1.925(9)	1.951(2)
Cu-N(2a)	1.925(8)	1.946(2)
Cu-N(1b)	1.987(8)	1.947(2)
Cu-N(2b)	1.900(8)	1.937(2)
Cu-O(1s)	2.537(10)	-
Bond angles/°		
N(1a)-Cu-N(2a)	91.2(3)	94.6(1)
N(1a)-Cu-N(1b)	86.8(4)	83.3(1)
N(1a)-Cu-N(2b)	168.7(4)	177.4(1)
N(1a)-Cu-O(1s)	86.0(4)	-
N(2a)-Cu-N(1b)	167.8(4)	177.6(1)
N(2a)-Cu-N(2b)	88.1(3)	87.7(1)
N(2a)-Cu-O(1s)	90.3(3)	-
N(1b)-Cu-N(2b)	91.6(3)	94.4(1)
N(1b)-Cu-O(1s)	101.4(3)	-
N(2b)-Cu-O(1s)	105.3(4)	-

Table 3.11 . Torsion angles/° in the inner great rings of the phenyl-substituted and unsubstituted complexes 3XIV and 3XV

	3XIV ($R''=C_6H_5$)		3 XV ($R''=H$)	
Torsion angles	part a	part b	part a	part b
N(2)'-C(1)'-C(1)-N(2)	0.0	-	4.5	-
C(1)'-C(1)-N(2)-C(2)	160.8	-165.6	176.1	179.1
C(1)-N(2)-C(2)-C(7)	170.9	-166.1	-170.6	163.7
N(2)-C(2)-C(7)-C(8)	-11.5	10.5	0.0	4.6
C(2)-C(7)-C(8)-N(1)	6.7	-6.9	0.0	0.0
C(7)-C(8)-N(1)-C(9)	-169.2	166.4	180.0	178.1
C(8)-N(1)-C(9)-C(9)'	-154.5	161.2	178.6	175.0
N(1)-C(9)-C(9)'-N(1)'	1.3	-	1.7	-

Table 3.12 . Deviations from theoretical values* for the flattened inner great ring

	3XIV $R = C_6H_5$		3XV $R = H$	
Torsion angles	part a	part b	part a	part b
N(2)-C(1)'-C(1)-N(2)	0.0	-	4.5	-
C(1)'-C(1)-N(2)-C(2)	19.2	14.4	3.9	0.9
C(1)-N(2)-C(2)-C(7)	9.1	13.9	9.4	16.3
N(2)-C(2)-C(7)-C(8)	11.5	10.5	0.0	4.6
C(2)-C(7)-C(8)-N(1)	6.7	6.9	0.0	0.0
C(7)-C(8)-N(1)-C(9)	10.8	13.6	0.0	1.9
C(8)-N(1)-C(9)-C(9)'	25.5	18.8	1.4	5.0
N(1)-C(9)-C(9)'-N(1)'	1.3	-	1.7	-
	Mean 11.6		Mean 3.5	

*0 or 180°

Table 3.13 . Intramolecular contacts involving ortho-hydrogen atoms in the phenyl-substituted and unsubstituted complexes 3 XIV and 3 XV

	3XIV	, $R''=C_6H_5$	3 XV	$R''=H$
	part a	part b	part a	part b
H(3) .... O(1)	2.21	2.17	2.13	2.16
H(6) .... H(8)	-	-	2.12	2.15
H(6) .... C(12)	2.34	2.38	-	-
H(6) .... C(13)	2.44	2.57	-	-
H(10).... H(8)	-	-	2.11	2.28
H(10).... C(12)	2.45	2.37	-	-
H(10).... C(13)	2.47	2.45	-	-

*Intramolecular contacts within benzene rings are excluded, other C .... H and H .... H contacts are $\geqslant 2.6$ or $\geqslant 2.3$ Å respectively.

Data for the R=H compound was kindly supplied by Mrs. S. Shaw

Table 3.14 . Least-squares planes and atom deviations in the phenyl-substituted and unsubstituted complexes 3XIV and 3XV

Plane 1, atoms	3XIV ($R''=C_6H_5$)	3XV ($R''=H$)
N1a	-0.01	0.00
N2a	0.01	0.00
N1b	0.01	0.00
N2b	-0.01	0.00
Cu*	-0.20*	0.02*
,equation		
P	8.708	-3.711
Q	-2.950	-5.602
R	-8.064	6.651
S	-1.227	-0.206
Plane 2, atoms		
N(2a)	-0.20	0.00
C(2a)	-0.03	0.00
C(7a)	0.19	0.00
C(8a)	0.01	0.00

N(1a)	-0.24	0.01
Cu	0.27,	-0.01
,equation		
P	-7.140	-3.737
Q	3.218	-5.679
R	11.195	6.635
S	2.116	-0.229
Plane 3, atoms		
N(2b)	0.17	0.01
C(2b)	0.03	-0.03
C(7b)	-0.17	0.02
C(8b)	-0.00	0.02
N(1b)	0.20	-0.03
Cu	-0.22	0.01
,equation		
P	8.990	-3.468
Q	-2.849	-5.219
R	-5.639	6.736
S	-0.503	-0.133
Plane 4, atoms		
N(2a)	0.11	-0.05
C(1a)	-0.06	0.01

C(1b)	-0.07	0.05
N(2b)	0.12	-0.08
Cu	-0.11	0.06
,equation		
P	8.476	-5.152
Q	6.056	-5.189
R	7.782	6.551
S	1.806	-1.010
Plane 5, atoms		
N(1a)	-0.12	0.01
C(9a)	0.06	0.01
C(9b)	0.06	-0.01
N(1b)	-0.12	0.02
Cu	0.11	-0.01
,equation		
P	8.150	-3.7466
Q	0.309	-5.6570
R	-7.587	6.6382
S	-1.140	-0.2299
Plane 6, atoms		
N(2a)	0.00	0.06
C(1a)	0.00	-0.02
O(1a)	0.00	-0.04

O(1b)	0.00	0.06
C(1b)	0.00	-0.02
N(2b)	0.00	-0.04
Cu*	-0.42	0.27
,equation		
P	-8.091	-6.4602
Q	7.293	-4.4657
R	7.452	6.4385
S	2.195	-1.9028

Table 3.15 . Angles between planes /°

3XIV $R''=C_6H_5$

Plane	1	2	3	4	5	6
1	0	13	9	18	17	26
2	13	0	22	21	22	28
3	9	22	0	160	19	27
4	18	21	160	0	8	35
5	17	22	19	8	0	43
6	26	28	27	35	43	0

3XV $R''=H$

Plane	1	2	3	4	5	6
1	0	0	2	6	0	12
2	0	0	2	6	0	12
3	2	2	0	7	2	12
4	6	6	7	0	6	8
5	0	0	2	6	0	12
6	12	12	12	8	12	0

Footnotes; *This atom not used in calculation of the plane

equations for planes are expressed in direct space as

$Px + Qy + Rz = S$

Data for the R=H complex was supplied by Mrs. S. Shaw;

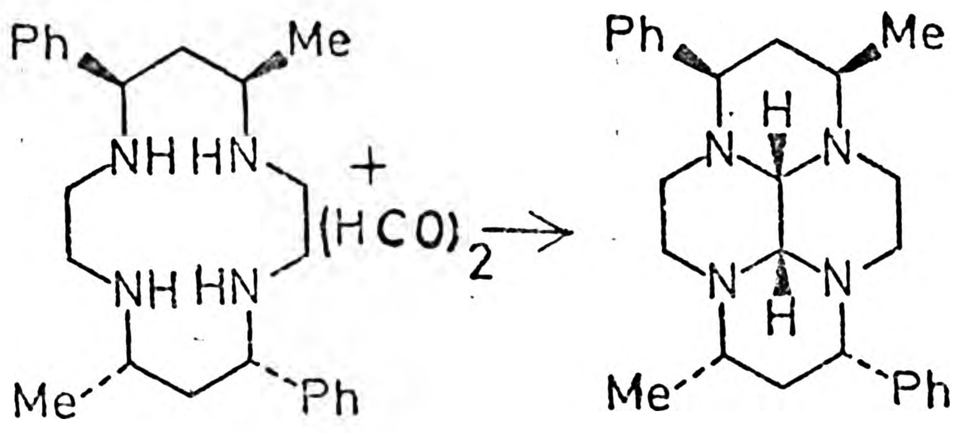
$a = 14.925(4)$, $b = 15.931(3)$, $c = 7.228(1)$,

Å, $\beta = 95.05(8)^{\circ}$.

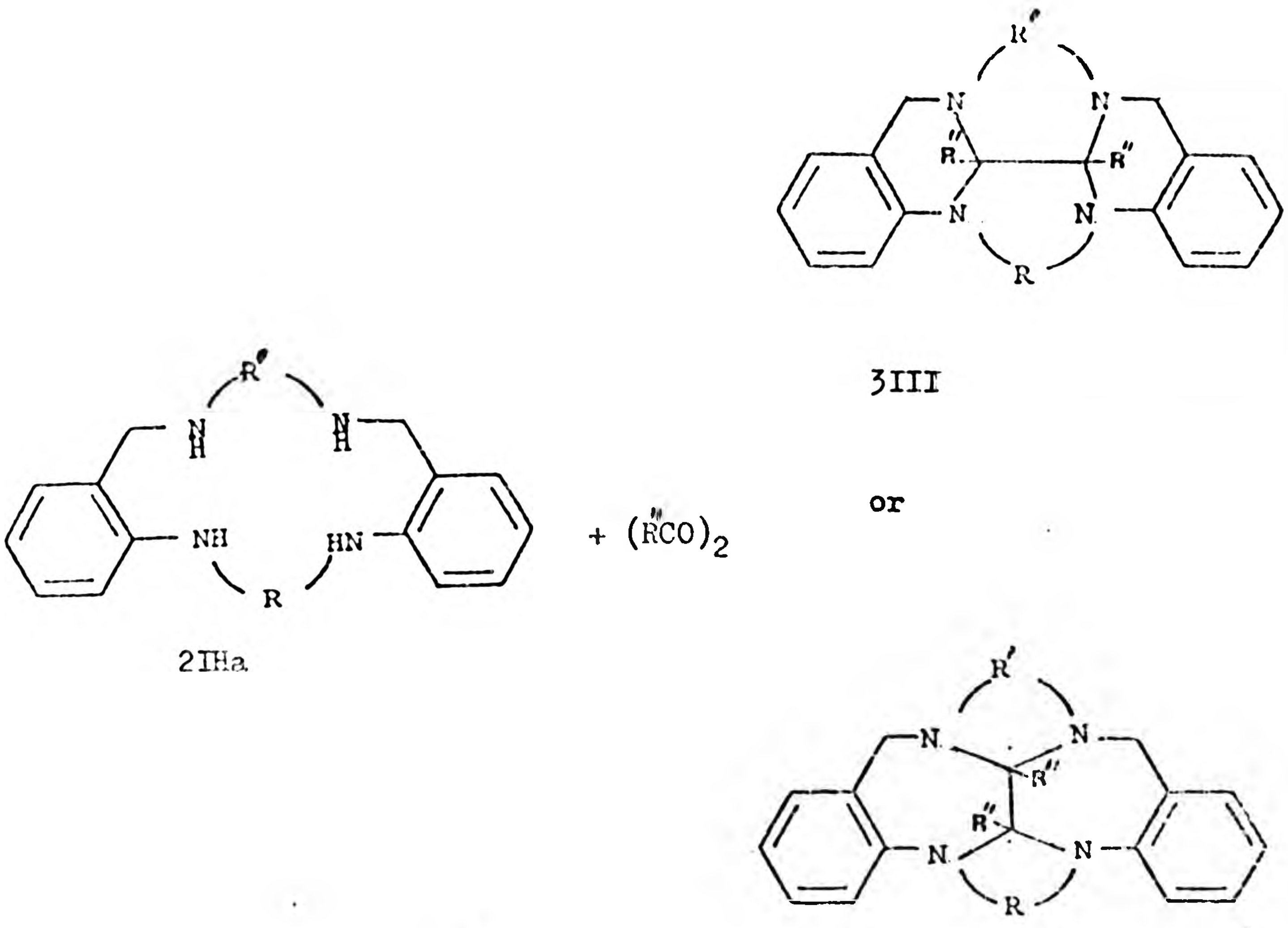
3.3 The bridged macrocycles

Polycyclic tetraamines have been formed by the reaction of substituted diamines with glyoxal and diacetyl.[16,17,18]

A typical reaction with glyoxal is as below;



The previous systems used were alicyclic, but it was thought that the tetraamine systems with fused benzene rings developed in this work could be modified to give polycyclic tetraaza compounds. A possible general reaction scheme is outlined below.



2IIa

3III

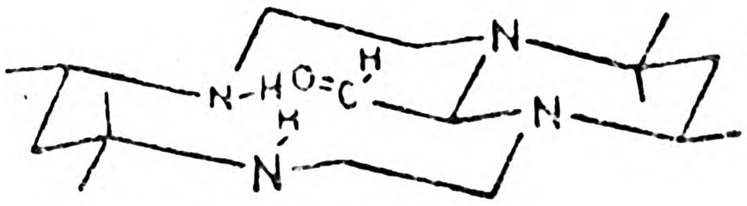
3IV

3IIIa, 3IVa R= (CH$_2$)$_3$, R'=C$_6$H$_4$, R''=H

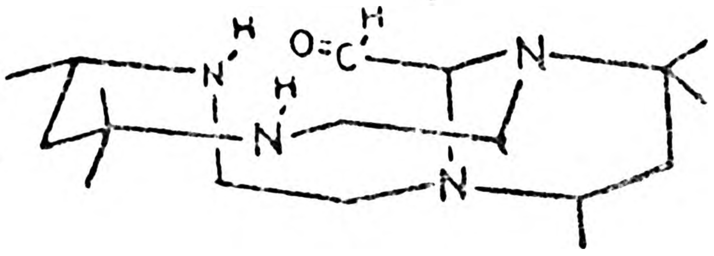
3IIIb, 3IVb R=(CH$_2$)$_2$, R'=(CH$_2$)$_3$, R''=H

Fig 3.8 General bridging reaction of the tetraamine ligands

For 1:1 reaction products there are two possible bridging modes, 3III and 3IV, and a possible *cis* or *trans-* fused stereochemistry at the central bridge. Previous X-ray crystallographic studies of bridged cyclam derivatives obtained from glyoxal have shown the central dimethylene bridge to be *cis-*[18,19]. Work on the cyclam systems[19] has led to the suggestion that the second stage of the condensation of glyoxal with the amine groups takes place along a folded edge of the intermediate molecule resulting in the C-H groups in a cis position(b). Condensation in the central region of the molecule, giving the trans form is more sterically crowded (a). Thus it is thought that the steric control associated with the final stage of the condensation results in the formation of the cis-isomer.



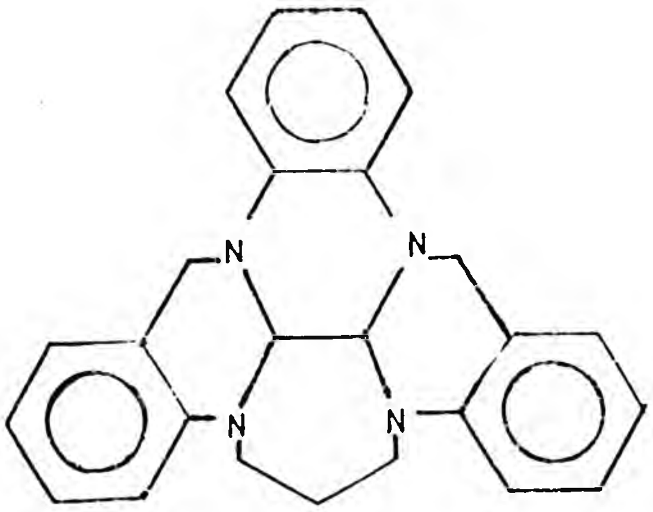
(a)



(b)

3.3.1. The treatment of 5,6,11,12,18,19,20,21-octahydro-17-*H*-tribenzo/ *f,j,n* // 1,5,9,12 /tetraazacyclopentadecine (2IIa) with glyoxal.

The above ligand(2IIa) was treated with glyoxal and the white product isolated as described in the Experimental Section 3.4.4. The compound was characterised using the spectroscopic techniques discussed below. The structure was formulated as 3IIIa (See Fig 3.8), as below;



3IIIa

3.3.1.2. ^{1}H spectrum of the bridged ligand 3IIIa

The ^{1}H nmr spectrum of 3IIIa showed, in addition to far more complex coupling than appeared in the spectrum of the unbridged ligand 3Ia, an additional singlet. This corresponded to two protons, and this evidence of their identical environments made it possible to assign the structure to the isomer 3IIIa, as above.

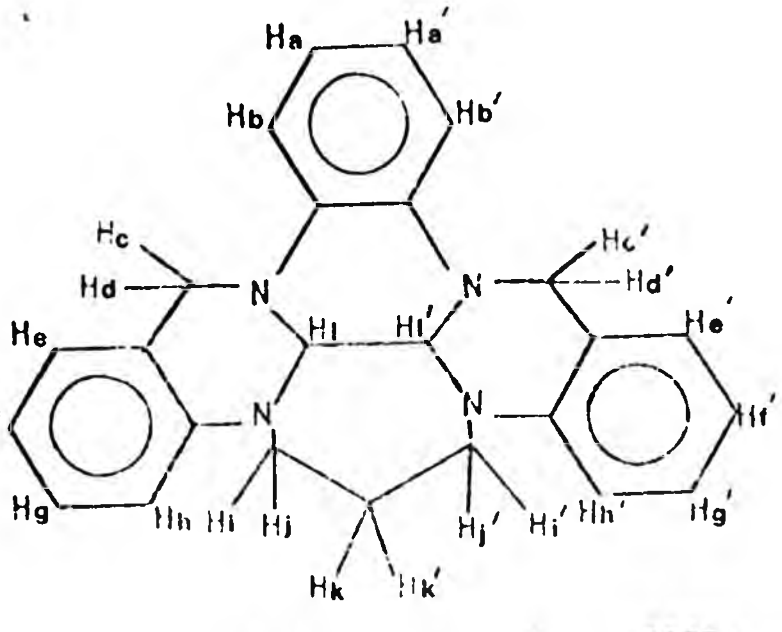


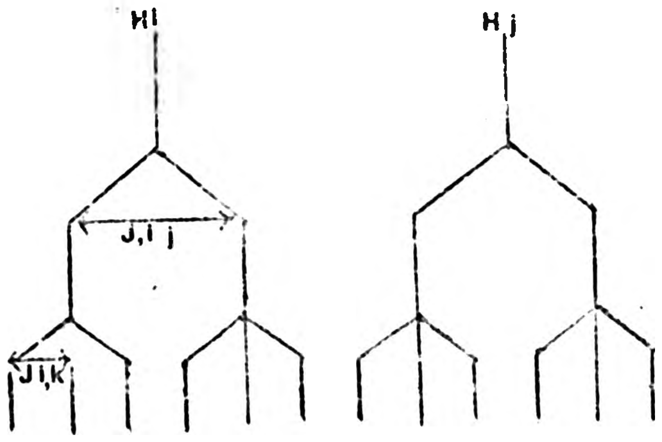
Fig. 3.9 Hydrogen labelling in the ligand 3IIIa.

The ^1H spectrum showed clearly that certain pairs of methylene protons were not equivalent, as a result of the rigidity of the structure imposed by the formation of the ring system. The signals are tabulated below.

Table 3.16 ^1H spectrum of the bridged ligand 3IIIa in $CDCl_3$

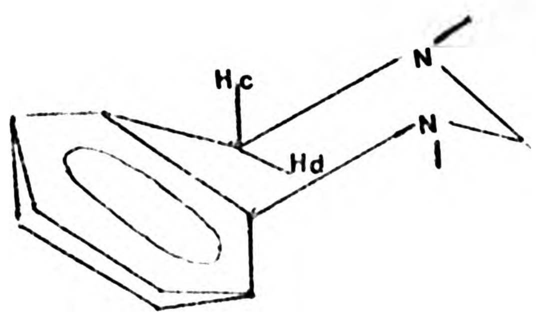
Assignment	δ/ppm (J/Hz)
Hk,Hk'	1.79 (m, 2H)
Hi,Hj,Hi',Hj'	3.65 (2x sext, 4H, Jij=45, Jik=Jjk=6.0)
Hc,Hd,Hc'Hd'	4.38 (d, 2H, J=9.0) 4.76 (d, 2H, J=9.0)
Hl,Hl'	5.16 (s, 2H)
Ha,Ha',Hb,Hb'	6.50-6.87 (m. 6H)
He-Hh,He'-Hh'	6.87-7.12 (m. 6H)

The hydrogen atoms of the central methylene group (Hk,k') gave a multiplet, indicating complex coupling between Hi(i') and Hj(j') and these protons, which were probably non-equivalent. The pair of sextuplets which constituted the signal from the methylene protons (Hi,i', Hk,k') were clearly shown. The coupling likely to produce this signal was as follows.



It is presumed that coupling took place between the methylene protons themselves (Hi,Hi',Hj,Hj') and, in addition, longer-range coupling between each proton and Hk(k') to give two sextuplets deriving from each methylene proton.

The 'benzylic' proton signal was centred at a similar chemical shift value to that of the untreated ligand. In this compound, the hydrogen atoms were constrained in non-equivalent positions in a six-membered ring. It was possible to visualise a puckered six-membered ring in which the methylene protons are fixed in 'axial' and 'equatorial' positions;



In this case coupling occurred between the two protons, to give two well-defined doublets.

The aromatic protons gave complex multiplets of the type seen in the unbridged ligand (2IIa).

3.3.1.3. ^{13}C spectrum of the bridged ligand 3IIIa.

The ^{13}C spectrum of the bridged ligand was consistent with the proposed structure of 3IIIa because it showed that the two halves of the molecule were symmetry-related. Only one additional signal was present, in comparison with the spectrum of the unbridged tetraamine 2IIa, in the area of the spectrum appropriate to sp^3-hybridised carbon attached to two nitrogen atoms. This signal was clearly due to the two bridging carbon atoms, which was strong evidence for their identical (cis-) environments. The remaining signals had chemical shift values which were very similar to those of the unbridged ligand 2IIa (See Fig. 3.5). The signals were assigned as shown below;

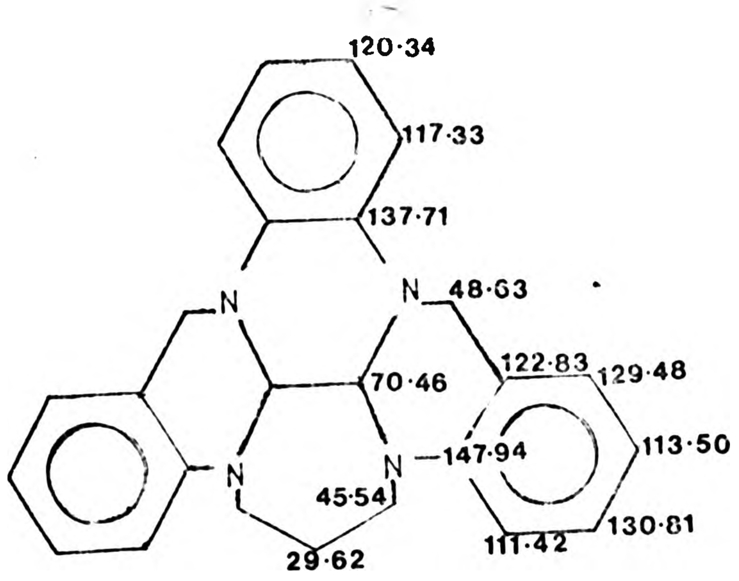


Fig 3.10. Chemical shifts in the ^{13}C spectrum of 3IIIa.

3.3.1.4. Infra-red spectra of the bridged ligand 3IIIa.

The infra-red spectrum in nujol mull showed a large number of very strong bands and was more complex than that of the unbridged ligand 2IIIa. The numerous strong bands in the region 1200-1460 cm^{-1} were probably due to complex C-H vibrations, due to non-equivalence of C-H groups imposed by steric restrictions which result from bridging. In particular, CH_2 in-plane deformations occur around 1450 cm^{-1} in six-membered rings.[20] The large number of peaks in the fingerprint region below 900 cm^{-1} might have been due to additional C-H deformations in the restricted ring systems.[21]

In HCB mull the spectrum of 3IIIa showed a complex group of peaks in the region 2800-3100 cm^{-1} - this was in contrast to the spectrum of the unbridged ligand where there were three main bands at 2760, 2800, 2830 cm^{-1}, attributable to C-H vibrations.[20]

3.3.1.5 U.v/visible spectrum of the bridged ligand 3IIIa

The u.v/visible spectrum of 3IIIa was more complex than that of the unbridged ligand. The λ_{max} values and extinction coefficients were of the same order, as shown below, and absorption was presumably due to $n-\sigma^*$ transitions. (ε = litre $mol^{-1}cm^{-1}$, λ = nm)

Bridged ligand 3IIIa	λ_{max}	233	265	310
(CH_2Cl_2)	ε	42560	35340	14400
Unbridged ligand 2IIIa	λ_{max}	242	-	380
(MeOH)	ε	33800	-	15000

3.3.1.6. Mass spectrum of the bridged ligand 3IIIa

The mass spectrum of the bridged ligand confirmed the atomic composition corresponding to the proposed structure 3IIIa. The mass peak was also the base peak, and the peak ca. 118 was present at high intensity as shown below. No peak corresponding to the unbridged ligand was seen, the largest mass unit after the mass peak corresponding to the loss of two hydrogen atoms. Other peaks indicated extensive breakdown. (See Experimental Section, 3.4.4).

Table 3.17 Peaks in the mass spectrum of 3IIIa

Formula	%	Measured mass	Calculated mass
$C_{25}H_{24}N_4$ (M^+)	100	380.2001	380.2008
$C_{25}H_{22}N_4$	15.8	378.1848	378.1844
C_8H_8N	74	118.0647	118.0656

The spectral evidence combined was sufficient to confirm the structure 3IIIa for this compound.

3.3.2. The treatment of 6,7,8,9,10,11,17,18-octahydro-5-*H*-dibenzo [*g*,*n*][1,4,8,12]tetraazacyclopentadecine with glyoxal.

The ligand 3XVI was treated with glyoxal as described in the Experimental Section 3.4 The expected reaction was as shown below (Fig. 3.11 from general scheme shown in Fig. 3.8)

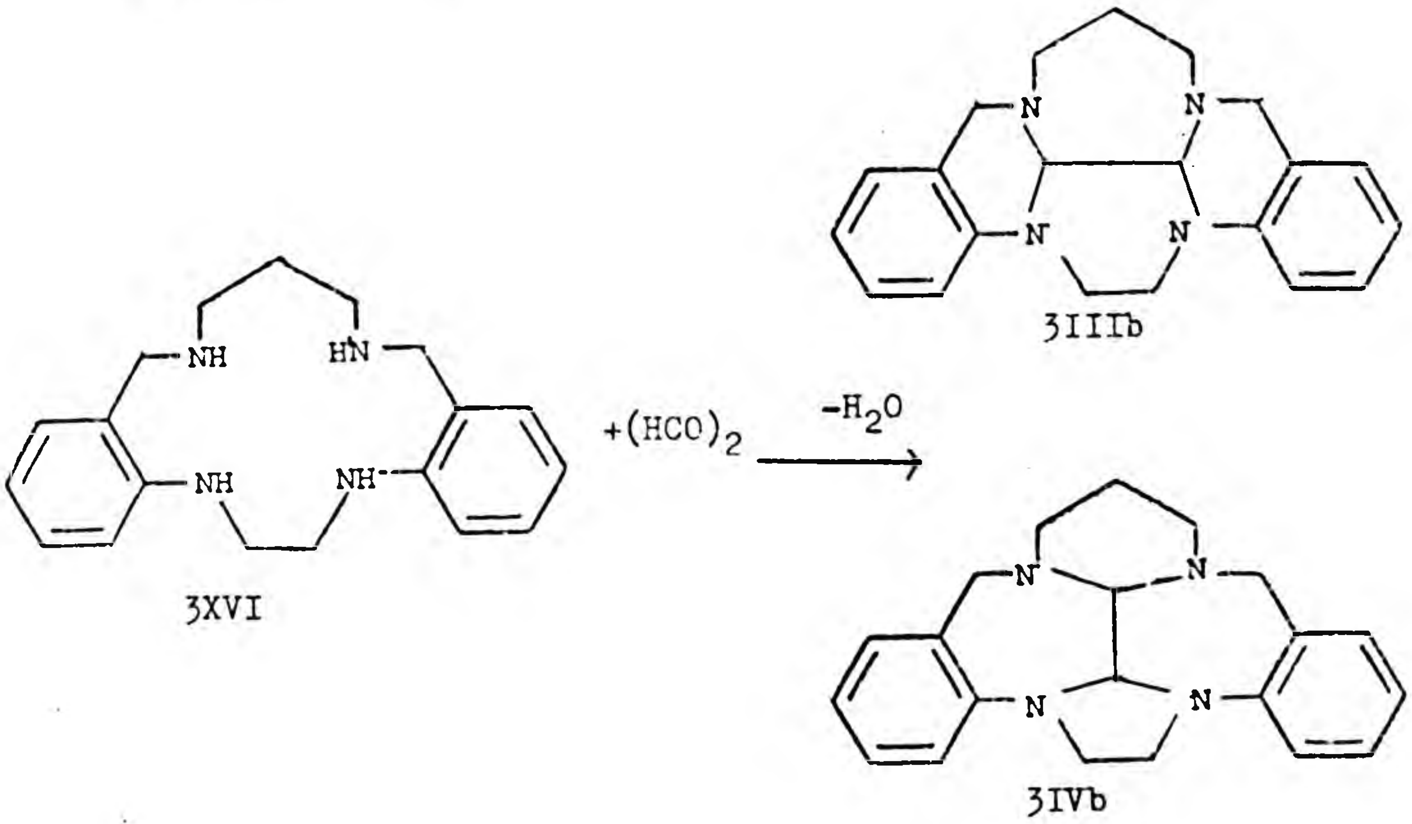
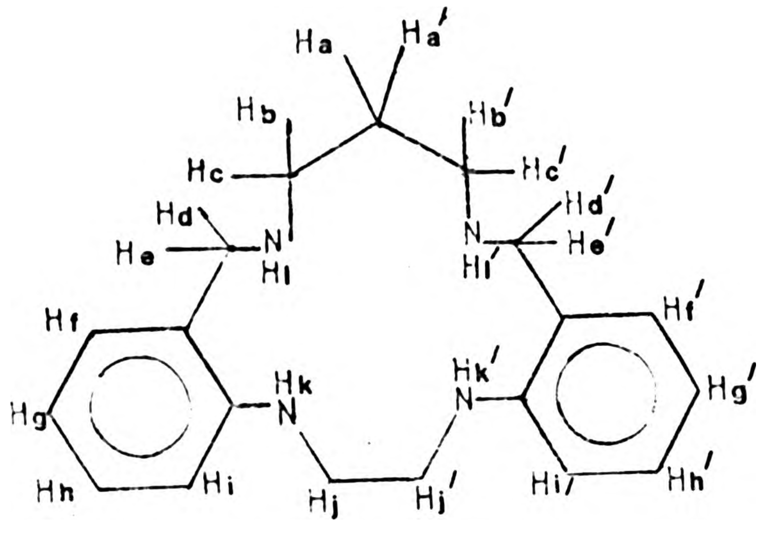


Fig. 3.11 Possible reactions of glyoxal with 3XVI

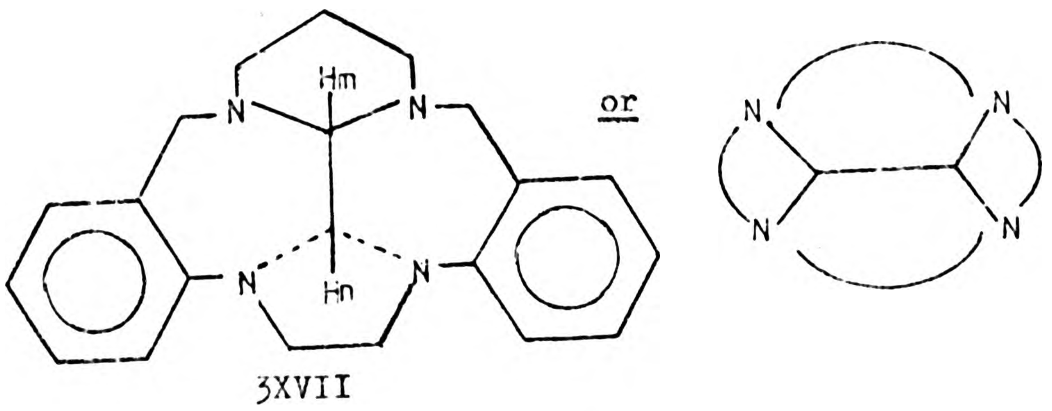
Spectral study of the white crystalline product, 3XVII, indicated that the bridging reaction was incomplete, and neither the structure 3IIIb or 3IVb could be assigned with certainty, since there was evidence of residual NH groups. Prolonged refluxing of the product 3XVII in benzene, using a Dean-Stark trap, did not result in further reaction, the compound remaining unchanged. However, under the conditions of mass spectrum analysis there was evidence that further dehydration occurred. The evidence for the structure of the product **3XVII** is discussed below.

3.3.2.1. ^{1}H spectrum of the glyoxal-treated ligand 3XVII

The labelling of hydrogen atoms in the tetraamine 3 XVI and the treated ligand is as below;



3XVI



3XVII

(other atoms labelled as above).

Fig 3.12 Hydrogen labelling in 3XVI and 3XVII

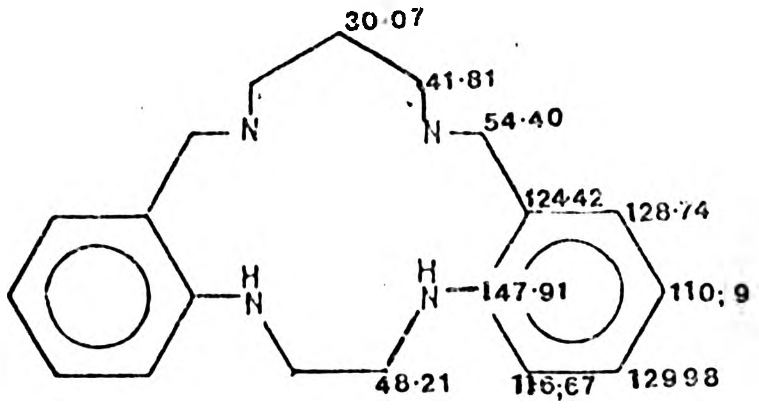
Comparison of the spectra (see below) showed that more complex coupling occurred in the treated ligand, and this was some indication of steric restriction resulting from bridging. This was particularly noticeable in the splitting of the benzylic proton signal (Hd,e) which indicated that they were non-equivalent in the treated compound. However, there was a residual NH proton signal, and an unidentified pair of signals at 4.83, 4.86 ppm as shown;

Table 3.18 Comparison of ^{1}H spectra 3XVI and 3XVII ($CDCl_3$)

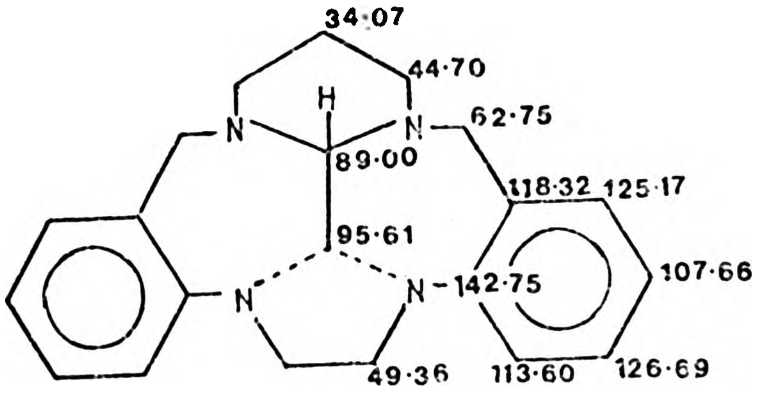
3XVI	3XVII	Assignment (ppm)
1.15 (s. 2H)	Not present	Hk,k' or Hl,l'
1.75 (quin. 2H.J=4.4)	1.5 (m. 2H)	Ha,a'
2.85 (t.4H.J=4.4)	2.6 (d.2H.J=13.0 3.3 (t.2H.J=13.0	Hb,b' c,c'
3.5 (s. 4H)	3.5 (m.4H)	Hj,j'
3.8 (s. 4H)	3.95(d.2H.J=13.0 4.10(d.2H.J=13.0	Hdd',He,e'
Not present	4.83 (s. 1H)	
Not present	4.86 (s. 1H)	
6.0 (s. 2H)	6.35 (s. 2H)	Hkk' or Hl,l'
6.6-6.8(m.8H) 7.0-7.1(m.2H) 7.15-7.2(m.2H)	6.6-6.7(m.8H) 7.0-7.1(m.2H) 7.2-7.3(m.2H)	Hf,f'-Hi,i'

3.3.2.2. The ^{13}C spectrum of 3XVII

The ^{13}C spectrum was clear and sharp, and the number of signals seemed to rule out the possibility of a mixture being present, and also showed that the two halves of the molecule were symmetry-related. Thus bridging must have occurred across one of the methylene bridges. In comparison with the untreated ligand, two extra carbon signals were seen. In the off-resonance spectrum each of these signals became a doublet, confirming that each had one attached hydrogen atom. These two carbons were the 'bridging' unit, but it was clear from their chemical shifts that they were in different environments. The ^{13}C chemical shifts in 3XVI and 3XVII are compared in Fig. 3.13



3XVI



3XVII

Fig. 3.13 Chemical shifts in the ^{13}C spectra of 3XVI and 3XVII

There is some evidence, from the large variation in shift of the benzylic C atoms, that bridging had occurred between their adjacent nitrogen atoms.

3.3.2.3. Infra-red spectrum of 3XVII

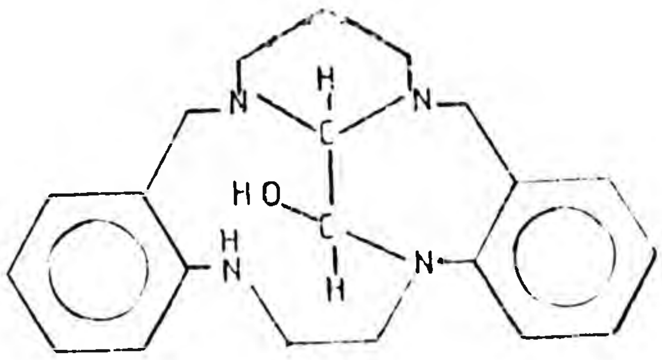
The infra-red spectrum provided additional evidence of the presence of NH, and, possibly, of OH groups in the treated ligand. A comparison of the spectra of 3XVI and 3XVII in the high-frequency region where NH and OH absorption bands are seen is given below. The remainder of the bands in the two spectra were significantly different, but it was not possible to make any definite assignments which would aid in characterisation.

Table 3.19 A comparison of infra-red spectra of 3XV and 3XVII (cm^{-1}, HCB)

3XVI	3XVII	Assignment
Not present	3400	OH
3320	Not present	NH stretch
3300	Not present	NH stretch
3280	3280	NH stretch
3240-3160	Not present	NH stretch
3090	3090	
3060	3060	CH stretch in methylene groups
Not present	3020	
2960-2860	2960-2860	
2720	2760	

3.3.2.4. Mass spectrum of 3XVII

The mass spectrum showed the presence of a peak at ca. 332 corresponding to $C_{21}H_{24}N_4$ which could be either the structure 3IIIb or 3IVb (See Fig. 3.11.) This was the base peak. However, the peak of the highest mass, m/e = ca. 350, corresponded to the formula $C_{21}H_{26}N_4O$ and might be assigned to the structure below in which partial reaction has occurred (3XVIII)(It is possible that this product was obtained as a result of dehydration during analysis, since ^{13}C evidence suggests a molecule in which the two halves are symmetry-related).



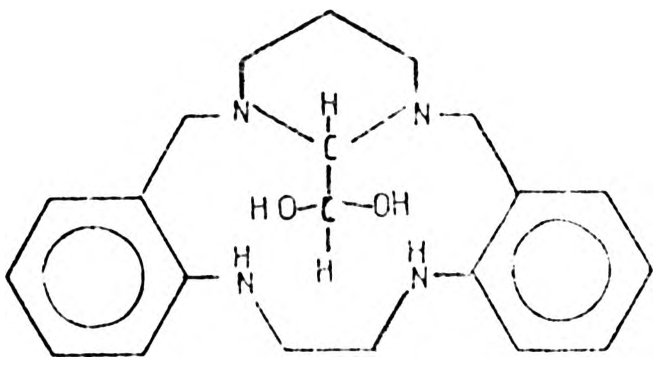
3XVIII

The main peaks are summarised below.

Table 3.20 Peaks in the mass spectrum of 3 XVII

Formula	%	Measured mass	Calculated mass
$C_{21}H_{26}N_4O$	20.0	350.2089	350.2106
$C_{21}H_{24}N_4$	100.0	332.1990	332.2000
C_8H_8N	78.0	118.0662	118.0656

The mass spectral evidence, combined with the other evidence suggests that 3XVII might have the structure below, although the presence of two -OH groups on one carbon atom would not normally be a stable arrangement. Analytical data agrees fairly well with the formula $C_{21}H_{28}N_4O_2$ (Section 3.4.3). Possibly dehydration occurs during the mass spectral measurement to give first, 3XVIII above and then the fully bridged ligand 3IVb (Fig 3.11).



3XVII

No further work was done to elucidate the structure of this compound at this stage.

Other experiments were carried out reacting glyoxal with the dimethylene-bridged tetrammine derived from 3X by reduction, and with diacetyl. These reactions led to oily products, which could not be isolated. No time was available to investigate this class of compounds any further at this stage.

Section 3.4. Experimental Data

3.4.1 Experimental data on the benzyl C-alkylated ligands

5,12-Dimethyl-5,6,11,12,18,19,20,21-octahydro-17-H-tribenzo[f,j,n][1,5,9,12]tetraazacyclopentadecine (3Ia)

The diimine 18,19,20,21-tetrahydro-17-H-tribenzo[f,j,n][1,5,9,12] tetraazacyclopentadecine (2Ia) (0.71g, 2 mmol) was added in portions to a solution of methyllithium in ether (20 cm^3, 32 mmol) in a dry box under nitrogen, with shaking after each addition. A clear cherry-red solution was formed. This was allowed to stand under nitrogen, and slow evaporation of the ether resulted in precipitation of a white solid. Water was added dropwise (5 cm^3) and then 2M HCl (5 cm^3) and finally 2M NaOH (5 cm^3). When all effervescence had ceased, chloroform (20 cm^3) was added and the chloroform solution filtered through anhydrous Na_2SO_4 to dry it and remove any insoluble material. On evaporation under vacuum, the filtrate yielded a friable white solid which was recrystallised from dichloromethane/petroleum ether (60-80%) and vacuum-dried to give 5-12-dimethyl-5,6,11,12,18,19,20,21-octahydro-17-H-tribenzo[f,j,n][1,5,9,12]tetraazacyclopentadecine (0.6g, 78%) as fine white needles, m.pt 142°C. (Found: C, 76.9; H, 7.9%; N, 14.2%. $C_{25}H_{30}N_4$ requires C, 77.72; H, 7.77; N, 14.50%); λ_{max} (CH_2Cl_2) 235 nm (ε = 10,580), 295 nm (ε = 6,690); ν_{max} (nujol) 3410(s, NH), 3300-3240(s,t, NH), 1600(s), 1590(s), 1530-1510(s.b), 1470(s), 1350(w), 1340(w), 1330(w), 1310(s), 1290(w), 1250(s), 1220(s), 1170(w), 1160(w), 1140(s), 1100(s), 1080(s), 1060(s), 990(w), 950(w), 930(w), 910(w), 875-865(w.d), 850(w), 750(s, o-substituted benzene). ^1H($CDCl_3$) 1.7(d.6H J=4.4, CH_3), 1.55(sept.2H. J=2.0, $CH_2C\underline{H}_2CH_2$), 3.5(m.4H. $C\underline{H}_2CH_2C\underline{H}_2$), 3.2(b.s.. 2H.N$\underline{H}$), 5.15(t.2H. J=2.2.CH.N$\underline{H}$), 4.5(quad.2H. J=4.4.$CH_3C\underline{H}$), 6.61-6.85(m.6H. aromatics), 7.39-7.7(m.6H. aromatics), $^{13}C(CDCl_3)$ See Fig. 3.5, Section 3.1.3; (Found; 386.2475. $C_{25}H_{30}N_4$ requires M, 386.2470;) m/e 386.2474 (M^+, 22.04), 278.1772(13.51), 263.1536 (15.08), 146.970(30.75), 134.0964(20.1), 132.0798(48.63), 130.0651 (23.72), 118.0647(23.62), 117.0575(16.65), 108.0697(100), 107.0613 (17.77).

5,12-Dibutyl-5,6,11,12,18,19,20,21-octahydro-17-*H*-tribenzo[*f*,*j*,*n*][1,5,9,12]tetraazacyclopentadecine hemihydrate (3Ib)

The diimine 18,19,20,21-tetrahydro-17-*H*-tribenzo(*f*,*j*,*n*)(1,5,9,12) tetraazacyclopentadecine (2Ia) (0.71g, 2 mmol) was added in portions to a solution of butyllithium in THF (20 cm^3, 28 mmol) in a dry box under nitrogen. The solution was shaken after each addition. A red solid was formed which turned pale yellow after standing overnight in a dry box. On gradually adding H_2O (10 cm^3) a white solid was formed. The mixture was shaken with 2M HCl (10 cm^3) and then 2M NaOH (10 cm^3). Chloroform (20 cm^3) was added to the mixture; all the solid dissolved to give a dark brown solution. On evaporating this to dryness a pale yellow solid was formed; this was recrystallised from dichloromethane/isopropylether and dried under vacuum to give 5,12,-dibutyl-5,6,11,12,18,19,20,21-octahydro-17-*H*-tribenzo[*f*,*j*,*n*][1,5,9,12]tetraazacyclopentadecine hemihydrate (0.71g, 74%) as fine off-white needles, m.pt 161°C. (Found: C, 77.9; H, 9.1; N, 11.5%. $C_{31}H_{43}N_4\frac{1}{2}O$ requires C, 77.66; H, 8.97; N, 11.69%). λ_{max} (MeOH) 254 nm (ε = 19,047), 302 nm (ε = 6,802); ν_{max} (nujol) 3400(s.b, NH), 1610(s, C=C), 1590(s. NH bend), 1530-1520(s.b), 1470(s,b), 1320(s), 1270(s), 1250(s), 1200(w), 1170(w), 1150(w), 1130(s), 1050(s), 1040(w), 940(w), 930(w), 910(w), 850(w), 750(s, o-substituted benzene); ^{1}H(CDCl$_3$) 0.92(t.6H. J=10.0, CH$_2$C$\underline{H}_3$), 1.2(sept.8H. J=5.0. C$\underline{H}_2$C$\underline{H}_2$CH$_3$), 1.8(quad.4H. J=10.0, CH C$\underline{H}_2$CH$_2$-), 1.8-2.0(m. 1H. CH$_2$ H-C-$\underline{H}$ CH$_2$), 2.0-2.2(m. 1H. CH$_2$$\underline{H}$-C-H CH$_2$), 3.18-3.3(m. 2H. C$\underline{H}_2CH_2CH_2$), 3.3-3.47(m. 2H. CH$_2CH_2C\underline{H}_2$), 3.58(s. 2H.N$\underline{H}$), 4.1(t. 2H. J=10.0.-CH$_2C\underline{H}$-), 4.9(s. 2H.N$\underline{H}$), 6.66-6.89(m. 8H. aromatics), 7.15-7.38(m. 4H. aromatics). ^{13}C See Fig 3.5, Section 3.1.3; (Found; 470.3405. $C_{31}H_{42}N_4$ requires M, 470.3409;) m/e 470.3405 (M^+, 47.35), 413.2675(27.02), 363.2751 (22.28), 224.1185(12.81), 202.1577(17.83), 200.1429(15.88), 190.1591 (25.63), 189.1454(12.26), 188.1443(83.57), 187.1370(12.81), 176.1454 (54.60), 175.1324(13.93), 174.1291(100), 162.1261(14.48), 146.0961 (10.86), 144.0809(20.89), 132.0792(65.46), 131.010(10.58), 130.0657 (50.14), 119.0625(21.45), 118.0659(74.09), 117.0581(22.28), 108.0688(17.27), 106.0646(32.59).

5,12-Dimethyl-5,6,11,12,17,18,19,20-octahydrotribenzo[c,i,m][1,4,8,11]tetraazacyclotetradecine (31c)

The diimine 17,18,19,20-tetrahydrotribenzo[c,i,m][1,4,8,11] tetraazacyclotetradecine (0.68g, 2 mmol) was added in portions to a solution of methyllithium in ether (20 cm^3, 32 mmol) in a dry box under nitrogen, with shaking after each addition. The solution was initially cherry-red, and became pale pink on standing. When no further colour change had occurred, H_2O was added dropwise (5 cm^3), followed by 2M HCl (5 cm^3) and 2M NaOH (5 cm^3). After all effervescence had ceased, chloroform (20 cm^3) was added. The chloroform solution was filtered through anhydrous Na_2SO_4, and evaporated to give a very soluble white powder which was recrystallised from methanol/water and vacuum-dried to give 5,12-dimethyl-5,6,11,12,17,18,19,20-octahydrotribenzo[c,i,m][1,4,8,11]tetraazacyclotetradecine (0.56g, 74%) as fine white needles, m.pt 171-173°C. (Found: C, 78.1; H, 8.1; N, 15.7%. $C_{24}H_{28}N_4$ requires C, 77.61; H, 7.52; N, 15.05%); λ_{max} (CH_2Cl_2) 235 nm (ε = 8,900), 300 nm (ε = 7,257); ν_{max} (nujol) 3310(s, NH), 3240(s, NH), 1605(s), 1585(s), 1520(s.b), 1470(s), 1360(w), 1330(w), 1310, 1290(w), 1260(s), 1230(s), 1200(w), 1170(s), 1140(s), 1090(s), 1065(s), 1050(s), 1035(w), 1010(s), 955, 930, 910(s), 860(s), 800(s), 750(s, o-substituted benzene); $^1H(CDCl_3)$ 1.6(d. 6H. J=6.0. $C\underline{H}_3$), 3.35(sext. 4H. J=6.0. $C\underline{H}_2C\underline{H}_2$), 4.4(quad. 2H. J=6.0. $CH_3C\underline{H}$), 4.9-5.2(m. 4H. N$\underline{H}$), 6.62-6.92(m. 8H. aromatics), 7.12-7.32 (m. 4H. aromatics); (Found; 372.2308, $C_{24}H_{28}N_4$ requires M, 372.2318;) m/e 372.2308 (M^+, 74.42), 265.1698(17.08), 249.1390 (19.24), 239.1393(12.96), 238.1353(73.20), 210.1024(20.26), 146.0967(15.99), 144.0795(14.67), 134.0963(30.77), 133.0846 (15.98), 132.0824(100), 130.0663(18.71), 120.0811(87.04), 118.0654 (44.02), 117.0585(22.88), 108.0690(23.90).

[illegible].4.2 Experimental data on the copper complexes of the [illegible] C-alkylated ligands

(5,12-Dimethyl-5,6,11,12,18,19,20,21-octahydro-17-H-tribenzo/[f,j,n/]/[1,5,9,12/]tetraazacyclopentadecine)copperII diperchlorate. $2H_2O$

The tetraamine 5,12-dimethyl-5,6,11,12,18,19,20,21-octahydro-17-H-tribenzo/[f,j,n/]/[1,5,9,12/]tetraazacyclopentadecine (3Ia) (0.19g 0.5 mmol) was dissolved in dichloromethane (10 cm^3) and a solution of copper diperchlorate 6 H_2O (0.19g, 0.5 mmol) was added in solution in methanol. A purple solid was deposited. This was recrystallised from hot dichloromethane to give (5,12-dimethyl-5,6,11,12,18,19,20,21-octahydro-17-H-tribenzo/[f,j,n/]/[1,5,9,12/] tetraazacyclopentadecine) copperII perchlorate. $2H_2O$ as fine purple crystals (0.24g, 68%). (Found: C, 42.6; H, 4.5; N, 7.8; Cu, 9.7%. $C_{25}H_{34}N_4CL_2O_{10}Cu$ requires C, 43.79; H, 4.96; N, 8.17; Cu, 9.34%). λ_{max} (DMF) 310 nm (ε = 6,485), 380 nm (ε = 2,804), 450 nm (ε = 1,051), 710 nm (ε = 1,893). ν_{max} (nujol) 3500(s.b.NH), 3200(b.NH), 1640(s), 1615(s), 1590, 1510, 1470(s), 1430(w), 1320(s), 1280, 1230(s), 1200(s), 1150-1000(v. strong, broad, ClO_4), 940(s), 920(s), 900(s), 830(s), 820, 770, 760(sh, o-substituted benzene), 730.

(5,12-Dibutyl-5,6,11,12,18,19,20,21-octahydro-17-*H*-tribenzo[*f*,*j*,*n*][1,5,9,12]tetraazacyclopentadecine)copperII diperchlorate

The tetraamine 5,12-dibutyl-5,6,11,12,18,19,20,21-octahydro-17-*H*-tribenzo[*f*,*j*,*n*][1,5,9,12]tetraazacyclopentadecine (31b) (0.235g, 0.5 mmol) was dissolved in dichloromethane (10 cm^3) and a solution of copper diperchlorate $6H_2O$ (0.19g, 0.5 mmol) in methanol was added. A dark brown solid was formed. The mixture was refluxed to ensure complete reaction. After cooling, the brown solid was recrystallised from hot dichloromethane to give (5,12-dibutyl-5,6,11,12,18,19,20,21-octahydro-17-*H*-tribenzo[*f*,*j*,*n*][1,5,9,12]tetraazacyclopentadecine)copperII diperchlorate as very dark brown crystals (0.25g, 69%). (Found: C, 50.1; H, 5.5; N, 7.4; Cu, 8.73%. $C_{31}H_{42}N_4Cl_2O_8Cu$ requires C, 50.75; H, 5.70; N, 7.63; Cu, 8.73%). λ_{max} (DMF) 267 nm (ε = 10,775), 375 nm (ε = 10,775), 440 nm (ε = 1,466). ν_{max} (nujol) 3280(s, broad, NH), 1620(s), 1600(s), 1520(s), 1490-1450(s, broad), 1300(s), 1260(s), 1240(s), 1200(s), 1150-1050(s, broad ClO_4), 1000(s), 940(w), 915(w), 850, 780-750 (s, broad, o-substituted benzene).

(5,12-Dimethyl-5,6,11,12,17,18,19,20-octahydrotribenzo[*e*,*i*,*m*][1,4,8,11]tetraazacyclotetradecine)copperII diperchlorate

The tetraamine 5,12-dimethyl-5,6,11,12,18,19,20,21-octahydro-17-*H*-tribenzo[*f*,*j*,*n*][1,5,9,12]tetraazacyclotetradecine (3Ic) (0.18g, 0.5 mmol) was dissolved in dichloromethane (10 cm^3), and a solution of copper diperchlorate $6H_2O$ (0.19g, 0.5 mmol) was added in solution in methanol. A purple solid was formed. This was recrystallised from hot dichloromethane to give (5,12-dimethyl-5,6,11,12,17,18,19,20-octahydrotribenzo[*e*,*i*,*m*][1,4,8,11]tetraazacyclotetradecine)copperII diperchlorate. $2H_2O$ as fine purple crystals (0.2g, 64.5%). (Found: C, 42.0; H, 4.4; N, 7.6, Cu, 10.0%. $C_{24}H_{32}N_4Cl_2O_{10}Cu$ requires C, 42.92; H, 4.76; N, 8.34; Cu, 9.53%). λ_{max} (DMF) 310 nm (ε = 9,807), 385 nm (ε = 3,015), 440 nm (ε = 1,753), 712 nm (ε = 1,907). γ_{max} (nujol) 3500(s, broad, OH), 3200(broad, NH), 1640(s), 1610, 1590, 1510, 1470(s), 1320, 1290, 1270(w), 1230(s), 1200(s), 1150-1030(v. strong broad, ClO_4), 1000(s), 935(s), 920(s), 900(w), 880(w), 850(s), 830(s), 820, 770(s), 760(s, o-substituted benzene), 745(w), 730.

3.4.3. Experimental data on the copper complexes of the oxalo-bridged ligands

[5,12-Diphenyl-18,19-dioxo-9,10,17,18,19,20-hexahydrodibenzo[e,m][1,4,8,11]tetraazacyclotetradecinato(2-)]-dimethylformamido copperII dihydrate

2,2'-(oxalyldiimino)bisbenzophenone (0.22g, 0.5 mmol) was refluxed in DMF with diaminoethane (0.07g, 1.1 mmol) and copper acetate (0.1g, 0.5 mmol) for 12 hours. On cooling the mixture, red crystals started to form, but some of the unreacted ketone was still present, so refluxing was continued for 24 hours. On cooling the mixture red needle crystals formed. These were recrystallised from hot DMF to give [5,12-diphenyl-18,19-dioxo-9,10,17,18,19,20-hexahydrodibenzo[e,m][1,4,8,11]tetraazacyclotetradecinato(2-)]-dimethylformamidocopperII dihydrate as large dark-red needle crystals (0.13g, 50%). (Found: C, 63.3; H, 5.3; N, 10.28%; $C_{30}H_{28}N_4O_4Cu$ requires C, 63.10; H, 4.56; N, 9.82%). λ_{max} (DMF) 375 nm (ϵ = 14,070), 420 nm (ϵ = 4,270); ν_{max} (nujol) 3400(s, CH), 1675(s), 1655(s), 1650-1600(s, v. broad), 1560(s), 1475(s), 1330(s), 1310(s), 1270(s), 1250(s), 1220(w), 1190(s), 1170(s), 1090(s), 1070(s), 1030(w), 1000, 920(s), 870(w), 850(w), 820(w), 780(s), 755(s), 735(s), 710(s).

[5,12-Diphenyl-18,19-dioxo-17,18,19,20-tetrahydrotribenzo[e,i,m][1,4,8,11]tetraazacyclotetradecinato(2-)]dimethylformamidocopper(II)

2,2'-(oxalyldiimino)bisbenzophenone (0.22g, 0.5 mmol) was refluxed in DMF with diaminobenzene (0.054g, 0.5 mmol) and triethylamine (0.1 cm^3, 1 mmol), and copper acetate (0.1g, 0.5 mmol). After 24 hours, there was some unreacted ketone deposited when the solution was cooled. This was filtered off, and the filtrate allowed to evaporate slowly, after the addition of a few drops of methanol. After several days, [5,12-diphenyl-18,19-dioxo-17,18,19,20-tetrahydrotribenzo[*e*,*i*,*m*][1,4,8,11]tetraazacyclotetradecinato(2-)]dimethylformamidocopperII was deposited as large, very dark green crystals (0.1g, 30%). (Found: C, 67.3; H, 4.4; N, 10.7%. $C_{38}H_{40}N_6O_4Cu$ requires C, 67.57; H, 4.71; N, 10.65%). λ_{max} (DMF) 365 nm (ε = 21,950), 395 nm (ε = 19,790), 460 nm (ε = 6,180). $\tilde{\nu}_{max}$ (nujol) 1740(w, C=O, DMF), 1670(s), 1650(s, sh), 1630(w), 1600(w), 1585(w), 1570(w), 1530(s), 1470(s), 1340(s), 1320(s), 1290(s), 1275(s), 1265(s), 1240(w), 1170, 1150, 1100(w), 1080(w), 1060(w), 1035(w), 1000(w), 970, 950(w), 930(s), 870, 800, 760(s), 740(s), 735, 710.

3.4.4. Experimental data on the bridged ligands

Reaction product of the tetraamine 2IIIa with glyoxal (3IIIa)

A very pure sample of the tetraamine 5,6,11,12,18,19,20,21-octahydro-17-H-tribenzo[f,i,n][1,5,9,12]tetraazacyclopentadecine (2IIIa) (0.18g, 0.5 mmol) was dissolved in acetonitrile (10 cm^3). Aqueous solution (40%) of glyoxal was added dropwise. (0.75 cm^3, 0.5 mmol). The solution changed from yellow to pale green during the two-hour reflux under nitrogen. The solution was cooled, evaporated to dryness and the cream-coloured residue digested with chloroform overnight. The mixture was filtered slowly through SiO_2 to give a clear bright solution which was evaporated under vacuum to give a brown oil, from which pale yellow crystals separated on addition of methanol. These were recrystallised from dichloromethane/methanol to give the reaction product as the hemihydrate of 3IIIa as very pale yellow crystals, (0.06g, 30%); m.pt 70°C. (Found: C, 77.2; H, 6.1; N, 13.8%. $C_{25}H_{25}N_4\frac{1}{2}O$ requires C, 77.12; H, 5.39; N, 14.39%). λ_{max} (CH_2Cl_2). 233 nm (ε = 42,560), 265 nm (ε = 35,340), 310 nm (ε = 14,400); ν_{max} (nujol) 3400(b,OH), 3080, 3050, 2820(C-H Stretch), 1610(s), 1580(s), 1500(s, broad), 1465(broad), 1400(s), 1350(s), 1340(s), 1330(s), 1320(s), 1300(s), 1270(s), 1250(s), 1230(s), 1210(s), 1200(s), 1170(s), 1150(s), 1125(s), 1110(s), 1060(s), 1050(s), 1030(s), 1010(s), 985(w), 975(s), 950(s), 925(s), 905(s), 865(s), 845(s), 820(s), 805(w), 790(s), 750(s,broad, o-substituted benzene) ^1H ($CDCl_3$) 1.78 (m, 2H, $CH_2\underline{CH_2}CH_2$), 3.65(2x sext), 4H, J=45, J=6.0, $\underline{CH_2}CH_2\underline{CH_2}$), 4.78 (d, 2H, J=9.0, $\underline{CH_2}$-N), 4.76(d, 2H, J=9.0, $\underline{CH_2}$-N), 5.16(s. 2H. $\overset{N}{\underset{N}{}}$ C$\underline{H}$-C$\underline{H}$ $\overset{N}{\underset{N}{}}$), 6.5-6.87(m. 6H. aromatics), 6.87-7.12 (m. 6H. aromatics). ^{13}C (CDCl$_3$) See Fig. 3.10 Section 3.3.1.3; (Found; 380.2001. $C_{25}H_{24}N_4$ requires M, 380.2008;) m/e 380.2001 (M$^+$, 100), 378.1848(15.75), 261.1377(10.07), 248.1201 (11.66), 236.1184(40.5), 234.1022(22.48), 233.0955(10.75), 232.0873(21.42), 221.0979(10.3), 220.0889(14.69), 207.0922(20.67), 158.0966(13.4), 144.0807(10.52), 132.0804(17.79), 131.0687(12.34), 130.0647(21.42), 118.0647(73.96), 117.0571(15.14)..

Reaction product of 3XVI with glyoxal (3XVII)

A pure sample of 6,7,8,9,10,11,17,18-octahydro-5-H-dibenzo[e,n] [1,4,8,12]tetraazacyclopentadecine (0.15g, 0.5 mmol) was dissolved in acetonitrile, and an aqueous solution (40%) of glyoxal was added dropwise (0.75 cm^3, 0.5 mmol) to the warm solution. A white precipitate formed after two minutes on stirring the mixture. This was dissolved in chloroform, and the solution filtered through silica gel. A few drops of diisopropyl ether were added to the solution giving a reaction product (tentatively formulated as 3XVII) as white crystals (0.09g, 60%); m.pt 213°C. (Found: C, 68.1; H, 7.0; N, 14.1%. $C_{21}H_{28}N_4O_2$ requires C, 68.47; H, 7.60; N, 15.21%). ν_{max} (nujol) 3390(s, OH), 3270(s, NH), 3090, 3060, 3020(w), 2730(w), 1610(s), 1580(s), 1520(s, broad), 1470(s), 1385(s), 1330, 1320, 1300(w), 1285, 1270(s), 1225(s), 1200(s), 1170(w), 1150(s), 1135(w), 1110(s), 1090(s), 1050(w), 1035(s), 980(w), 940(s, broad), 895(s), 860(s), 810(w), 800(w), 770-760(s, o-substituted benzene) 730(w), 720(w), ^1H ($CDCl_3$) 1.5 (m.2H) $CH_2\underline{CH_2}CH_2$), 2.6(d, 2H, J=13.0), 3.3(t. 2H, J=13.0), 3.5(m. 4H. $\underline{CH_2}$-$\underline{CH_2}$), 3.95(d, 2H. J=13.0), 4.10(d. 2H. J=13.0), 4.53(s. 1H), 4.86(s. 1H), 6.35(s. 2H. N$\underline{H}$), 6.6-6.7(m. 8H aromatics), 7.0-7.1(m. 2H. aromatics), 7.2-7.3(m. 2H aromatics). ^{13}C ($CDCl_3$) See Fig 3.15, Section 3.3.2.2; (Found: 350.2089. $C_{21}H_{26}N_4O$ requires M, 350.2106;) m/e 350.2089 (M^+, 20.07), 349.2043(29.45), 332.1990(100), 331.1891(12.81), 330.1832(28.02), 321.2089(34.90), 287.1282(10.05), 237.1373(10.21), 202.1338(41.71), 174.1156(41.78), 173.1075(40.71), 171.0[illegible](11.98), 166.0969(17.51), 165.0889(10.06), 159.0906(10.28), 14[illegible].05[illegible](1[illegible].84), 145.0771(13.91), 131.0612(41.53), 130.0604(18.69), 120.0[illegible]03(25.59), 118.0662(78.53), 117.0582(15.[illegible]), 116.0509(11.68), 106.0660(14.[illegible]).

3.5 References for Chapter 3

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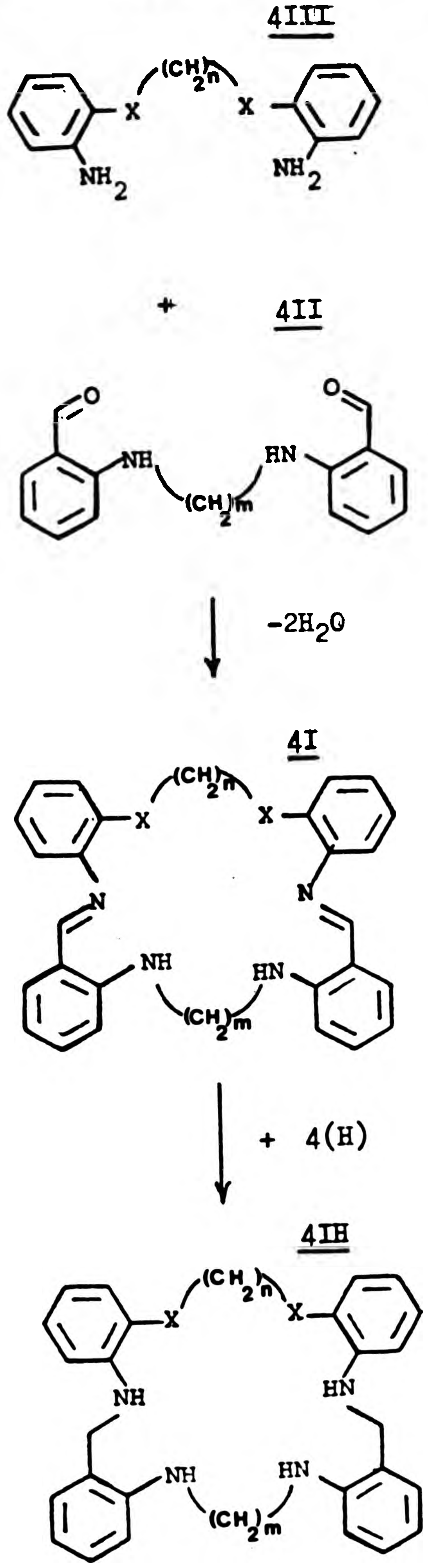
Chapter 4 The sexadentate macrocycles

4.1 Preparation of the sexadentate macrocycles

The sexadentate ligands were prepared by the reactions shown below;



4IIIa,b,c

4IIIa X=O, n=2
4IIIb X=O, n=3
4IIIc X=S, n=2
4IIId X=NH, n=2

4IIa,b
4IIa m=2
4IIb m=3

4Ia,b,c,d,e,f

4Ia X=O, n=m=2
4Ib X=O, n=2,m=3
4Ic X=O, n=m=3
4Id X=O n=3,m=2
4Ie X=S n=m=2
4If X=NH n=m=2

4IHa,b,c,d,e,f.

Fig 4.1 Preparative scheme for the sexadentate macrocycles.

4Ia has been prepared previously (see footnote), and certain metal complexes (Fe(II), Co(II), Ni(II) and Zn(II)) of 4Ia,* 4Ie and 4If have been isolated[1] from "metal-ion template" reactions in which the condensations outlined in the scheme above were performed in the presence of the appropriate divalent metal salt. For the present work both the free ligands and their Cu(II) complexes (none of which have been prepared previously) were required. As a result, considerable effort was expended in devising and optimising non-template conditions for the cyclocondensation reactions shown in the above scheme, and for the subsequent reduction of the resulting free ligand, as described below.

4.1.1. Preparation of the sexadentate diimines with an N_4O_2 donor set (4Ia-d, Fig 4.1)

A series of ligands with the N_4O_2donor set (4Ia-d) was made in order to investigate the effect of ring size upon possible mode of coordination. All the diimine ligands having the 'N_4O_2' donor set were yellow crystalline solids which were insoluble in methanol. In marked contrast to the preparations discussed below (4.1.2 and 4.1.3), they separated readily from the reactions shown in the scheme in section 4.1 when performed in methanol,

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*Footnote; 4Ia was obtained as a biproduct in the preparation of the zinc(II) perchlorate complex, when the condensation was performed in the presence of zinc(II) perchlorate.[1] A non-template route to 4Ia, using p-toluenesulphonic acid as a catalyst was demonstrated during a project[2] involving syn thesis of metal-free diimine quadridentate macrocyclic ligands.

using p-toluenesulphonic acid as catalyst. Their insolubility may contribute to the ease of formation of these macrocycles under conditions which approach thermodynamic control in the presence of the acid catalyst. Other ligands containing the ether linkage have been found to be both insoluble and to form easily.[3] However, insolubility, per se, was not found to be the sole criterion of ease of formation of the sexadentate ligands 4Ie and 4If; see 4.1.2 and 4.1.3 below.

All the 'N_4O_2' donor set ligands were formed from non-homogeneous reaction conditions, with the dialdehyde, (4IIa, b) in suspension in methanol. Intermediate products, however, were soluble and formed a deep orange solution in methanol from which the final product crystallised. At present it is assumed that these intermediates were carbinolamines,[4] and that for the series of compounds, 4Ia-f, the loss of water across the C-N bonds, to form the diimines was a thermodynamically favourable step. The electronic spectra of these ligands indicated that there was a relationship between ring size, (in particular the distance between possible donor oxygen atoms) and electronic properties of both the diimine and tetraamine ligands (4Ia-d , 4IHa-d) and of their copper complexes. In addition, there was an interesting variation in the character of the copper perchlorate complexes of these diimine ligands 4Ia-d, according to ring size.

4.1.2. Preparation of the sexadentate diimine with the N_4S_2 donor set (4Ie).

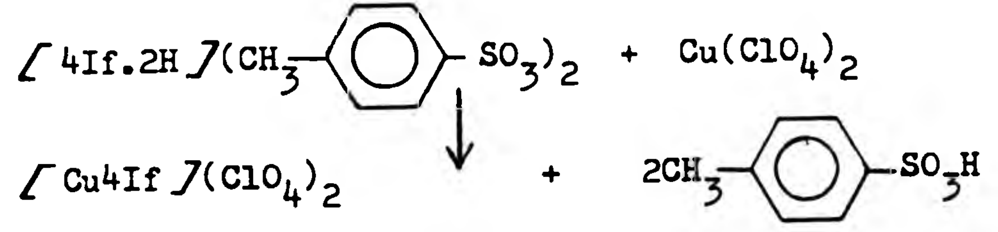
A lot of experimentation was required before a method was found for obtaining the metal-free ligand 4Ie. In many of the trial experiments the end-product contained a variable proportion of the unreacted dialdehyde, 4IIa, irrespective of the length of the reaction time. Eventually, a mixture of catalysts (p-toluenesulphonic acid and zinc acetate), was used to produce the pure ligand.

In contrast to the ligand series with an N_4O_2 donor set, homogeneous conditions were necessary at the start of the reaction. To achieve this, absolute ethanol was used to dissolve the dialdehyde completely. The ethanol may also assist in the 'dehydration' of a carbinolamine intermediate. The final product, however, was appreciably more soluble in ethanol than in methanol, and so the minimum possible volume of ethanol was used. With p-toluenesulphonic acid alone as catalyst, the product formed rapidly as a sticky red oil which hardened on cooling, and which usually contained unreacted dialdehyde. With zinc acetate alone the product formed very slowly, but always contained unreacted dialdehyde. It seemed that p-toluenesulphonic acid was needed to protonate the dialdehyde and promote condensation, but that zinc ions were beneficial in promoting formation of a pure microcrystalline product. The fact that crystals, rather than an oil, were formed using zinc acetate might indicate that formation of an intermediate, unstable zinc complex of the ligand occurred as one of the equilibrium stages of the reaction. Breakdown of this complex might occur in the final reaction stage to give the free ligand, causing the reaction sequence to move towards completion with the gradual deposition of the solid ligand. The reaction was found to take a minimum of 36 hours for completion. After completion most of the ligand was present as a bright yellow solid, with a small amount in solution in the ethanol.

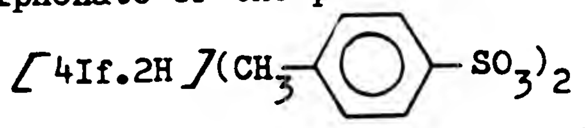
4.1.3. Preparation of the sexadentate diimine ligand with the 'N_6' donor set. (4If)

Preparation of the pure N_6 diimine was not achieved under any of the reaction conditions described above. Many trial experiments were carried out. Yellow products were frequently obtained which were shown by mass spectrometry to contain some of the desired ligand, but also non-volatile and polymeric material.[5]

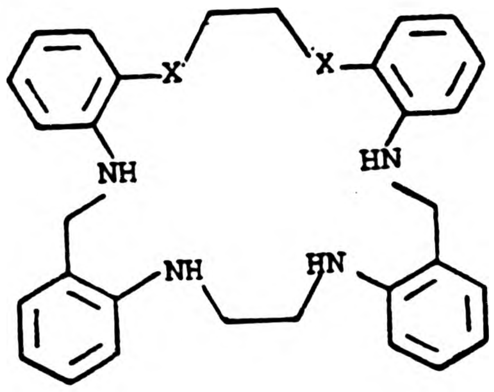
It was noticed that a pale green salt was separable from the yellow polymeric material by dissolving the latter in chloroform. This salt gave an infra-red spectrum which showed the characteristics of previous ligands in the series. In particular, there were three strong bands in the region 1590-1610 cm^{-1}, previously assumed to contain the C=N stretching modes, and a very strong broad band at 1200 cm^{-1} which indicated the presence of a sulphonate group. It seemed likely that the pale green material was a *p*-toluenesulphonate salt of the N_6 diimine. It appeared that the formation of this salt, which was insoluble in methanol, might be both kinetically and thermodynamically favourable in the presence of excess p-toluenesulphonic acid. Having recognised the strongly basic nature of the free ligand, the experiment was repeated in the presence of 2 moles of p-toluenesulphonic acid to 1 mole of dialdehyde, 1.25 moles of diamine and 1 mole of zinc acetate. It was found that homogeneous starting conditions were required, and absolute ethanol was used to dissolve the dialdehyde completely. Solutions of the diamine, zinc acetate, and p-toluenesulphonic acid were added, in that order. The order of the addition was important; addition of zinc acetate to the dialdehyde before the diamine had been added resulted in a yellow material containing free dialdehyde. Addition of p-toluenesulphonic acid at any stage but the last resulted in a yellow amorphous product. This order of addition, allowing a minute or two between each addition, must permit the reactants to equilibrate in the right sequence to allow the diimine salt as the end-product. The assumption was made at this stage that the free diimine would be unstable, so an attempt was made to form the copper complex of the diimine directly from the p-toluenesulphonic salt by reaction with copper perchlorate. Surprisingly, it was found that on stirring the pale green salt in a methanol solution of copper perchlorate, an insoluble white salt was obtained. This gave the same infra-red spectrum as the green salt except that the sulphonate band was replaced by a broad band at 1100 cm^{-1}, characteristic of perchlorate. From this and analytical data it was clear that anion exchange had occurred. The expected reaction



thus did not occur.

Further experiments on the salts led to the discovery that either of them, when added to a solution of the theoretical amount of LiOH in methanol, yielded an immediate bright yellow flocculent precipitate, which was insoluble in methanol and quite stable. This was shown to be the diimine, and it was produced in theoretical yield from the p-toluenesulphonate or the perchlorate salt, assuming that these had the formula  or [4If.2H]$(ClO_4)_2$. The strong proton affinity of this diimine, which was a vital clue to the successful preparative route, was reflected in its strong tendency to hydrate. It was not found possible, even after prolonged vacuum drying, to reduce the level of hydration below 1 mole of H_2O to 1 mole of ligand. In concluding this discussion of the preparative routes to the sexadentate ligands, it should be noted that most previous work on large macrocyclic imines has been limited to their formation as metal complexes under "template" conditions. Although it was not a trivial exercise to find the suitable reaction conditions for this series of free ligands to be formed, it was eventually possible to devise these after many trial experiments. It was unexpected that the ligands with different donor sets but otherwise similar structures required different conditions for formation.

4.1.4. Hydrogenation of the sexadentate diimine ligands, having 'N_4X_2' donor sets



4IHa X = O

4IHe X = S

4IHf X = NH 4 I

Borane-tetrahydrofuran was added in portions until the initially produced dark orange-yellow colour was discharged. In the case of these ligands(4 I)no problem was encountered with regard to removal of the boron from the complex[6] during the work up of the reduction mixtures.

A large excess of borane (15-20 moles:1 mole ligand) was found to be needed for complete reduction of diimine bonds. After cooling the reaction mixture, the excess diborane was decomposed with water. This usually gave a precipitate of boric acid which was removed by treating the mixture with 2M NaOH. At this stage the THF layer containing dissolved tetraamine, and the aqueous layer, were separated. It was sometimes necessary to 'salt out' the THF layer by addition of NaCl to the aqueous layer, since THF is miscible with water in certain proportions. Care was taken to carry out the separation under nitrogen and to keep all the handling operations under nitrogen as far as possible. Although the 'N_4O_2' donor set' ligand (4IHa) was stable to oxidation, the 'N_4S_2 donor set' ligand (4IHe) was easily oxidised when exposed to air, and slowly darkened on storage under nitrogen. Surprisingly, the 'N_6 donor set' ligand (4IHf) was fairly stable to oxidation, perhaps because of protection given by its crystallization as a hydrate.

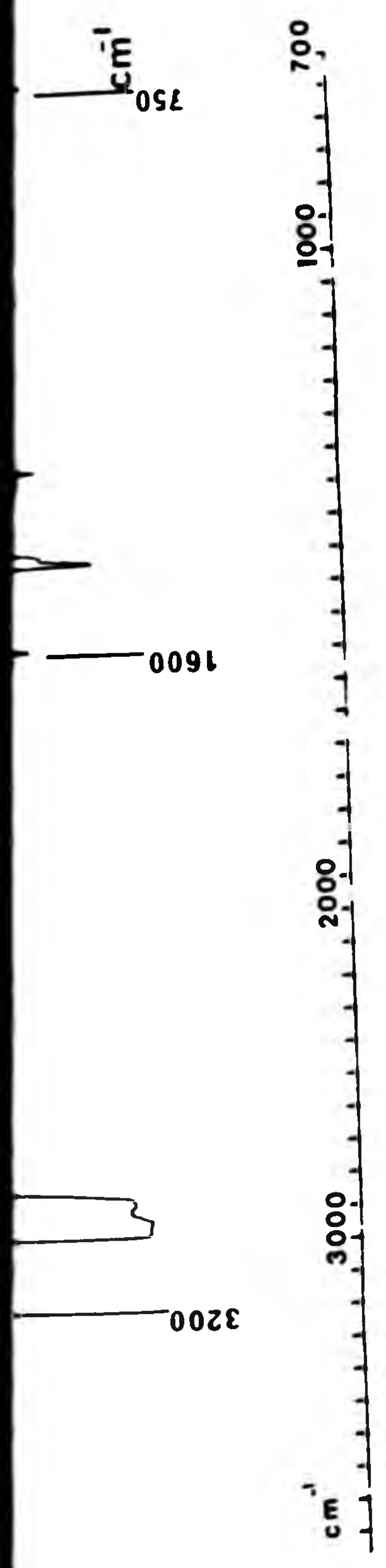
4.2. The physical properties of the metal-free 20-membered sexadentate ligands

The physical characteristics of the sexadentate diimines and tetraamines are discussed under the headings below.

4.2.1. Infra-red spectra of the 20-membered sexadentate ligands

The series of diimine ligands (4Ia-f) and the fully reduced counterparts (4IIa-f) showed complex infra-red absorption spectra. The spectra of the diimines showed many common characteristics, and many of the peaks were assigned. The remainder of the spectra, particularly that below 1000 cm^{-1}, was useful for 'fingerprinting' the particular compound. The main absorption bands in the diimine spectra together with tentative assignments are given below. (Table 4.1)

The peak ca. 750 cm^{-1}, assigned to C-H deformation in o-substituted benzene, was present in the spectrum of these and other similar macrocycles.[7] The absorption at 1510-1530 cm^{-1}, assigned to secondary N-H deformation was also found in other macrocycles prepared. The sexadentate ligands all showed a distinctive strong group of three peaks between 1570 and 1630 cm^{-1}, and these provided a useful mark of identification of the correct product. These bands were accentuated in the protonated p-toluenesulphonate and perchlorate salts of the N_6 donor set ligand, 4If. In the former, a broad band at 1150-1250 cm^{-1}



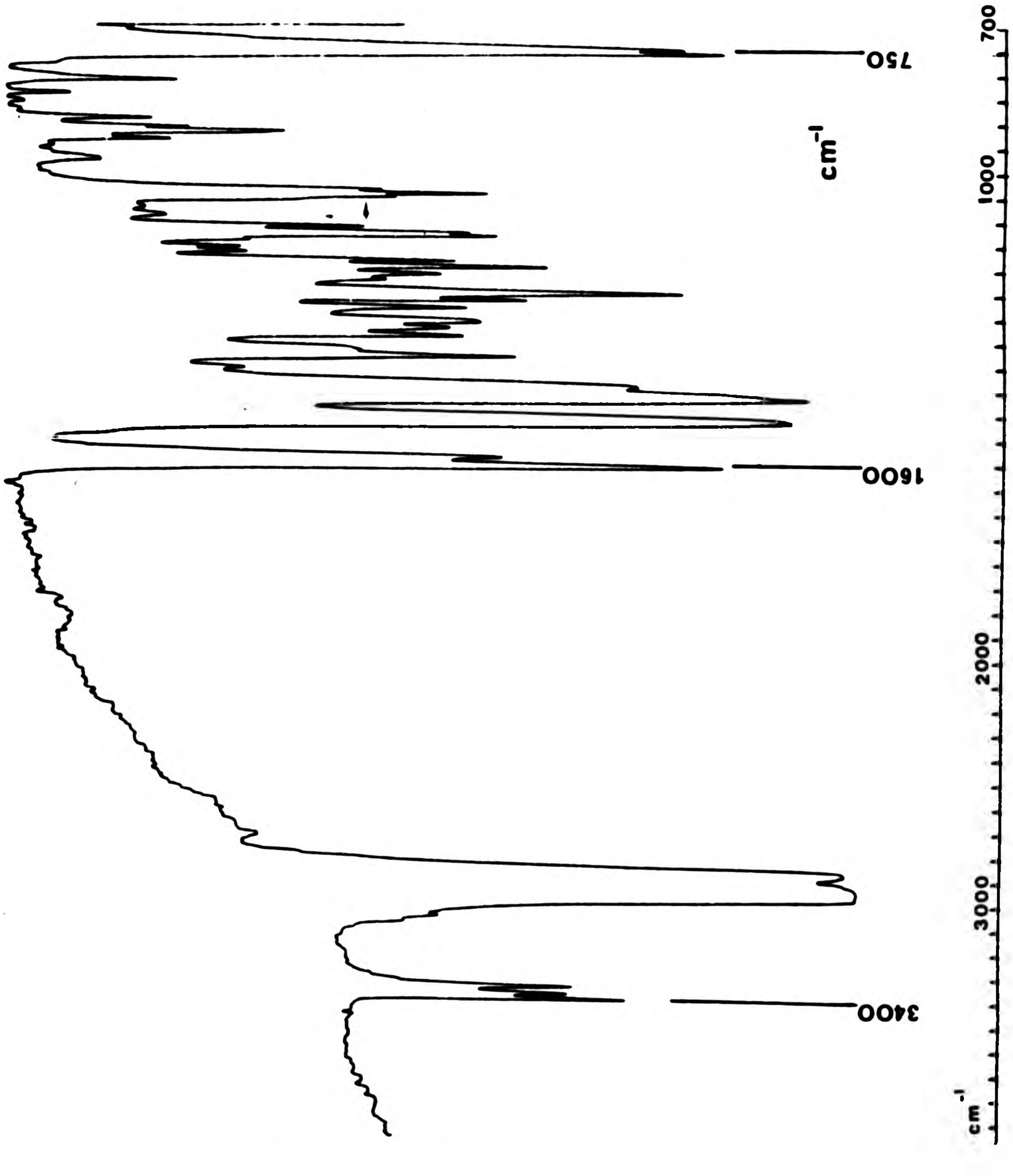
ine with an
ption bands.(Nujol)

due to S=O was present. This had a sub-peak at 1200 cm^{-1}, characteristic of p-toluenesulphonic and to its salts. Further identification was provided by a very sharp band at 1040 cm^{-1}, characteristic of sulphonic acids. In the perchlorate salt the very broad band at 1050-1150 cm^{-1} was characteristic of the symmetrical perchlorate anion with few infra-red active modes[8].

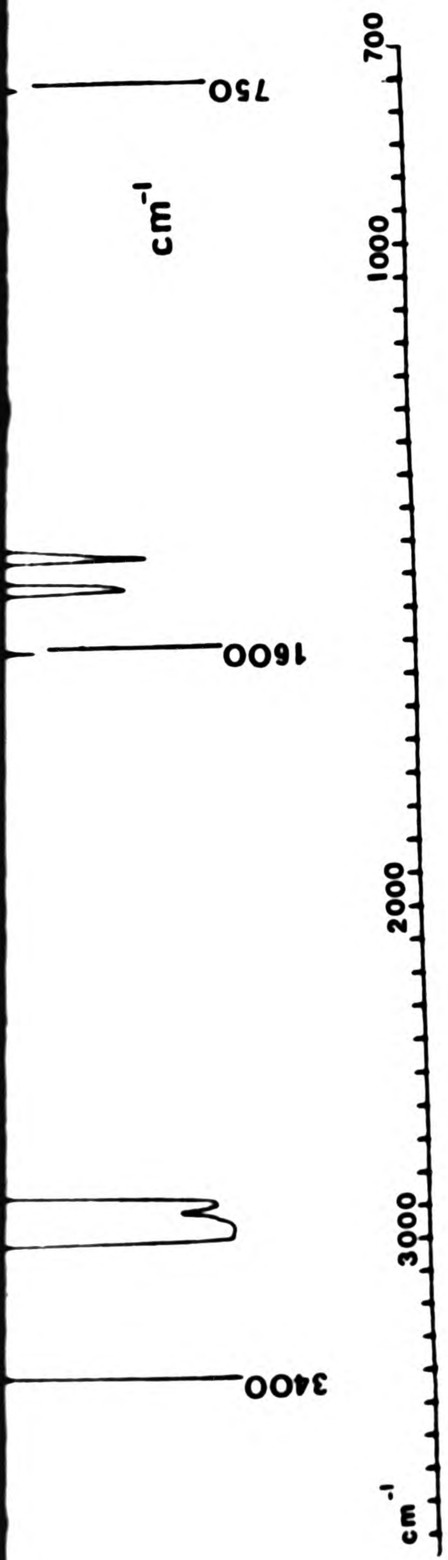
The peaks ca. 3300 cm^{-1} attributed to NH stretch were broad and weak. This feature was noted in other free diimine ligands and was probably due to intra-molecular hydrogen bonding involving the NH groups, for which some additional evidence was provided by the ^1H nmr data (see 4.2.2).

The main absorption peaks of the fully-reduced ligands are shown in Table 4.2. Peaks at ca. 1130 cm^{-1} were tentatively assigned as C-N stretching modes in aliphatic secondary amines. There were new peaks in the region 1270-1320 cm^{-1}, particularly strong in the 'N_4S_2' donor set' tetraamine (4IHe, see 4 I) These could not be definitely assigned, but were probably due to additional C-H infra-red active absorption modes.

The peak corresponding to N-H deformation in the diimines occurred at a lower wave number in the saturated macrocycles. The triple peak was reduced, in all three macrocycles, to two broad peaks, probably by elimination of the component corresponding to C=N stretch. There was a noticeable sharpening of the peak



Infra-red spectrum of the sexadentate tetraamine with an N_4O_2 donor set(4IIa), showing typical absorption bands.(Nujol)



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orption bands.(Nujol)

assigned to N-H stretch in the N_4O_2 donor set tetraamine, 4IHa, probably because of decrease in intramolecular hydrogen bonding in the reduced ligands as well as the additional HN bonds. The corresponding peak in the N_6 donor set hexaamine ligand 4IHf was a strong but broad peak. This compound contained a water of solvation and so intermolecular hydrogen bonding was expected.

Table 4.1 Absorption maxima (cm^{-1}) in the infrared spectra of the sexadentate diimines (nujol)

4Ia (X=O)	4Ie (X=S)	4If (X=NH)	Assignment
3220	3450-3300	3440-3300	NH stretch (OH)
1620	1630	1620	C=N stretch
1595	1595	1600	C=C stretch in benzene derivatives
1575	1570	1580	N-H bend
1550	1530	1530-1510	Secondary NH deformation
1250			C-O-C stretch in alkyl-aryl ethers
1160	1170	1170	Secondary aliphatic C-N stretch
740	745	750	C-H deformation in 1,2 disubstituted benzene

Table 4.2 Absorption maxima (cm^{-1}) in the infrared spectra of the reduced 20-membered ligands (nujol)

4IHa (X=O)	4IHe (X=S)	4IHf (X=NH)	Assignment
3380, 3340	3380, 3370	3420-3350	NH stretch (OH)
1610	1615	1610	Aromatic C=C stretch in benzene derivatives
1590	1590	1590	N-H bend
1515	1510	1520	Secondary NH deformation
1300	1320, 1270 1240	1270	CH_2 deformations
1250			C-O-C stretch in alkyl aryl ethers
1130	1140	1140	C-N stretch in aliphatic secondary amines
760	760	760	C-H deformation in 1, 2 disubstituted benzene

4.2.2. ^{1}H nmr spectra of the 20-membered sexadentate ligands

The spectra observed for the sexadentate diimines were consistent with the expected structures, and it was possible to assign the proton signals of the chemically equivalent halves of the molecule as shown in Figure 4.2, where X is O or S or the NH unit. The signals were assigned on the basis of their chemical shifts and

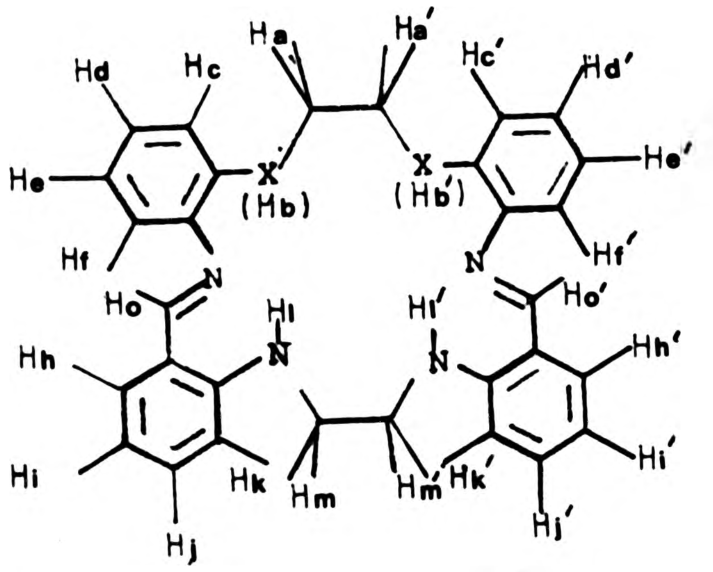

Fig. 4.2. Hydrogen labelling in the sexadentate diimines used in Table 4.3.

coupling. The azomethine proton, (H_o)signal occurred downfield of the aromatic proton signals, because of the deshielding due to the imine bond. The methylene protons (Ha, Hm) signals were upfield of the aromatic signals Hc-Hf, and Hh-Hk. (see Table 4.3)

The methylene proton signals Hm were assigned on the basis of the relatively small change in chemical shift (0.3 ppm) shown by

4.2.2. ^{1}H nmr spectra of the 20-membered sexadentate ligands

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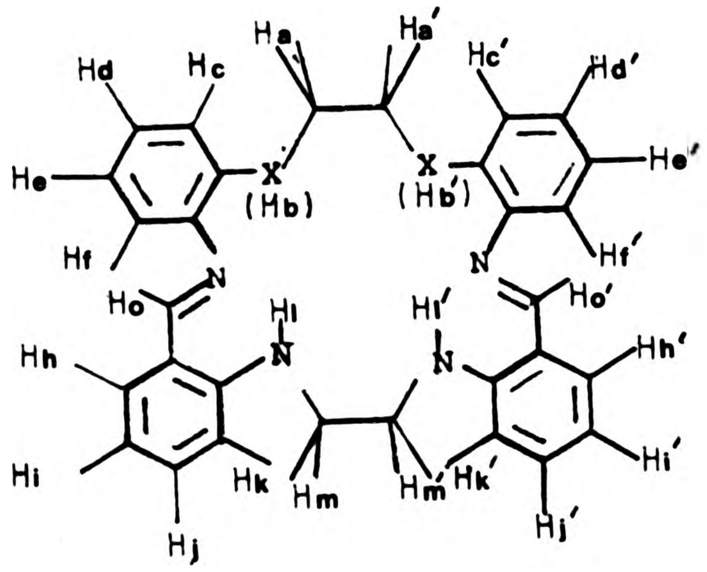


Fig. 4.2. Hydrogen labelling in the sexadentate diimines used in Table 4.3.

The methylene proton signals Hm were assigned on the basis of the relatively small change in chemical shift (0.3 ppm) shown by this signal between the spectra of all three diimine macrocycles. On the other hand the chemical shift of the signals of the methylene protons Ha adjacent to the O and S atoms and the NH unit, showed relative downfield shifts corresponding to the degree of electron withdrawal by the increasingly electronegative atoms or units, i.e. $S < NH < O$. This was consistent with literature values;[9, 10] for example where methylene protons adjacent to OH, NH_2 and SH showed chemical shifts of 3.59, 2.74 and 2.44 ppm respectively ($CDCl_3$). In these macrocycles values of 4.58, 3.46 and 3.25 ppm ($CDCl_3$) respectively were obtained. Exact structural comparisons were not available.

In the diimine with the N_6 donor set (4If) there were two types of NH protons, H_b and H_1. One signal appeared downfield of the azomethine proton signal in a comparable position to those in the diimines with the N_4O_2 and N_4S_2 donor sets (4Ia and 4Ie) in $CDCl_3$, and so by analogy this signal was assigned to the H1 protons derived from the dialdehyde. The other NH proton signal in the N_6 donor set was much further upfield. All NH signals were assigned after shaking with D_2O, when exchange of the labile NH protons with deuterium occurred causing the signal to disappear. Considerable solvent-dependent chemical shifts were observed for the NH proton signals; well-demonstrated in the case of the N_4S_2 donor set diimine studied in d-chloroform and d-pyridine. In d-pyridine the signal was shifted upfield to 6.0 ppm, from the more usual position around 10 ppm observed in d-chloroform which is close to the values which were also observed for H1 in the N_4O_2 donor set and

N_6 donor set diimines. In the case of amines, solvent-induced chemical shifts were thought to be mainly due to electrostatic changes involved in hydrogen bonding, especially in the case of strong hydrogen bonding solvents such as pyridine. Inversion of NH groups from an 'endo' to an 'exo' position has been shown to occur in polycyclic ring systems[12,13] and conformation changes caused by reorientation of NH groups between polar and non-polar solvents have also been studied.[14,15] Such a conformational change, if it occurred, should be reflected in marked chemical shift differences in the methylene group signals. However, where solvent dependent shifts were best observed, in the case of the N_4S_2 donor set ligand (4Ie) chemical shift changes of other groups were about 0.1 ppm. The maximum shift attributed to changes in bulk susceptibility of solutions in the study of some other large molecules was 0.3 ppm,[16,17] but values of 0.1-0.2 ppm were the most commonly encountered. The systems previously studied were not macrocyclic. Where solvent shifts of this magnitude occur in more flexible macrocycles, the possibility of conformational changes cannot be ruled out.

An interesting feature of the diimine systems is the evidence for intramolecular hydrogen bonding given by the ^1H n.m.r. spectra. Anilino systems normally show rapid NH proton exchange rates except where there is internal hydrogen bonding.[18] Studies in different solvents of the H-C-X-H system where X=O, N, or S have shown that an observably slow XH proton exchange rate is obtainable.[19] In the diimine macrocycles the NH exchange rate was slow enough for NH-CH_2 coupling to occur, and this was thought to be due to internal hydrogen bonding between NH protons and the lone pair of electrons on the nitrogen of the imine bond. This NH to CH_2 coupling was shown by simplification of the anilino methylene signal after shaking with

D_2O, in the N_4O_2 and N_4S_2 donor-set diimines. In the N_6 donor-set diimine both methylene protons Ha and Hm were split, indicating that coupling occurred with NH protons Hb and Hl respectively. After shaking with D_2O both methylene signals became singlets, thus confirming the NH-CH_2 coupling in both cases. This indicated the likelihood that both types of NH protons were hydrogen bonded.

The pattern of aromatic signals in d-chloroform was similar for all three diimines. It was not possible to assign specific protons to these signals due to the complexity and overlap of signals.

For the reduced macrocycles, the pattern of signals obtained was consistent with the expected structures. (Table 4.4)

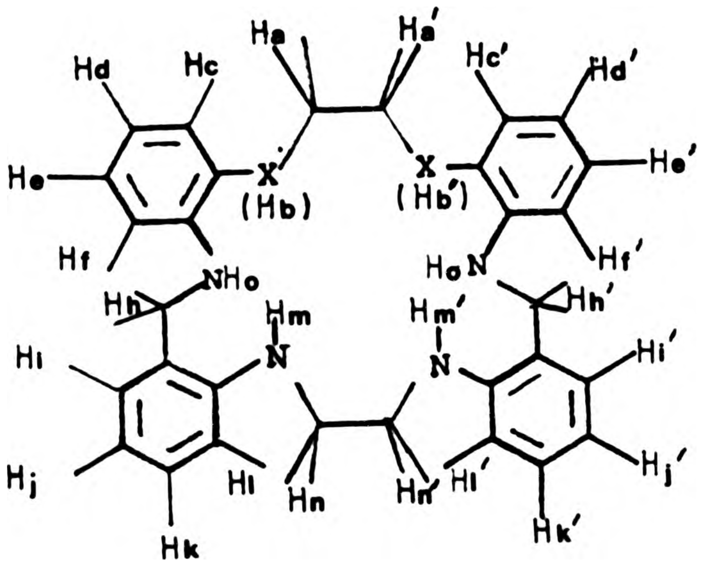


Fig. 4.3 Hydrogen labelling in the reduced 20-membered ligands.

The methylene protons, Ha, adjacent to the O, S, and the NH units were assigned by their comparatively large variation in chemical shift (see Table 4.3) as discussed for the diimine macrocycles. However, it was noted that these shifts were upfield of those shown by the corresponding methylene protons in the diimines; perhaps reflecting the lower extent of electron delocalisation throughout the reduced system.

The benzylic protons, Hh, were distinguished from the anilino protons both by reference to the position of the latter in the diimines and to the chemical shift of the benzylic protons observed in the quadridentate tetraamines already studied; (See Section 2.2.2.2)

Splitting of the benzylic protons Hh and the methylene protons Hn was noted in the reduced ligands with the N_4O_2 donor set (4IHa) and the N_4S_2 donor set (4IHe) but this splitting was not observed in the reduced ligand with the N_6 donor set (4IHf) and a single broad signal was assigned for the NH protons Hb, Ho, and Hm. This indicated a rapid exchange rate of NH protons with solvent leading to an averaging of the chemical shifts in the N_6 donor set macrocycle in d-chloroform. In d-pyridine as solvent for this macrocycle, the NH protons were not themselves observed, probably due to a very rapid proton exchange between the basic species. Both pairs of anilino methylene protons, Ha and Hn, appeared as a broad double peak over a range of 1 ppm. Throughout these experiments, the position of the NH proton signals varied greatly between d-chloroform and d-pyridine, as expected, due to changes in electrostatic forces caused by hydrogen bonding. Although solvent effects on the chemical shifts of other proton signals were below 0.3 ppm, the maximum value quoted in the literature[16,17] for such solvent-induced shifts for other compounds, the possibility of conformational changes cannot be ruled out, since the magnitude of solvent-induced shifts of comparable structures is not known.

On shaking the reduced ligand with N_4O_2 donor set (4IHa) in pyridine, with D_2O, there was near coincidence of the signals for the methylene protons Hh and Hn. The signals at 4.26 and 4.08 ppm respectively became almost coincident at 4.2, 4.18 ppm. In this case the shift was probably caused by changes in the solvent composition on adding the miscible D_2O.

Where the NH protons are seen (in the N_4O_2 and N_4S_2 donor set reduced ligands) the chemical shifts of some of the signals in d-pyridine are 1 - 4 ppm downfield of those in d-chloroform. This is consistent with increased hydrogen bonding in d-pyridine, which generally has the effect of moving the chemical shifts of the bonded protons downfield.[20] It has also been noted that equatorial protons in the cyclohexane ring give rise to resonances downfield from their axial counterparts.[10] Thus the change in chemical shift of the NH protons could also be consistent with a change in orientation of the NH units, and therefore a conformational change of the molecule.

Table 4.3 A comparison of the ^{1}H n.m.r. spectra of the sexadentate diimines with N_4X_2 donor set

Chemical Shifts (ppm) for Diimine protons

Compound	^{1}H chemical shift (ppm)		
X =	O*	NH	S
Ha,Ha'	4.58 (s.4H)	3.46 (s.4H)	3.25 (s.4H) 3.37 (s.4H)
Hb,Hb'	Not present	4.63 (s.2H)	Not present
Hc-f,G'-f,' Hh-k,h'-k,'	6.6-7.75 (c.16H)	6.68-7.25 (c.16H)	6.5-7.4 (c.16H) 6.5-7.66 (c.16H)
Ho,Ho'	8.76 (s.2H)	8.38 (s.2H)	8.47 (s.2H) 8.55 (s.2H)
Hl,Hl,	10.22 (s.2H)	9.17 (s.2H)	10.04 (s.2H) 6.00 (s.2H)
Hm,Hm'	3.76 (c.4H)	3.52 (c.4H)	3.75 (c.4H) 3.83 (c.4H)

*Recorded in C_5D_5N (0-5 ppm) and DMSO (5 - 10 ppm)

Upper and lower figures refer to measurements in $CDCl_3$ and C_5D_5N respectively.

s = singlet d = doublet c = complex multiplets

Table 4.4 A comparison of the ^{1}H n.m.r spectra of the reduced 20-membered ligands with N_4X_2 donor set

Compound	^{1}H Chemical shifts (ppm)		
X =	O	NH	S
Ha, Ha'	3.88 (s.4H) 4.08 (s.4H)	4.07 (s.4H) 3.3 (s.8H)	2.88 (s.4H) 2.88 (s.4H)
Hn, Hn'	3.46 (c.4H) 3.35 (c.4H)	3.2-3.3 (b.d.4H) 3.3 (s.8H)	3.49 (s.4H) 3.54-3.56 (b.d.4H)
Hh, Hh'	4.2 (s.4H) 4.26(d.4H J=4.0)	4.085 (s.4H) 4.3 (d.4H J=4.0)	4.12 (s.4H) 4.35 (b.d.4H J=4.0)
Hm, Hm' Ho, Ho' (Hb, Hb')	5.25 (b.s.2H), 4.4 (b.s.2H) 5.5 (b.s.4H)	3.44 (c.6H) Not seen	1.55 (b.s.2H), 4.81 (d.2H) 5.6 (b.s.4H)
Hc-f, c'-f' Hi-l, i'-l'	6.6-7.1 (m.8H), 7.1-7.7 (m.8H) 6.6-7.8 (c.16H)	6.8-7.23 (c.16H) 6.6-7.2 (c.16H)	6.6-7.8 (c.16H) 6.6-7.4 (c.16H)

•Upper and lower figures refer to measurements in $CDCl_3$ and C_5D_5N respectively throughout.

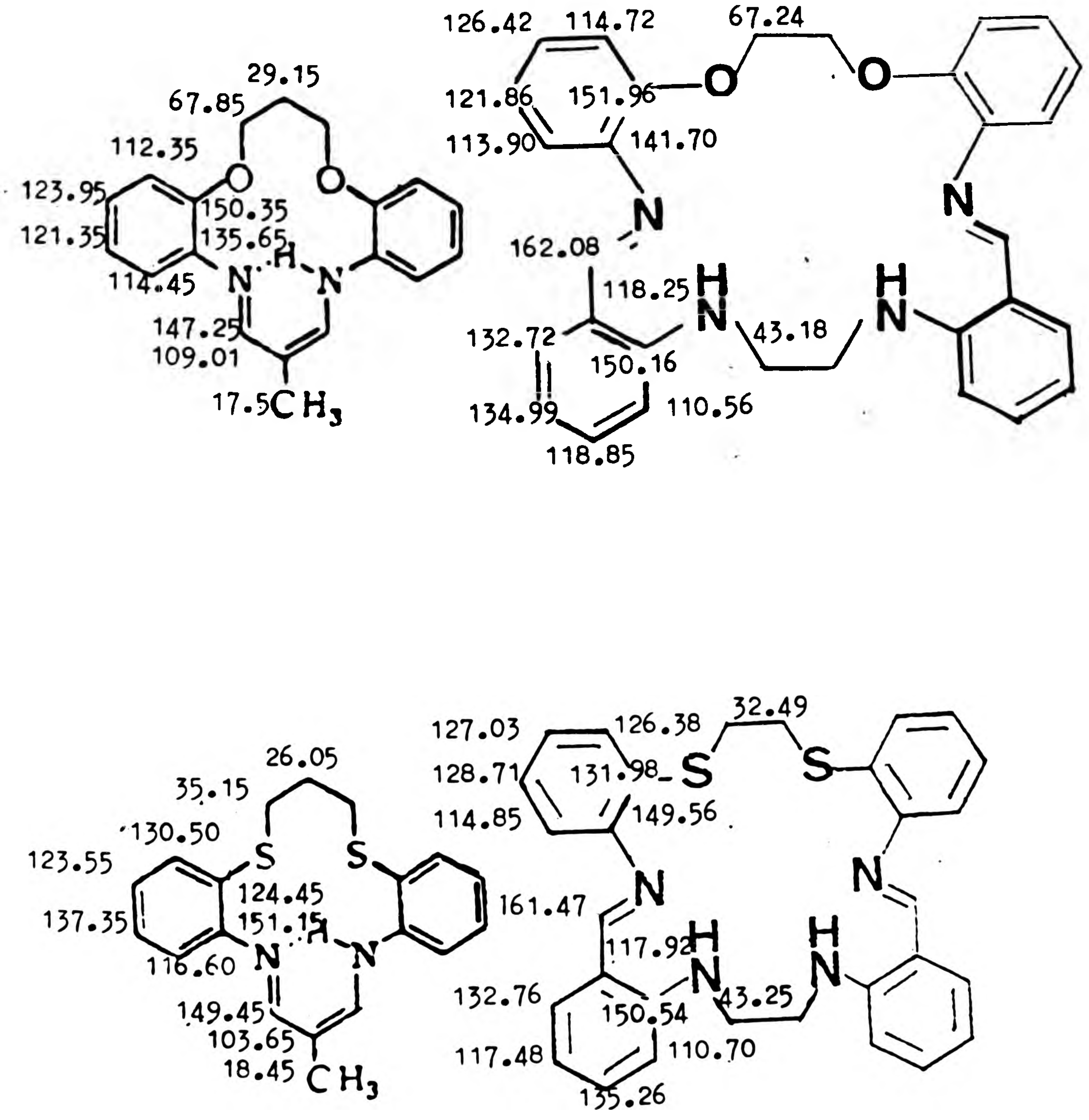
s = singlet d = doublet c = complex multiplet bs = broad singlet bd = broad doublet

4.2.3. ^{13}C spectra of the sexadentate ligands

The ^{13}C spectra of the diimines with the N_4O_2 donor set (4Ia) and the N_4S_2 donor set (4Ie) were obtained. The diimine with the N_6 donor set (4If) was found to be too insoluble for a ^{13}C spectrum to be obtained. The signals derived from the dialdehyde section of the molecules could be assigned as described previously (Section 2.2.3) because the chemical shifts were very similar to those seen in the quadridentate ligands. The assignment of the signals due to the amine part of the molecule agreed with those made in similar compounds[21] as shown , (See Fig. 4.4). As expected the spectra showed that the molecules were symmetrical; fifteen ^{13}C signals being seen. It was noticeable that the carbon atoms attached to the bridging oxygen atoms were at considerably lower field than those attached to the bridging sulphur atoms - an indication of the greater electron-withdrawing effect of the oxygen. The relaxation times of the quaternary carbon atoms were comparable in the two ligands 4Ia and 4Ie, with those of the azomethine carbon atoms being by far the shortest; as in the spectra of the quadridentate ligands (Section 2.2.3.1)

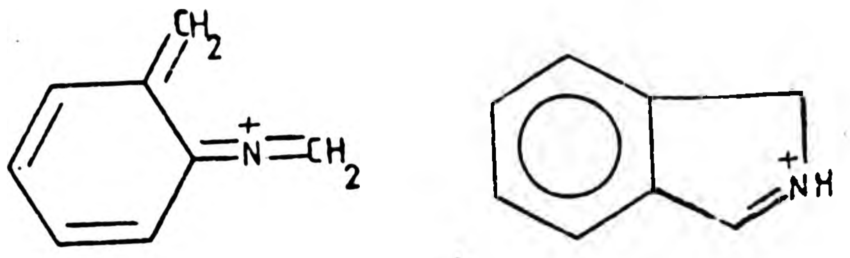
Fig 4.4. Comparison of ^{13}C chemical shift values obtained in the present work, and in previously studied compounds[21].

(Values in ppm ($CDCl_3$))



4.2.4. Mass spectra of the 20-membered sexadentate ligands (4Ia, 4Ie, 4If)

The m/e values for the molecular ions of the diimines were in good agreement with the calculated values. (Table 4.5) This was further evidence for the characterisation of these compounds. Only two splitting routes seemed to be common to this set of ligands. These are shown in Table 4.6. Route one consists of the splitting of the molecule to give the Fragment of m/e = 118 corresponding to C_8H_8N. This peak was a feature of the mass spectra of the quadridentate ligands (Section 2.2.4), having the suggested structures mentioned previously. (2XXIV) e.g.;



4II

In the spectra of the diimines with the N_4O_2 and N_4S_2 donor sets (4Ia and 4Ie), peaks corresponding to the fragments complementary to C_8H_8N were seen. In the diimine with the N_6 donor set (4If) the large complementary fragment was not seen. The next highest peak to the molecular ion in this spectrum was $C_{17}H_{17}N_3$(8.5%, Table 4.7) showing that more extensive breakdown had occurred in this compound resulting in a higher proportion of the peak at m/e 118 (Table 4.7)

The other common mode of splitting in the diimines was along an axis of symmetry to give a half-mass fragment containing half the donor set atoms (Table 4.7). The percentage of the half-mass peak was comparatively low for the N_4O_2 donor set ligand (4Ia). This was probably because the base peak, at m/e = 146, corresponded, on the basis of the closest fit of accurate masses, to the unit $C_8H_4NO_2$ which incorporates the O-C-C-O bridge (Table 4.8). The resistance of this bridging unit to cleavage could account for the comparatively low percentage of the symmetrical 'halves' (from route I (Table 4.6)) of this molecule. However, a comparable unit incorporating the $O-(CH_2)_n-O$ group was not seen in the 21- and 22-membered diimines with the N_4O_2 donor set (Section 4.3).

The accurate mass for the base peak of the N_4S_2 diimine fits best the formula $C_6H_{10}S_2$. It is difficult to propose a structural formula for this fragment. Either fragmentation of a benzene ring is required or an extremely complex fragmentation and rearrangement.

The base peak for the diimine with the N_6 donor set had the formula $C_{14}H_{12}N_2$. This could have a similar structure to that of the peak m/e = 222, seen in all the spectra of the quadridentate diimines (2XXIV). The possible structures are as follows;

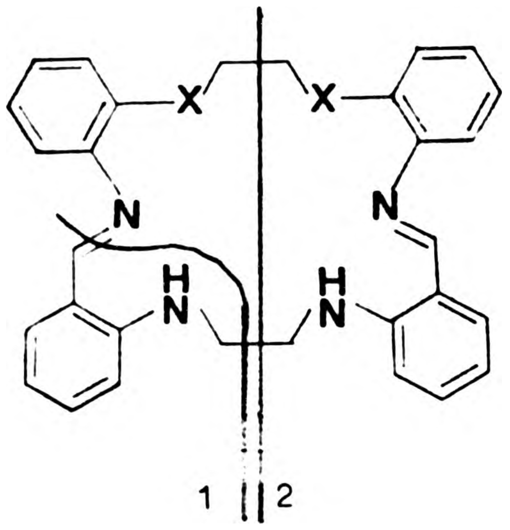
4 III

Both of these ions could be precursors of the unit C_8H_8N, which is next in percentage abundance to the base peak (Table 4.7). The spectra of the reduced 20-membered ligands contain molecular ion peaks in close agreement with the calculated values (Table 4.8). The peak corresponding to the molecular ion of the ligand with the N_6 donor set (4IHf) was much more intense than those for the reduced ligands with N_4O_2 and N_4S_2 donor sets (4IHa and 4IHe), perhaps indicating some greater stability for this ligand. However, the common splitting route 1 (Table 4.9), which was similar to that seen for the diimines, indicated that the large fragment, complementary to the peak of m/e = 118, was less stable for the N_6 donor set (Table 4.10). In the spectra of the reduced ligands, the base peak was that at m/e = 118 for 4IHa and 4IHf, with the addition of two hydrogen atoms giving m/e = 120 in the case of the N_6 donor set reduced ligand (4IHf). (Table 4.8)

Table 4.5 Molecular ions and base peaks in the spectra of the 20-membered sexadentate diimines

Ligand	4Ia, X=O	4Ie, X=S	4If, X=NH
Formula	$C_{30}H_{28}N_4O_2$	$C_{30}H_{28}N_4S_2$	$C_{30}H_{30}N_6$
Measured mass	476.2212	508.1752	474.2548
Intensity %	11.6	24	15
Calculated mass	476.2212	508.1755	474.2532
Formula base peak	$C_8H_4NO_2$	$C_6H_{10}S_2$	$C_{14}H_{12}N_3$
Measured mass	146.0270	146.0242	222.1033
Calculated mass	146.0242	146.0224	222.1031

Table 4.6 Common cleavage routes in the spectra of the 20-membered diimines



1

C_8H_8N

+

$C_{22}H_{20}N_3X_2$

m/e 358 for X=O

390 for X=S

$C_{17}H_{17}N_3$

m/e 263 [This is the largest fragment after the mass peak for X=NH]

2

$C_{15}H_{14}N_2X$

m/e 238 for X=O

254 for X=S

237 for X=NH

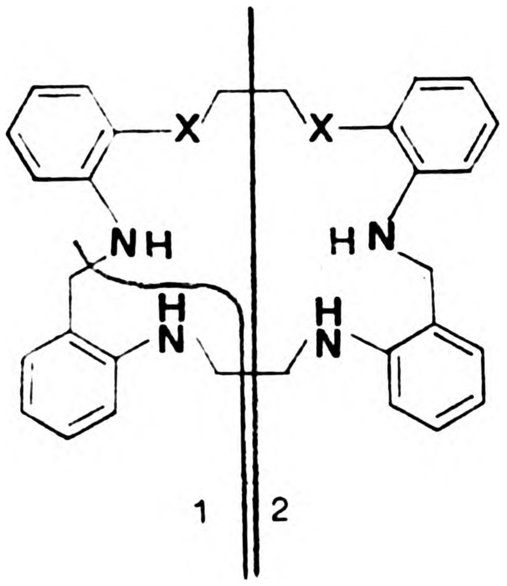
Table 4.7 m/e values and abundances for fragments arising from the common splitting routes of the 20-membered sexadentate diimines

Compound	$C_{22}H_{20}N_3X_2$	C_8H_8N	$C_{15}H_{14}N_2X$
4Ia (X=O)	358 (15.3%)	118 (13.5%)	238 (7%)
4Ie (X=S)	390 (16%)	118 (49%)	254 (25%)
4If (X=NH)	$C_{17}H_{17}N_3$ 263 (8.5%)	118 (96%)	237 (23%)

Table 4.8 Molecular ions and base peaks in the spectra of the reduced 20-membered ligands

Ligand	4IHa, X=O	4IHe, X=S	4IHf, X=NH
Formula	$C_{30}H_{32}N_4O_2$	$C_{30}H_{32}N_4S_2$	$C_{30}H_{34}N_6$
Measured mass	480.2522	512.2069	478.2844
Intensity %	6.0	4.0	53.6
Calculated mass	480.2525	512.2068	478.2844
Formula base peak	C_8H_8N	C_8H_8N	$C_8H_{10}N$
Measured mass	118.0649	118.0665	120.0809
Calculated mass	118.0657	118.0657	120.0813

Table 4.9 Common cleavage routes in the spectra of the reduced 20-membered ligands



1

C_8H_8N

+

$C_{22}H_{22}N_3X_2$

m/e 360 for X=O

392 for X=S

358 for X=NH

2

$C_{15}H_{16}N_2X$

m/e (for $\frac{m}{2}$ -H) = 239 for X=O

(for $\frac{m}{2}$ -H) = 255 for X=S

(for $\frac{m}{2}$) = 239 for X=NH

Table 4.10 M/e values and abundances for fragments arising from the common splitting routes of the reduced 20-membered ligands

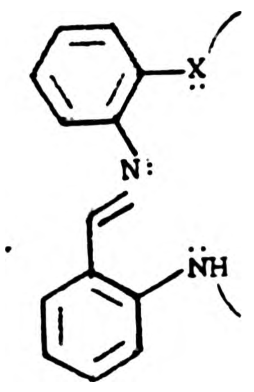
	I		II
Compound	$C_{22}H_{22}N_3X_2$	C_8H_8N	$C_{15}H_{16}N_2X^*$
4IHa (X=O)	360 (80%)	118 (100%)	239 (13%)
4IHe (X=S)	392 (42%)	118 (100%)	255 (5.3%)
4IHf (X=NH)	358 (16%)	118 (89%)	253 (11.6%)

$*(\frac{m}{2}$ -H for X=O, X=S)

4.2.5 Electronic spectra of the sexadentate ligands

The λ_{max} (nm) and ε (litre mol^{-1} cm^{-1}) values obtained for the diimines and the fully reduced free ligands are given below in Table 4.11.

The bright yellow diimines contained the benzaldehydeanil chromophore where X= O, S, or NH



4 IV

The absorption was shown as a broad band extending from the near u.v. into the visible region. Since a large part of the molecule was conjugated, the main absorption was probably due to $\pi \rightarrow \pi^*$ transitions which give intense bands (ε_{max} ca. 20,000 litre mol^{-1}cm^{-1} in conjugated polyenes). These transitions normally occur within the u.v. region for isolated bonds, but would be expected to occur at longer wavelengths in conjugated systems[22].

The n - π^* transitions which are possible with double bonds containing nitrogen having a lone pair, such as the imine bond, are symmetry forbidden, so that the band is weak ($\varepsilon_{max} \doteq 100$).[22] As discussed above, for the quadridentate diimines (section 2.2.5) the high extinction coefficients were probably due to overlapping $\pi \rightarrow \pi^*$ transitions. Again, the net effect was to allow sufficient absorption in the visible region to make all the sexadentate ligands bright yellow. There was a considerable decrease in the intensity of absorption when X=NH. See Table 4.11. There are two possible effects of varying X; a change in the energy of the π^* orbital effecting the energy of both $\pi - \pi^*$ and n - π^* transitions, and a change in energy of the n - π^* transitions resulting from changes in availability of the lone pairs of electrons.

The latter change might be directly associated with the electronegativity of the substituent X, and where X = O, λ_{max} is at higher energy than in the other two macrocycles. When X = S and HN, λ_{max} occurs at a similar energy but ε_{max} is considerably lower when X = NH. This might indicate less overlap of the $\pi \rightarrow \pi^*$ transitions with the n - π^* transitions in this compound due to a greater difference in the energies required for these two types of transition, perhaps due to a greater difference in the availability of lone pairs between this and the other ligands. Strong hydrogen bonding in this compound would have an effect on this availability, and thus on electronic transitions.

The fully-reduced sexadentate ligands were white substances and λ_{max} was within the u.v. region, this was to be expected since there was no fully conjugated chromophore in the molecule. The extinction coefficients were high since, in addition to possible $n - \pi^*$ transitions $n - \sigma^*$ transitions occur in saturated molecules and these are 'allowed' transitions.[8]

Table 4.11. Peaks in the u.v/visible spectra of the 20-membered sexadentate ligands.*

(ε = litre $mol^{-1}cm^{-1}$, λ = nm)

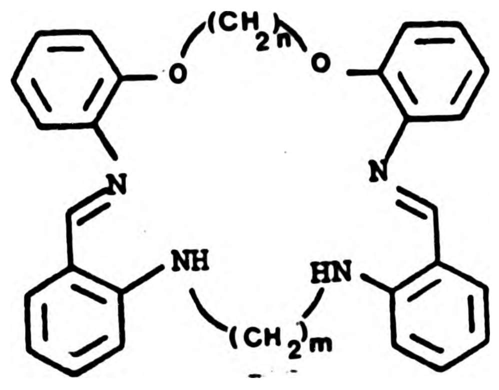
Diimine	λ max	ε	λ max	ε	λ max	ε
4Ia X=O	245	43,000	277(sh)	19,700	390	12,700
4Ie X=S	250	44,200	not present		410	11,800
4If X=NH	255	28,000	280(sh)	14,000	410	6,300

Reduced ligand	λ max	ε	λ max	ε
4IHa X=O	248	29,300	295	9,300
4IHe X=S	250	74,000	305	13,000
4IHf X=NH	254	51,400	300	15,000

*spectra measured in methanol

4.3 A comparison of the spectra of the series of ligands with the N_4O_2 donor set

The series of ligands with the N_4O_2 donor set had 20, 21 and 22-membered inner great rings, as shown below.



4V

n=m=2	4Ia (enen)*
n=2, m=3	4Ib (entn)
n=m=3	4Ic (tntn)
n=3, m=2	4Id (tnen)

The infra-red spectra of this series, as expected, showed little dependence on ring size and were very similar to that of 4Ia (Section 4.2.1) The ^1H nmr spectra of the oxygen-bridged diimines are summarised in Table 4.12a

*Footnote; the following additional notation is used for clarity in distinguishing the ligands with the N_4O_2 donor set: enen, n=m=2; entn, n=2, m=3; tntn, n=m=3; tnen n=3, m=2.

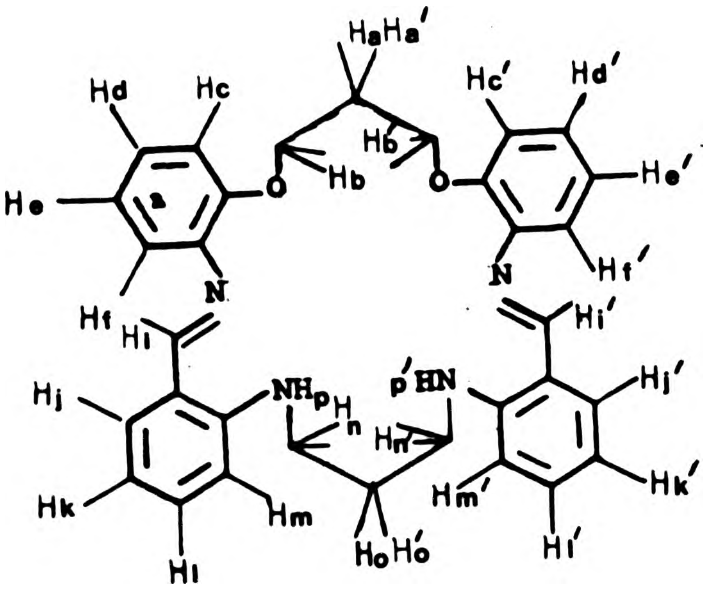


Fig. 4.5 Assignment of protons in the diimines with the N_4O_2 donor set.

The diimine 4Ia (enen) was the most insoluble of the series, and the spectrum had to be measured in d-pyridine; thus the small chemical shift differences between the signals in this spectrum, and the analogous signals in the other spectra are probably due to solvent effects. Apart from this; chemical shift values corresponded very closely between the diimines.

The spectra of the tetraamines are summarised in Table 4.12b

The signals of corresponding protons in the series had very similar ppm values, as expected; the greatest difference being between the NH proton signals in the di- and tri-methylene bridged species (Table 4.12). In these less well-resolved spectra it was not possible to see coupling between the NH hydrogen atoms and adjacent hydrogen atoms on adjacent methylene groups.

Table 4.12a A comparison of the 'H nmr spectra of the oxygen-bridged diimines (4Ia-d)

Chemical shifts (ppm, $CDCl_3$)

Protons	4Ia (enen*)	4Ib (entn)	4Ic (tntn)	4Id (tnen)
Ha,Ha'	Not present	Not present	1.7-2.4 (c.4H)	1.95(quin.2H, J=2)
Ho,Ho'	Not present	2.0(quin,2H, J=4)		Not present
Hn,Hn'	3.76 (s.4H)	3.35(t.4H. J=4)	3.3(t.4H. J=4)	3.3 (s.4H)
Hb,Hb'	4.58 (s.4H)	4.45 (s.4H)	4.0-4.3 (s.4H)	4.0-4.3 (s.4H)
Hc-Hf,Hc'-Hf'	6.6-7.75 (c.16H)	6.4-6.8 (m.8H)	6.4-6.75 (m.8H)	6.3-6.7 (m.8H)
Hj-Hm,Hj'-Hm'		6.8-7.2 (m.8H)	6.8-7.4 (m.8H)	6.8-7.1 (m.8H)
Hi,Hi'	8.76 (s.2H)	8.5 (s.2H)	8.5 (s.2H)	8.4 (s.2H)
Hp,Hp'	10.22 (s.2H)	9.6 (s.2H)	9.6 (s.2H)	9.6 (s.2H)

*measured in C_5D_5N

Table 4.12 b A comparison of the ^{1}H nmr spectra of the oxygen-bridged tetraamines

Chemical shifts (ppm, $CDCl_3$)

Protons	4IHa (enen)	4IHb (entn)	4IHc (tntn)	4Id (tnen)
Ha,Ha'	Not present	Not present	1.5-2.3 (c.4H)	2.2(quin.2H.J=8.0)
Ho,Ho'	Not present	1.8(quin.2H.J=8.0)		Not present
Hn,Hn'	3.46(s.4H)	3.2(t.4H. J=8.0)	3.2(t.4H. J=8.0)	3.35 (s.4H)
Hb,Hb'	3.88 (s.4H)	4.2 (s.4H)	4.2(t.4H. J=8.0)	4.1(t.4H. J=8.0)
Hi,Hi'	4.2 (s.4H)	4.3 (s.4H)	4.0 (s.4H)	4.0 (s.4H)
Hp,Hp'	4.4 (s.2H)	4.3 (s.2H)	5.3 (s.2H)	5.3 (s.2H)
Hq,Hq'	5.3 (s.2H)	5.3 (s.2H)	6.0 (s.2H)	5.9 (s.2H)
Hc-Hf,Hc'-Hf'	6.6-7.1 (m.8H)	6.5-6.9 (m.8H)	6.5-6.9 (m.8H)	6.3-6.7 (m.8H)
Hj-Hm,Hj'-Hm'	7.1-7.7 (m.8H)	7.0-7.3 (m.8H)	7.0-7.4 (m.8H)	6.8-7.2 (m.8H)

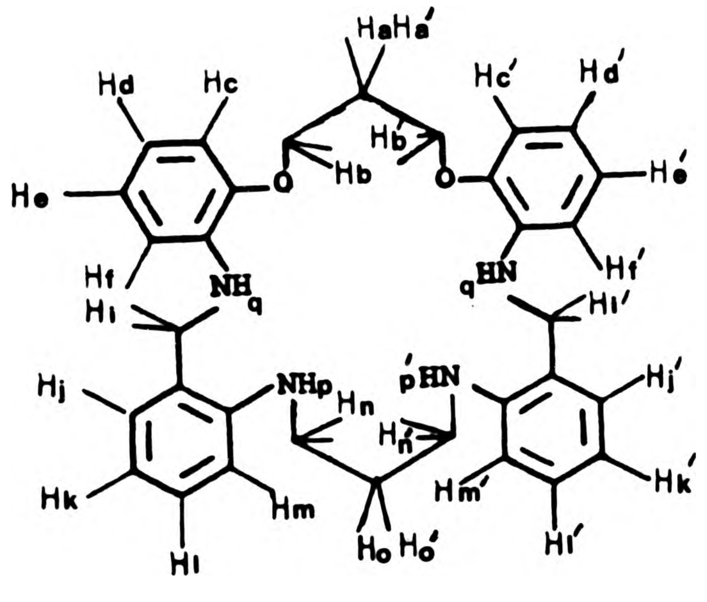
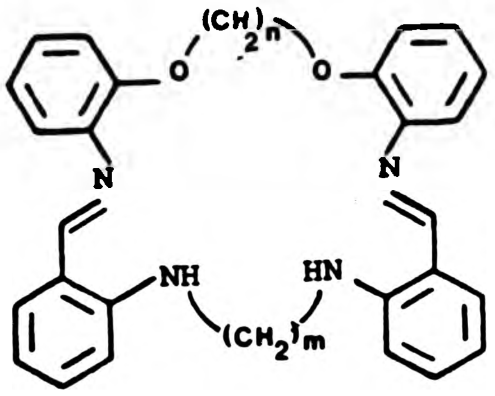


Fig. 4.6 Assignment of protons in the tetraamines with the N_4O_2 donor set

In the mass spectra the m/e values of the molecular ions of this series of diimines and their reduced tetraamine counterparts were very close to the calculated values, as shown in Tables 4.13 and 4.14. The common splitting routes shown in the spectra of this series of diimines were the same as those described for the 20-membered ligands (Table 4.6). However, the tetraamines with the N_4O_2 donor set seemed to fragment in a more random way, and no common splitting route could be discerned from the spectra obtained. The m/e values and the percentage of the fragments obtained from splitting routes 1 and 2 for the series of diimines is shown in Table 4.15. There was considerable difference in the intensities of the fragments $C_{23}H_{22}N_3O_2$ and the complementary peak at m/e = 118, in the spectra of the 21-membered diimines (4Ib(entn) and 4Id (tnen)). In the latter, the intensities of these peaks were the highest seen showing the difference in splitting between ligands with the same ring size; although the intensity of the 'half donor set' peak was the same for both the 21-membered ligands. The small base peak unit $C_8H_4NO_2$, in which the O-C-C-O bridging group was retained (Section 4.2.4), was not seen in the spectra of the other diimines with the N_4O_2 donor set, where the base peaks were the larger fragments shown in Table 4.13. In the spectra of the tetraamines in this series, the base peak was the peak at m/e = 118, (Table 4.14) in the spectra of all but the 22-membered tetraamine (4IHc). In the spectrum of this ligand the base peak unit included part of the O-C-C-C-O bridge.

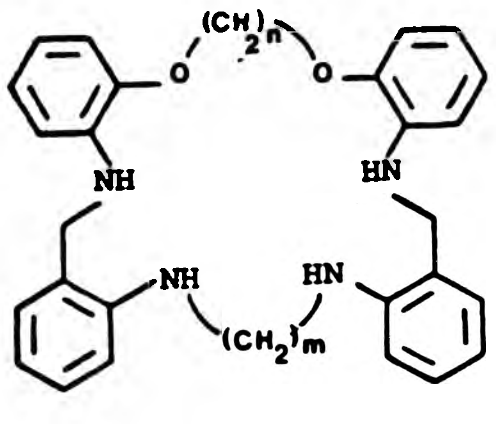
The u.v/visible spectra of all the N_4O_2 donor-set diimines are compared in Table 4.16. It seems that the intensity of absorption is strongly influenced by the size of the oxygen-bridged section of the molecule. The two dimethylene oxygen-bridged diimines 4Ia and 4Ib have similar extinction coefficients which are considerably higher than those of the trimethylene oxygen-bridged diimines, which are also very close in value. As discussed previously, (Section 4.2.5) n - π^* transitions are normally of low intensity and it was difficult to avoid the conclusion that the contribution of the lone pairs of the oxygen atoms to the overall electron density was particularly important in the π - π^* transitions; this contribution being dependent on the methylene chain length. A similar relationship was seen in the comparative u.v/visible spectra of the tetraamines of this series (Table 4.16). Here again, the contribution of the oxygen atoms would be important, because the energy of the possible n - π^* and n - σ^* transitions would depend on the availability of lone pair electrons. In all the spectra, the λ_{max} values were very close throughout the series of ligands.

Table 4.13 Molecular ions and base peaks in the spectra of the sexadentate diimines with the N_4O_2 donor set



Ligand	4Ia n=m=2 (enen)	4Ib n=2,m=3 (entn)	4Ic n=m=3 (tntn)	4Id n=3,m=2 (tnen)
Formula	$C_{30}H_{28}N_4O_2$	$C_{31}H_{30}N_4O_2$	$C_{32}H_{32}N_4O_2$	$C_{31}H_{30}N_4O_2$
Measured mass	476.2212	490.2367	504.2519	490.2364
Intensity %	11.6	49.0	48.0	72.8
Calculated mass	476.2212	490.2368	504.2524	490.2368
Formula base peak	$C_8H_4NO_2$	$C_{22}H_{22}N_3O_2$	$C_{28}H_{24}N$	$C_{23}H_{22}N_3O_2$
Measured mass	146.0270	360.1698	374.1908	372.1715
Calculated mass	146.0242	360.1711	374.1908	372.1711

Table 4.14 Molecular ions and base peaks in the spectra of the sexadentate tetraamines with the N_4O_2 donor set



Ligand	4IHa n=m=2 (enen)	4IHb n=2,m=3 (entn)	4IHc n=m=3 (tntn)	4IHd n=3,m=2 (tnen)
Formula	$C_{30}H_{32}N_4O_2$	$C_{31}H_{34}N_4O_2$	$C_{32}H_{36}N_4O_2$	$C_{31}H_{34}N_4O_2$
Measured mass	480.2522	494.2681	508.2831	494.2683
Intensity %	6	29	2.0	2.0
Calculated mass	480.2525	494.2681	508.2838	494.2681
Formula base peak	C_8H_8N	C_8H_8N	$C_9H_{12}NO$	C_8H_8N
Measured mass	118.0649	118.0651	150.0924	118.0659
Calculated mass	118.0657	118.0657	150.0918	118.0657

Table 4.15 M/e values and abundances for the fragments from splitting routes 1 and 2 of diimines with N_4O_2 donor-set

	1			2	
Diimine	C_8H_8N	Complementary Fragment Formula	Mass	'Half donor-set' Fragment Formula	Mass
en,en 4Ia n=m=2	118 (13.5%)	$C_{22}H_{22}N_3O_2$	358 (15%)	$C_{15}H_{15}N_2O$	238 (7%)
en tn 4Ib n=2,m=3	118 (44.5%)	$C_{23}H_{22}N_3O_2$	372 (9%)	$C_{15}H_{15}N_2O$	239 (21.5%)
tn,tn 4Ic n=m=3	118 (62%)	$C_{24}H_{24}N_3O_2$	386 (7.5%)	$C_{17}H_{18}N_2O$	265 (5%)
tn en 4Id n=3,m=2	118 (96%)	$C_{23}H_{22}N_3O_2$	372 (100%)	$C_{17}H_{17}N_2O$	265 (21%)

Table 4.15 M/e values and abundances for the fragments from splitting routes 1 and 2 of diimines with N_4O_2 donor-set

	1			2	
Diimine	C_8H_8N	Complementary Fragment Formula	Mass	'Half donor-set' Fragment Formula	Mass
en,en 4Ia n=m=2	118 (13.5%)	$C_{22}H_{22}N_3O_2$	358 (15%)	$C_{15}H_{15}N_2O$	238 (7%)
en tn 4Ib n=2,m=3	118 (44.5%)	$C_{23}H_{22}N_3O_2$	372 (9%)	$C_{15}H_{15}N_2O$	239 (21.5%)
tn,tn 4Ic n=m=3	118 (62%)	$C_{24}H_{24}N_3O_2$	386 (7.5%)	$C_{17}H_{18}N_2O$	265 (5%)
tn en 4Id n=3,m=2	118 (96%)	$C_{23}H_{22}N_3O_2$	372 (100%)	$C_{17}H_{17}N_2O$	265 (21%)

Table 4.16 Comparison of the u.v/visible spectra* of the diimines and tetraamines with the N_4O_2 donor set

(ε = litre $mol^{-1} cm^{-1}$, λ = nm)

Diimine	λ_{max}	ε	λ_{max}	ε	λ_{max}	ε
4Ia (n=m=2)	245	43,000	277	19,700	390	12,800
4Ib (n=2,m=3)	239	46,700	264	18,800	390	11,900
4Ic (n=m=3)	246	23,800	277	9,500	395	6,500
4Id (n=3,m=2)	245	23,300	280	8,100	400	7,900

Tetraamine	λ_{max}	ε	λ_{max}	ε
4IIa	248	29,200	295	9,300
4IIb	250	30,500	290	13,300
4IIc	250	43,300	297	13,600
4IId	256	36,300	290	10,700

*All spectra measured in methanol.

4.4. Preparation of the copper complexes of the sexadentate ligands, (4Ia-f, 4IIa-f)

The copper(II)diperchlorate complexes of the diimines were formed by stirring a suspension of the ligand in methanol with copper perchlorate, under gentle reflux. Attempts to prepare the neutral copper(II) complexes of the ligands deprotonated at the anilino nitrogen atoms were unsuccessful, except in the case of the 20-membered ligand with the N_4O_2 donor set (4Ia).

The cationic copper complex of the 20-membered ligand with the N_4O_2 donor set (4Ia) was a green dihydrate. In contrast, the copper complexes of the diimines with the N_4S_2 and N_6 donor sets, (4Ie and 4If) were red and were not hydrated. In addition it was found that warming suspensions of these red complexes with dilute perchloric acid resulted in green complexes corresponding to protonated tetraperchlorate salts, e.g.

$$\underset{\text{Red}}{[Cu(4Ie)](ClO_4)_2} + 2HClO_4 \rightarrow \underset{\text{Green}}{[Cu(4Ie + 2H^+)](ClO_4)_4}$$

In the sexadentate ligands it is probable that not all six donor atoms are coordinated to the copper atom. This has been demonstrated in the structure of the copper perchlorate complex of 4IIa (Section 4.5.2), in which only three out of the four ligand donor nitrogen atoms are coordinated. It is therefore quite feasible that in the copper complexes of the diimines with the N_4S_2 and N_6 donor sets (4Ie, 4If) two nitrogen donor atoms remain uncoordinated thus providing two basic sites available to accept protons. On the other hand the O(ether) atoms in the ligand with the N_4O_2 donor set

(4Ia) are poor donors, and the nitrogen atoms will coordinate preferentially to the copper atom. The uncoordinated oxygen atoms are not sufficiently basic to be proton acceptors, and so will not form protonated tetraperchlorate salts. As expected, these salts were not formed by the complexes of the other diimines with the N_4O_2 donor set. (4Ib - 4Id).

The analytical data for these complexes are summarised in Table 4.17.

The copperIIperchlorate complexes of the reduced ligands were formed by mixing a ligand suspension in methanol with copperII perchlorate, under nitrogen. Refluxing the copper diperchlorate salts of the reduced ligands with the N_4S_2 and N_6 donor sets produced the copper diperchlorate salts of the diimines. This oxidation was presumably catalysed by copper, and was particularly prone to occur with the N_6 donor set complex.

The copper perchlorate complexes of the tetraamines were very dark brown; the copper perchlorate complex of the hexaamine (4IHf) was a lighter brown powder.

(4Ia) are poor donors, and the nitrogen atoms will coordinate preferentially to the copper atom. The uncoordinated oxygen atoms are not sufficiently basic to be proton acceptors, and so will not form protonated tetraperchlorate salts. As expected, these salts were not formed by the complexes of the other diimines with the N_4O_2 donor set. (4Ib - 4Id).

The analytical data for these complexes are summarised in Table 4.17.

The copperII perchlorate complexes of the reduced ligands were formed by mixing a ligand suspension in methanol with copperII perchlorate, under nitrogen. Refluxing the copper diperchlorate salts of the reduced ligands with the N_4S_2 and N_6 donor sets produced the copper diperchlorate salts of the diimines. This oxidation was presumably catalysed by copper, and was particularly prone to occur with the N_6 donor set complex.

The copper perchlorate complexes of the tetraamines were very dark brown; the copper perchlorate complex of the hexaamine (4IHf) was a lighter brown powder.

Table 4.17 CopperIIperchlorate complexes of the 20-membered sexadentate diimines

Complex	Description		Analysis C	H	N	Cu
X = O $[Cu(4Ia)](ClO_4)_2 \cdot 2H_2O$	Green diperchlorate dihydrate	found	46.3	4.4	7.1	8.2
	$C_{30}H_{32}N_4CuCl_2O_{12}$	requires	46.57	4.14	7.24	8.27
	No tetraperchlorate formed					
X = S $[Cu(4Ie)](ClO_4)_2$	Red diperchlorate	found	46.8	4.3	7.3	8.3
	$C_{30}H_{28}N_4S_2CuCl_2O_8$	requires	46.73	3.66	7.27	8.24
$[Cu(4Ie)](ClO_4)_2 \cdot 2HClO_4$	Green tetraperchlorate	found	36.8	3.1	6.1	-
	$C_{30}H_{30}N_4S_2CuCl_4O_{16}$	requires	37.07	3.11	5.76	-
X = NH $[Cu(4If)](ClO_4)_2$	Red diperchlorate	found	48.2	4.2	10.9	8.3
	$C_{30}H_{30}N_6CuCl_2O_8$	requires	48.97	3.88	11.42	8.7
$[Cu(4If)](ClO_4)_2 \cdot 2HClO_4$	Green tetraperchlorate	found	40.0	3.4	9.3	
	$C_{30}H_{30}N_6CuCl_4O_{16}$	requires	38.54	3.21	8.99	

4.4.1 Infra-red spectra of the copper complexes of the 20-membered sexadentate ligands

The copper perchlorate complexes of both diimine and reduced ligands were all typified by the very large broad single peak at 1050-1150 cm^{-1} due to the Cl—O stretch of the perchlorate anion; which is characteristic of uncoordinated ClO_4^-[8]. In both the imine and reduced ligands the N-H stretches appear with greater strength and sharpness than in the free ligands, probably because complexation to the copper destroys intramolecular hydrogen bonding involving the N-H groups.

4.4.2 U.v/visible spectra of the copper complexes of the 20-membered sexadentate ligands

The copper perchlorate complexes of the diimines had λ_{max} values within the visible region, but the high ε_{max} values indicate that the d-d transitions, which usually have values of up to 1000 for six coordinate and square complexes[23] were obscured by strong charge-transfer bands. These values were consistent with those obtained previously[1] for the Co(II) and Fe(II) complexes of these ligands and for Cu(II) complexes of unsaturated aliphatic macrocycles.[24] Square planar copper complexes of tetraazamacrocycles have been shown to display a single band in the visible region[24], but in these cases ε_{max} values are consistent with a d-d transition.

There are a large number of possible modes of coordination of the sexadentate ligands with the copper, involving all or some of the donor set atoms. In solution, neutral and charged complexes may be in equilibrium

i.e. $(CuLH_2)^{2+} \rightarrow 2H^+ + CuL$

and each species will show a different spectra. In addition, the spectra of d^9 ions are not very useful in assigning coordination geometry

The positions of d-d bands in the spectra of d^9 ion complexes do not vary systematically with the nature and geometry of the donor sets; and, in copper complexes, are often observed to be solvent dependent.[24] As the spectra of the copper complexes under discussion were measured in DMF, it is possible that this could displace one or more of the donor atoms which were coordinated to copper in the solid samples isolated from methanol. Coordination to the oxygen atom in a DMF molecule in preference to a donor nitrogen atom is seen in the structure of the copper perchlorate complex of 4IHa (Section 4.5.2). Since the spectra of the copper complexes of the 20-membered ligands, measured in DMF, were not similar (Table 4.18) it is probable that they do not all exist in the same form, having a similar chromophore, in solution.

The λ_{max} (nm) and ε_{max} (litre mol^{-1} cm^{-1}) values for the copper perchlorate complexes of the diimine and fully-reduced ligands are given in Table 4.18.

Table 4.18 Peaks in the u.v/visible spectra of the copper perchlorate complexes of the sexadentate ligands*

(ε = litre mol^{-1} cm^{-1}, λ = nm)

Diimine complex	λ max	ε	λ max	ε	λ max	ε	λ max	ε	λ max	ε
$[Cu(4Ia)](ClO_4)_2$ (X=O)	270	31,500	340	9,900	395	10,300	460	5,900	550	1,200
$[Cu(4Ie)](ClO_4)_2$ (X=S)	273	34,600	-	-	410	6,300	515	8,500	-	-
$[Cu(4If)](ClO_4)_2$ (X=NH)	275	32,500	-	-	420	8,000	500	6,100	-	-

Reduced ligand complex	λ max	ε	λ max	ε	λ max	ε
$[Cu(4IHa)](ClO_4)_2$ (X=O)	272	11,600	375	3,600	455	1,500
$[Cu(4Ie)](ClO_4)_2$ (X=S)	270	31,500	310(sh)	27,500	505	7,100
$[Cu(4If)](ClO_4)_2$ (X=NH)	275	45,900	390	8,000	480	6,500

*All spectra measured in DMF

4.5 The copper complexes of the sexadentate ligands with the N_4O_2 donor set (4Ia-d)*

The copper perchlorate complexes of the series of ligands with the N_4O_2 donor set were made as described previously (Section 4.4), and investigated to discover if variations in ring size influenced the properties of the copper complexes. It was found that red or green forms of the complexes were isolated depending on reaction conditions (Section 4.6.4). Analytical data (Table 4.19) suggest that all the green complexes were isolated as hydrates, and this was consistent with the broad band attributable to -OH stretch in the infra red spectra of the green complexes $[Cu(4Ia\text{-}enen)](ClO_4)_2.2H_2O$, $[Cu(4Ib\text{-}entn)](ClO_4)_2.4H_2O$ and $[Cu(4Id\text{-}tnen)](ClO_4)_2.2H_2O$. The complex $[Cu(4Ib\text{-}entn)](ClO_4)_2$ could also be isolated in a red unhydrated form, and $[Cu(4Ic\text{-}tntn)](ClO_4)_2$ could only be isolated in a red unhydrated form, although on mixing the ligand and copperIIperchlorate, a transient green form was present.

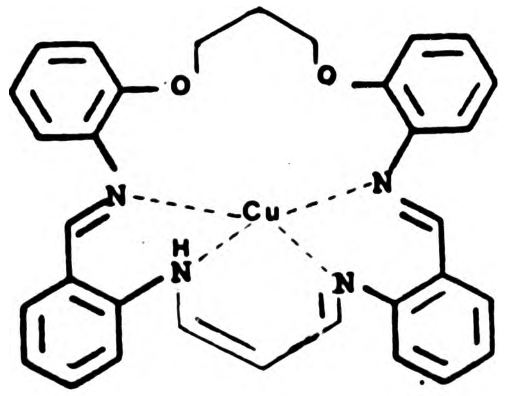
There was no evidence that the red complexes $[Cu(4Ib\text{-}entn)](ClO_4)_2$ and $[Cu(4Ic\text{-}tntn)](ClO_4)_2$ could be converted back to the green form. Also there was no indication that the green complexes $[Cu(4Ia\text{-}enen)](ClO_4)_2.2H_2O$, and $[Cu(4Id\text{-}tnen)](ClO_4)_2.2H_2O$ which have an ethane link between the anilino nitrogen atoms were

*Footnote: The following additional notation is again used for clarity in distinguishing the ligands with the N_4O_2 donor set, (4V)

enen, n=m=2	entn, n=2,m=3
tntn, n=m=3	tnen, n=3,m=2

capable of being converted to red forms. It is, therefore, possible that formation of the red form is dependent on an irreversible reaction which requires the presence of a propane link between the anilino nitrogen atoms.

Ligand dehydrogenation in nickel complexes of ligands with an N_4 donor set and three-carbon methylene bridge has been reported, in the presence of oxygen or a mild oxidising agent.[25] Copper complexes of this type were found to be less susceptible to oxidation but copper complexes of ligands with the N_4O_2 donor set had not been studied. It seemed that the colour change observed in solution, as described, might be due to dehydrogenation of the three-carbon bridge, although in the previously reported cases dehydrogenation resulted in reduction in oxidation state of the complex cation whereas in this work, both the red and green salts seemed to be diperchlorates. A tentative suggestion for the structure of the copper diperchlorate complex of the dehydrogenated ligand 4Ic, which would be more extensively conjugated, is as below.



4 VI

The series of tetraamines formed dark brown copper diperchlorate complexes.

Table 4.19 Copper diperchlorate complexes of the sexadentate ligands with N_4O_2 donor set

Complex	Description		Analysis			
			C	H	N	Cu
$\text{Cu}[4\text{Ia(enen)}](\text{ClO}_4)_2\cdot 2\text{H}_2\text{O}$	Green dihydrate	found	46.3	4.4	7.1	8.2
	$C_{30}H_{32}N_4CuCl_2O_{12}$	requires	46.33	4.40	7.20	8.02
$\text{Cu}[4\text{Ib(entn)}](\text{ClO}_4)_2\cdot 4\text{H}_2\text{O}$	Green tetrahydrate	found	44.3	4.2	6.7	8.1
	$C_{31}H_{38}N_4CuCl_2O_{14}$	requires	45.09	4.61	6.72	7.75
	Red salt. Not hydrated	found	48.2	4.2	7.7	8.8
	$C_{31}H_{30}N_4CuCl_2O_{10}$	requires	49.40	4.24	7.43	8.49
$\text{Cu}[4\text{Ic(tntn)}](\text{ClO}_4)_2$	Green salt, rapidly changing to red, non-hydrated salt	found	51.0	4.3	7.4	8.1
	$C_{32}H_{32}N_4CuCl_2O_{10}$	requires	50.06	4.17	7.30	8.30
$\text{Cu}[4\text{Id(tnen)}](\text{ClO}_4)_2\cdot 2\text{H}_2\text{O}$	Green dihydrate	found	47.2	4.8	7.0	7.9
	$C_{31}H_{34}N_4CuCl_2O_{12}$	requires	47.14	4.30	7.09	8.1

4.5.1 A comparison of the spectra of the copper perchlorate complexes of the ligands with the N_4O_2 donor set (4Ia-d)

The infra-red spectra of the green and red copper perchlorate complexes of the diimines discussed above showed certain differences, notably in the fingerprint region below 900 cm^{-1}. The spectrum of the 'intermediate' green salt $[Cu(4Ib\text{-}entn)](ClO_4)_2.4H_2O$ had bands at 1410 cm^{-1} and 1420 cm^{-1} which were not seen in the spectrum of the red salt. These bands were also seen in the spectrum of the green complex $[Cu(4Ia\text{-}enen)](ClO_4)_2.2H_2O$ and a weaker band was seen at 1410 cm^{-1} in the spectrum of $[Cu(4Id\text{-}tnen)](ClO_4)_2.2H_2O$. It was interesting that the NH stretch absorption band was considerably weaker in the spectra of the red complexes which would be expected for a dehydrogenated complex (4 VI)

On standing in methanol or DMF solution, the green copper perchlorate complex $[Cu(4Ib\text{-}entn)](ClO_4)_2$ gave a red solution on standing of which the u.v/visible spectrum was identical with that of the red complex, again indicating an irreversible chemical reaction involving the presence of a propane link between the anilino nitrogen atoms. The complexes with the corresponding ethane link showed no change in spectral characteristics on standing in solution. The more complex absorption pattern in the u.v region of complexes with the N_4O_2 donor set probably indicated the relative availability and significance of the oxygen lone pairs. The dissimilarity of the ε_{max} values for the series of copper complexes of the N_4O_2 donor set (Table 4.20) indicate that these may not exist in the same form in solution (4VI). Only the ε_{max} values of absorptions occurring further into the visible region, shown by the green copper perchlorate complexes were low enough to be considered as d-d bands.[23]

The copper perchlorate complex of the 21-membered ligand 4Ic(tntn) gave a spectrum with the highest series of extinction coefficients, indicating a possible dependence of these on ring size and mode of coordination.

In contrast, a comparison of the spectra of the copper perchlorate complexes of the tetraamine ligands (4IIa-d) showed very similar λ_{max} and ε values, indicating the probability of a similar structure in solution. All the complexes were brown and showed a d-d band in the visible region. (Table 4.20)

Table 4.20 Peaks in the u.v/visible spectra of the copper perchlorate complexes of the ligands with the N_4O_2 donor set (ε = litre mol^{-1} cm^{-1}, λ = nm)

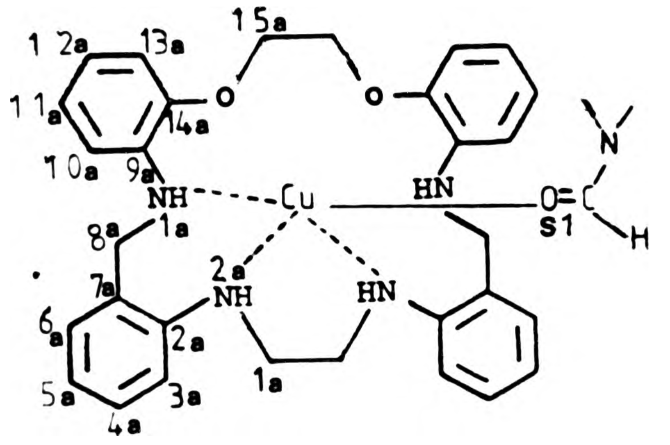
Diimine complex	λ_{max}	ε	λ_{max}	ε	λ_{max}	ε	λ_{max}	ε	λ_{max}	ε
$[Cu(4Ia\text{-}enen)](ClO_4)_2$	270	31,500	340	9,900	395	10,400	460	5,900	550	1,200
$[Cu(4Ib\text{-}entn)](ClO_4)_2$	270	31,700	330	13,800	380	11,500	470	5,200	500	8,000
$[Cu(4Ic\text{-}tntn)](ClO_4)_2$	270	51,500	330	25,400	380	24,200	480	9,600	510	8,800
$[Cu(4Id\text{-}tnen)](ClO_4)_2$	270	18,800	330	9,800	400	11,300	475	8,900	540	900
Tetraamine complex										
$[Cu(4IHa)](ClO_4)_2$	272	11,600	-	-	375	3,600	455	1,500		
$[Cu(4IHb)](ClO_4)_2$	270	13,800	290	12,000	380	3,600	445	1,500		
$[Cu(4IHc)](ClO_4)_2$	270	18,900	300	17,100	390	2,200	460	1,300		
$[Cu(4IHd)](ClO_4)_2$	270	14,700	295	14,600	385	1,400	455	1,000		

4.5.2 The crystal structure of bis(dimethylformamide) 5,6,12,13,19,20,25,26,27,28-decahydrotetrabenzo[*e*, *i*, *o*, *s*] [1,14,1,4,8,17]dioxatetraazacycloeicosine-N, N, N perchlorato-copper(II) perchlorate monodimethylformamide monohydrate

Crystals of the copper complex were obtained by the interaction of the ligand 4IHa in solution in DMF with a methanolic solution of copper(II) perchlorate, as described in Section 4.6.5. Crystal data and details of reflection intensity measurements are given in Appendix C, Tables 1 - 4.

The space group $P\bar{1}$ was assumed and confirmed by satisfactory solution and refinements of the structure. The position of the copper atom was identified from a Patterson synthesis, and inclusion of this atom in a Fourier synthesis revealed the positions of the remaining non-hydrogen atoms. Seven cycles of full-matrix least-squares refinement were carried out with all atoms, except the oxygen atoms [O(12)-O(10 2)] of the disordered perchlorate anion being assigned anisotropic thermal parameters. The hydrogen atoms were included in calculated positions with C-H lengths of 1.08 Å. Final R factors were R = 0.066, R' = 0.064 (Appendix C, Table 1). Tables of positional parameters, anisotropic thermal parameters and bond lengths and angles in the solvent molecules are given in Appendix C, Tables 2 - 4. Structure factors are listed in Appendix D, Table 3.

The atoms are labelled as shown below;



(Labelling the same in the 'b' half of the molecule).

4 VII

The unit cell contains 2 discrete monocations, $[Cu(C_{30}H_{32}N_4O_2)(DMF)_2(ClO_4)]^+$; 2 disordered perchlorate anions, two molecules of DMF and two molecules of water. The copper atom has a highly irregular octahedral coordination sphere (Table 4.21); only three of the four macrocyclic nitrogen atoms (N(1a), N(2a), N(2b)) being the equatorial donor atoms, together with the oxygen atom O(S1) of a DMF molecule. The oxygen atom O(S2) provides the apical donor atom, to give a square pyramidal arrangement which is modified by the weak coordination of an oxygen atom, O(11). The N_3O donor set provided by the macrocycle and the DMF oxygen O(S1) is planar to within ±0.07Å, with the copper displaced slightly (0.09Å) from the plane towards the apical donor oxygen atom O(S2) (Table 4.22).

The DMF oxygen O(S2) and the perchlorate oxygen O(11) are located at 2.29Å and 2.52Å from this plane respectively. The six-membered chelate ring (Cu, N(1a), C(8a), C(7a), C(2a), N(2a)) is inclined at 11° from the equatorial coordination plane and the five-membered chelate ring (Cu, N(2a), C(1a), C(1b), N(2b)) is inclined at an angle of 6.4°. (Table 4.23) This five-membered ring is puckered with the carbon atoms C(1a) and C(1b) displaced from the plane of the equatorial donor atoms including the copper atom, by 0.16Å and 0.52Å respectively.

Bond lengths and angles in the coordination sphere are given in Table 4.21. Equivalent bond lengths and angles in the two halves of the molecule are compared in Table 4.24. Because of the non-coordination of the nitrogen atom N(1b) the molecule is not symmetrical. However, the equivalent bond lengths and angles in the two halves (a and b) of the macrocycle agree closely. An exception is the point where the non-coordinating nitrogen atom N(1b) is incorporated into the large folded ring which included the atoms O(1a) to C(8b)

At this point, the values of bond angles around the nitrogen atoms N(1a), N(1b) and the bond lengths between the nitrogen atoms and the adjacent carbon atoms, diverge on each side of the molecule. In particular the C-N bonds are shown to be lengthened where the nitrogen atoms are coordinated to the copper. The general coordination of the macrocycle is saddle-shaped, with the large ring O(1a)-C(8b), and the five-membered ring, N(1a)-N(2a) folded away from the coordination plane, and the benzene rings C(9a)-C(14a) and C(2b)-C(7b) folded to the opposite side of the plane. The dimethylformamide molecule coordinated to the copper atom is enclosed in the cavity between the benzene rings, while the dimethylformamide molecule, which provides the apical oxygen atom of a square pyramidal coordination around the copper atom, is enclosed between the pair of rings on the opposite side of the molecule. The lack of symmetry of the macrocycle, caused by the bonding to copper of different donor atoms in each half of the ligand is manifest by the torsion angles (see Table 4.25). The irregular folding of the macrocycle is accompanied by a large divergence of the C(1)-N(2)-C(2)-C(7) and C(8)-N(1)-C(9)-C(14) angles in the a and b halves of the molecule. This creates the different environments for the benzene rings (C(9)-C(14)) on each side of the molecule.

In this complex, an oxygen atom, O(11), of one of the perchlorate anions is weakly coordinated (Cu-O(11), 2.67Å) to the copper atom in an axial site, (relative to the equatorial plane defined by the macrocycle donor atoms), giving a pseudo-octahedral geometry since this perchlorate oxygen atom O(11) is trans to the DMF oxygen O(S2). See Table 4.21.

The uncoordinated perchlorate anion centred on Cl(2) was found to be disordered. The site occupation factors were refined to give a total of 3.07 compared with the theoretical total of 4.0. The crystal lattice also incorporates one dimethylformamide molecule and one water molecule per complex unit $[Cu(C_{30}H_{32}N_4O_2)(DMF)_2(ClO_4)]$ DMF.H_2O.

Table 4.21 Bond lengths and angles in the coordination sphere of $[Cu(C_{30}H_{32}N_4O_2).(DMF)_2(ClO_4)](ClO_4).DMF.H_2O$

Bond lengths / Å

Cu-N(1a)	2.087(3)		
Cu-N(2a)	2.050(3)	Cu-N(2b)	2.075(3)
Cu-O(S1)	1.947(3)	Cu-O(S2)	2.236(4)
Cu-O(11)	2.668(5)		

Bond angles / Å

N(1a)-Cu-N(2a)	92.5(1)	N(1a)-Cu-N(2b)	176.3(1)
N(2a)-Cu-N(2b)	84.1(1)		
N(1a)-Cu-O(S1)	93.1(1)		
N(2a)-Cu-O(S1)	169.0(2)	N(2b)-Cu-O(S1)	90.1(1)
O(S1)-Cu-O(S2)	101.2(1)		
N(1a)-Cu-O(S2)	83.0(1)		
N(2a)-Cu-O(S2)	88.9(1)	N(2b)-Cu-O(S2)	98.1(2)
O(S1)-Cu-O(11)	94.5(1)	O(S2)-Cu-O(11)	160.1(1)
N(1a)-Cu-O(11)	84.1(1)		
N(2a)-Cu-O(11)	76.6(1)	N(2b)-Cu-O(11)	93.9(1)

Table 4.22 Least-squares planes and atom deviations in $[Cu(C_{30}H_{32}N_4O_2)(DMF)_2(ClO_4)](ClO_4). DMF.H_2O$

Plane 1

atoms	
N(1a)	-0.06
O(S1)	-0.07
N(2a)	0.06
N(2b)	-0.07
Cu*	-0.09

equation (-2.5300)X + (-9.1907)Y + (10.7122)Z = 0.4802

Plane 2

atoms	
Cu	-0.14
N(1a)	-0.22
N(2a)	0.40
C(2a)	-0.28
C(7a)	-0.23
C(8a)	0.47

equation (-2.7340)X + (-7.3391)Y + (11.4442)Z = 1.0924

Plane 3

atoms	
Cu	-0.08
O(S1)	0.08
N(1a)	-0.05
N(2a)	-0.09
N(2b)	-0.05

equation (-2.5327)X + (-9.1964)Y + (10.7085)Z = 0.4582

*This atom not used in calculation of the plane

Plane 4	atoms	
	Cu	0.02
	N(2a)	0.12
	N(2b)	-0.18
	C(1a)	-0.28
	C(1b)	-0.32

equation (-3.9592)X + (-9.6884)Y + (10.0988)Z = -0.1964

Table 4.23 Angles between planes/°

Plane	1	2	3	4
1	0	11.0	/	6.4
2	11.0	0	11.0	/
3	/	11.0	0	6.4
4	6.4	/	6.4	0

Table 4.24 Interatomic bond lengths and angles in the macrocycle in [$Cu(C_{30}H_{32}N_4O_2)(DMF)_2(ClO_4)$]$(ClO_4)$.DMF.$H_2O$

Cu-O(S1)	1.947(3)	Cu-O(S2)	2.236(4)
C(1a)-N(2a)	1.488(6)	C(1b)-N(2b)	1.488(5)
N(2a)-C(2a)	1.470(6)	N(2b)-C(2b)	1.469(6)
C(2a)-C(3a)	1.373(8)	C(2b)-C(3b)	1.375(8)
C(3a)-C(4a)	1.392(9)	C(3b)-C(4b)	1.380(8)
C(4a)-C(5a)	1.396(9)	C(4b)-C(5b)	1.374(8)
C(5a)-C(6a)	1.357(9)	C(5b)-C(6b)	1.380(10)
C(6a)-C(7a)	1.394(7)	C(6b)-C(7b)	1.383(7)
C(7a)-C(2a)	1.404(6)	C(7b)-C(2b)	1.400(6)
C(7a)-C(8a)	1.495(7)	C(7b)-C(8b)	1.492(8)
C(8a)-N(1a)	1.512(5)	C(8b)-N(1b)	1.419(6)
N(1a)-C(9a)	1.450(6)	N(1b)-C(9b)	1.402(8)
C(9a)-C(10a)	1.389(8)	C(9b)-C(10b)	1.375(8)
C(9a)-C(14a)	1.405(5)	C(9b)-C(14b)	1.411(7)
C(10a)-C(11a)	1.378(8)	C(10b)-C(11b)	1.383(12)
C(11a)-C(12a)	1.370(7)	C(11b)-C(12b)	1.354(11)
C(12a)-C(13a)	1.375(9)	C(12b)-C(13b)	1.352(11)
C(13a)-C(14a)	1.390(7)	C(13b)-C(14b)	1.380(9)
C(14a)-O(1a)	1.357(7)	C(14b)-O(1b)	1.374(7)
O(1a)-C(15a)	1.437(5)	O(1b)-C(15b)	1.428(6)
C(15a)-C(15b)	1.492(9)	C(1a)-C(1b)	1.499(7)
		O(S1)-Cu-O(S2)	101.2(1)
N(1a)-Cu-N(2a)	92.5(1)	N(1b)-Cu-N(2b)	-
N(1a)-Cu-O(S1)	93.1(1)	N(1b)-Cu-O(S1)	-

N(1a)-Cu-O(S2)	83.0(1)	N(1b)-Cu-O(S2)	-
N(2a)-Cu-O(S1)	169.0(2)	N(2b)-Cu-O(S1)	90.1(1)
N(2a)-Cu-O(S2)	88.9(1)	N(2b)-Cu-O(S2)	98.1(2)
N(1a)-Cu-N(2b)	176.3(1)	N(1b)-Cu-N(2a)	-
N(1a)-Cu-N(1b)	-	N(2b)-Cu-N(2a)	84.1(1)
C(1a)-N(2a)-C(2a)	114.8(4)	C(1b)-N(2b)-C(2b)	115.3(4)
C(1a)-N(2a)-Cu	107.5(2)	C(1b)-N(2b)-Cu	106.1(3)
C(2a)-N(2a)-Cu	115.7(2)	C(2b)-N(2b)-Cu	116.7(3)
N(2a)-C(1a)-C(1b)	108.4(4)		
N(2a)-C(2a)-C(3a)	122.2(4)	N(2b)-C(2b)-C(3b)	119.6(4)
N(2a)-C(2a)-C(7a)	116.5(4)	N(2b)-C(2b)-C(7b)	119.4(5)
C(3a)-C(2a)-C(7a)	121.3(5)	C(3b)-C(2b)-C(7b)	120.9(4)
C(2a)-C(3a)-C(4a)	119.0(5)	C(2b)-C(3b)-C(4b)	120.3(5)
C(3a)-C(4a)-C(5a)	119.9(6)	C(3b)-C(4b)-C(5b)	120.1(6)
C(4a)-C(5a)-C(6a)	120.1(4)	C(4b)-C(5b)-C(6b)	119.6(3)
C(5a)-C(6a)-C(7a)	120.3(5)	C(5b)-C(6b)-C(7b)	122.1(5)
C(6a)-C(7a)-C(8a)	120.2(4)	C(6b)-C(7b)-C(8b)	119.7(4)
C(6a)-C(7a)-C(2a)	118.6(5)	C(6b)-C(7b)-C(2b)	117.3(5)
C(2a)-C(7a)-C(8a)	121.2(4)	C(2b)-C(7b)-C(8b)	122.9(4)
C(7a)-C(8a)-N(1a)	110.6(4)	C(7b)-C(8b)-N(1b)	111.7(4)
C(8a)-N(1a)-C(9a)	113.4(3)	C(8b)-N(1b)-C(9b)	121.1(5)
C(8a)-N(1a)-Cu	113.3(2)	C(8b)-N(1b)-Cu	-
C(9a)-N(1a)-Cu	117.4(3)	C(9b)-N(1b)-Cu	-
N(1a)-C(9a)-C(10a)	122.9(3)	N(1b)-C(9b)-C(10b)	124.0(5)

N(1a)-C(9a)-C(14a)	117.3(4)	N(1b)-C(9b)-C(14b)	118.0(5)
C(10a)-C(9a)-C(14a)	119.8(4)	C(10b)-C(9b)-C(14b)	118.0(5)
C(9a)-C(10a)-C(11a)	120.1(4)	C(9b)-C(10b)-C(11b)	120.0(6)
C(9a)-C(14a)-C(13a)	119.4(5)	C(9b)-C(14b)-C(13b)	120.2(5)
C(9a)-C(14a)-O(1a)	115.3(4)	C(9b)-C(14b)-O(1b)	114.1(5)
C(10a)-C(11a)-C(12a)	119.6(6)	C(10b)-C(11b)-C(12b)	121.3(7)
C(11a)-C(12a)-C(13a)	121.9(5)	C(11b)-C(12b)-C(13b)	120.0(8)
C(12a)-C(13a)-C(14a)	119.4(5)	C(12b)-C(13b)-C(14b)	120.4(6)
C(13a)-C(14a)-C(9a)	119.4(5)	C(13b)-C(14b)-C(9b)	120.2(5)
C(13a)-C(14a)-O(1a)	125.3(4)	C(13b)-C(14b)-O(1b)	125.7(5)
C(14a)-O(1a)-C(15a)	117.4(4)	C(14b)-O(1b)-C(15b)	117.2(4)
O(1a)-C(15a)-C(15b)	108.5(4)	O(1b)-C(15b)-C(15a)	107.8(5)
O(11)-Cu-N(1a)	84.1(1)	O(11)-Cu-O(S1)	94.5(1)
O(11)-Cu-N(2a)	76.6(1)	O(11)-Cu-N(2b)	93.9(1)

Table 4.25 Torsion angles /° in the inner great ring of $[Cu(C_{30}H_{32}N_4O_2)(DMF)_2(ClO_4)](ClO_4)DMF.H_2O$*

	part a	part b
N(2')-C(1')-C(1)-N(2)	57.93	-
C(1)'-C(1)-N(2)-C(2)	-170.49	-176.26
C(1)-N(2)-C(2)-C(7)	180.0	-133.56
N(2)-C(2)-C(7)-C(8)	0	4.76
C(2)-C(7)-C(8)-N(1)	-64.67	-81.54
C(7)-C(8)-N(1)-C(9)	-161.59	-176.96
C(8)-N(1)-C(9)-C(14)	146.92	4.72
C(14)-O(1)-C(15)-C(15')	-169.57	-173.74
O(1)-C(15)-C(15')-O(1')	71.53	-

*Primes indicate atoms in the other part of the molecule.

4.6 Experimental Section

(Abbreviations used in this section are as listed previously).

4.6.1 General preparation of the sexadentate ligands

The preparation of the sexadentate ligands are shown in the scheme in Fig. 4.1. The starting materials 4Ia-b and 4IIIa-d were prepared as described previously.[1,26,27] The diimine ligands were purified by washing with ether. Recrystallisation was found to be difficult due to their insolubility, and deleterious due to the tendency of these ligands to solvate with polar solvents such as pyridine, dimethylformamide and dimethylsulphoxide. This was also the case with copper complexes, which had a high tendency to coordinate to the above solvents; exemplified in the crystal structure. (4.5.2.)

The diimine ligands were reduced to give the tetraamines 4IHa-e, and the hexaamine, 4IHf, using diborane as described in the following sections.

4.6.2 Experimental data on the sexadentate diimines

12,13,25,26,27,28-Hexahydrotetrabenzo [*e*,*i*,*o*,*s*] [11,14,1,4,8,17] dioxatetra-azacycloeicosine (4Ia(en en), X=O)

The dialdehyde (4IIa) (0.78 g, 3 mmol) and 1,2-di(*o*-aminophenoxy-ethane (4IIIa) (0.79 g, 3.25 mmol) were refluxed in methanol (125 cm^3) with p-toluenesulphonic acid (0.051 g, 0.3 mmol) until a flocculent yellow precipitate of the diimine separated. This was filtered from the orange supernatant liquid and washed with a little ether to give 12,13,25,26,27,28-hexahydrotetrabenzo [*e*,*i*,*o*,*s*] [11,14,1,4,8,17]dioxatetraazacycloeicosine (1.01 g, 70%) as fine yellow flocculent crystals m.pt 197-198°C. (Found: C, 76.6; H, 6.4; N, 11.1%. $C_{30}H_{28}N_4O_2$ requires C, 76.2; H, 6.39; N, 11.1%); λ_{max} (MeOH) 245 nm (ε = 43,000) 277 nm (ε = 19,700); 390nm(ε =12,700); ν_{max} (nujol) 3220(w,NH), 1620(s,C=N) 1595(s,C=C), 1575(s,C-N and NH), 1500(s), 1330, 1320, 1290, 1280, 1265, 1250(s), 1070, 1060, 970, 935(s), 915, 880, 850, 840, 740(s,o-substituted benzene); ^1H (C_5D_5N) 3.76(c,4H,NH-$\mathrm{C\underline{H}_2}$), 4.58(s, 4H,O-$\mathrm{C\underline{H}_2}$), 6.6-7.75 (m,16H, aromatics), 8.76(s,2H,N=C$\underline{\mathrm{H}}$), 10.22(s,2HN$\underline{\mathrm{H}}$); ^{13}C See Section 4.2.3. (Found: m/e 476.2212. $C_{30}H_{28}N_4O_2$ requires M, 476.2212): m/e 476.2212(M$^+$, 11.62), 358.1551(15.33), 356.0994(13.28, 224.0947 (19.41), 178.0493(49.81), 151.0634(32.44), 146.0245(100), 119.0370(19.54), 118.0654(13.54), 117.0575(13.03), 90.0358(14.94).

11,12,13,14,25,26,27,29-Octahydro-29-*H*-tetrabenzo[*f*,*j*,*p*,*t*][1,5,9,13]tetraazacycloheneicosine (4Ib(entn), X=O)

The dialdehyde (4IIb) (0.29g, 1 mmol) and 1,2-di(o-aminophenoxy)-ethane (4IIIa) (0.268g, 1.1 mmol) were refluxed in methanol (30 cm^3) with zinc acetate (0.11g, 0.5 mmol) until a yellow solid formed as small yellow crystals from a red supernatant liquid. The crystals were recrystallised from dichloromethane as fine yellow crystals of 11,12,13,14,25,26,27,29-octahydro-29-*H*-tetrabenzo-[*f*,*j*,*p*,*t*][1,5,9,13]tetraazacycloheneicosine (0.35g, 71%); m.pt 139°C. (Found: C, 76.3; H, 6.8; N, 11.39%. $C_{31}H_{30}N_4O_2$ requires C, 75.91; H, 6.12; N, 11.42%); λ_{max} (MeOH) 239 nm (ε = 46,700), 264 nm (ε = 18,800), 390 nm (ε = 11,900); ν_{max} (nujol) 3260(w,NH), 1630(s,C=N), 1600(s,C=C), 1580(s,C-N), 1530(w), 1500(s), 1470(s), 1340, 1290(w), 1250(s), 1230(s), 1190(s), 1170(s), 1125(s), 1050(s), 980, 950, 905, 850(w), 750(s, o-substituted benzene); ^1H ($CDCl_3$) 2.0 (quin. 2H. J=4.0, $CH_2C\underline{H}_2CH_2$), 3.35 (t. 4H. J=4.0, $C\underline{H}_2CH_2C\underline{H}_2$). 4.45(s.4H.O.$C\underline{H}_2$.$C\underline{H}_2$O), 6.4-6.8 (m. 8H. aromatics), 6.8-7.2 (m. 8H. aromatics), 8.5(s. 2H. N=C*H*), 9.6(s, 2H.N*H*); (Found: m/e 490.2367. $C_{31}H_{30}N_4O_2$ requires M, 490.2368); m/e 490.2368 (M^+, 49.03), 384.1716(13.46), 384.1716(13.46), 374.1815(13.34), 373.1786(55.47), 361.1741(22.6), 360.1698(100), 359.1631(20.5), 358.1547(21.23), 247.120'(23.0'), 246.1146(29.44), 245.1162(25.68), 244.1188(10.8), 239.1174(21.58), 238.1081(15.12), 225.1017(10.32), 224.0931(25.73), 223.0863(18.7), 222.0784(13.81), 221.0709(12.35), 148.0758(15.06), 136.0745(14.73), 135.0680(30.41), 132.0793(10.47), 130.0642(64.76), 129.0549(10.66), 120.0438(12.17), 118.0652(44.52), 117.0580(27.76), 106.0659(10.92).

11,12,13,14,26,27,28,29-Octahydro-15-*H*-tetrabenzo[*e*,*i*,*p*,*t*] [1,4,8,13]tetraazacyclohereicosine (4Id(tnen), X=O)

The dialdehyde(4IIa) (0.26g, 1 mmol) and 1,3-di(o-aminophenoxy)-propane*(4IIIb) (0.283g, 1.1 mmol) were refluxed in ethanol (30 cm^3) with zinc acetate (0.11g, 0.5 mmol). An orange solution was formed, in which a flocculent bright yellow solid slowly formed after 30 minutes. The solid was filtered and recrystallised from dichloromethane to give long needle crystals of 11,12,13,14,26,27,28,29-octahydro-15-*H*-tetrabenzo [*e*,*i*,*p*,*t*][1,4,8,13]tetraazacyclohereicosine dihydrate (0.34, 71%); m.pt 158°C. (Found: C, 70.1; H, 6.1; N, 10.6%. $C_{31}H_{34}N_4O_4$ requires C, 70.72; H, 5.7; N, 10.64%); λ_{max} (MeOH) 245 nm (ε = 23,300), 280 nm (ε = 8,100), 400 nm (ε = 7,900); ν_{max} (nujol) 3240(w,NH), 1630(s,C=N), 1600(s,C=C), 1580(s,C-N), 1530, 1500(s), 1470(s), 1300, 1290, 1270(w), 1250(s), 1230(w), 1185(s), 1160(s), 1135(w), 1120(s), 1095, 1070, 1040(s), 1015(s), 975(s), 920(w), 900(s), 815(s), 760(s, o-substituted benzene) ^{1}H ($CDCl_3$) 1.95 (quin. 2H. J=2.0, $OCH_2.C\underline{H}_2.CH_2O$), 3.3(s.4H. $C\underline{H}_2.C\underline{H}_2$), 4.0-4.3(s.4H.$OC\underline{H}_2.CH_2.C\underline{H}_2O$) 6.30-6.70 (m.8H. aromatics), 6.8-7.1(m.8H.aromatics). 8.4(s.2H.N=C$\underline{H}$), 9.6(s.2H.N$\underline{H}$); (Found: m/e 490.2364. $C_{31}H_{30}N_4O_2$ requires M, 490.2368); m/e 490.2364 (M$^+$, 72.86), 374.1808(13.67), 373.1775(55.55), 372.1715(100), 265.1342(20.90), 245.1166(43.95), 237.1005(12.81), 233.1072(19.60), 232.0984(21.62), 224.0957(69.00), 223.0854(26.74), 131.0614(27.83), 130.0637(35.24), 118.0651(96.24), 117.0570(55.38), 106.0668(15.76).

*Preparation of 1,2-di(o-aminophenoxy)propane

1,2di(o-nitrophenoxy)propane (10g) was suspended in ethanol (300 cm^3).

10% Pd on charcoal was added (0.5g), and hydrazine hydrate in 5 cm^3 portions (10 cm^3). The mixture was stirred under nitrogen until colourless. It was filtered through Celite, and the filtrate evaporated to small volume. 1,2-di(o-aminophenoxy)propane separated as small fluffy off-white needle crystals (6.5g, 83%).

11,12,13,14,26,27,28,29-Octahydro-15,29-2*H*-tetrabenzo[*f*,*j*,*q*,*u*] [1,5,9,19]tetraazacyclodecosane(4Ic(tntn),X=O)

The dialdehyde(4IIb) (0.29g, 1 mmol) and 1,3-di(o-aminophenoxy)-propane(4IIIb) (0.283g, 1.1 mmol) were refluxed in methanol with p-toluenesulphonic acid (0.019g, 0.1 mmol). An orange solution was formed, and after about twenty minutes a flocculent yellow solid was precipitated. The solid was filtered and recrystallised from dichloromethane to give 11,12,13,14,26,27,28,29,-octahydro-15,29-2*H*-tetrabenzo[*f*,*j*,*q*,*u*] 1,5,9,19]tetraazacyclodocosane as long yellow needle crystals (0.4g, 79.3%), m.pt 194°C. (Found: C, 76.6; H, 6.4; N, 11.1%. $C_{32}H_{32}N_4O_2$ requires C, 76.19; H, 6.34; N, 11.11%); λ_{max} (MeOH). 246 nm ($\mathcal{E}$ = 23,800), 277 nm ($\mathcal{E}$ = 9,500), 395 nm ($\mathcal{E}$ = 6,500); ν_{max} (nujol) 3270(w,NH), 1630(s,C=N), 1600(s, C=C), 1580(s,C-N), 1530, 1500(s), 1470(s), 1340(s), 1310, 1280(w), 1255(s), 1235(s), 1185(s), 1170(s), 1145, 1120(s), 1050(s), 1020(s), 980, 950(w), 925, 900(s), 830(s), 750(s, o-substituted benzene)

^1H ($CDCl_3$) (2.4 (c, 4H.CH_2.$C\underline{H}_2$.CH_2 , OCH_2 .$C\underline{H}_2$ .CH_2O) 3.3 (t. 4H. J=4.0 $C\underline{H}_2CH_2C\underline{H}_2$)4.0-4.3(s. 4H.$OC\underline{H}_2$.$CH_2$.$C\underline{H}_2O$) 6.40-6.75 (m.8H.aromatics), 6.80-7.40 (m.8H.aromatics), 8.5(s.2H.N=C$\underline{H}$), 9.6(s.2H. N$\underline{H}$); (found: m/e 504.2519. $C_{32}H_{32}N_4O_2$ requires 504.2525); m/e 504.2519 (M^+, 48.21), 400.1986(10.13), 399.1932(41.04), 398.1898(10.74), 388.2017(11.30), 387.1963(46.63), 375.1932(23.40), 374.1908(100), 373.1792(20.28), 372.1776(10.02), 258.1381(19.14), 252.1260(28.12), 247.1213(25.74), 246.1138(29.86), 237.1023(10.66), 224.0940(11.78), 223.0875(13.57), 150.0926(44.08), 149.0839(10.90), 144.0818(16.18), 132.0749(21.25), 131.0626(16.52), 130.0638(84.23), 122.0587(10.02), 120.0447(11.31), 118.0651(61.87), 117.0580(29.80), 109.0535(12.40), 108.0457(10.12), 106.0665(19.45).

4.4(b.s.2H.NH), 5.25(b.s.2H.NH), 4.2(s.4H.$C_6H_5-C\underline{H}_2$), 6.6-7.1 (m.8H aromatics), 7.1-7.7 (m.8H. aromatics). (C_5D_5N) 3.35(c.4H.NH-$C\underline{H}_2$), 4.08(s.4H.O-$C\underline{H}_2$), 4.26(d.4H. $C_6H_5-C\underline{H}_2$), 5.5(b.s.4H.NH), 6.6-7.8 (c.18H. aromatics). ^{13}C (See Section 4.2.3. (Found: m/e 480.2522. $C_{30}H_{32}N_4O_2$ requires M, 480.2525); 374.1852(12.99), 362.184(15.00), 361.1727(20.34), 360.1685(80.1), 349.1787(38.83), 349.1691(37.79), 348.1694(56.27), 244.1213(31.11), 239. 11.73(13.07), 237.1373(12.25), 136.0758(14.92), 135.0673(31.85), 132.0813(10.54), 130.0660(17.45), 120.0792(42.02), 119.0695(11.36), 118.0649(100), 117.0570(14.77), 109.0526(11.58), 106.0653(57.31), 91.0559(42.9).

4.6.3 Experimental data on the reduced sexadentate ligands

5,6,12,31,19,20,25,26,27,28-Decahydrotetrabenzo[*e*,*i*,*o*,*s*][11,14 1,4,8,17]dioxatetra-azacycloeicosine (4IHa(enen),X=O)

The diimine was reduced using a solution of diborane in THF as follows; the diimine ligand 4Ia (0.23g, 0.5 mmol) was placed in a flask previously flushed out with nitrogen. The diborane solution was added in 1 cm^3 portions with stirring 1 cm^3 = 1 mmol B_2H_6) and the mixture was refluxed gently. The yellow ligand dissolved in the THF solution and the resulting solution became paler as the ligand was reduced. After the addition of 10 cm^3 (10 mmol B_2H_6) of diborane solution, the solution was colourless. Distilled water was added (10 cm^3) and 2MNaOH (5 cm^3). The two resulting liquid layers were separated. The THF layer was evaporated to give a pale yellow oil which gave pale yellow crystals. On adding a few cm^3 of methanol fine white crystals were formed in a yellow supernatant solution. On recrystallisation from dichloromethane ethanol 15,6,12,13,19,20,25,26,27,28-decahydrotetrabenzo[*e*,*i*,*o*,*s*][11,14, 1,4,8,17]dioxatetra-azacycloeicosine was obtained as fine white crystals (0.144g, 60%) m.pt 180-182°C. (Found: C, 75.2; H, 6.8; N, 11.70%. $C_{30}H_{32}N_4O_2$ requires C, 74.97; H, 6.71; N, 11.66%); λ_{max} (MeOH) 248 nm (ε = 29,200), 295 nm (ε = 9,300); ν_{max} (nujol) 3395(s.NH), 3350(s,NH), 1610(s), 1595(s,C=C), 1515(s), 1340(w), 1325, 1310, 1305, 1280(s), 1250(s), 1215(w), 1200(s), 1130, 1050(s), 980(w), 930(w), 900, 820(w), 755(s), 745(s, o-substituted benzene); ^1H ($CDCl_3$) 3.46(c.4H.NH-$\underline{CH_2}$), 3.88(s.4H.O-$\underline{CH_2}$),

5,6,11,12,13,14,18,19,25,26,27,28-Dodecahydro-29-*H*-tetrabenzo[*f*,*j*,*p*,*t*][1,5,9,13]tetraazacycloheneicosine (4IHb(entn),X=O)

The diimine ligand (4Ib) (0.245g, 0.5 mmol) was reduced using a solution of diborane in THF (1.0M) as described previously for the homologous ligand, 4Ia. The crude material obtained from evaporation under vacuo of the THF layer was recrystallised from dichloromethane/methanol to give 5,6,11,12,13,14,18,19,25,26,27,28-dodecahydro-29-*H*-tetrabenzo[*f*,*j*,*p*,*t*][1,5,9,18]tetraazacycloheneicosine dihydrate as fine white crystals (0.15g, 61%), m.pt 182°C. (Found: C, 70.2; H, 6.6; N, 10.1%. $C_{31}H_{38}N_4O_4$ requires C, 70.18; H, 6.88; N, 10.50%). λ_{max} (MeOH) 250 nm (ε =30,500), 290 nm (ε = 13,300); ν_{max} (nujol) 3410(w,OH), 3385(s,NH), 3290(s,NH), 1610(s), 1595(s), 1520(s), 1470(s), 1335(s), 1320(s), 1250(s), 1220(s), 1205(s), 1165(w), 1130(s), 1050(s), 985, 940(s), 915, 880, 850(w), 750(s, o-substituted benzene); $^1H(CDCl_3)$1.8 (quin. 2H. J=8.0 $CH_2C\underline{H}_2CH_2$), 3.2 (t. 4H. J=8.0. $C\underline{H}_2CH_2C\underline{H}_2$), 4.25(s.4H. $O.C\underline{H}_2C\underline{H}_2O$), 4.35(s.4H. $C_6H_5C\underline{H}_2$), 4.3(s.2H.N$\underline{H}$), 5.3(s.2H.N$\underline{H}$) 6.5-6.95(m.8H.aromatics), 7.0-7.3(m.8H, aromatics); (Found: m/e 494.2681. $C_{31}H_{34}N_4O_2$ requires M, 494.2681); m/e 494.2681 (M^+, 22.85), 374.1860(11.63), 250.1484(16.91), 244.1208(46.3), 144.0817(29.34), 136.0758(30.28), 135.0697(72.21), 132.0800(51.90), 131.0728(68.85), 130.0653(33.98), 120.0812(82.93), 118.0651(100), 117.0574(16.00), 109.0536(27.35), 107.0737(16.80), 106.0665(39.92).

5,6,11,12,13,14,18,19,25,26,27,28-Dodecahydro-29-*H*-tetrabenzo-[*f*,*j*,*p*,*t*][1,5,9,13]tetraazacycloheneicosine (4IHb(entn),X=O)

The diimine ligand (4Ib) (0.245g, 0.5 mmol) was reduced using a solution of diborane in THF (1.0M) as described previously for the homologous ligand, 4Ia. The crude material obtained from evaporation under vacuo of the THF layer was recrystallised from dichloromethane/methanol to give 5,6,11,12,13,14,18,19,25,26,27,28-dodecahydro-29-*H*-tetrabenzo[*f*,*j*,*p*,*t*][1,5,9,18]tetraazacycloheneicosine dihydrate as fine white crystals (0.15g, 61%), m.pt 182°C. (Found: C, 70.2; H, 6.6; N, 10.1%. $C_{31}H_{38}N_4O_4$ requires C, 70.18; H, 6.88; N, 10.50%). λ_{max} (MeOH) 250 nm (ε =30,500), 290 nm (ε = 13,300); ν_{max} (nujol) 3410(w,OH), 3385(s,NH), 3290(s,NH), 1610(s), 1595(s), 1520(s), 1470(s), 1335(s), 1320(s), 1250(s), 1220(s), 1205(s), 1165(w), 1130(s), 1050(s), 985, 940(s), 915, 880, 850(w), 750(s, o-substituted benzene); $^1H(CDCl_3)$1.8 (quin. 2H. J=8.0 $CH_2\underline{H}_2CH_2$), 3.2 (t. 4H. J=8.0, $C\underline{H}_2CH_2C\underline{H}_2$), 4.25(s.4H. $O.C\underline{H}_2C\underline{H}_2O$), 4.35(s.4H. $C_6H_5C\underline{H}_2$), 4.3(s.2H.N$\underline{H}$), 5.3(s.2H.N$\underline{H}$) 6.5-6.95(m.8H.aromatics), 7.0-7.3(m.8H, aromatics); (Found: m/e 494.2681. $C_{31}H_{34}N_4O_2$ requires M, 494.2681); m/e 494.2681 (M^+, 22.85), 374.1860(11.63), 250.1484(16.91), 244.1208(46.3), 144.0817(29.34), 136.0758(30.28), 135.0697(72.21), 132.0800(51.90), 131.0728(68.85), 130.0653(33.98), 120.0812(82.93), 118.0651(100), 117.0574(16.00), 109.0536(27.35), 107.0737(16.80), 106.0665(39.92).

5,6,11,12,13,14,19,21,26,27,28,29-Dodecahydro-15,29-2*H*-tetrabenzo [*f*,*j*,*q*,*u*][1,5,9,12]tetraazacyclodocosane (4IIc(tntn),X=O)

The diimine ligand (4Ic) (0.252g, 0.5 mmol) was reduced using a solution of diborane in THF (1.0M), as described previously for the homologous ligands, 4Ia,b. The material obtained from the THF layer was recrystallised from dichloromethane to give 5,6,11,12,13-14,19,21,26,27,28,29-dodecahydro-15,29-2*H*-tetrabenzo[*f*,*j*,*q*,*u*] [1,5,9,12]tetraazacyclodocosane hemihydrate as small white crystals (0.18g, 72%), m.pt 186°C. (Found: C, 74.5; H, 6.3; N, 10.8%. $C_{32}H_{33}N_4O_{2.5}$ requires C, 74.20; H, 6.38; N, 10.83%); λ_{max} (MeOH) 250 nm (ε = 43,300), 297 nm (ε =13,600): ν_{max} (nujol) 3600(s,OH), 3400, 3300(s,NH), 1610(s), 1590(s), 1525(s,broad), 1470(s), 1350(s), 1310(s), 1260(s), 1230(s,broad), 1165, 1125(s), 1055-1035(s,broad), 935,960(s), 935, 900(s), 910, 895(s), 810, 760-740(s,broad, o-substituted benzene); ^1H ($CDCl_3$) 1.5-2.3(m, complex.4H $CH_2C\underline{H}_2CH_2$, $O-CH_2CH_2CH_2$)3.2 (t. 4H, J=8.0, $C\underline{H}_2CH_2CH_2$)4.0(s.2H. $C_6H_5C\underline{H}_2$), 4.1-4.25(t.4H. $OC\underline{H}_2CH_2C\underline{H}_2O$), 5.3(s.2H.N$\underline{H}$), 6.0(s.2H.N$\underline{H}$), 6.5-6.85 (m.8H. aromatics), 7.0-7.4(m.8H.aromatics); (Found: m/e 508.2821. $C_{32}H_{36}N_4O_2$ requires M, 508.2838); m/e 508.2821 (M^+, 1.43), 258.1373(35.19), 150.0924(70.17), 149.0846(16.59), 122.0580(22.74), 120.0796(13.94), 118.0632(15.81), 109.0525(31.82), 108.0447(31.01), 106.0657(11.17).

5,6,11,12,13,14,20,21,26,27,28,29-Dodeca-15-*H*-tetrabenzo[*e*,*i*,*f*,*t*][1,4,8,13]tetraazacycloheneicosine (4IHd(tnen), X=O)

The diimine ligand (4Id) (0.245g, 0.5 mmol) was reduced using a solution of diborane in THF (1.0M) as described for the homologous ligands, 4Ia-c. The material obtained by evaporation under vacuo of the THF layer was dissolved in chloroform and the solution filtered through anhydrous Na_2CO_3. The volume of the filtrate was reduced under vacuo, and petroleum ether (60-80°) added. 5,6,11,12,13,14,20,21,26,27,28,29-dodeca-15-*H*-tetrabenzo [*e*,*i*,*f*,*t*] [1,4,8,13]tetraazacycloheneicosine monohydrate was formed as white crystals (0.16g, 64%), m.pt 105°C. (Found: C, 73.1; H, 7.0; N, 10.9%. $C_{31}H_{36}N_4O_3$ requires C, 72.65; H, 7.03; N, 10.93%); λ_{max} (MeOH) 256 nm (ε = 36,300), 290 nm (ε = 10,700); ν_{max} (nujol), 3310, 3290(s, NH), 1615(s), 1595(s), 1520(s), 1500(s), 1470(s), 1325(s), 1315, 1260(s), 1235, 1225(s), 1200(s), 1190, 1180, 1170, 1145(s), 1090(s), 1055(s), 1015-1005(s,broad), 985(w), 960(s), 935(s), 890(s), 860(s), 830(s), 770, 750(s,broad, o-substituted benzene).

^{1}H ($CDCl_3$)2.2 (quin. 2H. J=8.0, $OCH_2\underline{CH_2}CH_2O$),3.35(s.4H. $\underline{CH_2}\underline{CH_2}$), 3.95(s.4H. $C_6H_5\underline{CH_2}$) 4.1 (t. 4H. J=0, $O\underline{CH_2}CH_2\underline{CH_2}O$) 5.3(s.2H.N$\underline{H}$), 5.9(s.2H.N$\underline{H}$), 6.3-6.7(m.8H. aromatics), 6.8-7.15(m.8H. aromatics); (Found: m/e 494.2683. $C_{31}H_{34}N_4O_2$ requires M, 494.2681); m/e 494.2683 (M^+, 2.07), 375.1921(13.02), 374.1871(54.0), 363.1963(25.76), 362.1895(42.82), 258.1362(28.28), 150.0923(43.12), 149.0845(12.05), 130.0658(18.67), 120.0804(28.85), 118.0659(100), 109.0522(10.94), 106.0656(55.22).

12,13,25,26,27,28-Hexahydrotetrabenzo[*e*,*i*,*o*,*s*][1,4,8,11,14,17] hexa-azacycloeicosine (4If, X=NH)

The dialdehyde(4IIa) (0.78g, 3 mmol) was completely dissolved in absolute ethanol (130 cm^3). 1,2-di(o-aminophenylamino)ethane (4IIId) (0.78g, 3.25 mmol) was then added directly as the solid, followed by zinc acetate 0.66g, 3 mmol), in that order. After refluxing the mixture overnight, a silky green precipitate of the diimine p-toluenesulphonate salt was found. To obtain the free diimine, the p-toluenesulphonate salt was added slowly to a stirred solution of the theoretical amount of lithium hydroxide in methanol. A bright yellow flocculent precipitate of the diimine formed immediately on addition. This was filtered, washed with methanol and vacuum-dried to give the free base 12,13,25,26,27,28-hexahydrotetrabenzo [*e*,*i*,*o*,*s*][1,4,8,11,14,17]hexaazacycloeicosine as the dehydrate (0.88g, 62%), m.pt 200°C, with decomposition. (Found: C, 71.1°; H, 6.11; N, 16.11%. $C_{30}H_{30}N_6 2H_2O$ requires C, 70.5; H, 6.27; N, 16.4%); λ_{max} (MeOH) 255 nm (ε =28,000) 280 nm(sh) (ε = 14,000), 410 nm (ε =6,300) ν_{max} (nujol) 3440(broad,w,OH), 3300(broad,w,NH), 1620(s,C=N), 1600(s,C=N), 1570(s,C-N and NH), 1510-1530(s,broad NH bend), 1330(s), 1285(w), 1250, 1220, 1150-1175(broad), 1135(w), 1100(w), 1050, 970, 930, 920, 880(w), 850(w), 750(s, o-substituted benzene;) ^1H (CDCl$_3$), 3.46(s, 4H.CH=N. C_6H_5-NH-C$\underline{H}_2$), 3.52 (c,4H, C_6H_5NH-C$\underline{H}_2$), 4.63(s,2H, CH=NC_6H_5N$\underline{H}$.CH$_2$); 6.68-7.25(m,16H, aromatics), 8.38 (s, 2H, C$\underline{H}$=NC_6H_5NH.CH$_2$), 9.17(s, 2H, C_6H_5N$\underline{H}$-CH$_2$); (Found: m/e 474.2548 $C_{30}H_{30}N_6$ requires M, 474.2532); m/e 474.2548 (M$^+$, 14.173), 472.2485 (10.85), 250.1315(23.26), 248.1125(24.81), 237.1241(23.26), 236.1185(54.26), 235.1088(38.76), 234.1039(43.41), 224.1177(30.23), 223.1099(35.66), 222.1033(100), 220.0914(37.98), 210.1013(28.68), 207.0933(35.66), 206.0815(21.71), 194.0834(26.36), 179.0736(10.85), 134.0851(15.5), 133.0786(23.26), 130.0679(63.57), 120.0808(13.18), 119.0631(78.29), 118.0657(96.12), 117.0588(34.11), 108.0684(16.28), 106.0646(27.91), 104.0498(15.5), 93.0571(15.5), 92.0505(25.58), 91.0551(59.69) The green p-toluenesulphonate salt of the diimine; ν_{max} (nujol) 3440(broad, OH), 3210(s,broad,NH), 1635(s,C=N), 1610(s, C=C), 1600, 1590, 1500(w), 1320(w), 1310, 1290, 1170-1250 (s,broad, sulphonate), 1130(s), 1070(w), 1060, 1040(s), 1015(s), 980(s), 930, 900(w), 850(w), 820(s), 780(w), 760(s, o-substituted benzene), 740(w), 725(w), 715.

12,13,25,26,27,28-Hexahydrotetrabenzo[*e*,*i*,*o*,*s*][11,14,1,4,8,17]dithiatetra-azacycloeicosine (4Ie,X=S)

The dialdehyde(4IIa) (0.78g, 3 mmol) was fully dissolved in absolute ethanol (130 cm^3) 1,2-di(o-aminophenylthio)ethane (4IIIc) (0.8g, 3.25 mmol) was added in solution in absolute ethanol together with p-toluenesulphonic acid (0.18g, 1.5 mmol) and zinc(II) acetate (0.55g, 2.5 mmol). The mixture was refluxed, some of the diimine forming after a few hours, but the reaction was complete after a total of 72 hours. 12,13,25,26,27,28-Hexahydrotetrabenzo-[*e*,*i*,*o*,*s*][11,14,1,4,8,17]dithiatetra-azacycloeicosine was formed as a yellow solid (0.75g, 50%), m.pt 180-182°C. (Found: C, 70.86; H, 5.52; N, 11.02%); λ_{max} (MeOH) 250 nm (ε = 44,200) 410 nm (ε = 11,800) ν_{max} (nujol) 1630(s,C=N), 1595(s,C=C), 1570(s,C-N and NH), 1530(s), 1360, 1340, 1310(w), 1285, 1270, 1250(w), 1190(w), 1170(s), 1140(w), 1100(w), 1075(s), 1075(s), 1050(s), 980(s), 940(w), 910(s), 850(w), 760(s), 745(s,p-substituted benzene); ^1H (C_5D_5N) 3.75(s. 4H. S-C$\underline{H}_2$), 3.83(c,4H.S-C$\underline{H}_2$), 6.0(s, 2H,N$\underline{H}$), 6.5-7.66 (m,16H, aromatics), 8.55(s,2H, NC$\underline{H}$); ($CDCl_3$) 3.25(s,4H, S-C$\underline{H}_2$), 3.75(d,4H, NH-C$\underline{H}_2$), 6.5-7.4(m, 16H, aromatics), 8.47(s, 2H,N=C$\underline{H}$), 10.04(s,2H, N$\underline{H}$); ^{13}C See Section 4.2.3. (Found: m/e 508.1752. $C_{30}H_{28}N_4S_2$ requires M, 508.1755); m/e 508.1752 (M^+, 23.96), 390.1086(15.66), 356.1035(15.35), 267.0981(21.37), 254.0884(24.69), 241.0752(14.52), 240.0720(63.8), 239.0642(44.92), 236.1176(21.16), 234.1046(11.0), 227.0631(10.68), 222.1017(19.29), 207.0907(14.52), 178.0509(53.94), 151.0637(34.65), 146.0242(100), 136.0205(19.09), 134.0590(19.92), 130.0659(15.25), 124.0222(18.46), 119.0381(18.26), 118.0655(49.69), 117.0574(26.87), 106.0651(11.0), 90.0360(15.15).

5,6,12,13,19,20,25,26,27,28-Decahydrotetrabenzo[e,i,o,s][11,14,1,4,8,17]dithiatetra-azacycloeicosine (4IHe, X=S)

The reduced ligand was prepared as described previously for the N_4O_2 donor set ligands, 4Ia-d. It was found that 0.5 mmol of ligand required 15 mls (15 mmol) of diborane for the complete discharge of the yellow colour of the solution, indicating complete reduction. On evaporation of the THF layer, a pinkish-brown residue was formed, from which a light brown powder separated on adding methanol. This was recrystallised from chloroform/methanol to give 5,6,12,13,19,20,25,26,27,28-decahydrotetrabenzo[e,i,o,s][11,14,1,4,8,17]dithiatetraazacycloeicosine as an off-white powder (0.154g, 60%); m.pt 148-150°C. (Found: C, 69.52; H, 6.44; N, 10.23% $C_{30}H_{32}N_4S_2$ requires C, 70.31; H, 6.25; N, 10.98%). λ_{max} (MeOH) 250 nm (ε =74,000), 305 nm (ε = 13,000); ν_{max} (nujol) 3380 (s,NH), 3340(s,NH), 1610(s), 1590(s), 1510(s), 320(broad,s), 1280, 1270(w), 1240(w), 1230, 1200(w), 1170(s), 1110(s), 1080-1095(s), 1055(w), 1040(s), 985(w), 945(w), 920(w), 880(w), 850(w), 810(w), 755(s, o-substituted benzene) ^1H ($CDCl_3$) 1.55(b.s. 2H.$N\underline{H}$) 2.88(s,4H,S-$C\underline{H}_2$), 3.49(s,4H,$NHC\underline{H}_2$), 4.12(s,4H,$C_6H_5C\underline{H}_2NH$), 4.81(d.2H.$N\underline{H}$), 6.6-7.8(c.16H, aromatics); (C_5D_5N) 2.88(s,4.1 S-$C\underline{H}_2$), 3.54-3.56(b.d,4H,$NHC\underline{H}_2$), 4.35 (b.d. 4H, $C_6H_5C\underline{H}_2NH$), 5.6(b.s. 4H, NH) 6.6-7.4(m, 16H, aromatics); Found m/e 512.2069. $C_{30}H_{32}N_4S_2$ requires M, 512.2068); m/e 512.2069 (M^+, 3.93), 393.1281(12.25), 392.1246(42.51), 381.1317 (10.89), 380.1251(26.63), 241.0797(17.25), 239.0649(4.22), 237.1385 (15.89), 227.0621(2012), 226.0551(11.65), 132.0800(11.95), 11.95), 130.0651(12.71), 124.0218(54.01), 120.0814(48.56), 119.0698(10.29), 118.0665(100), 117.0581(14.67), 106.0662(66.72), 91.0559(47.2)..

5,6,12,13,19,20,25,26,28-Decahydrotetrabenzo[*e*,*i*,*o*,*s*][1,4,8,11,14,17]hexaazacycloeicosine (4IHf, X=NH)

The reduction of the diimine was carried out as described previously, using a solution of diborane in THF to reduce 0.5 mmol of ligand. The residue after evaporation of the THF extract was a light brown friable powder. This was dissolved in CH_2Cl_2, filtered, and the tetraamine precipitated as a fine white powder by the addition of methanol. This product was further purified by conversion to the hydrochloride. The powder was suspended in methanol, and a few drops of concentrated hydrochloric acid were added. The yellow solution resulting was filtered and evaporated to dryness, giving a yellow solid. The acidification step was repeated. The solid after evaporation was washed out of the flask with a methanol/ether mixture, and washed on the filter with ether to give a pale pink solid. This solid was added to a methanol solution containing sufficient Li OH to liberate the free base, assuming all six amine groups to be protonated. An off-white powder was produced. This was filtered, triturated with methanol to remove traces of LiCl, and washed with ether. It was then vacuum-dried for several hours to give 5,6,12,13,19,20,25,26,27,28-decahydrotetrabenzo[*e*,*i*,*o*,*s*][1,4,8,11,14,17]hexaazacycloeicosine as the monohydrate. (0.155g, 65%), m.pt 178-180°C with decomposition. (Found: C, 71.8; H, 7.02; N, 16.43%. $C_{30}H_{36}N_6O$ requires C, 72.5; H, 6.8; N, 16.9%); λ_{max} (MeOH) 254 nm (ε = 51,400), 300 nm (ε =15,000); ν_{max} (nujol)3550(s,broad OH), 3410(s,broad,NH), 3360(s,NH), 1595-1610(s), 1595-1610(s), 1510-1540(s,broad), 1335(s), 1315, 1265(s), 1230, 1170(w), 1140(s), 1100(w), 1060(s), 1030, 950(w), 940, 920, 870, 750(s,broad, o-substituted benzene);

^1H ($CDCl_3$) 3.2-3.3(bd.4H.$NHC\underline{H}_2C\underline{H}_2NH$), 4.07(s.4H.NH $C\underline{H}_2C\underline{H}_2NH$), 4.08(s, 4H, $C_6H_5C\underline{H}_2NH$), 6.80-7.25(m, 16H, aromatics); (C_5D_5N), 3.3(c, 8H NHC_6H_5NH $C\underline{H}_2$, $C_6H_5NHC\underline{H}_2$), 4.3(d, 4H, J=4.0, $C_6H_5C\underline{H}_2NH$), 6.6-7.2(m, 16H, aromatics); Found m/e 478.2844. ($C_{30}H_{34}N_6$ requires M, 478.2844); m/e 478.2844 (M^+, 53.66), 357.2067(10.49), 344.1981(16.10), 253.1395(11.71), 238.1499(18.54), 237.1376(39.02), 224.1190(26.59), 133.0780(23.17), 132.0800(42.4), 130.0638(19.51), 122.0834(27.32), 121.0779(45.61), 120.0809(100), 119.0632(40.73), 118.0638(89.51), 117.0568(13.9), 108.0712(18.29), 106.0665(66.18), 94.0658(14.15), 91.0548(48.54).

4.6.4 Experimental data for the copper complexes of the sexadentate diimines

12,13,25,26,27,28-Hexahydrotetrabenzo[*e*,*i*,*o*,*s*][11,14,1,4,8,17]dioxatetraazacycloeicosine copper(II) diperchlorate dihydrate [Cu(4Ia-enen)]$(ClO_4)_2.2H_2O$ (X=O)

Copper(II) perchlorate (0.13g, 0.5 mmol) was added to a stirred suspension of the ligand 4Ia (0.25g, 0.5 mmol) in methanol. After gently refluxing the mixture for 15 minutes, a pale green solid was formed as the dehydrate (12,13,25,26,27,28-hexahydrotetrabenzo [*e*,*i*,*o*,*s*][11,14,1,4,8,17]dioxatetraazacycloeicosine copper(II) diperchlorate dihydrate (0.23g, 60%). This was washed down with a little ether. (Found: C, 46.3; H, 4.4; N, 7.1; Cu, 8.2%, $C_{30}H_{30}N_4O_{12}Cl_2Cu$ requires C, 46.33; H, 4.40; N, 7.21; Cu, 8.02%); λ_{max} (DMF) 270 nm (ε = 31,500), 340 nm (ε = 9,900), 395 nm (ε = 10,400), 460 nm (ε = 5,900), 550 nm (1200); ν_{max} (nujol) 3200(w,NH), 1620(s, C=N), 1610(s), 1600, 1580(s), 1415(w), 1410, 1325(w), 1310(w), 1290(w), 1270, 1260(w), 1210(s), 1180(w), 1075-1130(s,broad, ClO_4), 1025(s), 1010, 990(w), 970(w), 935(w), 900, 875(s), 860, 800(w), 765(s, o-substituted benzene).

(11,12,13,14,25,26,27,29-Octahydro-29-H-tetrabenzo[*f*,*j*,*p*,*t*][1,5,9,13]tetraazacycloheneicosine)copper(II)diperchlorate tetrahydrate[Cu(4Ib-entn)]$(ClO_4)_2 4H_2O$ (X=0)

Copper(II)diperchlorate (0.13g, 0.5 mmol) was added to a stirred suspension of the ligand 4Ib (0.245g, 0.5 mmol) in methanol. After a few minutes a pale green solid was formed. Some of this material was removed for analysis. The remaining material was gently refluxed for a further fifteen minutes, when it gradually became dark red. This solid was filtered, washed down with methanol and ether, and vacuum-dried to give red crystals of (11,12,13,14,25,26,27,29-octahydro-29-H-tetrabenzo[*f*,*j*,*p*,*t*][1,5,9,13]tetraazacycloheneicosine)copper(II)diperchlorate (0.3g, 77%) (Found: C, 48.2; H, 4.2; N, 7.7; Cu, 8.9%. $C_{31}H_{30}N_4O_8Cl_2Cu$ requires C, 48.25; H, 4.15; N, 7.26; Cu, 8.49%). λ_{max} (DMF) 270 nm (ε = 31,700), 330 nm (ε = 13,800), 380 nm (ε = 11,500), 470 nm (ε = 5,200), 500 nm (ε = 3,000); ν_{max} (nujol), 3300(w, NH), 1660(w), 1620(s), 1600, 1580(s), 1530, 1500(s), 1470(s), 1340, 1310, 1280(w), 1310(w), 1280(w), 1250(s), 1220, 1180, 1165(s), 1130-1050 (s,broad, ClO_4), 980, 935(s), 900(s), 850(w), 750(s, o-substituted benzene). Green salt; (Found C, 44.3; H, 4.2; N, 6.7; Cu, 8.1%. $C_{31}H_{38}N_4O_{12}Cl_2Cu$ requires C, 45.09; H, 4.61; N, 6.72; Cu, 7.75%). ν_{max} (nujol) 3450(w, OH), 3300(w, NH), 1630(s), 1600(sh), 1580(s), 1480(s), 1420(s), 1410(s), 1360(s), 1320, 1290(w), 1270(s), 1250, 1220(s), 1180, 1170, 1130-1030(s, broad, ClO_4), 1010, 990, 960, 940, 920, 900(s), 850(s), 840, 810(s), 805, 790(sh), 770-750(s, broad, o-substituted benzene).

(11,12,13,14,26,27,28,29-Octahydro-15,29-2*H*-tetrabenzo[*f*,*j*,*q*,*u*][1,5,9,19]tetraazacyclodocosane)copper(II)diperchlorate [Cu(4Ic-tntn)](ClO$_4$)$_2$ (X=O)

Copper(II)diperchlorate (0.13g, 0.5 mmol) was added to a stirred suspension of the ligand 4Ic (0.252g, 0.5 mmol) in methanol. After a few minutes a pale green solid was formed, which almost immediately began to turn red-brown. The change was complete after a few minutes gentle refluxing. The red solid was filtered, washed with methanol and ether and vacuum-dried to give red crystals of (11,12,13,14,26,27,28,29-octahydro-15,29-2*H*-tetrabenzo[*f*,*j*,*q*,*u*][1,5,9,19]tetraazacyclodocosane)copperIIdiperchlorate (0.3g, 78%). (Found: C, 51.0; H, 4.3; N, 7.4; Cu, 8.1%. $C_{32}H_{32}N_4O_{10}Cl_2Cu$ requires C, 50.06; H, 4.17; N, 7.30; Cu, 8.34%). λ_{max} (DMF) 270 nm (ε =51,500) 330 nm (ε = 25,400), 380 nm (ε = 24,200), 480 nm (ε = 9,600), 510 nm (ε = 8,800); ν_{max} (nujol) 3300(w, NH), 1630(s), 1600, 1580, 1560, 1530, 1500(s), 1470(s), 1310(s), 1280(s), 1255(s), 1230, 1170(s), 1150-1050(s, broad, ClO$_4$), 980, 935, 880, 860, 760(s, broad, o-substituted benzene).

(11,12,13,14,26,27,28,29-Octahydro-15-*H*-tetrabenzo[*e*,*i*,*p*,*t*][1,4,8,18]tetraazacycloheneicosine)copper(II) diperchlorate dihydrate [Cu(4Id-tnen)]$(ClO_4)_2$ $2H_2O$ X=O

CopperII diperchlorate (0.13g, 0.5 mmol) was added to a stirred suspension of the ligand 4Id (0.245g, 0.5 mmol) in methanol. A pale green solid was formed, which did not change colour on refluxing. The solid was filtered, washed with a little methanol and ether and vacuum-dried to give green crystals of (11,12,13,14,26,27,28,29-octahydro-15-*H*-tetrabenzo[*e*,*i*,*p*,*t*][1,4,8,18]tetraazacycloheneicosine)copper(II) diperchlorate dihydrate (0.35g, 88%). (Found: C, 47.2; H, 4.8; N, 7.0; Cu, 7.9%. $C_{31}H_{34}N_4O_{12}Cl_2Cu$ requires C, 47.12; H, 4.30; N, 7.09; Cu, 8.10%). λ_{max} (DMF) 270 nm (ε = 18,800), 330 nm (ε = 9,800), 400 nm (ε = 11,300), 475 nm (ε = 8,900), 540 nm (ε = 900); ν_{max} (nujol), 3450(broad, OH), 3300, 3200(w, NH), 1620(s), 1600, 1580(s), 1500(s), 1470(s), 1410(w), 1325(w), 1310, 1290(w), 1260, 1250(w), 1220(s), 1170-1050 (s, broad, ClO_4), 955(s), 930(s), 900(s), 875, 860(w), 780(s), 765(s, o-substituted benzene), 745(w), 730.

(12,13,25,26,27,28-Hexahydrotetrabenzo [*e*,*i*,*o*,*s*][11,14,1,4,8,17] dithiatetraazacycloeicosine)copper(II)diperchlorate[Cu(4Ie)] $(ClO_4)_2$. (X=S)

Copper(II) perchlorate (0.13g, 0.5 mmol) was added to a suspension of the ligand (0.25g, 0.5 mmol) in methanol. On refluxing gently, (12,13,25,26,27,28-hexahydrotetrabenzo[*e*,*i*,*o*,*s*][11,14,1,4,8,17] dithiatetraazacycloeicosine)copper(II) diperchlorate was obtained as red crystals. (0.3g, 78%). (Found: C, 46.83; H, 4.33; N, 7.55; Cu, 8.3% . $C_{30}H_{28}N_4O_8S_2Cl_2Cu$ requires C, 46.69; H, 3.63; N, 7.26; Cu, 8.3%). λ_{max} (DMF) 273 nm (ε = 34,600), 410 nm (ε = 6,300), 515 nm (ε = 8,500); ν_{max} (nujol) 3280(b, NH), 3240(b, NH), 1605(s), 1570(s), 1420, 1405(w), 325(w), 1295(w), 1280, 1270, 1215(w), 1190, 1170, 1050-1130(s, broad, ClO_4), 1000, 970, 930, 900(w), 880, 840(w), 770(s, o-substituted benzene), 725(w), When the red salt (0.18g, 0.25 mmol) was refluxed in methanol (10 cm^3) containing molar perchloric acid (5 cm^3, 5 mmol) a green salt, the protonated tetraperchlorate, was formed. (Found: C, 36.8; H, 3.1; N, 6.1%. $C_{30}H_{30}N_4O_{16}S_2Cl_4$ requires C, 37.11; H, 3.09; N, 5.77%).

(12,13,25,26,27,28-Hexahydrotetrabenzo[*e*,*i*,*o*,*s*][1,4,8,11,14,17]hexaazacycloeicosine)copper(II)diperchlorate[Cu(4If)]$(ClO_4)_2$

(X=NH)

Copper(II) perchlorate (0.13g, 0.5 mmol) was added to a methanol suspension of diimine ligand 4If (0.23g, 0.5 mmol) under nitrogen, and the mixture refluxed gently to give a red perchlorate salt. (Found: C, 48.2; H, 4.2; N, 10.9; Cu, 8.3%. $C_{30}H_{30}N_6O_8Cl_2Cu$ requires C, 48.71; H, 4.33; N, 10.94; Cu, 8.32%); λ_{max} (DMF) 275 nm (ε = 32,500), 420 nm (ε = 8,000), 500 nm (ε = 6,100); ν_{max} (nujol); 3400-3500(w, broad OH), 3230(s, broad NH), 3250(s, broad NH), 1615-1625(s, broad), 1600(s), 1580(s), 1500, 1430, 1320(w), 1305, 1290, 1280, 1215(s), 1185(w), 1170(w), 1030-1140(s, broad ClO_4), 990(w), 930-950(s, broad), 900, 890(w), 860(w), 845(w), 830(w), 810, 765(s, o-substituted benzene), 730(w). When the red diperchlorate salt (0.16g, 0.25 mmol) was refluxed in methanol (10 cm^3) containing molar perchloric acid (5 cm^3, 5 mmol) a green salt, the protonated tetraperchlorate, was formed. (Found: C, 40.0; H, 3.4; N, 9.3%. $C_{30}H_{32}N_6O_{16}Cl_4Cu$ requires C, 38.37; H, 3.41; N, 8.95%).

4.6.5 Experimental data on the copper complexes of the reduced sexadentate ligands

(5,6,12,13,19,20,25,26,27,28-Decahydrotetra[*e*,*i*,*o*,*s*][1,14,1,4,8,17]dioxatetraazacycloeicosine)copper(II) diperchlorate [Cu(4IHa-enen)]$(ClO_4)_2$

Copper(II) perchlorate (0.13g, 0.5 mmol) was added to a stirred suspension of the ligand 4IHa (0.25g, 0.5 mmol) methanol, under N_2 and with gentle refluxing. The dark brown crystals were washed with methanol and ether to give (5,6,12,13,19,20,25,26,27,28-deca hydrotetra[*e*,*i*,*o*,*s*][11,14,1,4,8,17]dioxatetraazacycloeicosine) copper(II) diperchlorate (0.30g, 80%). (Found: C, 48.30; H, 3.80; N, 7.3; Cu, 7.3% ; $C_{30}H_{28}N_4O_{10}ClCu$ requires C, 48.29; H, 3.79; N, 7.3; Cu, 7.6%); λ_{max} (DMF) 272 nm (ε = 11,600); 375 nm (ε = 3,600), 455 (ε = 1,500); ν_{max} (nujol) 3200(w, NH), 1620(s), 1610(s), 1600(s), 1600(m), 1580(s), 1500, 1415(w), 1410, 1325(w), 1310(w), 1290(w), 1270, 1260(w), 1210(w), 1210(s), 1180(w), 1075-1130(s, broad, ClO_4), 1025(s), 1010, 990(w), 970(w), 900, 875(w), 860, 800, 765(s, o-substituted benzene.) Formation of the copper complex by dissolving the ligand in DMF, cooling with liquid N_2 and allowing copper perchlorate in methanol to mix gradually gave large dark brown crystals of bis(dimethylformamide)(5,6,12,13,19,20,25,26,27,28-decahydrotetra[*e*,*i*,*o*,*s*][11,14,1,4,8,17]dioxatetraazacycloeicosine)copper(II) diperchlorate DMF monohydrate. The structure of this compound was investigated by X-ray crystallography; crystal data in Appendix C.

(5,6,11,12,13,14,18,19,25,26,27,28-Dodecahydro-29-*H*-tetrabenzo[*f*,*j*,*p*,*t*][1,5,9,13]tetraazacycloheneicosine)copper(II) diperchlorate [Cu(4IHb-entn)](ClO_4)$_2$

Copper(II) diperchlorate (0.13g, 0.5 mmol) was added to a stirred suspension of the ligand 4IHb (0.247g, 0.5 mmol) in methanol and gently refluxed under nitrogen. The dark brown crystals were filtered, and washed with a little methanol and ether to give (5,6,11,12,13,14,18,19,25,26,27,28-dodecahydro-29-*H*-tetrabenzo [*f*,*j*,*p*,*t*][1,5,9,13]tetraazacycloheneicosine)copper(II) diperchlorate hydrate (0.31g, 82%). (Found: C, 49.2; H, 4.12; N, 6.9; Cu, 8.8%. $C_{31}H_{36}N_4O_{11}Cl_2Cu$ requires C, 49.14; H, 4.49; N, 7.39; Cu, 8.25%); λ_{max} (DMF) 270 nm (ε = 13,800), 290 nm (ε = 12,000), 380 nm (ε = 3,600), 445 nm (ε = 1,500); ν_{max} (nujol) 3550(s, broad OH), 3260(s, NH), 1625(s), 1610(s), 1520(s), 1470(s), 1420, 1350(s), 1300(s), 1270(s), 1260(s), 1220(s), 1190(s), 1150-1030 (s, broad, ClO_4), 950, 930(s), 865(s), 830(s), 810(s), 770-750(s, broad, o-substituted benzene).

(5,6,11,12,13,14,19,21,26,27,28,29-Dodecahydro-15,29-2*H*-tetrabenzo[*f*,*j*,*q*,*u*][1,5,9,19]tetraazacyclodocosane)copper(II) diperchlorate[Cu(4IHc-tntn)]$(ClO_4)_2$

Copper(II) diperchlorate (0.13g, 0.5 mmol) was added to a stirred suspension of the ligand 4IHc (0.247g, 0.5 mmol) in methanol and gently refluxed under nitrogen. The dark brown crystals formed were filtered and washed with methanol and ether to give (5,6,11,12,13,14,19,21,26,27,28,29-dodecahydro-15,29-2*H*-tetrabenzo[*f*,*j*,*q*,*u*][1,5,9,19]tetraazacyclodocosane)copper(II) diperchlorate (0.3g, 78.9%). (Found: C, 49.3; H, 4.7; N, 7.2; Cu, 8.6%. $C_{32}H_{32}N_4O_{10}Cl_2Cu$ requires C, 49.80; H, 4.15; N, 7.26; Cu, 8.30%); λ_{max} (DMF) 270 nm (ε = 18,900), 300 nm (ε = 17,100), 390 nm (ε = 2,200), 460 nm (ε = 1,300); ν_{max} (nujol). 3200(s, NH), 1670(s), 1610(s), 1510(s), 1470(s), 1360, 1300(s), 1250(s, broad), 1190, 1150-1050(s, broad, ClO_4), 990, 950, 935, 880(s), 860(s), 790, 770-750(s, broad, o-substituted benzene).

(5,6,11,12,13,14,20,21,26,27,28,29-Dodeca-15-H-tetrabenzo[*e*,*i*,*p*,*t*][1,4,8,18]tetraazacycloheneicosine)copper(II) diperchlorate[Cu(4IHd-tnen)]$(ClO_4)_2$

Copper(II) diperchlorate (0.13g, 0.5 mmol) was added to a stirred suspension of the ligand 4IHd (0.247g, 0.5 mmol) in methanol and gently refluxed under nitrogen. The brown crystals formed were filtered and washed with methanol and ether to give (5,6,11,12,13,14,20,21,26,27,28,29-dodeca-15-*H*-tetrabenzo[*e*,*i*,*p*,*t*][1,4,8,18]tetraazacycloheneicosine)copper(II) diperchlorate dihydrate (0.3g, 77%). (Found: C, 47.16; H, 5.02; N, 6.8; Cu, 8.48%. $C_{31}H_{38}N_4O_{12}Cl_2Cu$ requires C, 46.90; H, 4.79; N, 7.06; Cu, 8.07%); λ_{max} (DMF) 270 nm (ε = 14,700), 295 nm (ε = 14,600), 385 nm (ε = 1,400), 455 nm (ε = 1,000); ν_{max} (nujol) 3500(s, OH), 3240(s, NH), 1660(sh), 1610(s), 1510(s), 1470(s), 1350(w), 1315(s), 1300(s), 1250(s, broad), 1220(s), 1195(s), 1150-1030(s, broad, ClO_4), 975(s), 930(s), 885, 850, 835(s), 795(w), 760(s, broad, o-substituted benzene.

(5,6,12,13,19,20,25,26,27,28-Decahydrotetrabenzo[*e*,*i*,*o*,*s*][11,14,1,4,8,17]dithiatetraazacycloeicosine)copper(II) diperchlorate (Cu[4IHe](ClO_4)$_2$)

Copper(II) perchlorate (0.13g, 0.5 mmol) was added to a stirred suspension of the ligand 4IHe (0.206g, 0.5 mmol) in methanol under nitrogen. After a few minutes (5,6,12,13,19,20,25,26,27,28-Decahydrotetrabenzo[*e*,*i*,*o*,*s*][11,14,1,8,17]dithiatetraazacycloeicosine)copper(II) diperchlorate was formed as dark green microcrystals (0.5g, 70%). Found: C, 45.83; H, 4.33; N, 7.39; Cu, 9.0%. $C_{30}H_{32}H_4O_8S_2Cl_2Cu$ requires C, 45.85; H, 4.07; N, 7.2; Cu, 8.25%); λ_{max} (DMF) 272 nm (ε = 31,500), 310 nm (ε = 27,500), 505 nm (ε = 7,100); ν_{max} (nujol) 3215(s, NH), 3190(s, NH), 1615, 1595, 1500, 1350, 1280, 1250, 1235, 1200, 1050-1130(broad, ClO_4), 1000, 975, 925, 880(w), 860(w), 835(w), 800(w), 770(s, o-substituted benzene), 730.

(5,6,12,13,19,20,25,26,27,28-Decahydrotetrabenzo[*e*,*i*,*o*,*s*][1,4,8,11,14,17]hexaazacycloeicosine)copper(II)diperchlorate [Cu(4IHf)]$(ClO_4)_2$

The complex was formed at room temperature to avoid the possible copper catalysed oxidation of the hexamine. Copper perchlorate (0.13g, 0.5 mmol) was added to a suspension of the ligand (0.23 g, 0.5 mmol) stirred in methanol under nitrogen. The copper perchlorate complex was formed as a brown powder, (0.26g, 70%). (Found: C, 49.19; H, 4.43; N, 11.02; Cu, 8.9%); $C_{30}H_{34}N_6O_8Cl_2Cu$ requires C, 48.5; H, 4.5; N, 11.33; Cu, 8.43%; λ_{max} (DMF) 275 nm (ε = 45,900), 390 nm (ε = 8,000), 480 nm (ε = 6,500); ν_{max} (nujol) 3260(s, broad NH), 1620(s), 1595(w), 1515(w), 1310(w), 1300, 1250, 1230(w), 1195(w), 1050-1150(s, broad, ClO_4), 1050-1150(s), 985, 935(w), 915, 900, 850(w), 750-780(s, broad, o-substituted benzene).

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APPENDICES (A-D)

Intensities were collected on a Phillips PW 1100 four-circle diffractometer operating in the θ-2θ scan mode using graphite-monochromated Mo-Kα radiation. The details of data collection and refinement are summarised in Tables 1A-1C in the Appendices. Background measurements were made at the extremities of the scan using a counting time proportional to Ib/Ii where Ib was the mean of two 5-s background measurements on either side of the peak. The standard deviation of the intensity (I) was calculated as $[\sigma c[I^2]+(0.04I)^2]^{\frac{1}{2}}$ where σc was the standard deviation. I and $\sigma[I]$ were corrected for Lorenz and polarisation factors with the use of a programme written for the PW 1100 diffractometer, and equivalent reflections were averaged giving the total number of reflections as recorded in Tables 1A-1C with $I/\sigma[I] \geq 3$

APPENDIX A

$[Cu(C_{25}H_{30}N_4)DMF](ClO_4)_2DMF$

Table 1A

Formula $[Cu(C_{25}H_{30}N_4)\,DMF](ClO_4)_2DMF$

M	867.5
Crystal system	Monoclinic
Space group	$P2_1/C$
a/A^o	19.806
b/A^o	11.422
c/A^o	16.401
α o	90
β o	95.255
γ o	90
V, A^{o3}	3694.71
Z	4
$D/g\ cm^{-3}$	1.5
F (000)	1659.96
Crystal dimensions	0.4 x 0.3 x 0.2
Reflections measured	2115
Unique reflections	2022
Scan width (w)°	1.0
Scan speed/°s^{-1}	0.05
θ range	$3 \leqslant \theta \leqslant 25$
$R = \Sigma \| \|Fo\| - \|Fc\| \| / \Sigma \|F_o\|$	0.0716
$R' = [\Sigma w(\|Fo\|-\|Fc\|)^2 / \Sigma w\|Fo\|^2]^{\frac{1}{2}}$	0.0671
Final no. of variables	263+
Average shift to error	0.007
Maximum shift to error*	0.216
$I/\sigma(I)$	$\geqslant 3$

Table 2A Final atomic parameters for [$Cu(C_{25}H_{30}N_4)DMF$][ClO_4]$_2$.2DMF. Fractional coordinates and isotropic thermal parameters ($^{o}A^2$) with estimated standard deviations in parenthesis

	x	y	2(x10^{4})	Ux10^{2}
Cu	7845(1)	6896(1)	4273(1)	†
N(1a)	8594(5)	7734(8)	4969(6)	4.1(3)
N(2a)	7800(5)	8215(9)	3404(5)	3.9(3)
C(1c)	7340(6)	6927(12)	2213(8)	5.4(4)
C(1a)	7907(6)	7768(12)	2556(8)	5.5(4)
C(2a)	8199(6)	9232(11)	3565(7)	3.9(3)
C(3a)	7936(7)	252(13)	3181(9)	6.4(5)
C(4a)	8306(7)	1301(13)	3200(9)	6.2(4)
C(5a)	8941(7)	1313(13)	3645(8)	5.9(4)
C(6a)	9189(7)	343(12)	4030(8)	5.3(4)
C(7a)	8821(6)	9254(11)	4006(7)	3.7(3)
C(8a)	9124(6)	8271(11)	4494(7)	4.5(4)
C(9a)	8871(6)	6903(12)	5614(7)	4.2(3)

	x	y	Z(x10^4)	Ux10^2
C(10a)	9386(6)	7269(12)	6203(8)	5.0(4)
C(11a)	9646(7)	6475(11)	6775(9)	5.6(4)
C(MEA)	9468(6)	7328(12)	4002(8)	5.8(4)
N(1b)	8034(5)	5547(8)	5043(6)	3.6(3)
N(2b)	7146(5)	5959(9)	3537(6)	4.5(3)
C(1b)	7308(7)	5814(13)	2684(8)	6.3(4)
C(2b)	6931(7)	4799(12)	3827(8)	4.4(4)
C(3b)	6257(7)	4483(14)	3592(9)	6.8(5)
C(4b)	6039(8)	3363(15)	3768(9)	8.3(5)
C(5b)	6470(9)	2615(18)	4174(11)	10.5(6)
C(6b)	7142(8)	2957(15)	4429(9)	8.1(5)
C(7b)	7358(6)	4057(12)	4263(8)	4.8(4)
C(8b)	8067(6)	4389(12)	4624(8)	5.3(4)
C(9b)	8613(6)	5832(11)	5626(7)	3.9(3)
C(10b)	8888(7)	4998(13)	6204(8)	5.7(4)
C(11b)	9411(7)	5328(13)	6778(9)	6.0(4)
C(MEB)	8610(7)	4419(13)	4038(8)	6.5(5)
N(1s)	6181(8)	8565(14)	5461(9)	8.0(4)

	x	y	Z(x10^4)	Ux10^2
O(1s)	7083(6)	7768(10)	4963(7)	7.3(4)
C(1s)	6615(14)	7784(28)	5185(12)	15.6(23)
C(2s)	6305(12)	9811(21)	5491(12)	21.1(24)
C(3s)	5560(11)	8322(25)	5710(15)	10.7(16)
Cl(2)	5745(3)	8658(5)	3118(3)	†
O(21)	5286(7)	9108(12)	3602(10)	†
O(22)	6362(6)	9240(12)	3205(8)	†
O(23)	5477(8)	8704(15)	2314(9)	†
O(24)	5869(6)	7507(15)	3356(10)	†
•Cl(1)	8606(2)	4159(4)	1278(3)	†
^{x}O(11A)	8132	4984	890	12.9(6)
O(12A)	8580	3175	790	12.9(6)
O(13A)	9268	4480	1175	12.9(6)
O(14A)	8602	3876	2050	12.9(6)
O(11B)	8942	4861	2020	12.9(6)
O(12B)	8044	3511	1666	12.9(6)
O(13B)	9090	3682	679	12.9(6)
O(14B)	8387	5417	1088	12.9(6)
O(11C)	8397	3141	1608	12.9(6)
O(12C)	8797	5198	881	12.9(6)
O(13C)	7947	4074	1179	12.9(6)
O(2s)	7024(7)	-70(13)	1104(8)	10.8(5)

	x	y	Z(x10^4)	Ux10^2
O(1s)	7083(6)	7768(10)	4963(7)	7.3(4)
C(1s)	6615(14)	7784(28)	5185(12)	15.6(23)
C(2s)	6305(12)	9811(21)	5491(12)	21.1(24)
C(3s)	5560(11)	8322(25)	5710(15)	10.7(16)
Cl(2)	5745(3)	8658(5)	3118(3)	†
O(21)	5286(7)	9108(12)	3602(10)	†
O(22)	6362(6)	9240(12)	3205(8)	†
O(23)	5477(8)	8704(15)	2314(9)	†
O(24)	5869(6)	7507(15)	3356(10)	†
•Cl(1)	8606(2)	4159(4)	1278(3)	†
^{x}O(11A)	8132	4984	890	12.9(6)
O(12A)	8580	3175	790	12.9(6)
O(13A)	9268	4480	1175	12.9(6)
O(14A)	8602	3876	2050	12.9(6)
O(11B)	8942	4861	2020	12.9(6)
O(12B)	8044	3511	1666	12.9(6)
O(13B)	9090	3682	679	12.9(6)
O(14B)	8387	5417	1088	12.9(6)
O(11C)	8397	3141	1608	12.9(6)
O(12C)	8797	5198	881	12.9(6)
O(13C)	7947	4074	1179	12.9(6)
O(2s)	7024(7)	-70(13)	1104(8)	10.8(5)

N(2s)	6312(9)	1263(16)	1405(10)	10.1(5)
† C(2sA)	6965(25)	863(51)	1245(29)	13.3(17)
C(3sA)	6432(37)	2279(62)	1837(40)	19.6(3)
C(4sA)	5617(25)	982(46)	1148(30)	14.8(17)
C(2sB)	6456(19)	258(33)	1092(20)	7.6(10)
C(3sB)	6884(26)	2114(47)	1707(30)	13.4(18)
C(4sB)	5672(22)	1950(43)	1569(27)	12.6(14)

*This perchlorate shows complex disorder. The model used for refinement has three superimposed sets of oxygen atoms with suffixes A, B, C in the table above. The main site has mean site occupation factors as follows [O(11A); 0.683, O(12A); 0.603, O(13A); 0.641, O(14A); 0.636.] Site occupation factors of the subsidiary site are as follows [O(11B); 0.328, O(12B); 0.30, O(13B); 0.296, O(14B); 0.290.] The minor site has site occupation factors as follows [O(11C); 0.07, O(12C); 0.055, O(13C); 0.062,]

†These atoms have site occupation factors = 0.5 corresponding to disorder of the DMF molecule which has a pseudo 2-fold rotation axis passing through O(2s) and N(2s).

ˣThese atoms have fixed thermal parameter

‡These atoms have anisotropic thermal parameters - see Table 3A

Table 3A Anisotropic thermal parameters ($^{o}A^{2}$) For $[Cu(C_{25}H_{30}N_{4})DMF][ClO_{4}]_{2}.DMF$

Atom	U11	U22	U33	U12	U13	U23
Cu	0.037(1)	0.041(1)	0.037(1)	-0.003(1)	0.001(1)	-0.001(1)
Cl(2)	0.053(3)	0.096(4)	0.008(4)	0.014(3)	0.009(3)	0.002(3)
O(21)	0.098(9)	0.133(13)	0.231(17)	0.037(9)	0.077(11)	0.027(12)
O(22)	0.066(8)	0.148(12)	0.129(11)	-0.004(8)	-0.004(8)	0.020(10)
O(23)	0.178(14)	0.230(19)	0.113(12)	-0.021(13)	-0.083(11)	0.002(12)
O(24)	0.082(10)	0.131(12)	0.189(15)	-0.006(12)	0.024(9)	0.006(9)
C(1s)	0.156(23)	0.326(38)	0.056(14)	0.123(25)	-0.039(15)	-0.027(18)
C(2s)	0.211(24)	0.136(21)	0.097(17)	0.005(18)	-0.055(17)	0.001(15)
C(3s)	0.107(16)	0.245(31)	0.176(23)	0.018(19)	0.032(16)	0.093(23)

C(3a)-C(2a)-C(7a)	120.1(12)	C(3b)-C(2b)-C(7b)	121.1(13)
			89.5(4)
C(2a)-C(3a)-C(4a)	121.9(13)	C(2b)-C(3b)-C(4b)	119.0(15)
C(3a)-C(4a)-C(5a)	117.5(14)	C(3b)-C(4b)-C(5b)	119.7(17)
C(4a)-C(5a)-C(6a)	120.7(14)	C(4b)-C(5b)-C(6b)	120.6(19)
C(5a)-C(6a)-C(7a)	122.4(13)	C(5b)-C(6b)-C(7b)	120.1(17)
C(6a)-C(7a)-C(2a)	117.3(12)	C(6b)-C(7b)-C(2b)	119.4(14)
C(6a)-C(7a)-C(8a)	117.6(11)	C(6b)-C(7b)-C(8b)	116.6(13)
C(2a)-C(7a)-C(8a)	125.0(11)	C(2b)-C(7b)-C(8b)	124.0(13)
C(7a)-C(8a)-C(MEA)	115.2(10)	C(7b)-C(8b)-C(MEB)	116.4(11)
C(7a)-C(8a)-N(1a)	109.0(9)	C(7b)-C(8b)-N(1b)	108.7(10)
C(MEA)-C(8a)-N(1a)	110.5(10)	C(MEB)-C(8b)-N(1b)	109.7(11)
C(8a)-N(1a)-C(9a)	113.7(9)	C(8b)-N(1b)-C(9b)	115.6(9)
C(8a)-N(1a)-Cu	114.4(7)	C(8b)-N(1b)-Cu	113.8(8)

Table 4A

Interatomic Bond Lengths and Angles

Cu-N(1a)	2.028(9)	Cu-N(1b)	2.007(9)
Cu-N(2a)	2.069(9)	Cu-N(2b)	2.052(10)
Cu-O(1s)	2.205(12)	-	-
C(1c)-C(1a)	1.544(16)	C(1c)-C(1b)	1.492(18)
C(1a)-N(2a)	1.515(14)	C(1b)-N(2b)	1.473(10)
N(2a)-C(2a)	1.417(14)	N(2b)-C(2b)	1.484(15)
C(2a)-C(3a)	1.402(17)	C(2b)-C(3b)	1.403(16)
C(3a)-C(4a)	1.403(17)	C(3b)-C(4b)	1.389(20)
C(4a)-C(5a)	1.396(17)	C(4b)-C(5b)	1.341(20)
C(5a)-C(6a)	1.346(16)	C(5b)-C(6b)	1.413(19)
C(6a)-C(7a)	1.440(16)	C(6b)-C(7b)	1.362(19)
C(7a)-C(8a)	1.474(16)	C(7b)-C(8b)	1.522(16)
C(8a)-C(MEA)	1.541(16)	C(8b)-C(MEB)	1.507(16)
C(8a)-N(1a)	1.495(13)	C(8b)-N(1b)	1.495(15)

N(1a)-C(9a)	1.489(14)	N(1b)-C(9b)	1.461(13)
C(9a)-C(10a)	1.403(15)	C(9b)-C(10b)	1.417(16)
C(10a)-C(11a)	1.370(16)	C(10b)-C(11b)	1.387(16)
C(11a)-C(11b)	1.391(17)	C(9b)-C(9a)	1.327(16)
N(1a)-Cu-N(2a)	91.6(4)	N(1b)-Cu-N(2b)	92.7(4)
N(1a)-Cu-O(1s)	89.9(4)	N(1b)-Cu-O(1s)	96.9(4)
N(2a)-Cu-O(1s)	92.1(4)	N(2b)-Cu-O(1s)	94.7(4)
N(1a)-Cu-N(2b)	175.3(4)	N(1b)-Cu-N(2a)	170.5(4)
N(1a)-Cu-N(1b)	85.6(4)	N(2b)-Cu-N(2a)	89.5(4)
-	-	C(1b)-C(1c)-C(1a)	113.9(11)
C(1c)-C(1a)-N(2a)	112.7(10)	C(1c)-C(1b)-N(2b)	114.8(12)
C(1a)-N(2a)-C(2a)	108.9(9)	C(1b)-N(2b)-C(2b)	107.3(1)
C(1a)-N(2a)-Cu	112.7(8)	C(1b)-N(2b)-Cu	115.1(8)
C(2a)-N(2a)-Cu	118.7(7)	C(2b)-N(2b)-Cu	118.4(8)
N(2a)-C(2a)-C(3a)	114.8(11)	N(2b)-C(2b)-C(3b)	115.8(12)
N(2a)-C(2a)-C(7a)	125.0(11)	N(2b)-C(2b)-C(3b)	123.0(12)

C(9a)-N(1a)-Cu	107.6(7)	C(9b)-N(1b)-Cu	109.3(7)
N(1a)-C(9a)-C(10a)	119.8(12)	N(1b)-C(9b)-C(10b)	121.2(11)
N(1a)-C(9a)-C(9b)	118.7(11)	N(1b)-C(9b)-C(9a)	118.5(11)
C(10a)-C(9a)-C(9b)	121.5(12)	C(10b)-C(9b)-C(9a)	120.3(12)
C(9a)-C(10a)-C(11a)	118.6(13)	C(9b)-C(10b)-C(11b)	119.2(14)
C(10a)-C(11a)-C(11b)	121.4(13)	C(10b)-C(11b)-C(11a)	118.9(14)

Table 5A Interatomic bond lengths and angles in the co-ordinated solvent molecule

O(1s)-C(1s)	1.027(26)
C(1s1)-N(1s)	1.345(25)
N(1s)-C(2s1)	1.443(24)
N(1s)-C(3s1)	1.359(21)
Cu-O(1s)-C(1s1)	150.8(21)
O(s1)-C(1s1)-N(1s)	139.1(34)
C(1s1)-N(1s)-C(2s1)	123.6(22)
C(1s1)-N(1s)-C(3s1)	126.0(23)
C(2s1)-N(1s)-C(3s1)	110.3(21)

APPENDIX B

$[Cu(C_{34}H_{22}N_4O_2)]$ DMF

Table IB

Formula	$[Cu(C_{34}H_{22}N_4O_2)]$ DMF
M	654.5
Crystal system	Triclinic
Space group	$P\bar{1}$
$a/Å$	9.072(2)
$b/Å$	11.049(4)
$c/Å$	16.873(5)
α°	78.82(3)
β°	102.77(3)
γ°	107.78(3)
$V, Å^3$	1556.02
Z	2
$D/g\ cm^{-3}$	1.5
F(000)	677.98
Crystal dimensions	0.5 x 0.4 x 0.2
Reflections measured	2362
Unique reflections	2283
Scan width $(w)^\circ$	1.0
Scan speed$/^\circ s^{-1}$	0.05
θ range	$3 \leqslant \theta \leqslant 25$
$R = \Sigma\|\|F_o\| - \|F_c\|\| / \Sigma\|F_o\|$	0.082
$R' = [\Sigma w(\|F_o\| - \|F_c\|)^2 / \Sigma w\|F_o\|^2]^{\frac{1}{2}}$	0.079
Final no of variables	346
Average shift to error	0.004
Maximum shift to error	0.169
$I/\sigma(I)$	$\geqslant 3$

Table 2B Final atomic parameters for Cu$[C_{34}H_{22}N_4O_2]$.DMF

Fractional coordinates and isotropic thermal parameters ($^{o}A^2$) with estimated standard deviations in parenthesis

	x	y	Z(x10^4)	Ux10^2
Cu	1206(2)	1023(1)	2695(1)	
N(1a)	324(10)	-293(8)	1991(5)	
N(2a)	1038(10)	2341(7)	1775(5)	
O(1a)	2545(8)	4396(7)	1411(5)	
C(1a)	2151(12)	3443(10)	1914(7)	3.2(3)
C(2a)	-201(13)	2166(10)	1102(7)	3.9(3)
C(3a)	-595(13)	3248(10)	615(7)	4.2(3)
C(4a)	-1941(14)	3091(12)	11(7)	5.5(3)
C(5a)	-2900(14)	1882(11)	115(7)	5.2(3)
C(6a)	-2495(13)	807(11)	340(7)	4.8(3)
C(7a)	-1178(12)	925(9)	954(6)	3.2(3)
C(8a)	-854(13)	-306(10)	1381(7)	3.8(3)
C(9a)	932(12)	-1413(10)	2371(7)	3.7(3)
C(10a)	954(13)	-2307(10)	1892(7)	4.8(3)
C(11a)	1766(15)	-3238(12)	2258(8)	6.4(4)
C(12a)	-1968(12)	-1541(10)	1136(6)	3.2(3)
C(13a)	-2084(13)	-1920(10)	393(7)	4.5(3)
C(14a)	-3098(14)	-3116(11)	226(8)	5.6(4)
C(15a)	-3997(14)	-3837(11)	787(7)	5.2(4)
C(16a)	-3956(14)	-3467(11)	1524(8)	5.4(4)
C(17a)	-2889(12)	-2281(10)	1708(7)	3.8(3)

	x	y	Z(x10^4)	Ux10^2
C(1b)	3018(13)	3475(11)	2818(7)	3.2(3)
C(2b)	2794(12)	2256(10)	4151(7)	3.4(3)
C(3b)	3385(13)	3304(11)	4596(7)	4.3(3)
C(4b)	3614(14)	3230(12)	5441(8)	5.2(4)
C(5b)	3244(13)	2015(11)	5895(8)	5.2(4)
C(6b)	2655(13)	929(11)	5511(7)	4.5(3)
C(7b)	2483(12)	972(10)	4654(7)	3.3(5)
C(8b)	2069(12)	-234(10)	4317(7)	3.1(3)
C(9b)	1670(13)	-1384(11)	3156(7)	4.2(3)
C(10b)	2535(13)	-2315(11)	3522(8)	5.0(3)
C(11b)	2533(15)	-3202(12)	3050(8)	6.6(4)
C(12b)	1981(13)	-1426(10)	4927(7)	3.9(3)
C(13b)	3373(14)	-1656(11)	5483(7)	4.8(3)
C(14b)	3246(16)	-2823(12)	5973(8)	5.8(4)
C(15b)	1870(16)	-3743(13)	5969(8)	6.7(4)
C(16b)	502(16)	-3529(12)	5466(8)	6.3(4)
C(17b)	599(14)	-2390(11)	4934(7)	5.1(4)

	x	y	Z (x10^2)
N(1b)	1786(10)	-332(7)	3561(6)
N(2b)	2458(10)	2336(8)	3333(5)
O(1b)	4045(8)	4435(6)	2992(5)
N(1s)	-3480(17)	1735(13)	2187(7)
O(1s)	-1602(10)	751(8)	2846(6)
C(1s)	-1999(19)	1708(15)	2553(8)
C(2s)	-3823(22)	2939(18)	1829(11)
C(3s)	-4720(20)	570(18)	2126(12)

	x	y	Z $(x10^2)$
N(1b)	1786(10)	-332(7)	3561(6)
N(2b)	2458(10)	2336(8)	3333(5)
O(1b)	4045(8)	4435(6)	2992(5)
N(1s)	-3480(17)	1735(13)	2187(7)
O(1s)	-1602(10)	751(8)	2846(6)
C(1s)	-1999(19)	1708(15)	2553(8)
C(2s)	-3823(22)	2939(18)	1829(11)
C(3s)	-4720(20)	570(18)	2126(12)

Table 3B Anisotropic thermal parameters ($\overset{o}{A}^2$) for Cu($C_{34}H_{22}N_4O_2$) DMF

Atom	U11	U22	U33	U12	U13	U23
Cu	0.038(1)	0.020(1)	0.045(1)	0.009(1)	-0.007(1)	0.005(1)
N(1a)	0.038(6)	0.043(6)	0.040(6)	0.014(5)	-0.009(5)	-0.008(5)
N(2a)	0.041(6)	0.019(5)	0.035(6)	-0.00L(4)	-0.007(5)	-0.004(4)
N(1b)	0.043(6)	0.025(5)	0.042(6)	0.017(5)	-0.004(5)	-0.001(5)
N(2b)	0.040(6)	0.046(6)	0.023(5)	0.011(5)	-0.004(5)	-0.011(5)
O(1a)	0.049(5)	0.037(5)	0.048(5)	0.00(4)	0.007(4)	0.014(4)
O(1b)	0.042(5)	0.028(5)	0.057(6)	-0.00(4)	-0.007(4)	0.00(4)
O(1s)	0.064(6)	0.062(6)	0.072(7)	0.033(5)	0.015(5)	0.012(5)
N(1s)	0.079(10)	0.106(11)	0.069(9)	0.059(9)	0.012(8)	0.013(8)
C(1s)	0.073(11)	0.074(11)	0.050(9)	0.023(9)	00.017(9)	0.005(8)
C(2s)	0.165(18)	0.133(16)	0.117(15)	0.113(14)	0.004(13)	0.034(13)
C(3s)	0.062(12)	0.142(18)	0.148(18)	0.038(13)	0.000(12)	0.004(15)

Table 4B Interatomic Bond Lengths and Angles

Bond lengths/Å

Cu-N(1a)	1.925(9)	Cu-N(1b)	1.987(8)
Cu-N(2a)	1.925(8)	Cu-N(2b)	1.900(8)
Cu-O(1s)	2.537(10)	C(1b)-C(1a)	1.556(14)
O(1a)-C(1a)	1.230(12)	O(1b)-C(1b)	1.214(12)
C(1a)-N(2a)	1.346(12)	C(1b)-N(2b)	1.406(13)
N(2a)-C(2a)	1.407(13)	N(2b)-C(2b)	1.338(14)
C(2a)-C(3a)	1.407(16)	C(2b)-C(3b)	1.405(17)
C(3a)-C(4a)	1.396(15)	C(3b)-C(4b)	1.385(17)
C(4a)-C(5a)	1.381(16)	C(4b)-C(5b)	1.392(16)
C(5a)-C(6a)	1.387(17)	C(5b)-C(6b)	1.379(18)
C(6a)-C(7a)	1.388(14)	C(6b)-C(7b)	1.413(16)
C(7a)-C(2a)	1.421(14)	C(7b)-C(2b)	1.486(14)
C(7a)-C(8a)	1.492(15)	C(7b)-C(8b)	1.461(16)
C(8a)-C(12a)	1.498(14)	C(8b)-C(12b)	1.499(14)
C(8a)-N(1a)	1.309(13)	C(8b)-N(1b)	1.263(15)

N(1a)-C(9a)	1.483(15)	N(1b)-C(9b)	1.426(16)
C(9a)-C(10a)	1.399(19)	C(9b)-C(10b)	1.444(18)
C10a)-C(11a)	1.413(19)	C(10b)-C(11b)	1.376(21)
C(11a)-C(11b)	1.365(18)	C(9b)-C(9a)	1.348(15)
C(12a)-C(13a)	1.371(17)	C(12b)-C(13b)	1.455(16)
C(13a)-C(14a)	1.399(15)	C(13b)-C(14b)	1.378(16)
C(14a)-C(15a)	1.359(17)	C(14b)-C(15b)	1.347(17)
C(15a)-C(16a)	1.374(20)	C(15b)-C(16b)	1.398(19)
C(16a)-C(17a)	1.414(15)	C(16b)-C(17b)	1.388(17)
C(17a)-C(12a)	1.389(15)	C(17b)-C(12b)	1.375(14)
O(1s)-C(7s)	1.20(2)	C(1s)-N(1s)	1.36(2)
N(1s)-C(2s)	1.44(3)	N(1s)-C(2s)	1.44(3)

Angles/°

N(1a)-Cu-N(2a)	91.2(3)	N(1b)-Cu-N(2b)	91.6(3)
N(1a)-Cu-O(1s)	86.0(4)	N(1b)-Cu-O(1s)	101.4(3)
N(2a)-Cu-O(1s)	90.3(3)	N(2b)-Cu-O(1s)	105.3(4)
N(1a)-Cu-N(2b)	168.7(4)	N(1b)-Cu-N(2a)	167.9(4)
N(1a)-Cu-N(1b)	86.8(4)	N(2b)-Cu-N(2a)	88.1(3)
O(1a)-C(1a)-C(1b)	118.0(8)	O(1b)-C(1b)-C(1a)	118.6(9)
O(1a)-C(1a)-N(2a)	127.4(9)	O(1b)-C(1b)-N(2b)	128.8(9)
C(1b)-C(1a)-N(2a)	114.6(8)	C(1a)-C(1b)-N(2b)	112.6(8)
C(1a)-N(2a)-C(2a)	126.4(8)	C(1b)-N(2b)-C(2b)	122.2(8)
C(1a)-N(2a)-Cu	110.7(6)	C(1b)-N(2b)-Cu	110.2(7)
C(2a)-N(2a)-Cu	122.6(6)	C(2b)-N(2b)-Cu	127.6(7)
N(2a)-C(2a)-C(3a)	119.2(9)	N(2b)-C(2b)-C(3b)	125.3(9)
N(2a)-C(2a)-C(7a)	121.6(9)	N(2b)-C(2b)-C(7b)	119.2(10)
C(3a)-C(2a)-C(7a)	118.8(9)	C(3b)-C(2b)-C(7b)	115.4(10)
C(2a)-C(3a)-C(4a)	120.0(10)	C(2b)-C(3b)-C(4b)	125.6(10)
C(3a)-C(4a)-C(5a)	120.7(11)	C(3b)-C(4b)-C(5b)	117.7(12)

C(4a)-C(5a)-C(6a)	119.8(10)	C(4b)-C(5b)-C(6b)	120.8(12)
C(5a)-C(6a)-C(7a)	121.0(10)	C(5b)-C(6b)-C(7b)	122.6(10)
C(6a)-C(7a)-C(2a)	119.6(10)	C(6b)-C(7b)-C(2b)	117.5(10)
C(6a)-C(7a)-C(8a)	115.5(9)	C(6b)-C(7b)-C(8b)	118.7(9)
C(2a)-C(7a)-C(8a)	124.9(9)	C(2b)-C(7b)-C(8b)	123.8(10)
C(7a)-C(8a)-N(1a)	119.8(9)	C(7b)-C(8b)-N(1b)	124.8(9)
C(7a)-C(8a)-C(12a)	118.6(9)	C(7b)-C(8b)-C(12b)	116.2(10)
N(1a)-C(8a)-C(12a)	121.4(9)	N(1b)-C(8b)-C(12b)	119.0(10)
C(8a)-N(1a)-C(9a)	124.9(9)	C(8b)-N(1b)-C(9b)	130.2(9)
C(8a)-N(1a)-Cu	125.2(9)	C(8b)-(1b)-Cu	123.0(8)
C(9a)-N(1a)-Cu	108.4(6)	C(9b)-N(1b)-Cu	106.6(7)
N(1a)-C(9a)-C(10a)	121(1)	N(4b)-C(9b)-C(10b)	121(1)
N(1a)-C(9a)-C(9b)	115(1)	N(1b)-C(9b)-C(9a)	120(1)
C(10a)-C(9a)-C(9b)	123(1)	C(10b)-C(9b)-C(9a)	119(1)
C(9a)-C(10a)-C(11a)	118(1)	C(9b)-C(10b)-C(11b)	118(1)
C(10a)-C(11a)-C(11b)	119(1)	C(10b)-C(11b)-C(11a)	123(1)

C(8a)-C(12a)-C(13a)	122(1)	C(8b)-C(12b)-C(13b)	121(1)
C(8a)-C(12a)-C(17a)	116(1)	C(8b)-C(12b)-C(17b)	121(1)
C(13a)-C(12a)-C(17a)	122(1)	C(13b)-C(12b)-C(17b)	118(1)
C(12a)-C(13a)-C(14a)	119(1)	C(12b)-C(13b)-C(14b)	119(1)
C(13a)-C(14a)-C(15a)	119(1)	C(13b)-C(14b)-C(15b)	122(1)
C(14a)-C(15a)-C(16a)	123(1)	C(14b)-C(15b)-C(16b)	120(1)
C(15a)-C(16a)-C(17a)	117(1)	C(15b)-C(16b)-C(17b)	119(1)
C(16a)-C(17a)-C(12a)	119(1)	C(16b)-C(17b)-C(12b)	122(1)
Cu-O(1s)-C(1s)	111(1)	O(1s)-C(1s)-N(1s)	125(1)
C(1s)-N(1s)-C(2s)	120(1)	C(1s)-N(1s)-C(3s)	121(1)
C(2s)-N(1s)-C(3s)	118(1)		

Equation of plane 1   N1aN1bN2aN2bCu

$$0.8603X + (-0.1772)Y + (-0.4780)Z = -1.2665$$

	DEVIAT-IONS FROM PLANE	WEIGHT		DEVIAT-IONS FROM PLANE	WEIGHT
Cu	-0.1576	1.0000*	H13A	0.4686	1.0000
N2A	0.0945	1.0000*	C14A	-0.6965	1.0000
N1A	0.0297	1.0000*	H14A	-0.1900	1.0000
O1A	1.0506	1.0000	C15A	-1.7133	1.0000
C1A	0.5826	1.0000	H15A	-2.0276	1.0000
C2A	-0.4346	1.0000	C16A	-2.3871	1.0000
C3A	-0.7039	1.0000	H16A	-3.2068	1.0000
H3A	-0.4141	1.0000	C17A	-1.9553	1.0000
C4A	-1.3426	1.0000	H17A	-2.42 3	1.0000
H4A	-1.5409	1.0000	N2B	0.030	1.0000*
C5A	-1.7203	1.0000	N1B	0.0477	1.0000*
H5A	-2.2360	1.0000	O1B	1.0698	1.0000
C6A	-1.4188	1.0000	C1B	0.5986	1.0000
H6A	-1.6835	1.0000	C2B	-0.3123	1.0000
C7A	-0.8013	1.0000	C3B	-0.4652	1.0000
C8A	-0.8000	1.0000	H3B	-0.1878	1.0000
C9A	0.5818	1.0000	C4B	-0.9250	1.0000
C10A	1.2508	1.0000	H4B	-1.0253	1.0000
H10A	1.2328	1.0000	C5B	-1.2559	1.0000
C11A	1.9363	1.0000	H5B	-1.6106	1.0000
H11A	2.4524	1.0000	C6B	-1.1395	1.0000
C12A	-0.9102	1.0000	H6B	-1.4660	1.0000
C13A	-0.2995	1.0000	C7B	-0.6111	1.0000

Equation of plane 1 N1aN1bN2aN2bCu

$$0.8603X + (-0.1772)Y + (-0.4780)Z = -1.2665$$

	DEVIAT- IONS FROM PLANE	WEIGHT		DEVIAT- IONS FROM PLANE	WEIGHT
Cu	-0.1576	1.0000*	H13A	0.4686	1.0000
N2A	0.0945	1.0000*	C14A	-0.6965	1.0000
N1A	0.0297	1.0000*	H14A	-0.1900	1.0000
O1A	1.0506	1.0000	C15A	-1.7133	1.0000
C1A	0.5826	1.0000	H15A	-2.0276	1.0000
C2A	-0.4346	1.0000	C16A	-2.3871	1.0000
C3A	-0.7039	1.0000	H16A	-3.2068	1.0000
H3A	-0.4141	1.0000	C17A	-1.9553	1.0000
C4A	-1.3426	1.0000	H17A	-2.42 3	1.0000
H4A	-1.5409	1.0000	N2B	0.030	1.0000*
C5A	-1.7203	1.0000	N1B	0.0477	1.0000*
H5A	-2.2360	1.0000	O1B	1.0698	1.0000
C6A	-1.4188	1.0000	C1B	0.5986	1.0000
H6A	-1.6835	1.0000	C2B	-0.3123	1.0000
C7A	-0.8013	1.0000	C3B	-0.4652	1.0000
C8A	-0.8000	1.0000	H3B	-0.1878	1.0000
C9A	0.5818	1.0000	C4B	-0.9250	1.0000
C10A	1.2508	1.0000	H4B	-1.0253	1.0000
H10A	1.2328	1.0000	C5B	-1.2559	1.0000
C11A	1.9363	1.0000	H5B	-1.6106	1.0000
H11A	2.4524	1.0000	C6B	-1.1395	1.0000
C12A	-0.9102	1.0000	H6B	-1.4660	1.0000
C13A	-0.2995	1.0000	C7B	-0.6111	1.0000

	DEVIATIONS FROM PLANE	WEIGHT
C8B	-0.3444	1.0000
C9B	0.5833	1.0000
C10B	1.3157	1.0000
H10B	1.3561	1.0000
C11B	1.9552	1.0000
H11B	2.4916	1.0000
C12B	-0.5630	1.0000
C13B	0.2694	1.0000
H13B	1.0053	1.0000
C14B	0.1069	1.0000
H14B	0.7371	1.0000
C15B	-0.8171	1.0000
H15B	-0.9062	1.0000
C16B	-1.6654	1.0000
H16B	-2.4478	1.0000

	DEVIATIONS FROM PLANE	WEIGHT
C17B	-1.4876	1.0000
H17B	-2.0977	1.0000
O1S	-2.6451	1.0000
N1S	-4.0392	1.0000
C1S	-3.0363	1.0000
H1S	-2.5637	1.0000
C2S	-4.4034	1.0000
H2S1	-4.4690	1.0000
S2	-4.0606	1.0000
H2S3	-4.8468	1.0000
C3S	-4.7264	1.0000
H3S1	-5.7214	1.0000
H3S2	-4.7856	1.0000
S3	-4.0218	1.0000

Equation of plane 6 N1a N1b N2a N2b

$$(8.7088) X + (-2.9498) Y + (-8.0641) Z = -1.2273$$

	DEVIATIONS FROM PLANE	WEIGHT		DEVIATIONS FROM PLANE	WEIGHT
Cu	-0.1971	1.0000	C11A	2.4154	1.0000
N2A	0.0093	1.0000*	C12A	-0.9486	1.0000
N1A	-0.0092	1.0000*	C13A	-0.3377	1.0000
O1A	1.0094	1.0000	H13A	0.4300	1.0000
C1A	0.5419	1.0000	C14A	-0.7342	1.0000
C2A	-0.4748	1.0000	H14A	-0.2275	1.0000
C3A	-0.7447	1.0000	C15A	-1.7557	1.0000
H3A	-0.4653	1.0000	H15A	-2.0645	1.0000
C4A	-1.3834	1.0000	C16A	-2.4246	1.0000
H4A	-1.5822	1.0000	H16A	-3.2439	1.0000
C5A	-1.7606	1.0000	C17A	-1.9934	1.0000
H5A	-2.2763	1.0000	H17A	-2.4674	1.0000
C6A	-1.4584	1.0000	N2B	-0.0092	1.0000*
H6A	-1.7227	1.0000	N1B	0.0091	1.0000*
C7A	-0.8409	1.0000	O1B	1.0288	1.0000
C8A	-0.5389	1.0000	C1B	0.5580	1.0000
C9A	0.5436	1.0000	C2B	-0.3521	1.0000
C10A	1.2130	1.0000	C3B	-0.5055	1.0000
H10A	1.1949	1.0000	H3B	-0.2287	1.0000

	DEVIATIONS FROM PLANE	WEIGHT
C4B	-0.9652	1.0000
H4B	-1.0659	1.0000
C5B	-1.2954	1.0000
H5B	-1.6500	1.0000
C6B	-1.1786	1.0000
H6B	-1.5046	1.0000
C7B	-0.6503	1.0000
C8B	-0.3830	1.0000
C9B	0.5452	1.0000
C10B	1.2781	1.0000
H10B	1.3185	1.0000
C11B	1.9180	1.0000
H11B	2.4548	1.0000
C12B	-0.6009	1.0000
C13B	0.2317	1.0000
H13B	0.9672	1.0000
C14B	0.0698	1.0000
H14B	0.7002	1.0000
C15B	-0.8538	1.0000
H15B	-0.9426	1.0000
C16B	-1.7023	1.0000
H16B	-2.4844	1.0000
C17B	-1.5251	1.0000
H17B	-2.1354	1.0000
O1S	-2.6845	1.0000
N1S	-4.0793	1.0000
C1S	-3.0762	1.0000
H1S	-2.6041	1.0000
C2S	-4.4441	1.0000
H2S1	-4.5102	1.0000
H2S2	-4.1016	1.0000
H2S3	-4.8872	1.0000
C3S	-4.7659	1.0000
H3S1	-5.7610	1.0000
H3S2	-4.8247	1.0000
H3S3	-4.0611	1.0000

APPENDIX C

$[Cu\ (C_{30}H_{32}N_4O_2)\ (DMF)_2(ClO_4)\ ](ClO_4)DMF.H_2O$

Table 1C

Formula $[\mathrm{Cu}(\mathrm{C}_{30}\mathrm{H}_{32}\mathrm{N}_4\mathrm{O}_2)(\mathrm{DMF})_2(\mathrm{ClO}_4)].\mathrm{ClO}_4.\mathrm{DMF}.\mathrm{H}_2\mathrm{O}$

M	888.5
Crystal system	Triclinic
Space group	$P\bar{1}$
a /Å	16.153
b /Å	12.753
c /Å	12.096
α /°	110.50
β /°	86.76
γ /°	84.46
V /Å^3	2312.14
Z	2
D /gcm^{-3}	1.52
F(000)	1025.98
Crystal dimensions	0.5 x 0.5 x 0.5
Reflections measured	7377
Unique reflections	6489
Scan width (w)°	1.0
Scan speed /°$^{-1}$	0.05
θ range	$3 \leqslant \theta \leqslant 25$
$R = \Sigma \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert \,\big\vert\, \Sigma \lvert F_o\rvert$	0.0661
$R' = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2 \,\big\vert\, \Sigma w \lvert F_o\rvert^2]^{\frac{1}{2}}$	0.0640
Final no. of variables	273
Av. shift to error	0.007
Max. shift to error	0.275
$I/\sigma(I)$	$\geqslant 3$

Table 2C Final atomic parameters for [$Cu(C_{30}H_{32}N_4O_2)$.$(DMF)_2(ClO_4)$] $ClO_4DMF.H_2O$. Fractional coordinates and isotropic thermal parameters ($Å^2$) with estimated standard deviations in parenthesis

Atom	x	y	Z (x10^4)	Site occupation factor
Cu	1958	2209	2716	1.0
O(S1)	2580(2)	753(3)	1767(2)	1.0
O(S2)	1935(2)	3085(3)	1406(3)	1.0
N(1a)	828(2)	1731(3)	2069(3)	1.0
N(2a)	1379(2)	3670(3)	3987(3)	1.0
N(2b)	3038(2)	2751(3)	3459(3)	1.0
N(1b)	4023(3)	1821(4)	745(3)	1.0
C(1a)	2043(3)	4368(4)	4516(4)	1.0
C(2a)	690(3)	4267(4)	3612(4)	1.0
C(3a)	661(3)	5388(4)	3756(4)	1.0
C(4a)	-8(4)	5895(5)	3371(5)	1.0
C(5a)	-402(3)	5482(2)	3452(4)	1.0
C(6a)	-613(3)	4164(5)	2732(6)	1.0
C(7a)	55(3)	3633(4)	3098(4)	1.0
C(8a)	92(1)	2412(4)	2934(4)	1.0
C(9a)	759(3)	534(4)	1582(4)	1.0
C(10a)	394(3)	-36(4)	2234(4)	1.0
C(11a)	369(3)	-1182(5)	1730(5)	1.0
C(12a)	717(3)	-1757(5)	592(5)	1.0
C(13a)	1090(3)	-1222(4)	-76(4)	1.0

Atom	x	y	Z $(x10^4)$	Site occup-ation factor
C(14a)	1106(3)	-63(4)	411(4)	1.0
C(15a)	1899(3)	-16(5)	-1293(4)	1.0
O(1a)	1442(2)	571(3)	-152(2)	1.0
C(1b)	2761(3)	3604(4)	4659(4)	1.0
C(2b)	3709(3)	1871(4)	3417(4)	1.0
C(3b)	3634(3)	1287(4)	4174(4)	1.0
C(4b)	4229(4)	402(5)	4087(5)	1.0
C(5b)	4894(4)	92(5)	3231(5)	1.0
C(6b)	4973(3)	695(5)	2489(5)	1.0
C(7b)	4390(3)	1590(4)	2555(4)	1.0
C(8b)	4504(3)	2204(4)	1722(4)	1.0
C(9b)	3997(3)	2309(4)	-128(4)	1.0
C(10b)	4472(3)	3135(5)	-172(5)	1.0
C(11b)	4411(5)	3562(6)	-1074(7)	1.0
C(12b)	3870(5)	3208(6)	-1905(6)	1.0
C(13b)	3401(4)	2389(5)	-1891(5)	1.0
C(14b)	3451(3)	1930(4)	-1016(4)	1.0
C(15b)	2343(3)	807(5)	-1647(4)	1.0
O(1b)	3011(2)	1093(3)	-915(3)	1.0
C(1S1)	2587(3)	-90(5)	2071(4)	1.0
C(2S1)	3660(4)	-1126(5)	444(5)	1.0
C(3S1)	3084(6)	-2015(6)	1856(8)	1.0

Atom	x	y	Z (x10^4)	Site occupation factor
N(S1)	3080(3)	-1041(4)	1483(4)	1.0
C(1S2)	2209(3)	3832(4)	1127(5)	1.0
C(2S2)	1034(5)	3985(8)	8(7)	1.0
C(3S2)	2217(7)	5168(3)	120(10)	1.0
N(S2)	1822(3)	4313(4)	457(4)	1.0
C(1S3)	4039(6)	5471(7)	3436(7)	1.0
C(2S3)	4674(8)	7026(11)	4730(9)	1.0
C(3S3)	3149(8)	7139(10)	4571(10)	1.0
N(S3)	4001(4)	6462(6)	4158(5)	1.0
OW	1109(8)	8135(11)	4784(11)	1.0
Cl(1)	1414(1)	1148(1)	5436(1)	1.0
O(11)	1452(2)	1545(3)	4477(3)	1.0
O(21)	1630(3)	2002(4)	6442(4)	1.0
O(31)	1992(3)	158(4)	5149(5)	1.0
O(41)	587(3)	942(5)	5639(5)	1.0
Cl(2)*	1109(8)	8135(11)	4784(11)	1.0
O(12)	2518(11)	6766(13)	8527(13)	0.28
O(22)	2667(6)	5356(8)	7305(8)	0.44
O(32)	3789(6)	5718(8)	6549(8)	0.44
O(42)	3408(7)	7462(8)	7576(8)	0.44
O(52)	3691(8)	6169(8)	8566(11)	0.43
O(62)	2795(10)	7220(12)	7598(12)	0.33

Atom	x	y	Z (x10^4)	Site occupation factor
O(72)	2441(13)	6853(17)	6991(19)	0.21
O(82)	3133(17)	5507(20)	6674(22)	0.17
O(92)	3000(20)	6548(21)	8841(22)	0.17
O(102)	4003(16)	6158(19)	7937(25)	0.18

*This perchlorate showed complex disorder. Ten resolved electron density maxima could be found in the region of the atom Cl(2). These were assigned a common thermal parameter of $0.08\,\text{Å}^2$. The positional parameters and site occupation factors for each atom were refined. Total site occupation factors for all oxygen atoms was 3.07

Table 3c Anisotropic thermal parameters (Å^2) for $[Cu(C_{30}H_{32}N_4O_2).2DMF](ClO_4)_2$ DMF. H_2O

Atom	U11	U22	U33	U12	U13	U23
Cu	0.030(3)	0.047(3)	0.038(3)	-0.001(2)	-0.005(2)	0.0063(2)
N(1a)	0.031(2)	0.048(2)	0.039(2)	-0.002(2)	-0.003(1)	0.008(2)
N(2a)	0.037(2)	0.051(2)	0.041(2)	-0.002(2)	-0.004(2)	0.005(2)
N(1b)	0.064(3)	0.074(3)	0.054(2)	-0.020(2)	-0.028(2)	0.029(2)
N(2b)	0.033(2)	0.057(2)	0.042(2)	-0.004(2)	-0.004(2)	0.008(2)
C(1a)	0.045(3)	0.054(3)	0.056(3)	-0.004(2)	-0.005(2)	-0.006(2)
C(2a)	0.038(2)	0.053(3)	0.040(2)	0.004(2)	0.001(2)	0.009(2)
C(3a)	0.054(3)	0.051(3)	0.062(3)	0.004(2)	0.002(2)	0.010(3)
C(4a)	0.083(4)	0.056(4)	0.077(4)	0.020(3)	0.017(3)	0.023(3)
C(5a)	0.056(3)	0.083(5)	0.066(4)	0.022(3)	-0.001(3)	0.022(3)
C(6a)	0.042(3)	0.068(4)	0.058(3)	0.013(2)	-0.005(2)	0.013(2)
C(7a)	0.038(2)	0.055(3)	0.043(3)	0.003(2)	0.001(2)	0.007(2)
C(8a)	0.029(2)	0.059(3)	0.047(3)	-0.001(2)	-0.001(2)	0.008(2)

Atom	U11	U22	U33	U12	U13	U23
C(9a)	0.035(2)	0.050(3)	0.039(2)	-0.004(2)	-0.009(2)	0.009(2)
C(10a)	0.048(3)	0.059(3)	0.058(3)	-0.012(2)	-0.006(2)	0.015(2)
C(11a)	0.071(4)	0.068(4)	0.087(4)	-0.021(3)	-0.008(3)	0.033(3)
C(12a)	0.079(4)	0.049(3)	0.086(4)	-0.018(3)	-0.011(3)	0.013(3)
C(13a)	0.061(3)	0.055(3)	0.053(3)	-0.008(2)	-0.015(2)	0.002(2)
C(14a)	0.041(2)	0.057(3)	0.042(3)	-0.006(2)	-0.013(2)	0.011(2)
C(15a)	0.056(3)	0.084(4)	0.035(3)	-0.005(3)	-0.011(2)	0.005(3)
O(2a)	0.057(2)	0.056(2)	0.035(2)	-0.001(2)	-0.003(1)	0.008(1)
C(1b)	0.049(3)	0.066(3)	0.046(2)	-0.003(2)	-0.014(2)	-0.003(2)
C(2b)	0.033(2)	0.057(3)	0.044(2)	0.015(2)	-0.013(2)	-0.005(2)
C(3b)	0.045(3)	0.074(3)	0.054(3)	-0.005(2)	-0.017(2)	0.023(2)
C(4b)	0.074(4)	0.085(4)	0.060(3)	-0.008(3)	-0.029(3)	0.033(3)
C(5b)	0.069(4)	0.077(4)	0.070(4)	0.019(3)	-0.023(3)	0.015(3)
C(6b)	0.047(3)	0.085(4)	0.053(3)	0.013(3)	-0.009(2)	0.008(3)
C(7b)	0.036(2)	0.061(3)	0.039(2)	-0.004(2)	-0.010(2)	0.007(2)

Atom	U11	U22	U33	U12	U13	U23
C(8b)	0.038(2)	0.074(3)	0.046(2)	-0.003(2)	-0.001(2)	0.012(2)
C(9b)	0.047(3)	0.053(3)	0.063(3)	-0.001(2)	-0.000(2)	0.023(2)
C(10b)	0.069(3)	0.067(4)	0.079(4)	-0.010(3)	-0.009(3)	0.033(3)
C(11b)	0.100(5)	0.084(5)	0.122(6)	-0.016(4)	-0.000(4)	0.062(4)
C(12b)	0.109(5)	0.110(6)	0.091(5)	-0.020(5)	-0.019(4)	0.066(5)
C(13b)	0.077(4)	0.078(4)	0.066(4)	-0.006(3)	-0.015(3)	0.034(3)
C(14b)	0.055(3)	0.058(3)	0.045(3)	0.004(2)	-0.002(2)	0.022(2)
C(15b)	0.056(3)	0.086(4)	0.039(3)	-0.006(3)	-0.008(2)	0.018(3)
O(2b)	0.055(2)	0.072(2)	0.044(2)	-0.006(2)	-0.014(1)	0.025(2)
Cl(1)	0.062(8)	0.070(9)	0.061(8)	-0.003(7)	-0.002(6)	0.032(7)
O(11)	0.079(3)	0.104(3)	0.065(2)	-0.008(2)	-0.008(2)	0.051(2)
O(21)	0.166(5)	0.102(3)	0.082(3)	-0.003(3)	-0.065(3)	0.009(3)
O(31)	0.133(4)	0.093(4)	0.149(4)	0.038(3)	0.011(3)	0.065(3)
O(41)	0.083(3)	0.155(5)	0.153(4)	-0.029(3)	0.027(3)	0.068(4)
Cl(2)	0.118(2)	0.095(1)	0.079(1)	-0.024(1)	-0.014(1)	0.005(1)
C(1S1)	0.047(3)	0.053(3)	0.055(3)	0.006(2)	-0.012(2)	0.005(2)

Atom	U11	U22	U33	U12	U13	U23
N(S1)	0.071(3)	0.055(3)	0.066(3)	0.004(2)	-0.016(2)	0.014(2)
C(2S1)	0.079(4)	0.080(4)	0.064(4)	0.004(2)	-0.016(2)	0.014(2)
C(3S1)	0.174(8)	0.074(5)	0.148(6)	0.014(5)	0.002(6)	0.055(5)
O(S1)	0.035(2)	0.049(2)	0.043(2)	0.002(1)	-0.006(1)	0.005(1)
C(1S2)	0.064(3)	0.055(3)	0.062(3)	0.011(2)	0.002(2)	0.016(3)
N(S2)	0.073(3)	0.071(3)	0.091(3)	0.006(3)	0.005(3)	0.046(3)
C(2S2)	0.084(5)	0.192(8)	0.133(6)	-0.016(5)	-0.048(5)	0.094(6)
C(3S2)	0.181(9)	0.111(7)	0.246(11)	0.004(6)	0.002(8)	0.123(7)
O(S2)	0.070(2)	0.067(2)	0.057(2)	-0.008(2)	-0.009(2)	0.030(2)
C(1S3)	0.165(8)	0.112(6)	0.104(5)	-0.089(6)	-0.0289(5)	0.020(5)
N(S3)	0.121(5)	0.107(4)	0.081(4)	-0.061(4)	-0.019(3)	0.026(3)
C(2S3)	0.195(11)	0.275(14)	0.153(8)	-0.148(11)	-0.050(8)	0.020(9)
C(3S3)	0.209(12)	0.165(10)	0.179(10)	0.023(9)	0.007(9)	0.094(8)
O(S3)	0.096(3)	0.104(3)	0.109(3)	-0.045(3)	-0.020(3)	0.009(3)

TABLE 4C **Interatomic bond lengths and angles in the DMF molecules**

O(S1)-C(1S1)	1.251(7)	O(S2)-C(1S2)	1.228(7)
C(1S1)-N(S1)	1.325(6)	C(1S2)-N(S2)	1.325(8)
N(S1)-C(2S1)	1.490(8)	N(S2)-C(2S2)	1.453(9)
N(S1)-C(3S1)	1.462(11)	N(S2)-C(3S2)	1.476(13)
Cu-O(S1)-C(1S1)	122.4(3)	Cu-O(S2)-C(1S2)	145.0(3)
O(S1)-C(1S1)-N(S1)	121.7(5)	O(S2)-C(1S2)-N(S2)	123.0(5)
C(1S1)-N(S1)-C(2S1)	120.4(5)	C(1S2)-N(S2)-C(2S2)	121.5(6)
C(1S1)-N(S1)-O(3S1)	120.9(5)	C(1S2)-N(S2)-C(3S2)	119.2(6)
C(2S1)-N(S1)-C(3S1)	118.7(5)	C(2S2)-N(S2)-C(3S2)	119.3(7)
O(S3)-C(1S3)	1.186(11)	O(S3)-C(1S3)-(NS3)	129.6(9)
C(1S3)-N(S3)	1.253(10)	C(153)-N(S3)-C(253)	127.7(8)
N(S3)-C(2S3)	1.437(14)	C(1S3)-N(S3)-C(3S3)	117.8(8)
N(S3)-C(3S3)	1.510(14)	C(2S3)-N(S3)-C(3S3)	114.3(7)

APPENDIX D STRUCTURE FACTORS

TABLE ID

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR [illegible]

H	K	L	FO	FC
3	[illegible]	[illegible]	1031	[illegible]
4	[illegible]	[illegible]	[illegible]	[illegible]
5	[illegible]	[illegible]	572	345
6	[illegible]	[illegible]	834	[illegible]
8	[illegible]	[illegible]	534	-48
9	[illegible]	[illegible]	355	[illegible]
10	[illegible]	[illegible]	[illegible]	[illegible]
11	[illegible]	[illegible]	37	-373
12	[illegible]	[illegible]	124	[illegible]
14	[illegible]	[illegible]	1131	1158
16	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	355	383
[illegible]	[illegible]	[illegible]	221	-174
4	1	[illegible]	835	[illegible]
5	1	[illegible]	2324	-2273
6	1	[illegible]	875	[illegible]
7	1	[illegible]	223	[illegible]
8	1	[illegible]	[illegible]	[illegible]
9	1	[illegible]	518	[illegible]
10	1	[illegible]	862	-871
11	1	[illegible]	476	-472
12	1	[illegible]	27	[illegible]
13	1	[illegible]	717	[illegible]
15	1	[illegible]	552	[illegible]
17	1	[illegible]	243	[illegible]
18	1	[illegible]	147	[illegible]
20	1	[illegible]	227	[illegible]
[illegible]	2	[illegible]	173	-211
1	2	[illegible]	534	541
3	2	[illegible]	385	[illegible]
4	2	[illegible]	[illegible]	[illegible]
5	2	[illegible]	835	[illegible]
6	2	[illegible]	754	745
7	2	[illegible]	353	377
8	2	[illegible]	[illegible]	[illegible]
9	2	[illegible]	575	[illegible]

H	K	L	FO	FC
11	2	[illegible]	597	525
[illegible]	2	[illegible]	431	[illegible]
[illegible]	2	[illegible]	521	[illegible]
16	2	[illegible]	334	[illegible]
[illegible]	2	[illegible]	237	-214
[illegible]	3	[illegible]	[illegible]	[illegible]
[illegible]	3	[illegible]	1738	1694
3	3	[illegible]	155	[illegible]
4	3	[illegible]	265	[illegible]
[illegible]	3	[illegible]	353	[illegible]
7	3	[illegible]	[illegible]	[illegible]
[illegible]	3	[illegible]	454	[illegible]
[illegible]	3	[illegible]	571	-577
13	3	[illegible]	[illegible]	-357
[illegible]	3	[illegible]	[illegible]	222
[illegible]	3	[illegible]	345	[illegible]
[illegible]	4	[illegible]	217	-63
1	4	[illegible]	[illegible]	559
[illegible]	4	[illegible]	[illegible]	[illegible]
[illegible]	4	[illegible]	793	775
[illegible]	4	[illegible]	[illegible]	[illegible]
7	4	[illegible]	545	-69
8	4	[illegible]	[illegible]	-411
10	4	[illegible]	274	291
11	4	[illegible]	163	-171
[illegible]	4	[illegible]	188	[illegible]
[illegible]	5	[illegible]	233	[illegible]
[illegible]	5	[illegible]	415	[illegible]
[illegible]	5	[illegible]	183	147
7	5	[illegible]	173	-13
[illegible]	5	[illegible]	383	-388
[illegible]	5	[illegible]	393	[illegible]
[illegible]	5	[illegible]	247	[illegible]
4	6	[illegible]	435	[illegible]
[illegible]	6	[illegible]	[illegible]	521
6	6	[illegible]	[illegible]	-474

H	K	L	FO	FC
7	[illegible]	[illegible]	[illegible]	-711
8	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
15	[illegible]	[illegible]	[illegible]	[illegible]
18	[illegible]	[illegible]	313	[illegible]
1	7	[illegible]	[illegible]	[illegible]
2	7	[illegible]	[illegible]	[illegible]
3	7	[illegible]	597	[illegible]
4	7	[illegible]	432	[illegible]
6	7	[illegible]	[illegible]	-447
8	7	[illegible]	[illegible]	593
11	7	[illegible]	[illegible]	-332
17	7	[illegible]	241	[illegible]
[illegible]	8	[illegible]	561	-571
1	8	[illegible]	[illegible]	[illegible]
2	8	[illegible]	[illegible]	[illegible]
3	8	[illegible]	[illegible]	577
4	8	[illegible]	357	-347
5	8	[illegible]	327	-344
7	8	[illegible]	458	[illegible]
9	8	[illegible]	368	[illegible]
12	8	[illegible]	[illegible]	[illegible]
14	8	[illegible]	298	[illegible]
15	8	[illegible]	248	[illegible]
1	9	[illegible]	474	[illegible]
2	9	[illegible]	239	[illegible]
3	9	[illegible]	467	-487
4	9	[illegible]	175	[illegible]
6	9	[illegible]	[illegible]	[illegible]
8	9	[illegible]	[illegible]	-588
11	9	[illegible]	321	[illegible]
17	9	[illegible]	234	[illegible]
[illegible]	10	[illegible]	249	[illegible]
2	10	[illegible]	414	-438
4	10	[illegible]	[illegible]	253

H	K	L	FO	FC
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	1	1	[illegible]	[illegible]
[illegible]	1	1	228	[illegible]
[illegible]	1	1	[illegible]	[illegible]
[illegible]	1	1	[illegible]	[illegible]
[illegible]	1	1	[illegible]	[illegible]
[illegible]	1	1	[illegible]	[illegible]
-7	1	1	445	[illegible]
[illegible]	1	1	[illegible]	[illegible]
[illegible]	1	1	[illegible]	[illegible]
-4	1	1	[illegible]	[illegible]
-3	1	1	437	[illegible]
[illegible]	1	1	[illegible]	[illegible]
3	1	1	1731	[illegible]
4	1	1	[illegible]	[illegible]
[illegible]	1	1	779	[illegible]
[illegible]	1	1	[illegible]	[illegible]
7	1	1	[illegible]	[illegible]
8	1	1	717	[illegible]
[illegible]	1	1	[illegible]	[illegible]
11	1	1	[illegible]	[illegible]
[illegible]	1	1	[illegible]	[illegible]
[illegible]	2	1	[illegible]	[illegible]
[illegible]	2	1	563	[illegible]
[illegible]	2	1	[illegible]	[illegible]
[illegible]	2	1	[illegible]	[illegible]
[illegible]	2	1	[illegible]	[illegible]
[illegible]	2	1	[illegible]	[illegible]
[illegible]	2	1	[illegible]	[illegible]
-7	2	1	[illegible]	[illegible]
[illegible]	2	1	434	[illegible]
[illegible]	2	1	194	231
-4	2	1	983	-871
[illegible]	2	1	[illegible]	[illegible]
[illegible]	2	1	3241	[illegible]
[illegible]	2	1	1372	[illegible]

H	K	L	FO	FC
[illegible]	[illegible]	1	[illegible]	[illegible]
4	[illegible]	1	71	-744
[illegible]	[illegible]	1	[illegible]	[illegible]
[illegible]	[illegible]	1	[illegible]	[illegible]
7	[illegible]	1	[illegible]	[illegible]
8	[illegible]	1	[illegible]	[illegible]
[illegible]	[illegible]	1	[illegible]	[illegible]
[illegible]	[illegible]	1	[illegible]	[illegible]
11	[illegible]	1	[illegible]	[illegible]
[illegible]	[illegible]	1	[illegible]	[illegible]
13	[illegible]	1	[illegible]	[illegible]
14	[illegible]	1	[illegible]	[illegible]
[illegible]	[illegible]	1	[illegible]	[illegible]
-17	3	1	[illegible]	[illegible]
-13	3	1	[illegible]	[illegible]
[illegible]	3	1	[illegible]	[illegible]
[illegible]	3	1	[illegible]	[illegible]
-7	3	1	[illegible]	[illegible]
[illegible]	3	1	[illegible]	[illegible]
[illegible]	3	1	[illegible]	[illegible]
[illegible]	3	1	[illegible]	[illegible]
-1	3	1	[illegible]	[illegible]
2	3	1	[illegible]	[illegible]
3	3	1	[illegible]	[illegible]
4	3	1	[illegible]	[illegible]
[illegible]	3	1	[illegible]	[illegible]
[illegible]	3	1	437	[illegible]
7	3	1	[illegible]	[illegible]
[illegible]	3	1	[illegible]	[illegible]
[illegible]	3	1	[illegible]	[illegible]
11	3	1	[illegible]	[illegible]
13	3	1	[illegible]	[illegible]
14	3	1	[illegible]	[illegible]
16	3	1	[illegible]	[illegible]
21	3	1	[illegible]	[illegible]
-22	4	1	[illegible]	[illegible]

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR [illegible]

H	K	L	10FO	10FC
-2	4	1	388	[illegible]
-17	4	1	226	[illegible]
-13	4	1	262	284
-12	4	1	14	-147
-11	4	1	57	[illegible]
-9	4	1	554	-558
-8	4	1	[illegible]	1
-7	4	1	254	-149
-6	4	1	474	-535
-4	4	1	2	227
-2	4	1	439	-489
-1	4	1	159	-173
0	4	1	772	785
1	4	1	522	498
2	4	1	152	173
3	4	1	848	-863
4	4	1	1148	-1137
6	4	1	1162	1101
7	4	1	188	-176
8	4	1	533	-537
10	4	1	239	225
11	4	1	256	245
12	4	1	29	-234
17	4	1	251	-271
19	4	1	328	[illegible]
20	4	1	352	319
-19	5	1	339	293
-16	5	1	271	-315
-14	5	1	27	234
-13	5	1	193	142
-12	5	1	391	-358
-11	5	1	357	-382
-10	5	1	386	355
-9	5	1	453	46
-8	5	1	252	-282
-7	5	1	374	-343

H	K	L	10FO	10FC
[illegible]	5	1	167	153
[illegible]	5	1	319	333
-4	5	1	436	-457
[illegible]	5	1	593	-59
-2	5	1	17	273
[illegible]	5	1	622	754
3	5	1	458	-482
4	5	1	[illegible]	589
5	5	1	245	[illegible]
6	5	1	381	-444
7	5	1	599	-611
9	5	1	555	55
11	5	1	468	-474
12	5	1	409	-424
18	5	1	245	[illegible]
-2	6	1	264	236
-12	6	1	354	-263
-11	6	1	301	247
-1	6	1	305	262
-9	6	1	512	-472
-8	6	1	374	-369
-6	6	1	979	993
-4	6	1	765	-786
-2	6	1	261	25
-1	6	1	448	444
0	6	1	242	-243
3	6	1	264	272
[illegible]	6	1	876	-867
[illegible]	6	1	477	-512
8	6	1	724	67
1	6	1	297	-21
13	6	1	364	32
17	6	1	227	21
-1	7	1	192	-18
-1	7	1	274	-313
-7	7	1	543	548

H	K	L	10FO	10FC
-6	7	1	352	374
-5	7	1	653	-634
-2	7	1	217	153
-1	7	1	432	-385
0	7	1	376	-365
1	7	1	299	358
2	7	1	265	283
3	7	1	153	213
4	7	1	279	-277
5	7	1	241	-237
7	7	1	281	315
8	7	1	354	343
-6	8	1	216	-271
-4	8	1	277	286
3	8	1	435	450
-6	9	1	239	-229
-5	9	1	273	-244
3	9	1	238	296
5	9	1	272	-306
-4	10	1	411	346
-3	10	1	298	301
-1	10	1	354	-338
8	10	1	196	-138
10	10	1	241	247
13	10	1	281	-224
15	10	1	261	158
-12	11	1	221	164
-2	11	1	259	-177
9	11	1	234	218
-4	12	1	252	-257
-2	12	1	216	199
1	12	1	258	-252
-20	[illegible]	2	313	366
-17	[illegible]	2	374	-429
-16	[illegible]	2	297	-296
-15	[illegible]	2	81	788

H	K	L	10FO	10FC
-14	[illegible]	2	81	[illegible]
-12	0	2	552	-49
-11	0	2	38	347
-1	0	2	712	67
-9	0	2	558	-573
-8	0	2	528	[illegible]
-7	0	2	1	[illegible]
-6	0	2	1614	15
-5	0	2	828	833
-4	0	2	1786	-1838
-3	0	2	1538	-1494
-2	0	2	1785	-1919
0	0	2	435	-329
3	0	2	972	841
4	0	2	546	627
5	0	2	1552	-16
6	0	2	642	-629
7	0	2	294	-327
8	0	2	452	48
9	0	2	1206	115
10	0	2	183	14
11	0	2	569	-55
12	0	2	559	-519
13	0	2	443	424
15	0	2	345	-37
18	0	2	332	291
19	0	2	249	-31
-23	1	2	273	-135
-2	1	2	215	[illegible]
-1	1	2	428	453
-14	1	2	506	-491
-13	1	2	44	[illegible]
-11	1	2	1141	117
-9	1	2	731	-73
-7	1	2	394	33
-6	1	2	465	4

H	K	L	10FO	10FC
-5	1	2	134	-17
-4	1	2	14	[illegible]
-3	1	2	11	[illegible]
-2	1	2	1	[illegible]
-1	1	2	733	7
0	1	2	1	-131
1	1	2	3	-3
2	1	2	17	-274
3	1	2	217	[illegible]
4	1	2	479	-449
7	1	2	31	[illegible]
8	1	2	841	[illegible]
9	1	2	71	-7
10	1	2	5	[illegible]
12	1	2	592	721
14	1	2	834	-849
17	1	2	3	245
19	1	2	2	-24
-16	2	2	277	255
-15	2	2	34	-317
-14	2	2	2	-237
-12	2	2	65	[illegible]
-10	2	2	494	-511
-9	2	2	[illegible]	16
-7	2	2	248	[illegible]
-6	2	2	429	-41
-5	2	2	273	3
-4	2	2	2	[illegible]
-2	2	2	2	-1
-1	2	2	111	-1178
[illegible]	2	2	5	-5
1	2	2	[illegible]	[illegible]
[illegible]	2	2	[illegible]	[illegible]
3	2	2	311	-357
4	2	2	34	-34
[illegible]	[illegible]	[illegible]	731	734

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR [illegible]

H	K	L	10FO	10FC
6	2	2	607	[illegible]
8	2	2	[illegible]7	-[illegible]
9	2	2	312	-[illegible]
10	2	2	[illegible]	[illegible]
11	2	2	3[illegible]4	[illegible]
13	2	2	[illegible]7	-[illegible]
14	2	2	33[illegible]	-[illegible]
15	2	2	383	437
16	2	2	3[illegible]	217
17	2	2	252	-[illegible]
18	2	2	254	-2[illegible]2
-15	3	2	227	-1[illegible]2
-13	3	2	314	[illegible]
-11	3	2	244	-[illegible]
-1[illegible]	3	2	29[illegible]	[illegible]4
-8	3	2	2[illegible]	-[illegible]
-7	3	2	55[illegible]	-6[illegible]
-5	3	2	263	[illegible]31
-4	3	2	232	[illegible]7
[illegible]	3	2	3[illegible]	-4[illegible]7
1	3	2	443	[illegible]
2	3	2	444	-4[illegible]
4	3	2	[illegible]	[illegible]4
5	3	2	111[illegible]	1199
6	3	2	[illegible]8	-[illegible]
7	3	2	357	-368
10	3	2	368	[illegible]
11	3	2	34	-[illegible]
16	3	2	2[illegible]	-2[illegible]7
17	3	2	2[illegible]	-[illegible]7
-14	4	2	314	321
-13	4	2	3[illegible]1	-3[illegible]1
-12	4	2	2[illegible]	-3[illegible]
-9	4	2	32[illegible]	3[illegible]
-7	4	2	5[illegible]7	4[illegible]
-6	4	2	[illegible]	[illegible]3

H	K	L	10FO	10FC
-[illegible]	4	2	[illegible]1	-[illegible]
-[illegible]	4	2	[illegible]7	-1[illegible]7
-1[illegible]	4	2	[illegible]	-45[illegible]
[illegible]	4	2	85[illegible]	8[illegible]7
[illegible]	4	2	[illegible]7	-2[illegible]
7	4	2	334	343
[illegible]	4	2	334	-325
1[illegible]	4	2	333	-2[illegible]8
12	4	2	327	31[illegible]
1[illegible]	4	2	2[illegible]2	-2[illegible]
-14	5	2	317	324
-1[illegible]	5	2	348	317
-[illegible]	5	2	282	25
-7	5	2	241	-3[illegible]4
-6	5	2	425	-451
-5	5	2	179	262
-4	5	2	185	17[illegible]
-2	5	2	513	-52[illegible]
-1	5	2	[illegible]21	-1[illegible]4
[illegible]	5	2	25	26
[illegible]	5	2	35	-3[illegible]7
[illegible]	5	2	175	-1[illegible]
4	5	2	323	33[illegible]
5	5	2	22[illegible]	[illegible]
7	5	2	498	-48[illegible]
[illegible]	5	2	467	-3[illegible]3
14	5	2	462	45[illegible]
17	5	2	268	-266
-15	6	2	268	274
-12	6	2	613	-543
-1	6	2	752	6[illegible]7
-8	6	2	27[illegible]	-267
-7	6	2	785	-4[illegible]
-4	6	2	375	-331
-3	6	2	227	-21[illegible]
-[illegible]	6	2	272	282

H	K	L	10FO	10FC
[illegible]	[illegible]	[illegible]	45[illegible]	-[illegible]
3	[illegible]	[illegible]	15[illegible]	234
4	[illegible]	[illegible]	411	3[illegible]8
6	[illegible]	[illegible]	33[illegible]	-341
7	[illegible]	2	2[illegible]4	-287
8	[illegible]	2	25	33[illegible]
9	[illegible]	2	2[illegible]	2[illegible]3
10	[illegible]	2	232	-245
12	[illegible]	2	388	38[illegible]
13	[illegible]	2	445	41[illegible]
15	6	2	328	-358
16	6	2	425	-386
18	6	2	317	2[illegible]
-11	7	2	285	317
-9	7	2	717	-739
-8	7	2	323	-362
-7	7	2	522	497
-6	7	2	403	429
-4	7	2	796	-764
-2	7	2	348	342
1	7	2	51[illegible]	-528
2	7	2	466	422
3	7	2	437	471
5	7	2	574	-565
6	7	2	258	-250
7	7	2	6[illegible]	626
8	7	2	328	358
9	7	2	226	-22[illegible]
10	7	2	22[illegible]	-27[illegible]
-1[illegible]	8	2	26[illegible]	-176
-14	8	2	32[illegible]	-271
-13	8	2	3[illegible]	243
-11	8	2	232	-176
-10	8	2	317	-322
-8	8	2	676	661
-7	8	2	142	214

H	K	L	10FO	10FC
-[illegible]	8	2	[illegible]7	-4[illegible]
-[illegible]	8	2	[illegible]7[illegible]	-441
-3	8	2	[illegible]7[illegible]	8[illegible]
-1	8	2	[illegible]	-[illegible]1[illegible]
[illegible]	8	2	47[illegible]	-[illegible]1[illegible]
1	8	2	[illegible]31	3[illegible]3
[illegible]	8	2	337	33[illegible]
4	8	2	[illegible]38	-27[illegible]
[illegible]	8	2	[illegible]4	-2[illegible]
[illegible]	8	2	[illegible]	617
8	8	2	271	-2[illegible]
9	8	2	337	-344
10	8	2	[illegible]	-185
11	8	2	472	43[illegible]
13	8	2	271	-174
-13	9	2	285	31[illegible]
-11	9	2	[illegible]31	-233
-9	9	2	558	3[illegible]4
-7	9	2	235	-3[illegible]
-4	9	2	193	25[illegible]
-3	9	2	391	-384
-2	9	2	557	-5[illegible]1
-1	9	2	283	168
[illegible]	9	2	763	67[illegible]
1	9	2	385	3[illegible]3
2	9	2	237	-2[illegible]
3	9	2	285	-1[illegible]
5	9	2	[illegible]59	25[illegible]
6	9	2	23[illegible]	19[illegible]
7	9	2	323	-2[illegible]
8	9	2	296	-274
10	9	2	47[illegible]	4[illegible]
12	9	2	554	-373
-8	10	2	219	-161
-5	10	2	345	323
-3	10	2	445	-4[illegible]

H	K	L	10FO	10FC
[illegible]	1	[illegible]	[illegible]	[illegible]
[illegible]	1	[illegible]	[illegible]	-[illegible]
11	1	[illegible]	[illegible]	-[illegible]
-1[illegible]	1	[illegible]	[illegible]	[illegible]
-1[illegible]	1	[illegible]	1[illegible]	-[illegible]
-16	1	3	31[illegible]	-33[illegible]
-15	1	3	36[illegible]	[illegible]
-13	1	3	[illegible]	-[illegible]
-1[illegible]	1	3	2[illegible]1	[illegible]7
-9	1	3	425	41[illegible]
-7	1	3	143	[illegible]
-6	1	3	1[illegible]	[illegible]
-5	1	3	793	7[illegible]
-4	1	3	122[illegible]	-1[illegible]
-3	1	3	24[illegible]	-23[illegible]
-2	1	3	673	-[illegible]
-1	1	3	1586	1497
[illegible]	1	3	772	82[illegible]
1	1	3	243	-273
2	1	3	2[illegible]3	-3[illegible]4
3	1	3	[illegible]14	-1[illegible]
4	1	3	3[illegible]	4[illegible]3
5	1	3	8[illegible]	76
6	1	3	6[illegible]8	-[illegible]
7	1	3	47	-4[illegible]3
8	1	3	23[illegible]	-[illegible]3
9	1	3	[illegible]	4[illegible]7
10	1	3	34[illegible]	[illegible]
1[illegible]	1	3	175	-[illegible]4
-18	2	3	31[illegible]	-[illegible]
-1[illegible]	2	3	311	3[illegible]7
-14	2	3	393	-37[illegible]
-1[illegible]	2	3	4[illegible]	441
-9	2	3	3[illegible]7	-8[illegible]
-7	2	3	[illegible]8[illegible]	[illegible]7[illegible]
-6	2	3	78[illegible]	7[illegible]4

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR [CU(C25H30N4)OH2][CLO4]2.DMF

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
-5	2	3	841	-838	[illegible]	3	3	786	[illegible]	15	4	3	346	335	3	6	3	[illegible]	[illegible]	[illegible]	0	4	[illegible]	[illegible]
-4	2	3	1054	[illegible]	7	3	3	[illegible]	[illegible]	17	4	3	184	-349	4	6	3	357	[illegible]	-18	0	4	[illegible]	[illegible]
-2	2	3	1821	-1774	8	3	3	477	[illegible]	19	4	3	333	319	5	6	3	[illegible]	[illegible]	-17	0	4	[illegible]	[illegible]
-1	2	3	[illegible]	[illegible]	9	3	3	559	-558	-17	5	3	352	-338	6	6	3	148	[illegible]	-16	0	4	[illegible]	[illegible]
1	2	3	[illegible]	[illegible]	10	3	3	563	[illegible]	-13	5	3	374	-399	7	6	3	582	[illegible]	-15	0	4	[illegible]	[illegible]
2	2	3	[illegible]	1118	11	3	3	587	534	-12	5	3	[illegible]	-439	8	6	3	[illegible]	[illegible]	-13	0	4	[illegible]	[illegible]
3	2	3	415	-397	12	3	3	376	[illegible]	-11	5	3	561	543	9	6	3	[illegible]	-437	-11	0	4	[illegible]	[illegible]
4	2	3	377	[illegible]	13	3	3	363	-374	-10	5	3	[illegible]	647	13	6	3	223	[illegible]	-10	0	4	[illegible]	[illegible]
5	2	3	1414	[illegible]	15	3	3	577	585	-8	5	3	528	-492	14	6	3	[illegible]	-341	-8	0	4	[illegible]	[illegible]
6	2	3	255	-263	17	3	3	352	-371	-7	5	3	217	-184	16	6	3	254	237	-7	0	4	249	[illegible]
7	2	3	1117	[illegible]	18	3	3	298	[illegible]	-6	5	3	[illegible]	514	17	6	3	225	274	-6	0	4	972	[illegible]
8	2	3	[illegible]	[illegible]	[illegible]	3	3	297	[illegible]	-5	5	3	419	435	-15	7	3	277	[illegible]	-5	0	4	1365	1339
9	2	3	534	[illegible]	-15	4	3	289	-274	-3	5	3	351	[illegible]	-12	7	3	266	314	-4	0	4	2533	[illegible]
10	2	3	565	[illegible]	-14	4	3	546	529	-1	5	3	[illegible]	564	-7	7	3	258	288	-3	0	4	1131	[illegible]
11	2	3	265	232	-13	4	3	337	291	0	5	3	[illegible]	-748	-6	7	3	425	-431	-2	0	4	862	[illegible]
14	2	3	226	[illegible]	-12	4	3	421	[illegible]	1	5	3	738	-699	-3	7	3	397	[illegible]	-1	0	4	[illegible]	-476
16	2	3	378	[illegible]	-11	4	3	553	-498	2	5	3	537	-529	-1	7	3	465	[illegible]	0	0	4	[illegible]	[illegible]
19	2	3	332	[illegible]	-10	4	3	[illegible]	-244	3	5	3	859	865	0	7	3	[illegible]	[illegible]	1	0	4	855	-886
-19	3	3	324	-372	-9	4	3	688	743	4	5	3	1469	1446	2	7	3	377	332	2	0	4	[illegible]	[illegible]
-15	3	3	244	[illegible]	-6	4	3	387	443	6	5	3	1041	[illegible]	8	7	3	388	-433	3	0	4	[illegible]	[illegible]
-14	3	3	213	[illegible]	-4	4	3	696	695	7	5	3	674	-671	13	7	3	285	-221	4	0	4	[illegible]	[illegible]
-13	3	3	[illegible]	[illegible]	-3	4	3	[illegible]	-655	8	5	3	565	631	-6	8	3	288	[illegible]	5	0	4	493	[illegible]
-12	3	3	[illegible]	[illegible]	-2	4	3	1117	-1136	9	5	3	435	[illegible]	1	8	3	299	-261	6	0	4	349	[illegible]
-8	3	3	[illegible]	[illegible]	-1	4	3	149	163	11	5	3	384	[illegible]	5	8	3	237	[illegible]	8	0	4	[illegible]	[illegible]
-7	3	3	194	[illegible]	0	4	3	[illegible]	1351	13	5	3	397	419	6	8	3	[illegible]	[illegible]	12	0	4	537	[illegible]
-6	3	3	187	[illegible]	1	4	3	459	[illegible]	17	5	3	211	144	8	8	3	388	[illegible]	16	0	4	545	-577
-5	3	3	625	[illegible]	2	4	3	696	-637	18	5	3	[illegible]	296	0	9	3	239	[illegible]	22	0	4	295	[illegible]
-4	3	3	648	592	3	4	3	1338	-1247	-16	6	3	378	324	2	9	3	222	[illegible]	-19	1	4	327	-315
-3	3	3	654	689	4	4	3	294	258	-11	6	3	495	479	-4	10	3	323	333	-17	1	4	[illegible]	371
-2	3	3	487	[illegible]	5	4	3	1345	1296	-9	6	3	[illegible]	-162	-2	10	3	310	[illegible]	-16	1	4	523	[illegible]
-1	3	3	931	-917	7	4	3	696	-782	-7	6	3	683	[illegible]	-1	10	3	288	[illegible]	-15	1	4	399	[illegible]
0	3	3	[illegible]	[illegible]	9	4	3	589	576	-6	6	3	262	258	4	10	3	321	[illegible]	-12	1	4	541	[illegible]
1	3	3	[illegible]	[illegible]	10	4	3	542	527	-5	6	3	772	-726	8	10	3	257	[illegible]	-11	1	4	[illegible]	[illegible]
2	3	3	124	[illegible]	11	4	3	621	[illegible]	-4	6	3	672	-638	3	11	3	[illegible]	[illegible]	-10	1	4	396	-372
4	3	3	893	-914	12	4	3	596	-711	-2	6	3	465	486	[illegible]	11	3	318	[illegible]	-8	1	4	468	476
5	3	3	[illegible]	[illegible]	14	4	3	[illegible]	343	1	6	3	388	[illegible]	-22	0	4	328	[illegible]	-7	1	4	772	[illegible]

```
OBSERVED AND CALCULATED STRUCTURE FACTORS FOR [CU(C2[illegible]H3[illegible]N4)DMF][CLO4]2.DMF

  H   K   L  10FO 10FC        H   K   L  10FO 10FC        H   K   L  10FO 10FC        H   K   L  10FO 10FC        H   K   L  10FO 10FC

 -6   1   4   770 -772        5   2   4  1275 1219       11   4   4   214  222      -15   7   4   216 -2[illegible]     1   9   4   285 -3[illegible]
 -5   1   4  1269-1188        6   2   4   768  357       17   4   4   215 -149      -14   7   4   381 -384        5   9   4   321  344
 -4   1   4  1152-1183        7   2   4   583 -548      -15   5   4   304  291      -12   7   4   218  229        6   9   4   332 -35[illegible]
 -3   1   4  1041 1119        8   2   4   571 -670      -13   5   4   228 -193      -11   7   4   345 -345        7   9   4   277 -285
 -1   1   4   347 -431       11   2   4   272  274      -10   5   4   279  261       -9   7   4   357 -319        9   9   4   476  431
  0   1   4    69 [illegible]  13   2   4   517 -528     -6   5   4   181  137       -7   7   4   343  354       11   9   4   304 -318
  1   1   4  2785-2575       15   2   4   365  412       -5   5   4   241 -245       -6   7   4   238  183       -4  10   4   201 -207
  2   1   4   738  642      -14   3   4   327  317       -3   5   4   597 -593       -5   7   4   293 -244        1  10   4   257 -255
  3   1   4   570  247      -12   3   4   440 -419       -2   5   4   193 -165       -3   7   4   334  350        2  10   4   293  254
  4   1   4  1131-1032      -11   3   4   267 -280       -1   5   4   755  826       -2   7   4   249  253        3  10   4   381  385
  5   1   4   512  546       -7   3   4   368 -328        0   5   4   489  472        0   7   4   690 -648        5  10   4   243 -209
  6   1   4   652  642       -6   3   4   296  286        2   5   4   517 -524        2   7   4   582  569        6  10   4   227 -257
  7   1   4  1214 1202       -5   3   4   432  387        3   5   4   270  257        4   7   4   479 -5[illegible]   5  11   4   194 -194
  9   1   4   534 -522       -4   3   4   220  228        5   5   4   210  192        5   7   4   528 -5[illegible] -18   1   5   224 -151
 11   1   4   260  326       -3   3   4   183  193        6   5   4   334  341        7   7   4   325  281      -14   1   5   335 -343
 12   1   4   299  305       -2   3   4   228 -272        7   5   4   255 -275       14   7   4   345 -286      -12   1   5   437  418
 13   1   4   311 -318       -1   3   4   761  384        8   5   4   213  165      -15   8   4   263 -248      -11   1   5   438  417
-18   2   4   354  319        0   3   4   910  973       13   5   4   312  301      -13   8   4   320  331      -10   1   5   323 -297
-15   2   4   241 -236        1   3   4   188 -271       16   5   4   374 -355      -11   8   4   368 -325       -9   1   5   355 -4[illegible]
-14   2   4   188 -167        2   3   4   862 -914      -15   6   4   372  353      -10   8   4   368  -33       -8   1   5   570 -6[illegible]3
-13   2   4   230 [illegible]  3   3   4  1097-1062    -10   6   4   231 -273       -9   8   4   485  457       -7   1   5   219 -155
-12   2   4   177  253        6   3   4   426 -434       -9   6   4   328 -327       -8   8   4   278  352       -6   1   5   786  803
-11   2   4   484 -539        7   3   4   283  234       -7   6   4   247  265       -6   8   4   237 -271       -5   1   5   416  337
 -8   2   4   233  222       14   3   4   364  352       -6   6   4   425  421       -4   8   4   343  349       -4   1   5   275 -293
 -7   2   4  1110-1203      -16   4   4   290 -277       -4   6   4   305 -347       -1   8   4    49 -493       -3   1   5   869 -838
 -6   2   4  1283-1312       -8   4   4   445  447       -3   6   4   232 -3[illegible]   1   8   4   577  569       -2   1   5   405  421
 -5   2   4  1110 1072       -7   4   4   268  253       -2   6   4   430  345        3   8   4   443 -451       -1   1   5  1848 1775
 -4   2   4   834  873       -5   4   4   572 -598       -1   6   4   256  295        4   8   4   455 -511        0   1   5   745 -513
 -3   2   4  1227 1122        1   4   4   265 -277        2   6   4   274  260        5   8   4   374  403        2   1   5  1024  975
 -2   2   4  1014  987        2   4   4   214 -201        3   6   4   181  169        6   8   4   333  323        4   1   5   423  405
 -1   2   4  1345-1322        3   4   4   681 -735        5   6   4   392 -422        9   8   4   232 -205        5   1   5   361 -333
  0   2   4  1352-1289        4   4   4   189 -111        6   6   4   294 -288       10   8   4   281  279        6   1   5 [illegible] -342
  1   2   4  1054  953        5   4   4   394  402        8   6   4   432  347      -14   9   4   266  318        7   1   5   333 -3[illegible]
  2   2   4   197  245        7   4   4   278  267       10   6   4   357 -365       -8   9   4   370 -307        8   1   5 [illegible] [illegible]8
  3   2   4   485 -443        8   4   4   196  224       13   6   4   132  122       -[illegible] 9 4  365  345     12   1   5   242 -176
  4   2   4   501  428        9   4   4   173  197       15   6   4   137 -213       [illegible] 9  4   265  215     13   1   5   348 -412
```

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR [illegible]

H	K	L	1FO1	FC
-15	2	5	514	-487
-14	2	5	251	-242
-12	2	5	478	457
-11	2	5	552	581
-10	2	5	354	-355
-8	2	5	181	190
-7	2	5	755	738
-5	2	5	1124	-1078
-4	2	5	241	-135
-3	2	5	175	180
-1	2	5	174	-185
0	2	5	583	-617
1	2	5	755	631
2	2	5	186	241
4	2	5	373	-383
5	2	5	876	-871
7	2	5	192	208
8	2	5	215	-237
9	2	5	353	-414
10	2	5	535	437
11	2	5	342	333
13	2	5	457	-425
14	2	5	255	-227
15	2	5	337	349
-20	3	5	253	-287
-18	3	5	326	361
-14	3	5	317	256
-13	3	5	334	310
-12	3	5	191	193
-11	3	5	347	-371
-10	3	5	302	-279
-8	3	5	170	-154
-7	3	5	394	-367
-6	3	5	1005	-1013
-5	3	5	435	454
-4	3	5	713	672

H	K	L	1FO1	FC
-3	3	5	325	-310
-1	3	5	523	-623
	3	5	1155	1148
1	3	5	931	870
2	3	5	551	-550
3	3	5	1021	-960
4	3	5	190	-186
5	3	5	1069	113
7	3	5	425	-433
8	3	5	489	-519
10	3	5	522	508
13	3	5	354	-382
14	3	5	503	495
15	3	5	331	382
19	3	5	259	304
-19	4	5	272	276
-17	4	5	399	-343
-16	4	5	291	-222
-15	4	5	256	137
-13	4	5	259	-34
-11	4	5	359	-372
-10	4	5	555	534
-8	4	5	545	-557
-7	4	5	521	-436
-5	4	5	1269	1241
-4	4	5	432	457
-3	4	5	938	-909
-2	4	5	318	-35
-1	4	5	1076	1071
	4	5	152	189
1	4	5	1207	-1181
2	4	5	1193	-1185
3	4	5	225	212
4	4	5	1193	118
5	4	5	497	[illegible]
6	4	5	388	-394

H	K	L	1FO1	FC
7	4	5	414	-453
9	4	5	524	545
11	4	5	515	-537
13	4	5	386	396
14	4	5	438	421
16	4	5	318	-317
18	4	5	345	334
-16	5	5	333	339
-15	5	5	285	268
-13	5	5	642	-668
-11	5	5	478	468
-9	5	5	346	-364
-8	5	5	290	-193
-7	5	5	257	271
-6	5	5	297	252
-5	5	5	239	249
-4	5	5	506	-536
-3	5	5	292	-232
-2	5	5	993	1012
-1	5	5	330	311
0	5	5	852	[illegible]
1	5	5	933	-948
2	5	5	432	375
3	5	5	772	769
7	5	5	266	194
9	5	5	379	-375
10	5	5	613	-663
12	5	5	821	791
13	5	5	417	416
14	5	5	193	-186
15	5	5	463	-412
17	5	5	312	256
-14	6	5	227	-213
-12	6	5	388	399
-9	6	5	146	-235
-7	6	5	366	349

H	K	L	1FO1	FC
-6	6	5	[illegible]	[illegible]
-4	6	5	262	-233
-3	6	5	352	238
-1	6	5	408	-42
	6	5	461	-451
1	6	5	286	252
2	6	5	591	574
6	6	5	537	265
7	6	5	552	577
8	6	5	257	-312
13	6	5	213	-507
-8	7	5	214	243
-7	7	5	449	-433
-6	7	5	257	-216
-5	7	5	263	-293
-4	7	5	237	331
-3	7	5	185	[illegible]
2	7	5	175	-197
3	7	5	334	-319
5	7	5	273	293
6	7	5	210	193
9	7	5	230	-223
10	7	5	132	-153
-2	8	5	226	223
-1	8	5	557	386
3	8	5	194	-224
-4	9	5	197	234
2	9	5	261	-271
3	9	5	283	-288
-3	10	5	422	-421
2	10	5	237	-234
4	10	5	288	221
5	10	5	251	264
-7	11	5	215	233
-5	11	5	314	327
-4	11	5	374	-355

H	K	L	1FO1	FC
5	11	5	285	301
6	11	5	[illegible]	-228
7	11	5	244	324
-3	12	5	[illegible]	-136
2	12	5	333	273
-21	[illegible]	[illegible]	243	312
-18	[illegible]	6	431	-435
-17	[illegible]	6	286	301
-16	[illegible]	6	299	319
-15	[illegible]	6	213	199
-14	[illegible]	6	254	-242
-13	[illegible]	6	685	-599
-12	[illegible]	6	390	410
-9	[illegible]	6	1076	-1041
-8	[illegible]	6	386	-372
-7	[illegible]	6	592	716
-6	[illegible]	6	651	613
-5	[illegible]	6	31	32
-4	[illegible]	6	883	-929
-2	[illegible]	6	1062	1039
-1	[illegible]	6	273	-248
	[illegible]	6	304	-323
1	[illegible]	6	1069	-1143
3	[illegible]	6	1083	1154
6	[illegible]	6	147	186
7	[illegible]	6	594	523
8	[illegible]	6	[illegible]	-227
9	[illegible]	6	315	-277
10	[illegible]	6	432	-407
11	[illegible]	6	524	508
12	[illegible]	6	388	403
13	[illegible]	6	625	-519
21	[illegible]	6	317	327
-19	1	6	282	-354
-17	1	6	353	371
-14	1	6	[illegible]	[illegible]

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR [CO(C[illegible]H3[illegible]N4)DMF][CLO4]2.DMF

H	K	L	10FO	10FC
-13	1	6	221	18
-11	1	6	181	-183
-10	1	6	545	-543
-8	1	6	1221	1205
-7	1	6	437	433
-6	1	6	325	-273
-5	1	6	517	-625
-4	1	6	510	427
-3	1	6	601	596
-2	1	6	910	-926
-1	1	6	370	-348
0	1	6	392	354
2	1	6	522	552
3	1	6	391	-405
4	1	6	543	-569
6	1	6	1076	1139
7	1	6	348	369
8	1	6	579	-637
9	1	6	378	-427
11	1	6	574	540
12	1	6	258	-289
13	1	6	250	-323
14	1	6	217	-164
16	1	6	285	264
20	1	6	314	302
-18	2	6	298	229
-12	2	6	193	-243
-9	2	6	571	539
-7	2	6	1248	-1261
-6	2	6	312	-316
-5	2	6	647	628
-4	2	6	549	533
-3	2	6	334	-284
-2	2	6	348	-314
-1	2	6	281	273
0	2	6	257	255
1	2	6	201	150
2	2	6	258	-320
3	2	6	472	-474
4	2	6	500	408
5	2	6	1055	1024
7	2	6	896	-917
8	2	6	313	-297
12	2	6	610	-571
14	2	6	403	346
19	2	6	298	251
-15	3	6	360	320
-12	3	6	301	-261
-9	3	6	358	-370
-8	3	6	367	-402
-6	3	6	959	961
-5	3	6	779	765
-4	3	6	262	-235
-3	3	6	786	-866
-1	3	6	657	655
0	3	6	738	751
2	3	6	448	-429
3	3	6	317	-351
5	3	6	569	-523
6	3	6	309	-340
7	3	6	224	-226
8	3	6	283	259
9	3	6	278	285
12	3	6	280	-281
13	3	6	259	245
-17	4	6	260	-226
-11	4	6	280	313
-3	4	6	219	-223
-2	4	6	303	321
0	4	6	423	-383
1	4	6	200	-148
2	4	6	277	-234
3	4	6	253	-274
8	4	6	389	349
11	4	6	245	-313
15	4	6	354	361
-15	5	6	282	184
-13	5	6	337	-239
-10	5	6	181	-110
-8	5	6	347	-335
-4	5	6	231	-230
-3	5	6	425	-427
-1	5	6	588	587
0	5	6	417	392
1	5	6	230	-172
3	5	6	345	-329
5	5	6	264	249
6	5	6	252	-241
9	5	6	255	291
10	5	6	294	275
-12	6	6	302	275
-10	6	6	312	-279
-9	6	6	303	-312
-7	6	6	283	278
-2	6	6	354	369
0	6	6	332	-367
2	6	6	299	278
3	6	6	252	282
5	6	6	341	-328
8	6	6	360	311
10	6	6	282	-359
16	6	6	225	204
-10	7	6	321	-284
-4	7	6	301	318
-3	7	6	419	415
-2	7	6	250	236
-1	7	6	425	-399
0	7	6	244	-267
1	7	6	330	35
3	7	6	220	-222
4	7	6	214	-243
8	7	6	263	-188
13	7	6	340	-339
-11	8	6	355	-357
-9	8	6	554	512
-6	8	6	337	-348
-2	8	6	556	-568
0	8	6	477	471
3	8	6	445	-412
10	8	6	225	155
-10	9	6	344	347
-8	9	6	252	-249
-7	9	6	481	-473
-5	9	6	452	444
0	9	6	272	-172
1	9	6	341	-355
4	9	6	286	329
7	9	6	259	-276
8	9	6	217	182
10	9	6	285	-279
-5	10	6	248	-251
-2	10	6	296	277
0	10	6	397	-351
1	10	6	206	-182
7	10	6	248	189
-6	11	6	223	-226
-15	1	7	351	-34
-12	1	7	245	305
-11	1	7	553	525
-9	1	7	345	-347
-8	1	7	512	-572
-7	1	7	199	-213
-6	1	7	294	-288
-3	1	7	562	583
-1	1	7	793	[illegible]
2	1	7	470	510
3	1	7	670	714
4	1	7	632	-543
9	1	7	223	[illegible]
10	1	7	370	373
13	1	7	244	-213
-15	2	7	325	-343
-12	2	7	408	403
-11	2	7	237	-272
-10	2	7	189	-183
-8	2	7	248	273
-7	2	7	295	-314
-6	2	7	1085	-1126
-5	2	7	189	124
-4	2	7	834	873
-3	2	7	573	554
-1	2	7	557	-544
0	2	7	282	265
1	2	7	548	453
2	2	7	218	235
4	2	7	255	-281
5	2	7	153	226
6	2	7	220	218
8	2	7	834	-819
10	2	7	293	318
11	2	7	338	330
13	2	7	531	-504
-16	3	7	457	-416
-14	3	7	333	336
-12	3	7	323	-345
-11	3	7	411	-418
-10	3	7	655	705
-9	3	7	430	510
-7	3	7	821	-874
-5	3	7	573	501

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR [illegible]

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-4	3	7	472	522	15	4	7	463	476	4	6	7	185	[illegible]	7	[illegible]	8	484	[illegible]	1	[illegible]	8	[illegible]	[illegible]
-3	3	7	[illegible]	-153	17	4	7	252	[illegible]	6	6	7	272	[illegible]	[illegible]	[illegible]	8	372	[illegible]	2	2	8	[illegible]	[illegible]
-2	3	7	833	[illegible]	-16	5	7	[illegible]	321	7	6	7	259	-276	14	[illegible]	8	[illegible]	[illegible]	4	[illegible]	8	[illegible]	341
-1	3	7	547	[illegible]	-15	5	7	297	[illegible]	8	6	7	257	-167	[illegible]	[illegible]	8	[illegible]	[illegible]	5	[illegible]	8	243	[illegible]
[illegible]	3	7	972	[illegible]	-14	5	7	416	-423	9	6	7	232	[illegible]	18	[illegible]	8	257	[illegible]	6	[illegible]	8	[illegible]	[illegible]
2	3	7	843	[illegible]	-13	5	7	487	465	10	6	7	[illegible]	[illegible]	19	[illegible]	8	[illegible]	[illegible]	7	[illegible]	8	421	[illegible]
3	3	7	834	[illegible]	-12	5	7	383	[illegible]	11	6	7	341	[illegible]	[illegible]	[illegible]	8	[illegible]	207	8	[illegible]	8	[illegible]	[illegible]
4	3	7	[illegible]	[illegible]	-9	5	7	327	-347	15	6	7	258	[illegible]	-18	1	8	[illegible]	371	9	[illegible]	8	[illegible]	[illegible]
7	3	7	413	-442	-8	5	7	341	[illegible]	-12	7	7	321	[illegible]	-13	1	8	214	[illegible]	10	[illegible]	8	[illegible]	277
9	3	7	[illegible]	[illegible]	-7	5	7	491	497	-9	7	7	317	[illegible]	-11	1	8	[illegible]	[illegible]	11	[illegible]	8	[illegible]	[illegible]
12	3	7	[illegible]	-658	-6	5	7	[illegible]	-657	-3	7	7	[illegible]	[illegible]	-10	1	8	[illegible]	-617	12	[illegible]	8	273	-243
14	3	7	[illegible]	[illegible]	-4	5	7	412	-444	-2	7	7	219	-234	-9	1	8	[illegible]	[illegible]	-12	3	8	[illegible]	[illegible]
18	3	7	243	[illegible]	-3	5	7	496	[illegible]	[illegible]	7	7	645	653	-8	1	8	[illegible]	[illegible]	-11	3	8	[illegible]	[illegible]
-15	4	7	439	425	[illegible]	5	7	345	-337	2	7	7	315	-298	-6	1	8	[illegible]	-438	-9	3	8	[illegible]	[illegible]
-13	4	7	568	-541	2	5	7	[illegible]	595	3	7	7	[illegible]	-252	-4	1	8	[illegible]	741	-8	3	8	313	[illegible]
-11	4	7	664	675	4	5	7	399	[illegible]	5	7	7	312	[illegible]	-3	1	8	[illegible]	[illegible]	-6	3	8	215	[illegible]
-10	4	7	676	685	5	5	7	419	-337	1	8	7	199	[illegible]	1	1	8	[illegible]	[illegible]	-5	3	8	[illegible]	[illegible]
-9	4	7	255	-322	6	5	7	237	[illegible]	-4	10	7	[illegible]	-315	4	1	8	[illegible]	[illegible]	-4	3	8	[illegible]	[illegible]
-8	4	7	518	-548	7	5	7	543	[illegible]	6	10	7	289	[illegible]	[illegible]	1	8	484	[illegible]	-3	3	8	[illegible]	[illegible]
-7	4	7	377	-368	9	5	7	547	[illegible]	8	10	7	259	225	6	1	8	[illegible]	[illegible]	-2	3	8	[illegible]	173
-6	4	7	521	524	10	5	7	377	-345	-5	11	7	[illegible]	-253	7	1	8	779	[illegible]	-1	3	8	[illegible]	-281
-5	4	7	[illegible]	318	11	5	7	379	456	-6	12	7	283	-255	8	1	8	461	-444	1	3	8	[illegible]	[illegible]
-4	4	7	522	[illegible]	12	5	7	354	[illegible]	-19	[illegible]	8	319	-307	10	1	8	[illegible]	[illegible]	3	3	8	[illegible]	[illegible]
-3	4	7	377	[illegible]	14	5	7	[illegible]	-329	-16	[illegible]	8	[illegible]	189	12	1	8	325	[illegible]	5	3	8	[illegible]	[illegible]
-2	4	7	648	653	16	5	7	[illegible]	289	-13	[illegible]	8	412	[illegible]	13	1	8	263	[illegible]	6	3	8	328	[illegible]
-1	4	7	647	[illegible]	18	5	7	295	-193	-10	[illegible]	8	516	-498	-16	2	8	[illegible]	-237	8	3	8	[illegible]	[illegible]
1	4	7	1131	-1187	-13	6	7	[illegible]	342	-9	[illegible]	8	883	-813	-10	2	8	[illegible]	[illegible]	9	3	8	[illegible]	[illegible]
2	4	7	561	-583	[illegible]	6	7	318	-374	-8	[illegible]	8	454	439	-9	2	8	398	[illegible]	13	3	8	[illegible]	[illegible]
3	4	7	717	729	[illegible]	6	7	285	324	-7	[illegible]	8	[illegible]	884	-8	2	8	[illegible]	-277	-15	4	8	[illegible]	[illegible]
4	4	7	[illegible]	[illegible]	[illegible]	6	7	177	[illegible]	-5	[illegible]	8	[illegible]	-1125	-7	2	8	[illegible]	[illegible]	[illegible]	4	8	41	[illegible]
6	4	7	[illegible]	[illegible]	-6	6	7	294	275	-4	[illegible]	8	[illegible]	[illegible]	[illegible]	2	8	[illegible]	[illegible]	7	4	8	[illegible]	[illegible]
7	4	7	246	[illegible]	-5	6	7	171	168	-3	[illegible]	8	228	[illegible]	-4	2	8	187	[illegible]	8	4	8	[illegible]	[illegible]
8	4	7	349	[illegible]	[illegible]	6	7	225	-237	3	[illegible]	8	269	[illegible]	-3	2	8	[illegible]	[illegible]	-11	[illegible]	8	283	[illegible]
10	4	7	621	[illegible]	-1	6	7	354	[illegible]	4	[illegible]	8	[illegible]	[illegible]	[illegible]	2	8	[illegible]	[illegible]	-9	[illegible]	8	273	[illegible]
11	4	7	218	[illegible]	1	6	7	659	657	5	[illegible]	8	[illegible]	[illegible]	-1	2	8	[illegible]	[illegible]	-6	[illegible]	8	[illegible]	[illegible]
12	4	7	396	[illegible]	[illegible]	6	7	[illegible]	-234	6	[illegible]	8	[illegible]	[illegible]	[illegible]	2	8	[illegible]	[illegible]	-5	[illegible]	8	[illegible]	[illegible]

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR [illegible]

H	K	L	10FO	10FC
-1	5	8	488	478
1	5	8	437	-488
4	5	8	435	410
5	5	8	307	-301
6	5	8	359	-331
9	5	8	251	291
1	5	8	275	-140
12	5	8	251	-193
-14	6	8	305	-328
-12	6	8	256	335
-6	6	8	198	-159
-5	6	8	307	-295
-3	6	8	502	519
-2	6	8	315	354
-1	6	8	377	-316
0	6	8	652	-742
1	6	8	282	-299
3	6	8	377	343
4	6	8	231	-269
7	6	8	237	301
9	6	8	280	-304
11	6	8	289	226
12	6	8	210	173
-8	7	8	253	292
-6	7	8	273	-275
-2	7	8	281	-273
-1	7	8	512	-403
1	7	8	237	234
3	7	8	215	-213
5	7	8	448	462
6	7	8	248	319
8	7	8	512	-508
-12	8	8	272	-321
-10	8	8	383	383
-7	8	8	329	-369
-1	8	8	258	313

H	K	L	10FO	10FC
0	8	8	294	286
2	8	8	448	-447
4	8	8	313	239
7	8	8	262	-241
9	8	8	357	374
11	8	8	256	-220
-8	9	8	294	-24
-6	9	8	225	215
-4	9	8	304	-294
-2	9	8	427	430
-1	9	8	233	237
1	9	8	279	-257
2	9	8	280	-273
3	9	8	221	251
8	9	8	314	267
10	9	8	299	-292
-7	10	8	250	224
-3	10	8	226	203
-2	10	8	199	193
-17	1	9	246	212
-1	1	9	203	197
-8	1	9	301	251
-4	1	9	219	228
-3	1	9	597	626
-2	1	9	329	-324
-1	1	9	419	-422
1	1	9	608	-617
[illegible]	1	9	319	320
6	1	9	179	213
8	1	9	512	-521
11	1	9	294	335
-13	2	9	349	378
-11	2	9	423	-433
-9	2	9	232	165
-7	2	9	653	-568
-6	2	9	242	196

H	K	L	10FO	10FC
-5	2	9	475	536
-4	2	9	315	333
-3	2	9	416	-395
-2	2	9	625	-635
1	2	9	302	344
3	2	9	848	-841
4	2	9	301	380
5	2	9	360	364
6	2	9	306	315
7	2	9	470	-505
10	2	9	321	373
12	2	9	377	-366
13	2	9	263	217
15	2	9	328	180
-13	3	9	492	-486
-12	3	9	617	-635
-10	3	9	376	365
-8	3	9	517	-538
-6	3	9	672	692
-3	3	9	411	-412
-2	3	9	255	-274
-1	3	9	597	612
0	3	9	397	418
1	3	9	414	-454
2	3	9	979	-948
3	3	9	481	463
4	3	9	439	558
5	3	9	252	-264
6	3	9	261	-277
8	3	9	654	662
9	3	9	228	247
11	3	9	454	-462
13	3	9	211	246
15	3	9	277	-259
-13	4	9	251	-173
-18	4	9	264	-347

H	K	L	10FO	10FC
-15	4	9	391	[illegible]
-14	4	9	312	-495
-12	4	9	254	321
-11	4	9	444	453
-9	4	9	297	-305
-7	4	9	343	343
-6	4	9	532	580
-5	4	9	235	-244
-4	4	9	850	[illegible]
-3	4	9	334	-287
-2	4	9	675	649
-1	4	9	412	421
0	4	9	338	[illegible]
1	4	9	496	-511
2	4	9	308	271
3	4	9	364	385
4	4	9	174	-181
5	4	9	206	-247
7	4	9	453	411
9	4	9	203	-241
-15	5	9	227	-339
-13	5	9	497	439
-12	5	9	212	228
-10	5	9	473	-512
-8	5	9	257	257
-7	5	9	288	253
-5	5	9	334	[illegible]
-3	5	9	327	[illegible]
-1	5	9	497	-487
1	5	9	572	665
2	5	9	537	534
3	5	9	236	-141
4	5	9	633	-647
5	5	9	234	334
13	5	9	301	-307
15	5	9	329	274

H	K	L	10FO	10FC
-11	6	9	[illegible]	-139
-5	6	9	385	407
-4	6	9	291	287
-2	6	9	[illegible]	-312
-1	6	9	294	[illegible]
0	6	9	[illegible]	[illegible]
1	6	9	235	261
2	6	9	271	-273
3	6	9	225	-243
5	6	9	341	344
6	6	9	293	-307
7	6	9	333	-331
9	6	9	293	280
10	6	9	435	445
12	6	9	239	[illegible]
-12	7	9	267	[illegible]
-10	7	9	[illegible]	199
-7	7	9	373	341
-6	7	9	297	274
-4	7	9	344	-357
-3	7	9	311	[illegible]
-2	7	9	[illegible]	[illegible]
-1	7	9	[illegible]	[illegible]
0	7	9	459	457
5	7	9	336	[illegible]
6	7	9	[illegible]	[illegible]
8	7	9	334	247
-11	8	9	184	144
-17	0	10	[illegible]	212
-15	0	10	[illegible]	-443
-13	0	10	342	[illegible]
-12	0	10	298	323
-10	0	10	549	-555
-7	0	10	[illegible]	478
-6	0	10	341	-342
-5	0	10	[illegible]	-375

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR CU(C25H33N4)DMF)(CLO4)2.DMF

H	K	L	10FO	10FC
-4	0	10	456	439
-3	0	10	386	369
-1	0	10	[illegible]	[illegible]
1	0	10	1193	1161
2	0	10	338	331
3	0	10	312	-262
4	0	10	772	-764
6	0	10	393	404
7	0	10	213	213
8	0	10	683	-731
10	0	10	261	254
13	0	10	582	-561
15	0	10	445	419
18	0	10	247	-303
-16	1	10	297	-274
-14	1	10	263	213
-11	1	10	388	-413
-10	1	10	338	372
-9	1	10	497	497
-7	1	10	541	-535
-6	1	10	611	-599
-5	1	10	63	[illegible]
-4	1	10	592	555
-2	1	10	556	-555
-1	1	10	243	-245
0	1	10	[illegible]	[illegible]
2	1	10	214	-223
3	1	10	339	-379
4	1	10	193	172
5	1	10	573	587
7	1	10	636	-635
8	1	10	522	-512
9	1	10	440	473
14	1	10	343	391
-19	2	10	191	172
-17	2	10	41	399

H	K	L	10FO	10FC
[illegible]	2	10	382	-408
[illegible]	2	10	368	375
-5	2	10	517	413
-3	2	10	563	-555
-2	2	10	251	-199
-1	2	10	517	495
0	2	10	167	223
1	2	10	181	-212
3	2	10	167	231
4	2	10	197	252
[illegible]	2	10	354	-305
[illegible]	2	10	548	-555
7	2	10	341	-327
9	2	10	453	44
13	2	10	234	218
-15	3	10	275	-279
-12	3	10	294	311
-11	3	10	333	367
-10	3	10	458	435
-8	3	10	453	-398
-6	3	10	351	354
-4	3	10	409	-415
-3	3	10	352	364
-2	3	10	243	250
-1	3	10	463	-461
0	3	10	616	-621
1	3	10	259	-267
2	3	10	335	368
3	3	10	187	172
4	3	10	177	166
[illegible]	3	10	231	-245
-17	4	10	299	136
-12	4	10	257	-194
-8	4	10	136	223
-5	4	10	377	-388
-4	4	10	273	-259

H	K	L	10FO	10FC
-2	4	10	268	-236
-1	4	10	218	242
2	4	10	327	354
4	4	10	179	209
5	4	10	167	-231
6	4	10	236	250
-14	5	10	208	-239
-11	5	10	263	280
-2	5	10	328	325
0	5	10	336	-363
3	5	10	318	325
9	5	10	245	-218
-8	6	10	208	221
-6	6	10	226	-177
-5	6	10	232	[illegible]
-4	6	10	347	367
-3	6	10	354	413
-1	6	10	238	-322
3	6	10	385	-357
5	6	10	274	205
6	6	10	277	319
8	6	10	358	-364
-13	7	10	261	141
-9	7	10	190	185
-8	7	10	214	207
-3	7	10	433	-376
-2	7	10	594	-521
0	7	10	440	467
2	7	10	396	-383
4	7	10	219	266
5	7	10	331	311
7	7	10	232	-248
12	7	10	281	-249
-10	8	10	257	221
-8	8	10	358	-348
-5	8	10	214	193

H	K	L	10FO	10FC
-4	8	10	257	-123
-3	8	10	412	-391
-1	8	10	266	[illegible]
0	8	10	228	22
1	8	10	251	-236
2	8	10	234	-222
3	8	10	279	-282
-7	9	10	437	[illegible]
-4	9	10	317	-334
4	9	10	[illegible]	-177
5	9	10	392	[illegible]
7	9	10	374	363
-1	10	10	286	[illegible]
3	10	10	[illegible]	[illegible]
-11	1	11	277	-271
-8	1	11	223	247
-5	1	11	283	[illegible]
1	1	11	393	421
3	1	11	350	[illegible]
5	1	11	324	[illegible]
6	1	11	212	254
-14	2	11	418	347
-12	2	11	245	-237
-8	2	11	409	-319
-6	2	11	565	511
-5	2	11	379	345
-3	2	11	425	-431
-2	2	11	214	-198
0	2	11	383	372
[illegible]	2	11	243	-251
[illegible]	2	11	261	278
[illegible]	2	11	[illegible]	[illegible]
9	2	11	265	[illegible]
10	2	11	364	373
11	2	11	348	-363
-13	3	11	261	-324

H	K	L	10FO	10FC
[illegible]	3	11	[illegible]	[illegible]
-8	3	11	325	-317
-7	3	11	434	432
-6	3	11	351	[illegible]
-4	3	11	473	-445
-3	3	11	[illegible]	-243
-2	3	11	183	212
1	3	11	521	-518
3	3	11	328	333
5	3	11	[illegible]	-254
6	3	11	259	-217
[illegible]	3	11	312	[illegible]
12	3	11	241	211
-12	4	11	234	224
-1	4	11	257	-217
-9	4	11	452	-453
-7	4	11	534	523
-6	4	11	257	234
-5	4	11	441	-453
-4	4	11	227	-235
-3	4	11	215	[illegible]
1	4	11	247	257
2	4	11	343	327
4	4	11	257	-219
5	4	11	367	-391
-15	5	11	281	[illegible]
-13	5	11	214	222
-12	5	11	272	197
-6	5	11	[illegible]	-458
-4	5	11	[illegible]	521
-3	5	11	[illegible]	354
-2	5	11	334	-348
-1	5	11	[illegible]	[illegible]
0	5	11	217	[illegible]
8	5	11	254	[illegible]
10	5	11	[illegible]	[illegible]

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR [CU(C3H7NO)4DMF][CLO4]2.DMF

H	K	L	10FO	10FC
-7	6	11	2?8	-2?1
-5	6	11	434	422
-2	6	11	217	-212
-1	6	11	248	268
4	6	11	579	563
7	6	11	295	-224
9	6	11	357	375
3	7	11	362	333
5	7	11	231	-321
1	8	11	334	-273
-17	0	12	227	175
-11	0	12	413	-435
-1	0	12	25	182
-9	0	12	499	463
-7	0	12	612	-575
-6	0	12	6 3	-524
-4	0	12	519	537
-3	0	12	468	416
-2	0	12	593	-552
-1	0	12	312	-299
0	0	12	289	[illegible]
1	0	12	363	398
2	0	12	555	-351
3	0	12	855	-816
4	0	12	564	555
5	0	12	594	562
6	0	12	459	491
7	0	12	334	-241
8	0	12	478	-483
9	0	12	245	13
12	0	12	288	-282
14	0	12	334	363
17	0	12	369	-351
-17	1	12	259	-237
-1	1	12	5 3	352
-1	1	12	360	-352

H	K	L	10FO	10FC
-11	1	12	[illegible]	197
-1	1	12	521	553
-8	1	12	244	-239
-7	1	12	488	-485
-5	1	12	317	297
-4	1	12	377	421
-3	1	12	457	-486
-1	1	12	731	723
0	1	12	184	243
1	1	12	355	-338
2	1	12	564	-579
4	1	12	623	620
5	1	12	273	256
7	1	12	483	-490
11	1	12	399	-39
13	1	12	377	417
-16	2	12	239	256
-15	2	12	261	276
-11	2	12	374	452
-9	2	12	288	-377
-8	2	12	349	-375
-5	2	12	226	-131
-4	2	12	234	-218
-2	2	12	557	534
0	2	12	465	-481
1	2	12	245	-243
2	2	12	274	221
3	2	12	332	349
6	2	12	554	-320
10	2	12	397	-318
12	2	12	337	366
-5	3	12	473	-384
-4	3	12	250	197
-3	3	12	352	335
0	3	12	365	-35
-3	4	12	297	-313

H	K	L	10FO	10FC
4	4	12	389	-341
8	4	12	241	-225
-13	5	12	217	224
-11	5	12	292	-267
-5	5	12	193	249
-3	5	12	277	-234
-2	5	12	335	-332
-8	7	12	332	-334
-5	7	12	347	341
-3	7	12	446	-397
-1	7	12	371	373
0	7	12	321	272
6	7	12	343	-358
9	7	12	245	275
-9	8	12	323	-350
-5	8	12	332	366
-4	8	12	336	-319
4	8	12	254	97
5	8	12	286	-285
13	8	12	211	-166
1	9	12	213	225
4	9	12	237	-286
-6	1	13	255	-254
-3	1	13	241	-266
-1	1	13	275	-281
0	1	13	277	317
1	1	13	186	232
3	1	13	212	-136
5	1	13	251	245
-10	2	13	299	298
-8	2	13	292	-259
-7	2	13	304	-231
-3	2	13	315	319
2	2	13	383	-365
4	2	13	474	454
6	2	13	238	-276

H	K	L	10FO	10FC
[illegible]	2	13	313	33[illegible]
-9	3	13	214	-241
-4	3	13	263	-231
-1	3	13	231	144
0	3	13	392	-349
3	3	13	355	39
5	3	13	227	-235
-14	4	13	257	-215
-12	4	13	243	231
-6	4	13	318	-317
-5	4	13	294	-298
-3	4	13	337	261
2	4	13	354	320
4	4	13	381	-330
8	4	13	277	-264
10	4	13	285	220
-9	5	13	327	341
-7	5	13	334	-331
-4	5	13	248	295
3	5	13	394	-373
5	5	13	476	439
7	5	13	433	-375
-8	6	13	292	-23
-3	6	13	412	-383
2	6	13	301	-242
4	6	13	248	25
9	6	13	232	217
-2	7	13	231	14
7	7	13	253	145
-14	0	14	224	161
-13	0	14	248	-155
-10	0	14	433	-435
-9	0	14	309	482
-3	0	14	236	-251
-1	0	14	301	273
0	0	14	372	383

H	K	L	10FO	10FC
[illegible]	0	14	464	-442
2	0	14	51[illegible]	-3[illegible]9
5	0	14	31[illegible]	347
13	0	14	[illegible]	[illegible]
-4	1	14	53[illegible]	-3[illegible]
-3	1	14	4[illegible]	-428
-2	1	14	237	32[illegible]
-1	1	14	257	323
1	1	14	472	-47[illegible]
3	1	14	372	447
12	1	14	248	252
-2	2	14	244	324
0	2	14	32[illegible]	-37[illegible]
2	2	14	237	332
6	2	14	237	[illegible]
-11	3	14	25[illegible]	-144
-7	3	14	27[illegible]	23[illegible]
1	3	14	214	[illegible]
-5	5	14	245	218
-11	7	14	234	211
-9	7	14	218	-14[illegible]
-1	7	14	277	31[illegible]
0	8	14	297	-3[illegible]
2	8	14	27	254
-6	9	14	28[illegible]	-219
-7	1	15	297	-261
-5	1	15	234	25[illegible]
-11	2	15	[illegible]	[illegible]
-6	2	15	217	142
-4	2	15	234	-218
-2	2	15	3[illegible]	349
-1	2	15	24[illegible]	[illegible]
0	2	15	24[illegible]	-276
1	2	15	231	-314
2	2	15	[illegible]1	-[illegible]35
8	2	15	314	[illegible]

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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR  [CU(C28H32N4)DMF][CL04]2.DMF

  H  K  L  10FO 10FC     H  K  L  10FO 10FC     H  K  L  10FO 10FC     H  K  L  10FO 10FC     H  K  L  10FO 10FC

 -1  3 15  212 -[illegible]    [illegible]  4 15  341 -347    -5    16  239  246     [illegible]  7 16  [illegible] -143    [illegible]  4 17  [illegible]  [illegible]
 -5  3 15  345 -347    [illegible]  4 15  363  333    -3    16  367 -370   -11  2 17  257   73    -4    18  [illegible] -24[illegible]
 [illegible]  3 15  [illegible] -[illegible]    [illegible]  4 15  362 -3[illegible]    -1    16  325  340    -7  2 17  348  311    -3    18  [illegible] -3[illegible]
  2  3 15  3[illegible]   35[illegible]    -5  5 15  2[illegible]3  2[illegible]     [illegible]    16  499  437    -[illegible]  2 17  38[illegible]  3[illegible]1     3    18  23[illegible]  [illegible]13
  4  3 15  21[illegible] -247    -3  5 15  235 -234    -4  1 16  257 -258    -8  3 17  22[illegible]  17[illegible]     [illegible]    18  272 -2[illegible]
  9  3 15  245 -245     [illegible]  5 15  3[illegible]  268     [illegible]  1 16  24[illegible] -243     5  3 17  251 -211    -2  1 18  231  [illegible]
 -3  4 15  275  [illegible]     [illegible]  [illegible] 15  347 -321    -3  2 16  244  218     8  3 17  244 -25[illegible]     4  1 18  27[illegible] -152
 -6  4 15  383 -41     -4  5 15  261 -3[illegible]1    -2  3 16  257 -282     [illegible]  4 17  273 -296    -1    18  274 -[illegible]7
  1  4 15  21[illegible]  188     1  6 15  283 -2[illegible]
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TABLE 2D

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR CU(C34H22N4O2).DMF

H	K	L	10FO	10FC
2	0	0	1453	-1352
3	0	0	167	-166
4	0	0	244	-257
5	0	0	161	-164
6	0	0	126	-124
-7	1	0	207	-198
-6	1	0	233	-216
-5	1	0	387	-375
-4	1	0	145	-106
-3	1	0	932	-802
-2	1	0	771	-623
1	1	0	796	807
2	1	0	248	232
3	1	0	471	-485
4	1	0	251	-255
5	1	0	185	-176
6	1	0	290	283
7	1	0	288	281
-6	2	0	279	-276
-5	2	0	155	144
-3	2	0	742	-603
-2	2	0	1697	1386
-1	2	0	177	-160
0	2	0	958	-926
1	2	0	221	204
2	2	0	334	-315
3	2	0	532	-530
4	2	0	161	-163
5	2	0	145	131
6	2	0	177	163
7	2	0	181	179
-7	3	0	363	-390
-5	3	0	230	205
-4	3	0	288	250
-3	3	0	724	631
-2	3	0	152	158
-1	3	0	76	65
0	3	0	136	107
1	3	0	329	-351
2	3	0	136	107
3	3	0	214	-215
5	3	0	140	141
6	3	0	165	171
-8	4	0	211	-222
-7	4	0	175	-175
-6	4	0	251	-225
-5	4	0	224	-205
-4	4	0	912	831
-3	4	0	655	577
-2	4	0	103	114
-1	4	0	269	-268
0	4	0	482	-466
2	4	0	204	172
3	4	0	168	140
4	4	0	136	124
5	4	0	200	198
6	4	0	151	104
-9	5	0	147	-124
-8	5	0	220	-205
-7	5	0	231	-236
-5	5	0	402	373
-4	5	0	568	542
-3	5	0	380	341
-2	5	0	98	69
0	5	0	224	-238
1	5	0	297	-312
3	5	0	302	282
4	5	0	248	253
5	5	0	157	129
8	5	0	146	-137
-9	6	0	179	-165
-8	6	0	344	-347
-7	6	0	225	-249
-6	6	0	382	362
-5	6	0	387	361
-4	6	0	168	165
-2	6	0	392	-379
-1	6	0	360	-372
0	6	0	142	-153
1	6	0	113	-93
2	6	0	108	126
3	6	0	235	267
5	6	0	167	204
7	6	0	176	-184
-6	7	0	246	242
-5	7	0	295	264
-3	7	0	163	-154
-2	7	0	327	-328
-1	7	0	415	-426
0	7	0	265	-255
1	7	0	138	153
2	7	0	332	346
-3	8	0	165	-193
-1	8	0	244	-249
1	8	0	553	582
2	8	0	179	178
5	8	0	168	-160
-8	9	0	201	195
-6	9	0	234	-167
-5	9	0	187	-188
-3	9	0	162	-110
-2	9	0	236	-206
0	9	0	460	460
1	9	0	243	266
5	9	0	168	-148
-8	10	0	148	144
-5	10	0	279	-272
-1	10	0	182	215
4	10	0	174	-155
-6	11	0	175	-181
-5	11	0	158	-139
-2	11	0	131	135
-6	12	0	157	-126
-1	12	0	184	151
3	-12	1	171	-165
4	-12	1	211	-209
3	-11	1	192	-189
7	-11	1	138	118
-3	-10	1	174	161
3	-10	1	142	-169
5	-10	1	205	167
0	-9	1	274	-267
1	-9	1	278	-257
2	-9	1	126	-120
4	-9	1	171	175
5	-9	1	167	142
6	-9	1	280	241
7	-9	1	151	116
-3	-8	1	307	336
-2	-8	1	246	239
-1	-8	1	529	-506
0	-8	1	597	-570
1	-8	1	355	-345
3	-8	1	143	143
5	-8	1	191	200
-4	-7	1	228	238
-3	-7	1	372	358
-2	-7	1	172	-202
-1	-7	1	404	-433
0	-7	1	375	-374
1	-7	1	238	-248
3	-7	1	150	146
4	-7	1	366	315
5	-7	1	167	142
6	-7	1	174	-103
7	-7	1	295	-240
8	-7	1	265	-267
-4	-6	1	264	271
-3	-6	1	287	-293
-2	-6	1	312	-320
-1	-6	1	285	-289
0	-6	1	264	-263
1	-6	1	234	238
2	-6	1	221	215
3	-6	1	455	395
4	-6	1	342	306
7	-6	1	378	-347
8	-6	1	259	-231
-8	-5	1	147	135
-5	-5	1	226	194
-4	-5	1	140	-162
-3	-5	1	233	-245
-2	-5	1	256	-268
-1	-5	1	309	-310
0	-5	1	215	219
2	-5	1	406	392
3	-5	1	170	168
4	-5	1	142	102
5	-5	1	234	-191
6	-5	1	444	-395
-6	-4	1	308	319
-4	-4	1	324	-327
-3	-4	1	405	-414
-1	-4	1	381	363
0	-4	1	160	165
1	-4	1	129	164
2	-4	1	238	250
4	-4	1	105	-78
5	-4	1	709	-597
6	-4	1	283	-268
-7	-3	1	228	213
-5	-3	1	158	-177
-4	-3	1	228	-249
-3	-3	1	635	-618
-2	-3	1	129	-133
-1	-3	1	187	195
0	-3	1	629	625
3	-3	1	262	227
4	-3	1	565	-489
5	-3	1	465	-385
6	-3	1	201	-188
8	-3	1	187	182
-8	-2	1	352	348
-5	-2	1	262	-254
-4	-2	1	202	-201
-2	-2	1	206	-203
-1	-2	1	255	261
0	-2	1	294	281
1	-2	1	344	-298
2	-2	1	733	621
3	-2	1	119	-121
4	-2	1	733	-616
5	-2	1	532	-468
7	-2	1	195	205
8	-2	1	161	135
10	-2	1	160	-172
-9	-1	1	190	226
-6	-1	1	186	-191
-5	-1	1	361	-351
-3	-1	1	465	463
-2	-1	1	690	702
-1	-1	1	101	102
1	-1	1	322	309
3	-1	1	376	-329
4	-1	1	678	-571
5	-1	1	105	-69
6	-1	1	224	225
7	-1	1	219	205
-7	0	1	228	-254
-6	0	1	328	-359
-2	0	1	1396	1391
2	0	1	676	-569
3	0	1	216	-163
6	0	1	143	153
7	0	1	309	316
-8	1	1	142	-141
-5	1	1	135	-132
-3	1	1	697	618
-2	1	1	1153	1068
2	1	1	368	-366
3	1	1	150	-151
4	1	1	204	180
5	1	1	244	246
-9	2	1	168	-173
-8	2	1	196	-204
-6	2	1	228	234
-5	2	1	307	-307
-4	2	1	287	294
-3	2	1	1079	963
-2	2	1	392	-330

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR CU(C34H22N4)2).DMF

H	K	L	10FO	10FC
-1	2	1	367	-382
0	2	1	255	-270
1	2	1	221	-251
3	2	1	383	365
4	2	1	575	555
5	2	1	295	301
6	2	1	255	-242
7	2	1	333	-322
-7	3	1	172	207
-6	3	1	285	308
-5	3	1	152	160
-3	3	1	166	-152
-2	3	1	137	125
-1	3	1	127	-146
0	3	1	548	-569
1	3	1	255	-261
2	3	1	308	321
3	3	1	709	719
4	3	1	380	379
5	3	1	196	184
6	3	1	177	-212
7	3	1	336	-343
8	3	1	176	-144
-6	4	1	204	233
-5	4	1	441	399
-4	4	1	194	195
-3	4	1	147	136
-2	4	1	373	-367
-1	4	1	324	-337
1	4	1	262	247
2	4	1	404	403
3	4	1	282	288
4	4	1	185	185
-6	5	1	168	206
-4	5	1	229	206
-3	5	1	138	76
-2	5	1	279	-295
-1	5	1	179	-187
1	5	1	341	345
2	5	1	250	251
3	5	1	272	290
5	5	1	148	-184
-8	6	1	143	135
-7	6	1	226	250
-4	6	1	431	-409
-3	6	1	141	-170
0	6	1	409	412
1	6	1	241	258
3	6	1	211	-229
-5	7	1	175	-180
-4	7	1	357	-363
-3	7	1	346	-373
-1	7	1	483	509
0	7	1	368	375
1	7	1	253	255
5	7	1	233	-198
-5	8	1	321	-296
-4	8	1	251	-264
-2	8	1	363	400
-1	8	1	576	629
0	8	1	277	302
4	8	1	275	-285
-4	9	1	245	-236
-2	9	1	424	414
-1	9	1	730	763
1	9	1	253	-275
2	9	1	179	-171
3	9	1	175	-172
-7	10	1	211	-174
-2	10	1	155	227
2	10	1	174	-206
-7	11	1	141	-126
-4	11	1	153	144
-3	11	1	138	145
-1	11	1	162	-125
-4	12	1	142	161
0	12	1	142	-184
1	-12	2	175	-181
2	-12	2	175	-187
1	-11	2	182	-177
4	-11	2	181	165
5	-11	2	145	176
-2	-10	2	166	-123
4	-10	2	377	324
5	-10	2	256	214
8	-10	2	163	-156
-1	-9	2	175	-141
0	-9	2	267	-261
3	-9	2	199	186
4	-9	2	307	267
5	-9	2	127	127
7	-9	2	199	-195
-3	-8	2	175	-192
-2	-8	2	249	-234
-1	-8	2	371	-362
0	-8	2	143	-130
2	-8	2	260	239
5	-8	2	176	122
6	-8	2	196	-167
-5	-7	2	177	162
-3	-7	2	376	-372
-2	-7	2	528	-510
-1	-7	2	133	-106
0	-7	2	162	136
1	-7	2	244	243
2	-7	2	236	234
3	-7	2	141	130
4	-7	2	180	-124
5	-7	2	361	-355
-4	-6	2	195	-204
-3	-6	2	312	-294
-2	-6	2	119	-112
0	-6	2	268	299
1	-6	2	246	261
2	-6	2	360	318
4	-6	2	553	-531
5	-6	2	367	-319
6	-6	2	117	130
-5	-5	2	151	-136
-4	-5	2	215	-198
-3	-5	2	157	-158
-1	-5	2	341	341
0	-5	2	387	394
1	-5	2	224	205
3	-5	2	727	-627
4	-5	2	473	-450
6	-5	2	155	106
7	-5	2	332	279
8	-5	2	209	191
-5	-4	2	219	-219
-4	-4	2	240	-211
-2	-4	2	357	361
0	-4	2	179	204
1	-4	2	218	199
2	-4	2	668	-611
3	-4	2	1012	-881
4	-4	2	414	-351
5	-4	2	143	133
6	-4	2	137	123
7	-4	2	171	194
8	-4	2	143	170
-7	-3	2	143	-119
-6	-3	2	189	-158
-5	-3	2	287	-292
-4	-3	2	191	-188
-1	-3	2	235	237
0	-3	2	122	135
1	-3	2	192	-185
2	-3	2	738	-696
3	-3	2	171	-163
4	-3	2	105	67
6	-3	2	136	110
7	-3	2	118	139
-6	-2	2	244	-237
-4	-2	2	187	184
-3	-2	2	194	-183
-2	-2	2	223	-203
0	-2	2	260	-231
1	-2	2	529	-522
3	-2	2	133	122
4	-2	2	168	-181
5	-2	2	185	165
6	-2	2	253	220
7	-2	2	158	199
9	-2	2	156	-183
-7	-1	2	131	-137
-6	-1	2	150	-182
-5	-1	2	302	291
-4	-1	2	744	755
-3	-1	2	668	658
-2	-1	2	529	-531
-1	-1	2	939	-881
0	-1	2	620	-656
1	-1	2	72	90
2	-1	2	147	-143
3	-1	2	148	-125
4	-1	2	319	267
5	-1	2	209	213
-8	0	2	234	-240
-5	0	2	150	158
-4	0	2	709	721
-3	0	2	653	622
-2	0	2	332	-317
-1	0	2	1022	-1069
1	0	2	292	272
2	0	2	409	-334
3	0	2	820	671
4	0	2	407	376
5	0	2	307	291
7	0	2	264	-277
-5	1	2	126	140
-4	1	2	410	443
-3	1	2	258	273
-2	1	2	1760	-1870
-1	1	2	1039	-1162
1	1	2	185	-196
2	1	2	239	301
3	1	2	187	188
4	1	2	333	314
5	1	2	236	234
6	1	2	248	-241
7	1	2	131	-126
8	1	2	177	-172
-8	2	2	246	277
-6	2	2	107	103
-5	2	2	443	467
-4	2	2	140	158
-3	2	2	928	-918
-2	2	2	669	-682
-1	2	2	189	174
0	2	2	488	-497
1	2	2	166	156
2	2	2	99	-62
3	2	2	443	453
4	2	2	298	269
5	2	2	499	-502
6	2	2	390	-409
7	2	2	191	-197
-8	3	2	158	179
-7	3	2	195	198
-6	3	2	207	222
-5	3	2	201	204
-4	3	2	773	-773
-3	3	2	373	-393
-2	3	2	588	571
0	3	2	260	271
1	3	2	439	503
2	3	2	517	501
3	3	2	318	294
4	3	2	407	-398
5	3	2	214	-198
6	3	2	218	-220
-9	4	2	151	146
-8	4	2	142	174
-7	4	2	152	193
-5	4	2	445	-476
-4	4	2	269	-308
-3	4	2	161	155
-2	4	2	331	-344
-1	4	2	327	325

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR CU(C34H22N4O2).DMF

H	K	L	10FO	10FC
0	4	2	98	137
1	4	2	381	394
2	4	2	474	442
3	4	2	218	-223
4	4	2	319	-333
5	4	2	145	-162
-7	5	2	147	192
-5	5	2	262	-268
-4	5	2	309	-311
-2	5	2	429	441
-1	5	2	179	197
0	5	2	109	110
1	5	2	322	328
3	5	2	246	-251
4	5	2	319	-343
5	5	2	120	-117
-10	6	2	147	142
-6	6	2	134	-219
-5	6	2	260	-275
-4	6	2	334	-357
-2	6	2	147	175
-1	6	2	226	257
0	6	2	321	327
3	6	2	211	-242
4	6	2	151	-139
-10	7	2	192	172
-9	7	2	244	224.
-6	7	2	175	-165
-5	7	2	171	-176
-4	7	2	151	139
-2	7	2	219	241
-1	7	2	293	327
1	7	2	220	-231
4	7	2	163	-183
6	7	2	202	190
-7	8	2	210	-191
-4	8	2	260	238
-3	8	2	480	490
-2	8	2	416	456
0	8	2	151	-164
1	8	2	145	-129
2	8	2	142	-169
3	8	2	192	-206
5	8	2	171	148
-7	9	2	224	-194
-4	9	2	197	182
-3	9	2	438	442
-2	9	2	240	229
-1	9	2	201	-231
0	9	2	171	-186
4	9	2	205	179
-4	10	2	191	240
-2	10	2	229	-244
-1	10	2	174	-206
1	10	2	146	-131
3	10	2	185	168
-4	11	2	177	185
-3	11	2	191	-181
-2	11	2	182	-210
1	12	2	182	131
3	-12	3	163	169
4	-12	3	190	157
2	-11	3	165	179
3	-11	3	176	136
0	-10	3	165	152
1	-10	3	199	199
2	-10	3	218	201
5	-10	3	153	-124
6	-10	3	219	-185
-4	-9	3	162	-160
1	-9	3	211	188
2	-9	3	274	255
-4	-8	3	163	-163
1	-8	3	185	148
4	-8	3	293	-265
5	-8	3	259	-246
8	-8	3	128	176
9	-8	3	181	166
-4	-7	3	240	-219
-2	-7	3	440	424
-1	-7	3	346	340
0	-7	3	192	162
3	-7	3	171	-169
4	-7	3	304	-283
5	-7	3	243	-186
7	-7	3	260	239
8	-7	3	150	172
-6	-6	3	166	-204
-5	-6	3	332	-301
-3	-6	3	267	256
-2	-6	3	282	293
-1	-6	3	289	289
1	-6	3	127	64
3	-6	3	421	-380
5	-6	3	115	111
6	-6	3	235	211
7	-6	3	424	413
-6	-5	3	279	-272
-4	-5	3	297	298
-3	-5	3	160	128
-2	-5	3	211	208
0	-5	3	278	-235
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2	-5	3	782	-741
3	-5	3	225	200
5	-5	3	377	360
6	-5	3	436	394
7	-5	3	219	179
-7	-4	3	230	-239
-5	-4	3	197	227
-3	-4	3	306	316
-1	-4	3	192	186
0	-4	3	166	-208
1	-4	3	1358	-1175
2	-4	3	752	-678
4	-4	3	570	545
5	-4	3	556	539
-8	-3	3	176	-172
-4	-3	3	200	240
0	-3	3	619	-583
1	-3	3	104	-146
2	-3	3	492	-494
3	-3	3	356	369
4	-3	3	642	611
5	-3	3	110	105
7	-3	3	129	-124
-5	-2	3	163	158
-4	-2	3	194	-218
-3	-2	3	136	117
-2	-2	3	395	382
-1	-2	3	459	-397
0	-2	3	575	-564
1	-2	3	405	-426
2	-2	3	544	532
3	-2	3	678	686
4	-2	3	186	-145
5	-2	3	120	117
6	-2	3	118	-103
7	-2	3	225	-220
8	-2	3	147	-142
-7	-1	3	156	156
-6	-1	3	270	280
-4	-1	3	255	-235
-3	-1	3	492	-544
-2	-1	3	577	-577
-1	-1	3	596	534
0	-1	3	251	-266
1	-1	3	95	108
2	-1	3	383	400
3	-1	3	655	578
4	-1	3	646	532
5	-1	3	165	-130
6	-1	3	225	-217
-7	0	3	300	317
-6	0	3	216	215
-5	0	3	160	153
-4	0	3	298	-276
-3	0	3	1095	-1073
-2	0	3	1088	-1135
-1	0	3	1007	-964
0	0	3	317	-350
1	0	3	846	761
3	0	3	400	326
4	0	3	241	181
5	0	3	150	-142
-8	1	3	142	149
-7	1	3	272	309
-6	1	3	307	337
-4	1	3	626	-636
-3	1	3	317	-303
-2	1	3	851	-924
-1	1	3	407	-454
0	1	3	321	299
1	1	3	168	184
3	1	3	518	-487
4	1	3	226	-200
5	1	3	114	-93
6	1	3	185	-195
-8	2	3	156	-183
-7	2	3	119	119
-6	2	3	346	386
-5	2	3	158	-162
-4	2	3	718	-758
-3	2	3	441	-460
-2	2	3	207	240
-1	2	3	906	934
0	2	3	859	845
1	2	3	292	321
3	2	3	421	-432
4	2	3	470	-470
8	2	3	158	164
-6	3	3	172	-213
-5	3	3	504	-530
-4	3	3	244	-270
-3	3	3	190	184
-1	3	3	128	-110
0	3	3	373	393
1	3	3	397	379
2	3	3	287	-305
3	3	3	572	-550
6	3	3	201	203
-8	4	3	140	162
-6	4	3	370	-423
-4	4	3	199	195
-2	4	3	147	150
-1	4	3	137	134
1	4	3	493	-482
2	4	3	665	-645
3	4	3	201	-230
6	4	3	290	281
-7	5	3	259	-285
-6	5	3	136	-166
-5	5	3	108	119
-3	5	3	146	195
-2	5	3	238	253
-1	5	3	115	106
0	5	3	174	-201
1	5	3	507	-472
2	5	3	225	-242
3	5	3	248	-254
5	5	3	168	173
-8	6	3	219	-250
-7	6	3	148	-163
-4	6	3	260	281
-3	6	3	142	176
-1	6	3	163	-178
0	6	3	120	-128
2	6	3	224	-239
4	6	3	194	178
-7	7	3	120	-99
-6	7	3	117	108
-5	7	3	254	268
-4	7	3	141	176
-1	7	3	265	-271
1	7	3	140	-166
3	7	3	152	150
-6	8	3	192	210
-5	8	3	387	381
-4	8	3	234	253
-3	8	3	225	-203

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR CU(C34H22N4O2).DMF

H	K	L	10FO	10FC
-2	8	3	375	-394
-1	8	3	140	-150
0	8	3	205	-237
2	8	3	174	220
3	8	3	228	202
-6	9	3	122	128
-5	9	3	292	314
-4	9	3	145	113
-3	9	3	279	-342
-2	9	3	297	-326
-1	9	3	209	-209
2	9	3	184	228
3	9	3	194	201
-6	10	3	192	149
-3	10	3	133	-202
-2	10	3	148	-204
1	10	3	226	212
-4	11	3	244	-242
0	11	3	196	185
1	-12	4	224	216
2	-12	4	191	204
0	-11	4	165	180
1	-11	4	235	249
3	-11	4	176	-157
4	-11	4	245	-193
0	-10	4	249	244
2	-10	4	163	-152
3	-10	4	199	-144
4	-10	4	195	-205
-3	-9	4	162	133
3	-9	4	259	-243
4	-9	4	148	-145
7	-9	4	221	181
-2	-8	4	386	390
-1	-8	4	317	299
0	-8	4	206	-194
1	-8	4	163	-134
2	-8	4	304	-282
4	-8	4	126	103
-3	-7	4	269	271
-2	-7	4	419	418
-1	-7	4	197	167
0	-7	4	146	-155
1	-7	4	406	-372
2	-7	4	117	-125
4	-7	4	168	133
5	-7	4	417	382
-4	-6	4	464	450
-3	-6	4	465	462
-2	-6	4	225	-235
-1	-6	4	116	-96
1	-6	4	341	-298
2	-6	4	153	-155
5	-6	4	251	249
6	-6	4	361	324
-5	-5	4	294	280
-4	-5	4	321	303
-1	-5	4	319	-315
0	-5	4	304	-333
1	-5	4	150	-148
2	-5	4	180	190
3	-5	4	485	486
5	-5	4	147	181
6	-5	4	133	126
7	-5	4	182	-204
8	-5	4	185	-164
-6	-4	4	226	235
-5	-4	4	283	290
-4	-4	4	185	-187
-3	-4	4	129	-126
-2	-4	4	128	-139
-1	-4	4	580	-535
0	-4	4	404	-401
1	-4	4	565	532
2	-4	4	336	396
3	-4	4	214	220
4	-4	4	337	346
6	-4	4	230	-212
-7	-3	4	141	141
-6	-3	4	187	189
-3	-3	4	191	-210
-2	-3	4	411	-401
-1	-3	4	331	-309
0	-3	4	177	163
1	-3	4	404	454
2	-3	4	317	320
3	-3	4	346	371
5	-3	4	378	-340
6	-3	4	206	-185
-7	-2	4	272	292
-5	-2	4	148	-154
-2	-2	4	125	-144
-1	-2	4	113	124
0	-2	4	321	323
1	-2	4	399	462
2	-2	4	146	147
5	-2	4	228	-224
6	-2	4	216	-225
8	-2	4	243	271
9	-2	4	262	287
-7	-1	4	186	188
-6	-1	4	109	-121
-5	-1	4	176	-196
-4	-1	4	196	-237
-3	-1	4	344	-352
-2	-1	4	131	172
-1	-1	4	646	593
0	-1	4	401	440
1	-1	4	235	266
2	-1	4	104	71
3	-1	4	112	-114
4	-1	4	191	-190
5	-1	4	280	-271
6	-1	4	195	-161
8	-1	4	255	243
-6	0	4	122	-144
-5	0	4	380	-393
-4	0	4	216	-246
-3	0	4	127	-167
-2	0	4	714	-709
-1	0	4	631	586
0	0	4	704	727
2	0	4	557	485
3	0	4	341	-317
4	0	4	404	-378
6	0	4	189	201
-9	1	4	171	174
-6	1	4	341	-373
-5	1	4	287	-274
-4	1	4	155	167
-2	1	4	326	-343
-1	1	4	406	-493
0	1	4	632	650
2	1	4	391	-406
3	1	4	337	-317
4	1	4	147	-150
5	1	4	221	191
6	1	4	280	277
-7	2	4	216	-222
-6	2	4	205	-200
-4	2	4	112	-98
-3	2	4	791	843
-2	2	4	1083	1176
-1	2	4	821	-862
0	2	4	463	-438
1	2	4	219	-238
2	2	4	440	-471
3	2	4	358	-354
4	2	4	152	144
5	2	4	218	181
6	2	4	229	249
7	2	4	285	276
-7	3	4	235	-275
-6	3	4	132	-125
-4	3	4	519	553
-3	3	4	474	529
-2	3	4	401	418
-1	3	4	155	-135
0	3	4	482	-501
1	3	4	382	-377
2	3	4	412	-417
4	3	4	317	367
5	3	4	239	234
6	3	4	329	312
-8	4	4	212	-236
-7	4	4	155	-159
-5	4	4	254	260
-4	4	4	321	351
-3	4	4	93	-89
-1	4	4	202	-211
0	4	4	961	-947
1	4	4	891	-843
2	4	4	456	444
3	4	4	414	416
5	4	4	250	260
-9	5	4	161	-156
-8	5	4	166	-126
-6	5	4	200	199
-2	5	4	166	150
-1	5	4	376	-383
0	5	4	974	-952
1	5	4	294	-291
2	5	4	314	331
3	5	4	238	259
4	5	4	209	224
7	5	4	145	-117
-6	6	4	176	215
-3	6	4	160	-150
-2	6	4	199	-214
-1	6	4	256	-274
3	6	4	243	229
-5	7	4	109	-92
-4	7	4	123	-169
-2	7	4	347	-368
-1	7	4	132	-160
0	7	4	106	99
1	7	4	210	225
2	7	4	170	176
-8	8	4	212	226
-7	8	4	275	290
-5	8	4	167	-154
-4	8	4	360	-379
-3	8	4	279	-312
0	8	4	153	166
1	8	4	228	238
-8	9	4	152	193
-5	9	4	125	-153
-4	9	4	434	-479
-3	9	4	343	-370
-1	9	4	121	137
0	9	4	190	217
1	9	4	176	181
2	9	4	167	146
-6	10	4	140	-107
-5	10	4	225	-223
-3	10	4	148	-178
2	10	4	204	-175
3	10	4	161	-170
-3	11	4	168	158
-1	11	4	129	153
1	11	4	163	-158
2	11	4	215	-179
2	-11	5	265	-225
3	-11	5	211	-197
1	-10	5	210	-201
2	-10	5	298	-281
5	-10	5	172	167
0	-9	5	185	-166
1	-9	5	220	-218
2	-9	5	132	-149
5	-9	5	282	258
6	-9	5	171	159
0	-8	5	288	-252
1	-8	5	275	-277
7	-8	5	141	-157
-3	-7	5	182	155
-2	-7	5	122	137
0	-7	5	182	-198
2	-7	5	218	204
3	-7	5	238	238

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR CU(C34H22N4O2).DMF

H	K	L	10FO	10FC
7	-7	5	200	-186
-3	-6	5	158	-189
-2	-6	5	180	-182
0	-6	5	230	180
1	-6	5	171	173
2	-6	5	163	141
3	-6	5	319	332
5	-6	5	175	-159
-7	-5	5	165	132
-6	-5	5	191	133
-4	-5	5	207	-196
-3	-5	5	365	-351
-2	-5	5	342	-335
0	-5	5	210	222
1	-5	5	488	512
2	-5	5	216	239
4	-5	5	137	-137
5	-5	5	512	-511
6	-5	5	248	-223
-7	-4	5	251	250
-4	-4	5	167	-156
-3	-4	5	299	-320
-2	-4	5	226	-242
-1	-4	5	280	249
0	-4	5	933	861
3	-4	5	148	-184
4	-4	5	327	-352
5	-4	5	331	-365
6	-4	5	244	-239
-5	-3	5	168	179
-4	-3	5	199	-220
-3	-3	5	500	-515
-1	-3	5	945	850
0	-3	5	829	792
1	-3	5	194	203
2	-3	5	175	175
3	-3	5	554	-578
4	-3	5	341	-354
6	-3	5	124	101
-5	-2	5	150	177
-4	-2	5	255	245
-3	-2	5	111	-120
-2	-2	5	400	370
-1	-2	5	307	316
0	-2	5	128	140
1	-2	5	190	197
2	-2	5	361	-385
3	-2	5	470	-477

H	K	L	10FO	10FC
4	-2	5	180	-201
6	-2	5	121	154
7	-2	5	197	233
8	-2	5	298	321
-7	-1	5	172	-181
-6	-1	5	180	-194
-5	-1	5	161	-144
-4	-1	5	111	138
-3	-1	5	772	757
-2	-1	5	407	375
0	-1	5	255	264
1	-1	5	502	-521
2	-1	5	115	-96
6	-1	5	165	138
7	-1	5	250	265
-7	0	5	215	-204
-6	0	5	136	-132
-5	0	5	220	-260
-4	0	5	298	308
-3	0	5	698	706
-1	0	5	708	-620
2	0	5	493	-428
3	0	5	118	-143
4	0	5	190	177
5	0	5	168	170
6	0	5	295	320
-7	1	5	204	-182
-6	1	5	174	-191
-5	1	5	375	404
-4	1	5	614	662
-3	1	5	603	644
-2	1	5	718	737
-1	1	5	649	-706
0	1	5	508	-509
1	1	5	433	-487
2	1	5	216	-240
3	1	5	283	271
4	1	5	189	170
-9	2	5	186	-168
-8	2	5	214	-188
-7	2	5	117	-103
-6	2	5	145	153
-5	2	5	182	180
-4	2	5	480	510
-3	2	5	438	495
-2	2	5	685	742
-1	2	5	331	372
0	2	5	1032	-953

H	K	L	10FO	10FC
1	2	5	167	-178
2	2	5	348	386
3	2	5	216	249
4	2	5	499	523
5	2	5	304	305
7	2	5	172	-157
-8	3	5	195	-221
-6	3	5	230	220
-5	3	5	233	251
-4	3	5	161	128
-3	3	5	438	-480
-2	3	5	412	-485
-1	3	5	288	-266
0	3	5	142	-149
2	3	5	150	177
3	3	5	295	305
4	3	5	395	401
5	3	5	350	349
-6	4	5	317	376
-4	4	5	199	-221
-3	4	5	106	-110
-2	4	5	655	-667
-1	4	5	479	-475
0	4	5	113	118
1	4	5	199	194
2	4	5	272	272
3	4	5	156	171
5	4	5	151	-164
-10	5	5	158	-147
-8	5	5	156	201
-7	5	5	209	212
-5	5	5	147	-172
-3	5	5	184	-198
-2	5	5	424	-408
-1	5	5	112	-61
0	5	5	509	507
1	5	5	458	459
2	5	5	118	112
4	5	5	246	-250
5	5	5	228	-192
-8	6	5	168	176
-4	6	5	278	-306
-3	6	5	303	-321
-1	6	5	327	339
0	6	5	267	274
1	6	5	166	153
2	6	5	176	156
4	6	5	175	-172

H	K	L	10FC	10FC
-5	7	5	124	-115
-4	7	5	220	-223
-2	7	5	235	249
-1	7	5	226	217
0	7	5	125	107
1	7	5	150	137
2	7	5	156	-133
3	7	5	133	-82
-6	8	5	333	-338
-5	8	5	245	-235
-2	8	5	181	208
-1	8	5	152	201
0	8	5	140	123
-6	9	5	162	-185
-5	9	5	228	-191
3	9	5	190	-142
-5	10	5	141	127
-4	10	5	133	171
1	10	5	226	-236
2	10	5	205	-183
-7	11	5	145	-152
-5	11	5	166	170
-4	11	5	229	209
-3	11	5	179	174
-1	11	5	166	-154
1	11	5	136	-126
-1	12	5	201	-218
0	12	5	187	-154
0	-11	6	197	-210
1	-11	6	200	-171
3	-11	6	163	145
-1	-10	6	175	-187
0	-10	6	267	-244
2	-10	6	197	146
3	-10	6	206	158
-2	-9	6	175	-179
-1	-9	6	258	-221
1	-9	6	146	148
7	-9	6	231	-215
0	-8	6	168	155
1	-8	6	192	175
2	-8	6	189	226
5	-8	6	268	-261
6	-8	6	153	-199
-3	-7	6	303	-275
0	-7	6	175	171
1	-7	6	341	336
2	-7	6	181	179

H	K	L	10FO	10FC
4	-7	6	212	-247
-4	-6	6	205	-184
-3	-6	6	140	-140
0	-6	6	171	152
2	-6	6	174	157
3	-6	6	260	-256
4	-6	6	420	-395
5	-6	6	228	-286
-5	-5	6	395	-344
-3	-5	6	190	146
-2	-5	6	316	299
-1	-5	6	328	333
1	-5	6	155	155
3	-5	6	263	-335
4	-5	6	385	-408
5	-5	6	480	-483
-7	-4	6	150	-148
-6	-4	6	395	-373
-5	-4	6	157	-146
-3	-4	6	172	163
-2	-4	6	368	357
-1	-4	6	282	283
0	-4	6	568	542
1	-4	6	127	-175
2	-4	6	336	-353
3	-4	6	162	-193
7	-4	6	172	148
-7	-3	6	174	-163
-3	-3	6	341	365
-2	-3	6	308	324
0	-3	6	235	-233
1	-3	6	344	-367
2	-3	6	404	-407
3	-3	6	151	-160
4	-3	6	288	294
5	-3	6	228	237
-4	-2	6	323	315
-3	-2	6	355	345
-2	-2	6	295	272
-1	-2	6	176	-174
0	-2	6	507	-496
1	-2	6	612	-659
2	-2	6	215	-227
3	-2	6	300	317
4	-2	6	185	219
5	-2	6	283	305
6	-2	6	234	199
8	-2	6	233	-218

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR CU(C34H22N4O2).DMF

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
-9	-1	6	201	-184	6	3	6	150	-179	3	9	6	135	154	-2	-3	7	229	-246	4	1	7	383	-392
-5	-1	6	272	297	-7	4	6	138	154	-4	10	6	157	214	-1	-3	7	522	-508	5	1	7	221	-252
-4	-1	6	251	291	-5	4	6	312	-360	-2	10	6	223	-220	0	-3	7	138	-154	-6	2	7	192	-206
-3	-1	6	161	175	-4	4	6	312	-318	-1	10	6	207	-230	3	-3	7	425	466	-4	2	7	293	-339
-1	-1	6	162	-145	-3	4	6	225	-235	0	10	6	174	-172	4	-3	7	218	237	-3	2	7	127	-113
0	-1	6	611	-644	-2	4	6	282	280	2	10	6	152	153	7	-3	7	195	-221	-2	2	7	299	337
1	-1	6	468	-491	-1	4	6	737	754	-3	11	6	151	-116	-5	-2	7	110	116	-1	2	7	492	524
2	-1	6	166	176	0	4	6	430	399	-1	11	6	165	-183	-3	-2	7	104	-141	0	2	7	485	490
3	-1	6	118	126	1	4	6	407	414	1	11	6	150	147	-2	-2	7	676	-631	1	2	7	377	380
4	-1	6	210	240	3	4	6	300	-325	2	-11	7	224	229	-1	-2	7	453	-418	2	2	7	131	-102
5	-1	6	290	264	4	4	6	459	-438	1	-10	7	394	342	0	-2	7	133	-139	3	2	7	444	-471
7	-1	6	206	-212	5	4	6	260	-233	2	-10	7	191	159	1	-2	7	142	145	4	2	7	196	-197
8	-1	6	260	-267	-8	5	6	135	155	0	-9	7	280	276	2	-2	7	415	447	-9	3	7	147	145
-5	0	6	189	184	-6	5	6	295	-325	1	-9	7	158	152	3	-2	7	186	215	-7	3	7	231	-237
-4	0	6	321	346	-5	5	6	116	-95	4	-9	7	171	-201	4	-2	7	138	153	-6	3	7	228	-203
-3	0	6	199	215	-3	5	6	235	-236	5	-9	7	191	-189	6	-2	7	313	-324	-5	3	7	142	-140
-1	0	6	527	-493	-2	5	6	224	218	-2	-8	7	155	139	7	-2	7	278	-284	-4	3	7	202	-232
1	0	6	143	112	-1	5	6	611	620	-1	-8	7	306	302	-6	-1	7	171	164	-3	3	7	104	-153
2	0	6	478	-372	0	5	6	424	403	4	-8	7	289	-274	-4	-1	7	297	-333	-2	3	7	211	207
4	0	6	383	339	2	5	6	174	-166	-2	-7	7	211	187	-3	-1	7	399	-433	-1	3	7	331	327
5	0	6	132	112	3	5	6	246	-247	-1	-7	7	197	178	-1	-1	7	351	-347	1	3	7	94	-98
6	0	6	290	-269	4	5	6	189	-229	0	-7	7	146	127	0	-1	7	179	-170	2	3	7	272	-277
7	0	6	174	-190	-6	6	6	179	223	2	-7	7	138	-191	1	-1	7	556	565	3	3	7	264	-301
-7	1	6	170	187	-4	6	6	267	-272	6	-7	7	133	150	2	-1	7	187	231	4	3	7	189	-208
-6	1	6	233	241	-3	6	6	182	172	-4	-6	7	138	-139	3	-1	7	141	139	-7	4	7	135	-160
-4	1	6	130	195	-2	6	6	368	367	-2	-6	7	153	155	5	-1	7	192	-180	-6	4	7	238	-244
-3	1	6	91	116	-1	6	6	245	258	-1	-6	7	119	116	6	-1	7	314	-315	-4	4	7	231	262
-2	1	6	129	-138	1	6	6	126	-135	0	-6	7	114	-102	7	-1	7	236	-253	-3	4	7	646	705
-1	1	6	196	201	2	6	6	284	-302	1	-6	7	292	-306	-7	0	7	249	248	-2	4	7	405	397
2	1	6	259	267	6	6	6	141	131	2	-6	7	220	-239	-6	0	7	162	179	-1	4	7	137	-144
3	1	6	153	193	-8	7	6	204	-242	-4	-5	7	138	134	-5	0	7	135	-145	0	4	7	155	-166
5	1	6	165	-142	-4	7	6	179	197	-3	-5	7	194	202	-4	0	7	353	-349	1	4	7	297	-294
-7	2	6	184	176	-3	7	6	250	264	0	-5	7	287	-272	-3	0	7	181	-172	2	4	7	248	-272
-6	2	6	245	249	-2	7	6	123	97	1	-5	7	341	-375	-2	0	7	314	-294	3	4	7	278	-321
-2	2	6	160	-183	1	7	6	220	-191	2	-5	7	231	-228	-1	0	7	179	157	4	4	7	282	-327
-1	2	6	140	-143	2	7	6	195	-165	3	-5	7	143	-176	1	0	7	129	-111	-7	5	7	224	-237
1	2	6	531	571	5	7	6	151	144	4	-5	7	141	130	2	0	7	390	-322	-4	5	7	327	345
2	2	6	346	397	-8	8	6	162	-185	5	-5	7	258	316	3	0	7	145	116	-3	5	7	459	511
4	2	6	248	-246	-7	8	6	219	-212	-7	-4	7	185	-184	5	0	7	337	-297	-2	5	7	298	320
-8	3	6	174	156	-5	8	6	195	214	-5	-4	7	219	248	6	0	7	210	-207	-1	5	7	260	232
-6	3	6	195	222	-4	8	6	375	396	-4	-4	7	367	355	-7	1	7	175	210	0	5	7	235	-204
-4	3	6	580	-667	-3	8	6	181	169	-3	-4	7	172	149	-5	1	7	185	-195	1	5	7	302	-302
-2	3	6	191	215	0	8	6	264	-254	0	-4	7	309	-318	-3	1	7	126	-85	2	5	7	125	-136
-1	3	6	113	111	1	8	6	167	-167	1	-4	7	295	-309	-1	1	7	665	657	-5	6	7	204	203
0	3	6	527	502	-7	9	6	181	-144	4	-4	7	249	245	0	1	7	328	322	-4	6	7	323	317
1	3	6	290	294	-5	9	6	121	158	5	-4	7	181	193	1	1	7	123	158	-1	6	7	206	-228
4	3	6	239	-216	-4	9	6	238	216	-5	-3	7	156	148	2	1	7	151	-132	0	6	7	172	-171
5	3	6	219	-219	-3	9	6	187	195	-4	-3	7	241	281	3	1	7	353	-357	1	6	7	113	-140

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR CU(C34H22N4O2).DMF

H	K	L	10FO	10FC
3	6	7	300	307
4	6	7	205	187
-5	7	7	219	243
-4	7	7	189	192
-2	7	7	269	-235
-1	7	7	215	-207
0	7	7	174	-172
2	7	7	167	156
4	7	7	234	223
-6	8	7	334	335
-5	8	7	167	164
-3	8	7	145	-157
0	8	7	174	-172
-6	9	7	131	145
-5	9	7	151	139
0	10	7	143	150
1	10	7	150	119
0	11	7	294	286
1	11	7	180	164
3	-10	8	210	-196
-2	-9	8	212	181
2	-9	8	182	-200
6	-9	8	236	232
-3	-8	8	180	197
-2	-8	8	218	222
5	-8	8	272	311
6	-8	8	156	187
2	-7	8	146	-143
4	-7	8	429	446
5	-7	8	218	267
-4	-6	8	146	133
-3	-6	8	197	-179
-2	-6	8	156	-155
0	-6	8	277	-266
1	-6	8	224	-215
3	-6	8	210	246
-5	-5	8	176	137
-4	-5	8	167	185
-2	-5	8	298	-322
-1	-5	8	223	-227
2	-5	8	262	275
3	-5	8	316	332
4	-5	8	115	113
-6	-4	8	256	268
-3	-4	8	187	-170
-2	-4	8	231	-253
-1	-4	8	302	-300
1	-4	8	346	327

H	K	L	10FO	10FC
2	-4	8	140	186
3	-4	8	388	420
4	-4	8	158	188
-7	-3	8	187	139
-6	-3	8	145	143
-4	-3	8	268	-265
-3	-3	8	260	-252
-2	-3	8	415	-398
-1	-3	8	415	-390
0	-3	8	148	171
1	-3	8	433	445
2	-3	8	220	231
5	-3	8	172	-214
-4	-2	8	182	-164
-3	-2	8	461	-478
-2	-2	8	146	-129
-1	-2	8	392	415
0	-2	8	206	235
1	-2	8	285	314
2	-2	8	127	139
4	-2	8	360	-390
5	-2	8	416	-459
8	-2	8	151	134
-6	-1	8	150	-148
-5	-1	8	201	-207
-4	-1	8	352	-368
-3	-1	8	312	-317
-2	-1	8	120	132
-1	-1	8	429	435
0	-1	8	411	439
1	-1	8	174	176
3	-1	8	344	-365
4	-1	8	419	-397
-7	0	8	140	-106
-6	0	8	165	-161
-5	0	8	143	-170
-1	0	8	229	213
0	0	8	125	-114
1	0	8	280	295
3	0	8	609	-564
4	0	8	225	-212
6	0	8	255	259
7	0	8	182	188
-7	1	8	128	-135
-6	1	8	246	-254
-5	1	8	255	-284
-3	1	8	547	589
-2	1	8	365	373

H	K	L	10FO	10FC
-1	1	8	351	-329
2	1	8	146	-131
3	1	8	201	-194
4	1	8	140	-106
5	1	8	243	253
6	1	8	191	196
-7	2	8	145	-143
-6	2	8	135	-122
-5	2	8	284	-337
-4	2	8	152	-180
-3	2	8	405	404
-2	2	8	104	-118
1	2	8	500	-532
2	2	8	181	-201
4	2	8	195	193
5	2	8	137	123
-2	3	8	421	469
-1	3	8	265	-313
0	3	8	785	-712
1	3	8	324	-340
3	3	8	157	175
-9	4	8	180	-143
-5	4	8	285	323
-4	4	8	219	220
-3	4	8	241	260
-1	4	8	401	-398
0	4	8	376	-351
1	4	8	150	-151
2	4	8	158	143
3	4	8	160	119
4	4	8	123	171
-6	5	8	190	187
-5	5	8	153	120
-4	5	8	160	162
-3	5	8	202	-231
-2	5	8	278	-293
-1	5	8	187	-182
0	5	8	268	-255
2	5	8	239	237
3	5	8	230	227
4	5	8	150	166
-7	6	8	131	122
-6	6	8	136	154
-3	6	8	262	-285
-2	6	8	302	-334
-1	6	8	230	-226
0	6	8	165	155
1	6	8	209	163

H	K	L	10FO	10FC
2	6	8	200	196
3	6	8	143	115
5	6	8	153	-139
6	6	8	202	-181
-4	7	8	145	-136
-3	7	8	267	-259
-2	7	8	300	-290
-1	7	8	123	148
0	7	8	306	326
5	7	8	265	-265
-7	8	8	156	114
-5	8	8	199	-188
-4	8	8	191	-186
-1	8	8	166	170
0	8	8	122	87
-8	9	8	166	180
-4	9	8	132	-133
-2	9	8	209	236
-1	9	8	152	120
3	9	8	152	-105
-3	10	8	127	166
-2	10	8	195	220
-3	11	8	162	154
-1	11	8	175	138
1	-10	9	229	-200
2	-10	9	174	-129
0	-9	9	166	-203
3	-8	9	150	152
4	-8	9	197	229
6	-8	9	177	-155
-3	-7	9	243	-205
-2	-7	9	220	-199
3	-7	9	231	262
5	-7	9	142	-188
-2	-6	9	157	-148
0	-6	9	133	160
1	-6	9	191	200
2	-6	9	367	398
3	-6	9	180	165
4	-6	9	304	-319
7	-6	9	171	-147
-3	-5	9	170	-198
0	-5	9	157	178
1	-5	9	295	318
2	-5	9	195	196
-7	-4	9	143	119
-4	-4	9	172	-201
-3	-4	9	234	-237

H	K	L	10FO	10FC
0	-4	9	151	141
1	-4	9	259	269
4	-4	9	179	130
8	-4	9	146	142
-5	-3	9	200	-184
-1	-3	9	194	176
0	-3	9	234	246
1	-3	9	121	127
2	-3	9	221	-241
3	-3	9	395	-405
-6	-2	9	201	-208
-5	-2	9	171	-206
-3	-2	9	197	192
-2	-2	9	316	315
-1	-2	9	245	259
0	-2	9	99	86
1	-2	9	211	-209
2	-2	9	293	-308
3	-2	9	230	-237
4	-2	9	131	-140
5	-2	9	194	181
6	-2	9	192	236
-7	-1	9	146	-115
-6	-1	9	205	-251
-5	-1	9	136	-138
-4	-1	9	177	180
-3	-1	9	399	382
-2	-1	9	194	190
-1	-1	9	113	83
0	-1	9	107	-101
1	-1	9	347	-372
2	-1	9	192	-215
3	-1	9	112	-156
4	-1	9	133	143
5	-1	9	294	289
6	-1	9	255	254
-4	0	9	290	326
-3	0	9	229	229
-1	0	9	132	-139
1	0	9	201	-231
2	0	9	195	-194
3	0	9	126	139
4	0	9	293	268
5	0	9	298	306
6	0	9	155	207
-5	1	9	135	112
-4	1	9	102	121
-3	1	9	174	190

OBSERVED AND CALCULATED STRUCTURE FACTORS FOF CU(C34H22N4O2).DMF

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FC	10FC	H	K	L	10FO	10FC
-2	1	9	151	-147	-4	7	9	171	-154	1	-3	10	331	-355	-2	2	10	101	-97	0	8	10	137	-115
-1	1	9	350	-364	0	7	9	235	226	2	-3	10	259	-273	0	2	10	151	149	4	8	10	160	162
3	1	9	239	228	2	7	9	215	-200	4	-3	10	265	268	1	2	10	229	210	-3	9	10	151	-179
4	1	9	334	325	3	7	9	244	-245	5	-3	10	175	198	2	2	10	279	298	0	9	10	147	-109
5	1	9	137	133	4	7	9	202	-217	-5	-2	10	158	141	4	2	10	235	-214	3	9	10	201	157
-4	2	9	132	-204	-7	8	9	127	-125	-4	-2	10	172	194	-7	3	10	156	139	-2	11	10	152	-102
-3	2	9	358	-343	-6	8	9	155	-160	-3	-2	10	391	393	-6	3	10	133	174	0	-9	11	171	154
-2	2	9	97	144	-2	8	9	131	144	-2	-2	10	263	261	-5	3	10	211	-195	-2	-7	11	139	231
0	2	9	249	-241	-1	8	9	176	190	-1	-2	10	298	-306	-2	3	10	211	-236	0	-7	11	133	-149
2	2	9	117	142	1	8	9	132	-123	0	-2	10	401	-389	-1	3	10	240	248	1	-7	11	248	-231
3	2	9	360	385	2	8	9	123	-114	1	-2	10	262	-299	0	3	10	287	304	2	-7	11	166	-183
4	2	9	259	291	3	8	9	152	-134	3	-2	10	165	159	1	3	10	289	295	-4	-6	11	155	184
-7	3	9	132	113	2	9	9	180	-194	4	-2	10	220	214	3	3	10	246	-260	-3	-6	11	135	176
-6	3	9	211	238	-4	10	9	181	187	5	-2	10	138	162	6	3	10	179	-166	1	-6	11	323	-363
-4	3	9	371	-412	-3	10	9	236	219	-7	-1	10	122	93	-6	4	10	135	-133	2	-6	11	311	-314
-3	3	9	508	-562	-4	11	9	205	195	-4	-1	10	194	197	-5	4	10	142	-118	5	-6	11	150	176
-1	3	9	141	-144	-1	12	9	235	-212	-3	-1	10	163	168	-4	4	10	189	-193	6	-6	11	204	195
0	3	9	196	-201	1	-9	10	145	171	-1	-1	10	186	-186	-2	4	10	244	272	0	-5	11	221	-211
1	3	9	180	201	2	-9	10	192	195	0	-1	10	396	-385	-1	4	10	239	238	1	-5	11	274	-305
2	3	9	288	312	-3	-8	10	179	-141	1	-1	10	170	-167	0	4	10	402	390	4	-5	11	162	202
3	3	9	112	97	1	-8	10	218	227	2	-1	10	230	243	3	4	10	263	299	5	-5	11	214	252
7	3	9	170	-160	4	-8	10	143	-160	3	-1	10	360	386	5	4	10	147	-199	-1	-4	11	339	-353
-7	4	9	172	184	5	-8	10	136	-194	4	-1	10	240	265	-7	5	10	143	-152	0	-4	11	157	-139
-6	4	9	240	222	4	-7	10	194	-267	5	-1	10	135	120	-6	5	10	191	-198	1	-4	11	189	187
-3	4	9	446	-466	0	-6	10	171	188	-6	0	10	265	239	-5	5	10	152	-148	2	-4	11	235	-219
-2	4	9	547	-587	1	-6	10	147	154	-5	0	10	181	185	-4	5	10	277	-311	3	-4	11	255	-260
0	4	9	132	136	2	-6	10	278	-294	-3	0	10	194	-183	-2	5	10	210	187	4	-4	11	170	185
1	4	9	199	166	3	-6	10	361	-367	-2	0	10	136	-148	-1	5	10	168	193	5	-4	11	212	228
2	4	9	282	325	7	-6	10	185	205	-1	0	10	168	-167	0	5	10	123	-118	-5	-3	11	192	186
-8	5	9	153	163	-4	-5	10	190	169	1	0	10	151	155	1	5	10	184	-176	-4	-3	11	168	128
-4	5	9	192	-177	-3	-5	10	118	114	2	0	10	327	335	2	5	10	181	207	-2	-3	11	245	-239
-3	5	9	239	-212	-2	-5	10	148	148	3	0	10	243	226	-7	6	10	135	-137	-1	-3	11	265	-275
-2	5	9	170	-173	-1	-5	10	263	251	4	0	10	138	113	-6	6	10	185	-135	0	-3	11	123	183
-1	5	9	104	114	0	-5	10	233	230	-7	1	10	153	161	-4	6	10	233	265	-6	-2	11	152	133
0	5	9	223	229	1	-5	10	113	-115	-6	1	10	182	188	-2	6	10	121	61	-3	-2	11	129	-115
1	5	9	134	173	2	-5	10	226	-251	-4	1	10	220	-200	0	6	10	220	-200	-2	-2	11	309	-317
2	5	9	288	288	7	-5	10	153	177	-3	1	10	274	-247	1	6	10	221	-218	1	-2	11	233	215
4	5	9	167	-198	-3	-4	10	201	165	-2	1	10	137	-131	2	6	10	373	-362	2	-2	11	278	300
-5	6	9	240	-235	-2	-4	10	190	202	-1	1	10	147	-151	4	6	10	181	179	-8	-1	11	177	165
-4	6	9	235	-239	-1	-4	10	226	238	0	1	10	201	186	-8	7	10	179	-207	-7	-1	11	207	189
-3	6	9	138	-113	0	-4	10	165	-183	1	1	10	552	571	-7	7	10	127	-118	-3	-1	11	273	-271
0	6	9	358	351	1	-4	10	365	-363	2	1	10	333	314	-5	7	10	155	159	-2	-1	11	207	-194
1	6	9	360	367	2	-4	10	165	151	3	1	10	142	119	-4	7	10	186	206	-1	-1	11	211	-228
2	6	9	179	-168	3	-4	10	115	89	-7	2	10	170	163	-3	7	10	210	233	0	-1	11	214	201
3	6	9	260	-300	-7	-3	10	138	-130	-6	2	10	119	96	1	7	10	287	-287	1	-1	11	334	335
4	6	9	185	-148	-4	-3	10	151	133	-5	2	10	147	-118	2	7	10	282	-266	2	-1	11	162	182
-6	7	9	141	-163	-2	-3	10	160	161	-4	2	10	323	-358	5	7	10	162	164	3	-1	11	129	130
-5	7	9	145	-104	0	-3	10	304	-311	-3	2	10	365	-344	-4	8	10	187	136	4	-1	11	171	-180

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR CU(C34H22N4O2).DMF

H	K	L	10FO	10FC
5	-1	11	167	-193
-4	0	11	209	-190
-2	0	11	132	-125
-1	0	11	103	110
0	0	11	274	309
1	0	11	251	262
2	0	11	184	188
3	0	11	189	-174
4	0	11	307	-285
5	0	11	199	-210
-5	1	11	155	-188
-3	1	11	195	-192
-1	1	11	275	282
0	1	11	254	263
1	1	11	262	252
2	1	11	176	-189
3	1	11	288	-265
4	1	11	214	-211
-7	2	11	171	-134
-2	2	11	110	108
0	2	11	104	130
2	2	11	204	-217
3	2	11	206	-235
7	2	11	163	161
-7	3	11	184	-204
-5	3	11	138	173
-3	3	11	167	168
-2	3	11	172	172
-1	3	11	197	236
1	3	11	254	-243
2	3	11	207	-165
6	3	11	182	174
-8	4	11	133	-105
-6	4	11	120	-103
-4	4	11	167	190
-3	4	11	150	103
-2	4	11	236	249
-1	4	11	128	116
0	4	11	253	-269
1	4	11	235	-187
-4	5	11	279	257
-3	5	11	321	362
-1	5	11	302	-326
0	5	11	333	-311
2	5	11	147	156
-5	6	11	175	134
-4	6	11	140	152
-3	6	11	143	184

H	K	L	10FO	10FC
-2	6	11	124	-109
-1	6	11	317	-306
0	6	11	255	-219
3	6	11	245	234
4	6	11	155	127
-5	7	11	137	119
-2	7	11	187	-167
-1	7	11	284	-287
0	7	11	184	-151
1	7	11	150	103
2	7	11	182	154
3	7	11	148	157
4	7	11	131	120
-7	8	11	147	139
-2	8	11	191	-157
-1	8	11	131	-145
1	8	11	189	162
2	8	11	132	110
-7	9	11	142	117
-4	9	11	165	-134
-4	10	11	131	-108
0	10	11	170	138
1	-8	12	192	-243
-4	-7	12	148	113
-1	-7	12	127	-114
0	-7	12	161	-196
4	-7	12	196	186
-5	-6	12	197	145
-1	-6	12	220	-234
0	-6	12	162	-176
3	-6	12	153	194
4	-6	12	153	164
-2	-5	12	182	-154
2	-5	12	190	197
-3	-4	12	123	-128
-2	-4	12	303	-292
0	-4	12	221	246
6	-4	12	166	-157
-4	-3	12	215	-223
-3	-3	12	253	-251
-1	-3	12	245	247
4	-3	12	161	-191
5	-3	12	200	-211
-4	-2	12	351	-376
-2	-2	12	306	333
-1	-2	12	155	164
1	-2	12	235	206
3	-2	12	177	-175

H	K	L	10FO	10FC
4	-2	12	158	-179
-5	-1	12	120	-111
-4	-1	12	259	-234
-2	-1	12	255	237
-1	-1	12	295	285
0	-1	12	152	169
2	-1	12	125	-129
3	-1	12	210	-220
4	-1	12	153	-158
-5	0	12	153	-140
-2	0	12	174	153
-1	0	12	150	151
2	0	12	256	-249
3	0	12	300	-282
-7	1	12	142	-131
-6	1	12	175	-163
-4	1	12	202	238
-3	1	12	314	296
0	1	12	189	-166
1	1	12	254	-241
2	1	12	219	-183
6	1	12	153	128
-4	2	12	196	182
-3	2	12	236	184
-1	2	12	184	-210
0	2	12	404	-427
1	2	12	292	-289
5	2	12	230	262
-6	3	12	175	247
-5	3	12	299	328
-1	3	12	239	-214
0	3	12	303	-308
1	3	12	156	-172
4	3	12	251	242
5	3	12	163	211
-6	4	12	192	185
-1	4	12	109	-96
3	4	12	234	206
4	4	12	206	237
-7	5	12	138	120
-3	5	12	243	-272
-2	5	12	306	-298
0	5	12	230	255
1	5	12	190	-228
3	5	12	214	229
-8	6	12	168	129
-5	6	12	174	201
-3	6	12	370	-377

H	K	L	10FO	10FC
-2	6	12	225	-224
-1	6	12	158	180
2	6	12	182	129
-3	7	12	137	-129
0	7	12	216	173
1	7	12	357	343
-1	8	12	175	143
0	8	12	299	313
3	8	12	155	-100
-1	9	12	185	164
2	-8	13	187	160
2	-7	13	163	142
0	-6	13	192	215
1	-6	13	262	228
2	-6	13	224	221
4	-6	13	146	-164
-5	-5	13	189	-183
0	-5	13	142	137
1	-5	13	226	238
2	-5	13	174	148
4	-5	13	234	-244
-4	-4	13	129	-92
2	-4	13	262	-222
3	-4	13	205	-208
-3	-3	13	196	216
-2	-3	13	229	217
2	-3	13	210	-206
3	-3	13	255	-273
-6	-2	13	253	-268
-5	-2	13	204	-221
-4	-2	13	221	189
-3	-2	13	269	258
3	-2	13	153	-132
5	-2	13	157	167
-6	-1	13	189	-151
-4	-1	13	161	134
-2	-1	13	129	117
-1	-1	13	131	131
0	-1	13	321	-314
1	-1	13	304	-301
4	-1	13	127	127
-3	0	13	282	290
-1	0	13	308	-315
0	0	13	236	-233
1	0	13	231	-234
-3	1	13	175	195
-2	1	13	199	-185
-1	1	13	230	-219

H	K	L	10FO	10FC
0	1	13	272	-292
2	1	13	225	232
3	1	13	213	182
-5	2	13	182	167
-3	2	13	251	-274
-2	2	13	132	-117
-1	2	13	225	-219
2	2	13	121	106
3	2	13	220	233
-5	3	13	207	246
-4	3	13	121	-131
-3	3	13	215	-201
-2	3	13	225	-199
0	3	13	166	166
1	3	13	146	107
2	3	13	179	162
-3	4	13	230	-232
0	4	13	131	-169
-4	5	13	157	-114
-2	5	13	196	232
1	5	13	135	-155
-5	6	13	244	-281
-4	6	13	176	-144
-3	6	13	245	308
-2	6	13	205	199
-6	7	13	168	-156
-5	7	13	262	-304
-3	7	13	226	217
0	7	13	179	170
-2	8	13	181	163
-4	10	13	182	132
-1	-7	14	160	182
0	-7	14	171	157
-2	-6	14	197	193
-1	-6	14	248	259
2	-6	14	172	-144
-2	-5	14	176	150
1	-5	14	128	-137
2	-5	14	202	-173
5	-4	14	157	155
4	-3	14	141	182
5	-3	14	157	175
-5	-2	14	202	202
-2	-2	14	160	-189
3	-2	14	151	171
-6	-1	14	241	220
-5	-1	14	140	105
-3	-1	14	161	-153

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR CU(C34H22N4O2).DMF

H	K	L	10FO	10FC
0	-1	14	200	-209
2	-1	14	184	210
3	-1	14	210	173
-7	0	14	140	128
-1	0	14	174	-196
1	0	14	155	164
2	0	14	170	152
-2	1	14	218	-214
0	1	14	181	194
1	1	14	278	273
2	1	14	145	84
-1	2	14	147	116
0	2	14	253	222
1	2	14	202	202
-3	3	14	194	-194
-1	3	14	333	315
0	3	14	181	205
3	3	14	185	-198
-7	4	14	187	-190
0	4	14	218	191
2	4	14	185	-148
3	4	14	150	-166
-5	5	14	140	-123
-3	5	14	205	158
1	5	14	226	-168
2	5	14	168	-184
-6	6	14	158	-135
-4	6	14	215	185
1	6	14	197	-163
-7	7	14	195	-219
-5	7	14	205	199
-4	7	14	179	208
-1	8	14	182	-161
0	8	14	148	-157
-2	9	14	175	-169
-1	9	14	194	-171
1	-6	15	180	-133
1	-5	15	146	-109
-1	-4	15	182	-148
3	-4	15	199	144
-2	-3	15	135	-113
-1	-3	15	167	-147
1	-3	15	292	281
2	-3	15	197	202
-3	-2	15	185	-146
1	-2	15	265	253
2	-2	15	224	228
-4	-1	15	156	-143
2	-1	15	126	115
-3	0	15	133	-114
-1	0	15	205	176
0	0	15	155	151
5	0	15	137	-127
-2	1	15	223	207
-1	1	15	162	197
-5	2	15	160	-149
-3	2	15	214	228
-2	2	15	235	246
-1	2	15	186	151
2	2	15	146	-131
-7	3	15	200	-163
-6	3	15	176	-146
-3	3	15	238	191
-2	3	15	256	260
1	3	15	153	-123
-7	4	15	185	-150
0	4	15	137	-106
1	4	15	166	-150
0	5	15	153	-114
3	5	15	167	138
-6	6	15	157	108
-4	10	15	143	-107
-1	-5	16	151	-89
1	-4	16	132	139
2	-4	16	205	212
1	-3	16	226	219
-1	-1	16	187	165
2	-1	16	152	-140
3	-1	16	146	-142
-2	0	16	225	175
-3	1	16	231	196
-2	1	16	176	123
0	1	16	176	-160
-4	2	16	298	273
-3	2	16	212	219
-1	2	16	168	-144
0	2	16	158	-139
-4	3	16	147	159
-1	3	16	137	-140
2	4	16	145	100
3	4	16	140	116
-3	5	16	181	-120
0	5	16	155	127
2	5	16	185	160
-3	6	16	145	-119
0	6	16	160	162
1	6	16	219	182
0	7	16	197	149
1	7	16	135	101
-2	9	16	174	119
-1	-2	17	155	-139
0	-2	17	234	-212
0	-1	17	230	-202
1	-1	17	177	-145
3	1	17	167	128
-5	2	17	127	107
-4	2	17	160	-171
-3	2	17	229	-227
-6	3	17	185	174
-4	3	17	194	-193
-3	3	17	240	-223
0	3	17	123	72
1	3	17	160	135
0	4	17	187	163
-1	5	17	158	134
0	5	17	147	102
-2	-2	18	167	-144
-1	-2	18	134	-182
0	-2	18	206	-171
1	0	18	138	78
-4	2	18	168	-117
-5	3	18	190	-170
-1	7	18	194	-160

TABLE 3D

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR SEXACU

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
3	0	0	34	-33	3	1	0	1029	-985	3	2	0	362	-364	2	3	0	753	-757	5	4	0	247	223
4	0	0	537	-567	4	1	0	1229	1290	4	2	0	297	285	3	3	0	69	10	6	4	0	452	410
5	0	0	208	227	5	1	0	90	-104	5	2	0	106	-87	4	3	0	587	574	7	4	0	246	-243
6	0	0	336	330	6	1	0	251	-277	6	2	0	490	-466	5	3	0	346	-343	8	4	0	591	-537
7	0	0	284	-251	7	1	0	158	-147	7	2	0	145	-147	6	3	0	493	506	9	4	0	233	-209
8	0	0	467	-471	8	1	0	188	190	8	2	0	190	186	7	3	0	708	697	10	4	0	189	184
9	0		66	-59	9	1	0	108	83	9	2	0	278	-250	8	3	0	76	62	11	4	0	463	459
10	0	0	289	264	11	1	0	266	-274	10	2	0	309	-312	9	3	0	352	-391	12	4	0	192	213
11	0	0	79	88	12	1	0	259	-241	11	2	0	70	-83	10	3	0	61	53	13	4	0	286	-282
12	0	0	120	-136	13	1	0	104	88	12	2	0	377	351	11	3	0	240	263	14	4	0	184	-193
13	0	0	77	-82	14	1	0	125	118	13	2	0	73	103	12	3	0	318	304	15	4	0	78	93
14	0	0	168	182	15	1	0	113	-97	14	2	0	84	68	13	3	0	122	94	16	4	0	93	90
15	0	0	291	285	16	1	0	205	-212	15	2	0	122	-135	14	3	0	238	-217	19	4	0	78	-87
16	0	0	252	269	17	1	0	243	-259	16	2	0	151	-132	15	3	0	233	-233	-16	5	0	88	93
17	0	0	111	-110	18	1	0	117	-118	18	2	0	100	112	18	3	0	102	88	-15	5	0	96	88
18	0	0	166	-164	19	1	0	120	114	19	2	0	113	129	-20	4	0	82	87	-14	5	0	131	-130
20	0		134	138	20	1	0	97	105	20	2	0	64	-60	-18	4	0	61	-42	-13	5	0	96	-84
-21	1		71	72	21	1	0	55	-59	21	2	0	81	-78	-15	4	0	133	144	-12	5	0	65	48
-19	1	0	140	-147	-20	2	0	118	-122	-21	3	0	92	-73	-13	4	0	252	-271	-11	5	0	304	318
-18	1	0	86	-87	-18	2	0	61	67	-19	3	0	87	94	-12	4	0	216	-204	-10	5	0	254	267
-17	1	0	73	81	-17	2	0	131	146	-18	3	0	73	59	-11	4	0	53	46	-9	5	0	203	-211
-16	1	0	233	231	-15	2	0	84	-101	-15	3	0	94	87	-10	4	0	318	295	-8	5	0	365	-360
-15	1	0	52	-59	-11	2	0	394	-391	-13	3	0	64	-60	-9	4	0	214	220	-7	5	0	58	-58
-14	1	0	116	-134	-10	2	0	396	-378	-12	3	0	161	-158	-8	4	0	160	-167	-6	5	0	387	389
-13	1	0	297	-290	-9	2	0	176	-170	-11	3	0	410	-409	-7	4	0	688	-668	-5	5	0	528	530
-12	1	0	196	184	-8	2	0	518	512	-10	3	0	96	112	-6	4	0	288	-265	-4	5	0	93	-97
-11	1	0	68	68	-7	2	0	150	-123	-9	3	0	479	476	-5	4	0	785	775	-3	5	0	491	-432
-10	1	0	212	-205	-6	2	0	434	-417	-8	3	0	374	341	-4	4	0	753	762	-2	5	0	227	229
-9	1	0	354	-352	-5	2	0	708	-688	-6	3	0	552	-545	-3	4	0	316	-286	-1	5	0	582	545
-8	1	0	188	196	-4	2	0	270	256	-5	3	0	45	62	-2	4	0	205	-201	0	5	0	625	556
-7	1	0	531	502	-3	2	0	99	35	-4	3	0	856	821	-1	4	0	266	-270	1	5	0	41	-74
-6	1	0	434	422	-2	2	0	109	-131	-3	3	0	73	-61	0	4	0	231	-231	2	5	0	96	-89
-5	1	0	434	-442	-1	2	0	1640	1514	-2	3	0	746	734	1	4	0	32	71	3	5	0	46	-43
-4	1	0	1537	-1428	0	2	0	176	-175	-1	3	0	446	-483	2	4	0	245	-223	4	5	0	84	-58
-3	1	0	491	-545	1	2	0	327	-333	0	3	0	233	-246	3	4	0	489	-482	5	5	0	446	441
-2	1	0	849	607	2	2	0	708	694	1	3	0	432	-440	4	4	0	75	81	6	5	0	226	-228

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $[Cu(C_{30}H_{32}N_4O_2)(DMF)_2(ClO_4)_2].ClO_4.DMF.H_2O$.....'SEXACU'.

H	K	L	10FO	10FC
7	5	0	544	-547
8	5	0	95	-102
9	5	0	391	388
10	5	0	344	349
11	5	0	59	49
13	5	0	270	-266
14	5	0	54	59
15	5	0	230	214
17	5	0	125	-127
-14	6	0	133	-146
-12	6	0	178	189
-11	6	0	149	142
-10	6	0	156	-156
-9	6	0	107	-97
-7	6	0	51	44
-6	6	0	137	137
-5	6	0	98	101
-4	6	0	519	-480
-3	6	0	64	-77
-2	6	0	353	337
-1	6	0	140	145
1	6	0	490	-505
3	6	0	61	-38
4	6	0	181	193
5	6	0	253	-248
6	6	0	463	-453
8	6	0	171	178
9	6	0	119	109
11	6	0	77	-78
12	6	0	179	-171
14	6	0	108	120
15	6	0	86	-87
16	6	0	147	-157
-16	7	0	69	-63
-15	7	0	122	-118
-13	7	0	89	79

H	K	L	10FO	10FC
-11	7	0	98	-91
-10	7	0	148	-161
-9	7	0	102	-113
-7	7	0	86	77
-5	7	0	212	-219
-4	7	0	65	-68
-3	7	0	269	293
-2	7	0	58	62
-1	7	0	115	106
0	7	0	329	-332
1	7	0	170	161
2	7	0	497	503
3	7	0	187	-196
4	7	0	63	-91
5	7	0	143	-142
6	7	0	201	-204
7	7	0	47	49
8	7	0	162	172
10	7	0	96	-82
12	7	0	69	-85
14	7	0	70	-77
15	7	0	142	-144
17	7	0	69	78
18	7	0	74	82
-16	8	0	85	-97
-14	8	0	119	128
-12	8	0	172	-178
-11	8	0	131	-139
-10	8	0	77	86
-9	8	0	137	134
-8	8	0	110	107
-7	8	0	47	60
-4	8	0	187	183
-3	8	0	232	219
-2	8	0	272	-262
-1	8	0	190	-178

H	K	L	10FO	10FC
0	8	0	161	157
1	8	0	255	245
2	8	0	82	106
4	8	0	256	-275
5	8	0	84	-101
6	8	0	414	437
7	8	0	279	283
9	8	0	133	130
12	8	0	62	49
13	8	0	110	-126
14	8	0	157	-164
15	8	0	84	-72
16	8	0	88	75
-15	9	0	114	124
-13	9	0	155	-171
-12	9	0	156	-165
-11	9	0	57	73
-10	9	0	156	160
-8	9	0	64	-67
-7	9	0	66	-65
-6	9	0	71	80
-5	9	0	210	198
-3	9	0	167	-158
-2	9	0	135	-154
0	9	0	340	342
1	9	0	231	240
2	9	0	177	-180
3	9	0	270	-251
5	9	0	286	274
6	9	0	219	202
8	9	0	145	-162
9	9	0	117	-111
10	9	0	128	130
12	9	0	165	-153
13	9	0	96	-102
14	9	0	104	-101

H	K	L	10FO	10FC
18	9	0	65	-58
20	9	0	68	73
-14	10	0	101	-118
-11	10	0	96	92
-9	10	0	136	-149
-8	10	0	53	-57
-7	10	0	120	126
-6	10	0	184	187
-5	10	0	62	-60
-4	10	0	197	-197
-3	10	0	88	-88
-1	10	0	192	174
0	10	0	138	122
1	10	0	150	-145
2	10	0	193	-176
4	10	0	209	226
5	10	0	99	105
6	10	0	58	-52
7	10	0	288	-287
9	10	0	190	189
11	10	0	61	-64
12	10	0	133	-126
14	10	0	54	45
16	10	0	72	-69
-7	11	0	104	105
-5	11	0	250	-258
-4	11	0	107	-102
-3	11	0	115	123
-2	11	0	69	58
1	11	0	62	-50
3	11	0	178	192
4	11	0	109	106
5	11	0	108	-100
6	11	0	120	-118
8	11	0	64	69
11	11	0	128	-123

H	K	L	10FO	10FC
12	11	0	54	56
13	11	0	125	121
-8	12	0	86	79
-6	12	0	124	-123
-4	12	0	116	118
-3	12	0	79	83
-2	12	0	56	54
-1	12	0	104	-94
0	12	0	93	-81
1	12	0	66	81
2	12	0	101	111
9	12	0	91	-81
10	12	0	63	-56
11	12	0	77	58
12	12	0	118	111
15	12	0	70	-64
-7	13	0	83	-81
-5	13	0	76	80
-4	13	0	137	138
-2	13	0	108	-119
-1	13	0	95	-86
1	13	0	90	87
3	13	0	124	-119
5	13	0	87	85
11	13	0	72	47
13	13	0	98	-95
-6	14	0	73	67
-5	14	0	86	76
-3	14	0	88	-87
2	14	0	99	-91
4	14	0	131	122
13	14	0	77	-53
3	15	0	71	49
8	15	0	73	69
2	16	0	69	43
-3	-15	1	77	-80

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR SEXACU

H	K	L	10FO	10FC
-2	-15	1	82	-77
0	-15	1	72	56
-14	-14	1	75	-59
-6	-14	1	75	79
-3	-14	1	104	-121
-1	-14	1	93	91
-10	-13	1	84	-74
-8	-13	1	75	87
-7	-13	1	96	83
-4	-13	1	132	-127
-2	-13	1	142	142
1	-13	1	87	-95
5	-13	1	64	-55
6	-13	1	84	-89
-13	-12	1	68	56
-11	-12	1	119	-105
-9	-12	1	78	54
-8	-12	1	111	106
-6	-12	1	158	-160
-5	-12	1	74	-74
-3	-12	1	113	122
-2	-12	1	64	80
0	-12	1	79	-64
2	-12	1	64	55
4	-12	1	138	-141
5	-12	1	69	-96
6	-12	1	65	72
7	-12	1	117	122
9	-12	1	103	-108
12	-12	1	67	66
-12	-11	1	124	-121
-10	-11	1	77	81
-9	-11	1	220	229
-8	-11	1	101	101
-7	-11	1	279	-271
-5	-11	1	84	78

H	K	L	10FO	10FC
-4	-11	1	102	95
-3	-11	1	109	119
-2	-11	1	86	-77
-1	-11	1	58	-42
0	-11	1	67	-67
1	-11	1	56	-38
2	-11	1	63	-71
3	-11	1	170	-170
4	-11	1	102	-100
5	-11	1	143	144
6	-11	1	165	160
7	-11	1	79	62
8	-11	1	120	-112
9	-11	1	75	-86
11	-11	1	78	83
13	-11	1	78	-73
14	-11	1	80	-73
-14	-10	1	65	-82
-13	-10	1	119	-114
-11	-10	1	148	127
-10	-10	1	210	205
-8	-10	1	252	-241
-7	-10	1	138	-141
-5	-10	1	185	185
-3	-10	1	212	-244
-1	-10	1	197	205
0	-10	1	55	84
1	-10	1	120	-114
2	-10	1	126	-114
3	-10	1	64	-57
4	-10	1	78	79
5	-10	1	225	214
6	-10	1	71	-57
7	-10	1	178	-198
8	-10	1	133	-139
10	-10	1	74	67

H	K	L	10FO	10FC
12	-10	1	96	-108
13	-10	1	90	-91
15	-10	1	78	76
-17	-9	1	79	78
-15	-9	1	165	-155
-14	-9	1	197	-188
-12	-9	1	163	146
-11	-9	1	205	198
-10	-9	1	93	95
-9	-9	1	143	135
-8	-9	1	57	-22
-7	-9	1	343	361
-6	-9	1	314	330
-5	-9	1	163	-160
-4	-9	1	194	-189
-3	-9	1	106	109
-2	-9	1	143	137
-1	-9	1	123	122
0	-9	1	53	-50
1	-9	1	484	-459
2	-9	1	146	-147
3	-9	1	414	406
4	-9	1	234	260
8	-9	1	80	69
9	-9	1	192	193
10	-9	1	64	108
11	-9	1	105	-105
12	-9	1	124	-134
-18	-8	1	108	106
-16	-8	1	108	-107
-15	-8	1	190	-192
-13	-8	1	133	140
-11	-8	1	78	-93
-9	-8	1	121	113
-8	-8	1	55	53
-7	-8	1	109	-93

H	K	L	10FO	10FC
-6	-8	1	208	-228
-5	-8	1	181	-151
-4	-8	1	187	-195
-3	-8	1	393	392
-2	-8	1	107	116
-1	-8	1	270	-279
0	-8	1	166	-178
2	-8	1	348	331
3	-8	1	327	357
5	-8	1	425	-414
6	-8	1	320	-302
8	-8	1	85	-83
9	-8	1	122	-127
10	-8	1	105	-126
11	-8	1	167	-160
13	-8	1	100	111
15	-8	1	140	-139
17	-8	1	91	99
-19	-7	1	72	68
-17	-7	1	101	-101
-16	-7	1	176	-180
-15	-7	1	85	-76
-14	-7	1	122	125
-12	-7	1	123	-120
-10	-7	1	152	149
-8	-7	1	47	10
-6	-7	1	237	-252
-5	-7	1	148	151
-4	-7	1	277	316
-3	-7	1	165	-147
-2	-7	1	194	-176
-1	-7	1	197	-181
0	-7	1	190	-188
1	-7	1	361	360
2	-7	1	398	352
4	-7	1	318	-287

H	K	L	10FO	10FC
5	-7	1	229	-242
6	-7	1	100	90
7	-7	1	150	164
8	-7	1	65	37
9	-7	1	59	-52
11	-7	1	196	176
12	-7	1	105	119
13	-7	1	141	-142
14	-7	1	150	-172
15	-7	1	93	-92
16	-7	1	128	126
17	-7	1	83	90
19	-7	1	78	-83
-18	-6	1	75	-82
-17	-6	1	93	-101
-15	-6	1	186	178
-12	-6	1	71	-74
-11	-6	1	66	-43
-10	-6	1	179	184
-9	-6	1	98	95
-8	-6	1	377	-386
-7	-6	1	201	-207
-6	-6	1	44	38
-5	-6	1	344	336
-4	-6	1	264	251
-1	-6	1	154	169
0	-6	1	637	637
1	-6	1	506	438
2	-6	1	450	430
3	-6	1	149	-156
4	-6	1	48	-96
5	-6	1	51	76
6	-6	1	46	44
7	-6	1	248	-239
8	-6	1	275	-270
9	-6	1	52	70

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR SEXACU

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
10	-6	1	266	268	14	-5	1	60	72	-18	-3	1	84	85	-14	-2	1	59	28	-9	-1	1	275	254
11	-6	1	82	91	15	-5	1	114	115	-17	-3	1	105	-119	-13	-2	1	104	-84	-7	-1	1	221	-189
12	-6	1	78	-111	17	-5	1	88	-87	-13	-3	1	63	61	-12	-2	1	177	-164	-6	-1	1	125	-152
13	-6	1	87	-85	20	-5	1	87	84	-11	-3	1	160	-182	-10	-2	1	196	204	-5	-1	1	158	145
15	-6	1	168	158	-19	-4	1	70	-71	-10	-3	1	368	-357	-9	-2	1	569	582	-4	-1	1	1235	1199
16	-6	1	161	178	-18	-4	1	70	71	-9	-3	1	354	364	-8	-2	1	337	378	-3	-1	1	367	341
18	-6	1	68	-54	-17	-4	1	61	68	-8	-3	1	601	584	-7	-2	1	108	-128	-2	-1	1	48	-34
-19	-5	1	83	-75	-16	-4	1	62	-81	-7	-3	1	166	-156	-6	-2	1	232	-271	2	-1	1	785	-808
-17	-5	1	65	52	-14	-4	1	56	-46	-6	-3	1	253	-257	-4	-2	1	280	270	3	-1	1	340	273
-16	-5	1	74	80	-13	-4	1	147	108	-5	-3	1	490	-481	-3	-2	1	124	120	4	-1	1	603	-567
-15	-5	1	75	77	-12	-4	1	259	257	-4	-3	1	489	-440	-2	-2	1	53	-25	5	-1	1	49	-36
-14	-5	1	74	-78	-10	-4	1	239	-249	-2	-3	1	385	392	-1	-2	1	272	212	6	-1	1	39	58
-13	-5	1	170	-153	-9	-4	1	393	-420	-1	-3	1	223	-202	0	-2	1	562	-548	7	-1	1	323	-347
-12	-5	1	107	105	-8	-4	1	443	442	0	-3	1	205	-181	1	-2	1	133	-86	8	-1	1	535	-540
-11	-5	1	312	288	-7	-4	1	603	652	1	-3	1	338	324	2	-2	1	480	457	9	-1	1	135	-114
-9	-5	1	574	-542	-6	-4	1	263	271	2	-3	1	249	-222	3	-2	1	1853	-1715	10	-1	1	576	568
-8	-5	1	274	-271	-5	-4	1	414	-412	3	-3	1	449	-466	4	-2	1	287	-282	11	-1	1	318	308
-7	-5	1	126	-115	-3	-4	1	48	32	4	-3	1	625	-653	5	-2	1	402	386	12	-1	1	114	-112
-6	-5	1	358	396	-2	-4	1	143	-121	5	-3	1	469	-472	6	-2	1	72	60	13	-1	1	58	-38
-5	-5	1	714	719	-1	-4	1	720	706	6	-3	1	134	166	7	-2	1	298	292	15	-1	1	268	253
-4	-5	1	558	-589	0	-4	1	226	-233	7	-3	1	134	152	8	-2	1	223	215	16	-1	1	150	160
-3	-5	1	357	-377	1	-4	1	65	-70	8	-3	1	151	119	9	-2	1	572	-585	17	-1	1	205	-213
-2	-5	1	277	276	2	-4	1	366	365	9	-3	1	512	-499	11	-2	1	626	608	-19	0	1	149	-140
0	-5	1	207	225	3	-4	1	60	-82	10	-3	1	637	-603	12	-2	1	149	141	-17	0	1	234	233
1	-5	1	38	73	4	-4	1	161	-173	12	-3	1	299	296	13	-2	1	201	-200	-16	0	1	100	112
2	-5	1	47	-53	5	-4	1	423	-383	13	-3	1	112	120	14	-2	1	96	-113	-15	0	1	114	-133
4	-5	1	421	425	7	-4	1	304	281	14	-3	1	96	123	15	-2	1	109	-96	-14	0	1	354	-340
5	-5	1	475	-482	8	-4	1	531	508	15	-3	1	164	-169	16	-2	1	208	219	-13	0	1	93	-92
6	-5	1	331	-322	9	-4	1	158	154	17	-3	1	65	62	21	-2	1	80	72	-12	0	1	397	386
7	-5	1	170	-173	10	-4	1	345	-343	18	-3	1	97	81	-20	-1	1	90	101	-11	0	1	399	385
8	-5	1	143	143	11	-4	1	394	-388	20	-3	1	91	-101	-18	-1	1	222	-222	-9	0	1	143	-151
9	-5	1	240	246	12	-4	1	111	122	-20	-2	1	66	48	-16	-1	1	245	232	-8	0	1	243	-214
10	-5	1	72	67	14	-4	1	214	189	-19	-2	1	71	85	-15	-1	1	151	163	-7	0	1	42	30
11	-5	1	236	-212	15	-4	1	93	111	-18	-2	1	105	-111	-13	-1	1	207	-217	-6	0	1	64	116
12	-5	1	199	-174	16	-4	1	87	-83	-17	-2	1	195	-203	-11	-1	1	287	301	-5	0	1	385	374
13	-5	1	69	-85	-19	-3	1	73	73	-16	-2	1	93	-84	-10	-1	1	372	360	-4	0	1	509	-455

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR SEXACU

H	K	L	10FO	10FC
-3	0	1	397	357
-2	0	1	231	267
3	0	1	100	-111
4		1	635	674
5	0	1	626	-576
6	0	1	978	-910
7	0	1	470	-421
9	0	1	549	520
10	0	1	276	275
11	0	1	156	-156
12	0	1	309	-287
13	0	1	58	24
14	0	1	93	-95
15	0	1	114	-97
16	0	1	203	-213
17	0	1	177	-173
18	0	1	84	78
19	0	1	69	79
-18	1	1	92	98
-17	1	1	70	69
-16	1	1	147	-146
-15	1	1	228	-228
-14	1	1	83	-83
-13	1	1	329	352
-12	1	1	214	209
-11	1	1	241	-244
-10	1	1	360	-350
-9	1	1	308	-307
-8	1	1	308	303
-7	1	1	176	201
-6	1	1	280	-323
-4	1	1	183	-158
-3	1	1	1473	1437
-2	1	1	650	-653
-1	1	1	210	203
1	1	1	396	-205
2	1	1	1595	1444
3	1	1	624	560
4	1	1	436	-436
5	1	1	1608	-1486
6	1	1	295	-323
7	1	1	419	372
8	1	1	507	503
9	1	1	66	57
10	1	1	184	-180
11	1	1	254	-243
12	1	1	71	50
13	1	1	54	-34
16	1	1	206	-193
17	1	1	176	164
18	1	1	158	165
20	1	1	84	-76
21	1	1	87	-85
-19	2	1	132	126
-17	2	1	100	-78
-16	2	1	81	-93
-13	2	1	314	316
-12	2	1	239	-224
-11	2	1	502	-492
-9	2	1	429	416
-8	2	1	203	198
-7	2	1	102	-112
-6	2	1	168	171
-5	2	1	385	-406
-4	2	1	946	927
-3	2	1	109	-76
-2	2	1	1859	-1842
-1	2	1	80	38
0	2	1	558	419
1	2	1	1576	1550
2	2	1	529	-390
3	2	1	881	782
4	2	1	759	-831
5	2	1	830	-837
6	2	1	931	942
7	2	1	856	822
8	2	1	51	-79
9	2	1	315	-297
10	2	1	129	-133
11	2	1	119	136
12	2	1	76	57
13	2	1	67	-70
14	2	1	124	-100
15	2	1	198	-215
16	2	1	123	105
17	2	1	214	235
20	2	1	68	-49
22	2	1	99	115
-21	3	1	73	63
-20	3	1	93	108
-18	3	1	96	-105
-17	3	1	75	-82
-15	3	1	104	104
-12	3	1	325	-338
-11	3	1	86	93
-10	3	1	109	92
-9	3	1	261	240
-8	3	1	47	-48
-7	3	1	99	-106
-6	3	1	66	58
-5	3	1	765	739
-4	3	1	114	91
-3	3	1	1248	-1169
-2	3	1	316	253
0	3	1	342	394
1	3	1	1422	1356
2	3	1	643	-657
3	3	1	125	-118
4	3	1	221	-175
5	3	1	282	304
6	3	1	569	529
7	3	1	155	180
8	3	1	551	-517
9	3	1	57	30
10	3	1	143	131
11	3	1	217	203
12	3	1	229	-215
13	3	1	234	-253
16	3	1	230	230
18	3	1	154	-141
21	3	1	84	81
-19	4	1	102	-102
-18	4	1	86	-89
-16	4	1	120	112
-15	4	1	61	67
-13	4	1	79	-84
-12	4	1	124	-106
-11	4	1	199	193
-10	4	1	113	-107
-9	4	1	228	-223
-8	4	1	85	-91
-7	4	1	377	383
-6	4	1	93	79
-5	4	1	376	350
-4	4	1	675	-655
-3	4	1	636	-632
-2	4	1	172	157
-1	4	1	836	799
0	4	1	217	250
1	4	1	293	-295
2	4	1	122	-111
3	4	1	87	-116
4	4	1	208	-215
5	4	1	369	407
6	4	1	178	-143
7	4	1	413	-425
8	4	1	274	257
9	4	1	100	109
10	4	1	70	[illegible]
11	4	1	122	-140
12	4	1	238	-247
14	4	1	122	124
15	4	1	252	251
16	4	1	85	-73
17	4	1	215	-229
20	4	1	67	39
-20	5	1	86	-90
-19	5	1	74	-53
-18	5	1	70	54
-17	5	1	105	110
-14	5	1	64	-55
-13	5	1	60	52
-12	5	1	116	112
-11	5	1	101	-116
-10	5	1	324	-326
-9	5	1	149	161
-8	5	1	244	248
-6	5	1	105	-130
-5	5	1	348	-343
-4	5	1	598	-596
-3	5	1	391	363
-2	5	1	778	767
-1	5	1	441	411
0	5	1	241	-216
1	5	1	454	-426
2	5	1	405	-376
3	5	1	125	145
4	5	1	255	-256
5	5	1	351	-382
6	5	1	75	-70

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR SEXACU

H	K	L	10FO	10FC
7	5	1	238	245
9	5	1	63	-38
10	5	1	141	-136
11	5	1	259	-239
12	5	1	87	93
13	5	1	296	265
14	5	1	65	69
15	5	1	64	-61
16	5	1	226	-239
18	5	1	91	84
-16	6	1	124	-110
-12	6	1	66	-83
-11	6	1	145	-148
-9	6	1	324	311
-8	6	1	110	109
-7	6	1	118	-96
-6	6	1	253	-257
-5	6	1	257	-280
-4	6	1	154	178
-3	6	1	587	573
-2	6	1	153	141
0	6	1	619	-585
1	6	1	125	-81
2	6	1	177	200
3	6	1	417	-386
4	6	1	272	-251
6	6	1	141	-145
7	6	1	334	314
8	6	1	109	112
9	6	1	279	-280
10	6	1	307	-303
11	6	1	183	177
12	6	1	213	201
13	6	1	61	71
14	6	1	66	-72
15	6	1	18[illegible]	-183

H	K	L	10FO	10FC
17	6	1	152	150
18	6	1	98	94
-15	7	1	89	98
-13	7	1	97	-102
-12	7	1	174	-170
-11	7	1	64	-66
-10	7	1	143	131
-9	7	1	187	199
-7	7	1	77	-90
-6	7	1	217	-196
-4	7	1	354	327
-3	7	1	296	305
-2	7	1	138	-132
-1	7	1	121	86
1	7	1	200	195
3	7	1	380	-364
4	7	1	335	-317
5	7	1	215	207
6	7	1	339	339
8	7	1	177	-199
9	7	1	189	-186
11	7	1	215	226
12	7	1	157	173
13	7	1	165	-146
14	7	1	212	-194
16	7	1	106	108
17	7	1	101	104
21	7	1	74	62
-14	8	1	88	-99
-13	8	1	175	-166
-11	8	1	194	201
-10	8	1	262	277
-9	8	1	235	236
-7	8	1	119	-117
-6	8	1	116	99
-5	8	1	215	223

H	K	L	10FO	10FC
-4	8	1	142	139
-3	8	1	155	-157
0	8	1	68	-72
1	8	1	95	88
2	8	1	340	-347
4	8	1	307	323
5	8	1	268	274
7	8	1	229	-229
8	8	1	120	-109
9	8	1	73	-88
10	8	1	210	200
11	8	1	125	94
12	8	1	206	-194
13	8	1	145	-160
14	8	1	89	-92
16	8	1	82	74
-14	9	1	152	-164
-11	9	1	143	135
-9	9	1	212	-217
-8	9	1	99	-113
-7	9	1	71	86
-6	9	1	74	66
-4	9	1	95	-88
-3	9	1	83	-65
-2	9	1	73	84
-1	9	1	68	-81
0	9	1	101	-88
1	9	1	106	-109
3	9	1	135	125
4	9	1	167	151
5	9	1	78	-69
6	9	1	398	-383
7	9	1	226	-232
9	9	1	113	117
11	9	1	64	-78
12	9	1	92	-95

H	K	L	10FO	10FC
13	9	1	70	-77
-15	10	1	101	-117
-8	10	1	142	149
-7	10	1	171	181
-5	10	1	17[illegible]	-179
-3	10	1	160	163
-2	10	1	114	-122
-1	10	1	128	-119
0	10	1	56	54
1	10	1	110	-115
2	10	1	145	145
3	10	1	365	361
4	10	1	66	-54
5	10	1	169	-187
6	10	1	73	-75
8	10	1	167	159
11	10	1	104	-107
-7	11	1	67	-65
-6	11	1	107	-96
-4	11	1	179	175
-3	11	1	102	123
-1	11	1	122	-113
1	11	1	206	211
2	11	1	127	141
4	11	1	133	-127
5	11	1	201	-204
7	11	1	112	105
12	11	1	140	134
-5	12	1	84	81
-4	12	1	86	86
-3	12	1	92	-111
-2	12	1	178	-180
-1	12	1	87	-66
0	12	1	151	148
1	12	1	137	133
3	12	1	118	-118

H	K	L	10FO	10FC
4	12	1	69	-64
5	12	1	63	69
6	12	1	67	50
11	12	1	96	67
13	12	1	136	-125
-5	13	1	65	76
-4	13	1	77	-55
-3	13	1	86	-86
-1	13	1	79	91
0	13	1	120	139
2	13	1	137	-128
4	13	1	100	103
5	13	1	62	28
9	13	1	75	39
12	13	1	99	-93
15	13	1	74	48
-4	14	1	81	-73
0	14	1	96	-84
1	14	1	86	-77
2	15	1	69	47
0	-16	2	69	71
-4	-15	2	82	-84
-1	-15	2	68	59
1	-15	2	75	-69
-3	-14	2	82	65
-1	-14	2	65	-54
0	-14	2	91	-91
3	-14	2	98	71
5	-14	2	65	-35
-11	-13	2	66	-49
-6	-13	2	68	-75
-4	-13	2	93	85
-3	-13	2	75	72
0	-13	2	105	-115
2	-13	2	127	132
4	-13	2	89	-106

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR SEKACU

H	K	L	10FO	10FC
7	-13	2	94	85
-10	-12	2	90	90
-7	-12	2	170	-154
-5	-12	2	139	137
-4	-12	2	93	83
-2	-12	2	146	-144
-1	-12	2	114	-117
0	-12	2	73	-81
1	-12	2	163	137
3	-12	2	228	-222
4	-12	2	120	-114
5	-12	2	102	107
6	-12	2	126	107
7	-12	2	64	73
8	-12	2	109	-112
10	-12	2	81	83
14	-12	2	80	-84
-15	-11	2	69	68
-11	-11	2	108	104
-7	-11	2	105	-105
-6	-11	2	157	155
-5	-11	2	133	148
-4	-11	2	107	-115
-3	-11	2	248	-249
-1	-11	2	143	134
0	-11	2	6	59
1	-11	2	128	118
2	-11	2	95	-81
3	-11	2	156	-151
4	-11	2	84	78
5	-11	2	178	198
6	-11	2	82	-76
7	-11	2	94	-109
8	-11	2	68	-65
9	-11	2	102	108
10	-11	2	92	81
12	-11	2	116	-109
14	-11	2	87	96
15	-11	2	103	109
-16	-10	2	83	57
-15	-10	2	92	-73
-13	-10	2	121	89
-11	-10	2	116	113
-8	-10	2	100	96
-7	-10	2	246	253
-6	-10	2	118	111
-5	-10	2	197	-204
-4	-10	2	226	-200
-3	-10	2	91	-79
-2	-10	2	125	126
-1	-10	2	188	186
0	-10	2	112	-113
1	-10	2	152	-157
3	-10	2	56	58
8	-10	2	109	88
9	-10	2	187	196
10	-10	2	114	-96
11	-10	2	120	-116
12	-10	2	71	-68
14	-10	2	87	84
-16	-9	2	101	-94
-15	-9	2	93	-110
-14	-9	2	104	95
-13	-9	2	107	112
-11	-9	2	118	-94
-9	-9	2	143	146
-8	-9	2	158	142
-6	-9	2	220	-231
-5	-9	2	368	-374
-4	-9	2	194	-204
-3	-9	2	311	318
-2	-9	2	87	97
-1	-9	2	262	-266
0	-9	2	153	-145
2	-9	2	133	131
3	-9	2	71	65
4	-9	2	233	-245
5	-9	2	190	-196
7	-9	2	70	-78
9	-9	2	118	-112
10	-9	2	180	-184
13	-9	2	142	150
-17	-8	2	112	-107
-16	-8	2	78	-80
-14	-8	2	166	150
-12	-8	2	230	-218
-10	-8	2	230	235
-9	-8	2	239	247
-8	-8	2	223	235
-7	-8	2	189	-181
-6	-8	2	352	-363
-5	-8	2	109	118
-4	-8	2	300	286
-3	-8	2	94	49
-2	-8	2	303	-301
-1	-8	2	313	-309
0	-8	2	64	66
1	-8	2	401	401
3	-8	2	270	-263
4	-8	2	363	-356
6	-8	2	254	254
7	-8	2	152	145
9	-8	2	147	-152
11	-8	2	129	151
12	-8	2	88	111
14	-8	2	108	-108
16	-8	2	69	66
17	-8	2	86	89
-18	-7	2	124	-107
-16	-7	2	131	112
-15	-7	2	126	135
-13	-7	2	129	-132
-12	-7	2	110	-106
-11	-7	2	118	133
-10	-7	2	431	406
-9	-7	2	186	176
-8	-7	2	336	-313
-7	-7	2	252	-252
-6	-7	2	370	374
-5	-7	2	54	-43
-4	-7	2	196	186
-3	-7	2	138	120
-2	-7	2	323	-351
-1	-7	2	327	297
0	-7	2	641	636
2	-7	2	455	-447
3	-7	2	458	-444
4	-7	2	80	-74
5	-7	2	266	277
6	-7	2	265	250
7	-7	2	169	-187
8	-7	2	365	-388
10	-7	2	256	278
11	-7	2	156	161
13	-7	2	70	-53
15	-7	2	80	76
16	-7	2	87	107
18	-7	2	86	-94
-19	-6	2	82	-80
-17	-6	2	133	134
-16	-6	2	110	111
-14	-6	2	162	-158
-12	-6	2	87	94
-11	-6	2	237	215
-10	-6	2	103	98
-9	-6	2	210	-216
-8	-6	2	120	-118
-6	-6	2	231	255
-5	-6	2	85	117
-4	-6	2	49	-41
-3	-6	2	95	-130
-2	-6	2	324	349
-1	-6	2	58	-57
0	-6	2	135	154
1	-6	2	240	-245
2	-6	2	753	-721
3	-6	2	232	309
4	-6	2	538	541
5	-6	2	73	-56
6	-6	2	302	-284
7	-6	2	324	-319
9	-6	2	289	267
10	-6	2	203	200
11	-6	2	105	-108
12	-6	2	161	-170
16	-6	2	78	-80
17	-6	2	73	-69
19	-6	2	94	89
-18	-5	2	124	134
-17	-5	2	68	74
-16	-5	2	73	-89
-15	-5	2	138	-139
-13	-5	2	84	69
-12	-5	2	114	127
-11	-5	2	113	105
-10	-5	2	98	-120
-9	-5	2	168	-165
-8	-5	2	188	166
-7	-5	2	235	235
-6	-5	2	506	-528

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR SEXACU

H	K	L	10FO	10FC
-5	-5	2	166	-183
-4	-5	2	96	128
-3	-5	2	233	-206
-2	-5	2	102	79
-1	-5	2	156	151
0	-5	2	578	-561
1	-5	2	306	-297
2	-5	2	411	384
3	-5	2	499	483
4	-5	2	286	-236
5	-5	2	304	-294
6	-5	2	120	-139
8	-5	2	286	283
10	-5	2	205	-238
11	-5	2	69	-61
12	-5	2	142	154
13	-5	2	68	64
14	-5	2	59	-67
15	-5	2	82	-70
16	-5	2	77	-67
17	-5	2	82	73
18	-5	2	73	79
-22	-4	2	93	-68
-19	-4	2	96	103
-18	-4	2	96	87
-17	-4	2	110	-97
-16	-4	2	94	-101
-13	-4	2	230	214
-9	-4	2	283	271
-8	-4	2	161	138
-7	-4	2	740	-720
-6	-4	2	374	-368
-4	-4	2	321	339
-3	-4	2	313	337
-2	-4	2	618	-635
-1	-4	2	435	-442
0	-4	2	614	-668
1	-4	2	193	176
2	-4	2	510	531
3	-4	2	349	326
5	-4	2	65	36
7	-4	2	148	149
8	-4	2	219	-201
9	-4	2	190	-180
11	-4	2	63	46
12	-4	2	226	204
14	-4	2	148	-146
16	-4	2	108	102
17	-4	2	114	125
20	-4	2	88	-118
-22	-3	2	77	-86
-20	-3	2	93	87
-17	-3	2	155	-161
-16	-3	2	121	-99
-15	-3	2	161	147
-14	-3	2	139	113
-13	-3	2	78	-42
-11	-3	2	142	121
-10	-3	2	52	78
-9	-3	2	368	373
-8	-3	2	598	-566
-7	-3	2	804	-828
-6	-3	2	95	71
-5	-3	2	428	499
-4	-3	2	448	444
-3	-3	2	555	-559
-2	-3	2	390	-441
-1	-3	2	1023	-1078
0	-3	2	86	91
1	-3	2	1422	1364
2	-3	2	499	476
3	-3	2	80	90
4	-3	2	272	-266
6	-3	2	319	-308
7	-3	2	344	317
9	-3	2	181	-169
10	-3	2	181	184
11	-3	2	454	456
12	-3	2	92	-95
13	-3	2	270	-280
14	-3	2	72	-61
15	-3	2	109	114
16	-3	2	212	212
17	-3	2	73	69
19	-3	2	113	-118
21	-3	2	71	64
-21	-2	2	118	96
-20	-2	2	78	69
-18	-2	2	143	-133
-16	-2	2	159	139
-15	-2	2	69	89
-12	-2	2	173	185
-11	-2	2	313	304
-10	-2	2	100	79
-8	-2	2	746	-718
-6	-2	2	168	163
-5	-2	2	582	573
-4	-2	2	282	303
-3	-2	2	1428	-1482
-2	-2	2	626	-577
-1	-2	2	1544	1524
0	-2	2	111	110
1	-2	2	79	58
2	-2	2	219	-251
3	-2	2	778	-740
4	-2	2	823	-713
5	-2	2	124	126
6	-2	2	164	152
7	-2	2	138	95
8	-2	2	72	92
9	-2	2	457	442
10	-2	2	335	331
11	-2	2	58	73
12	-2	2	463	-431
13	-2	2	140	-149
14	-2	2	128	113
15	-2	2	381	366
17	-2	2	169	-169
-18	-1	2	67	61
-17	-1	2	211	210
-16	-1	2	115	115
-14	-1	2	98	-80
-13	-1	2	151	126
-12	-1	2	355	322
-11	-1	2	73	-68
-10	-1	2	363	-384
-9	-1	2	358	-347
-8	-1	2	179	-175
-7	-1	2	242	233
-6	-1	2	274	294
-5	-1	2	386	372
-4	-1	2	894	-879
-3	-1	2	427	360
-2	-1	2	614	675
-1	-1	2	695	838
0	-1	2	43	69
1	-1	2	183	184
2	-1	2	212	-242
3	-1	2	759	-765
4	-1	2	1003	-1003
5	-1	2	470	-474
6	-1	2	579	-541
7	-1	2	184	193
8	-1	2	511	418
9	-1	2	235	242
11	-1	2	262	-270
12	-1	2	173	-177
13	-1	2	188	190
14	-1	2	140	142
15	-1	2	139	143
16	-1	2	262	-266
17	-1	2	107	-105
19	-1	2	89	80
21	-1	2	71	-81
-16	0	2	165	-163
-15	0	2	140	-153
-14	0	2	85	64
-13	0	2	213	242
-12	0	2	116	-129
-11	0	2	354	-373
-10	0	2	353	-330
-8	0	2	497	497
-7	0	2	432	427
-6	0	2	224	-276
-5	0	2	136	135
-4	0	2	1016	-935
-3	0	2	1164	-1121
-2	0	2	965	930
-1	0	2	199	-250
0	0	2	518	-526
1	0	2	610	704
2	0	2	772	-855
3	0	2	939	-863
4	0	2	1389	-1276
5	0	2	663	-638
6	0	2	282	-305
7	0	2	643	635
8	0	2	355	378
10	0	2	157	-181
11	0	2	108	-119

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR SEXACU

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
13	0	2	96	86	18	1	2	64	-36	16	2	2	114	114	-17	4	2	102	113	-7	5	2	288	-265
15	0	2	87	-74	21	1	2	94	84	18	2	2	111	-120	-15	4	2	177	-191	-6	5	2	286	-204
16	0	2	264	-256	-21	2	2	80	79	21	2	2	74	83	-13	4	2	75	94	-5	5	2	127	123
17	0	2	167	166	-20	2	2	72	77	-19	3	2	102	-110	-12	4	2	257	257	-4	5	2	72	110
18	0	2	109	107	-18	2	2	125	-98	-17	3	2	84	82	-11	4	2	162	-163	-3	5	2	307	205
-20	1	2	73	62	-16	2	2	73	74	-16	3	2	115	119	-9	4	2	68	77	-2	5	2	274	-263
-19	1	2	76	91	-15	2	2	77	55	-14	3	2	141	-145	-7	4	2	359	351	-1	5	2	603	-572
-15	1	2	111	98	-13	2	2	201	-201	-13	3	2	220	-226	-6	4	2	350	-347	0	5	2	496	-506
-14	1	2	182	186	-12	2	2	364	-378	-11	3	2	319	309	-5	4	2	113	-79	1	5	2	106	108
-13	1	2	118	106	-11	2	2	211	228	-9	3	2	154	-140	-4	4	2	108	-108	2	5	2	85	106
-12	1	2	508	-484	-10	2	2	605	597	-8	3	2	488	-491	-3	4	2	425	403	3	5	2	106	-107
-11	1	2	437	-426	-9	2	2	656	632	-7	3	2	426	415	-2	4	2	765	726	4	5	2	123	-98
-10	1	2	93	76	-8	2	2	68	-70	-6	3	2	248	261	-1	4	2	181	-207	5	5	2	158	-164
-9	1	2	514	506	-7	2	2	323	-351	-5	3	2	267	-262	0	4	2	753	-724	6	5	2	94	-102
-8	1	2	507	487	-6	2	2	540	524	-4	3	2	199	-165	1	4	2	443	-433	7	5	2	302	326
-7	1	2	96	-106	-5	2	2	351	359	-3	3	2	675	-672	2	4	2	96	111	8	5	2	130	127
-6	1	2	165	-167	-4	2	2	261	223	-2	3	2	612	576	3	4	2	119	150	10	5	2	120	116
-5	1	2	221	-253	-3	2	2	138	-103	-1	3	2	507	516	4	4	2	272	265	12	5	2	233	241
-3	1	2	1602	1506	-2	2	2	1094	-1092	0	3	2	62	-54	5	4	2	113	-138	14	5	2	225	-241
-2	1	2	378	-381	-1	2	2	234	-208	1	3	2	1113	-1097	7	4	2	391	356	15	5	2	135	-124
-1	1	2	408	416	0	2	2	765	745	2	3	2	540	-536	8	4	2	55	33	17	5	2	229	225
0	1	2	753	732	1	2	2	466	419	3	3	2	49	-40	9	4	2	192	190	19	5	2	64	-57
1	1	2	161	-109	2	2	2	939	-915	4	3	2	222	234	10	4	2	129	96	20	5	2	75	-54
3	1	2	551	489	3	2	2	75	-90	5	3	2	433	474	11	4	2	230	-227	-17	6	2	74	-67
4	1	2	2033	-1929	4	2	2	275	-254	6	3	2	472	-467	13	4	2	422	418	-15	6	2	143	157
5	1	2	270	-267	5	2	2	1261	1249	7	3	2	537	-568	14	4	2	170	-156	-14	6	2	114	108
6	1	2	1106	1079	6	2	2	765	701	8	3	2	71	-62	15	4	2	161	-184	-13	6	2	68	-79
7	1	2	597	494	7	2	2	275	-250	9	3	2	352	354	16	4	2	147	-146	-12	6	2	108	-118
8	1	2	513	-506	8	2	2	997	-926	12	3	2	323	-333	18	4	2	159	155	-10	6	2	145	152
9	1	2	320	-304	9	2	2	87	-96	13	3	2	65	87	-16	5	2	195	-190	-7	6	2	172	-181
10	1	2	208	-202	10	2	2	437	441	14	3	2	221	203	-15	5	2	70	-73	-5	6	2	225	217
11	1	2	205	206	11	2	2	171	174	16	3	2	100	-96	-14	5	2	97	108	-4	6	2	439	424
12	1	2	301	273	12	2	2	104	-77	17	3	2	134	-158	-13	5	2	75	58	-3	6	2	188	-164
13	1	2	136	130	13	2	2	128	-141	19	3	2	72	69	-11	5	2	203	-206	-2	6	2	226	-227
14	1	2	67	91	14	2	2	52	-48	22	3	2	84	-88	-10	5	2	94	106	0	6	2	155	152
17	1	2	226	244	15	2	2	86	-75	-18	4	2	114	115	-8	5	2	154	154	1	6	2	380	359

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR SEXACU

H	K	L	10FO	10FC
2	6	2	187	162
3	6	2	367	-375
4	6	2	314	-321
5	6	2	127	129
6	6	2	279	278
7	6	2	80	95
9	6	2	112	112
11	6	2	120	118
12	6	2	169	158
13	6	2	281	-274
14	6	2	98	-64
15	6	2	145	145
16	6	2	164	171
17	6	2	107	115
19	6	2	71	-67
21	6	2	81	72
-14	7	2	78	-66
-13	7	2	110	-96
-12	7	2	100	103
-11	7	2	195	185
-10	7	2	165	177
-9	7	2	178	179
-7	7	2	91	-107
-6	7	2	362	347
-5	7	2	122	127
-4	7	2	302	-288
-3	7	2	393	-404
-2	7	2	270	-253
0	7	2	280	273
1	7	2	52	-38
2	7	2	243	-243
3	7	2	109	-118
4	7	2	270	263
5	7	2	238	236
6	7	2	104	108
7	7	2	179	-180
8	7	2	61	-40
9	7	2	183	18
12	7	2	270	-246
13	7	2	152	-161
14	7	2	93	98
15	7	2	96	94
16	7	2	64	68
19	7	2	66	57
-15	8	2	75	-72
-14	8	2	69	-74
-12	8	2	66	62
-10	8	2	110	-111
-9	8	2	151	-160
-7	8	2	86	90
-6	8	2	60	58
-5	8	2	156	-166
-4	8	2	359	-338
-3	8	2	245	-240
-2	8	2	270	244
-1	8	2	139	122
0	8	2	77	-53
1	8	2	96	-87
4	8	2	95	89
5	8	2	137	-145
6	8	2	544	-535
8	8	2	228	247
9	8	2	124	-122
10	8	2	98	-92
11	8	2	149	-140
12	8	2	91	-85
13	8	2	89	96
14	8	2	123	129
-9	9	2	135	138
-8	9	2	275	270
-7	9	2	153	160
-6	9	2	142	-148
-5	9	2	242	-232
1	9	2	147	-127
2	9	2	161	174
3	9	2	107	136
4	9	2	145	-132
6	9	2	143	146
7	9	2	169	172
8	9	2	122	90
9	9	2	91	-82
10	9	2	144	-137
12	9	2	105	108
13	9	2	86	76
18	9	2	76	92
-14	10	2	68	65
-12	10	2	66	-63
-11	10	2	67	-75
-9	10	2	93	104
-8	10	2	71	69
-7	10	2	151	-153
-6	10	2	161	-145
-4	10	2	79	72
-3	10	2	169	169
3	10	2	71	-65
4	10	2	80	-70
5	10	2	121	-119
8	10	2	160	-157
9	10	2	96	-96
11	10	2	122	125
12	10	2	150	153
14	10	2	78	-82
-10	11	2	96	103
-7	11	2	99	-104
-5	11	2	114	111
-4	11	2	90	84
-2	11	2	114	-117
3	11	2	65	-55
5	11	2	71	70
8	11	2	105	-103
9	11	2	65	-50
11	11	2	146	143
13	11	2	124	-127
-8	12	2	70	-75
-1	12	2	117	121
0	12	2	68	67
1	12	2	134	-134
2	12	2	95	-95
3	12	2	118	96
4	12	2	104	95
7	12	2	118	-100
8	12	2	84	-93
9	12	2	87	81
12	12	2	89	-86
-2	13	2	62	50
0	13	2	113	-116
1	13	2	67	-62
3	13	2	132	129
5	13	2	102	-98
6	13	2	74	-71
1	14	2	66	66
2	14	2	98	100
4	14	2	80	-62
7	14	2	82	76
1	15	2	73	67
-4	-16	3	71	-73
-5	-15	3	72	-82
5	-15	3	130	-118
-14	-14	3	74	61
-11	-14	3	82	-55
1	-14	3	99	71
4	-14	3	115	-112
6	-14	3	104	119
-12	-13	3	84	-74
-10	-13	3	95	98
-9	-13	3	73	49
-3	-13	3	71	-67
3	-13	3	77	-70
5	-13	3	134	124
6	-13	3	100	91
-13	-12	3	78	-67
-11	-12	3	80	84
-6	-12	3	73	71
-4	-12	3	89	-109
-2	-12	3	128	143
2	-12	3	119	-103
3	-12	3	86	-91
4	-12	3	215	183
5	-12	3	147	177
14	-12	3	80	72
-18	-11	3	68	58
-15	-11	3	69	-60
-14	-11	3	63	-56
-11	-11	3	69	63
-9	-11	3	116	-98
-8	-11	3	71	68
-6	-11	3	107	-100
-5	-11	3	163	-172
-4	-11	3	150	-160
-3	-11	3	91	74
-2	-11	3	358	341
0	-11	3	210	-196
1	-11	3	196	-194
3	-11	3	108	124
4	-11	3	179	171
6	-11	3	116	-100
8	-11	3	76	75
10	-11	3	92	-92
11	-11	3	105	-113
13	-11	3	96	96

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR SEXACU

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
2	6	2	187	162	8	7	2	61	-40	-5	9	2	242	-232	6	11	2	71	70	-10	-13	3	95	98
3	6	2	367	-375	9	7	2	183	18	1	9	2	147	-127	8	11	2	105	-103	-9	-13	3	73	49
4	6	2	314	-321	12	7	2	270	-246	2	9	2	161	174	9	11	2	65	-50	-3	-13	3	71	-67
5	6	2	127	129	13	7	2	152	-161	3	9	2	107	136	11	11	2	146	143	3	-13	3	77	-70
6	6	2	279	278	14	7	2	93	98	4	9	2	145	-132	13	11	2	124	-127	5	-13	3	134	124
7	6	2	80	95	15	7	2	96	94	6	9	2	143	146	-8	12	2	70	-75	6	-13	3	100	91
9	6	2	112	112	16	7	2	64	68	7	9	2	169	172	-1	12	2	117	121	-13	-12	3	78	-67
11	6	2	120	118	19	7	2	66	57	8	9	2	122	90	0	12	2	68	67	-11	-12	3	80	84
12	6	2	169	158	-15	8	2	75	-72	9	9	2	91	-82	1	12	2	134	-134	-6	-12	3	73	71
13	6	2	281	-274	-14	8	2	69	-74	10	9	2	144	-137	2	12	2	95	-95	-4	-12	3	89	-109
14	6	2	98	-64	-12	8	2	66	62	12	9	2	105	108	3	12	2	118	96	-2	-12	3	128	143
15	6	2	145	145	-10	8	2	110	-111	13	9	2	86	76	4	12	2	104	95	2	-12	3	119	-103
16	6	2	164	171	-9	8	2	151	-160	18	9	2	76	92	7	12	2	118	-100	3	-12	3	86	-91
17	6	2	107	115	-7	8	2	86	90	-14	10	2	68	65	8	12	2	84	-93	4	-12	3	215	183
19	6	2	71	-67	-6	8	2	60	58	-12	10	2	66	-63	9	12	2	87	81	5	-12	3	147	177
21	6	2	81	72	-5	8	2	156	-166	-11	10	2	67	-75	12	12	2	89	-86	14	-12	3	80	72
-14	7	2	78	-66	-4	8	2	359	-338	-9	10	2	93	104	-2	13	2	62	50	-18	-11	3	68	58
-13	7	2	110	-96	-3	8	2	245	-240	-8	10	2	71	69	0	13	2	113	-116	-15	-11	3	69	-60
-12	7	2	100	103	-2	8	2	270	244	-7	10	2	151	-153	1	13	2	67	-62	-14	-11	3	63	-56
-11	7	2	195	185	-1	8	2	139	122	-6	10	2	161	-145	3	13	2	132	129	-11	-11	3	69	63
-10	7	2	165	177	0	8	2	77	-53	-4	10	2	79	72	5	13	2	102	-98	-9	-11	3	116	-98
-9	7	2	178	179	1	8	2	96	-87	-3	10	2	169	169	6	13	2	74	-71	-8	-11	3	71	68
-7	7	2	91	-107	4	8	2	95	89	3	10	2	71	-65	1	14	2	66	66	-6	-11	3	107	-100
-6	7	2	362	347	5	8	2	137	-145	4	10	2	80	-70	2	14	2	98	100	-5	-11	3	163	-172
-5	7	2	122	127	6	8	2	544	-535	5	10	2	121	-119	4	14	2	80	-62	-4	-11	3	150	-160
-4	7	2	302	-288	8	8	2	228	247	8	10	2	160	-157	7	14	2	82	76	-3	-11	3	91	74
-3	7	2	399	-404	9	8	2	124	-122	9	10	2	96	-96	1	15	2	73	67	-2	-11	3	358	341
-2	7	2	270	-253	10	8	2	98	-92	11	10	2	122	125	-4	-16	3	71	-73	0	-11	3	210	-196
0	7	2	280	273	11	8	2	149	-140	12	10	2	150	153	-5	-15	3	72	-82	1	-11	3	196	-194
1	7	2	52	-38	12	8	2	91	-85	14	10	2	78	-82	5	-15	3	130	-118	3	-11	3	108	124
2	7	2	243	-243	13	8	2	89	96	-10	11	2	96	103	-14	-14	3	74	61	4	-11	3	179	171
3	7	2	109	-118	14	8	2	123	129	-7	11	2	99	-104	-11	-14	3	82	-55	6	-11	3	116	-100
4	7	2	270	263	-9	9	2	135	138	-5	11	2	114	111	1	-14	3	99	71	8	-11	3	76	75
5	7	2	238	236	-8	9	2	275	270	-4	11	2	90	84	4	-14	3	115	-112	10	-11	3	92	-92
6	7	2	104	108	-7	9	2	153	160	-2	11	2	114	-117	6	-14	3	104	119	11	-11	3	105	-113
7	7	2	179	-180	-6	9	2	142	-148	3	11	2	65	-55	-12	-13	3	84	-74	13	-11	3	96	96

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR SEXACU

H	K	L	10FO	10FC
-15	-10	3	89	-88
-14	-10	3	86	107
-12	-10	3	87	90
-11	-10	3	95	106
-9	-10	3	116	117
-7	-10	3	178	-176
-6	-10	3	251	-245
-5	-10	3	311	-322
-3	-10	3	302	299
-2	-10	3	67	53
-1	-10	3	324	-333
0	-10	3	167	-165
2	-10	3	262	264
3	-10	3	95	77
5	-10	3	75	-74
8	-10	3	86	73
10	-10	3	124	-126
12	-10	3	136	142
14	-10	3	86	-92
15	-10	3	90	-83
-17	-9	3	73	-61
-16	-9	3	69	-61
-14	-9	3	125	111
-9	-9	3	66	38
-8	-9	3	71	-81
-7	-9	3	349	-339
-6	-9	3	270	-268
-5	-9	3	63	-43
-4	-9	3	124	125
-3	-9	3	80	51
-2	-9	3	102	-88
-1	-9	3	191	-189
1	-9	3	327	307
2	-9	3	197	184
3	-9	3	253	-233
4	-9	3	122	-141

H	K	L	10FO	10FC
7	-9	3	107	-118
9	-9	3	117	-118
11	-9	3	120	150
14	-9	3	66	-82
16	-9	3	96	86
-20	-8	3	74	57
-18	-8	3	78	-74
-15	-8	3	113	126
-13	-8	3	80	-67
-11	-8	3	131	134
-10	-8	3	320	307
-8	-8	3	255	-243
-7	-8	3	105	-113
-6	-8	3	87	94
-4	-8	3	192	202
-3	-8	3	204	-204
-2	-8	3	291	-284
[illegible]	-8	3	358	342
1	-8	3	54	66
2	-8	3	145	-153
4	-8	3	52	66
5	-8	3	351	349
7	-8	3	198	-186
8	-8	3	96	87
9	-8	3	160	162
10	-8	3	260	251
13	-8	3	122	-118
15	-8	3	86	61
18	-8	3	72	-75
-21	-7	3	69	32
-17	-7	3	129	128
-16	-7	3	98	105
-14	-7	3	176	-158
-13	-7	3	84	79
-12	-7	3	199	194
-11	-7	3	100	110

H	K	L	10FO	10FC
-10	-7	3	139	-119
-9	-7	3	414	-442
-8	-7	3	218	-222
-7	-7	3	346	331
-6	-7	3	363	355
-5	-7	3	226	-216
-4	-7	3	140	-155
-3	-7	3	115	129
-2	-7	3	203	231
-1	-7	3	129	127
0	-7	3	251	270
1	-7	3	486	-497
2	-7	3	207	-204
3	-7	3	371	384
4	-7	3	223	198
5	-7	3	298	-295
6	-7	3	553	-528
7	-7	3	82	-89
8	-7	3	139	149
9	-7	3	358	349
10	-7	3	154	161
11	-7	3	246	-249
12	-7	3	127	-139
14	-7	3	84	94
-18	-6	3	91	108
-16	-6	3	102	-90
-15	-6	3	140	-142
-14	-6	3	107	94
-13	-6	3	174	158
-11	-6	3	197	-188
-10	-6	3	457	-477
-9	-6	3	95	-76
-8	-6	3	383	394
-7	-6	3	282	279
-6	-6	3	400	-385
-5	-6	3	264	-271

H	K	L	10FO	10FC
-4	-6	3	232	219
-3	-6	3	189	177
-1	-6	3	579	-566
0	-6	3	334	-381
1	-6	3	158	-128
2	-6	3	221	225
3	-6	3	337	343
4	-6	3	152	-142
5	-6	3	746	-766
6	-6	3	216	-213
7	-6	3	325	324
8	-6	3	384	370
9	-6	3	102	112
10	-6	3	368	-378
11	-6	3	257	-273
12	-6	3	59	73
13	-6	3	161	149
15	-6	3	136	-133
16	-6	3	72	-79
20	-6	3	91	-84
-19	-5	3	98	98
-17	-5	3	114	-89
-14	-5	3	86	98
-13	-5	3	128	111
-12	-5	3	163	-177
-11	-5	3	309	-303
-10	-5	3	179	191
-9	-5	3	172	183
-7	-5	3	66	-72
-6	-5	3	364	-340
-5	-5	3	205	167
-4	-5	3	400	412
-3	-5	3	369	376
-2	-5	3	70	-16
-1	-5	3	143	-128
0	-5	3	205	220

H	K	L	10FO	10FC
1	-5	3	406	353
2	-5	3	426	481
3	-5	3	175	-185
4	-5	3	515	-513
5	-5	3	186	-191
6	-5	3	271	260
7	-5	3	485	467
8	-5	3	81	-81
9	-5	3	237	-248
10	-5	3	187	-159
11	-5	3	134	121
12	-5	3	336	331
13	-5	3	68	97
14	-5	3	125	-139
16	-5	3	104	114
17	-5	3	115	102
19	-5	3	84	-74
-18	-4	3	84	-97
-15	-4	3	105	106
-14	-4	3	102	88
-13	-4	3	128	-120
-12	-4	3	107	-103
-11	-4	3	87	-111
-10	-4	3	48	54
-8	-4	3	163	-156
-7	-4	3	493	-465
-6	-4	3	177	-155
-5	-4	3	369	372
-4	-4	3	187	136
-3	-4	3	53	-43
-2	-4	3	62	-60
0	-4	3	553	609
1	-4	3	366	365
2	-4	3	556	-578
3	-4	3	313	-274
4	-4	3	64	-63

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR SEXACU

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
6	-4	3	64	91	11	-3	3	90	-87	15	-2	3	61	-80	17	-1	3	197	196	-10	1	3	360	348
7	-4	3	151	149	12	-3	3	111	-114	16	-2	3	233	-229	18	-1	3	108	107	-9	1	3	122	111
8	-4	3	385	-375	14	-3	3	151	143	18	-2	3	117	105	20	-1	3	124	-108	-8	1	3	248	-250
9	-4	3	109	-116	15	-3	3	70	89	19	-2	3	77	85	-20	0	3	120	112	-7	1	3	125	-136
10	-4	3	197	195	16	-3	3	113	-135	21	-2	3	89	-106	-19	0	3	147	144	-6	1	3	314	325
11	-4	3	142	156	17	-3	3	136	-142	-19	-1	3	107	99	-14	0	3	156	137	-5	1	3	220	-208
12	-4	3	70	-71	20	-3	3	95	97	-18	-1	3	113	98	-12	0	3	277	-260	-4	1	3	224	-240
13	-4	3	128	-129	-20	-2	3	78	-71	-16	-1	3	240	-240	-10	0	3	284	272	-3	1	3	196	-209
15	-4	3	117	110	-18	-2	3	179	183	-15	-1	3	136	-146	-9	0	3	79	76	-2	1	3	791	-750
16	-4	3	107	114	-17	-2	3	206	212	-11	-1	3	317	-314	-8	0	3	155	140	-1	1	3	1216	-1145
18	-4	3	120	-134	-15	-2	3	105	-101	-10	-1	3	62	-43	-7	0	3	423	-410	0	1	3	127	137
19	-4	3	72	-88	-14	-2	3	158	-140	-9	-1	3	224	219	-6	0	3	75	50	1	1	3	292	274
-19	-3	3	82	-99	-12	-2	3	332	318	-8	-1	3	376	354	-5	0	3	209	210	2	1	3	746	695
-18	-3	3	69	-72	-11	-2	3	151	-108	-7	-1	3	308	-317	-4	0	3	221	257	3	1	3	571	-503
-16	-3	3	102	88	-10	-2	3	243	-242	-6	-1	3	154	-173	-3	0	3	467	457	4	1	3	187	152
-14	-3	3	70	-76	-9	-2	3	69	-84	-5	-1	3	181	-153	-2	0	3	211	221	5	1	3	411	370
-13	-3	3	133	-135	-8	-2	3	112	-124	-4	-1	3	482	-470	-1	0	3	491	431	6	1	3	425	441
-11	-3	3	329	327	-7	-2	3	107	135	-3	-1	3	70	-74	1	0	3	59	-58	7	1	3	139	-137
-10	-3	3	202	199	-6	-2	3	118	-116	-2	-1	3	321	-291	2	0	3	1351	1269	8	1	3	365	-380
-8	-3	3	101	-91	-5	-2	3	251	-269	-1	-1	3	1717	-1750	3	0	3	349	-336	9	1	3	181	166
-7	-3	3	94	115	-4	-2	3	568	-598	0	-1	3	2238	-2250	4	0	3	1061	-993	10	1	3	334	331
-6	-3	3	234	221	-3	-2	3	958	925	1	-1	3	382	328	5	0	3	359	370	11	1	3	69	-61
-5	-3	3	103	-71	-2	-2	3	1441	1500	2	-1	3	695	628	6	0	3	347	349	12	1	3	302	-299
-4	-3	3	170	-172	-1	-2	3	482	-452	3	-1	3	552	-480	7	0	3	421	376	13	1	3	297	-305
-3	-3	3	727	-797	0	-2	3	235	-334	4	-1	3	228	-204	10	0	3	278	266	14	1	3	116	-104
-2	-3	3	65	105	1	-2	3	1139	-1082	5	-1	3	88	42	11	0	3	248	264	15	1	3	87	95
-1	-3	3	1479	1499	2	-2	3	178	-114	6	-1	3	85	44	12	0	3	294	282	16	1	3	210	189
0	-3	3	443	-397	3	-2	3	465	497	7	-1	3	778	765	13	0	3	87	-57	17	1	3	111	-104
1	-3	3	778	-732	4	-2	3	121	-122	8	-1	3	913	853	16	0	3	210	217	-15	2	3	104	-84
2	-3	3	296	237	5	-2	3	656	-645	9	-1	3	386	-375	17	0	3	208	205	-13	2	3	95	-80
3	-3	3	94	-153	6	-2	3	64	-82	10	-1	3	96	-67	19	0	3	67	-77	-12	2	3	167	154
4	-3	3	349	333	7	-2	3	55	81	11	-1	3	136	99	21	0	3	94	90	-11	2	3	217	219
5	-3	3	327	324	8	-2	3	587	548	12	-1	3	158	-148	-20	1	3	113	109	-10	2	3	185	-176
6	-3	3	326	332	9	-2	3	370	388	14	-1	3	134	-145	-14	1	3	71	83	-9	2	3	467	-467
7	-3	3	87	63	10	-2	3	169	-174	15	-1	3	305	-293	-13	1	3	79	-105	-8	2	3	89	-89
9	-3	3	621	574	13	-2	3	115	131	16	-1	3	73	-104	-11	1	3	294	310	-7	2	3	142	148

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR SEXACU

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
-6	2	3	547	566	-3	3	3	392	398	3	4	3	232	-265	9	5	3	257	-263	-14	7	3	103	-88
-5	2	3	275	-243	-2	3	3	611	561	4	4	3	417	-381	11	5	3	110	112	-12	7	3	142	110
-4	2	3	830	-822	-1	3	3	176	-133	5	4	3	420	-438	12	5	3	126	119	-10	7	3	163	-170
-3	2	3	632	-634	0	3	3	488	-489	6	4	3	830	796	13	5	3	105	-101	-6	7	3	101	-114
-2	2	3	190	194	3	3	3	224	252	7	4	3	273	304	16	5	3	105	113	-5	7	3	392	-398
-1	2	3	363	358	4	3	3	71	-106	8	4	3	114	118	18	5	3	90	-98	-4	7	3	185	-174
0	2	3	500	483	5	3	3	627	-631	9	4	3	346	-349	-16	6	3	107	106	-3	7	3	80	88
1	2	3	86	105	6	3	3	326	340	10	4	3	161	-156	-14	6	3	138	-137	-2	7	3	334	328
3	2	3	151	-196	7	3	3	343	315	11	4	3	111	-113	-13	6	3	124	-125	-1	7	3	49	40
4	2	3	388	398	8	3	3	412	421	12	4	3	157	167	-11	6	3	215	229	0	7	3	211	-213
5	2	3	562	-516	9	3	3	181	198	13	4	3	179	171	-10	6	3	116	97	1	7	3	288	-294
6	2	3	367	-410	10	3	3	372	-374	14	4	3	160	-178	-9	6	3	81	97	3	7	3	224	245
7	2	3	524	-509	11	3	3	439	-426	15	4	3	137	-139	-7	6	3	262	-267	4	7	3	367	367
8	2	3	48	95	12	3	3	84	59	17	4	3	122	134	-6	6	3	189	204	5	7	3	203	-203
9	2	3	509	497	13	3	3	333	320	22	4	3	80	77	-5	6	3	221	-222	6	7	3	420	-430
10	2	3	63	-65	15	3	3	170	-188	-16	5	3	70	50	-4	6	3	235	-247	7	7	3	138	-156
11	2	3	277	-275	16	3	3	87	-84	-15	5	3	175	182	-3	6	3	52	-64	8	7	3	240	237
12	2	3	314	-310	18	3	3	105	102	-14	5	3	63	71	-2	6	3	134	148	10	7	3	58	-54
14	2	3	372	342	-17	4	3	96	-106	-13	5	3	131	-123	-1	6	3	201	215	12	7	3	71	-67
15	2	3	59	84	-16	4	3	110	-102	-12	5	3	238	-250	0	6	3	140	145	13	7	3	188	178
16	2	3	113	-103	-14	4	3	192	192	-10	5	3	244	255	1	6	3	421	-417	14	7	3	86	90
17	2	3	118	-126	-13	4	3	93	79	-8	5	3	307	305	2	6	3	404	-418	15	7	3	95	-94
22	2	3	69	-89	-12	4	3	187	-180	-7	5	3	162	-151	3	6	3	133	-116	18	7	3	94	99
-20	3	3	81	-62	-11	4	3	391	-404	-6	5	3	146	-144	4	6	3	424	449	20	7	3	82	-67
-18	3	3	98	97	-10	4	3	111	116	-5	5	3	143	125	5	6	3	491	474	-11	8	3	71	-78
-15	3	3	129	-134	-8	4	3	266	260	-4	5	3	245	235	6	6	3	70	70	-9	8	3	185	190
-13	3	3	242	244	-7	4	3	80	81	-3	5	3	102	-114	7	6	3	183	-196	-8	8	3	113	97
-12	3	3	163	166	-6	4	3	491	-489	-1	5	3	325	346	8	6	3	315	-313	-7	8	3	62	-66
-11	3	3	281	-302	-5	4	3	96	-102	0	5	3	345	348	9	6	3	192	221	-6	8	3	313	-325
-10	3	3	114	-111	-4	4	3	285	269	1	5	3	311	304	10	6	3	80	79	-5	8	3	229	-229
-9	3	3	77	-86	-3	4	3	405	400	2	5	3	328	-313	11	6	3	149	-155	-4	8	3	185	174
-8	3	3	190	188	-2	4	3	282	-255	3	5	3	616	-634	13	6	3	86	-109	-3	8	3	129	135
-7	3	3	753	747	-1	4	3	798	-775	4	5	3	72	-97	14	6	3	82	8	0	8	3	315	-320
-6	3	3	71	-91	0	4	3	336	331	5	5	3	510	523	17	6	3	102	-108	2	8	3	412	418
-5	3	3	1113	-1125	1	4	3	407	425	6	5	3	623	611	-17	7	3	74	63	3	8	3	147	153
-4	3	3	125	-89	2	4	3	77	73	7	5	3	54	25	-15	7	3	100	-122	4	8	3	98	-99

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR SEXACU

H	K	L	10FO	10FC
5	8	3	196	-191
7	8	3	82	72
8	8	3	186	186
10	8	3	104	-109
11	8	3	124	128
12	8	3	176	155
14	8	3	75	-65
17	8	3	78	92
18	8	3	93	92
20	8	3	75	-51
-10	9	3	95	103
-9	9	3	112	124
-7	9	3	186	-201
-6	9	3	68	-81
-5	9	3	134	139
-4	9	3	132	123
-3	9	3	67	59
-2	9	3	114	-101
-1	9	3	207	-208
1	9	3	199	194
2	9	3	153	149
4	9	3	136	-129
7	9	3	59	62
9	9	3	76	-104
10	9	3	143	157
11	9	3	154	143
12	9	3	66	72
14	9	3	139	-132
16	9	3	75	61
-7	10	3	79	-99
-6	10	3	79	78
-5	10	3	226	229
-3	10	3	168	-163
-2	10	3	67	-63
1	10	3	125	114
2	10	3	103	-96
3	10	3	122	-123
10	10	3	131	117
11	10	3	96	90
12	10	3	121	-117
13	10	3	120	-123
-9	11	3	77	-87
-6	11	3	87	101
-4	11	3	124	-107
-3	11	3	86	-89
-1	11	3	142	144
1	11	3	144	-145
3	11	3	82	74
7	11	3	73	-63
9	11	3	91	98
11	11	3	86	-94
12	11	3	74	-56
14	11	3	68	73
-5	12	3	84	-81
-2	12	3	104	105
0	12	3	69	-73
3	12	3	112	126
5	12	3	104	-100
13	12	3	87	73
-6	13	3	75	-67
1	13	3	68	66
2	13	3	92	93
4	13	3	100	-93
6	14	3	90	86
2	15	3	77	-57
-5	-16	4	105	-94
-6	-15	4	100	-95
-10	-14	4	83	84
-5	-14	4	100	72
-4	-14	4	68	82
1	-14	4	66	62
2	-14	4	76	-97
5	-14	4	110	91
7	-14	4	85	-93
-11	-13	4	71	77
-9	-13	4	84	-89
-8	-13	4	69	-54
-6	-13	4	113	124
-4	-13	4	65	-77
-1	-13	4	58	-64
0	-13	4	89	79
1	-13	4	124	-125
3	-13	4	103	98
4	-13	4	71	47
6	-13	4	75	-97
-10	-12	4	80	-95
-9	-12	4	78	-87
-7	-12	4	127	130
-3	-12	4	119	134
1	-12	4	84	-80
2	-12	4	173	186
6	-12	4	69	-55
8	-12	4	68	69
10	-12	4	73	-76
-16	-11	4	99	-92
-14	-11	4	66	89
-8	-11	4	86	92
-6	-11	4	100	-99
-5	-11	4	127	-137
-4	-11	4	66	85
-3	-11	4	131	133
-2	-11	4	82	-77
-1	-11	4	60	51
1	-11	4	133	125
2	-11	4	136	118
3	-11	4	60	-68
5	-11	4	124	-124
7	-11	4	143	149
8	-11	4	63	73
9	-11	4	75	-86
10	-11	4	98	-91
12	-11	4	67	75
-15	-10	4	148	130
-13	-10	4	100	-94
-12	-10	4	80	-72
-11	-10	4	116	-108
-7	-10	4	245	-246
-6	-10	4	135	-152
0	-10	4	207	201
1	-10	4	412	418
2	-10	4	96	-97
3	-10	4	448	-457
4	-10	4	113	-129
7	-10	4	86	64
8	-10	4	104	-95
9	-10	4	176	-171
11	-10	4	111	105
16	-10	4	75	76
-18	-9	4	81	-74
-16	-9	4	93	83
-15	-9	4	95	102
-13	-9	4	123	-116
-11	-9	4	96	93
-10	-9	4	174	163
-9	-9	4	60	75
-5	-9	4	95	86
-3	-9	4	136	-162
-2	-9	4	151	152
-1	-9	4	291	304
0	-9	4	134	126
1	-9	4	51	62
2	-9	4	324	-329
3	-9	4	168	-175
4	-9	4	300	315
5	-9	4	441	431
6	-9	4	191	188
7	-9	4	73	-60
8	-9	4	92	77
9	-9	4	77	92
10	-9	4	68	83
12	-9	4	67	-62
13	-9	4	94	-121
15	-9	4	76	80
-17	-8	4	116	114
-16	-8	4	101	87
-14	-8	4	204	-208
-12	-8	4	59	74
-11	-8	4	58	77
-10	-8	4	61	-54
-9	-8	4	128	-152
-8	-8	4	96	-76
-7	-8	4	138	132
-5	-8	4	187	-207
-3	-8	4	129	151
-2	-8	4	161	155
-1	-8	4	254	225
1	-8	4	423	-445
2	-8	4	309	-314
3	-8	4	235	253
4	-8	4	63	56
6	-8	4	233	-242
7	-8	4	191	-209
8	-8	4	102	110
9	-8	4	120	113
10	-8	4	63	-51
11	-8	4	86	-65
14	-8	4	71	77
16	-8	4	124	-109
-20	-7	4	80	-49
-18	-7	4	82	99

A-5

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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR  SEXACU

  H  K  L 10FO 10FC       H  K  L 10FO 10FC       H  K  L 10FO 10FC       H  K  L 10FO 10FC       H  K  L 10FO 10FC

-15 -7  4  146 -148       1 -6  4  213  221      11 -5  4  125  146      17 -4  4  114 -127     -14 -2  4  108  133
-14 -7  4   89  -84       2 -6  4  332  355      12 -5  4  199 -204      20 -4  4   70   77     -13 -2  4   65   73
-13 -7  4  101  102       3 -6  4   46  -61      13 -5  4  226 -226     -18 -3  4  145  161     -11 -2  4  360 -361
-10 -7  4  215 -229       4 -6  4   51   50      14 -5  4  134 -129     -17 -3  4   89   95     -10 -2  4  339 -338
 -8 -7  4  430  462       6 -6  4  105  119      15 -5  4   89   85     -16 -3  4   78  -86      -9 -2  4  261  234
 -6 -7  4  416 -425       8 -6  4  133 -129      16 -5  4  148  149     -15 -3  4  165 -159      -8 -2  4   98  141
 -5 -7  4  162 -175       9 -6  4  115 -113      18 -5  4  102 -111     -13 -3  4  199  205      -7 -2  4  123 -113
 -4 -7  4  154 -156      11 -6  4  299  293     -19 -4  4   78  -90     -12 -3  4   96  104      -6 -2  4   57   25
 -3 -7  4  297  311      12 -6  4  163  173     -17 -4  4  104  114     -11 -3  4   76  -85      -5 -2  4  248 -229
 -2 -7  4  157  177      14 -6  4  124 -130     -14 -4  4   77  -83     -10 -3  4  363 -355      -4 -2  4  100   75
 -1 -7  4  429 -478      16 -6  4   74   99     -13 -4  4   62   59      -9 -3  4  378 -384      -3 -2  4  201  199
  0 -7  4  382 -438      17 -6  4  100   96     -12 -4  4  168  186      -8 -3  4  124 -124      -2 -2  4  389 -321
  1 -7  4  388 -358     -18 -5  4   80  -98     -11 -4  4  261  258      -7 -3  4  166  183      -1 -2  4   97 -131
  2 -7  4  134  105     -13 -5  4   86  -79      -9 -4  4  441 -452      -6 -3  4   58   57       0 -2  4  191 -196
  3 -7  4  194  216     -11 -5  4  149  140      -8 -4  4  174 -178      -5 -3  4  229 -244       1 -2  4  714  706
  7 -7  4  288  280     -10 -5  4  228  219      -7 -4  4   60   55      -4 -3  4  100  102       2 -2  4  167  165
  8 -7  4  152  137      -9 -5  4   89  -71      -6 -4  4  210  216      -2 -3  4  625  609       3 -2  4  596 -596
  9 -7  4   68  -48      -8 -5  4  512 -549      -5 -4  4  264  265       0 -3  4  482 -473       4 -2  4  109  -82
 10 -7  4  156 -155      -7 -5  4  324 -330      -4 -4  4   41   58       1 -3  4   65   62       6 -2  4  398  394
 14 -7  4   63  -62      -6 -5  4  165  165      -3 -4  4  216 -219       2 -3  4  286  263       7 -2  4  695  682
 15 -7  4  161 -165      -5 -5  4  336  348      -1 -4  4  695  711       3 -3  4  474  492       8 -2  4  491  433
 18 -7  4   86   86      -4 -5  4  325  343       0 -4  4  365  347       4 -3  4  244 -228       9 -2  4  277 -278
-19 -6  4  104  109      -3 -5  4  101  -97       1 -4  4  277 -305       5 -3  4  720 -696      10 -2  4  119 -121
-14 -6  4  109  103      -2 -5  4  830 -857       2 -4  4  114  -48       6 -3  4  134 -140      11 -2  4  210 -225
-12 -6  4  169 -167      -1 -5  4  115  109       3 -4  4  303  301       8 -3  4  467  443      12 -2  4  193 -171
-11 -6  4   85  -93         -5  4  361  387       4 -4  4  346  349       9 -3  4  153  152      13 -2  4   86  -96
-10 -6  4  262  251       1 -5  4  521  563       5 -4  4  383  368      10 -3  4  342 -347      14 -2  4  176 -182
 -9 -6  4  307  302       2 -5  4  445 -422       6 -4  4  159 -184      11 -3  4  379 -363      15 -2  4  124 -131
 -7 -6  4  297 -308       3 -5  4  213  194       7 -4  4  468 -457      13 -3  4  138  141      16 -2  4  112  105
 -6 -6  4  394 -399       4 -5  4   76   64       8 -4  4  251  251      15 -3  4   95 -120      17 -2  4  158  169
 -5 -6  4  167  179       5 -5  4  363 -361       9 -4  4  551  550      16 -3  4  133 -125     -20 -1  4   87   92
 -4 -6  4  598  632       6 -5  4  238  252      10 -4  4  120  117      18 -3  4  114  113     -19 -1  4   84   77
 -3 -6  4  663  663       7 -5  4  247 -230      11 -4  4  371 -376      21 -3  4   72  -89     -17 -1  4   89  -94
 -2 -6  4  486 -496       8 -5  4  483 -491      12 -4  4  345 -357     -18 -2  4   89   89     -15 -1  4  111  103
 -1 -6  4  369 -393       9 -5  4  126  119      14 -4  4  182  171     -17 -2  4  167 -158     -14 -1  4  138  117
  0 -6  4   65 -112      10 -5  4  441  442      15 -4  4  106  103     -16 -2  4  239 -231     -13 -1  4  165 -150
```

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR SEXACU

H	K	L	10FO	10FC
-12	-1	4	316	-324
-11	-1	4	165	-190
-10	-1	4	259	252
-9	-1	4	150	143
-7	-1	4	103	-72
-6	-1	4	83	46
-5	-1	4	395	429
-4	-1	4	197	218
-3	-1	4	98	-148
-2	-1	4	191	240
-1	-1	4	306	325
0	-1	4	554	543
1	-1	4	327	385
2	-1	4	176	129
3	-1	4	448	-482
4	-1	4	396	-440
5	-1	4	701	688
6	-1	4	433	451
8	-1	4	296	277
9	-1	4	194	-197
10	-1	4	125	122
11	-1	4	91	-74
12	-1	4	122	117
15	-1	4	88	82
16	-1	4	185	207
18	-1	4	80	-74
19	-1	4	95	-100
21	-1	4	79	96
-21	0	4	82	86
-15	0	4	109	123
-14	0	4	104	-92
-13	0	4	194	-226
-11	0	4	195	207
-10	0	4	192	173
-8	0	4	252	-255
-7	0	4	77	70
-6	0	4	565	594
-5	0	4	382	-395
-4	0	4	333	-322
-3	0	4	412	-415
-2	0	4	76	-112
-1	0	4	272	268
0	0	4	650	665
1	0	4	246	254
2	0	4	210	-209
3	0	4	443	-436
4	0	4	340	317
5	0	4	413	368
6	0	4	353	-300
7	0	4	153	-141
8	0	4	65	45
9	0	4	194	219
10	0	4	144	124
11	0	4	146	-126
12	0	4	119	-107
13	0	4	263	-284
15	0	4	160	161
17	0	4	194	-182
20	0	4	111	116
22	0	4	104	-89
-20	1	4	85	-71
-19	1	4	88	-71
-14	1	4	102	-96
-13	1	4	87	-81
-12	1	4	98	82
-11	1	4	203	210
-10	1	4	257	-247
-9	1	4	169	-178
-8	1	4	186	184
-7	1	4	93	90
-5	1	4	142	-114
-4	1	4	920	-905
-3	1	4	369	-352
-2	1	4	875	899
-1	1	4	94	85
0	1	4	141	-171
1	1	4	298	291
2	1	4	196	-171
3	1	4	592	-562
4	1	4	538	540
5	1	4	274	-245
6	1	4	502	-523
7	1	4	120	133
8	1	4	269	278
9	1	4	161	156
10	1	4	260	-233
11	1	4	244	-261
12	1	4	96	-81
13	1	4	171	166
14	1	4	329	305
16	1	4	208	-210
17	1	4	103	-115
18	1	4	61	57
21	1	4	76	-105
22	1	4	105	-82
-15	2	4	140	-142
-13	2	4	68	82
-11	2	4	55	-67
-10	2	4	71	-63
-9	2	4	56	-65
-8	2	4	219	218
-7	2	4	273	278
-6	2	4	321	-339
-5	2	4	543	-549
-4	2	4	298	-267
-3	2	4	302	309
-2	2	4	366	328
-1	2	4	66	-49
0	2	4	250	-256
1	2	4	149	-175
2	2	4	188	-148
3	2	4	206	224
4	2	4	56	27
5	2	4	221	-186
6	2	4	354	343
7	2	4	237	-266
8	2	4	395	428
9	2	4	176	-176
10	2	4	468	-457
11	2	4	75	88
12	2	4	345	329
13	2	4	216	229
15	2	4	207	-235
16	2	4	73	-90
17	2	4	94	113
18	2	4	67	77
21	2	4	87	-76
-19	3	4	80	100
-17	3	4	74	-82
-16	3	4	77	-96
-14	3	4	148	145
-12	3	4	95	-100
-10	3	4	109	93
-9	3	4	188	184
-8	3	4	114	120
-6	3	4	230	-233
-5	3	4	313	-318
-4	3	4	414	406
-3	3	4	609	618
-2	3	4	223	-190
-1	3	4	580	-588
0	3	4	172	165
2	3	4	147	-156
3	3	4	416	416
4	3	4	298	-275
6	3	4	525	533
7	3	4	45	71
9	3	4	282	-284
11	3	4	84	87
12	3	4	152	145
14	3	4	269	-280
15	3	4	60	-76
16	3	4	120	130
17	3	4	104	130
-18	4	4	74	-70
-15	4	4	119	130
-13	4	4	146	-149
-12	4	4	98	-101
-11	4	4	129	129
-10	4	4	149	155
-8	4	4	78	-89
-7	4	4	165	-135
-6	4	4	91	-96
-5	4	4	315	308
-4	4	4	283	299
-3	4	4	167	-174
-2	4	4	419	-432
0	4	4	330	304
2	4	4	275	-239
3	4	4	124	-141
4	4	4	69	-46
5	4	4	656	681
6	4	4	112	105
7	4	4	139	-150
8	4	4	112	-107
9	4	4	226	-229
10	4	4	154	149
11	4	4	158	153
12	4	4	156	-151
13	4	4	252	-230

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR SEXACU

H	K	L	10FO	10FC
15	4	4	80	88
16	4	4	124	142
18	4	4	105	-112
-14	5	4	175	-185
-11	5	4	196	207
-10	5	4	97	99
-9	5	4	230	-222
-8	5	4	271	-271
-7	5	4	185	182
-6	5	4	167	187
-4	5	4	85	-107
-3	5	4	171	-158
-1	5	4	347	332
0	5	4	89	86
1	5	4	221	-224
2	5	4	227	-241
3	5	4	205	205
4	5	4	405	405
5	5	4	316	294
6	5	4	421	-418
7	5	4	200	-183
8	5	4	59	-71
9	5	4	284	293
10	5	4	219	224
11	5	4	390	-382
12	5	4	116	-130
13	5	4	86	-102
15	5	4	134	145
17	5	4	119	-124
-15	6	4	113	-115
-13	6	4	125	148
-12	6	4	138	156
-11	6	4	70	77
-10	6	4	255	-276
-9	6	4	100	-98
-7	6	4	215	217
-6	6	4	63	-84
-5	6	4	380	-361
-4	6	4	207	-176
-2	6	4	138	134
2	6	4	139	146
3	6	4	374	348
4	6	4	140	122
5	6	4	497	-486
6	6	4	342	-334
7	6	4	300	313
8	6	4	127	131
9	6	4	147	144
10	6	4	131	-148
11	6	4	286	-309
12	6	4	99	-89
13	6	4	150	167
14	6	4	89	96
15	6	4	63	-69
18	6	4	80	59
20	6	4	85	-85
21	6	4	102	-101
-16	7	4	98	-77
-14	7	4	75	93
-11	7	4	162	-171
-10	7	4	159	-174
-9	7	4	120	132
-8	7	4	87	71
-6	7	4	383	-389
-4	7	4	75	81
-3	7	4	66	70
-2	7	4	154	134
-1	7	4	157	155
1	7	4	262	253
2	7	4	262	262
3	7	4	188	-192
4	7	4	233	-257
5	7	4	220	-221
6	7	4	126	155
7	7	4	250	246
10	7	4	256	-256
12	7	4	188	199
13	7	4	85	82
17	7	4	68	60
20	7	4	75	-51
-15	8	4	94	106
-14	8	4	74	73
-10	8	4	125	149
-9	8	4	185	188
-7	8	4	99	-112
-6	8	4	96	-94
-3	8	4	78	75
-2	8	4	92	-90
-1	8	4	75	76
0	8	4	221	242
1	8	4	221	220
4	8	4	165	-150
5	8	4	196	191
6	8	4	264	259
9	8	4	124	-125
11	8	4	138	160
13	8	4	62	-73
14	8	4	103	-108
-12	9	4	77	-81
-8	9	4	74	-80
-7	9	4	85	-90
-6	9	4	86	68
-5	9	4	84	98
-4	9	4	133	-138
-1	9	4	102	89
0	9	4	105	98
2	9	4	305	-306
3	9	4	176	-179
4	9	4	65	52
5	9	4	154	155
6	9	4	105	-113
7	9	4	72	-70
8	9	4	59	-61
10	9	4	176	178
12	9	4	138	-139
13	9	4	73	-76
18	9	4	84	-66
-11	10	4	84	78
-5	10	4	73	-75
-4	10	4	156	-166
-2	10	4	129	130
-1	10	4	111	133
0	10	4	128	-136
1	10	4	252	-248
3	10	4	112	124
4	10	4	130	132
5	10	4	113	128
6	10	4	134	-135
8	10	4	73	64
9	10	4	118	106
11	10	4	93	-103
16	10	4	79	-82
-3	11	4	167	183
-2	11	4	116	105
-1	11	4	88	-104
0	11	4	149	-152
2	11	4	93	92
3	11	4	104	82
5	11	4	118	-116
12	11	4	99	96
-6	12	4	81	-65
-1	12	4	92	-82
1	12	4	84	92
4	12	4	67	-64
9	14	4	73	62
1	-16	5	73	59
4	-16	5	73	-76
-5	-15	5	65	41
-3	-15	5	63	-64
-1	-15	5	73	63
0	-15	5	83	87
3	-15	5	71	-55
-7	-14	5	94	98
-6	-14	5	65	63
-4	-14	5	119	-132
-1	-14	5	102	93
1	-14	5	68	-77
2	-14	5	158	-155
3	-14	5	62	53
11	-14	5	78	-83
-9	-13	5	63	70
-8	-13	5	112	112
-7	-13	5	103	101
-6	-13	5	82	-78
-5	-13	5	183	-153
-3	-13	5	131	139
-2	-13	5	156	165
1	-13	5	115	-115
3	-13	5	114	116
7	-13	5	74	86
10	-13	5	119	-112
12	-13	5	71	83
13	-13	5	125	114
-9	-12	5	96	96
-7	-12	5	78	-74
-6	-12	5	217	-206
-4	-12	5	149	159
-3	-12	5	147	154
-2	-12	5	110	-140
1	-12	5	87	-101

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR SEXACU

H	K	L	10FO	10FC
3	-12	5	86	-82
6	-12	5	68	66
8	-12	5	92	-95
9	-12	5	98	-91
10	-12	5	67	-68
12	-12	5	69	76
14	-12	5	73	-96
-15	-11	5	92	72
-13	-11	5	62	-51
-10	-11	5	68	82
-8	-11	5	108	-101
-7	-11	5	181	-172
-5	-11	5	78	62
-4	-11	5	173	174
-3	-11	5	113	117
-1	-11	5	217	222
0	-11	5	84	-76
2	-11	5	183	-192
8	-11	5	121	-95
11	-11	5	109	111
12	-11	5	67	46
-16	-10	5	73	77
-14	-10	5	105	-103
-11	-10	5	192	183
-9	-10	5	75	-50
-8	-10	5	112	-131
-7	-10	5	56	-79
-5	-10	5	147	143
-4	-10	5	169	191
-3	-10	5	79	-82
-2	-10	5	217	225
-1	-10	5	154	152
0	-10	5	52	-59
2	-10	5	273	-254
3	-10	5	145	158
4	-10	5	191	190

H	K	L	10FO	10FC
5	-10	5	137	141
6	-10	5	77	-72
9	-10	5	92	98
10	-10	5	132	117
12	-10	5	119	-127
-17	-9	5	69	67
-15	-9	5	92	-106
-14	-9	5	76	-67
-12	-9	5	139	132
-11	-9	5	102	101
-10	-9	5	239	-245
-9	-9	5	168	-173
-8	-9	5	88	-75
-7	-9	5	54	42
-6	-9	5	73	88
-4	-9	5	124	-147
-3	-9	5	104	113
-2	-9	5	265	263
0	-9	5	76	-69
1	-9	5	327	-338
3	-9	5	461	468
5	-9	5	260	-269
6	-9	5	369	-364
7	-9	5	76	-57
8	-9	5	194	190
9	-9	5	148	150
10	-9	5	63	-79
11	-9	5	76	-77
12	-9	5	118	-127
16	-9	5	78	-71
-16	-8	5	110	-111
-15	-8	5	84	-77
-11	-8	5	163	-175
-10	-8	5	307	-292
-9	-8	5	120	112
-8	-8	5	232	229

H	K	L	10FO	10FC
-6	-8	5	53	-70
-5	-8	5	51	48
-4	-8	5	167	-159
-3	-8	5	105	116
-2	-8	5	68	83
-1	-8	5	273	-294
0	-8	5	245	-235
1	-8	5	180	175
2	-8	5	405	381
3	-8	5	187	178
4	-8	5	282	-270
5	-8	5	197	-181
6	-8	5	124	-117
7	-8	5	324	329
8	-8	5	255	268
9	-8	5	149	-152
10	-8	5	180	-192
17	-8	5	77	75
-20	-7	5	74	62
-17	-7	5	80	-84
-14	-7	5	105	96
-12	-7	5	96	-100
-11	-7	5	129	-115
-9	-7	5	157	176
-6	-7	5	50	-43
-4	-7	5	116	124
-3	-7	5	87	93
-2	-7	5	127	-139
-1	-7	5	52	-54
1	-7	5	166	183
2	-7	5	307	323
3	-7	5	250	-252
4	-7	5	342	-357
5	-7	5	193	184
7	-7	5	184	194
8	-7	5	48	44

H	K	L	10FO	10FC
9	-7	5	210	-195
11	-7	5	230	216
13	-7	5	107	-95
17	-7	5	69	68
-18	-6	5	86	-91
-16	-6	5	107	99
-15	-6	5	80	75
-13	-6	5	61	-51
-12	-6	5	111	-115
-11	-6	5	64	-63
-10	-6	5	207	222
-8	-6	5	165	-165
-7	-6	5	63	47
-6	-6	5	270	275
-5	-6	5	250	247
-4	-6	5	145	125
-3	-6	5	76	-82
-2	-6	5	377	-399
-1	-6	5	423	424
0	-6	5	215	253
1	-6	5	66	-60
2	-6	5	153	-162
3	-6	5	279	-252
6	-6	5	268	264
7	-6	5	60	49
8	-6	5	293	-290
10	-6	5	203	212
12	-6	5	133	-147
15	-6	5	116	112
18	-6	5	95	-106
-19	-5	5	117	-110
-17	-5	5	126	126
-16	-5	5	75	75
-14	-5	5	151	-149
-13	-5	5	113	-127
-12	-5	5	143	142

H	K	L	10FO	10FC
-11	-5	5	154	156
-10	-5	5	82	-78
-9	-5	5	261	-250
-7	-5	5	296	302
-6	-5	5	302	275
-5	-5	5	161	-167
-4	-5	5	293	-310
-3	-5	5	106	-115
-2	-5	5	720	728
-1	-5	5	528	537
0	-5	5	234	-230
1	-5	5	452	-448
2	-5	5	888	-868
3	-5	5	77	50
4	-5	5	243	251
5	-5	5	91	101
6	-5	5	109	-127
7	-5	5	252	-255
9	-5	5	210	218
10	-5	5	136	131
11	-5	5	236	-228
12	-5	5	152	-149
13	-5	5	71	63
14	-5	5	140	149
16	-5	5	122	-134
17	-5	5	124	-133
19	-5	5	112	117
-20	-4	5	100	-79
-18	-4	5	112	115
-15	-4	5	217	-230
-13	-4	5	215	212
-11	-4	5	49	-53
-10	-4	5	102	-99
-9	-4	5	95	-74
-8	-4	5	269	272
-7	-4	5	394	393

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR SEXACU

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
-6	-4	5	316	-315	-2	-3	5	327	-332	3	-2	5	370	-348	7	-1	5	339	-363	9	0	5	114	102
-5	-4	5	538	-554	-1	-3	5	926	-919	4	-2	5	114	110	8	-1	5	46	-42	10	0	5	230	-228
-4	-4	5	397	372	0	-3	5	130	137	5	-2	5	778	745	9	-1	5	453	463	11		5	320	-318
-3	-4	5	545	557	1	-3	5	36	-19	6	-2	5	238	214	10	-1	5	77	-81	12	0	5	254	-247
-2	-4	5	881	877	2	-3	5	509	508	7	-2	5	118	-110	11	-1	5	105	-102	13	0	5	62	52
-1	-4	5	477	-441	3	-3	5	99	67	8	-2	5	159	-148	12	-1	5	103	-106	14	0	5	66	72
0	-4	5	931	-932	4	-3	5	506	-487	10	-2	5	65	59	13	-1	5	253	-250	15	0	5	64	-73
1	-4	5	532	-544	5	-3	5	358	-378	11	-2	5	102	-119	14	-1	5	99	121	16	0	5	76	-97
2	-4	5	129	-127	6	-3	5	288	296	12	-2	5	76	-72	15	-1	5	172	162	21	0	5	80	-90
3	-4	5	714	685	7	-3	5	477	486	13	-2	5	190	-191	17	-1	5	103	-95	-19	1	5	82	78
5	-4	5	379	-345	8	-3	5	194	-206	14	-2	5	142	-154	22	-1	5	78	-83	-16	1	5	95	-89
6	-4	5	195	-190	9	-3	5	278	-280	15	-2	5	98	103	-20	0	5	86	-85	-15	1	5	95	-106
8	-4	5	290	283	10	-3	5	88	-93	16	-2	5	228	233	-16	0	5	66	-74	-14	1	5	91	91
9	-4	5	160	157	11	-3	5	109	-114	17	-2	5	66	73	-15	0	5	118	-103	-13	1	5	188	193
10	-4	5	327	-318	12	-3	5	157	147	18	-2	5	79	-78	-14	0	5	181	-169	-11	1	5	200	-214
11	-4	5	278	-299	14	-3	5	226	-215	-14	-1	5	133	-129	-13	0	5	120	116	-10	1	5	352	-352
12	-4	5	94	91	15	-3	5	94	-100	-13	-1	5	163	-173	-12	0	5	381	361	-8	1	5	234	248
13	-4	5	167	182	16	-3	5	123	128	-12	-1	5	222	232	-11	0	5	60	74	-6	1	5	387	-390
15	-4	5	158	-153	17	-3	5	195	200	-11	-1	5	284	293	-10	0	5	359	-337	-5	1	5	90	-100
16	-4	5	131	-133	19	-3	5	71	-68	-10	-1	5	129	119	-9	0	5	219	-221	-4	1	5	117	123
18	-4	5	147	164	-17	-2	5	71	-83	-9	-1	5	248	-239	-8	0	5	63	58	-3	1	5	701	676
20	-4	5	89	-77	-13	-2	5	189	-169	-8	-1	5	261	-249	-7	0	5	138	141	-2	1	5	264	260
-21	-3	5	76	-67	-11	-2	5	250	240	-7	-1	5	212	198	-5	0	5	422	-407	-1	1	5	103	-102
-17	-3	5	111	-125	-10	-2	5	351	350	-6	-1	5	404	389	-4	0	5	1074	-1078	1	1	5	237	234
-16	-3	5	107	-118	-9	-2	5	190	198	-5	-1	5	259	246	-3	0	5	100	-90	2	1	5	376	409
-15	-3	5	62	-80	-8	-2	5	69	-67	-4	-1	5	114	138	-2	0	5	369	379	4	1	5	158	-179
-12	-3	5	122	-130	-7	-2	5	73	-84	-3	-1	5	129	-122	-1	0	5	67	54	5	1	5	477	-428
-11	-3	5	152	-159	-6	-2	5	212	-228	-2	-1	5	270	-252	0	0	5	58	-49	6	1	5	305	-309
-10	-3	5	80	88	-5	-2	5	182	221	-1	-1	5	525	463	1	0	5	81	-90	7	1	5	284	260
-9	-3	5	298	298	-4	-2	5	360	375	0	-1	5	575	551	2	0	5	127	101	8	1	5	506	521
-8	-3	5	133	124	-3	-2	5	426	-465	1	-1	5	105	-114	3	0	5	148	187	9	1	5	109	-118
-7	-3	5	40	-43	-2	-2	5	492	-501	2	-1	5	176	-186	4	0	5	388	401	10	1	5	430	-424
-6	-3	5	295	-291	-1	-2	5	66	-80	3	-1	5	277	299	5	0	5	249	-249	11	1	5	249	254
-5	-3	5	38	64	0	-2	5	120	128	4	-1	5	327	333	6	0	5	939	-934	12	1	5	171	156
-4	-3	5	389	374	1	-2	5	275	292	5	-1	5	210	190	7	0	5	220	215	13	1	5	141	156
-3	-3	5	675	666	2	-2	5	131	129	6	-1	5	298	-285	8	0	5	428	412	15	1	5	69	-72

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR SEXACU

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  H  K  L 10FO 10FC      H  K  L 10FO 10FC      H  K  L 10FO 10FC      H  K  L 10FO 10FC      H  K  L 10FO 10FC

 17  1  5  105  108    -10  3  5  103 -113     -4  4  5  116 -112      2  5  5   61  -48     13  6  5   87   86
 22  1  5   75   56     -9  3  5   56   60     -3  4  5  248 -242      3  5  5  363  338     14  6  5   63  -72
-19  2  5   80   82     -8  3  5   83   82     -2  4  5  156  150      5  5  5  520 -498     15  6  5   83  -88
-17  2  5  109 -112     -7  3  5  135 -148     -1  4  5  513  520      7  5  5  290  275    -14  7  5   69   76
-15  2  5  111  117     -6  3  5   51   57      0  4  5  266  273      8  5  5  179 -183    -11  7  5  118  116
-14  2  5  192  193     -5  3  5  233  234      1  4  5  319 -331      9  5  5   82  110    -10  7  5  187  193
 -9  2  5  127  116     -4  3  5  295 -280      2  4  5  452 -468     10  5  5  264 -265     -9  7  5  102  105
 -8  2  5   60   63     -3  3  5  261 -247      4  4  5  320  330     11  5  5  172 -161     -8  7  5  103 -100
 -7  2  5   43  -45     -2  3  5   85  -91      5  4  5  307  296     13  5  5  187  172     -7  7  5  202 -207
 -6  2  5   58  -57     -1  3  5  131  126      6  4  5  167 -184     14  5  5   75   69     -5  7  5   96  109
 -5  2  5   73   65      0  3  5  331  320      7  4  5   50  -45     15  5  5   84  -96     -4  7  5  187  181
 -4  2  5  149  162      1  3  5  205  222      8  4  5  120 -122     16  5  5   96 -107     -3  7  5  114  125
 -3  2  5   40  -32      2  3  5  403 -408      9  4  5   95   84     21  5  5   91 -101     -2  7  5  130 -111
 -2  2  5  521 -530      3  3  5  231 -239     10  4  5  176 -158    -12  6  5  139 -132     -1  7  5  113  113
 -1  2  5  179  155      4  3  5  406 -406     11  4  5  158 -142    -11  6  5  138 -141      0  7  5  128  130
  0  2  5  261  287      5  3  5  255  255     14  4  5  188  191     -9  6  5  106  120      1  7  5   98  106
  1  2  5  640  634      6  3  5   45  -41     15  4  5  158  161     -8  6  5  196  204      5  7  5   84   65
  2  2  5  176  178      7  3  5  182  185     16  4  5   96 -106     -7  6  5  129 -120      6  7  5  255  248
  3  2  5   74   73      8  3  5  111 -108     17  4  5  116 -127     -6  6  5  439 -437      7  7  5  221 -213
  4  2  5   82 -103      9  3  5  302 -284     19  4  5   82   93     -5  6  5   50   42      8  7  5  123 -127
  5  2  5  124 -132     12  3  5  158 -145    -15  5  5  102 -104     -4  6  5  303  320     10  7  5   59   47
  6  2  5   59   67     13  3  5  133 -133    -14  5  5   86  -91     -3  6  5  380  372     11  7  5  197  200
  7  2  5  314  321     14  3  5  118  113    -13  5  5  145  144     -2  6  5  313  304     13  7  5  132 -155
  8  2  5   67   51     15  3  5  207  227    -12  5  5   89  103      0  6  5  208 -204     14  7  5  127 -134
  9  2  5  196 -197     17  3  5  109 -111    -10  5  5  118 -113      1  6  5  104   95    -14  8  5   82  -83
 10  2  5  125 -122     18  3  5  120 -106     -9  5  5   87  -94      2  6  5  102  109    -13  8  5  119 -127
 11  2  5   93  101     21  3  5   73   73     -8  5  5  158  154      3  6  5  234 -219     -9  8  5  101 -104
 13  2  5  102 -106    -17  4  5   68   64     -7  5  5  280  291      4  6  5  276 -270     -8  8  5  136 -130
 14  2  5  181 -166    -16  4  5   74   77     -6  5  5  211 -232      5  6  5   59  -64     -7  8  5   73  -84
 15  2  5  125  118    -14  4  5  145 -141     -5  5  5  460 -466      6  6  5  122  138     -6  8  5  173  168
 16  2  5  165  164    -11  4  5   91   96     -4  5  5  284 -273      7  6  5  168  156     -5  8  5   61   60
 21  2  5   87   90    -10  4  5   66   88     -3  5  5  274  272      8  6  5   81  -98     -1  8  5   75   76
-18  3  5  104 -107     -9  4  5   77  -82     -2  5  5  250  258      9  6  5  149 -135      0  8  5   98   98
-15  3  5  133  140     -8  4  5  119 -121     -1  5  5  221  236     10  6  5   83  -82      2  8  5  243 -245
-13  3  5  138 -145     -7  4  5  355  342      0  5  5  141 -161     11  6  5  202  217      3  8  5   67  -68
-12  3  5   73  -56     -6  4  5  109  100      1  5  5  488 -479     12  6  5  156  154      6  8  5  137 -135
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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR SEXACU

H	K	L	10FO	10FC
7	8	5	132	-149
8	8	5	73	-53
10	8	5	260	248
12	8	5	208	-203
-12	9	5	98	80
-7	9	5	89	70
-6	9	5	89	85
-5	9	5	112	-121
-4	9	5	112	-98
-2	9	5	100	110
-1	9	5	76	84
0	9	5	102	-104
1	9	5	129	-125
2	9	5	90	100
3	9	5	166	174
4	9	5	92	90
5	9	5	149	139
6	9	5	185	-171
7	9	5	68	-74
8	9	5	164	171
9	9	5	129	115
11	9	5	152	-158
12	9	5	75	-67
-11	10	5	69	-54
-10	10	5	85	-71
-3	10	5	122	133
-1	10	5	124	-120
0	10	5	98	-93
2	10	5	185	186
5	10	5	139	-124
6	10	5	85	-88
7	10	5	124	143
8	10	5	113	84
10	10	5	71	-72
12	10	5	109	90
-9	11	5	72	54

H	K	L	10FO	10FC
-1	11	5	77	-97
1	11	5	151	165
3	11	5	128	-139
6	11	5	91	72
0	12	5	71	57
2	12	5	100	-96
3	12	5	77	-62
7	12	5	85	-72
1	-17	6	73	24
2	-16	6	66	-38
5	-16	6	82	76
-7	-15	6	71	46
1	-15	6	70	-57
3	-15	6	62	39
-6	-14	6	71	-72
0	-14	6	80	-101
3	-14	6	69	72
5	-14	6	89	-87
-7	-13	6	69	-69
-6	-13	6	107	-92
-5	-13	6	103	107
-4	-13	6	131	121
-2	-13	6	64	-92
-1	-13	6	169	-169
1	-13	6	109	91
4	-13	6	143	-142
-8	-12	6	72	-57
-6	-12	6	95	89
-5	-12	6	172	188
-3	-12	6	95	-84
-2	-12	6	156	-162
0	-12	6	277	273
2	-12	6	158	-171
3	-12	6	118	-131
5	-12	6	68	63
6	-12	6	111	92

H	K	L	10FO	10FC
9	-12	6	84	65
15	-12	6	87	69
-9	-11	6	87	-74
-7	-11	6	103	105
-6	-11	6	221	226
-4	-11	6	61	-44
-1	-11	6	303	316
1	-11	6	238	-244
2	-11	6	172	-162
3	-11	6	68	-59
9	-11	6	69	74
11	-11	6	74	-64
12	-11	6	78	-79
14	-11	6	111	106
-15	-10	6	71	-62
-10	-10	6	103	-108
-9	-10	6	71	67
-8	-10	6	163	152
-7	-10	6	169	164
-5	-10	6	165	-172
-4	-10	6	64	76
-3	-10	6	133	-126
-2	-10	6	167	167
-1	-10	6	173	189
0	-10	6	69	-46
1	-10	6	242	-247
3	-10	6	52	41
4	-10	6	120	-127
7	-10	6	119	135
8	-10	6	66	66
10	-10	6	102	-95
11	-10	6	107	-95
13	-10	6	83	74
15	-10	6	86	-72
-13	-9	6	73	-57
-12	-9	6	61	-49

H	K	L	10FO	10FC
-11	-9	6	221	-221
-9	-9	6	300	295
-8	-9	6	106	112
-6	-9	6	217	-240
-4	-9	6	57	-75
-3	-9	6	85	81
-2	-9	6	328	338
-1	-9	6	119	-123
0	-9	6	111	-95
1	-9	6	205	-204
3	-9	6	194	-198
4	-9	6	71	-56
5	-9	6	68	-60
6	-9	6	111	110
7	-9	6	200	187
8	-9	6	118	-113
9	-9	6	235	-233
10	-9	6	103	-100
12	-9	6	94	77
13	-9	6	100	97
14	-9	6	80	-77
18	-9	6	74	71
-13	-8	6	136	-141
-10	-8	6	311	319
-9	-8	6	253	258
-8	-8	6	60	43
-7	-8	6	341	-329
-6	-8	6	171	-169
-5	-8	6	132	125
-4	-8	6	56	-62
-3	-8	6	125	128
-2	-8	6	39	-39
-1	-8	6	143	-146
1	-8	6	79	96
2	-8	6	55	47
3	-8	6	187	-195

H	K	L	10FO	10FC
4	-8	6	310	322
5	-8	6	272	259
6	-8	6	217	203
8	-8	6	270	-232
9	-8	6	259	-245
10	-8	6	181	183
11	-8	6	190	180
12	-8	6	66	58
13	-8	6	124	-127
14	-8	6	75	-91
17	-8	6	71	74
-14	-7	6	119	-120
-11	-7	6	107	112
-10	-7	6	334	344
-9	-7	6	63	-61
-8	-7	6	215	-216
-7	-7	6	228	-242
-6	-7	6	175	209
-5	-7	6	211	211
-4	-7	6	67	25
-2	-7	6	56	56
-1	-7	6	95	101
0	-7	6	40	-21
1	-7	6	232	-264
4	-7	6	194	190
5	-7	6	235	230
7	-7	6	378	-368
8	-7	6	190	-196
9	-7	6	217	205
10	-7	6	272	243
11	-7	6	94	97
12	-7	6	88	-95
13	-7	6	223	-215
14	-7	6	100	109
15	-7	6	72	72
-17	-6	6	70	66

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR SEXACU

H	K	L	10FO	10FC
-15	-6	6	82	-62
-14	-6	6	135	-141
-12	-6	6	156	175
-11	-6	6	211	198
-9	-6	6	215	-219
-8	-6	6	183	-182
-7	-6	6	167	-159
-6	-6	6	210	215
-5	-6	6	85	99
-4	-6	6	194	-201
-3	-6	6	268	-278
-2	-6	6	164	173
-1	-6	6	153	-147
0	-6	6	421	-422
1	-6	6	276	-282
2	-6	6	56	16
3	-6	6	182	194
4	-6	6	364	396
5	-6	6	75	-75
6	-6	6	259	-277
7	-6	6	306	-289
8	-6	6	132	147
9	-6	6	237	231
11	-6	6	90	-90
12	-6	6	199	-191
14	-6	6	149	161
19	-6	6	77	81
-18	-5	6	105	102
-16	-5	6	68	-70
-15	-5	6	179	-172
-13	-5	6	243	236
-12	-5	6	149	151
-11	-5	6	97	117
-10	-5	6	156	-180
-9	-5	6	292	-312
-8	-5	6	100	87

H	K	L	10FO	10FC
-7	-5	6	152	160
-6	-5	6	116	124
-5	-5	6	179	-202
-4	-5	6	104	107
-3	-5	6	296	303
-2	-5	6	56	36
-1	-5	6	350	-336
0	-5	6	430	-435
2	-5	6	498	534
3	-5	6	201	202
4	-5	6	44	-65
5	-5	6	277	-277
6	-5	6	163	-148
7	-5	6	89	74
8	-5	6	373	371
10	-5	6	58	-49
12	-5	6	52	-48
14	-5	6	77	53
15	-5	6	112	-113
17	-5	6	102	88
18	-5	6	124	130
20	-5	6	94	-88
-20	-4	6	82	87
-19	-4	6	100	96
-17	-4	6	109	-116
-16	-4	6	120	-111
-14	-4	6	169	166
-13	-4	6	131	130
-12	-4	6	112	-123
-11	-4	6	239	-254
-9	-4	6	69	63
-8	-4	6	104	-115
-6	-4	6	80	-81
-5	-4	6	129	132
-4	-4	6	344	355
-2	-4	6	222	-215

H	K	L	10FO	10FC
-1	-4	6	843	-839
0	-4	6	421	391
1	-4	6	235	273
2	-4	6	67	-69
3	-4	6	108	-116
4	-4	6	571	-527
5	-4	6	430	-450
6	-4	6	444	433
7	-4	6	271	301
8	-4	6	205	-198
9	-4	6	104	-100
10	-4	6	60	-50
11	-4	6	121	-109
14	-4	6	80	-64
16	-4	6	198	207
17	-4	6	105	112
19	-4	6	111	-115
-20	-3	6	98	74
-18	-3	6	100	-107
-17	-3	6	80	-76
-15	-3	6	82	96
-14	-3	6	69	77
-13	-3	6	126	-122
-11	-3	6	237	226
-10	-3	6	231	260
-8	-3	6	129	-134
-6	-3	6	91	92
-5	-3	6	193	189
-4	-3	6	73	-61
-3	-3	6	448	-478
-2	-3	6	517	-507
-1	-3	6	246	231
0	-3	6	641	638
1	-3	6	262	281
3	-3	6	578	-567
4	-3	6	201	194

H	K	L	10FO	10FC
5	-3	6	509	514
6	-3	6	370	350
7	-3	6	163	-166
8	-3	6	328	-339
9	-3	6	106	-114
10	-3	6	68	62
12	-3	6	138	-110
13	-3	6	96	-104
15	-3	6	235	254
16	-3	6	239	236
18	-3	6	96	-84
20	-3	6	72	78
-17	-2	6	62	42
-14	-2	6	69	-103
-12	-2	6	160	167
-11	-2	6	201	208
-9	-2	6	345	-330
-8	-2	6	52	73
-7	-2	6	314	308
-6	-2	6	199	198
-5	-2	6	185	175
-4	-2	6	49	16
-3	-2	6	73	-81
-2	-2	6	120	-101
-1	-2	6	1048	1038
0	-2	6	424	436
1	-2	6	604	-605
2	-2	6	435	-474
3	-2	6	126	-133
4	-2	6	88	101
5	-2	6	92	96
6	-2	6	265	-245
7	-2	6	544	-554
9	-2	6	491	494
10	-2	6	83	100
11	-2	6	213	-203

H	K	L	10FO	10FC
12	-2	6	241	-227
13	-2	6	61	-42
14	-2	6	277	266
15	-2	6	275	253
17	-2	6	128	-127
-20	-1	6	95	-37
-19	-1	6	80	-79
-18	-1	6	79	-56
-15	-1	6	77	-66
-14	-1	6	152	-134
-13	-1	6	103	99
-12	-1	6	233	227
-11	-1	6	57	-39
-10	-1	6	200	-178
-8	-1	6	87	87
-7	-1	6	178	196
-5	-1	6	720	-705
-4	-1	6	423	-441
-3	-1	6	127	-130
-2	-1	6	109	111
-1	-1	6	214	210
0	-1	6	248	-235
1	-1	6	265	-279
2	-1	6	100	-106
3	-1	6	193	196
4	-1	6	154	145
5	-1	6	610	-592
6	-1	6	371	-336
7	-1	6	170	178
8	-1	6	250	236
10	-1	6	396	-399
11	-1	6	459	-443
12	-1	6	119	-126
13	-1	6	279	251
14	-1	6	98	104
15	-1	6	102	-83

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR SEXACU

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
16	-1	6	80	-100	-9	1	6	233	217	1	2	6	62	-67	7	3	6	175	-175	17	4	6	64	[illegible]
19	-1	6	82	86	-7	1	6	288	-285	2	2	6	650	-648	8	3	6	203	189	-14	5	6	111	113
21	-1	6	94	-73	-6	1	6	66	-77	3	2	6	134	-122	9	3	6	93	[illegible]	-11	5	6	120	-131
-16	0	6	86	-80	-5	1	6	258	251	4	2	6	365	375	10	3	6	58	-49	-9	5	6	91	104
-13	0	6	113	119	-4	1	6	389	406	5	2	6	130	127	12	3	6	181	-176	-8	5	6	87	100
-12	0	6	75	-82	-3	1	6	280	-261	6	2	6	111	-115	14	3	6	271	266	-7	5	6	113	-113
-11	0	6	177	-176	-2	1	6	629	-637	7	2	6	192	-182	16	3	6	104	-102	-6	5	6	93	-94
-10	[illegible]	6	142	-158	-1	1	6	380	370	8	2	6	182	-181	19	3	6	68	69	-5	5	6	87	91
-9	0	6	194	202	0	1	6	398	382	9	2	6	87	-105	21	3	6	93	-90	-4	5	6	142	147
-8	0	6	369	366	1	1	6	111	114	10	2	6	265	269	-16	4	6	80	-60	-3	5	6	168	164
-7	0	6	87	-79	2	1	6	103	-99	11	2	6	75	87	-15	4	6	102	-113	-2	5	6	91	94
-6	0	6	279	-269	3	1	6	241	-246	12	2	6	102	-96	-13	4	6	154	172	-1	5	6	73	-73
-5	0	6	88	97	4	1	6	64	-81	13	2	6	128	-139	-12	4	6	107	105	0	5	6	57	[illegible]
-4	0	6	477	477	5	1	6	271	301	14	2	6	98	98	-10	4	6	109	-111	1	5	6	107	110
-3	0	6	489	447	6	1	6	260	264	15	2	6	167	180	-9	4	6	85	-96	2	5	6	179	177
-2	0	6	304	303	8	1	6	122	-119	17	2	6	91	-93	-8	4	6	66	61	3	5	6	279	-280
-1	0	6	60	51	9	1	6	208	-210	18	2	6	86	-87	-7	4	6	48	50	4	5	6	343	-350
1	0	6	176	177	11	1	6	174	167	20	2	6	70	45	-6	4	6	62	-61	5	5	6	109	-118
3	0	6	317	-324	13	1	6	179	-177	-17	3	6	73	77	-5	4	6	116	-113	6	5	6	228	[illegible]
4	0	6	385	-373	14	1	6	163	-163	-15	3	6	91	-104	-4	4	6	180	-178	7	5	6	142	141
5	0	6	373	-363	15	1	6	129	138	-14	3	6	100	-96	-2	4	6	111	110	8	5	6	153	131
6	0	6	48	51	16	1	6	71	79	-12	3	6	154	150	-1	4	6	103	[illegible]	9	5	6	255	-248
7	0	6	351	365	21	1	6	86	76	-11	3	6	120	133	0	4	6	44	-37	11	5	6	203	201
8	0	6	201	215	-16	2	6	122	120	-9	3	6	105	-99	1	4	6	403	-385	-15	6	6	69	64
9	0	6	197	-199	-14	2	6	134	-114	-8	3	6	58	-25	2	4	6	221	221	-10	6	6	161	166
10	0	6	77	-96	-13	2	6	120	-125	-6	3	6	94	88	3	4	6	401	398	-8	6	6	82	-98
11	0	6	334	325	-11	2	6	89	88	-4	3	6	145	-145	4	4	6	207	-211	-7	6	6	108	-112
12	0	6	273	265	-8	2	6	140	-143	-3	3	6	252	-255	5	4	6	460	-453	-6	6	6	124	121
13	0	6	219	217	-7	2	6	235	-224	-2	3	6	351	343	7	4	6	185	186	-5	6	6	120	121
14	0	6	119	-143	-6	2	6	347	366	-1	3	6	76	100	8	4	6	63	65	-4	6	6	186	189
15	0	6	77	-75	-5	2	6	294	294	0	3	6	138	-141	9	4	6	98	85	-3	6	6	143	-135
-17	1	6	84	-88	-4	2	6	381	-399	1	3	6	223	-227	10	4	6	160	-172	-2	6	6	154	-153
-15	1	6	122	114	-3	2	6	354	-347	2	3	6	232	-218	11	4	6	154	-147	-1	6	6	232	227
-14	1	6	61	69	-2	2	6	272	268	3	3	6	409	398	12	4	6	75	64	0	6	6	156	146
-12	1	6	87	-83	-1	2	6	239	231	4	3	6	446	448	13	4	6	129	137	2	6	6	114	-137
-10	1	6	165	159	0	2	6	122	124	6	3	6	346	-358	15	4	6	66	-50	3	6	6	331	-340

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR SEXACU

H	K	L	10FO	10FC
4	6	6	97	-77
5	6	6	85	80
6	6	6	234	235
7	6	6	87	-65
8	6	6	64	-64
10	6	6	131	135
11	6	6	70	79
12	6	6	63	-71
13	6	6	157	-166
-13	7	6	69	-74
-9	7	6	90	-99
-8	7	6	96	-88
-7	7	6	78	86
-6	7	6	208	214
-5	7	6	77	-67
-4	7	6	80	-77
-3	7	6	158	-158
-2	7	6	117	118
-1	7	6	261	252
0	7	6	145	140
1	7	6	201	-210
2	7	6	353	-348
3	7	6	102	-94
7	7	6	59	-85
8	7	6	107	-89
9	7	6	84	74
10	7	6	230	226
11	7	6	293	-291
12	7	6	149	-153
-8	8	6	71	78
-7	8	6	134	133
-5	8	6	188	-191
-4	8	6	85	-85
-2	8	6	291	301
-1	8	6	82	71
0	8	6	177	-177
1	8	6	140	-132
4	8	6	113	99
6	8	6	62	-75
8	8	6	122	95
9	8	6	75	80
11	8	6	186	-183
13	8	6	73	70
18	8	6	90	95
-8	9	6	98	106
-6	9	6	100	-113
-5	9	6	113	-107
-4	9	6	100	103
-3	9	6	122	122
-1	9	6	106	-102
2	9	6	179	183
3	9	6	85	85
4	9	6	77	-95
10	9	6	105	-92
12	9	6	136	133
17	9	6	87	78
-9	10	6	75	88
-1	10	6	113	-114
0	10	6	84	89
3	10	6	109	-121
6	10	6	80	81
8	10	6	106	-93
11	10	6	77	77
14	10	6	73	-50
-7	11	6	86	-53
2	11	6	93	-88
3	11	6	73	-69
4	11	6	74	104
5	11	6	81	91
7	11	6	114	-110
10	11	6	86	61
2	12	6	69	-77
4	12	6	89	66
9	12	6	74	73
0	13	6	74	-52
-6	-16	7	78	57
-11	-15	7	69	-47
-5	-15	7	69	-57
4	-15	7	74	-48
-6	-14	7	69	-75
1	-14	7	78	59
6	-14	7	106	102
11	-14	7	72	59
-10	-13	7	66	65
-7	-13	7	68	-90
0	-13	7	86	73
2	-13	7	133	-148
5	-13	7	122	115
6	-13	7	109	93
8	-13	7	78	-66
-11	-12	7	87	65
-9	-12	7	66	-59
-6	-12	7	73	63
-4	-12	7	73	-81
-2	-12	7	126	132
-1	-12	7	80	77
1	-12	7	287	-294
2	-12	7	171	-173
4	-12	7	210	194
5	-12	7	85	89
7	-12	7	60	-69
9	-12	7	88	106
10	-12	7	80	79
-15	-11	7	83	-61
-12	-11	7	71	91
-6	-11	7	71	-51
-5	-11	7	145	-162
-3	-11	7	128	136
-2	-11	7	70	43
0	-11	7	396	-393
1	-11	7	237	-255
2	-11	7	245	259
3	-11	7	206	213
4	-11	7	78	67
5	-11	7	62	-78
8	-11	7	93	76
10	-11	7	77	-74
11	-11	7	89	-105
15	-11	7	75	-73
-9	-10	7	115	108
-8	-10	7	113	-91
-7	-10	7	104	-117
-6	-10	7	72	-99
-5	-10	7	64	-55
-4	-10	7	310	312
-2	-10	7	133	-122
-1	-10	7	186	-200
0	-10	7	165	-159
1	-10	7	69	69
2	-10	7	73	45
3	-10	7	127	-115
4	-10	7	184	-180
5	-10	7	158	-155
6	-10	7	107	109
11	-10	7	66	52
12	-10	7	76	71
-11	-9	7	93	97
-10	-9	7	200	209
-8	-9	7	159	-157
-6	-9	7	57	-51
-5	-9	7	250	254
-3	-9	7	187	-203
-1	-9	7	116	-115
0	-9	7	100	89
1	-9	7	214	216
2	-9	7	108	120
4	-9	7	152	171
6	-9	7	133	128
8	-9	7	68	-45
10	-9	7	149	135
12	-9	7	104	-97
15	-9	7	74	70
16	-9	7	129	121
-11	-8	7	61	69
-10	-8	7	68	74
-9	-8	7	247	-256
-6	-8	7	219	233
-5	-8	7	277	263
-4	-8	7	219	-243
-3	-8	7	138	-102
-2	-8	7	89	-94
-1	-8	7	172	154
0	-8	7	209	228
1	-8	7	63	58
3	-8	7	127	-100
4	-8	7	188	-199
7	-8	7	249	-252
8	-8	7	99	107
9	-8	7	97	115
10	-8	7	169	162
11	-8	7	117	-125
12	-8	7	75	-73
14	-8	7	77	72
15	-8	7	95	93
18	-8	7	111	-86
-10	-7	7	210	-212
-8	-7	7	136	138
-6	-7	7	396	391
-5	-7	7	289	-280
-4	-7	7	513	-511

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR SEXACU

H	K	L	10FO	10FC
-3	-7	7	44	-47
-2	-7	7	230	243
-1	-7	7	186	194
0	-7	7	112	-117
1	-7	7	118	-108
2	-7	7	203	-205
3	-7	7	80	84
4	-7	7	104	95
6	-7	7	86	-91
8	-7	7	196	196
9	-7	7	71	66
10	-7	7	178	-175
11	-7	7	273	-265
14	-7	7	134	147
16	-7	7	88	-88
-18	-6	7	68	51
-13	-6	7	66	32
-10	-6	7	244	-237
-9	-6	7	179	182
-8	-6	7	176	168
-7	-6	7	102	93
-5	-6	7	252	-276
-3	-6	7	321	341
-2	-6	7	241	220
-1	-6	7	249	-259
0	-6	7	296	-269
1	-6	7	143	-130
2	-6	7	185	189
3	-6	7	46	-41
5	-6	7	101	118
7	-6	7	293	270
8	-6	7	223	232
9	-6	7	250	-238
10	-6	7	244	-242
11	-6	7	147	133
12	-6	7	104	112
13	-6	7	98	108
15	-6	7	161	-149
17	-6	7	78	73
-17	-5	7	82	-69
-14	-5	7	80	74
-12	-5	7	178	-182
-11	-5	7	156	-142
-10	-5	7	136	140
-9	-5	7	270	273
-8	-5	7	93	-108
-6	-5	7	266	-246
-5	-5	7	154	-156
-4	-5	7	215	191
-1	-5	7	187	-193
0	-5	7	272	-277
1	-5	7	109	122
2	-5	7	100	-104
3	-5	7	218	-222
4	-5	7	95	-97
5	-5	7	191	174
6	-5	7	358	357
8	-5	7	94	-122
9	-5	7	251	-247
11	-5	7	181	175
14	-5	7	131	-115
16	-5	7	115	129
19	-5	7	95	-89
-16	-4	7	69	68
-15	-4	7	119	117
-13	-4	7	143	-144
-11	-4	7	238	241
-10	-4	7	351	365
-9	-4	7	123	111
-8	-4	7	243	-245
-7	-4	7	244	-235
-6	-4	7	152	-161
-5	-4	7	145	163
-4	-4	7	124	132
-2	-4	7	86	-88
0	-4	7	82	-97
1	-4	7	112	92
2	-4	7	197	-199
4	-4	7	459	468
5	-4	7	382	389
6	-4	7	80	60
8	-4	7	277	-250
9	-4	7	109	-126
10	-4	7	188	182
11	-4	7	56	69
15	-4	7	182	201
16	-4	7	86	90
20	-4	7	72	53
-17	-3	7	91	76
-16	-3	7	96	75
-14	-3	7	167	-167
-12	-3	7	245	252
-11	-3	7	350	354
-10	-3	7	125	118
-9	-3	7	347	-371
-8	-3	7	237	-231
-7	-3	7	73	90
-6	-3	7	101	-98
-5	-3	7	243	216
-4	-3	7	172	-167
-3	-3	7	227	-236
-2	-3	7	86	81
-1	-3	7	59	50
1	-3	7	205	-205
2	-3	7	190	-195
3	-3	7	304	330
4	-3	7	138	145
5	-3	7	45	20
6	-3	7	261	-246
7	-3	7	383	-383
8	-3	7	75	-71
9	-3	7	238	259
10	-3	7	255	256
12	-3	7	102	-94
14	-3	7	114	129
15	-3	7	160	166
16	-3	7	90	-92
17	-3	7	64	-75
-15	-2	7	149	-136
-14	-2	7	77	-60
-13	-2	7	248	250
-12	-2	7	251	233
-10	-2	7	158	-148
-9	-2	7	148	-171
-6	-2	7	43	-58
-5	-2	7	495	-506
-4	-2	7	236	-257
-3	-2	7	264	283
-2	-2	7	58	-38
-1	-2	7	68	-87
0	-2	7	233	-229
1	-2	7	237	-218
3	-2	7	656	624
4	-2	7	100	-74
5	-2	7	529	-539
6	-2	7	169	-183
7	-2	7	71	75
8	-2	7	192	186
9	-2	7	217	225
10	-2	7	152	-152
11	-2	7	300	-318
13	-2	7	97	103
14	-2	7	86	70
16	-2	7	89	-88
20	-2	7	73	-73
21	-2	7	91	-98
-16	-1	7	113	-108
-14	-1	7	120	127
-13	-1	7	168	171
-10	-1	7	113	-104
-9	-1	7	66	68
-8	-1	7	78	64
-7	-1	7	145	-140
-6	-1	7	217	-215
-4	-1	7	512	493
-3	-1	7	154	162
-2	-1	7	186	-154
-1	-1	7	284	-298
0	-1	7	297	-301
1	-1	7	291	292
2	-1	7	432	439
3	-1	7	78	-42
4	-1	7	520	-527
5	-1	7	224	-231
6	-1	7	112	102
7	-1	7	468	463
9	-1	7	142	-136
10	-1	7	82	80
11	-1	7	135	146
12	-1	7	224	229
14	-1	7	152	-135
16	-1	7	120	122
17	-1	7	114	117
20	-1	7	96	-97
-15	0	7	84	100
-14	0	7	95	100
-9	0	7	68	75
-8	0	7	128	-122
-5	0	7	405	401
-4	0	7	484	481

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR SEXACU

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
-3	-7	7	44	-47	13	-6	7	98	108	-5	-4	7	145	163	6	-3	7	261	-246	20	-2	7	73	-73
-2	-7	7	230	243	15	-6	7	161	-149	-4	-4	7	124	132	7	-3	7	383	-383	21	-2	7	91	-98
-1	-7	7	186	194	17	-6	7	78	73	-2	-4	7	86	-88	8	-3	7	75	-71	-16	-1	7	113	-108
0	-7	7	112	-117	-17	-5	7	82	-69	0	-4	7	82	-97	9	-3	7	238	259	-14	-1	7	120	127
1	-7	7	118	-108	-14	-5	7	80	74	1	-4	7	112	92	10	-3	7	255	256	-13	-1	7	168	171
2	-7	7	203	-205	-12	-5	7	178	-182	2	-4	7	197	-199	12	-3	7	102	-94	-10	-1	7	113	-104
3	-7	7	80	84	-11	-5	7	156	-142	4	-4	7	459	468	14	-3	7	114	129	-9	-1	7	66	68
4	-7	7	104	95	-10	-5	7	136	140	5	-4	7	382	389	15	-3	7	160	166	-8	-1	7	78	64
6	-7	7	86	-91	-9	-5	7	270	273	6	-4	7	80	60	16	-3	7	90	-92	-7	-1	7	145	-140
8	-7	7	196	196	-8	-5	7	93	-108	8	-4	7	277	-250	17	-3	7	64	-75	-6	-1	7	217	-215
9	-7	7	71	66	-6	-5	7	266	-246	9	-4	7	109	-126	-15	-2	7	149	-136	-4	-1	7	512	493
10	-7	7	178	-175	-5	-5	7	154	-156	10	-4	7	188	182	-14	-2	7	77	-60	-3	-1	7	154	162
11	-7	7	273	-265	-4	-5	7	215	191	11	-4	7	56	69	-13	-2	7	248	250	-2	-1	7	186	-154
14	-7	7	134	147	-1	-5	7	187	-193	15	-4	7	182	201	-12	-2	7	251	233	-1	-1	7	284	-298
16	-7	7	88	-88	0	-5	7	272	-277	16	-4	7	86	90	-10	-2	7	158	-148	0	-1	7	297	-301
-18	-6	7	68	51	1	-5	7	109	122	20	-4	7	72	53	-9	-2	7	148	-171	1	-1	7	291	292
-13	-6	7	66	32	2	-5	7	100	-104	-17	-3	7	91	76	-6	-2	7	43	-58	2	-1	7	432	439
-10	-6	7	244	-237	3	-5	7	218	-222	-16	-3	7	96	75	-5	-2	7	495	-506	3	-1	7	78	-42
-9	-6	7	179	182	4	-5	7	95	-97	-14	-3	7	167	-167	-4	-2	7	236	-257	4	-1	7	520	-527
-8	-6	7	176	168	5	-5	7	191	174	-12	-3	7	245	252	-3	-2	7	264	283	5	-1	7	224	-231
-7	-6	7	102	93	6	-5	7	358	357	-11	-3	7	350	354	-2	-2	7	58	-38	6	-1	7	112	102
-5	-6	7	252	-276	8	-5	7	94	-122	-10	-3	7	125	118	-1	-2	7	68	-87	7	-1	7	468	463
-3	-6	7	321	341	9	-5	7	251	-247	-9	-3	7	347	-371	0	-2	7	233	-229	9	-1	7	142	-136
-2	-6	7	241	220	11	-5	7	181	175	-8	-3	7	237	-231	1	-2	7	237	-218	10	-1	7	82	80
-1	-6	7	249	-259	14	-5	7	131	-115	-7	-3	7	73	90	3	-2	7	656	624	11	-1	7	135	146
0	-6	7	296	-269	16	-5	7	115	129	-6	-3	7	101	-98	4	-2	7	100	-74	12	-1	7	224	229
1	-6	7	143	-130	19	-5	7	95	-89	-5	-3	7	243	216	5	-2	7	529	-539	14	-1	7	152	-135
2	-6	7	185	189	-16	-4	7	69	68	-4	-3	7	172	-167	6	-2	7	169	-183	16	-1	7	120	122
3	-6	7	46	-41	-15	-4	7	119	117	-3	-3	7	227	-236	7	-2	7	71	75	17	-1	7	114	117
5	-6	7	101	118	-13	-4	7	143	-144	-2	-3	7	86	81	8	-2	7	192	186	20	-1	7	95	-97
7	-6	7	293	270	-11	-4	7	238	241	-1	-3	7	59	50	9	-2	7	217	225	-15	0	7	84	100
8	-6	7	223	232	-10	-4	7	351	365	1	-3	7	205	-205	10	-2	7	152	-152	-14	0	7	95	100
9	-6	7	250	-238	-9	-4	7	123	111	2	-3	7	190	-195	11	-2	7	300	-318	-9	0	7	68	75
10	-6	7	244	-242	-8	-4	7	243	-245	3	-3	7	304	330	13	-2	7	97	103	-8	0	7	128	-122
11	-6	7	147	133	-7	-4	7	244	-235	4	-3	7	138	145	14	-2	7	86	70	-5	0	7	405	401
12	-6	7	104	112	-6	-4	7	152	-161	5	-3	7	45	20	16	-2	7	89	-88	-4	0	7	484	481

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR SEXACU

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
-3	0	7	485	-488	9	1	7	131	121	-13	3	7	140	160	2	4	7	128	-116	3	6	7	59	64
-2	0	7	513	-518	10	1	7	139	147	-11	3	7	174	-159	3	4	7	372	-372	6	6	7	104	95
-1	0	7	260	272	11	1	7	236	-225	-10	3	7	113	-112	5	4	7	109	142	7	6	7	111	-115
0	0	7	409	405	12	1	7	198	-212	-9	3	7	100	86	6	4	7	336	335	9	6	7	210	198
1	0	7	116	123	14	1	7	166	167	-8	3	7	190	194	7	4	7	125	113	10	6	7	95	70
2	0	7	171	170	15	1	7	129	145	-6	3	7	171	-171	8	4	7	110	-107	11	6	7	185	-197
3	0	7	315	-317	17	1	7	112	-137	-5	3	7	163	-153	9	4	7	259	-242	12	6	7	68	-40
4	0	7	549	-540	18	1	7	84	-87	-4	3	7	78	-57	11	4	7	210	216	14	6	7	66	69
5	0	7	208	208	-15	2	7	115	-112	-3	3	7	95	104	12	4	7	98	87	-7	7	7	128	145
6	0	7	336	321	-14	2	7	66	-56	-2	3	7	208	217	14	4	7	70	-66	-5	7	7	83	-104
7	0	7	152	-170	-12	2	7	97	96	1	3	7	72	-55	19	4	7	95	-92	-2	7	7	216	228
8	0	7	55	-60	-10	2	7	192	-185	2	3	7	277	267	-10	5	7	144	156	-1	7	7	59	-55
9	0	7	133	136	-9	2	7	136	-132	4	3	7	333	-314	-8	5	7	100	-106	0	7	7	268	-278
10	0	7	215	210	-8	2	7	75	72	5	3	7	77	-76	-7	5	7	95	-84	1	7	7	141	-145
11	0	7	109	102	-7	2	7	96	88	6	3	7	187	165	-6	5	7	59	78	4	7	7	91	84
12	0	7	157	-148	-6	2	7	178	174	7	3	7	201	210	-5	5	7	190	176	5	7	7	88	-92
13	0	7	277	-268	-5	2	7	89	-95	8	3	7	113	114	-1	5	7	104	96	6	7	7	93	-104
15	0	7	139	149	-4	2	7	416	-419	9	3	7	101	-103	0	5	7	57	-58	7	7	7	84	82
16	0	7	127	147	-3	2	7	96	-106	10	3	7	190	-179	1	5	7	110	-122	8	7	7	102	90
18	0	7	76	-70	-2	2	7	313	324	11	3	7	89	-89	2	5	7	165	-168	9	7	7	93	109
-16	1	7	116	115	-1	2	7	174	169	12	3	7	161	171	3	5	7	316	-297	11	7	7	69	-71
-14	1	7	66	-42	1	2	7	191	-206	13	3	7	196	194	4	5	7	143	158	-9	8	7	78	87
-8	1	7	218	-217	3	2	7	67	73	15	3	7	113	-104	5	5	7	276	245	-8	8	7	93	80
-6	1	7	380	373	4	2	7	96	96	-14	4	7	100	101	8	5	7	71	-68	-6	8	7	167	-166
-5	1	7	190	170	5	2	7	93	-94	-12	4	7	105	-105	10	5	7	219	238	-4	8	7	89	82
-4	1	7	358	-362	6	2	7	297	-302	-11	4	7	114	-111	11	5	7	77	71	-3	8	7	86	88
-3	1	7	322	-311	7	2	7	65	73	-10	4	7	91	89	13	5	7	160	-166	-1	8	7	105	-105
-2	1	7	78	71	8	2	7	168	173	-9	4	7	209	206	15	5	7	69	69	1	8	7	96	92
-1	1	7	210	210	11	2	7	95	-94	-7	4	7	253	-253	-9	6	7	71	-82	2	8	7	260	255
0	1	7	401	404	12	2	7	87	-73	-6	4	7	69	-73	-8	6	7	113	-125	3	8	7	87	77
2	1	7	389	-382	13	2	7	111	111	-5	4	7	64	77	-6	6	7	82	94	4	8	7	140	-154
3	1	7	192	-189	14	2	7	291	297	-3	4	7	129	126	-4	6	7	69	-62	6	8	7	88	80
4	1	7	55	42	16	2	7	117	-141	-2	4	7	70	95	-3	6	7	107	-119	9	8	7	63	-65
5	1	7	57	57	17	2	7	71	-70	-1	4	7	173	-153	-1	6	7	147	144	10	8	7	97	-77
7	1	7	87	-100	-15	3	7	78	-58	0	4	7	82	62	1	6	7	228	-227	11	8	7	169	94
8	1	7	61	-59	-14	3	7	93	113	1	4	7	80	72	2	6	7	276	-277	17	8	7	101	92

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR SEXACU

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
-9	9	7	84	72	-8	-12	8	89	66	-1	-10	8	142	146	1	-8	8	217	-220	-5	-6	8	262	258
-5	9	7	80	87	-7	-12	8	103	105	0	-10	8	275	254	3	-8	8	143	167	-4	-6	8	389	379
-2	9	7	140	-160	-5	-12	8	76	-76	1	-10	8	78	105	4	-8	8	139	148	-3	-6	8	78	-57
0	9	7	114	123	-4	-12	8	84	-79	2	-10	8	269	-250	5	-8	8	172	151	-2	-6	8	361	-344
2	9	7	71	-76	-2	-12	8	71	55	3	-10	8	133	-140	6	-8	8	252	-234	-1	-6	8	241	-267
3	9	7	111	-117	-1	-12	8	65	-67	5	-10	8	342	355	7	-8	8	71	-59	0	-6	8	73	68
6	9	7	89	88	0	-12	8	93	-106	6	-10	8	213	224	11	-8	8	125	-131	1	-6	8	392	396
8	9	7	116	-117	2	-12	8	71	89	7	-10	8	114	-122	12	-8	8	91	78	2	-6	8	208	185
10	9	7	81	64	7	-12	8	123	121	8	-10	8	164	-151	13	-8	8	111	116	3	-6	8	111	-103
14	9	7	73	-68	10	-12	8	118	-126	10	-10	8	69	67	-16	-7	8	88	-83	4	-6	8	68	71
-8	10	7	77	-64	11	-12	8	114	-124	-11	-9	8	129	140	-10	-7	8	69	-84	5	-6	8	138	136
-2	10	7	75	-80	-12	-11	8	102	-112	-9	-9	8	66	-64	-9	-7	8	89	92	6	-6	8	100	113
-1	10	7	71	94	-11	-11	8	111	-110	-8	-9	8	102	-89	-7	-7	8	299	-274	8	-6	8	221	-232
4	10	7	66	83	-9	-11	8	108	94	-7	-9	8	134	136	-6	-7	8	158	-165	9	-6	8	93	109
5	10	7	92	88	-6	-11	8	104	-102	-6	-9	8	75	-92	-4	-7	8	187	206	10	-6	8	109	-110
1	11	7	91	88	-5	-11	8	75	-65	-5	-9	8	103	-134	-3	-7	8	293	295	11	-6	8	225	208
1	11	7	76	-81	-3	-11	8	111	107	-3	-9	8	86	-77	-1	-7	8	383	-378	13	-6	8	145	-142
8	11	7	74	69	-2	-11	8	101	-103	-2	-9	8	188	186	0	-7	8	266	-251	14	-6	8	89	-97
0	12	7	76	-82	-1	-11	8	154	-155	-1	-9	8	306	312	1	-7	8	133	128	15	-6	8	68	67
7	12	7	87	83	0	-11	8	62	62	0	-9	8	55	-13	2	-7	8	143	140	16	-6	8	131	151
-3	-16	8	68	54	1	-11	8	148	142	1	-9	8	297	-311	3	-7	8	194	174	-13	-5	8	104	-85
0	-16	8	66	-43	3	-11	8	123	-139	2	-9	8	134	-125	4	-7	8	129	137	-12	-5	8	110	112
1	-15	8	7[illegible]	76	4	-11	8	184	-187	4	-9	8	63	20	6	-7	8	245	-250	-10	-5	8	99	85
-8	-14	8	79	-76	6	-11	8	254	269	5	-9	8	318	323	7	-7	8	241	239	-9	-5	8	145	-147
-5	-14	8	68	62	7	-11	8	89	104	6	-9	8	100	-97	8	-7	8	127	-117	-8	-5	8	349	-337
5	-14	8	78	62	9	-11	8	86	-92	7	-9	8	224	-232	12	-7	8	141	163	-6	-5	8	92	98
12	-14	8	86	-67	10	-11	8	124	-112	9	-9	8	91	85	14	-7	8	143	-138	-5	-5	8	416	431
-9	-13	8	92	-31	12	-11	8	84	69	13	-9	8	73	81	15	-7	8	77	-78	-4	-5	8	163	-157
-7	-13	8	69	64	-13	-10	8	83	-68	17	-9	8	69	-72	16	-7	8	77	45	-3	-5	8	141	-147
-6	-13	8	116	101	-11	-10	8	77	71	-15	-8	8	66	-33	17	-7	8	131	136	-2	-5	8	193	-138
3	-13	8	71	46	-10	-10	8	169	165	-6	-8	8	172	-182	-17	-6	8	67	-70	0	-5	8	342	334
4	-13	8	62	56	-9	-10	8	77	79	-5	-8	8	161	-163	-12	-6	8	77	-79	1	-5	8	173	172
9	-13	8	77	63	-8	-10	8	68	-74	-4	-8	8	105	-99	-10	-6	8	77	65	2	-5	8	223	-197
11	-13	8	75	-74	-7	-10	8	63	-66	-3	-8	8	295	292	-9	-6	8	135	133	3	-5	8	63	47
-15	-12	8	77	-41	-3	-10	8	120	-141	-2	-8	8	95	100	-8	-6	8	291	-301	4	-5	8	235	234
-10	-12	8	118	-107	-2	-10	8	112	-101	0	-8	8	174	-177	-7	-6	8	125	-120	5	-5	8	94	93

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR SEXACU

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
6	-5	8	69	-85	-4	-3	8	237	-227	7	-2	8	491	482	-12	0	8	64	72	4	1	8	145	127
7	-5	8	297	-274	-3	-3	8	212	211	8	-2	8	131	-122	-11	0	8	78	85	5	1	8	181	-178
9	-5	8	121	91	-2	-3	8	179	186	9	-2	8	178	-172	-10	0	8	151	132	6	1	8	205	-190
11	-5	8	139	156	-1	-3	8	88	72	10	-2	8	73	-74	-8	0	8	279	-271	8	1	8	120	121
12	-5	8	196	-207	0	-3	8	84	71	12	-2	8	146	154	-7	0	8	68	74	9	1	8	190	185
13	-5	8	123	-125	1	-3	8	152	-111	14	-2	8	99	-103	-6	0	8	98	115	10	1	8	111	115
15	-5	8	172	161	3	-3	8	117	89	16	-2	8	75	83	-5	0	8	185	-196	11	1	8	108	-108
18	-5	8	91	-102	4	-3	8	291	-252	-15	-1	8	131	122	-4	0	8	221	-221	13	1	8	198	205
-13	-4	8	73	75	5	-3	8	315	-314	-13	-1	8	159	-186	-3	0	8	228	-209	14	1	8	66	57
-12	-4	8	159	173	6	-3	8	100	-95	-12	-1	8	133	-100	-1	0	8	293	298	15	1	8	116	-107
-10	-4	8	90	-87	7	-3	8	369	370	-10	-1	8	175	154	0	0	8	94	98	16	1	8	92	-94
-9	-4	8	378	-363	8	-3	8	122	89	-9	-1	8	136	154	1	0	8	319	-338	-16	2	8	75	-72
-8	-4	8	124	-128	10	-3	8	185	-166	-8	-1	8	89	-92	2	0	8	312	-282	-14	2	8	95	102
-6	-4	8	142	122	11	-3	8	134	-150	-7	-1	8	86	-77	3	0	8	98	-117	-13	2	8	127	144
-5	-4	8	235	218	12	-3	8	78	90	-6	-1	8	152	155	4	0	8	293	272	-8	2	8	117	148
-4	-4	8	241	-232	13	-3	8	120	138	-5	-1	8	354	370	5	0	8	263	281	-6	2	8	137	-140
-3	-4	8	264	-248	14	-3	8	76	85	-4	-1	8	347	360	7	0	8	354	-352	-5	2	8	123	-103
-2	-4	8	179	166	16	-3	8	87	-78	-3	-1	8	263	-265	8	0	8	248	-241	-4	2	8	167	167
-1	-4	8	230	229	-16	-2	8	77	-69	-2	-1	8	174	-183	9	0	8	205	195	-3	2	8	197	179
1	-4	8	154	143	-14	-2	8	171	168	-1	-1	8	265	264	10	0	8	69	84	-1	2	8	111	-99
2	-4	8	87	-101	-12	-2	8	141	-149	0	-1	8	116	112	11	0	8	86	-101	0	2	8	217	-226
3	-4	8	167	167	-11	-2	8	124	-128	3	-1	8	499	-500	12	0	8	223	-232	1	2	8	188	218
4	-4	8	78	65	-9	-2	8	143	130	4	-1	8	249	-238	14	0	8	76	73	2	2	8	564	567
6	-4	8	409	-408	-7	-2	8	267	-243	5	-1	8	430	423	15	0	8	66	27	3	2	8	73	45
8	-4	8	314	319	-6	-2	8	297	-309	6	-1	8	508	534	17	0	8	111	-130	4	2	8	332	-319
11	-4	8	87	-89	-5	-2	8	151	-148	8	-1	8	215	-209	-15	1	8	112	-122	6	2	8	98	90
12	-4	8	214	-206	-4	-2	8	107	98	9	-1	8	55	69	-14	1	8	68	-92	8	2	8	136	132
14	-4	8	177	170	-3	-2	8	252	260	10	-1	8	165	151	-12	1	8	82	82	10	2	8	129	-122
15	-4	8	65	45	-2	-2	8	68	-65	11	-1	8	240	233	-9	1	8	186	-183	12	2	8	115	142
-13	-3	8	170	162	-1	-2	8	151	-134	13	-1	8	160	-168	-7	1	8	120	118	13	2	8	110	125
-11	-3	8	130	-116	1	-2	8	147	144	15	-1	8	63	69	-4	1	8	163	-163	14	2	8	96	-126
-10	-3	8	200	-209	2	-2	8	112	104	16	-1	8	69	85	-3	1	8	141	148	19	2	8	82	-79
-9	-3	8	199	-204	3	-2	8	167	-163	18	-1	8	80	-85	-2	1	8	244	239	-15	3	8	88	69
-8	-3	8	104	107	4	-2	8	257	-269	-16	0	8	102	93	0	1	8	378	-366	-14	3	8	84	83
-7	-3	8	112	120	5	-2	8	122	-122	-14	0	8	105	-89	1	1	8	315	-302	-12	3	8	110	-129
-5	-3	8	255	-250	6	-2	8	324	332	-13	0	8	86	-107	3	1	8	219	242	-11	3	8	59	-48

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR SEXACU

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
-8	3	8	125	-131	12	4	8	187	-194	15	6	8	77	-88	-3	-13	9	98	77	4	-10	9	118	78
-7	3	8	284	-292	13	4	8	98	-97	-9	7	8	113	114	-2	-13	9	66	65	6	-10	9	149	-155
-5	3	8	153	152	15	4	8	66	59	-6	7	9	158	-159	0	-13	9	96	-110	7	-10	9	107	-132
-4	3	8	111	108	18	4	8	71	-76	-4	7	8	69	64	2	-13	9	74	71	8	-10	9	68	74
-3	3	8	102	103	-9	5	8	119	-121	1	7	8	156	161	10	-13	9	94	-97	9	-10	9	121	125
-2	3	8	251	-246	-7	5	8	94	91	2	7	8	155	161	-7	-12	9	80	-79	11	-10	9	93	-86
-1	3	8	265	-255	-5	5	8	113	-110	4	7	8	100	-100	-6	-12	9	81	-89	12	-10	9	79	-69
0	3	8	196	197	-4	5	8	219	-227	5	7	8	73	61	-4	-12	9	69	68	-11	-9	9	70	-76
1	3	8	356	344	-3	5	8	71	-71	6	7	8	109	104	-3	-12	9	96	102	-10	-9	9	138	-138
2	3	8	110	-95	-1	5	8	114	101	7	7	8	110	125	-1	-12	9	72	-88	-9	-9	9	118	-106
3	3	8	336	-368	1	5	8	99	-82	9	7	8	130	-128	1	-12	9	72	65	-7	-9	9	203	178
4	3	8	93	-114	2	5	8	199	-204	10	7	8	83	-92	2	-12	9	60	47	-5	-9	9	198	-191
5	3	8	85	107	3	5	8	71	51	11	7	8	117	130	6	-12	9	68	60	-4	-9	9	59	66
6	3	8	252	250	5	5	8	79	110	14	7	8	75	-68	8	-12	9	104	-97	-3	-9	9	119	131
7	3	8	63	62	6	5	8	107	101	-10	8	8	78	93	9	-12	9	102	-99	0	-9	9	157	-166
8	3	8	176	-174	7	5	8	90	-89	-8	8	8	71	-73	11	-12	9	80	74	1	-9	9	161	-159
11	3	8	94	94	8	5	8	79	93	-2	8	8	124	-129	-13	-11	9	72	-71	2	-9	9	108	112
13	3	8	86	-96	9	5	8	176	165	0	8	8	94	106	-10	-11	9	74	83	4	-9	9	134	-133
14	3	8	105	-111	10	5	8	133	-148	2	8	8	133	-132	-8	-11	9	133	-128	5	-9	9	157	-152
19	3	8	100	-109	11	5	8	200	-209	3	8	8	161	-160	-7	-11	9	78	-79	6	-9	9	184	-183
-11	4	8	86	97	12	5	8	107	-101	5	8	8	90	79	-5	-11	9	90	93	7	-9	9	89	96
-9	4	8	88	-94	14	5	8	93	81	6	8	8	77	96	-4	-11	9	81	73	8	-9	9	161	150
-8	4	8	152	-157	-8	6	8	85	86	8	8	8	125	-110	-2	-11	9	96	-91	10	-9	9	135	-136
-6	4	8	224	243	-7	6	8	73	98	10	8	8	73	68	0	-11	9	72	62	11	-9	9	89	-103
-5	4	8	257	249	-5	6	8	108	-111	14	8	8	75	-86	1	-11	9	59	67	-13	-8	9	80	76
-4	4	8	73	-85	-3	6	8	78	90	-8	9	8	88	-68	4	-11	9	70	95	-11	-8	9	114	-123
-3	4	8	162	-156	-2	6	8	103	112	-1	9	8	115	116	7	-11	9	97	-95	-8	-8	9	114	113
-1	4	8	61	57	0	6	8	133	-134	2	9	8	75	-82	8	-11	9	114	-106	-6	-8	9	214	-221
0	4	8	125	128	1	6	8	82	-85	4	9	8	119	125	10	-11	9	75	75	-4	-8	9	152	167
1	4	8	142	141	2	6	8	110	-119	7	9	8	69	-67	-12	-10	9	102	99	-2	-8	9	169	-175
2	4	8	235	-262	4	6	8	64	62	8	9	8	81	-72	-11	-10	9	113	112	-1	-8	9	151	-145
3	4	8	189	-175	7	6	8	207	197	0	10	8	91	-98	-9	-10	9	177	-160	0	-8	9	78	67
4	4	8	188	201	8	6	8	129	143	3	11	8	86	80	-8	-10	9	69	-85	1	-8	9	265	252
5	4	8	279	263	10	6	8	138	-143	-7	-14	9	68	56	-6	-10	9	109	102	2	-8	9	181	181
8	4	8	58	29	12	6	8	64	43	-2	-14	9	78	79	-1	-10	9	176	188	3	-8	9	60	-84
10	4	8	125	123	13	6	8	94	101	1	-14	9	95	-74	3	-10	9	75	85	4	-8	9	109	-115

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR SEXACU

H	K	L	10FO	10FC
5	-8	9	143	-143
6	-8	9	133	109
7	-8	9	196	201
8	-8	9	89	-78
9	-8	9	95	-87
10	-8	9	112	-130
12	-8	9	93	105
14	-8	9	91	-79
17	-8	9	82	93
-15	-7	9	91	72
-12	-7	9	156	-166
-10	-7	9	100	110
-8	-7	9	168	163
-5	-7	9	159	151
-4	-7	9	93	95
-3	-7	9	87	-84
-2	-7	9	173	-169
-1	-7	9	142	145
0	-7	9	219	239
1	-7	9	79	87
2	-7	9	84	-93
3	-7	9	285	-266
5	-7	9	134	127
6	-7	9	194	208
8	-7	9	104	-113
11	-7	9	90	86
12	-7	9	67	64
15	-7	9	78	99
16	-7	9	95	105
-16	-6	9	86	83
-13	-6	9	145	-133
-11	-6	9	127	114
-7	-6	9	80	-85
-6	-6	9	63	69
-4	-6	9	126	-123
-3	-6	9	65	-72
-1	-6	9	107	119
0	-6	9	192	172
1	-6	9	175	-184
2	-6	9	313	-308
4	-6	9	229	246
5	-6	9	90	70
6	-6	9	116	105
7	-6	9	290	-268
8	-6	9	118	-127
10	-6	9	124	-114
14	-6	9	68	69
15	-6	9	71	74
17	-6	9	102	-108
-12	-5	9	182	184
-10	-5	9	88	-70
-7	-5	9	98	-108
-6	-5	9	66	58
-5	-5	9	63	-68
-4	-5	9	98	-108
-3	-5	9	200	195
-2	-5	9	311	296
-1	-5	9	167	165
0	-5	9	124	-108
1	-5	9	148	-157
2	-5	9	124	-125
3	-5	9	185	205
4	-5	9	282	260
5	-5	9	73	-56
6	-5	9	123	-150
7	-5	9	179	-211
8	-5	9	259	280
9	-5	9	103	-115
13	-5	9	136	127
14	-5	9	80	75
15	-5	9	76	-51
-11	-4	9	155	-144
-7	-4	9	122	-148
-6	-4	9	129	-115
-5	-4	9	162	-152
-4	-4	9	259	266
-3	-4	9	350	351
-2	-4	9	183	195
-1	-4	9	143	-153
0	-4	9	325	-332
1	-4	9	259	-232
2	-4	9	55	46
3	-4	9	114	112
4	-4	9	185	-164
6	-4	9	130	-123
7	-4	9	134	159
8	-4	9	199	199
9	-4	9	329	-324
12	-4	9	161	164
13	-4	9	86	80
14	-4	9	91	-94
15	-4	9	124	-136
-13	-3	9	73	80
-10	-3	9	66	71
-8	-3	9	185	-174
-7	-3	9	344	-342
-6	-3	9	170	-177
-4	-3	9	435	447
-3	-3	9	159	162
-1	-3	9	314	-302
1	-3	9	152	158
2	-3	9	235	250
4	-3	9	102	102
7	-3	9	183	185
8	-3	9	268	-273
9	-3	9	187	-198
10	-3	9	171	178
11	-3	9	139	139
12	-3	9	115	103
13	-3	9	155	-145
14	-3	9	176	-165
16	-3	9	107	118
-13	-2	9	84	-68
-11	-2	9	88	80
-10	-2	9	122	118
-8	-2	9	193	-199
-7	-2	9	112	-123
-6	-2	9	213	213
-5	-2	9	536	545
-4	-2	9	239	245
-3	-2	9	201	-218
-1	-2	9	105	-105
0	-2	9	69	-65
1	-2	9	236	232
2	-2	9	71	60
3	-2	9	277	-259
4	-2	9	247	242
6	-2	9	116	114
9	-2	9	230	247
10	-2	9	217	206
12	-2	9	146	-142
13	-2	9	216	-234
15	-2	9	94	93
16	-2	9	74	80
18	-2	9	74	-79
-12	-1	9	84	89
-11	-1	9	75	88
-9	-1	9	244	-254
-8	-1	9	253	-242
-7	-1	9	83	71
-6	-1	9	193	192
-5	-1	9	103	-113
-4	-1	9	208	-195
-3	-1	9	193	-197
-2	-1	9	161	-198
-1	-1	9	59	53
0	-1	9	131	131
3	-1	9	181	164
5	-1	9	122	-129
7	-1	9	250	-249
9	-1	9	91	99
10	-1	9	71	-91
11	-1	9	197	-205
12	-1	9	219	-232
13	-1	9	102	-95
14	-1	9	116	103
15	-1	9	92	104
-16	0	9	104	-95
-15	0	9	89	-97
-12	0	9	67	59
-11	0	9	80	-64
-10	0	9	141	-125
-9	0	9	155	-142
-8	0	9	91	77
-7	0	9	249	257
-6	0	9	128	147
-5	0	9	97	-103
-4	0	9	110	-105
-3	0	9	54	49
-2	0	9	100	104
-1	0	9	111	-107
0	0	9	64	-53
2	0	9	68	60
3	0	9	206	219
4	0	9	163	-180
5	0	9	306	-314
7	0	9	102	101
8	0	9	308	318
9	0	9	178	165
11	0	9	214	-205

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR SEXACU

H	K	L	10FO	10FC
13	0	9	183	193
15	0	9	71	-78
-16	1	9	93	-92
-14	1	9	141	130
-12	1	9	64	-50
-11	1	9	91	-102
-8	1	9	174	181
-7	1	9	78	77
-6	1	9	120	-124
-5	1	9	154	-141
-4	1	9	120	125
-3	1	9	69	43
0	1	9	93	-105
1	1	9	295	292
2	1	9	438	435
3	1	9	239	-236
4	1	9	476	-469
6	1	9	220	222
7	1	9	200	207
8	1	9	186	186
9	1	9	219	-221
10	1	9	247	-247
12	1	9	173	182
13	1	9	110	116
14	1	9	96	-120
17	1	9	73	81
-15	2	9	105	109
-13	2	9	78	-58
-12	2	9	145	-165
-10	2	9	71	65
-9	2	9	73	74
-7	2	9	71	-80
-4	2	9	169	176
-3	2	9	75	70
-2	2	9	183	-187
-1	2	9	71	-59
0	2	9	270	267
1	2	9	163	141
2	2	9	190	-183
3	2	9	392	-390
4	2	9	217	-223
5	2	9	329	339
6	2	9	270	263
8	2	9	237	-235
9	2	9	147	-146
10	2	9	77	85
11	2	9	80	67
12	2	9	91	107
13	2	9	90	-95
14	2	9	108	-132
15	2	9	68	58
18	2	9	96	-99
-13	3	9	75	-100
-11	3	9	111	112
-8	3	9	105	-100
-6	3	9	154	155
-5	3	9	93	99
-3	3	9	79	-73
-1	3	9	88	80
	3	9	151	142
2	3	9	314	-321
3	3	9	84	-67
4	3	9	241	233
5	3	9	243	228
7	3	9	128	-117
8	3	9	84	-92
10	3	9	89	89
11	3	9	63	-73
12	3	9	114	-125
18	3	9	75	-73
-9	4	9	86	-87
-7	4	9	119	125
-5	4	9	134	-136
-4	4	9	112	-123
-3	4	9	73	69
-2	4	9	113	119
0	4	9	79	-95
1	4	9	172	-154
2	4	9	60	-39
3	4	9	77	66
4	4	9	129	142
5	4	9	114	112
6	4	9	62	-64
7	4	9	100	-84
8	4	9	78	80
9	4	9	68	68
10	4	9	206	-224
11	4	9	181	-178
-8	5	9	86	114
-6	5	9	115	-126
-5	5	9	78	-84
-3	5	9	214	205
-1	5	9	201	-198
0	5	9	67	-57
3	5	9	139	145
7	5	9	150	137
8	5	9	94	109
9	5	9	108	-113
10	5	9	149	-169
12	5	9	66	61
13	5	9	73	85
15	5	9	78	-82
17	5	9	71	47
-9	6	9	97	99
-7	6	9	122	-101
-6	6	9	96	-89
-5	6	9	64	46
-4	6	9	121	116
-1	6	9	104	-108
1	6	9	222	222
2	6	9	102	87
3	6	9	118	-105
5	6	9	58	52
6	6	9	66	71
7	6	9	142	155
9	6	9	167	-168
11	6	9	94	95
14	6	9	71	-76
16	6	9	83	95
-10	7	9	76	79
-8	7	9	95	-87
-3	7	9	64	-58
-2	7	9	90	-80
-1	7	9	72	71
0	7	9	145	152
2	7	9	113	-105
3	7	9	125	-132
7	7	9	88	-73
8	7	9	79	-78
10	7	9	71	54
-9	8	9	73	-71
-5	8	9	75	-72
-1	8	9	75	67
2	8	9	98	-100
4	8	9	104	112
-2	9	9	77	95
2	9	9	71	72
8	9	9	84	81
-1	10	9	73	-71
-1	-14	10	67	-59
1	-14	10	70	81
0	-13	10	92	65
1	-13	10	127	107
3	-13	10	76	-54
9	-13	10	116	-138
-6	-12	10	66	84
-1	-12	10	77	67
0	-12	10	104	97
2	-12	10	99	-111
3	-12	10	71	-80
5	-12	10	63	42
-4	-11	10	98	-81
-2	-11	10	127	133
-1	-11	10	113	132
2	-11	10	101	-81
4	-11	10	129	119
-11	-10	10	73	-69
-10	-10	10	68	-60
-8	-10	10	80	62
-7	-10	10	63	60
-6	-10	10	91	-84
-5	-10	10	133	-137
-3	-10	10	87	91
-2	-10	10	170	165
0	-10	10	119	-102
1	-10	10	180	-174
2	-10	10	162	-185
5	-10	10	81	-91
8	-10	10	76	81
9	-10	10	74	-64
12	-10	10	71	83
15	-10	10	77	-76
-9	-9	10	112	117
-7	-9	10	114	-122
-6	-9	10	172	-171
-5	-9	10	72	-96
-4	-9	10	189	174
-3	-9	10	228	209
-1	-9	10	176	-169
2	-9	10	138	130

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR SEXACU

H	K	L	10FO	10FC
3	-9	10	113	90
4	-9	10	96	-89
6	-9	10	159	153
7	-9	10	75	95
8	-9	10	98	-98
9	-9	10	158	-165
11	-9	10	67	78
12	-9	10	102	105
16	-9	10	80	63
-16	-8	10	77	43
-13	-8	10	72	-77
-12	-8	10	75	-71
-10	-8	10	136	149
-7	-8	10	134	-118
-6	-8	10	95	-92
-5	-8	10	215	210
-4	-8	10	204	190
-3	-8	10	82	-67
-2	-8	10	183	-165
0	-8	10	154	160
3	-8	10	178	-167
5	-8	10	183	193
6	-8	10	91	94
7	-8	10	127	-149
8	-8	10	138	-127
10	-8	10	152	139
11	-8	10	145	163
13	-8	10	94	-82
-12	-7	10	89	88
-11	-7	10	165	154
-9	-7	10	131	-122
-8	-7	10	115	-101
-7	-7	10	60	-56
-3	-7	10	123	-116
-1	-7	10	212	213
0	-7	10	86	-127
1	-7	10	229	-232
3	-7	10	122	118
4	-7	10	190	191
6	-7	10	152	-136
7	-7	10	309	-299
10	-7	10	136	140
12	-7	10	84	-72
15	-7	10	71	53
17	-7	10	71	-79
-15	-6	10	81	-76
-13	-6	10	76	83
-12	-6	10	147	139
-10	-6	10	172	-173
-6	-6	10	116	108
-4	-6	10	59	65
-3	-6	10	82	86
-1	-6	10	87	-83
0	-6	10	166	-165
1	-6	10	58	-79
2	-6	10	113	135
3	-6	10	227	224
4	-6	10	65	54
5	-6	10	238	-213
6	-6	10	199	-207
8	-6	10	93	101
9	-6	10	79	59
10	-6	10	89	95
11	-6	10	135	-129
13	-6	10	72	68
14	-6	10	64	53
-16	-5	10	87	-86
-14	-5	10	64	67
-11	-5	10	154	-152
-10	-5	10	117	-103
-4	-5	10	214	223
-1	-5	10	219	-245
0	-5	10	155	-151
1	-5	10	55	69
2	-5	10	85	66
4	-5	10	239	-246
5	-5	10	262	-268
7	-5	10	140	141
8	-5	10	162	152
11	-5	10	81	-73
12	-5	10	122	142
-17	-4	10	70	-59
-15	-4	10	94	75
-11	-4	10	106	-99
-9	-4	10	76	77
-7	-4	10	104	-98
-5	-4	10	260	259
-4	-4	10	288	288
-2	-4	10	136	-131
-1	-4	10	203	-194
0	-4	10	208	205
1	-4	10	160	157
3	-4	10	100	-114
4	-4	10	306	-288
5	-4	10	56	63
6	-4	10	214	192
7	-4	10	109	128
9	-4	10	96	-109
12	-4	10	62	62
13	-4	10	149	-150
16	-4	10	69	83
-15	-3	10	73	47
-12	-3	10	62	-76
-6	-3	10	199	204
-5	-3	10	343	354
-4	-3	10	125	-130
-3	-3	10	204	-193
-2	-3	10	77	82
0	-3	10	247	238
2	-3	10	196	-190
3	-3	10	372	-381
4	-3	10	116	108
5	-3	10	228	234
7	-3	10	71	88
9	-3	10	60	47
12	-3	10	134	-131
13	-3	10	78	-97
14	-3	10	125	139
18	-3	10	88	-86
-15	-2	10	81	-73
-9	-2	10	62	-30
-7	-2	10	120	127
-5	-2	10	87	-82
-4	-2	10	246	-243
-2	-2	10	87	98
-1	-2	10	217	212
1	-2	10	249	-239
2	-2	10	159	-166
4	-2	10	228	247
9	-2	10	67	-63
10	-2	10	170	-180
11	-2	10	109	-107
12	-2	10	95	-106
14	-2	10	124	126
-16	-1	10	77	-68
-12	-1	10	71	33
-10	-1	10	60	-40
-8	-1	10	74	73
-5	-1	10	179	-178
-4	-1	10	75	-66
-3	-1	10	224	230
-2	-1	10	100	78
-1	-1	10	60	-59
0	-1	10	174	-171
2	-1	10	104	-101
3	-1	10	283	278
4	-1	10	79	81
5	-1	10	165	-168
10	-1	10	69	-68
11	-1	10	64	-66
12	-1	10	93	75
13	-1	10	145	152
15	-1	10	86	-114
-16	0	10	111	-108
-14	0	10	86	64
-9	0	10	147	164
-8	0	10	113	96
-7	0	10	72	-66
-6	0	10	137	-123
-4	0	10	176	170
-3	0	10	160	151
-1	0	10	158	-170
0	0	10	176	-173
1	0	10	145	147
2	0	10	190	195
4	0	10	136	-152
7	0	10	173	155
9	0	10	115	-112
10	0	10	63	-77
11	0	10	93	91
12	0	10	159	170
14	0	10	118	-131
16	0	10	77	70
17	0	10	74	80
-15	1	10	107	107
-10	1	10	131	119
-8	1	10	172	-167
-5	1	10	143	135
-4	1	10	271	276
-2	1	10	264	-273

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR SEXACU

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
0	1	10	104	109	0	3	10	85	-82	16	5	10	91	84	-5	-9	11	132	133	11	-7	11	113	-10[illegible]
3	1	10	114	-117	1	3	10	84	-85	-10	6	10	75	63	-3	-9	11	65	-50	13	-7	11	95	102
4	1	10	110	-123	2	3	10	125	115	-8	6	10	73	-61	0	-9	11	130	141	16	-7	11	90	-79
5	1	10	187	192	6	3	10	142	-139	-3	6	10	66	-59	3	-9	11	86	-93	-14	-6	11	72	70
8	1	10	113	-136	8	3	10	135	122	-1	6	10	131	136	5	-9	11	60	72	-12	-6	11	85	-90
9	1	10	80	-85	10	3	10	214	-219	0	6	10	178	172	6	-9	11	77	64	-9	-6	11	100	87
10	1	10	85	83	11	3	10	153	-153	2	6	10	149	-152	7	-9	11	68	49	-8	-6	11	151	136
11	1	10	129	113	13	3	10	69	63	3	6	10	93	-103	8	-9	11	68	-64	-6	-6	11	218	-208
13	1	10	162	-157	14	3	10	69	79	5	6	10	89	86	-7	-8	11	77	75	-5	-6	11	57	-54
14	1	10	88	-96	-10	4	10	100	-89	7	6	10	100	-95	-6	-8	11	70	95	-4	-6	11	155	158
15	1	10	73	75	-8	4	10	127	134	14	6	10	75	38	-4	-8	11	131	-117	-3	-6	11	96	91
-14	2	10	73	-74	-6	4	10	111	-112	-1	7	10	68	48	-3	-8	11	128	-117	-2	-6	11	64	77
-11	2	10	91	97	-5	4	10	88	-83	1	7	10	126	-131	-1	-8	11	265	251	-1	-6	11	129	-143
-9	2	10	119	-125	-3	4	10	116	120	2	7	10	113	-115	1	-8	11	191	-174	0	-6	11	218	-236
-8	2	10	121	-124	-1	4	10	93	-99	4	7	10	72	67	4	-8	11	93	106	1	-6	11	72	60
-7	2	10	80	82	2	4	10	102	102	-2	8	10	117	121	6	-8	11	69	-80	4	-6	11	169	-177
-6	2	10	161	163	3	4	10	103	95	8	8	10	70	69	7	-8	11	66	-63	6	-6	11	219	226
-5	2	1	116	142	4	4	10	95	-98	-1	9	10	80	-64	9	-8	11	70	71	7	-6	11	169	160
-3	2	10	145	-142	5	4	10	138	-138	7	9	10	91	56	14	-8	11	89	73	8	-6	11	71	-65
-2	2	10	147	-154	6	4	10	113	107	-7	-14	11	71	-65	-13	-7	11	77	71	9	-6	11	77	-79
1	2	10	90	-100	7	4	10	100	92	-12	-12	11	90	64	-11	-7	11	76	-70	10	-6	11	116	-117
2	2	10	118	-109	9	4	10	130	-125	-2	-12	11	63	80	-10	-7	11	89	-78	12	-6	11	143	153
4	2	10	138	128	10	4	10	216	-221	1	-12	11	62	-48	-8	-7	11	73	73	13	-6	11	89	74
6	2	10	80	-81	12	4	10	72	88	6	-12	11	105	-110	-7	-7	11	113	95	15	-6	11	111	-99
7	2	10	72	-64	-9	5	10	104	115	-1	-11	11	64	-70	-5	-7	11	210	-201	-12	-5	11	80	-80
9	2	10	174	169	-7	5	10	86	-86	0	-11	11	110	-99	-4	-7	11	122	-117	-10	-5	11	82	79
10	2	10	93	73	-4	5	10	67	73	5	-11	11	114	-115	-3	-7	11	107	98	-9	-5	11	97	105
11	2	10	90	-105	-2	5	10	78	-85	7	-11	11	100	93	-2	-7	11	138	125	-7	-5	11	152	-140
12	2	10	116	-122	-1	5	10	68	-74	-2	-10	11	66	-54	-1	-7	11	83	83	-6	-5	11	93	-101
17	2	10	66	-47	0	5	10	113	118	-1	-10	11	84	-96	0	-7	11	229	-234	-5	-5	11	188	185
-10	3	10	83	-103	1	5	10	205	199	4	-10	11	95	-78	1	-7	11	116	-116	-4	-5	11	131	150
-9	3	10	108	-109	3	5	10	173	-143	5	-10	11	77	-78	2	-7	11	75	88	-2	-5	11	77	-83
-8	3	10	93	88	6	5	10	143	141	6	-10	11	82	77	3	-7	11	118	108	-1	-5	11	136	-127
-7	3	10	170	175	7	5	10	120	107	7	-10	11	104	112	5	-7	11	171	-172	0	-5	11	60	-68
-4	3	10	82	-86	8	5	10	75	-73	11	-10	11	71	64	7	-7	11	86	90	1	-5	11	89	-84
-1	3	10	77	67	9	5	10	153	-165	-10	-9	11	62	43	9	-7	11	63	56	3	-5	11	73	-76

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR SEXACU

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
4	-5	11	97	-85	6	-3	11	289	-273	1	-1	11	484	489	-1	2	11	137	129	-8	5	11	84	-96
5	-5	11	255	237	7	-3	11	91	-77	3	-1	11	87	-92	0	2	11	95	-107	-7	5	11	68	-79
6	-5	11	227	232	8	-3	11	117	109	4	-1	11	86	-78	1	2	11	154	-144	-3	5	11	74	-90
7	-5	11	96	-74	9	-3	11	98	95	5	-1	11	109	-103	2	2	11	81	88	-1	5	11	114	108
8	-5	11	219	-228	11	-3	11	74	-57	6	-1	11	84	92	3	2	11	107	96	2	5	11	125	-138
11	-5	11	184	155	12	-3	11	134	-142	7	-1	11	263	261	6	2	11	82	-87	5	5	11	65	66
13	-5	11	89	-76	13	-3	11	86	99	8	-1	11	66	86	8	2	11	139	141	7	5	11	110	-135
14	-5	11	79	-94	-13	-2	11	107	99	-8	0	11	105	-108	9	2	11	91	-75	8	5	11	68	-60
-11	-4	11	90	97	-12	-2	11	74	63	-5	0	11	84	74	10	2	11	145	-157	12	5	11	64	-50
-8	-4	11	109	-112	-11	-2	11	66	-43	-4	0	11	63	70	13	2	11	117	120	0	6	11	102	-98
-6	-4	11	124	122	-10	-2	11	75	-79	-3	0	11	210	-219	14	2	11	86	91	1	6	11	140	-163
-5	-4	11	189	189	-6	-2	11	68	-80	-2	0	11	102	-102	-8	3	11	95	93	3	6	11	102	92
-4	-4	11	106	-107	-5	-2	11	99	-104	0	0	11	241	233	-6	3	11	122	-121	-3	7	11	80	85
-3	-4	11	87	105	-4	-2	11	83	88	1	0	11	128	123	-5	3	11	91	-90	-2	7	11	86	90
-1	-4	11	89	-90	-3	-2	11	157	169	2	0	11	186	-180	-4	3	11	76	79	5	7	11	73	-51
1	-4	11	145	-142	-2	-2	11	152	-162	8	0	11	84	-96	-3	3	11	74	72	7	7	11	98	97
2	-4	11	156	-146	-1	-2	11	73	-69	12	0	11	79	-76	0	3	11	179	-193	-1	8	11	70	-48
4	-4	11	183	166	0	-2	11	244	-234	13	0	11	91	-78	2	3	11	145	156	7	8	11	86	82
5	-4	11	252	263	1	-2	11	137	149	15	0	11	86	80	3	3	11	73	79	-1	-16	12	86	-58
6	-4	11	68	-52	2	-2	11	270	274	-7	1	11	122	125	4	3	11	104	-98	0	-15	12	71	70
7	-4	11	293	-210	3	-2	11	138	126	-6	1	11	138	142	5	3	11	98	-110	-10	-13	12	71	-52
9	-4	11	113	113	5	-2	11	298	-310	-4	1	11	179	-173	6	3	11	77	83	-11	-12	12	75	-71
10	-4	11	78	56	6	-2	11	142	-168	-3	1	11	116	-111	7	3	11	75	83	-6	-12	12	72	-77
12	-4	11	168	-171	7	-2	11	93	115	-2	1	11	59	-63	9	3	11	142	-153	-2	-12	12	65	55
15	-4	11	69	66	8	-2	11	102	98	0	1	11	105	116	10	3	11	125	-131	6	-12	12	63	50
-15	-3	11	81	-87	10	-2	11	109	-110	1	1	11	235	-256	12	3	11	116	127	5	-11	12	64	47
-14	-3	11	93	-82	11	-2	11	103	-89	2	1	11	151	-141	-10	4	11	74	66	6	-11	12	88	92
-12	-3	11	96	96	13	-2	11	114	123	9	1	11	122	124	-9	4	11	92	94	-7	-10	12	75	-56
-7	-3	11	75	75	17	-2	11	86	95	11	1	11	100	-92	-7	4	11	109	-110	-1	-10	12	77	86
-4	-3	11	66	-70	-14	-1	11	67	60	12	1	11	80	-84	-4	4	11	104	106	2	-10	12	87	-79
-3	-3	11	138	141	-9	-1	11	95	93	-10	2	11	82	-73	1	4	11	124	112	4	-10	12	93	94
0	-3	11	253	-269	-8	-1	11	91	96	-8	2	11	131	141	6	4	11	142	151	5	-10	12	69	75
1	-3	11	236	-231	-5	-1	11	117	119	-7	2	11	107	102	8	4	11	134	-127	8	-10	12	77	-77
2	-3	11	69	67	-4	-1	11	152	142	-5	2	11	115	-102	9	4	11	115	-125	-6	-9	12	63	40
3	-3	11	164	167	-2	-1	11	91	-89	-4	2	11	92	-91	10	4	11	68	54	-2	-9	12	77	72
4	-3	11	179	180	-1	-1	11	172	-178	-2	2	11	86	83	11	4	11	89	94	0	-9	12	106	-39

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR SEXACU

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
1	-9	12	114	-115	8	-6	12	78	-83	0	-3	12	80	-80	-6	0	12	69	73	3	3	12	63	-62
2	-9	12	91	-87	12	-6	12	80	-76	2	-3	12	127	136	-4	0	12	73	-78	4	3	12	91	-93
3	-9	12	74	63	13	-6	12	76	-52	4	-3	12	131	-125	-3	0	12	61	-51	6	3	12	104	99
4	-9	12	109	98	16	-6	12	81	78	5	-3	12	61	-63	-1	0	12	73	-86	8	3	12	80	-76
6	-9	12	75	-57	-11	-5	12	69	80	10	-3	12	127	-139	1	0	12	226	-217	-3	4	12	145	-136
-5	-8	12	72	-94	-8	-5	12	89	-81	11	-3	12	71	-62	3	0	12	205	211	-2	4	12	71	73
-3	-8	12	111	100	-7	-5	12	95	101	12	-3	12	172	187	4	0	12	125	121	-1	4	12	143	128
-2	-8	12	75	75	-6	-5	12	170	171	-10	-2	12	82	80	6	0	12	143	-132	2	4	12	100	-104
0	-8	12	98	-89	-4	-5	12	149	-133	-9	-2	12	118	114	8	0	12	84	86	-4	5	12	93	-99
2	-8	12	73	66	-3	-5	12	125	-105	-8	-2	12	66	72	9	0	12	124	119	-2	5	12	110	127
3	-8	12	174	153	0	-5	12	71	74	-4	-2	12	123	120	11	0	12	115	-118	1	5	12	144	-146
5	-8	12	95	-102	1	-5	12	63	-64	-1	-2	12	113	-142	12	0	12	78	-84	9	5	12	74	72
6	-8	12	78	-67	4	-5	12	98	97	1	-2	12	184	192	-12	1	12	73	79	-3	6	12	104	101
-4	-7	12	133	135	5	-5	12	103	134	2	-2	12	75	-86	-10	1	12	77	-76	-2	6	12	95	73
-3	-7	12	132	142	7	-5	12	81	-92	3	-2	12	128	-129	-1	1	12	67	-75	7	6	12	90	111
-1	-7	12	109	-103	9	-5	12	119	107	5	-2	12	96	102	2	1	12	161	167	6	7	12	102	75
0	-7	12	147	-151	10	-5	12	64	65	6	-2	12	147	148	3	1	12	136	130	0	-14	13	78	-55
1	-7	12	65	66	11	-5	12	102	-106	7	-2	12	91	99	4	1	12	73	72	1	-14	13	68	-37
2	-7	12	138	130	12	-5	12	152	-144	9	-2	12	81	-79	5	1	12	133	-119	3	-14	13	70	62
3	-7	12	66	78	15	-5	12	107	120	11	-2	12	108	116	6	1	12	65	-77	-4	-13	13	68	57
4	-7	12	82	-105	-8	-4	12	111	97	12	-2	12	83	81	7	1	12	68	77	2	-13	13	71	63
6	-7	12	107	119	-7	-4	12	125	135	13	-2	12	86	-76	8	1	12	95	101	-5	-12	13	73	72
7	-7	12	104	81	-5	-4	12	124	-126	-8	-1	12	86	-108	13	1	12	84	93	-3	-12	13	64	-48
-12	-6	12	78	-74	-4	-4	12	148	-135	-7	-1	12	122	-119	-7	2	12	79	-66	-2	-12	13	69	-76
-8	-6	12	98	-89	0	-4	12	185	-194	-3	-1	12	103	-130	-4	2	12	78	71	-6	-11	13	92	77
-5	-6	12	156	150	1	-4	12	121	-123	0	-1	12	98	93	-2	2	12	99	-104	-1	-11	13	63	55
-4	-6	12	114	125	3	-4	12	61	58	2	-1	12	184	-170	0	2	12	82	-88	0	-11	13	94	69
-3	-6	12	143	-152	8	-4	12	91	89	4	-1	12	164	152	2	2	12	203	214	5	-11	13	67	66
-2	-6	12	168	-149	10	-4	12	78	-76	5	-1	12	89	103	5	2	12	84	-84	-4	-10	13	108	-102
-1	-6	12	95	-103	11	-4	12	199	-203	7	-1	12	172	-173	7	2	12	78	66	-2	-10	13	67	53
1	-6	12	102	81	13	-4	12	136	115	8	-1	12	125	-132	9	2	12	88	-87	6	-10	13	73	-73
3	-6	12	67	-51	16	-4	12	105	-113	10	-1	12	78	95	12	2	12	95	95	-5	-9	13	104	-88
4	-6	12	89	-81	-8	-3	12	73	65	12	-1	12	90	-111	-3	3	12	81	-87	10	-9	13	86	-80
5	-6	12	199	205	-6	-3	12	136	-122	14	-1	12	95	88	-2	3	12	96	-89	-9	-8	13	69	56
6	-6	12	76	87	-5	-3	12	141	-154	-9	0	12	69	-69	0	3	12	71	72	-8	-8	13	71	51
7	-6	12	97	-104	-3	-3	12	89	86	-8	0	12	73	-55	1	3	12	109	102	-3	-8	13	104	90

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR SEXACU

H	K	L	10FO	10FC
6	-8	13	92	85
7	-8	13	93	77
9	-8	13	67	-73
-10	-7	13	73	69
3	-7	13	95	-78
4	-7	13	82	69
5	-7	13	154	143
8	-7	13	104	-97
9	-7	13	66	-58
-11	-6	13	74	56
-8	-6	13	69	-77
-6	-6	13	91	82
-4	-6	13	56	-39
-3	-6	13	66	-66
-1	-6	13	92	92
1	-6	13	109	-102
2	-6	13	82	-68
3	-6	13	71	61
4	-6	13	221	220
5	-6	13	97	95
7	-6	13	113	-99
9	-6	13	67	29
-9	-5	13	81	-69
-7	-5	13	76	74
-6	-5	13	78	-82
-5	-5	13	98	-103
-3	-5	13	64	58
-2	-5	13	127	118
0	-5	13	177	-168
1	-5	13	152	-154
2	-5	13	78	99
3	-5	13	188	182
4	-5	13	152	137
6	-5	13	79	-67
11	-5	13	80	-90
-7	-4	13	77	-78

H	K	L	10FO	10FC
-6	-4	13	142	-132
-4	-4	13	106	88
-3	-4	13	101	104
-1	-4	13	140	-129
0	-4	13	114	-103
2	-4	13	221	216
3	-4	13	85	94
4	-4	13	62	-60
10	-4	13	73	-70
12	-4	13	131	150
-7	-3	13	116	-107
-5	-3	13	68	78
-4	-3	13	93	101
-2	-3	13	90	-79
-1	-3	13	86	-103
0	-3	13	97	92
1	-3	13	111	113
6	-3	13	89	77
11	-3	13	81	103
13	-3	13	120	-124
-9	-2	13	73	-64
-8	-2	13	103	-96
-6	-2	13	101	92
-5	-2	13	83	80
-3	-2	13	80	-84
0	-2	13	109	100
3	-2	13	66	-69
5	-2	13	66	76
7	-2	13	129	-135
10	-2	13	75	72
12	-2	13	136	-141
14	-2	13	87	79
-10	-1	13	70	-88
-9	-1	13	109	-105
-7	-1	13	130	127
-6	-1	13	67	64

H	K	L	10FO	10FC
-1	-1	13	66	69
1	-1	13	95	-101
6	-1	13	122	-126
8	-1	13	127	117
9	-1	13	89	81
11	-1	13	111	-105
12	-1	13	89	-94
-11	0	13	74	-63
-8	0	13	87	87
-6	0	13	73	-41
-5	0	13	75	-62
0	0	13	76	-57
1	0	13	62	81
2	0	13	107	90
5	0	13	130	-130
7	0	13	122	128
13	0	13	100	96
1	1	13	130	135
9	1	13	91	-81
-2	2	13	80	-81
0	2	13	98	82
2	2	13	128	-98
6	2	13	75	83
8	2	13	83	-89
-1	3	13	116	113
1	3	13	94	-92
2	3	13	82	-93
4	3	13	78	65
7	3	13	87	-71
9	3	13	69	63
-2	4	13	86	95
0	4	13	100	-107
1	4	13	104	-90
8	4	13	82	83
-3	5	13	81	74
5	-13	14	87	83

H	K	L	10FO	10FC
6	-13	14	73	69
-1	-12	14	92	85
-2	-11	14	90	77
0	-11	14	77	-86
4	-11	14	88	60
-3	-10	14	78	73
-1	-10	14	83	-64
-5	-9	14	71	65
-4	-9	14	84	68
-2	-9	14	68	-56
-6	-8	14	86	75
-5	-8	14	78	65
-2	-8	14	69	-68
2	-8	14	70	-65
4	-8	14	100	93
7	-8	14	100	-93
-6	-7	14	74	75
4	-7	14	82	90
6	-7	14	110	-103
-7	-6	14	66	61
-5	-6	14	75	-66
3	-6	14	112	121
5	-6	14	97	-81
10	-6	14	86	-63
13	-6	14	94	78
-6	-5	14	91	-74
1	-5	14	71	57
2	-5	14	80	79
4	-5	14	76	-66
9	-5	14	102	-90
12	-5	14	69	73
-7	-4	14	71	-73
-5	-4	14	73	78
-4	-4	14	72	69
0	-4	14	105	107
5	-4	14	88	77

H	K	L	10FO	10FC
6	-4	14	64	57
8	-4	14	68	-72
9	-4	14	72	-80
-11	-3	14	73	76
-8	-3	14	68	-52
-6	-3	14	88	78
-3	-3	14	64	-64
-1	-3	14	113	101
1	-3	14	115	-104
2	-3	14	102	-89
4	-3	14	86	99
5	-3	14	86	98
7	-3	14	68	-81
9	-3	14	74	62
10	-3	14	77	69
12	-3	14	68	-68
-10	-2	14	75	-82
-2	-2	14	107	87
-1	-2	14	82	76
0	-2	14	111	-114
1	-2	14	114	-104
3	-2	14	68	76
6	-2	14	89	-92
9	-2	14	83	80
10	-2	14	70	-64
-3	-1	14	80	73
0	-1	14	104	-109
2	-1	14	77	76
3	-1	14	92	83
5	-1	14	70	-49
-5	0	14	80	78
-1	0	14	88	-73
1	0	14	167	105
4	0	14	97	-85
9	0	14	75	-77
11	0	14	77	76

```
OBSERVED AND CALCULATED STRUCTURE FACTORS FOR  SEXACU

 H  K  L 10FO 10FC      H  K  L 10FO 10FC      H  K  L 10FO 10FC      H  K  L 10FO 10FC      H  K  L 10FO 10FC

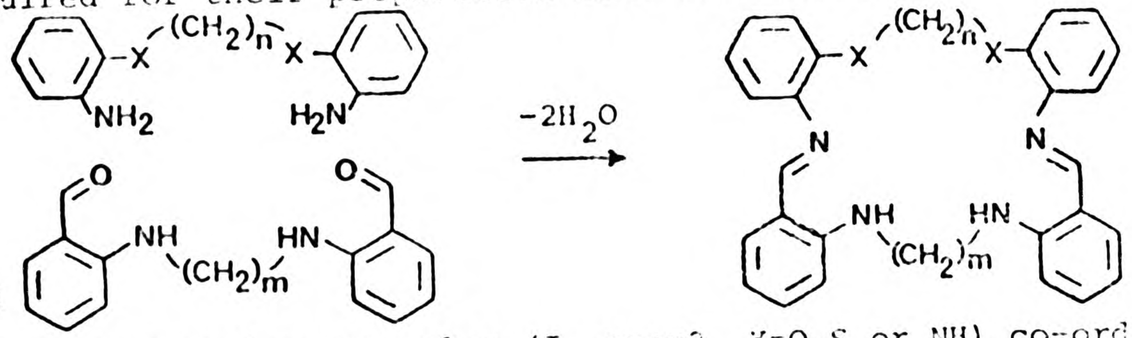
-2  1 14   91  -88      2  1 14  105  -95      7  1 14   70  -69     10  1 14   78   87      5  2 14  104   95
 0  1 14   85   80      5  1 14   81   73      8  1 14   83  -75      6  2 14   91  -97
```

Abstract of oral communication presented at the Toulouse XXI Conference Internationale de Chimie de Coordination, July 1980.

MACROCYCLIC SEXADENTATE LIGANDS WITH 'N_4X_2' DONOR SETS (X = O,S OR NH) AND THEIR COPPER COMPLEXES.

P.M.Judd, P.A.Tasker and R.W.Turner, Department of Chemistry, The Polytechnic of North London, London N7 8DB and ICI Pharmaceuticals Division, Mereside Alderley Park, Macclesfield, Cheshire SK10 4TG UK.

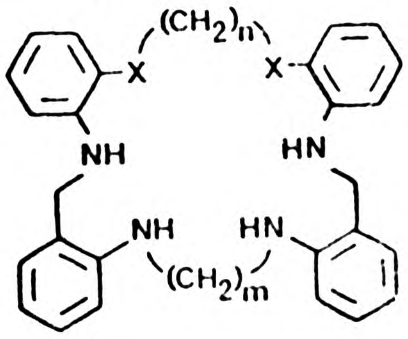
Metal-free sexadentate di-imine ligands of the type I have been prepared from the dialdehydes II. The range of distinctive physical properties of the ligands I is reflected in the considerable variation of reaction conditions and methods of isolation which are required for their preparation from the reactions



II[1]

I

The 20-membered macrocycles (I, m=n=2, X=O,S or NH) co-ordinate readily to Cu(II). The co-ordination numbers and geometries in the resulting complexes will be discussed. Preliminary experiments showed that it was not possible to prepare the Cu(II) complexes directly from condensation reactions of II in the presence of Cu(II) salts under conditions which had previously[2] been successful for other 1st row transition metal ions. The di-imine ligands have been reduced to form tetramines (III, X=O,S) and hexamines (III, X=NH) which are also potentially sexadentate ligands and form stable Cu(II) complexes. Effects of variation of the donor set on the properties of the free ligands and their Cu(II) complexes will be described.



III

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P.M.Judd,P.A.Tasker,R.W.Turner

Inorganica Chimica Acta, 53 (1981) L265–L266
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The Preparation of Sterically-crowded Macrocyclic Copper(II) Complexes from N,N'-di(o-benzoylphenyl)oxalodiamide: the X-ray Structure Determination of {5,12-diphenyl-18,19-dioxo-17,18,19,20-tetrahydrotribenzo[*c,i,m*][1,4,8,11]tetra-azacyclotetradecinato(2−)}dimethylformamidocopper(II)

K. HENRICK, P. M. JUDD*, M. McPARTLIN, P. A. TASKER*

Department of Chemistry, The Polytechnic of North London, London N7 8DB, U.K.

and R. W. TURNER

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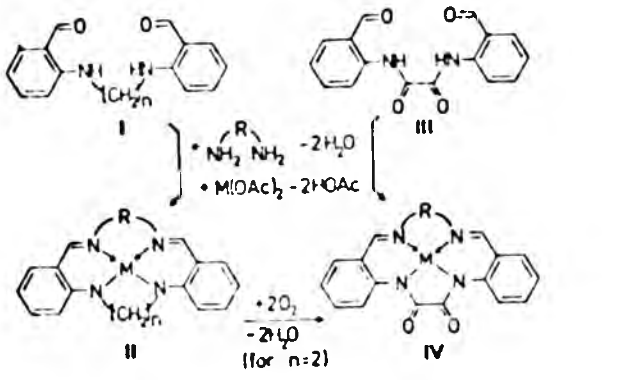
Received December, 23, 1980

The use of N,N'-bis(2-aminobenzaldehyde) compounds I as precursors in the synthesis of metal complexes II of macrocyclic quadridentate imine ligands has been well documented [1, 2]. Recently [3] this approach was extended by using 2,2'-(oxalyldiimino)-bisbenzaldehyde III in condensation reactions with di-primary amines in the presence of metal(II) acetates. These gave (see Scheme) the neutral complexes IV, in which the deprotonated amide nitrogen atoms are co-ordinated to the metal ions. In certain cases the same oxamido complexes IV can be also obtained [4] by oxygenation of an ethane bridge between the anilino nitrogen atoms in the complexes II (see Scheme).



We report here the preparation of complexes related to IV which carry a phenyl substituent at the azomethine carbon atom, and are thus subject to severe steric constraints which are likely to reduce the planarity of the macrocycles and possibly force them to present non-regular geometries of their 'N_4^{2-}' donor sets to any complexed metal ion. The complexes V and VI were obtained by refluxing a solution of N,N'-di(*o*-benzoylphenyl)oxalodiamide [5], copper(II) acetate and 1,2-diaminoethane or 1,2-diaminobenzene in dimethylformamide under conditions similar to those described [3] for the preparation of the related aldimine complexes IV. After 48 hours the solutions were filtered, and crystals separated on cooling after addition of a small volume of methanol, giving V as its dihydrate and VI as a dimethylformamide adduct, as judged by infrared spectra and analytical data.

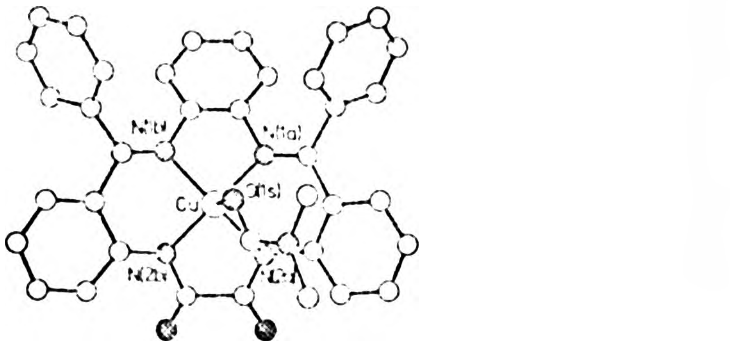
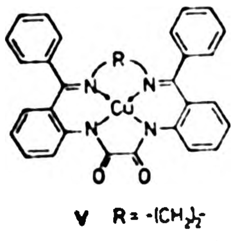


Fig. 1. The molecular structure of the dimethylformamide complex VI. Bond lengths to the Cu atom (Å) are: N(1a), 1.925(9); N(2a), 1.925(8); N(1b), 1.987(8), N(2b), 1.9[illegible](8); O(1s), 2.537(10); and angles subtended at the Cu atom by pairs of donor atoms are: N(1a), N(2a) 91.2(3); N(1a), N(1b) 86.8(4); N(1a), N(2b) 168.7(4); N(1a), O(1s) 86.[illegible](4); N(2a), N(1b) 167.8(4); N(2a), N(2b) 83.1(3); N(2a), O(1s) 90.3(3); N(1b), N(2b) 91.6(3); N(1b), O(1s) 101.4(3); N(2b), O(1s) 105.3(4)°.



V R = $-(CH_2)_2-$

VI R = $-(C_6H_4\text{-}o)-$

Crystal data for VI: $C_{34}H_{22}N_4O_2Cu \cdot C_3H_7NO$ dark brown prisms from dmf, $M = 655.2$, triclinic, space group $P\bar{1}$, $a = 9.072(2)$, $b = 11.049(4)$, $c = 16.873(5)$ Å, $\alpha = 78.82(3)$, $\beta = 102.77(3)$, $\gamma = 107.78°$, $Z = 2$, $I/\sigma(I) > 3.0$, θ-range 3–25°, $R = 0.082$ for 2283 data obtained on a Philips PW1100 diffractometer with Mo-K_α radiation.

The structure determination shows that the copper atom in the complex VI has an approximately square pyramidal coordination geometry (see Fig. 1). The apical donor atom is provided by the dimethylformamide oxygen atom, which is more weakly bonded than the basal nitrogen atoms.

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*Authors to whom correspondence should be addressed.

Inorganica Chimica Acta, 53 (1981) L265–L266

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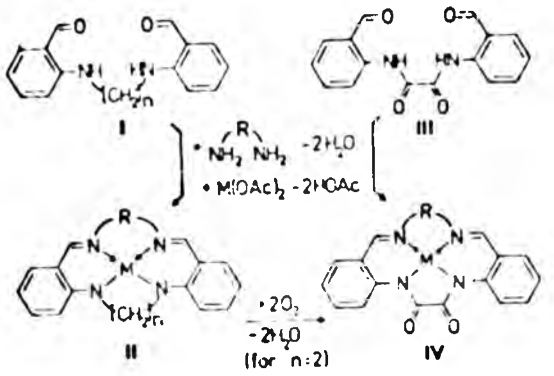

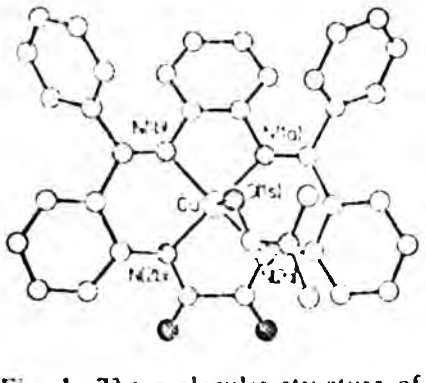

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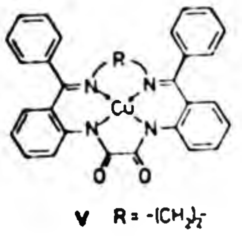

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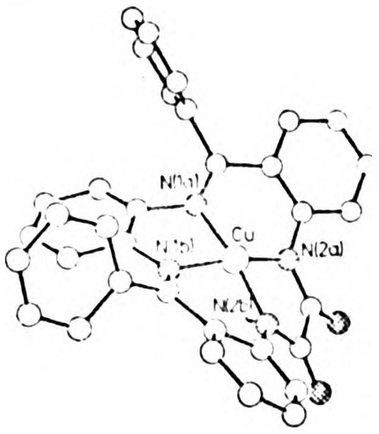

Fig. 2. The 'saddle-shaped' configuration of the chelate rings in VI. The co-ordinated dimethylformamide has been omitted for clarity.

The macrocyclic complex has an arrangement of its chelate rings which can be described as "saddle-shaped" [6]. The two 5-membered chelate rings containing the oxanilide nitrogens [N(2a) and N(2b)], and the *o*-phenylene nitrogen atoms [N(1a) and N(1b)], are tilted approximately equally (18° and 17° respectively) to the same side of the 'N_4' plane. The two *o*-anilino-imino six-membered chelate rings are bent to the other side of the 'N_4' plane by 13° and 9°. This conformation of the ligand increases the separation between the β-hydrogen atoms on the phenyl rings, and there are no particularly short intramolecular contacts between these hydrogen atoms (all > 2.5 Å). .

Despite the "saddle-shape" of the macrocycle, its 'N_4^{2-}' donor set is very nearly planar (deviations of individual nitrogen atoms from the least squares plane are all less than 0.01 Å). It is therefore possible that other related phenylketimine macrocycles [7] may give complexes which have square planar, square pyramidal or *trans*-octahedral structures.

Acknowledgements

We thank the S.R.C. for a studentship (P.M.J.) and for diffractometer equipment and computing facilities.

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Dinucleating Octaaza Macrocyclic Ligands from Simple Imine Condensations

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Received February 19, 1981

Macrocyclic ligands which are capable of incorporating two metal ions[1] offer the possibility of studying unusual electronic and chemical properties which depend upon proximity of two metal centers. An advantage of macrocyclic systems for this type of investigation is that variation of ring size or other geometric constraints should allow the separation and disposition of the two metal ions to be controlled in a systematic manner. In this paper we describe a series of such ligands which have been obtained in high yields from simple imine condensation reactions and have been characterized by field desorption mass spectrometry and X-ray structure determination.

We have reported[2] that under appropriate conditions the dialdehyde **1a** can be condensed with a range of diamines **2** to give tetraaza macrocycles **3** with a wide range of ring sizes. These reactions proceed without addition of "metal-ion templates",[3] provided that reaction conditions and solvents are selected which allow the free ligands to separate from solution before they can undergo conversion to species which are less soluble or thermodynamically more stable. It was noted,[2] for example, that on prolonged heating in methanol, **3a** is converted to a species of higher relative molecular mass (*m*.). We have now characterized a number of the higher *m*. materials obtained from condensations under conditions defined in Scheme I and shown them to be an

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(1) (a) Groh, S. E. *Isr. J. Chem.* 1976, *15*, 277–307. (b) Fenton, D. E.; Lintvedt, R. L. *J. Am. Chem. Soc.* 1978, *100*, 6367–6372. (c) Fenton, D. E.; Bresciani Pahor, N.; Calligaris, M.; Nardin, G.; Randaccio, L. *J. Chem. Soc., Chem. Commun.* 1979, 39–40. (d) Gagné, R. R.; Henling, L. M.; Kistenmacher, T. J. *Inorg. Chem.* 1980, *19*, 1226–1231. (e) Burnett, M. G.; McKee, V.; Nelson, S. M.; Drew, M. G. B. *J. Chem. Soc., Chem. Commun.* 1980, 829–831. (f) Kahn, O.; Morgenstern-Badarau, I.; Audiere, J. P.; Lehn, J. M.; Sullivan, S. A. *J. Am. Chem. Soc.* 1980, *102*, 5936–5938. (g) Coughlin, P. K.; Lippard, S. J.; Martin, A. E.; Bulkowski, J. E. *J. Am. Chem. Soc.* 1980, *102*, 7616–7617.

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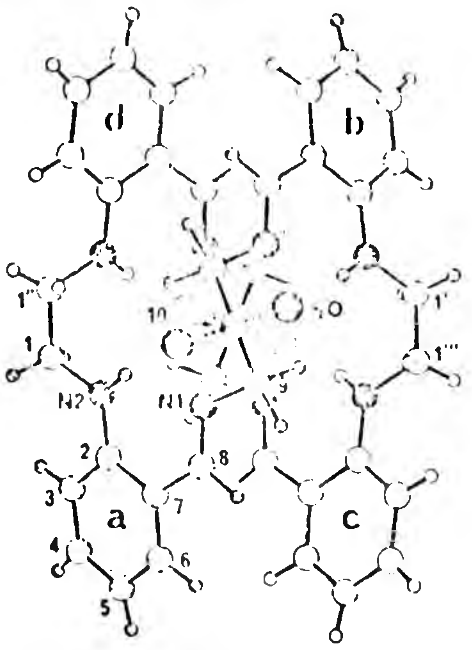


Figure 1. Tetraimine 5b, showing the disorder of the hydroxyl groups about the 2-fold axis which passes through carbon atoms C(10). Another crystallographic C_2 axis passes through the midpoints of the C(1)–C(1) bonds. Shaded C and H atoms are in the half of the molecule nearer the viewer.

interesting new class of potentially octadentate macrocycles 5.

These high m_r compounds, which were obtained (see Scheme I) from reactions of the diamines 2a–c, are relatively insoluble and involatile, and cryoscopic methods and electron-impact mass spectrometry could not be used to determine their relative molecular masses. However, the samples showed simple field desorption (FD) mass spectra,[4] giving molecular ions compatible with the [2 + 2] condensation products:[5] 5a, m/e 584, 5b, m/e 645 $(M + 1)^+$, 5c, m/e 697 $(M - 1)^+$. No fragmentation products were observed in the range m/e 400–800.

FDMS also proved useful in identifying compounds which were present when mixtures of products were obtained from similar condensation reactions. For example, a mixture (ca. 1:4) of the diimine 4 and the tetraimine 6 [m/e 307 $(M + 1)^+$ and m/e 613 $(M + 1)^+$, respectively] was obtained from the condensation of the trimethylene-bridged dialdehyde 1b and 1,2-diaminoethane (1:1.1, 4 h in 15-cm^3 refluxing $CHCl_3$). These substrates have been used previously,[6] but under conditions of high dilution, to prepare the diimine 4.

An X-ray structure determination[7] confirmed the presence of a 30-membered ring in 5b (see Figure 1). The inner great ring has a configuration which effectively creates two "N_4" donor sets (from the o-iminoanilino units of a with d and b with c, see Figure 1), in the two halves of the molecule. Such an arrangement would cause close approximation of two metal ions in a dinuclear complex, because the centroids of the two donor sets are separated by only 3.44 Å. A similar ligand geometry is found[8] in a dicopper complex of the smaller ring 5a in which the two copper ions are forced to adopt a very short Cu–Cu bond [2.445 (5) Å].

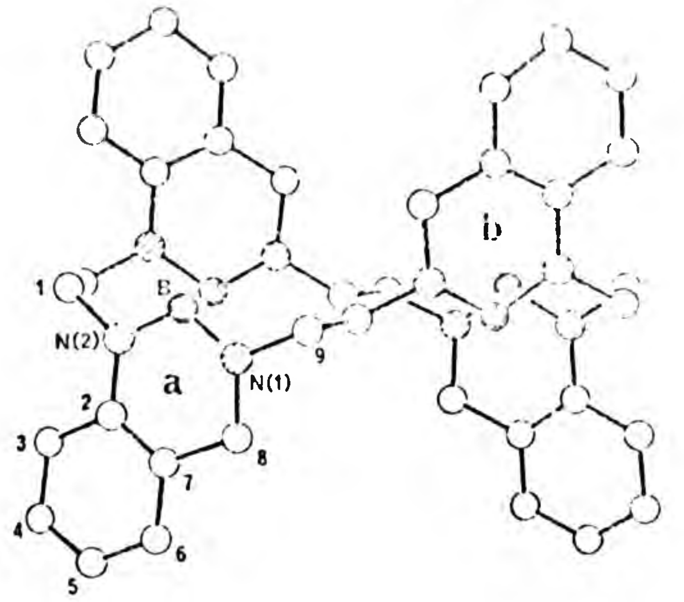
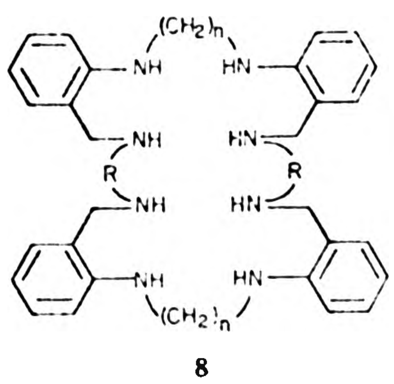


Figure 2. The 20-membered B–N heterocycle 7.

A crystallographic 2-fold axis passes through the carbon atoms having the hydroxyl substituents, and the oxygen atoms are statistically disordered with half-occupancies of the sites shown in Figure 1. Consequently, the structure determination does not allow a distinction to be made between meso and racemic isomeric forms for 5b.

We conclude that ease of isolation of the metal-free macrocycles 5 is dependent on the presence of strong *intra*molecular hydrogen bonding in the o-iminoanilino units. The geometry of the o-iminoanilino unit in 5b is very similar to that found[2] in the related tetraaza macrocycles 3. Reactions of 2,6-diacetylpyridine with certain diamines have also been observed[9] to give large ring ligands by [2 + 2] condensations,[9] but for these systems the new chelate rings are of the α-diimine type and do not have the facility to form *intra*molecular H bonds. In these cases the free ligands have not been isolated, but an extensive range of mono- and binuclear complexes have been prepared[9] by carrying out transmetalation reactions on complexes prepared in the presence of certain metal ion templates.

The 28-membered ring structure for 5a was indirectly confirmed by x-ray structure analysis[10] of an unusual borane adduct (7) which was obtained as an intermediate in the reduction with borane–THF to give the corresponding octaamine 8. Crystals of 7 which



8

separated from a suspension of 5a in borane–THF gave a sharp infrared absorption band at 2510 cm^{-1}, a region in which B–H stretching modes are known to occur. They were found to be surprisingly stable to hydrolysis, and X-ray diffraction data were

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(4) Spectra were obtained on a KRATOS MS50 spectrometer, operated at 8 kV accelerating voltage and with a potential difference of [illegible] kV between the emitter and extractor plate. Spectra, recorded on oscillograph paper, were calibrated with the EI spectrum of [illegible] (Heimann, J.; [illegible] H. [illegible] *[illegible]* 1977, 27, 171–175). High-temperature activated emitters were loaded by dipping into either a solution (5c and 4, 6) or a suspension (5a,b 8a) in $CHCl_3$. Emitter heating currents in the range 15–21 mA were required to desorb these compounds.

(5) The hydrogenated octaaza macrocycle (8, R = $(CH_2)_2$, n = 2) and a related "N_4O_2" system (with phenoxo groups replacing the anilino units; Lindoy, L. F. et al., unpublished results) were also identified by FDMS measurements [m/e 592 $(M)^+$ and 597 $(M + 1)^+$, respectively].

(6) Black, D. St. C.; Hartshorn, A. J.; Horner, M.; Hünig, S. *Aust. J. Chem.* 1977, 30, 2493–2514.

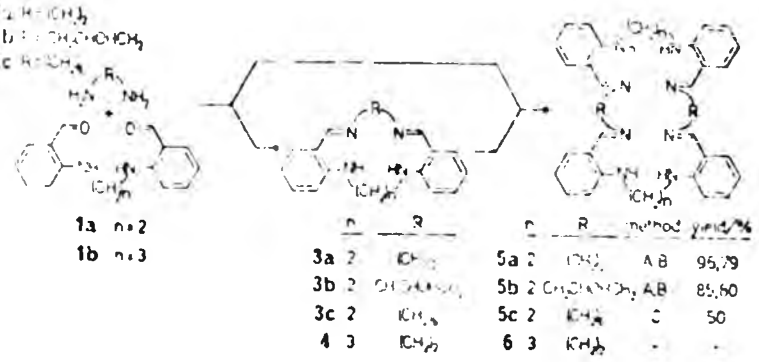
(7) Crystal data for 5b, 7,8,9,16,17,18,19,26,27,28,35,36,37,38-tetradecahydro-8,27-dihydroxytetrabenzo[[illegible]]-1,4,8,12,16,19,23,27-octaazacyclotriacontine: $C_{38}H_{44}N_8O_2$, M_r 644.8, orthorhombic, space group $Fdd2$, a = 33.076 (3), b = 17.4[illegible] (2), c = 11.787 (3) Å, V = 6789.3 Å^3, Z = 8, D_c = 1.26 g cm^{-3}, μ(Mo Kα) = 0.45 cm^{-1}, 2047 intensities were recorded on a Philips PW1100 four-circle diffractometer and merged to give 701 unique observed reflections [$I > 3\sigma(I)$]. The residuals are R = 0.040 and R_w = $\sum w^{1/2}\Delta/\sum w^{1/2}|F_o|$ = 0.069. The structure was solved by direct methods and refined by the full matrix least squares method.

(8) Dancey, K. P.; Tasker, P. A.; Price, R.; Hatfield, W. E.; Brower, D. C. *J. Chem. Soc., Chem. Commun.* 1980, 1248–1250.

(9) (a) Drew, M. G. B.; Knox, C. V.; Nelson, S. M. *J. Chem. Soc., Dalton Trans.* 1980, 942–948. (b) Drew, M. G. B.; McFall, S. G.; Nelson, S. M.; Waters, C. P. *J. Chem. Res., Synop.* 1979, 16–17. (c) Drew, M. G. B.; McCann, M. *J. Chem. Soc., Chem. Commun.* 1979, 481–482.

(10) Crystal data for 7: $C_{36}H_{44}B_4N_8$, M_r 632.1, orthorhombic, space group $Pcca$, a = 20.162 (2), b = 10.541 (2), c = 16.469 (2) Å, V = 3500.4 Å^3, Z = 4, D_c = 1.20 g cm^{-3}, μ(Mo Kα) = 0.39 cm^{-1}, 3469 intensities were recorded on a Philips PW1100 four-circle diffractometer and merged to give [illegible] unique observed reflections [$I > 3\sigma(I)$]. The residuals are R = [illegible] and R_w = $\sum w^{1/2}\Delta/\sum w^{1/2}|F_o|$ = 0.096. The structure was solved by direct methods and refined by the full matrix least squares method.

Scheme I[a]



[a] Reaction conditions are (A) **1a** (2 mmol) + **2** (2.2 mmol) in MeOH (40–50 cm^3) refluxed 6 h and a further 24 h after addition of CHCl$_3$ (5 cm^3); (B) **3** heated 24 h in refluxing MeOH containing acetic acid (1 mol l^{-1}); (C) **1a** (10 mmol) + **2c** (11.5 mmol) in EtOH (50 cm^3) refluxed for 1.5 h, filtered, and set aside for 12 h.

collected without special precautions to protect the crystals from atmospheric moisture. Structure determination showed this material to be tetrabenzo[*a,g,o,u*]-1,5,8,12,15,19,22,26-octaaza-29,30,31,32-tetraborapentacyclo[$1^{1,5}.1^{8,12}.1^{15,19}.1^{22,26}$]dotriacontane in which a B–H unit has been incorporated between each pair of *o*-amino anilino nitrogen to give the unusual 20 membered B–N heterocycle shown in Figure 2. The two halves of the molecule are related by a crystallographic 2-fold axis perpendicular to the best plane through the inner great ring.

The isolation of the potentially octadentate macrocycles **5** and **8** presents the interesting possibility of preparing a series of dinuclear complexes in which the separation and disposition of the two metal ions is controlled by ring sizes and other geometric constraints in the ligands.

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Supplementary Material Available: Fractional coordinates, thermal parameters, bond distances, bond angles and observed and calculated structure factors for compounds 5a and 7 (7 pages). Ordering information is given on any current masthead page.