Some Studies in the Chemistry of Mercury and Lithium

A Thesis Submitted for the Degree

of

Doctor of Philosophy

by

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To my wife.

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The enhanced stability of perfluoroaromatic lithium species (compared with their hydrogen analogues) has been used to study their thermal degredation reactions and the reactions of the unstable intermediates thus produced, as effectively only one thermal reaction path exists. Attempts have been made to test exisiting hypotheses, and also to rationalise results by theoretical MO calculations. Especial emphasis has been put on ^{80m}Br radio-labelling studies.

A similar enhancement of stability for the perfluoro organo-mercurials makes some of them ideal substrates for solid state kinetic studies and a wide range of organo-mercury complexes has been studies by thermal and other techniques. Partly by way of comparison and partly as an extension of the work X-ray structure determinations have been carried out on the hydrogen analogue compounds as well as the fluoro compounds.

Publications

1. The Addition of $Li^{80m}Br$ to Polyhalogenoarynes; D.J. Malcolme-Lawes, A.G. Massey and D. Wickens; J. Chem. Soc. Chem. Commun. 1977 933-934.

2. A Reinvestigation of o-Phenylenemercurials II: The Structure of Tribenzo [b,e,h][1,4,7] trimercuronin; D.S. Brown, A.G. Massey and D.A. Wickens; Acta Cryst. B34 1695-1697 (1978).

3. A Reinvestigation of o-Phenylenemercurials III: On the Decarboxylation of Mercury (II) Tetrafluorophthallate; D.S. Brown, A.G. Massey and D.A. Wickens; submitted to J. Chem. Soc. Dalton Trans.

4. A Reinvestigation of o-Phenylenemercurials IV; The adducts of perfluorotribenzo [b,e,h][1,4,7] trimercuronin and the crystal and molecular structure of its 1:1 4-phenylpyridine solvate; M.C. Ball, D.S.Brown, A.G. Massey and D.A. Wickens; submitted to J. Chem. Soc. Dalton Trans.

Conference Papers

1. Some studies on the fluoroaromatic compounds of mercury; M.C.Ball, D.S.Brown, A.G. Massey and D.A.Wickens; 9th International Symposium on Fluorine Chemistry, Avignon, Sept. 3-7 1979.

2. o-Phenylenemercurials; D.S.Brown, A.G. Massey and D.A. Wickens; 9th International Conference on Organometallic Chemistry, Dijon, Sept. 3-7 1979.

3. o-Phenylenemercurials; D.A.Wickens; Midland Region Post-Graduate Meeting, Dalton Division, Chemical Society, Leicester, 27 March 1979.

Acknowledgements

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Chapter 1

Introduction

Summary: the chemistry pertaining to highly fluorinated aromatic systems and the organolithium compounds derived from them is reviewed. The chemistry of organomercury compounds is briefly presented as is that of polyalkylbenzenes.

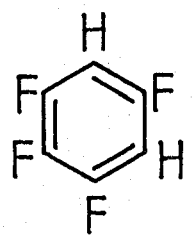
Introduction

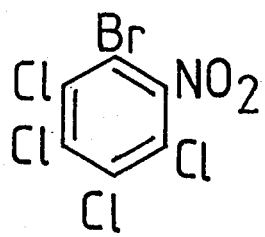
Conventional ("perhydro") organometallic chemistry has produced a large number of interesting and unusual compounds which span a very wide range of bonding characteristics from the simple σ-bonds of tetramethyltitanium [1] via the π-bonding of ferrocene [2,3] to bis(cyclooctatetraene)uranium [4] in which the bonding is believed to involve f-orbitals. In addition there are many compounds such as methylcyclopentadienylmolybdenum tricarbonyl [5] which possess more than one type of metal-carbon bond. Given that this is so it seems at first odd that considerable effort has been expended to make the same compounds again save for halogen atoms or methyl groups in place of most or all of the hydrogen atoms. The reason is that, whilst many of the per-substituted compounds are very similar to the "parent" compounds, the differences in reactivities, properties and preparation techniques are often more informative than investigations on wholely new compounds.

Nomenclature

The normal rules for naming organic and organo-metallic compounds start on the assumption that all "spare" positions on carbon atoms are occupied by hydrogen atoms: any atom or group present other than hydrogen is specified. This rule is less reasonable when most or all sites are substituted by identical atoms or groups and thus in perhalo chemistry the fully halogenated molecules are regarded as the parent species with hydrogen regarded as a substituent

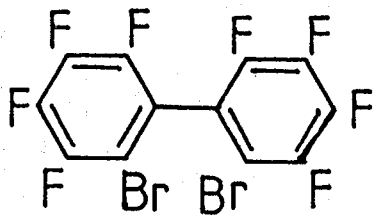
e.g.





1,3-dihydrotetra-fluorobenzene (1,3,5,6-tetra-fluorobenzene)

1-bromo-2-nitrotetrachloro-benzene (1-bromo-2,3,4,5-tetrachloro-6-nitrobenzene)



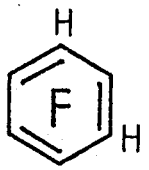
2,2'-dibromoocta-fluorobiphenyl

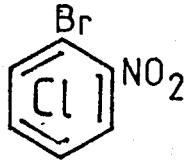
(2,2'-dibromo-3,3',4,4',5,5',6,6'-octa-fluorobiphenyl)

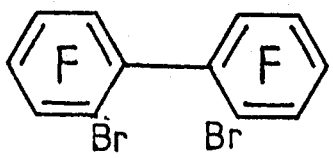
As can be seen the above semi-systematic names are usually shorter than the wholely systematic names which are given in parentheses. The major reason, however, for the adoption of the semi-systematic approach is that, with no loss in clarity, it emphasises the similarities between conventional and perhalo molecules. Thus for the third example above, many of the reactions of 2,2'-dibromooctafluorobiphenyl are close or exact analogues of the reactions of 2,2'-dibromobiphenyl.

For the purposes of this thesis the spirit of the system has been extended to polyalkylbenzenes and their derivatives. The trivial names for the parent hydrocarbons are given together with the semi-systematic names in Table 1 as much of the literature cited uses the trivial names. Abbreviations used are also given in this Table.

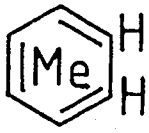
A similar shorthand is employed for structural formulae, and F, Cl or Me in the middle of an aromatic ring indicates that all unmarked positions are appropriately substituted. The above examples thus become







and 1,2-dihydrotetramethylbenzene becomes

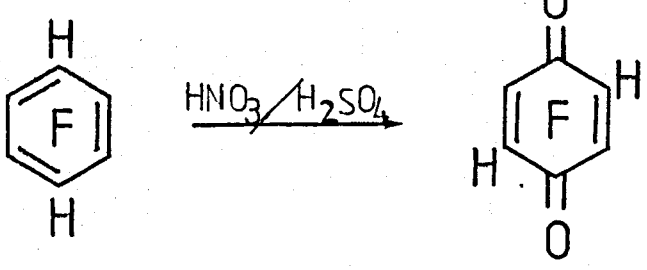

Me
H
H

Syntheses of Poly fluoro-aromatic Systems

The Balz-Schiemann reaction [6] is the classical organic method for the introduction of fluorine into an aromatic system:

$$ArH \longrightarrow ArNO_2 \longrightarrow ArNH_2 \longrightarrow ArN_2.BF_4 \longrightarrow ArF+N_2+BF_3$$

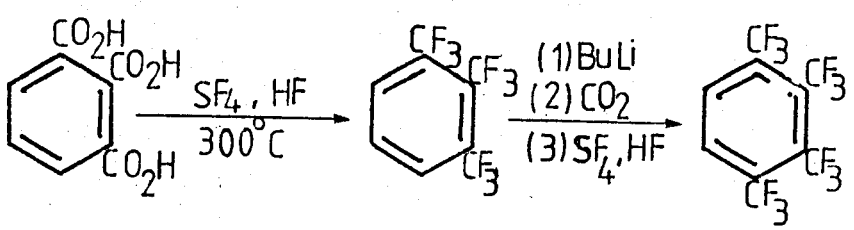
It has the advantage that, after the initial nitration stage, no isomerisation is possible. The disadvantages are the several steps and the progressively more severe conditions required for the nitration as more electron-withdrawing fluorine atoms are introduced. After four fluorines have been inserted oxidation occurs instead of nitration:[7,8]

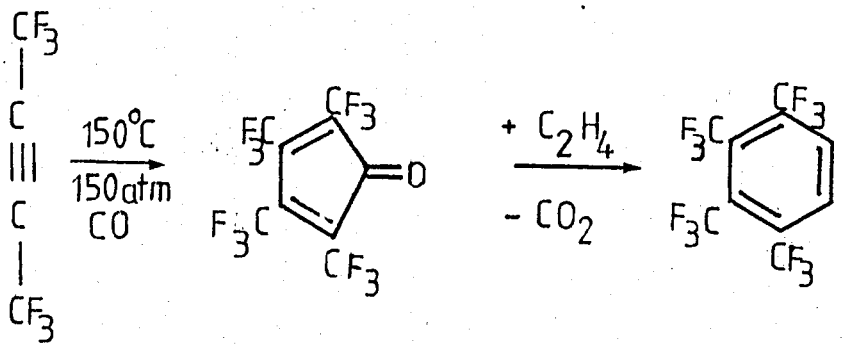


Pyrolyses (of, for example [9], tribromofluoromethane) produce wholely halogenated aromatic systems but the commercially practical routes involve fluorinating agents such as bromine trifluoride,[10] cobalt (III) fluoride [11,12] and gaseous fluorine [13] which simultaneously fluorinate and de-aromatise phenyl and biphenyl systems. Re-aromatisation under vigorous conditions [11,13,14,15,16,

gives a mixture of highly fluorinated aromatic systems. The more readily available perchloroaromatic compounds (produced by similar chlorination reaction schemes) can have the halogens exchanged with potassium fluoride either directly at high temperature [17,18] or in an aprotic solvent.[19,20]

Some more exotic syntheses [21,22,23] have been reported more recently for fluoromethylated arenes and are summarised below. The extreme conditions employed make these derivatives still very much a specialised research area.





Reactions of Fluoro-aromatic Compounds

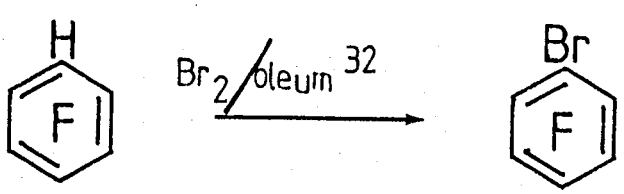
The combined electron-withdrawing effect of the fluorine atoms in hexafluorobenzene is shown both theoretically by SCF MO calculations [24] and by the relative ease with which it undergoes nucleophilic attack [25,26,27]:

$$X^{\ominus} + C_6F_6 \longrightarrow C_6F_5X + F^{\ominus} \quad X=OH,SH,OCH_3,NH_2 \text{ etc.}$$

These reactions have been studied kinetically [28,29] as well as by analysis of reaction products. The calculations show that in benzene the mean electronic charge on the carbon atom is 6.061 electrons, whereas in hexafluorobenzene it is 5.889 electrons.

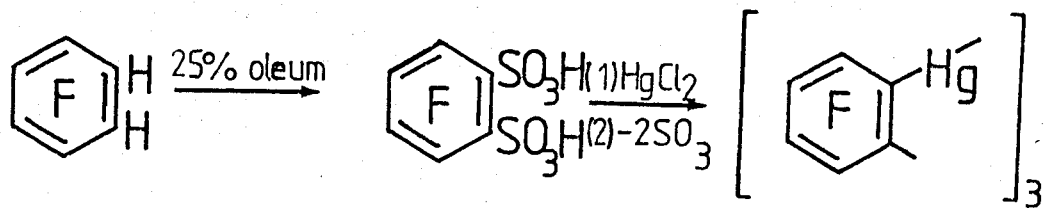
Further nucleophilic attack occurs typically para to any substituent [25], giving 1,4-disubstituted tetrafluorobenzenes. On the basis that a biphenyl can be treated as two mono-substituted phenyl systems, decafluorobiphenyl undergoes nucleophilic attack to produce 4,4'-disubstituted biphenyls.[30]

Halogenation of hydrofluoroaromatics can be carried out in oleum,[31-35] the forcing conditions being necessary because of the electrophilic nature of the reaction.[36]

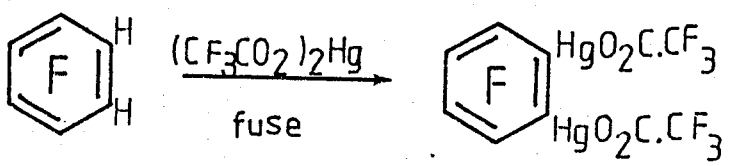


This is in complete contrast to methylated benzenes where, for example, the bromination of pentamethylbenzene occured at the speed of mixing at room temperature in glacial acetic acid.

Similarly, sulphonation of hydrofluoroarenes has been achieved in oleum [37], and the corresponding desulphonation has been used to prepare organomercurials:[37]

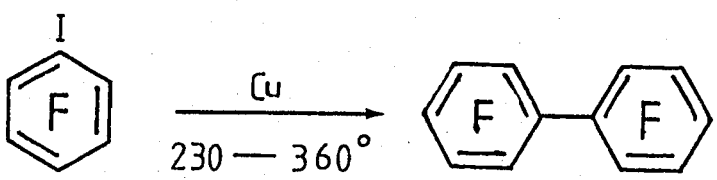


Mercuration is another electrophilic reaction that has been performed [38], and permercuration can also be achieved [39,40]:



The reaction can be used to prepare halogenated derivatives by cleavage of the carbon-mercury bonds with trihalide ions. [39,40]

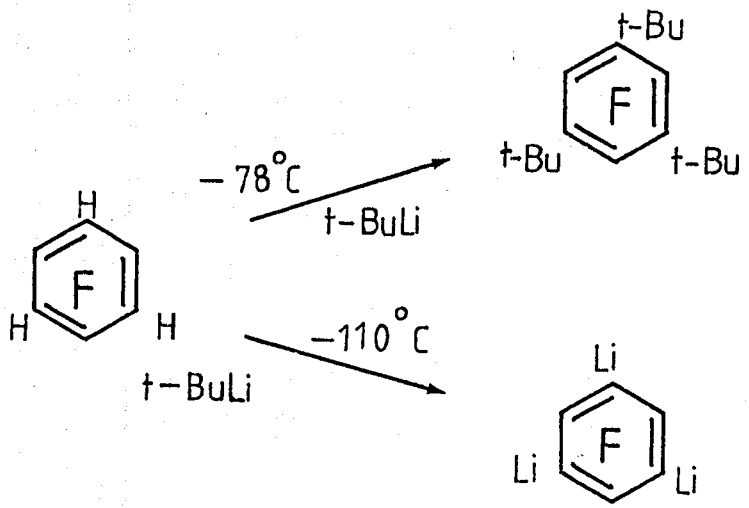
Ullman coupling [41] occurs in good yield to give biphenyls:



Pentafluorobenzene and the various halopentafluorobenzenes all react with n-butyllithium to give pentafluorophenyllithium.[42,43,44] These are the most convenient preparations of this compound, but lithium metal will produce pentafluorophenyllithium with pentafluorobenzene[42] as will lithium amalgam with bromopentafluorobenzene.[45] The n-butyllithium reaction is mechanically the easiest preparation as it proceeds wholely in solution and, furthermore, n-butyllithium is available commercially in hexane solution. The usual practice is to inject a known volume of standardised n-butyllithium solution into a solution of a fluoroarene in ether or THF at -78°C. Standardisation is necessary as the commercial preparations of organolithium reagents often have alkoxide contaminants: the double titration method of Gilman[46] is used to assay both total and organic lithium. Empirically a cloudy solution is useless. Lithiation of C_6F_5X (X=H,Cl,Br,I) proceeds quantitatively in ether/hexane at -78°C, the only variations being those of reaction times: generally lithium/hydrogen exchange either takes longer or requires more forcing conditions, such as hexane/THF as solvent.[42] Lithium/halogen exchange occurs in preference to lithium/hydrogen exchange[47] as would be expected from the above observations.

Dilithiation requires still more forcing conditions and specifically this means more reactive lithium alkyls: methyllithium has been reported both as giving 1,2-dilithiotetrafluorobenzene[48] and 1,2-dimethyltetra-

fluorobenzene [49] with 1,2-dibromotetrafluorobenzene. Of the two reactions that can occur (lithiation with production of alkyl halide and alkylation with production of lithium halide) metallation seems to predominate at low temperature. Gilman made 1,3,5-trilithiotrifluorobenzene at -110°C using t-butyllithium and 1,3,5-trifluorobenzene, but at -78°C the major product was 1,3,5-tris(t-butyl)-trifluorobenzene.[51]



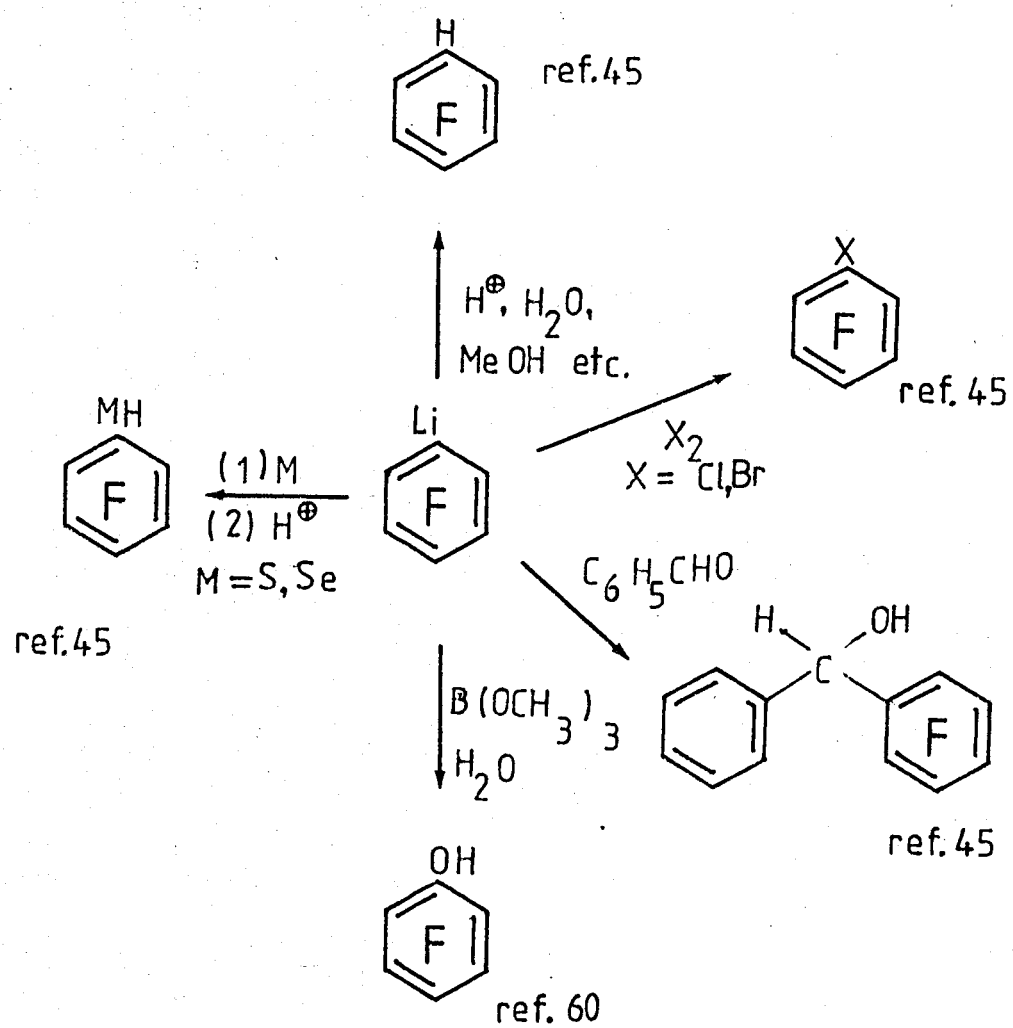
Formation of Grignard reagents is generally more difficult than the analogous lithiation, but has been achieved both from magnesium metal and halopentafluoro-benzenes [51] and from the action of alkylmagnesium halides on pentafluorobenzene [42] and bromopentafluorobenzene.[52] The Grignard reagents can be refluxed unchanged in diethyl ether, but unfortunately reaction yields can be very low from that solvent: carbonation gives pentafluorobenzoic acid in yields of 3% or less.[33,51,53] In THF, where

yields of acid were up to 70%.[53,54] nucleophilic attack by pentafluorophenyl "anions" takes place at -10°C [55,56,57] and solutions rapidly decompose on refluxing,[55,58,59] presumably by elimination of magnesium halofluoride.

To summarise, electrophilic attack on the polyfluoro-aromatic system requires rather forcing conditions, whereas nucleophilic attack occurs much more easily. This is the reverse of the situation for perhydroaromatic systems.

Properties of Polyfluoroaryllithium Compounds

The standard reactions of conventional aryllithium species are echoed for polyfluoroaryllithium compounds and a selection is given below.



Intermolecular elimination of lithium halide occurs with metal and metalloidal halides, to give organometallic compounds of boron,[61] selenium, [62] copper [63] and mercury[64] amongst many others. The reaction is not confined to monolithio species and perfluoro-o-phenyleneantimony has

been claimed [48] as have polymers from cadmium and mercury halides with 1,4-dilithiotetrafluorobenzene.[65]

$$MX_n + nAr_F Li \longrightarrow M(Ar_F)_n + n\ LiX$$

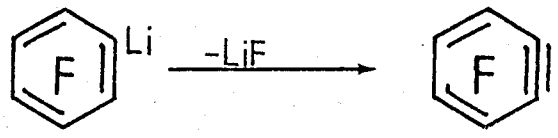
Two major pathways exist for the thermal decomposition of lithium polyfluoroaryls that do not for conventional lithium aryls and both involve elimination of lithium fluoride [66, 67]. At low temperature the elimination is due to intermolecular nucleophilic attack, building up para-linked polyfluoropolyphenylenes.[66]

$$Ar_F - F + Ar'_F - Li \longrightarrow Ar_F - Ar'_F + LiF$$

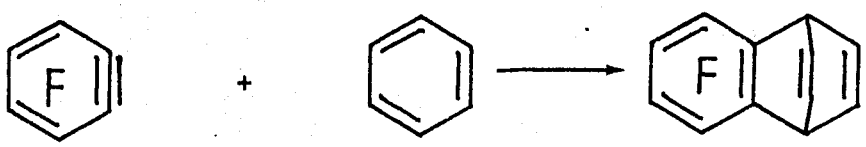
Typically, reaction times of about 7 days and temperatures of $-40^{\circ}C$ are used. Not all reactions give totally para-substituted products: nitropentafluorobenzene forms first 4-nitrononafluorobiphenyl, then the 2-position on the original ring is attacked in preference to the 4'-position, giving 2,4-bis(pentafluorophenyl)-1-nitrotrifluorobenzene, and considerably smaller amounts of 4-nitro-4'-(pentafluorophenyl)octafluorobiphenyl.[66] The greater polarity of the carbon-lithium bond compared with carbon-magnesium bonds presumably accounts for the greater thermal stability of polyfluoroaryl Grignard reagents; the lower effective negative charge on the organic moiety making it less effective in nucleophilic reactions.

The other possible elimination of lithium fluoride

is intramolecular, producing a reactive species best formulated as a polyfluorobenzyne:



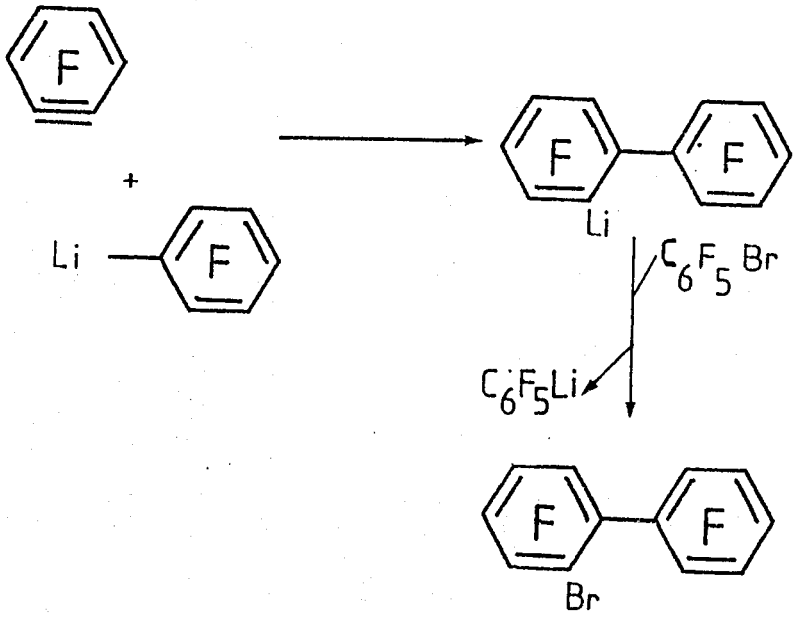
Benzyne itself (C_6H_4:) can be produced by lithiation of fluorobenzene, followed by elimination of lithium fluoride because lithiation occurs totally ortho to the fluorine atom.[68] Support for postulation of benzyne formation is given by a variety of chemical evidence. Tetrafluorobenzyne would be expected to be a very efficient dienophile in the Diels-Alder 1,4-addition reaction and products from 1,4-addition have been isolated from experiments with furan,[45] benzene,[64] and substituted benzenes.[69]



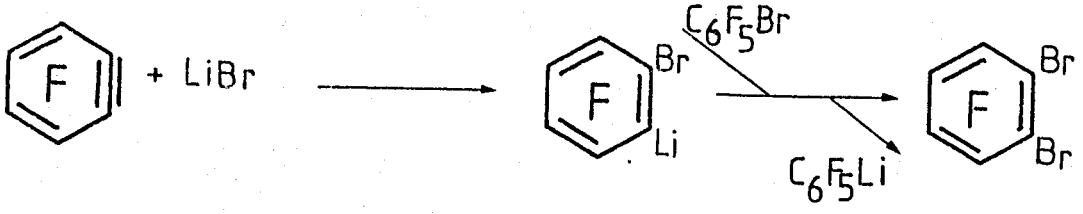
These adducts form a convenient rigid diene group for the formation of transition metal complexes and several have been made.[70]

Polyfluorobenzynes are also capable of 1,2-addition across polar bonds and this provides more evidence for their presence: the production of 2-bromonona-fluoro-

biphenyl[44] would be quite difficult to account for otherwise:



Similarly lithium halides have been shown to add across tetrafluorobenzyne:



In the presence of excess lithium bromide and bromopentafluorobenzene, 1,2-dibromotetrafluorobenzene is the major product. 1,2-Diiodotetrafluorobenzene can similarly be produced from iodopentafluorobenzene and lithium iodide.[66] This "inorganic addition" is discussed more fully in the light of experimental work presented in Chapter 4 of this thesis. Similarly, benzynes generated from Grignard reagents have been shown to exhibit 1,4-addition to dienes.[71]

Syntheses of Organomercurials

Organomercury compounds provide, in their preparation, a microcosm of general organometallic procedures. The only major synthetic route not used in mercury chemistry is transmetallation:

$$R_2M + Hg \longrightarrow R_2Hg + M$$

On the contrary, mercury compounds are often used as the starting organometallic in this class of synthesis as mercury metal, being very inert and low in the electrochemical series, is eliminated by most metals as a readily-separable liquid or colloid.

The reaction of alkyl and aryl halides with alkali metal amalgams often gives organomercurials and only two specific examples are quoted:

$$2\ C_6F_5Br \xrightarrow{Li/Hg} (C_6F_5)_2\ Hg \qquad \text{ref 45}$$

$$o\text{-}C_6H_4Br_2 \xrightarrow{Na/Hg} (C_6H_4Hg)_3 \qquad \text{ref 72}$$

These examples were chosen to illustrate the care needed in the examination of reaction-mixtures where reactive intermediates are possible: lithium amalgam has been used to prepare both bis(pentafluorophenyl)mercury and pentafluorophenyllithium[45]. The other example is valid where the 1,2-dibromobenzene is dissolved in diethyl ether[72],

but in more strongly basic ethers (THF,1,2-dimethoxyethane) the major mercury-containing species is dimeric o-terphenylenemercury:[73]

$$o\text{-}C_6H_4Br_2 \xrightarrow[THF]{Na/Hg} \left[(C_6H_4)_3Hg\right]_2$$

As discussed in the previous sections, mercurials can be made from lithium aryls and mercuric halides:[64]

$$2\ C_6F_5Li + HgCl_2 \xrightarrow{ether} (C_6F_5)_2Hg + 2LiCl$$

Mercury(I) compounds disproportionate under these reaction conditions, and give mercury metal and mercury(II) organometallics.[64] However, organomercury(I) compounds have been postulated as intermediates in electrochemical reactions.[74] The intermolecular halide eliminations are performed by preparation of the organolithium species at -78°C in an ether solvent, followed by addition of mercuric halide, either as a solid or in solution (normally in THF) and allowing the stirred system to warm up to room temperature. This procedure minimises the production of benzyne decomposition products and has been used to prepare, for example, bis(2,3-dihydrotrifluorophenyl)-mercury (this work). The analogous Grignard reactions have been employed to prepare, amongst others, bis(pentafluorophenyl)mercury.[75]

$$2\ C_6F_5MgBr + HgCl_2 \longrightarrow (C_6F_5)_2Hg + 2\ MgClBr$$

The organometallics of the other electropositive elements may be used in a similar manner, and some examples are given:

$$Zn(CH_2\text{-}CH{=}CH_2)_2 + 2HgCl_2 \rightarrow 2(CH_2{=}CH\text{-}CH_2)HgCl + ZnCl_2$$ ref 76

$$2Et_3Al + 3HgCl_2 \longrightarrow 3Et_2Hg + 2AlCl_3$$ ref 77

$$2C_5H_5Na + HgCl_2 \longrightarrow (C_5H_5)_2Hg + 2NaCl$$ ref 78

The major preparative routes, however, are from the lithium derivatives and Grignard reagents rather than the above reaction-types.

Intramolecular elimination reactions provide another route to organomercurials. The presence, in aromatic systems, of electron-withdrawing substituents makes the reactions either occur more easily or at temperatures which do not degrade the product mercurial. Eliminations of N_2, CO_2, SO_2 and SO_3 have all been shown:

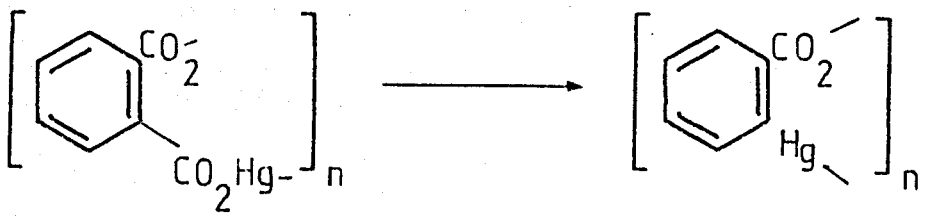
$$2C_6H_5N_2Cl + 2HgCl_2 \longrightarrow 2C_6H_5N_2Cl.HgCl_2 \xrightarrow[(2)\ NH_4OH]{(1)\ Cu} (C_6H_5)_2Hg + 2N_2 + HgCl_2$$ ref 79

$$3C_6F_4(CO_2)_2Hg \longrightarrow (C_6F_4Hg)_3 + 6CO_2$$ ref 80

$$3C_6F_4(SO_3)_2Hg \longrightarrow (C_6F_4Hg)_3 + 6SO_3$$ ref 37

$$m\text{-}NO_2.C_6H_4SO_2Na + HgCl_2 \rightarrow m\text{-}NO_2.C_6H_4HgCl + SO_2 + NaCl$$ ref 81

The usefulness of these methods largely depends on the ease of preparation of the starting materials: normally carboxylic acids are readily available, but decarboxylation may not be easy. Phthallic acid gives a monodecarboxylated cyclic internal salt:



ref 82

Further heating to 370°C caused only charring.[83] The monodecarboxylation also occured in mercury(II) tetrafluorophthallate, but the second decarboxylation proceeds at temperatures of about 300°C.[80]

Desulphination follows the same trend in that it occurs more readily and at lower temperatures in compounds with electron-withdrawing substituents, and desulphonation is of use only in the fluoro-aromatic series.[84] The sulphonates are the least easy derivatives to prepare as sulphonation is reversible and the solubility properties of the products do not lead to easy separation from the reaction mixture. Continuous extraction was used to achieve the purification[37] of the tetrafluorobenzene-1,2-disulphonic acid employed in the example above.

The easiest synthesis for aromatic mercurials is probably the diazo preparation: the diazotisation of aromatic amines is normally quite straightforward.

Mercuric chloride forms insoluble double salts with the diazonium halides and as it is soluble in concentrated hydrochloric acid the precipitation can be carried out without jeopardising the stability of the diazonium compound. The double salt is then reduced with copper to form the arylmercuric chloride. This preparation also shows the effectiveness of electron-withdrawing groups and in their presence the reaction may not be possible due to decomposition of the diazonium salt:

$$ArN_2^{\oplus}Cl^{\ominus} \longrightarrow ArCl + N_2$$

Replacement of a hydrogen atom by HgX (where X is an anion) is possible with active protons and is called mercuration; under forcing conditions less active hydrogen atoms may be replaced (third example below):

$$2CH_3\text{-}C{\equiv}C\text{-}H + HgI_2 \xrightarrow{NaOH} (CH_3\text{-}C{\equiv}C)_2Hg \qquad \text{ref 86}$$

$$C_6H_6 + (CH_3CO_2)_2Hg \xrightarrow{EtOH} C_6H_5Hg(O_2C.CH_3) \qquad \text{ref 87}$$

$$2\ C_6F_5H + HgF_2 \xrightarrow{SbF_5} (C_6F_5)_2Hg \qquad \text{ref 88}$$

The reaction is electrophilic in nature and thus requires more forcing conditions for compounds with electron-withdrawing substituents.[89] The co-ordination of an aromatic system to mercury-presumably an intermediate state in the reaction - has been demonstrated by

preparation of a series of complexes of the form $(SbF_6)_2$ Hg.Ar where Ar represents benzene, toluene, etc.[90] Permercuration, as mentioned in the previous section can be accomplished using mercuric trifluoroacetate, either fusing it with the arene [39] or in a trifluoroacetic acid/trifluoromethylsulphonic acid solvent system.[91]

Mercury metal will replace halogens both in alkyl and aryl halides, in halogenonium compounds and in favourable conditions will replace hydrogen:

$$MeX + Hg \longrightarrow MeHgX \qquad \text{ref 92}$$

$$o\text{-}C_6F_4I_2 + Hg \xrightarrow{300^\circ C} (o\text{-}C_6F_4Hg)_3 \qquad \text{ref 93}$$

$$(C_6H_5)_2Br.Cl + 2Hg \longrightarrow C_6H_5HgBr + C_6H_5HgCl \qquad \text{ref 94}$$

$$2C_6F_5H + Hg \xrightarrow{SbF_5} (C_6F_5)_2Hg \qquad \text{ref 88}$$

Organomercurials can also be produced from organomercury salts by a process known as symmetrisation. The reaction

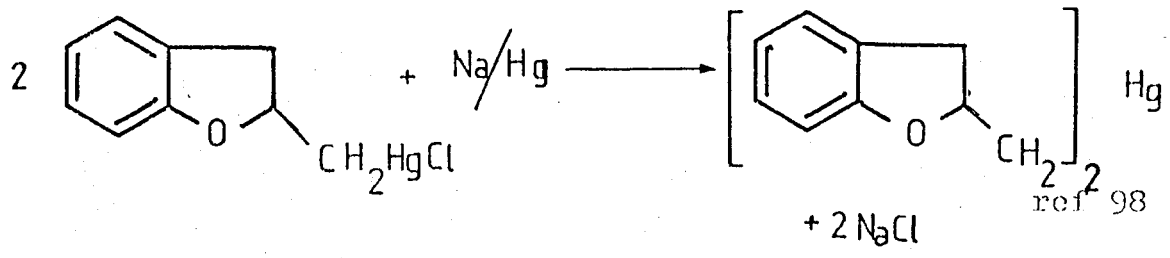
$$R_2Hg + HgX_2 \longrightarrow 2RHgX$$

is reversible and can be driven to the left as the mercuric salt is removed either by reduction or by complex formation:

$$2(o\text{-}C_6H_5.C_6H_4.HgI) + 2KI \longrightarrow (o\text{-}C_6H_5.C_6H_4)_2Hg + K_2HgI_4 \qquad \text{ref 95}$$

$$2CH_3COCH_2HgCl + 2NH_3 \longrightarrow (CH_3COCH_2)_2Hg + (NH_3)_2HgCl_2 \qquad \text{ref 96}$$

$2C_6H_5CH_2HgI + Na_2SnO_2 + H_2O \rightarrow (C_6H_5CH_2)_2Hg + Hg + 2NaI + H_2SnO_3$ ref 97



ref 98

Properties of Organomercurials

The carbon-mercury bond is thermally stable and is stable to moisture, light, bases and nucleophilic reagents. Hydrazine thus substitutes the aromatic ring in bis(pentafluorophenyl)mercury:[99]

$$(C_6F_5)_2Hg \xrightarrow{H_2N.NH_2} (p\text{-}C_6F_4NHNH_2)_2Hg$$

However, the action of organolithium species is to give the mercurial with the less negative organic fragment:[99]

$$2\ n\text{-}C_4H_9Li + (C_6F_5)_2Hg \rightarrow 2\ C_6F_5Li + (n\text{-}C_4H_9)_2Hg$$

Symmetrisation was covered in the previous section as a preparative technique. The reverse reaction ("desymmetrisation") cleaves one of the carbon-mercury bonds:[100]

$$(n\text{-}C_{18}H_{37})_2Hg + HgCl_2 \xrightarrow{\text{ether}} 2\ n\text{-}C_{18}H_{37}HgCl$$

Halogens and trihalide ions also cleave carbon-mercury bonds[39] as mentioned in a previous section:

$$C_6H_5CO_2H \xrightarrow{(CF_3CO_2)_2Hg} (CF_3CO_2Hg)_5C_6CO_2H \xrightarrow{I_3^{\ominus}} C_6I_5CO_2H$$

The greater stability of polyfluoroarylmercurials to acids is shown by the recrystallisation of bis(penta-

fluorophenyl)mercury from conc. sulphuric acid[75], whereas this reagent cleaves diphenylmercury.[101] Organomercurials are still less stable to complexing acids, particularly hydrochloric acid.[101]

The action of more electropositive metals is to deposit mercury metal and form organometallics, a particularly unexpected example being:[102]

$$(C_6H_5\text{-}C{\equiv}C)_2Hg + Yb \longrightarrow (C_6H_5\text{-}C{\equiv}C)Yb + Hg$$

A main-group example is[103]

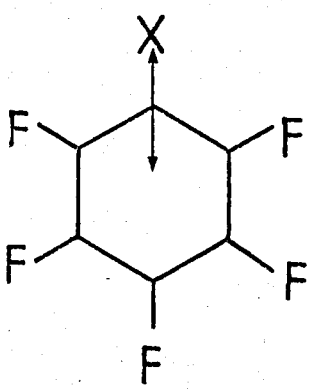
$$2(C_6F_5)_2Hg + Sn \longrightarrow (C_6F_5)_4Sn + 2Hg$$

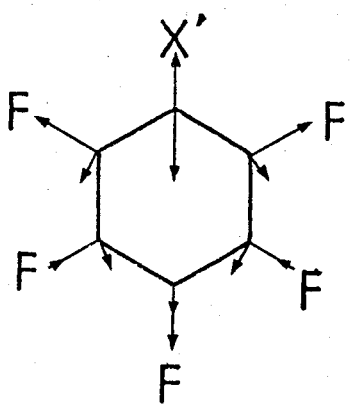
However, alternative reactions can occur where one carbon-mercury is retained:[104]

$$(C_6F_5)_2Hg + \left[\left((C_6H_5)_3P\right)_3 . Pt\right] \rightarrow C_6F_5\text{-}Hg\text{-}\underset{\displaystyle P(C_6H_5)_3}{\overset{\displaystyle P(C_6H_5)_3}{Pt}}\text{-}C_6F_5$$

Spectroscopic investigation of mercury compounds is not simple for a variety of reasons: infra-red spectra suffer from the disadvantage that the Hg atom is both heavy, and fairly weakly bonded, so that vibrations involving it are at low frequency and tend to be coupled to other vibrations. By way of example, in the spectrum of diphenylmercury, all bonds involving mercury directly are below 375cm^{-1} and none correspond directly to a C-Hg stretching mode.[105] In perhaloaryl compounds the

situation is even more complex as calculations on the C_6F_5X system display. The diagrams below show the atoms involved in C-X stretching for hydrogen and a number of halogens,[106,107] but the principle extends to all heavy substituents:[106]





X = H	D = 3105cm^{-1}	X' = Cl	D = 885cm^{-1}
X = D	D = 2315cm^{-1}	X' = Br	D = 836cm^{-1}
		X' = I	D = 808cm^{-1}

No direct allocation of a band to a C-Hg stretching mode was made in a far infra-red study of bis(pentafluorophenyl) mercury.[108]

Mercury has a range of stable isotopes and two of these have magnetically quantized nuclei:[199] Hg (spin quantum number 1/2, abundance 16.86%) and ^{201}Hg (spin quantum number 3/2, abundance 13.24%). Almost no quadrupole resonance studies have been carried out on

^{201}Hg samples, probably because of its high absorbtion frequencies (300-350 MHz in a series of dioxan mercuric halide complexes[109]) and because Zeeman studies are necessary to give value for the asymmetry parameter η. ^{201}Hg nmr is largely unexplored[110] since the nucleus both has a five-fold lower magnetic susceptibility than ^{199}Hg, and also suffers from quadrupolar relaxation.[110] The magnetic susceptibility of ^{199}Hg in a natural abundance sample is 9.5×10^{-6} that of the proton[111] and shifts are up to 2300 ppm.[112] Shielding effects have been shown to be consistent in organocadmium and organomercury compounds[113] and shifts have been shown to vary with sample concentration,[111,114,115] solvent,[111,114,115] temperature,[111,115,116] and pH.[117] ^{199}Hg nmr was used to show that cyclohexylmercurials adopt an equatorial configuration, virtually irrespective of the other group on the mercury atom.[115]

Moessbauer studies have been briefly described for ^{199}Hg [118,119], ^{197}Hg,[120] ^{193}Hg[121] and ^{201}Hg[122] but no detailed chemical work has been reported.

Polyalkylbenzenes

The preparation of these compounds is normally accomplished by one of two routes: alkylation of benzene or cyclisation of acetylenes. Alkylation by alkyl halides with an aluminium halide catalyst (the Friedel-Crafts reaction) is of the form:[123]

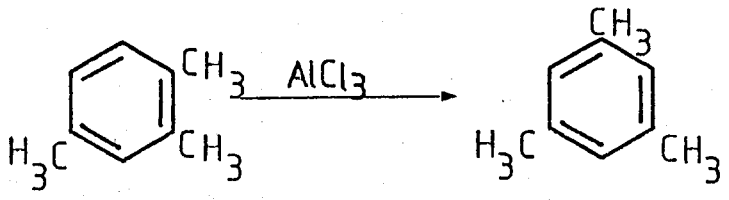
$$RX + AlX_3 \longrightarrow R[AlX_4]$$

$$C_6H_6 + R[AlX_4] \longrightarrow [C_6H_6R][AlX_4] \rightarrow C_6H_5R + HX + AlX_3$$

Since the species $R[AlX_4]$ is quite ionic the alkyl group has to support substantial positive charge and this has two consequences: the reaction with the aromatic system is electrophilic (and thus favoured by alkyl substituents) and, where possible, rearrangements to form secondary or tertiary carbon atoms are strongly favoured (for example, n-butyl halides can give t-butyl benzenes[123]). Since the reaction products are activated towards further reaction, compared with the starting aromatic, and since aluminium halides also catalyse both intermolecular disproportionations,

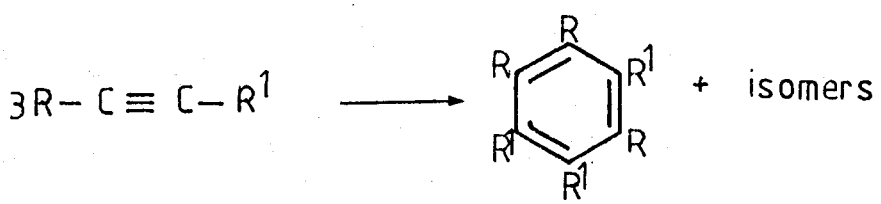
$$2(CH_3)_5C_6H \xrightarrow{AlCl_3} (CH_3)_4C_6H_2 + (CH_3)_6C_6$$

and intramolecular rearrangements



the reaction products form a Friedel-Crafts alkylation tend to be produced as a complex mixture.

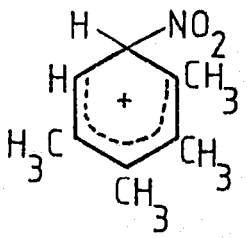
Cyclisation has been used as an alternative route to alkylbenzenes. The general reaction is of the form:



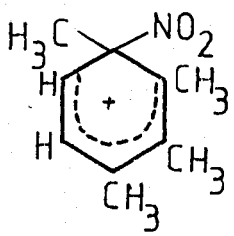
To simplify the preparation normally either R = R^1 or R^1 = H, and tris(t-butyl)benzenes[124] have been produced by this route as has hexakis(trifluoromethyl)benzene.[125]

The reactions of highly alkylated benzenes cannot be predicted from those of benzene. Nitration of benzene to nitrobenzene and then to m-dinitrobenzene requires forcing conditions (2-3 hours reflux in a conc.sulphuric acid fuming nitric acid mixture[126]) but dinitration of 1,2-dihydrotetramethylbenzene has to be done in the cold and in the presence of an organic solvent immiscible with conc.sulphuric acid to prevent oxidative attack on the methyl groups of the 1,2-dinitrotetramethylbenzene produced.[127] The total reaction time is about 30 minutes. Pentamethyl-

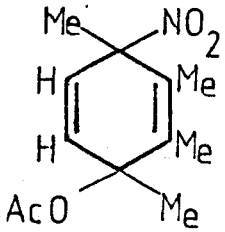
benzene readily gives 1,2-dinitrotetramethylbenzene,[127] whereas pentaethylbenzene gives 1,4-dinitrotetraethylbenzene.[128] The course of the reaction in acetic anhydride solution has been studied and shown to involve formation of classical Wheland intermediates where attack has been on an unsubstituted carbon atom and of ipso-Wheland intermediates where attack has been on a substituted carbon atom. Some of the wide range of products and isolable intermediates have been prepared by low temperature chromatography and characterised.[129]



Wheland intermediate



ipso-Wheland intermediate



isolable

Although kinetic studies in trifluoroacetic acid[130] appeared to give mononitration, our preparative scale reaction gave alkyl-substituted products.[131] Mononitration is also claimed using methyl nitrate in nitromethane with a boron trifluoride catalyst.[132]

Bromination is also an electrophilic reaction and proceeds very readily.[133] The only problem is the choice of solvent when multi-bromination is required, as the usual solvent (glacial acetic acid) will not dissolve all bromohydropolymethylbenzenes. Iodination is more difficult and oxidative conditions are necessary for the

introduction of iodine.[134] Mercuration followed by cleavage of carbon-mercury bonds by triiodide will introduce iodine into all available sites.[39]

Sulphonation occurs readily and reversibly, but often causes rearrangements (the Jacobsen reaction). Polymethylbenzenes are reluctant to rearrange,[135] but polyethylbenzenes rearrange readily:[136]

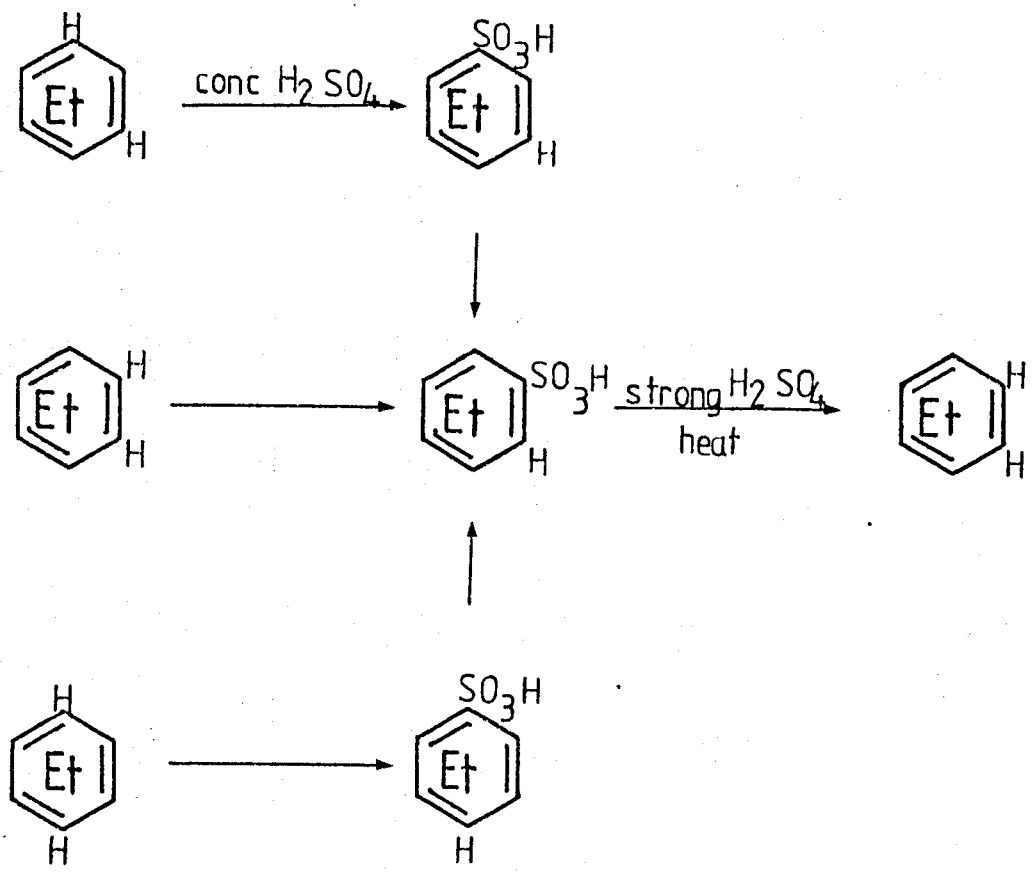


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Table 1

(a) Nomenclature employed for polymethylbenzenes

Trivial Name	Formula	Semi-Systematic Name
Mesitylene	$(CH_3)_3C_6H_3$	1,3,5-trihydrotrimethylbenzene
Pseudocumene	$(CH_3)_3C_6H_3$	1,2,4-trihydrotrimethylbenzene
Hemimellitene	$(CH_3)_3C_6H_3$	1,2,3-trihydrotrimethylbenzene
Prehnitene	$(CH_3)_4C_6H_2$	1,2-dihydrotetramethylbenzene
Isodurene	$(CH_3)_4C_6H_2$	1,3-dihydrotetramethylbenzene
Durene	$(CH_3)_4C_6H_2$	1,4-dihydrotetramethylbenzene
-	$(CH_3)_5C_6H$	Pentamethylbenzene
-	$(CH_3)_6C_6$	Hexamethylbenzene

(b) Abbreviations employed for solvents

Acronym	Chemical
DMF	N,N-dimethylformamide
DMA	N,N-dimethylacetamide
DPF	N,N-diphenylformamide
DEF	N,N-diethylformamide
DMSO	Dimethylsulphoxide
TMED	N,N,N',N'-Tetramethylethylene-diamine
THF	Tetrahydrofuran
Py	Pyridine
2-Pic	2-Methylpyridine (2-picoline)

3-Pic	3-Methylpyridine (3-picoline)
4-Pic	4-Methylpyridine (4-picoline)
2,6-Lut	2,6-Dimethylpyridine (2,6-lutidine)

Chapter 2

X-Ray Crystallography

Summary: The practical, theoretical and computational aspects of single-crystal X-ray structure analysis are reviewed. Some unsuccessful preliminary studies are presented and the completed analyses of monoclinic and orthorhombic tribenzo [b,e,h][1,4,7] trimercuronin, bis(2-hydrotetrafluorophenyl)mercury and perfluorotribenzo [b,e,h][1,4,7] trimercuronin.4-phenylpyridine are given and discussed.

X-ray Crystallography

Theory and Technique

Suitable crystals for X-ray study are small (the optimum size is $2/\mu$ where μ is the linear absorbtion co-efficient) and well-formed. The former reduces absorbtion effects and the latter makes optical alignment simpler and absorbtion corrections possible. The three simplest methods of growing crystals are (a) sublimation (b) cooling a hot saturated solution and (c) vapour diffusion. This third technique involves the production of a saturated solution at room temperature of the substance under investigation, followed by diffusion of the vapour of a second, denser, liquid into that solution. If the compound is insoluble in the second liquid, which will mix because of its greater density, crystals will slowly form.

After separation from the mother liquor a sample of the crystals is then inspected on a polarising microscope and a crystal chosen. It must be physically single (not, for example, a fan-shaped cluster of smaller crystals) and as far as possible untwinned. This defect may show up on inspection when the crystal is rotated between crossed Nicol prisms: if there are substantial zones where the lattice is orientated differently then extinction (the crystal should be light against a dark background and go dark four times in a complete revolution) is

observed in different parts of the crystal at different times. If extinction is not parallel to the edges of the crystal then the overall symmetry is monoclinic or triclinic. A crystal that is bent, cracked or grossly damaged should be rejected.

The crystal is then mounted on a goniometer head either by cementing it to a glass fibre with an epoxy-resin glue or by inserting it into a thin-walled glass tube, either of which is then secured with wax or plasticine. Glass tubes, which are normally sealed after the crystal is inside, are used where the compound studied is sensitive to some component of the atmosphere or liable to effloresce. Glasses and glues produce diffuse background scattering only, which do not affect data collection. Optical alignment is then performed and since this relies on the fact that the direction of extension of a needle-like crystal, or the edge of a plate-like crystal, is almost always one of the short unit cell axes (often the shortest) it is worthwhile adjusting a needle-like crystal so that it is as far as possible an extension of the fibre. Alignment is performed by rotation of the mounted crystal on its goniometer head and adjusting the arcs (for tilt) and the sledges (for centring at the focal point of the arcs) so that the crystal is perpendicular to the X-ray beam during a complete rotation. It must not move up or down and on goniometer heads where the sledges can be locked it is good practice to do this after each adjustment. Optical alignment normally produces

recognisable diffraction lines on X-ray analysis, and if it fails, lines can often be produced by alteration of the setting of one arc in 15° steps. The final adjustments have to be performed with X-rays.

The Davies (double-oscillation) technique[137] is probably the best rapid alignment method. Deviations from alignment on the horizontal arc cause the layer lines to be curved, whereas misalignment on the vertical arc causes them to be tilted. The Davies method assumes that, for small angles of deviation, the curvature is negligable when the arcs are at 45° to the vertical. The tilt is measured, and corrected as it is projected by 45°. To eliminate as many sources of internal error as possible a double exposure is taken: an initial long exposure followed by another of half the original time with the goniometer head rotated through 180°. This doubles the tilt to be measured and by reference to the orientation of the lines (heavy on one side, light on the other) the direction of adjustment can be found. Other methods exist but the technique described is as accurate as any, is rapid and is easy enough to be the method of choice. In its disfavour are the facts that it is specific to a cylindrical camera and it is difficult to apply to long axes of oscillation as the layer lines may then be as close as the lines produced by the second exposure. This can make it virtually impossible to sort the weak exposure lines from weak spots on the strong exposure lines. In this work no precession-method

photographs were taken. This technique is considerably more complex to operate and has the general disadvantage compared with cylindrical camera techniques that considerably fewer reflections are available for study.

The "usual" cylindrical camera is the Weissenberg camera, and with this device alignment photographs are taken with the camera stationary and the crystal oscillating through 10-15°. This brings sufficient reflections into their diffracting positions that patterns can be seen. Oscillation photographs can yield three pieces of information: from the spacing of the lines the repeating distance along the needle axis can be determined; from the presence or absence of symmetry, information about the symmetry class of the crystal can be gleaned; and the presence of an n-fold axis of rotation can be shown if oscillation photographs taken 360/n° apart are the same.

The next stage is to obtain Weissenberg pictures: oscillation photographs display a fraction of the possible reflections as a series of lines and the Weissenberg technique was developed to display a single line spread out over a complete film. An oscillation range greater than 180° is chosen for the crystal and both it and the camera then move. Since the zero layer (indexing of the lines starts at 0, then proceeds outwards to ± 1, ± 2 etc) is directly in line with the crystal and higher layers are not, when these are studied by the equi-inclination or flat-cone techniques the angle of the camera assembly to

the beam is adjusted. In the equi-inclination method, the commonest as it makes most reflections available, both the camera and the screens (inserted to block reflections from other layers) are moved whereas in the other approaches only one of these adjustments is made.

The position of the spots and the size of the unit cell are related by Bragg's Law and as this involves an inverse relationship the positions of the reflections are called a reciprocal lattice. This lattice is determined solely by the wavelength of the radiation and the physical size of the unit cell: the contents determine the intensities of the spots but not their position. A Weissenberg photograph gives a distorted view of one section through a reciprocal lattice and a precession photograph gives an undistorted picture. Either can be used to calculate lattice parameters. These can be calculated as follows: the length of the axis of rotation is obtained from the oscillation photograph using the relationship

$$b = \frac{n\lambda}{\sin(\tan^{-1} y_n/D)}$$

where b is the direct lattice parameter (in Å)

n is the index number of the layer lines

y_n is the separation (in mm) of the layer lines $\pm$ n

D is the camera diameter (in mm)

λ is the wavelength of the X-rays used (in Å)

Usual practice is to calculate b for each layer-line pair and to use the mean value; y_n is best measured near the backstop shadow to minimise misalignment errors. The other axes are obtained as the reciprocal parameter from the zero-layer Weissenberg photograph. In the case of monoclinic crystals rotated about the unique axis (conventionally b) and all higher symmetry crystals the oscillation and zero layer Weissenberg photographs together give sufficient information to define the unit cell completely. Conventionally an asterisk is used to denote a parameter defining a distance or angle in the reciprocal unit cell. In an orthorhombic cell the relationships

$$a = \frac{1}{a^*} \qquad b = \frac{1}{b^*} \qquad c = \frac{1}{c^*}$$

hold, and in a monoclinic system

$$a = \frac{1}{a^* \sin\beta^*} \quad b = \frac{1}{b^*} \quad c = \frac{1}{c^* \sin\beta^*} \quad \beta = (180 - \beta^*)$$

In a triclinic system the relationships are considerably more complex. The reciprocal parameters are obtained from the zero-layer Weissenberg picture as follows: the angle between the reciprocal axes is obtained directly and the reciprocal spacings from the relationship

$$a^* = \frac{2\sin(y_n/\sqrt{5})}{n\lambda}$$

where a^* is the reciprocal lattice dimension (in Å^{-1})

y_n is the separation (in mm) of the $\pm$nth spots on the axial rows

λ is the wavelength of the x-rays used

$\sqrt{5}$ arises from the usual ratio of 2° crystal oscillation to 1mm of camera transverse for a 57.3 mm diameter camera.

There are only 230 ways in which identical objects can be arranged into a regularly repeating 3-dimensional array and which of these is present is determined by the internal arrangement of the unit cell. The symmetry operations possible are rotations, mirrors, centres of symmetry and combinations of the first two operations with translation. This produces screw axes and glide planes respectively. The other possible symmetry operations involve centring of the crystal lattice. The sum total of the symmetry operations in a unit cell define the space group and their number and nature decide the crystal class. The clues to the space group of a crystal under examination are twofold: the unit cell dimensions decide the crystal class and any translational symmetry shows up in systematically absent reflections. These also affect lattice calculations: if every alternate spot on an axial row is absent then the apparent reciprocal dimension will be twice its true value. Translational symmetry produces these absent reflections because certain projections of the unit cell will appear to repeat at shorter intervals and thus satisfy Bragg's Law for a value

that is a sub-multiple of the true value. A two-fold screw axis about an axis a means that a projection onto the one dimension of a will appear to repeat at units of a/2: thus odd-indexed spots must have zero intensity. Since this shorter apparent axis is only valid for the one special projection only reflections whose indices involve a alone will be affected.

For triclinic crystals, and monoclinic crystals rotated about a or c, a single axis is not enough to define completely the unit cell: a second axis has to be examined. It is possible to obtain lattice parameters from the deviations of axial spots from linearity on higher axes but such values tend to be imprecise. A second axis can also give information about the crystal's space group through the absences (or lack of them) on the original oscillation axis.

Preliminary alignment and cell dimensions are always obtained by photographic techniques, but final alignment and measurement of cell dimensions is most often done with a diffractometer. These devices also measure reflection intensities by scintillation or proportional counting. Photographic techniques (microdensitometry) have the grave disadvantages of imprecise inter-layer scaling, absence of error estimates and the very long exposures to the X-ray beam needed.

The raw data is corrected for background, Lorentz and polarisation effects and, if necessary, absorbtion in order to obtain observed structure amplitudes. These

are then manipulated by one of a number of the available crystallographic computer packages until the structure is solved. The relationship between the intensity value and the structure factor is of the form:

$$I = K\,|F|^2(Lp)(Abs)(Tv)$$

where I is the intensity

$|F|$ is the magnitude of the structure factor

(Lp) indicates a factor for Lorenz and polarisation corrections

(Abs) indicates a factor for absorption corrections

(Tv) indicates a factor for overall thermal vibration

K is a scale factor

The structure factor is composed of two terms, A and B, corresponding to the amplitude and phase of the reflection. Each of these terms is obtained by summing all the scattered radiation taking into account that the atoms will not all scatter in phase. If f_j is the scattering power of the jth atom, at co-ordinates x,y,z, towards the point h,k,l then the phase of the difracted radiation is $2\pi(hx + ky + lz)$ and

$$A(hkl) = \sum_j f_j \cos 2\pi (hx_j + ky_j + lz_j)$$

$$B(hkl) = \sum_j f_j \sin 2\pi (hx_j + ky_j + lz_j)$$

Since $|F| = (A^2 + B^2)^{1/2}$ and is derived from the intensity

there is insufficient data to calculate both A and B. This is known as the phase problem since the parameter α is defined to make the unknown sought independent of any individual set of data for a particular compound. α is called the phase angle.

$$\alpha = \tan^{-1} \frac{B}{A}$$

Structure Analysis Methods

There are two approaches to solving the phase problem in current use, called direct and indirect methods. The latter most usually work with the Patterson function:

$$P(U,V,W) = \frac{1}{Vc} \sum_h \sum_k \sum_l |F|^2 \cos 2\pi (hU+kV+lW)$$

All the terms in this are known (V_c is the volume of the unit cell and P(U,V,W) is the value of the function at the point U,V,W) and so three-dimensional maps can be calculated by Fourier synthesis. The disadvantage of this treatment of the data is that the units of P are (electron density)^2 and for N atoms a Patterson synthesis produces N(N-1) unique peaks and a large peak at the origin. The heights of these peaks, which correspond to one "view" of the unit cell per atom, that atom being treated as the origin, are proportional to the electron density of both viewed and viewing atoms. On a Patterson map, therefore, any atoms which have many more electrons

than the other atoms present will give rise to considerably larger, higher peaks. The unit cell contents may thus be viewed neglecting the lighter atoms and a first trial structure obtained.

Direct methods consist of comparison of experimental values for intensities with those generated by a statistically random distribution of atoms in the unit cell. Thus the unit cell contents must be known: it can be calculated from the density, the unit cell volume and an empirical formula derived from elemental analysis. The difference between the two sets of values is used to define the (non-random) positions of atoms in the unit cell. Since the generation of a random set of data requires a random set of phases, direct methods work best in centrosymmetric space groups (where the phase angle is constrained to be π or 0) and in space groups with considerable translational symmetry. Similarly equal-atom structures are best for direct methods, but large, planar molecules can be difficult to solve: both these generalisations are concerned with the assumption of random distribution built into the calculated set of values.

Once initial atomic positions have been determined the refinement of the model structure they define proceeds by least square analysis. Intensities are calculated based on the trial structure and small modifications are made to it to minimise the difference between observed and theoretical values. The residual term R is defined to

act as a gauge of the reliability of the optimised model:

$$R = \frac{\sum|(|F_o|-|F_c|)|}{\sum|F_o|}$$

Whilst a wide range of values of R is possible depending on how much of the complete structure forms the model and the amount of that that is correct, empirically if $R \leq \sim 10\%$ few structural features are incorrect and if $R \leq \sim 20\%$ the trial structure is substantially correct. Exceptions to these rules of thumb exist.

Extra features are normally added to a model structure by difference electron-density maps: these are generated by subtraction of all features of the model structure after a Fourier synthesis of the structure factors where the trial structure determines the phases. If the model phases are correct then the intensity values the model cannot account for will produce maxima on the difference map corresponding to the remaining atoms. If the model phases are not correct then the map will show no meaningful patterns. The fewer electrons an atom has the more of the structure has to be correctly determined before it will show up on a difference map.

Preliminary Investigations

The following substances were examined for suitability for single-crystal X-ray analysis but were rejected. Since some of the diffraction patterns obtained seemed at first quite eligible for further study and data collection, details are given below together with the reason for abandonment of the analysis.

(1) General

No untwinned crystals could be found in samples of o-biphenylenemercury, perfluoro-o-biphenylenemercury, bis(pentachlorophenyl)mercury, 1,2-diiodobenzene or the triphenylphosphine adduct of perfluoro-o-phenylenemercury. Adducts of this lattermost mercurial with DEF and DMA decomposed rapidly in the X-ray beam and the DPF adduct was shown to be twinned when two alternate oscillation axes gave values for the unit cell volume which differed by a factor of two. All three adducts gave triclinic systems.

(2) Bis(2,3-dihydrotrifluorophenyl)mercury.1,10-phenanthroline. Oscillation photographs showed no symmetry and a zero-layer Weissenberg showed the reciprocal lattice to be hexagonal (or rhombohedral), with absences $h + k = 2n + 1$. This is not a possible condition in either a hexagonal system or a rhombohedral system defined on hexagonal axes and the study was terminated.

(3) o-Terphenylenemercury.1DMF

Crystals were studied both after preparation of the adduct in DMF solution and after recrystallisation from chloroform. Oscillation photographs showed m_x symmetry on both needle and alternate axes; the needle-axis spacing was 27.51Å. A zero-layer Weissenberg photograph showed no meaningful patterns.

(4) Bis(perfluoro-2-biphenyl)mercury.1,10-phenanthroline

Well-formed needle-like crystals were grown by diffusion of water into a chloroform/methanol solution of the sample. The needle-axis showed m_x symmetry but zero and higher layer Weissenberg pictures showed no systematic absences that corresponded to standard space group. Crystal data (oscillation about a): Orthorhombic or Tetragonal, a = 16.17Å, b = 16.37Å, c = 31.79Å; absences: 0kl when k = 2n + 1, 00l when l = 2n + 1; no hhl absences.

(5) Perfluoro-o-phenylenemercury.2DMF

Crystals were grown by diffusion of water into a DMF solution of the parent mercurial and were allowed to effloresce. The study was terminated when several crystals had decomposed in the beam. The needle-axis dimension was 19.22Å and showed no symmetry on oscillation photographs.

(6) Perfluoro-o-phenylenemercury.1DMF

Crystals of the above DMF recrystallisation were heated at 120°C overnight then recrystallised by diffusion of water into a methanol solution. The presence of DMF in the resulting crystals was shown by i-r spectroscopy;

on standing in the open the crystals did not become opaque, but after X-ray examination over 7-10 days no diffraction patterns could be detected. Oscillation axis spacings were 13.31Å and 11.31Å; neither axis showed any symmetry on the oscillation pictures.

(7) Bis(pentamethylphenyl)mercury

Crystals were grown by slow cooling from boiling of a solution in DMF. There was a fair approximation of m_x symmetry on needle-axis oscillation photographs. The only absences on Weissenberg pictures were alternate festoons on the zero layer; one axial row became curved on higher layers. These two facts are irreconcilable with a standard space group and in addition the extra reflections on the first layer (compared with the zero layer) were displaced slightly from their festoons. The crystal was assumed to be twinned and X-ray studies abandoned.

Structure Determinations

1 Tribenzo [b,e,h][1,4,7] trimercuronin (orthorhombic form) Crystals were prepared by slow cooling from boiling of a DMF solution. The compound was prepared by Dr. S. B. Awad via the reaction of sodium amalgam with 1,2-dibromo-benzene in either solution.

Crystal data

orthorhombic a = 5.56(2)Å Dx = 3.49Mg/m^3
b = 23.36(2)Å Z = 4 F(000)=1440
c = 12.24(2)Å U = 1589.8Å^3

Absences 00l when l odd
0k0 when k odd
h00 when h odd

Space group $P2_12_12_1$ (No.19)

Radiation:Mo - Kα λ= 0.71069Å μ = 8.35mm^{-1}

Crystal size: 0.05 x 0.05 x 0.5mm

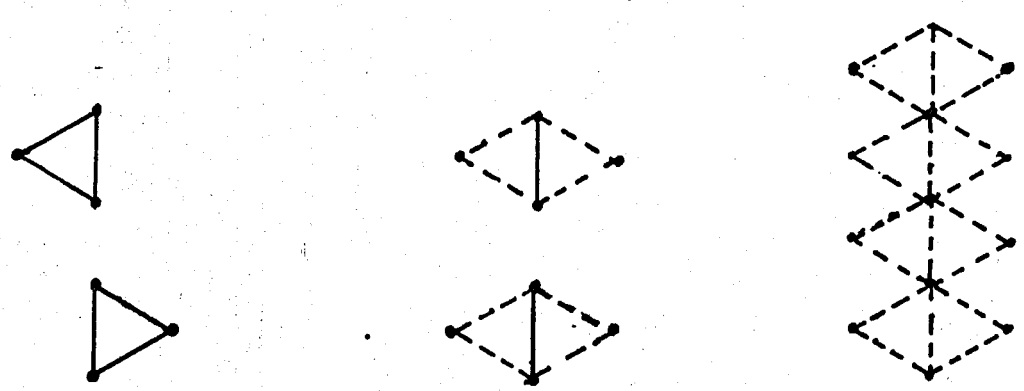
Intensity Data

Intensities were measured on a Stoë automatic Weissenberg diffractometer equipped with a graphite monochromator. Rotation was about the crystallographic a axis; each reflection was counted for 60 seconds with variable ω scan and a twenty second background measurement was made at the beginning and end of each scan. A strong reflection was measured every 30 reflections but the data

was not scaled to it and a new reflection was chosen for each layer. Systematically absent reflections were measured, checked and omitted from further data reduction; reflections where $F \leq 3\sigma(F)$ were classed as unobserved. Lorentz and polarisation effects were corrected but absorbtion was neglected.

Structure Determination and Refinement

After data reduction a Patterson map was calculated but only two major unique peaks appeared: at 0,0,0 and 0,0,$\frac{1}{3}$. Both also gave symmetry and vector related peaks, but there was no trace of the third mercury atom. Refinement of approximate atomic co-ordinates of 0,0,0 and 0,0,$\frac{1}{3}$ as isotropic mercury sites left R at 39.4%. A difference Fourier map showed four approximately equal peaks instead of a single maximum and trial structures involving both single and double disorder were calculated. The R factor would not reduce below about 25% nor would the resulting difference maps show any recognisable shapes.



order

single disorder

double disorder

6 x full weight atoms

4 x full-weight atoms
4 x 0.5 weight atoms

4 x fullweight atoms
8 x 0.25 weight atoms

The two sites which had seemed most amenable to refinement as mercury sites were then separately tried as the basis of new, ordered, models and one of these gave an anisotropic R of 13.6%. All the carbon atoms showed clearly on a difference map and isotropic refinement of these reduced R to 10.4%

At this stage it was noticed that the initial data had been incorrectly reduced as only reflections calculating less than background were classed as unobserved. Alteration of this that $F \leq 3\sigma(F)$ was the criterion for less-than status lead to a conventional R of 7.8% with mercury anisotropic, carbon isotropic and hydrogen atoms neglected. As no absorbtion correction had been applied further refinement was not attempted.

The structure obtained shows unequivocally the trimeric nature of orthorhombic o-phenylenemercury: the same as the proposed structure for its perfluoro analogue.[37,80,93] Structure and temperature factors are listed in Appendix I; bond lengths (Tables 2,3), bond angles (Table 4) and positional parameters (Table 5) are given together with the equivalent values for the monoclinic form. Figure I shows the atomic numbering scheme adopted for both crystal modifications, Figure 2 shows the packing arrangement of the two atoms discovered first and Figure 3 shows the unit cell contents in projection. In Figure 2 the a and c axes are shown in small letters and of the contact distances shown only B is bridged; the distances involved are 3.98Å (A), 3.54Å (B) and 3.44Å (C).

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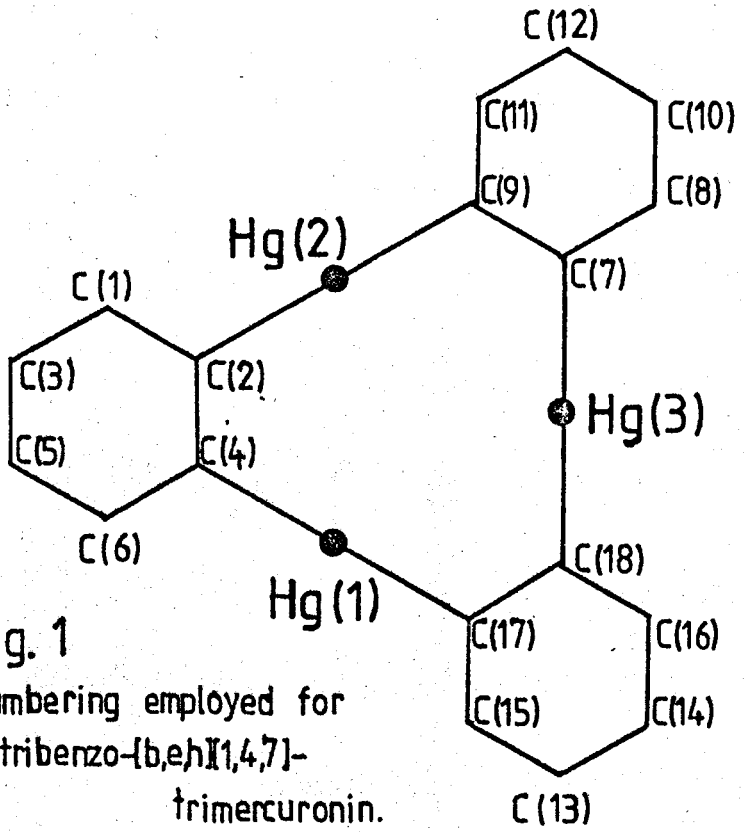
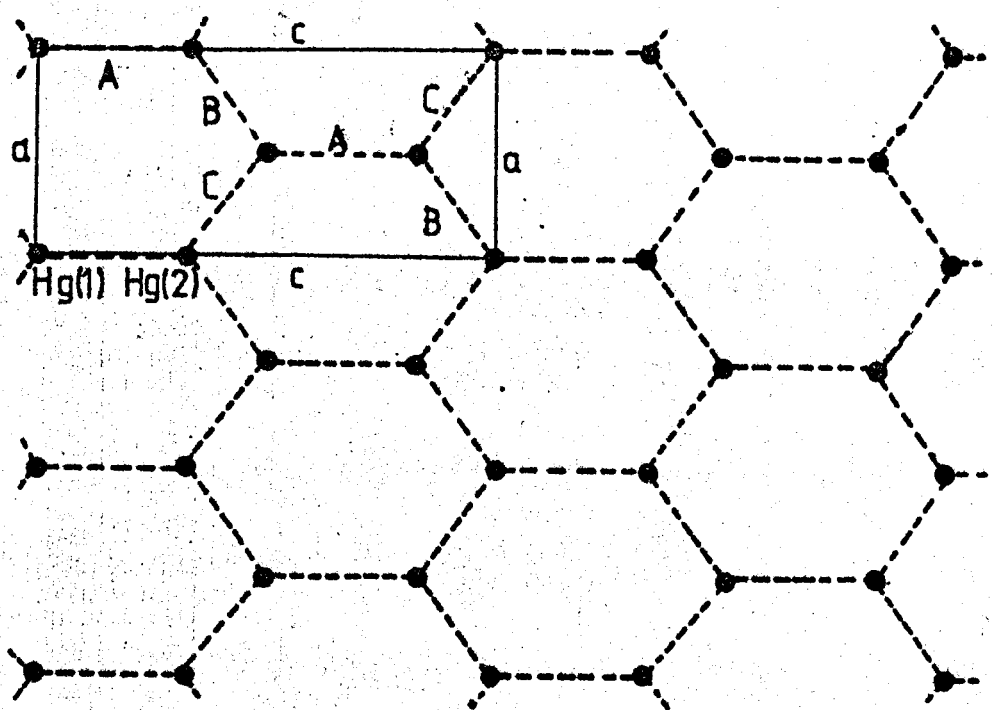


Fig. 1

Numbering employed for -tribenzo-[b,e,h][1,4,7]- trimercuronin.

Fig. 2



"Honeycomb" array of Hg(1),Hg(2) : projection of ½ unit cell down b.

a,c outline one unit cell

A,B,C are contact distances

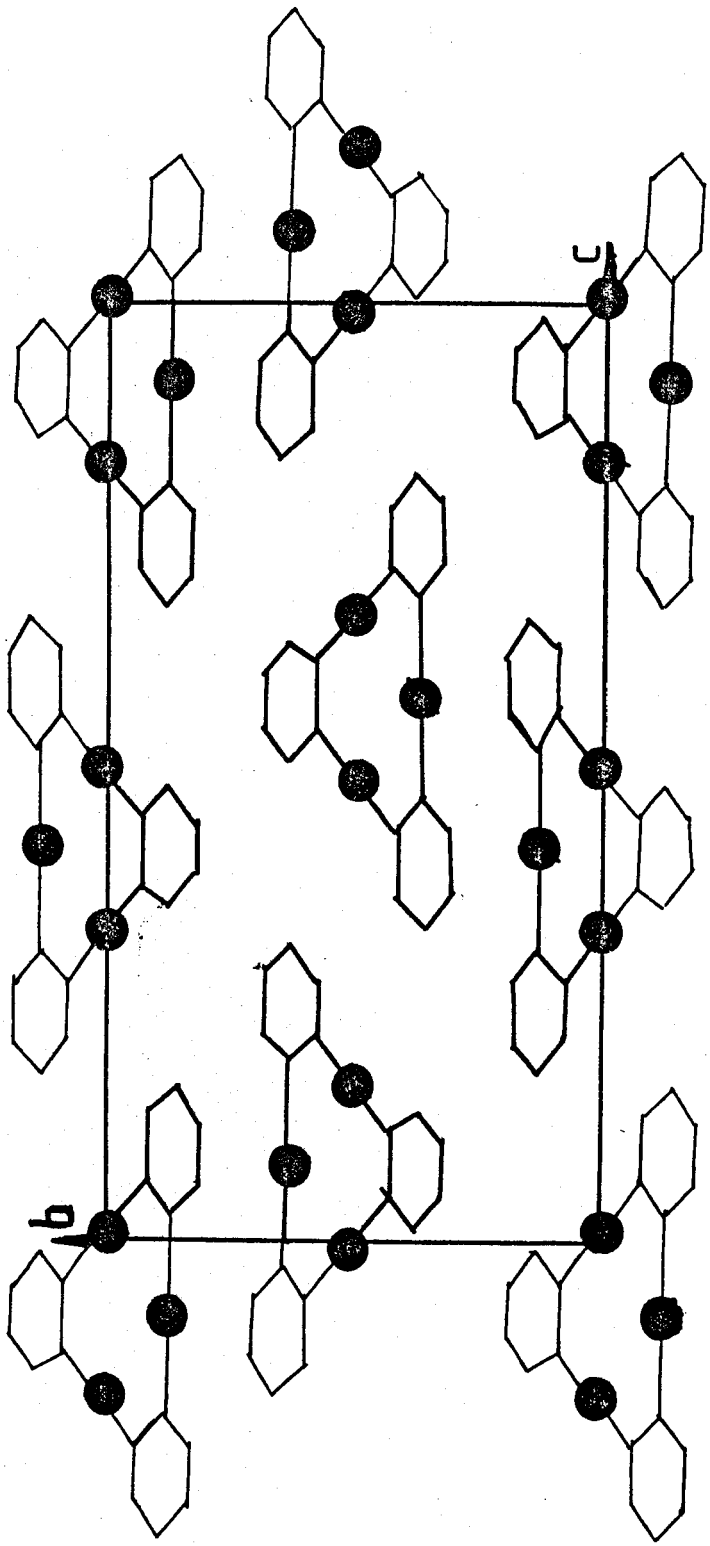


Fig 3.
Orthorhombic unit cell ; Tribenzo[b,e,h][1,4,7]-trimercuronin

Table 2

Carbon-Mercury Bond-lengths in o-Phenylenemercury

(a) Orthorhombic Form

Atom 1	Atom 2	Bondlength(Å)
C(4)	Hg(1)	2.13(4)
C(17)	Hg(1)	2.12(4)
C(2)	Hg(2)	2.08(5)
C(9)	Hg(2)	2.09(5)
C(7)	Hg(3)	2.12(4)
C(18)	Hg(3)	2.07(5)

(b) Monoclinic Form

Atom 1	Atom 2	Bondlength(Å)
C(4)	Hg(1)	2.17(5)
C(17)	Hg(1)	2.05(3)
C(2)	Hg(2)	2.06(3)
C(9)	Hg(2)	2.07(2)
C(7)	Hg(3)	2.07(3)
C(18)	Hg(3)	2.04(2)

Table 3

Carbon-Carbon Bondlengths in o-Phenylenemercury

(a) Orthorhombic Form

Atom 1	Atom 2	Bondlength (Å)
C(1)	C(2)	1.47(8)
C(2)	C(4)	1.38(7)
C(3)	C(1)	1.46(7)
C(4)	C(6)	1.44(6)
C(5)	C(3)	1.38(7)
C(6)	C(5)	1.38(6)
C(7)	C(8)	1.43(6)
C(8)	C(10)	1.45(7)
C(9)	C(7)	1.49(6)
C(10)	C(12)	1.30(6)
C(11)	C(9)	1.38(7)
C(12)	C(11)	1.38(6)
C(13)	C(14)	1.43(8)
C(14)	C(16)	1.39(9)
C(15)	C(13)	1.47(8)
C(16)	C(18)	1.43(7)
C(17)	C(15)	1.49(7)
C(18)	C(17)	1.42(6)

(b) Monoclinic Form

Atom 1	Atom 2	Bondlength(Å)
C(1)	C(2)	1.33(6)
C(2)	C(4)	1.30(5)
C(3)	C(1)	1.39(5)
C(4)	C(6)	1.51(7)
C(5)	C(3)	1.32(5)
C(6)	C(5)	1.41(6)
C(7)	C(8)	1.42(4)
C(8)	C(10)	1.35(4)
C(9)	C(7)	1.41(4)
C(10)	C(12)	1.39(5)
C(11)	C(9)	1.37(4)
C(12)	C(11)	1.45(4)
C(13)	C(14)	1.45(5)
C(14)	C(16)	1.29(4)
C(15)	C(13)	1.33(5)
C(16)	C(18)	1.45(5)
C(17)	C(15)	1.44(4)
C(18)	C(17)	1.45(4)

Table 4

Bondangles in o-Phenylenemercury

(a) Orthorhombic Form

Atom 1	Atom 2	Atom 3	Angle 1-2-3(°)
C(4)	Hg(1)	C(17)	176.5(1.8)
C(2)	Hg(2)	C(9)	178.1(1.9)
C(7)	Hg(3)	C(18)	178.5(1.6)
C(2)	C(1)	C(3)	117.4(5.1)
C(1)	C(2)	C(4)	117.0(4.4)
C(1)	C(3)	C(5)	122.0(4.2)
C(2)	C(4)	C(6)	121.7(4.0)
C(3)	C(5)	C(6)	119.3(4.2)
C(4)	C(6)	C(5)	120.3(4.4)
C(8)	C(7)	C(9)	121.0(4.1)
C(7)	C(8)	C(10)	116.0(3.9)
C(7)	C(9)	C(11)	115.8(3.9)
C(8)	C(10)	C(12)	120.7(4.4)
C(9)	C(11)	C(12)	121.1(4.4)
C(10)	C(12)	C(11)	124.4(4.9)
C(14)	C(13)	C(15)	123.5(5.7)
C(13)	C(14)	C(16)	118.7(5.2)
C(13)	C(15)	C(17)	112.5(4.4)
C(14)	C(16)	C(18)	123.7(5.2)
C(15)	C(17)	C(18)	125.0(3.8)
C(16)	C(18)	C(17)	116.6(4.4)
Hg(1)	C(4)	C(2)	119.6(3.2)

Hg(1)	C(4)	C(6)	118.5(3.2)
Hg(1)	C(17)	C(15)	118.6(2.9)
Hg(1)	C(17)	C(18)	116.3(3.1)
Hg(2)	C(2)	C(1)	116.9(4.0)
Hg(2)	C(2)	C(4)	123.9(3.3)
Hg(2)	C(9)	C(7)	116.5(3.4)
Hg(2)	C(9)	C(11)	127.6(3.3)
Hg(3)	C(7)	C(8)	117.0(3.1)
Hg(3)	C(7)	C(9)	121.4(3.1)
Hg(3)	C(18)	C(16)	118.0(3.5)
Hg(3)	C(18)	C(17)	125.2(3.0)

(b) Monoclinic Form

Atom 1	Atom 2	Atom 3	Angle (°)
C(2)	C(1)	C(3)	125.4(3.4)
C(1)	C(2)	C(4)	116.3(3.3)
C(1)	C(3)	C(5)	118.2(3.8)
C(2)	C(4)	C(6)	124.4(4.4)
C(3)	C(5)	C(6)	123.1(3.2)
C(4)	C(6)	C(5)	112.5(3.5)
C(8)	C(7)	C(9)	118.0(2.4)
C(7)	C(8)	C(10)	119.2(3.1)
C(7)	C(9)	C(11)	120.4(2.4)
C(8)	C(10)	C(12)	125.7(2.7)
C(9)	C(11)	C(12)	122.3(3.0)
C(10)	C(12)	C(11)	113.9(2.6)
C(14)	C(13)	C(15)	121.1(3.1)
C(13)	C(14)	C(16)	120.5(3.6)

C(13)	C(15)	C(17)	118.6(2.8)
C(14)	C(16)	C(18)	121.5(1.7)
C(15)	C(17)	C(18)	118.8(2.9)
C(16)	C(18)	C(17)	117.1(2.3)
Hg(1)	C(4)	C(2)	124.5(3.1)
Hg(1)	C(4)	C(6)	111.0(3.0)
Hg(1)	C(17)	C(15)	121.3(2.2)
Hg(1)	C(17)	C(18)	119.9(2.0)
Hg(2)	C(2)	C(1)	124.5(2.4)
Hg(2)	C(2)	C(4)	118.4(3.1)
Hg(2)	C(9)	C(7)	120.8(1.7)
Hg(2)	C(9)	C(11)	118.4(2.2)
Hg(3)	C(18)	C(16)	122.0(1.8)
Hg(3)	C(18)	C(17)	120.9(2.1)
Hg(3)	C(7)	C(8)	119.4(2.3)
Hg(3)	C(7)	C(9)	121.7(1.7)
C(4)	Hg(1)	C(17)	175.7(1.3)
C(2)	Hg(2)	C(9)	176.4(1.2)
C(7)	Hg(3)	C(18)	177.1(1.1)

C(13)	C(15)	C(17)	118.6(2.8)
C(14)	C(16)	C(18)	121.5(1.7)
C(15)	C(17)	C(18)	118.8(2.9)
C(16)	C(18)	C(17)	117.1(2.3)
Hg(1)	C(4)	C(2)	124.5(3.1)
Hg(1)	C(4)	C(6)	111.0(3.0)
Hg(1)	C(17)	C(15)	121.3(2.2)
Hg(1)	C(17)	C(18)	119.9(2.0)
Hg(2)	C(2)	C(1)	124.5(2.4)
Hg(2)	C(2)	C(4)	118.4(3.1)
Hg(2)	C(9)	C(7)	120.8(1.7)
Hg(2)	C(9)	C(11)	118.4(2.2)
Hg(3)	C(18)	C(16)	122.0(1.8)
Hg(3)	C(18)	C(17)	120.9(2.1)
Hg(3)	C(7)	C(8)	119.4(2.3)
Hg(3)	C(7)	C(9)	121.7(1.7)
C(4)	Hg(1)	C(17)	175.7(1.3)
C(2)	Hg(2)	C(9)	176.4(1.2)
C(7)	Hg(3)	C(18)	177.1(1.1)

Table 5

Positional Parameters ($x10^4$) for o-Phenylene Mercury

(a) Orthorhombic Form

Atom	x	y	z
Hg(1)	-116(4)	-55(1)	76(1)
Hg(2)	5075(4)	32(1)	8317(2)
Hg(3)	2095(4)	1317(1)	4197(2)
C(1)	4325(118)	1311(26)	8597(47)
C(2)	3181(105)	755(20)	8800(38)
C(3)	3038(87)	1821(17)	8957(32)
C(4)	1275(86)	745(18)	9528(35)
C(5)	891(91)	1789(19)	9515(37)
C(6)	91(95)	1264(18)	9878(35)
C(7)	5832(82)	8738(18)	8094(35)
C(8)	6942(93)	8210(18)	7771(35)
C(9)	6905(98)	9299(18)	7786(36)
C(10)	9070(95)	8260(20)	7094(39)
C(11)	8999(98)	9274(19)	7185(39)
C(12)	9861(96)	8760(18)	6792(39)
C(13)	5893(126)	8519(25)	1648(55)
C(14)	7145(122)	8024(23)	1248(45)
C(15)	6530(100)	9109(20)	1346(40)
C(16)	9176(119)	8104(25)	603(51)
C(17)	8717(82)	9136(17)	647(35)
C(18)	35(87)	8653(17)	269(32)

(b) Monoclinic Form

Atom	x	y	z
Hg(1)	-255(1)	2890(2)	-823(1)
Hg(2)	2710(1)	4758(2)	211(1)
Hg(3)	729(1)	2459(1)	1093(1)
C(1)	2826(39)	5825(52)	-1284(19)
C(2)	2195(34)	4901(42)	-913(17)
C(3)	2413(38)	6076(49)	-2038(19)
C(4)	1069(45)	4255(59)	-1290(22)
C(5)	1280(33)	5405(43)	-2422(17)
C(6)	478(46)	4448(59)	-2106(22)
C(7)	2420(28)	3695(35)	1682(13)
C(8)	2750(33)	3743(41)	2458(16)
C(9)	3134(26)	4722(33)	1339(13)
C(10)	3819(28)	4624(37)	2838(14)
C(11)	4217(30)	5585(39)	1746(15)
C(12)	4619(32)	5583(43)	2539(16)
C(13)	-3165(37)	-348(46)	-405(18)
C(14)	-2819(36)	-437(46)	383(18)
C(15)	-2608(34)	759(44)	-735(17)
C(16)	-1745(32)	253(41)	783(16)
C(17)	-1386(30)	1535(30)	-319(15)
C(18)	- 943(27)	1311(34)	469(13)

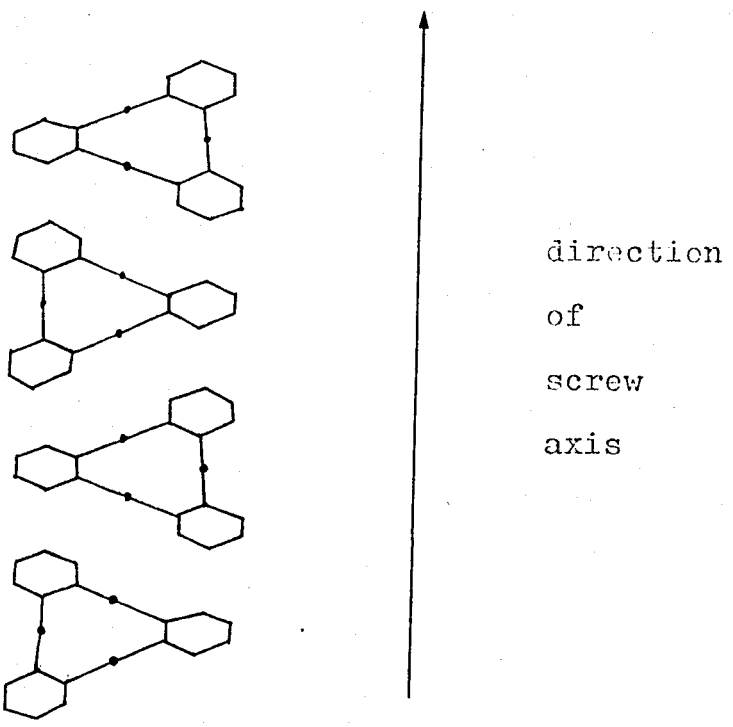
Discussion

The crystallographic point of interest in this structure lies in its failure to comply with some of the basic truisms of heavy atom X-ray analysis. Firstly, the Patterson map should have shown an arrangement based on a triangle of mercury atoms since the mathematics produces peaks proportional to the product of the electron densities of the two atoms concerned. A mercury atom (nominally) has 80 electrons to the 6 of a carbon atom. The projection Patterson synthesis for a triangle (a) and the observed map (b), however, are given below:

(a) (b)

The subsequent different maps should have given a single major unique peak corresponding to the remaining mercury atom rather than four smaller maxima. The disordered models tried attempted to reconcile the presence of mercury as the only heavy atom present (this was shown by X-ray fluorescence for the particular batch of crystals

concerned) with the smaller peaks and failed. In retrospect the problem appears to have arisen from the similarity in distance of the third mercury atom and the bridging phenyl ring from the two atoms located first. The phenylene bridge has 38 electrons in it and in a poorly defined structure (as shown by the R value of 39%) this was enough to produce features on the difference map indistinguishable from the heavy atom. The space group also contributed as shown below:



The screw axes meant that the three phenylene bridges and the remaining mercury formed an array virtually identical to that theoretically given by disorder.

The bond-lengths and angles are those one would expect from an organometallic: the values involving only light atoms have high standard deviations and this explains why some appear to deviate quite sharply from "normal".

The mercury atoms are shown to be bonded linearly to their two phenyl rings and the carbon-mercury bond-lengths are within normal values for aromatic mercurials. Some literature bond-lengths are given in Table 9.

The chemical points of interest are two-fold: the molecular structure of o-phenylenemercury is shown to be trimeric (this is discussed more fully in Chapter 7), and the van der Waals radius for mercury in its compounds is shown in a new light. Mercury metal is known in its solid state[138] to have two short interatomic contact distances of 3.000Å and 3.466Å; its three crystalline forms are all distorted forms of metallic close-packing.[139] The question of a van der Waals radius for mercury could then produce answers between 1.50Å and 1.74Å. Grdenic suggests that the lesser value be used, but that interatomic separations up to distances involving the larger radius can still involve bonding interactions.[140] The orthorhombic form of o-phenylenemercury appears to be held together by mercury-mercury contacts (Figure 2) and the shortest of these at 3.44Å suggests that a truer van der Waals radius would be about 1.72Å This structure is probably the only published case other than the metal where intermetallic contacts between uncharged mercury atoms are made. The phenylene bridges hold the metal atoms just further apart than this higher van der Waals distance, the separations being 3.54Å, 3.56Å and 3.61Å.

2. Tribenzo[b,e,h][1,4,7]trimercuronin (monoclinic form)
Crystals were grown by slow cooling from boiling of a DMF

solution. The compound was prepared via the reaction of a 1,2-dibromobenzene solution (in 1,4-dioxan) with sodium amalgam.

Crystal Data

Monoclinic $a = 10.512(3)\text{Å}$ $Dx = 3.49\text{Mg/m}^3$

$b = 8.116(2)\text{Å}$ $Z = 4$

$c = 19.128(7)\text{Å}$ $U = 1561.2\text{Å}$

$\beta = 106.92(3)^\circ$ $F(000) = 1440$

Absences hOl when l odd

OkO when k odd

Space Group $P2_I/c$ (No.14)

Radiation: Mo-Kα, λ=0.71069Å, $\mu = 8.35\text{mm}^{-1}$

Crystal size: 0.2 x 0.05 x 0.6mm

Intensity Data

Intensities were reasured on a Hilger-Watt automatic Eulerian geometry diffractometer equipped with a graphite monochromator. Rotation was about the crystallographic b axis; each reflection was counted for 28 seconds using an ω, ϑ scan. Background measurements were made for 7 seconds at the beginning and end of each scan. Three strong reflections were measured every 100 reflections and the data scaled to them. Cell dimensions were obtained by least-squares refinement of 30 reflections; systematically absent reflections were measured but omitted from data reduction after checking as were all reflections for which $I \leq 3\sigma(I)$. Lorenz and polarisation corrections were applied.

Structure Determination and Refinement

A Patterson function was calculated and was sufficiently well-defined to prove a trimeric structure but gave no idea as to the absolute position of that trimer. A variety of solutions was tried to no avail. Direct methods were then tried and the solutions with the best figures of merit refined by least-squares techniques. The second best set gave an R factor of 16.8% on anisotropic refinement of the mercury atoms: a difference map from this located all the carbon atoms and isotropic refinement of these atoms lead R to converge at 11.2%. The high value of R was attributed to the lack of absorbtion corrections.

Structure and temperature factors are given in Appendix I, bond lengths in Tables 2 and 3, bond angles in Table 4 and positional parameters in Table 5. The molecular numbering scheme used is shown in Figure 1 and the unit cell contents in Figure 4.

Discussion

The structure obtained shows unequivocally the trimeric nature of monoclinic o-phenylenemercury, a fact which was underlined during the course of this study when the orthorhombic form was produced from the monoclinic simply by recrystallisation from boiling quinoline. Since the Patterson map in projection was the same as the earlier work suggesting a hexamer,[72, 141] and our unit cell is a simple diagonal to this (as shown both by dimensions and

p77

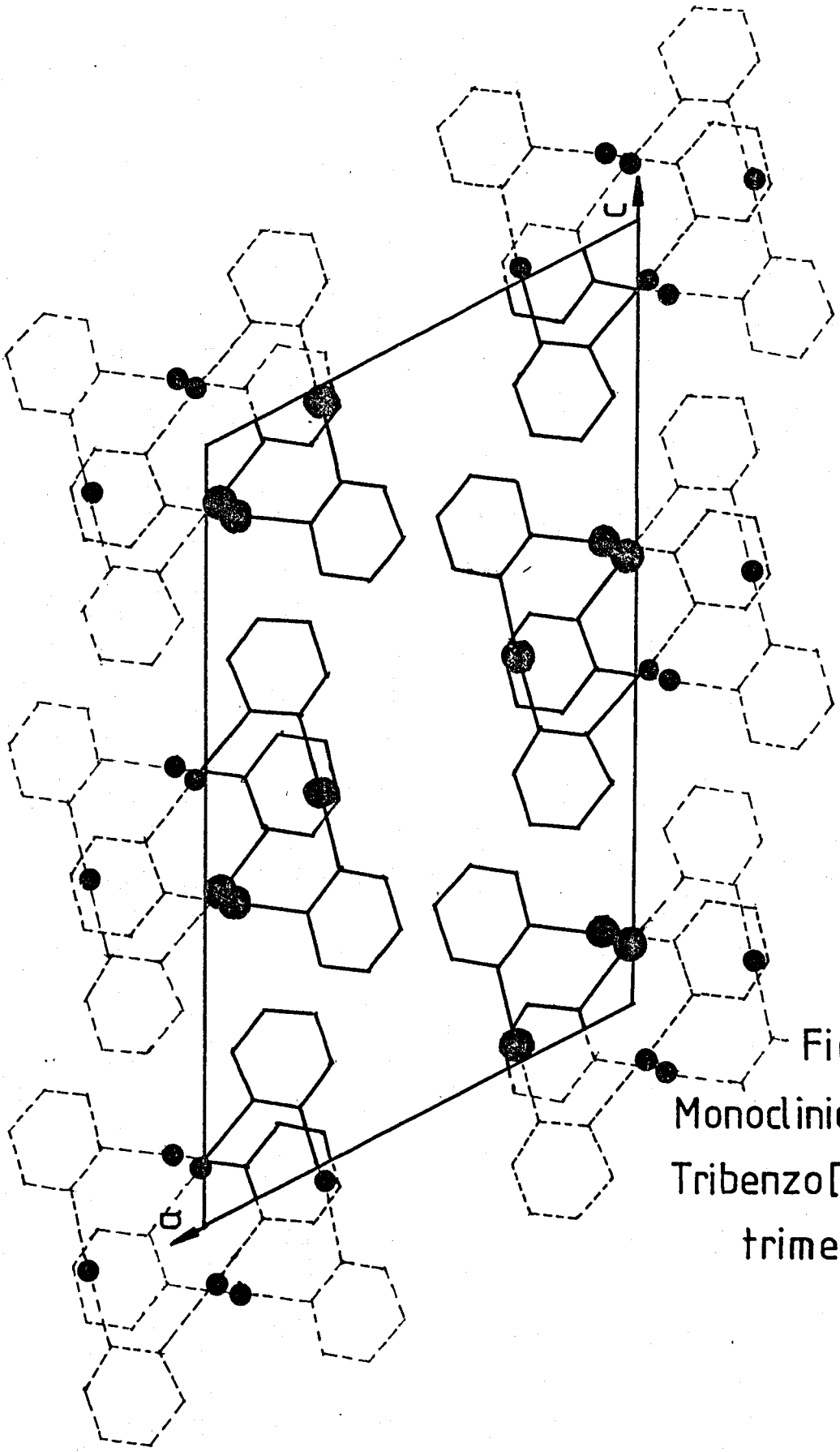


Fig. 4
Monoclinic unit cell;
Tribenzo[b,e,h][1,4,7]-
trimercuronin

p75 ▷
the change of space group to $P2_1/c$) a hexameric formulation for o-phenylenemercury is disproved.

In contrast to the orthorhombic form the van der Waals forces holding the crystal together shed no light on the appropriate radius for mercury: the closest (non-bridged) mercury-mercury contact distances are 3.67(0)Å and 3.82(0)Å. No trace of a mercury honeycomb is visible in the packing and no great deviation from linear geometry about the mercury atom is observed. The C-Hg bond-lengths are normal and those involving the light atoms show the effect of the high R-factor.

The most puzzling fact about o-phenylenemercury is that the reluctance of the two forms to interconvert in solution (either can be recrystallised from DMF) implies an ordering the DMF temperatures ($\sim 152°C$) are unable to break whereas quinoline temperatures ($\sim 235°$) can. Both solvents are strongly solvating and it is probably this that produces the solution structure conversion. Dry heating at temperatures up to 320°C during thermal analysis showed no energy changes, nor did it change the respective i-r spectra.

3. Bis(2-hydrotetrafluorophenyl)mercury

Crystals were prepared by sublimation of a specimen of "perfluorotribenzo [b,e,h][1,4,7] trimercuronin" recrystallised from cyclohexanone.

Crystal Data

First Set

Monoclinic

a = 11.07(5)Å Dx = 2.78Mg/m^3

b = 4.87(1)Å Z = 2

c = 13.11(5)Å F(000) = 452

β = 122.6(1)° U = 595.3Å^3

Absences hOl when l odd

OkO when k odd

hkl weak when k + l odd

Space group: $P2_1/c$ (No.14)

Radiation: Cu - Kα (Ni-filtered), λ = 1.5418, μ = 24.4mm^{-1}

Crystal size: 0.1 x 0.025 x 0.9mm

Second Set

Monoclinic

a = 11.786(7)Å Dx = 2.78Mg/m^3

b = 4.871(6)Å Z = 2

c = 13.114 (5)Å F(000) = 452

β = 127.41(6)° U = 598.0Å^3

Absences: hOl when l odd

OkO when k odd

hkl weak when k + l odd

Space group: $P2_1/c$ (No.14)

Radiation: Mo - Kα, λ = 0.71069Å, μ = 12.47mm^{-1}

Crystal size: 0.1 x 0.005 x 0.65mm

Intensity Data

Set 1 was collected by multiple exposure Weissenberg techniques. The films were then submitted to the SRC microdensitometer service who measured integrated intensities, rejected equivalent reflections which gave differing values, scaled the data and returned the output as condensed format SHELX[152] cards.

Set 2 consists of values measured on a Stoë automatic Weissenberg diffractometer equipped with a graphite monochromator. Rotation was about the crystallographic b axis; each reflection was scanned with variable ω and a 20 second background count was made at the start and end of every relection. A strong reflection was measured every 30 reflections but the data was not scaled to it and a new standard was chosen for each layer. Systematically absent reflections were measured but were omitted from data reduction after checking; reflections where $I \leq 4\sigma(I)$ were classed as unobserved. Lorentz, polarisation and absorbtion effects were corrected, the lattermost after structure solution.

Structure Determination and Refinement

Initial work was performed using the XRAY 72 [153] suite of programs: the mercury atom was located from the pseudo A symmetry as being at 0,0,0 and $0,\frac{1}{2},\frac{1}{2}$. The structure refinement was conducted in space group $P\bar{1}$ as this introduces no assumptions about symmetry: the reason

for this was the method of preparation of the crystals. The bulk solid had complied with the i-r spectrum of $(C_6F_4Hg)_3$ and so the crystals were assumed to be that compound. This, however, gave a value of Z = 1 for any realistic density and in $P2_1/c$ only 2 or 4 are possible. The R factor in P1 was 19.2% (isotropic), refining to 16.3% (anisotropic), and the subsequent difference map located the light atoms and hence the symmetry and molecular structure. R converged at 8.1% with light atoms isotropic. In order to apply absorbtion corrections the data was transferred to the SHELX [152] suite of programs; R refined to 5.1% with light atoms isotropic and the proton omitted from consideration.

Data set 1 was accumulated on an earlier crystal and the diffractometer data was obtained because the changes in spot-shapes during the long exposures required for photographic data indicated that the crystal had suffered decomposition. Solution of this data in $P2_1/c$ for anisotropic mercury gave R = 22.4% compared with R = 18.5% for the diffractometer data. The unit cell chosen for the photographic work had a different a* axis (and hence an alternate β^*) but comparison of the unit cell volumes (598 and 595$\AA^3$) shows that it is a valid alternative. The a* and b* axes are common, but the photographic cell is left-handed: the common axes mean the space group is unchanged.

Structure and temperature factors are given in Appendix 1, bondlengths are in Table 6, bond angles in

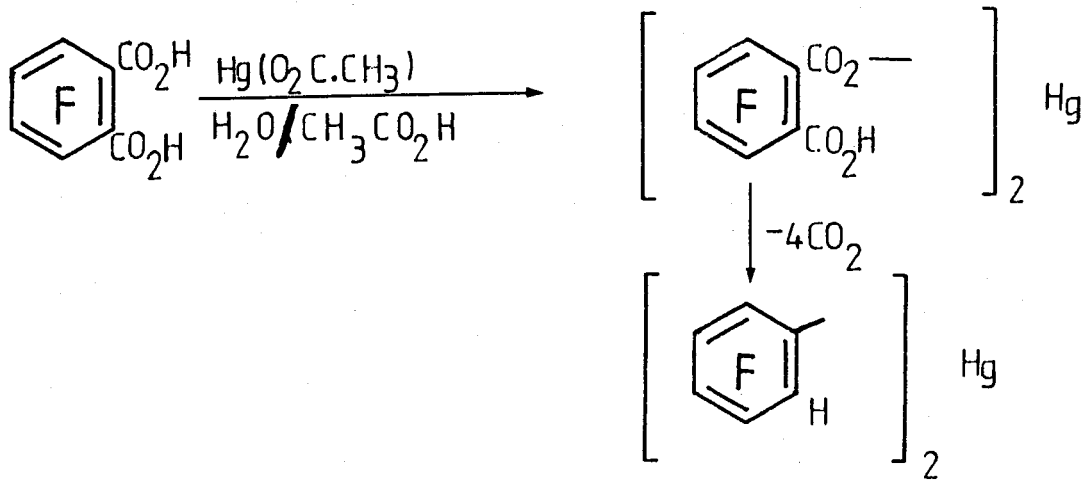
Table 7. The positional parameters are given in Table 8; the numbering scheme adopted is shown in Figure 5 and the unit cell contents in Figure 6.

Discussion

Preparation of perfluoro-o-phenylenemercury is most conveniently performed by the method of Sartori[80], and it was decided to recrystallise the product of this reaction

$$3\ C_6F_4(CO_2)_2Hg \xrightarrow{300^\circ C} (C_6F_4Hg)_3 + 6\ CO_2$$

from cyclohexanone to study the solvent/mercurial complex expected to form. On drying the sample in an oven a small quantity of feathery crystals grew on the neck of the flask. Proof of the identity of the compound as bis(2-hydrotetrafluorophenyl)mercury came as somewhat of a surprise; later thermogravimetric analysis showed it to comprise only about 1% of the mercurials produced. It presumably arises from the reaction sequence



p86

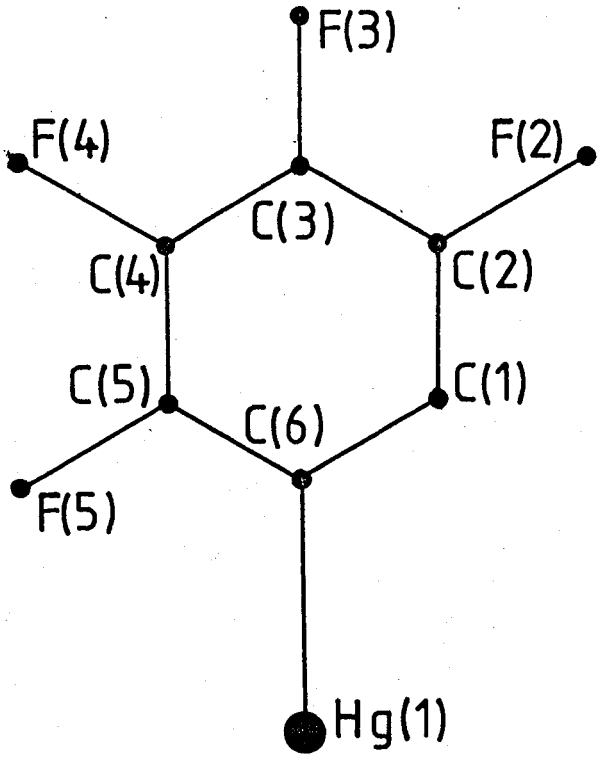


Fig. 5

Numbering scheme adopted for the assymmetric unit : Bis(2-hydrotetrafluorophenyl)mercury.

Fig. 6

Unit cell contents.

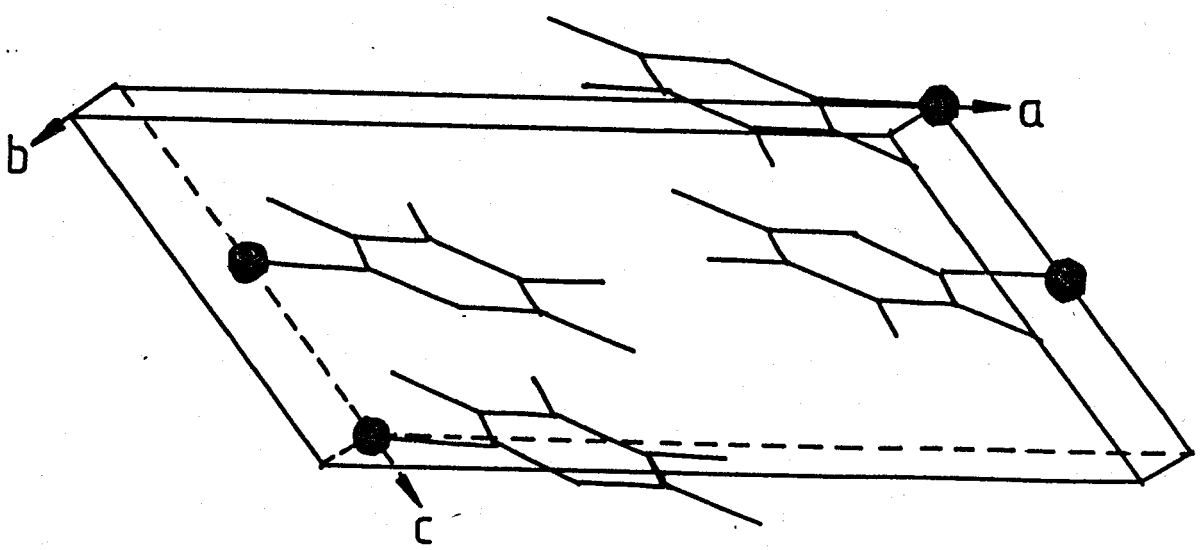


Table 6

Bondlengths(Å) in bis(2-hydrotetrafluorophenyl)mercury with estimated standard deviations in parentheses

C(6)	-	Hg(1)	2.096(16)
C(6)	-	C(1)	1.346(23)
C(1)	-	C(2)	1.405(23)
C(2)	-	C(3)	1.369(22)
C(3)	-	C(4)	1.325(25)
C(4)	-	C(5)	1.380(26)
C(5)	-	C(6)	1.336(22)
C(2)	-	F(2)	1.388(21)
C(3)	-	F(3)	1.394(21)
C(4)	-	F(4)	1.337(17)
C(5)	-	F(5)	1.378(21)

Table 7

Bondangles (^{o}) with their estimated standard deviations in parentheses

C(6)	-	Hg(1)	-	C(6)'	180.0*
C(1)	-	C(6)	-	Hg(1)	119.8(1.2)
C(5)	-	C(6)	-	Hg(1)	120.4(1.3)
C(5)	-	C(6)	-	C(1)	119.8(1.7)
C(6)	-	C(1)	-	C(2)	117.7(1.6)
C(1)	-	C(2)	-	C(3)	120.4(1.7)
C(1)	-	C(2)	-	F(2)	121.8(1.7)
C(3)	-	C(2)	-	F(2)	118.0(1.8)
C(2)	-	C(3)	-	C(4)	121.0(0.8)
C(2)	-	C(3)	-	F(3)	119.8(1.7)
C(4)	-	C(3)	-	F(3)	119.1(1.6)
C(3)	-	C(4)	-	C(5)	117.3(1.5)
C(3)	-	C(4)	-	F(4)	122.4(1.9)
C(5)	-	C(4)	-	F(4)	120.1(1.7)
C(4)	-	C(5)	-	C(6)	123.4(1.7)
C(4)	-	C(5)	-	F(5)	115.5(1.5)
C(6)	-	C(5)	-	F(5)	120.9(1.7)

* Fixed by symmetry considerations

Table 8

Final positional parameters ($x10^4$) with their standard deviations in parentheses

	x	y	z
Hg(1)	0	5000	5000*
C(1)	2232(18)	-576(41)	6211(17)
C(2)	3232(17)	1193(39)	6303(16)
C(3)	3294(18)	1447(43)	5298(17)
C(4)	2514(14)	-144(54)	4271(14)
C(5)	1578(17)	-1941(44)	4224(17)
C(6)	1449(16)	-2185(37)	5164(15)
F(2)	4075(12)	2038(30)	2334(11)
F(3)	4235(12)	3323(31)	5373(11)
F(4)	2534(11)	87(38)	3266(10)
F(5)	832(12)	-3642(28)	3168(11)

* fixed atom, hence no standard deviation values

p81 ▷

The successful structure solution shows that abandonment of chemical and symmetry considerations for a compound is no bar to a final, true, structure determination from X-ray data. Although it must be said that the case involved was favourable in that the single heavy atom in a cetrosymmetric special position weighted the data such that initial stages of structure determination were easy, the employment of P1 symmetry has been shown to be a very powerful analytical tool. The drawbacks of P1 were two-fold: true A symmetry for the heavy atoms produced an ill-conditioned matrix and the second atom refined away from its true position (the first atom was used to fix the origin). Secondly, the true symmetry was not easy to pick out because of the very short b axis: this meant the possible space-groups of P1, P2, P2/c and $P2_1/c$ could not be easily distinguished by the locations of the better-defined light atoms. P2 and P2/c would have meant a non-linear C-Hg-C system and they additionally gave higher values for R. The anisotropic heavy-atom value for R was 16.3% in P1 and 18.5% in $P2_1/c$. This can be attributed to two circumstances: P1 refinement used 15 variables (compared to 6), and the positional flexibility of the second heavy atom made it possible for the incomplete model to account for the data better.

The structure itself is interesting because it proves the supposition made about the structure of bis(penta-fluorophenyl)mercury:[144] this is non-planar, which was attributed to electrostatic repulsion between the ortho

fluorine atoms. Both the other phenyl mercurials studied (diphenylmercury [146] and bis(4-methylphenyl)mercury [147]) are planar and crystallise in $P2_1/c$ with $Z = 2$. The 2-hydrotetrafluorophenyl moiety would be expected to be chemically very similar to the pentafluorophenyl fragment, save that any electrostatic repulsions would tend to make it ordered and planar. The consideration of ordering is illustrated by the structure of 2-hydrononafluorobiphenyl which is non-randomly disordered.[142]

An early study on bis(pentafluorophenyl)mercury[45], which could not be reproduced during the course of this work, stated that on fresh sublimation the melting point was lower (115-117°C) than after standing or solvent crystallisation (135-137°C). This suggests that a metastable crystalline form exists and one possibility is that condensation from the gas phase can occur to give a planar molecule, this ordering then breaking down on standing.

Unfortunately the determination of hydrogen positions in the presence of heavy atoms is not reliable and so hydrogen / fluorine interactions between molecules cannot be proved, although the orientation of the rings suggests that some association is geometrically possible (Figure 6).

The infra-red spectrum of the compound was inconclusive as an identity test as most peaks were considerably broadened, but the mass spectrum clearly corroborated the structure as $(C_6F_4H)_2Hg$. The only major degredative pathway was cleavage of the C-Hg bond

(i.e. loss of C_6F_4H or HC_6F_4Hg) but small peaks corresponding to loss of HF, F, $F^{\oplus}$ or Hg could also be seen. Loss of $F^{\oplus}$ to give a doubly charged ion was several times more favourable than the loss of F.

The carbon-mercury bondlength is normal (Table 9) as are the carbon-carbon bondlengths and angles. The worst-defined atom is C(4) which is involved in the shortest carbon-carbon value and both the bondangles which deviate most from 120°. This casts some doubt upon the value for C(4) - F(4) as it deviates from the other carbon-fluorine distances. The other three carbon-fluorine separations, at about 1.38Å, are about 0.04Å higher than in non-metallic polyfluoroaromatic derivatives such as 2-hydrononafluorobiphenyl [142] and 2,6-bis(pentafluorophenyl)-1-bromotrifluorobenzene.[143] The values for bis(pentafluorophenyl)mercury average 1.38Å range but fall in the range 1.33Å - 1.47Å. [144]

4. Perfluorotribenzo [b,e,h][1,4,7]trimercuronin. 4-phenylpyridine

Crystals were prepared by slow evaporation of 1:1 methanol solution of the two separate compounds.

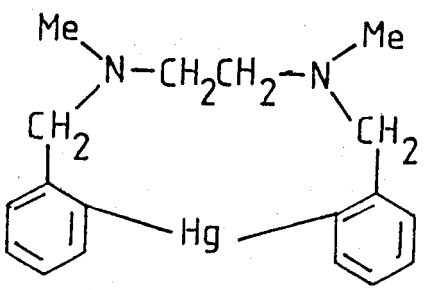
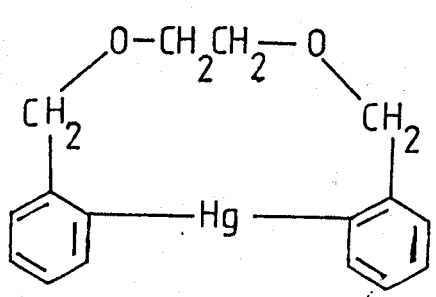
Crystal Data

Monoclinic	a = 11.223(9)Å	Dx = 2.83 Mgm^{-3}
	b = 27.308(15)Å	Z = 4
	c = 9.529(10)Å	F(000) = 2052
	β = 105.20(5)°	U = 2818.2$Å^3$

▷p90

Table 9

Carbon-Mercury bondlengths in aromatic mercurials

Compound	C-Hg bondlengths (Å)*	Reference
$(C_6F_5)_2Hg$	2.10(-); 2.10(-)	144
C_6H_5HgCN	2.05(2)	145
$(C_6H_5)_2Hg$	2.085(7)	146
$(p\text{-}MeC_6H_4)_2Hg$	2.08(-)	147
$(2\text{-}C_4H_3S)_2Hg$	2.08(-)	148
$(C_6H_5)_2Hg.1,10\text{-}C_{14}H_{12}N_2$	2.10(-)	149
$(C_6H_5)_2Hg.1,10C_{16}H_{16}N_2$	2.10(-);2.13(-)	149
$((C_6F_5)_2Hg)_2.C_{13}H_{12}As_2$	2.15(4);2.07(4)	150
	2.07(2);2.12(2)	151
	2.07(5);2.13(6)	151

*values in parentheses are standard deviations

p88▷

Absences: hOl when h + l = 2n + l

OkO when k = 2n + l

Space Group: $P2_1/n$ (No. 14)

Radiation: Cu-Kα, λ=1.54178Å, μ= 30.1mm^{-1}

Crystal size: 0.077 x 0.170 x 0.56mm

Intensity Data

Reflections were measured on a Stoe automatic Weissenberg diffractometer equipped with a graphite monochromator. Rotation was about the crystallographic a axis; each reflection was scanned with variable ω based on at 2.2° mosaic spread and a 20 second background count was made at the start and end of every reflection. A strong reflection was measured after every 25 scans, but the data was not scaled to it and a new standard was chosen for each layer. The decomposition observed during the course of data collection was not severe enough to necessitate correction of measured values: it was typically of the order of 10% in the intensity value. Systematically absent reflections were measured but omitted from data reduction after inspection; reflections where $I \leq 4\sigma(I)$ were classed as unobserved and omitted from least-squares refinement; 0kl and 1kl less-thans were included in direct-methods structure solution attempts. Lorentz, polarisation and absorbtion effects were corrected.

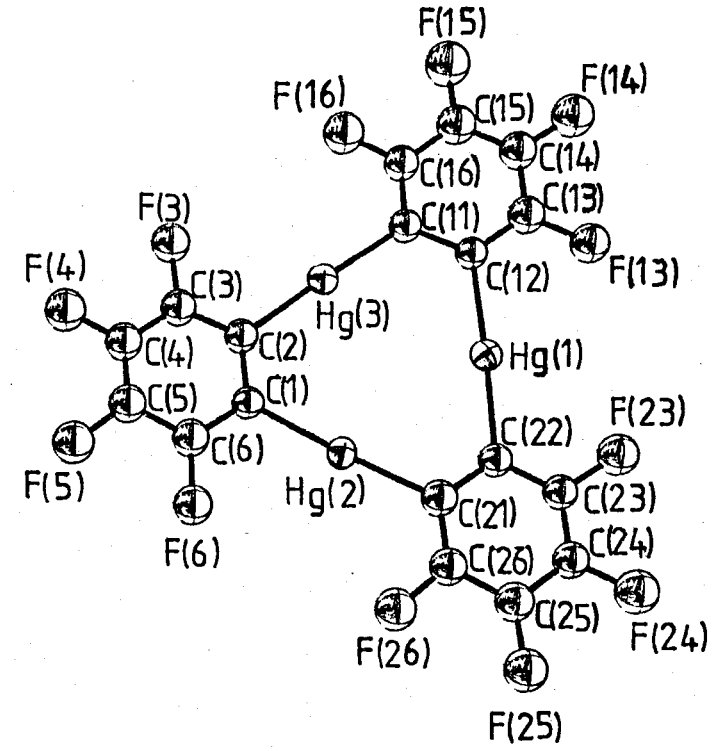
Structure Determination and Refinement

The direct-methods routine of the SHELX suite of programs [152] was used initially, but gave no success on least-squares refinement of the trial structure proposed. A set of data was then generated for the MULTAN 74 program [154]: the solution with the best figure of merit refined anisotropically for the heavy atoms to give an R value of 16.4%. A difference map located all the light atoms and of the 43 highest peaks 42 were real. Values for the scale-factor and for inter-layer factors were obtained by an isotropic refinement of all atoms (R was 8.8% at convergence) and then fixed during anisotropic refinement of the heavy atoms. No attempts were made either to refine the light atoms anisotropically or to locate hydrogen atoms. The nitrogen atom was allocated to position (34) rather than (44) on the basis of temperature factors. The final value of R was 7.4% for the 3533 observed reflections

Structure and temperature factors are given in Appendix I, positional parameters in Table 10, bond-lengths in Table 11, bond-angles in Table 12 and short contact distances in Table 13. The numbering scheme adopted is shown in Figure 7; Figures 8 and 9 are two different projection views of the unit cell contents.

Discussion

There are two main chemical points of interest in this structure: the oligomeric nature of $(C_6F_4Hg)_n$ and



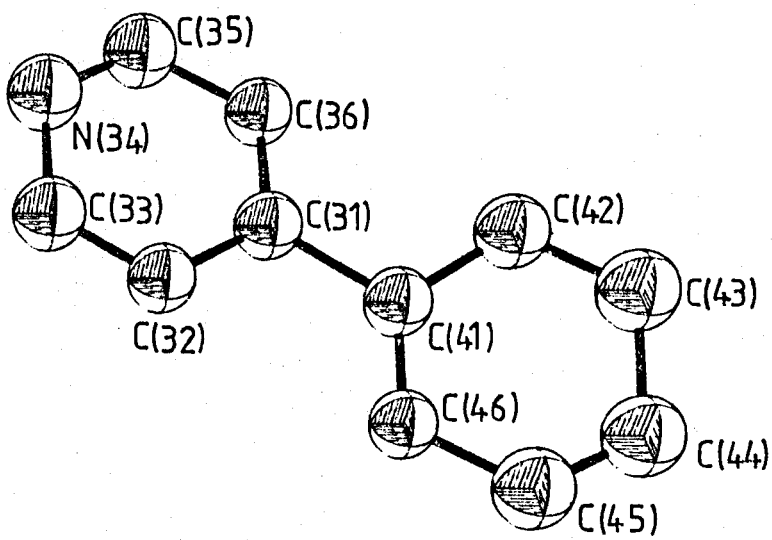


Fig. 7

Numbering employed for perfluorotribenzo[b,e,h][1,4,7]trimercuronin and 4-phenylpyridine (to different scales).

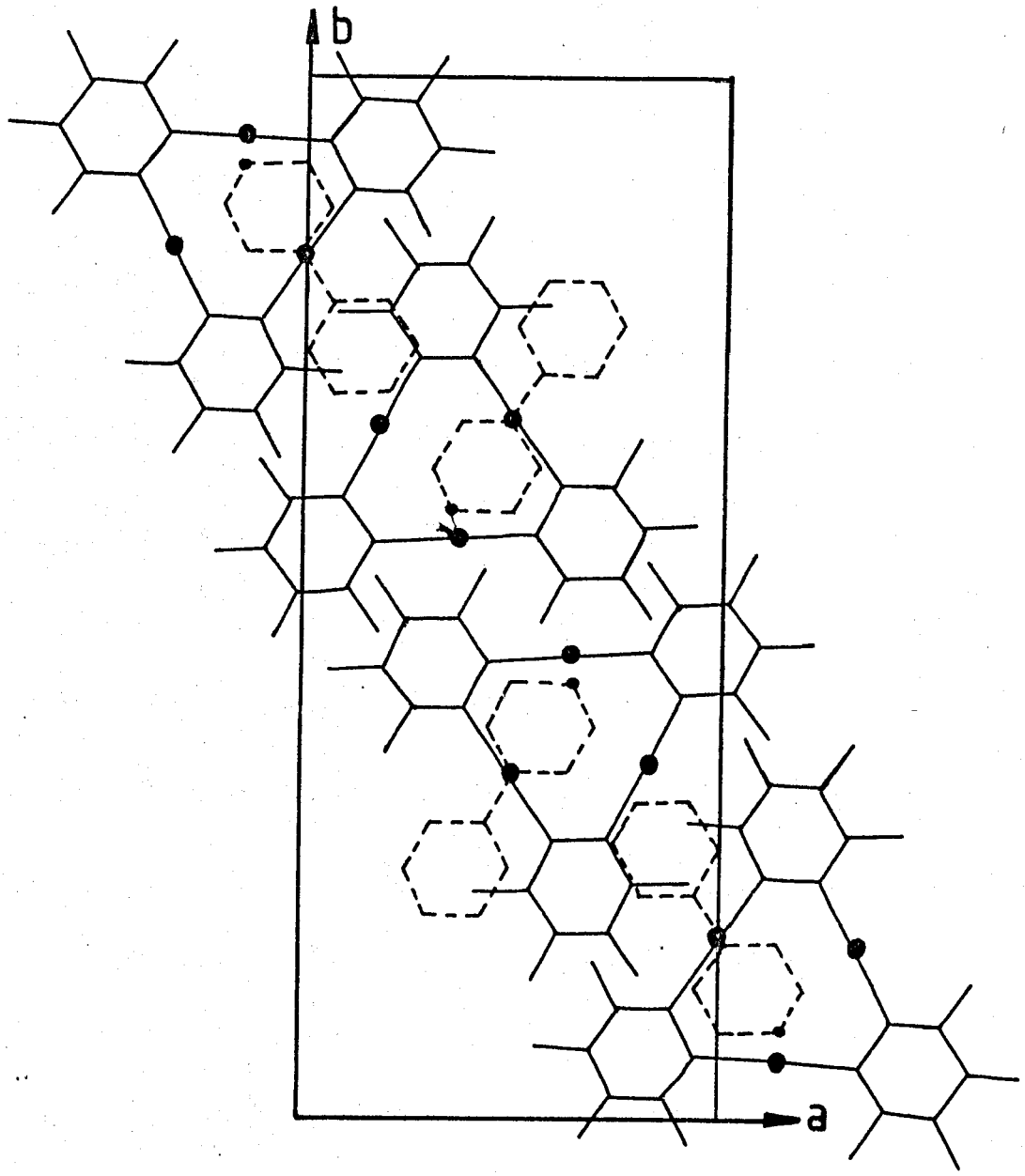


Fig.8

Unit cell contents : c axis projection.

- Nitrogen
- Mercury

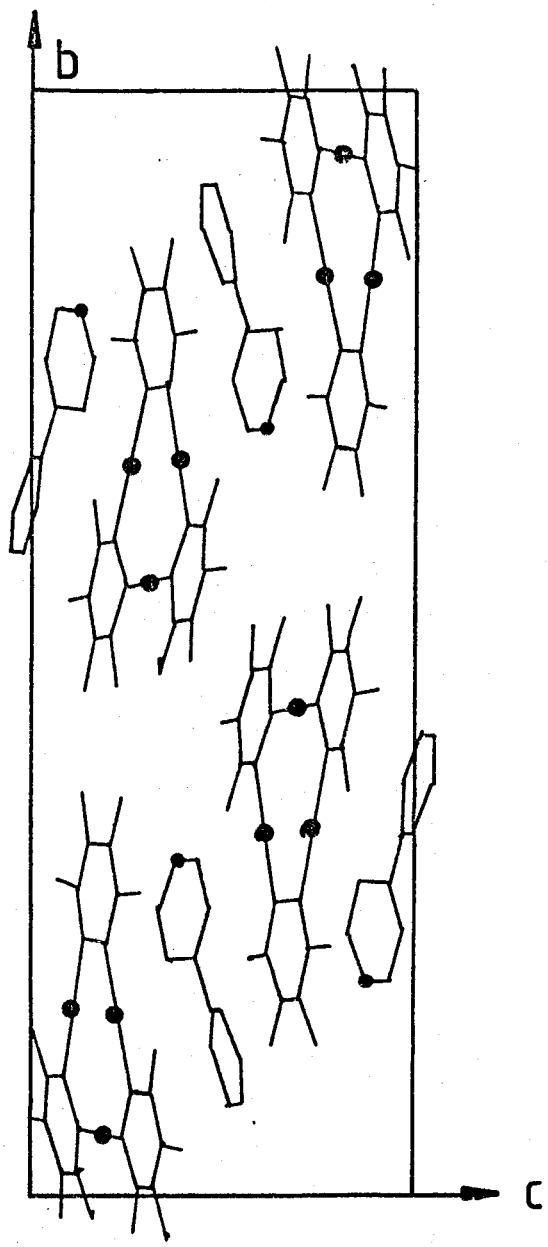


Fig.9
Unit cell contents : a axis projection.

- Nitrogen
- Mercury

Table 10

Positional parameters ($x10^4$, with their estimated standard deviations in parentheses) for perfluorotribenzo(b,e,h)-(1,4,7) trimercuronin.4-phenylpyridine

	x	y	z
Hg(1)	8212(1)	3359(0)	7389(1)
Hg(2)	4911(1)	3287(0)	6066(1)
Hg(3)	6376(1)	4451(0)	6963(1)
C (1)	3874(26)	3921(10)	5874(28)
C (2)	4439(25)	4388(9)	6316(27)
C (3)	3704(30)	4801(11)	6238(33)
C (4)	2447(31)	4772(11)	5797(34)
C (5)	1904(32)	4334(12)	5422(36)
C (6)	2646(29)	3912(11)	5482(31)
C(11)	8308(26)	4482(9)	7507(28)
C(12)	9021(28)	4059(10)	7749(31)
C(13)	10245(29)	4095(11)	8185(32)
C(14)	10864(30)	4548(11)	8472(33)
C(15)	10108(28)	4966(11)	8279(31)
C(16)	8895(27)	4920(10)	7895(29)
C(21)	6023(27)	2661(10)	6436(29)
C(22)	7285(25)	2689(9)	6977(27)
C(23)	7962(29)	2255(11)	7275(33)
C(24)	7339(30)	1795(11)	7072(32)
C(25)	6195(30)	1777(11)	6541(32)
C(26)	5487(28)	2199(11)	6223(31)

C(31)	4347(29)	2835(11)	9333(32)
C(32)	4915(29)	2383(11)	9676(32)
C(33)	4260(32)	1955(12)	9350(36)
N(34)	2971(27)	1969(10)	8766(30)
C(35)	2470(33)	2387(12)	8380(37)
C(36)	3116(29)	2856(11)	8639(32)
C(41)	5120(29)	3317(11)	9736(32)
C(42)	4445(31)	3749(12)	9855(35)
C(43)	5041(35)	4185(13)	10261(39)
C(44)	6437(34)	4172(13)	10550(38)
C(45)	6936(35)	3769(13)	10448(39)
C(46)	6317(28)	3316(11)	9990(31)
F(3)	4274(16)	5236(6)	6640(18)
F(4)	1786(18)	5180(7)	5814(21)
F(5)	675(20)	4297(7)	5006(22)
F(6)	2020(18)	3490(7)	5114(21)
F(13)	11017(17)	3703(7)	8324(20)
F(14)	12055(18)	4592(7)	8920(20)
F(15)	10665(18)	5405(7)	8607(20)
F(16)	8208(16)	5342(6)	7803(18)
F(23)	9199(16)	2255(6)	7808(18)
F(24)	8077(17)	1390(7)	7397(20)
F(25)	5568(18)	1343(7)	6336(20)
F(26)	4213(16)	2154(6)	5712(18)

Table 11

Bondlengths (Å) for perfluorotribenzo[b,e,h][1,4,7]-trimercuronin.4-phenylpyridine with their estimated standard deviations in parentheses

Hg(1)	-	C(12)	2.105(29)
Hg(1)	-	C(22)	2.089(25)
Hg(2)	-	C(1)	2.067(27)
Hg(2)	-	C(21)	2.090(27)
Hg(3)	-	C(2)	2.111(27)
Hg(3)	-	C(11)	2.095(28)
C (1)	-	C(2)	1.436(35)
C (2)	-	C(3)	1.385(38)
C (3)	-	C(4)	1.361(43)
C (4)	-	C(5)	1.343(42)
C (5)	-	C(6)	1.417(41)
C (6)	-	C(1)	1.332(40)
C(11)	-	C(12)	1.391(37)
C(12)	-	C(13)	1.331(41)
C(13)	-	C(14)	1.411(40)
C(14)	-	C(15)	1.405(40)
C(15)	-	C(16)	1.320(41)
C(16)	-	C(11)	1.367(36)
C(21)	-	C(22)	1.376(37)
C(22)	-	C(23)	1.396(38)
C(23)	-	C(24)	1.427(41)
C(24)	-	C(25)	1.289(41)

C(25)	-	C(26)	1.367(40)
C(26)	-	C(21)	1.391(38)
C(31)	-	C(32)	1.389(39)
C(32)	-	C(33)	1.371(42)
C(33)	-	N(34)	1.408(41)
N(34)	-	C(35)	1.284(40)
C(35)	-	C(36)	1.460(43)
C(36)	-	C(31)	1.367(41)
C(31)	-	C(41)	1.569(40)*
C(41)	-	C(42)	1.421(32
C(42)	-	C(43)	1.372(44)
C(43)	-	C(44)	1.518(52)
C(44)	-	C(45)	1.249(46)
C(45)	-	C(46)	1.431(44)
C(46)	-	C(41)	1.301(41)
C(3)	-	F(3)	1.359(32)
C(4)	-	F(4)	1.342(34)
C(5)	-	F(5)	1.333(37)
C(6)	-	F(6)	1.350(32)
C(13)	-	F(13)	1.362(33)
C(14)	-	F(14)	1.297(35)
C(15)	-	F(15)	1.349(32)
C(16)	-	F(16)	1.378(30)
C(23)	-	F(23)	1.348(34)
C(24)	-	F(24)	1.368(34)
C(25)	-	F(25)	1.346(33)
C(26)	-	F(26)	1.390(33)

* taken from rigid body refinement of the two phenyl rings

Table 12

Bondangles (°) for perfluorotribenzo [b,e,h][1,4,7]-trimercuronin.4-phenylpyridine

Hg(1)	-	Hg(2)	-	Hg(3)	60.0(0)
Hg(2)	-	Hg(3)	-	Hg(1)	60.2(0)
Hg(3)	-	Hg(1)	-	Hg(2)	59.8(0)
C(22)	-	Hg(1)	-	C(12)	175.8(1.1)
C(21)	-	Hg(2)	-	C(1)	175.3(1.0)
C(2)	-	Hg(3)	-	C(11)	176.6(1.0)
Hg(1)	-	C(22)	-	C(23)	119.1(2.0)
Hg(1)	-	C(22)	-	C(21)	122.1(1.9)
Hg(1)	-	C(12)	-	C(11)	121.6(2.2)
Hg(1)	-	C(12)	-	C(13)	118.9(2.2)
Hg(2)	-	C(1)	-	C(2)	121.7(2.0)
Hg(2)	-	C(1)	-	C(6)	122.0(2.1)
Hg(2)	-	C(21)	-	C(22)	121.9(2.0)
Hg(2)	-	C(21)	-	C(26)	120.0(2.1)
Hg(3)	-	C(2)	-	C(1)	119.8(1.9)
Hg(3)	-	C(2)	-	C(3)	120.1(2.0)
Hg(3)	-	C(11)	-	C(16)	119.8(2.0)
Hg(3)	-	C(11)	-	C(12)	121.3(2.0)
C(2)	-	C(1)	-	C(6)	116.0(2.6)
C(1)	-	C(2)	-	C(3)	119.9(2.5)
C(12)	-	C(11)	-	C(16)	117.8(2.6)
C(11)	-	C(12)	-	C(13)	119.4(2.7)
C(22)	-	C(21)	-	C(26)	118.0(2.6)

C(1)	-	C(2)	-	C(3)	119.9(2.5)
C(2)	-	C(3)	-	F(3)	117.9(2.6)
C(4)	-	C(3)	-	F(3)	120.7(2.7)
C(2)	-	C(3)	-	C(4)	121.4(2.8)
C(3)	-	C(4)	-	F(4)	118.7(2.8)
C(5)	-	C(4)	-	F(4)	121.6(3.0)
C(3)	-	C(4)	-	C(5)	119.7(3.1)
C(4)	-	C(5)	-	F(5)	120.8(3.0)
C(6)	-	C(5)	-	F(5)	119.8(2.9)
C(4)	-	C(5)	-	C(6)	119.3(3.1)
C(5)	-	C(6)	-	F(6)	115.4(2.7)
C(1)	-	C(6)	-	F(6)	121.0(2.7)
C(5)	-	C(6)	-	C(1)	123.6(2.9)
C(12)	-	C(13)	-	F(13)	123.4(2.7)
C(14)	-	C(13)	-	F(13)	113.7(2.7)
C(12)	-	C(13)	-	C(14)	122.8(2.9)
C(13)	-	C(14)	-	F(14)	123.8(2.8)
C(15)	-	C(14)	-	F(14)	120.3(2.8)
C(13)	-	C(14)	-	C(15)	115.9(2.9)
C(14)	-	C(15)	-	F(15)	117.6(2.7)
C(16)	-	C(15)	-	F(15)	122.1(2.7)
C(14)	-	C(15)	-	C(16)	120.2(2.8)
C(15)	-	C(16)	-	F(16)	117.2(2.5)
C(11)	-	C(16)	-	F(16)	119.5(2.5)
C(15)	-	C(16)	-	C(11)	123.2(2.7)
C(22)	-	C(23)	-	F(23)	122.1(2.6)
C(24)	-	C(23)	-	F(23)	118.0(2.7)
C(22)	-	C(23)	-	C(24)	119.9(2.8)

C(23)	-	C(24)	-	F(24)	115.8(2.7)
C(25)	-	C(24)	-	F(24)	123.8(2.9)
C(23)	-	C(24)	-	C(25)	120.3(3.1)
C(24)	-	C(25)	-	F(25)	120.5(2.9)
C(26)	-	C(25)	-	F(25)	119.2(2.8)
C(24)	-	C(25)	-	C(26)	120.3(3.1)
C(25)	-	C(26)	-	F(26)	117.3(2.7)
C(21)	-	C(26)	-	F(26)	119.9(2.6)
C(25)	-	C(26)	-	C(21)	122.7(2.8)
C(41)	-	C(31)	-	C(32)	119.9(2.7)
C(41)	-	C(31)	-	C(36)	120.5(2.7)
C(32)	-	C(31)	-	C(36)	119.6(2.8)
C(31)	-	C(32)	-	C(33)	121.2(3.0)
C(32)	-	C(33)	-	N(34)	120.1(3.0)
C(33)	-	N(34)	-	C(35)	117.7(3.0)
N(34)	-	C(35)	-	C(36)	124.8(3.2)
C(35)	-	C(36)	-	C(31)	116.0(2.8)
C(31)	-	C(41)	-	C(42)	116.3(2.7)
C(31)	-	C(41)	-	C(46)	121.4(2.8)
C(42)	-	C(41)	-	C(46)	122.2(3.0)
C(41)	-	C(42)	-	C(43)	120.8(3.2)
C(42)	-	C(43)	-	C(44)	115.7(3.2)
C(43)	-	C(44)	-	C(45)	118.0(3.5)
C(44)	-	C(45)	-	C(46)	126.4(3.6)
C(45)	-	C(46)	-	C(41)	116.7(3.0)

Table 13

Short contact distances in perfluorotribenzo[b,e,h]-[1,4,7]trimercuronin.4-phenylpyridine. Only distances less than 4.0Å are given.

(a) Intramolecular distances (Å) involving mercury and fluorine atoms

Hg(1)	-	F(13)	3.181
Hg(1)	-	F(23)	3.201
Hg(2)	-	F(6)	3.180
Hg(2)	-	F(26)	3.188
Hg(3)	-	F(3)	3.143
Hg(3)	-	F(16)	3.151

(b) Intermolecular distances (Å) involving mercury atoms

Hg(1)	-	F(26)	3.374
Hg(2)	-	F(24)	3.669
Hg(2)	-	F(23)	3.341
Hg(2)	-	C(23)	3.983
Hg(3)	-	F(4)	3.891
Hg(3)	-	F(3)	3.420
Hg(3)	-	C(4)	3.872
Hg(3)	-	C(3)	3.656

(c) Contact distances (Å) involving mercury atoms and the 4-phenylpyridine system

Hg(1) - C(45)	3.741	Hg(1) - C(33)	3.506
Hg(1) - C(46)	3.667	Hg(1) - N(34)	3.507
Hg(2) - C(31)	3.557	Hg(2) - C(41)	3.445
Hg(2) - C(36)	3.747	Hg(2) - C(42)	3.987
Hg(2) - C(46)	3.659	Hg(3) - C(43)	3.888
Hg(3) - C(44)	3.484	Hg(3) - C(45)	3.713

(d) Short contact distances (Å) between light atoms. Distances less than 3.50 Å are given, and all values are intermolecular

C(1) - F(24)	3.308	F(4) - F(5)	3.030
C(4) - F(16)	3.329	F(5) - F(15)	3.478
C(5) - F(16)	3.165	F(5) - F(16)	3.387
C(6) - F(24)	3.120	F(6) - F(24)	3.134
C(11) - F(4)	3.273	C(13) - F(25)	3.165
C(14) - F(16)	3.429	C(15) - C(15)	3.354
C(15) - F(15)	3.451	C(16) - F(4)	3.423
C(16) - F(15)	3.356	F(13) - F(25)	3.042
F(14) - F(16)	3.220	F(15) - F(25)	2.921
C(22) - N(34)	3.472	C(22) - C(35)	3.493
C(24) - F(6)	3.106	C(25) - F(6)	3.366
C(25) - F(13)	3.298	C(32) - F(6)	3.303
C(32) - F(23)	3.434	C(33) - F(26)	3.496
C(33) - F(6)	3.228	C(36) - F(13)	3.260
C(42) - F(24)	3.212	c(43) - F(3)	3.258

C(44)	-	F(3)	3.398	C(44)	-	F(15)	3.346
C(45)	-	F(15)	3.447	C(46)	-	F(26)	3.396

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the location of the 4-phenylpyridine relative to this mercurial. The former observation is discussed more fully in Chapter 7, and the only note that will be made here is that a trimeric formulation is unequivocally proved as it was for $(C_6H_4Hg)_n$.

The adducts of the $(C_6F_4Hg)_n$ trimer are very numerous and are discussed in terms of their thermal decomposition kinetics in Chapter 3. 4-Phenylpyridine was chosen for a recrystallisation with X-ray studies in mind because it is a solid and the thermal stability of the adducts appeared to be linked to the vapour pressure of the free organic molecule. The 1:1 stoichiometry was chosen also for reasons of stability. The decomposition in the X-ray beam could not be attributed to thermal degradation since the sample from the recrystallisation had been allowed to stand for a considerable time before preliminary structure studies began and a mounted crystal was left for six months without deterioration. This decomposition probably accounts in large part for the relatively poor values for bond-lengths and angles involving light atoms: the intensity measurements were affected directly by a lessening of the numerical value for the reflection and indirectly as the spots became broader during data collection. This smearing effect added to values for background. The size of the crystal chosen also adversely affected intensity values: the optimum size for a crystal of the adduct is about 0.03mm and all

crystal dimensions were greater than this.

The bond-lengths and angles are within the normal range of values for carbon-mercury and for fluoroaromatic systems. The Hg-Hg-Hg angles are quoted to show that there is no significant deviation of the mercurial moiety from an ideal triangular array. The carbon-fluorine distances were not sufficiently well-defined to determine if the "norm" value of 1.38Å found in bis(2-hydrotetrafluorophenyl)mercury and bis(pentafluorophenyl)mercury [144] is consistent with perfluorotribenzo[b,e,h][1,4,7]trimercuronin, but the mean of the twelve unique lengths is 1.35Å. The mercury atoms were very close to isotropic in character and this explains the small change in R (from 8.8% to 7.4%) upon anisotropic heavy-atom refinement.

The position of the 4-phenylpyridine relative to the mercurial system was surprising since a classical complex had been expected with donation from the nitrogen to one of the metal atoms. The table of contact distances together with the two projection views (Figures 8 and 9) shows that the geometry of the molecular arrangement rules out hydrogen/fluorine bonding and charge-transfer effects as well as nitrogen-mercury interactions. The contact distances are quoted extensively to give inter-mercurial light atom separations for comparison with 4-phenylpyridine values. The only explanation remaining is that the 4-phenylpyridine acts as an inert spacer, intercalating

between the negatively charged fluorine atoms on the perimeter of the mercurial, and it is probably best described as a solvent of crystallisation. The van der Walls forces which hold molecular crystals together are caused by interactions between induced dipole moments,[155] and are a balance between attractive and repulsive forces. With this in mind the insertion of a molecular spacer between the negative fluorine atoms becomes reasonable on empirical grounds: it would not reduce the overall level of the attractive forces whilst decreasing electrostatic repulsions.

Chapter 3

Solid State Chemistry

Summary: the chemistry of the solid state is reviewed with particular reference to the analysis of reaction kinetics. Experimental data is presented for the complexes of perfluorotribenzo[b,e,h][1,4,7]trimercuronin and a model cobalt system.

Solid State Chemistry

Introduction

Reactions in the solid state are characterised by several important differences to those in the liquid and gaseous states. These are shown in their kinetics by the following effects: sample history can greatly influence reaction rates; and classical laws (with consequent equations) based on continuously homogenous systems do not usually apply. The first effect is not only due to such things as particle size, shape and, where relevant, crystal form, but also to more subtle influences such as the number and type of defects in the solid lattice. The second effect is caused by the non-homogeneity of solid systems during reactions: if a solid is heated and a reaction occurs it often starts on the surface and progresses inwards. Endothermic reactions inhibit heat transfer into the body of a particle and exothermic reactions start by increasing the temperature of the surface. Reactions, therefore, that are rapid compared with thermal equilibrium would hardly be expected to comply with kinetic models for homogenous systems. Where a gas or vapour is involved it has to diffuse in or out of the particle through a surface layer of reacted material: this surface changes in depth during the course of the reaction.

Solid state reactions can be regarded as occuring in three steps: nucleation, phase-boundary reaction, and

diffusion of the reaction products out of the solid. Any of these steps may be rate determining and all have different kinetics (although each overall type may be best described by one of a variety of mathematical equations). Polymerisation is the classic example of a nucleation-controlled reaction: formation of the initial reaction "nucleus" or particle of product is the highest energy step and further product rapidly forms around that nucleus. Typically this means a slow start to a reaction then it proceeds rapidly to completion. Phase-boundary controlled reactions are the most similar to liquid or gas phase reactions: nucleation is rapid and product forms smoothly on the nuclei. The reaction must, however, be treated as starting on the outside of a solid particle and proceeding towards its centre. This implies reactions that start a little more slowly and go to completion a little more rapidly than liquid phase reactions. Diffusion controlled reactions occur where nucleation is rapid and product is smoothly formed on these nuclei, but one or more products have a high energy barrier to diffusion from the reaction site to the outside of the particle. Additionally, if a high energy barrier exists to diffusion and one of the starting materials is present in a fluid phase, kinetics may be determined by this step. If the system that monitors such a reaction does so on the basis of weight changes then it will appear to start rapidly and go to completion very slowly.

The following conventions have been adopted in

studies where thermogravimetry (TG) has been used as the analytical technique: the weight-loss curve is normalised by expression as a percentage of the total loss (either experimental or theoretical) and the reaction time is expressed as a multiple of the half-time. This, the time for the weight to change by 50% of the total value, does not imply any kinetic conclusion but merely puts all data on a common scale that favours no particular part of it. The half-time is obtained graphically from a plot of normallised weight loss ($\Delta W/W$) against time: two such curves are shown in each of Figures 10 and 11. Reaction times are normallised for further data processing only where the analysis has been carried out isothermally. In general the best temperatures for isothermal data collection are the lower ones as this minimises the errors due to partial reaction during attainment of thermal equilibrium.

TG is by far the most common kinetic probe used since spectroscopic techniques have the grave drawbacks either of poor signal/noise ratio (e.g. n m r, reflectance spectroscopy), limited availability (e.g. n q r) or are limited by the method of sample preparation (e.g. i-r and absorbance U-V). The results from a typical temperature programmed experiment are shown in Figure 12: the reactions involved are two sequential losses of one molecule each of DMF from its 2:1 adduct with perfluoro-o-phenylenemercury.

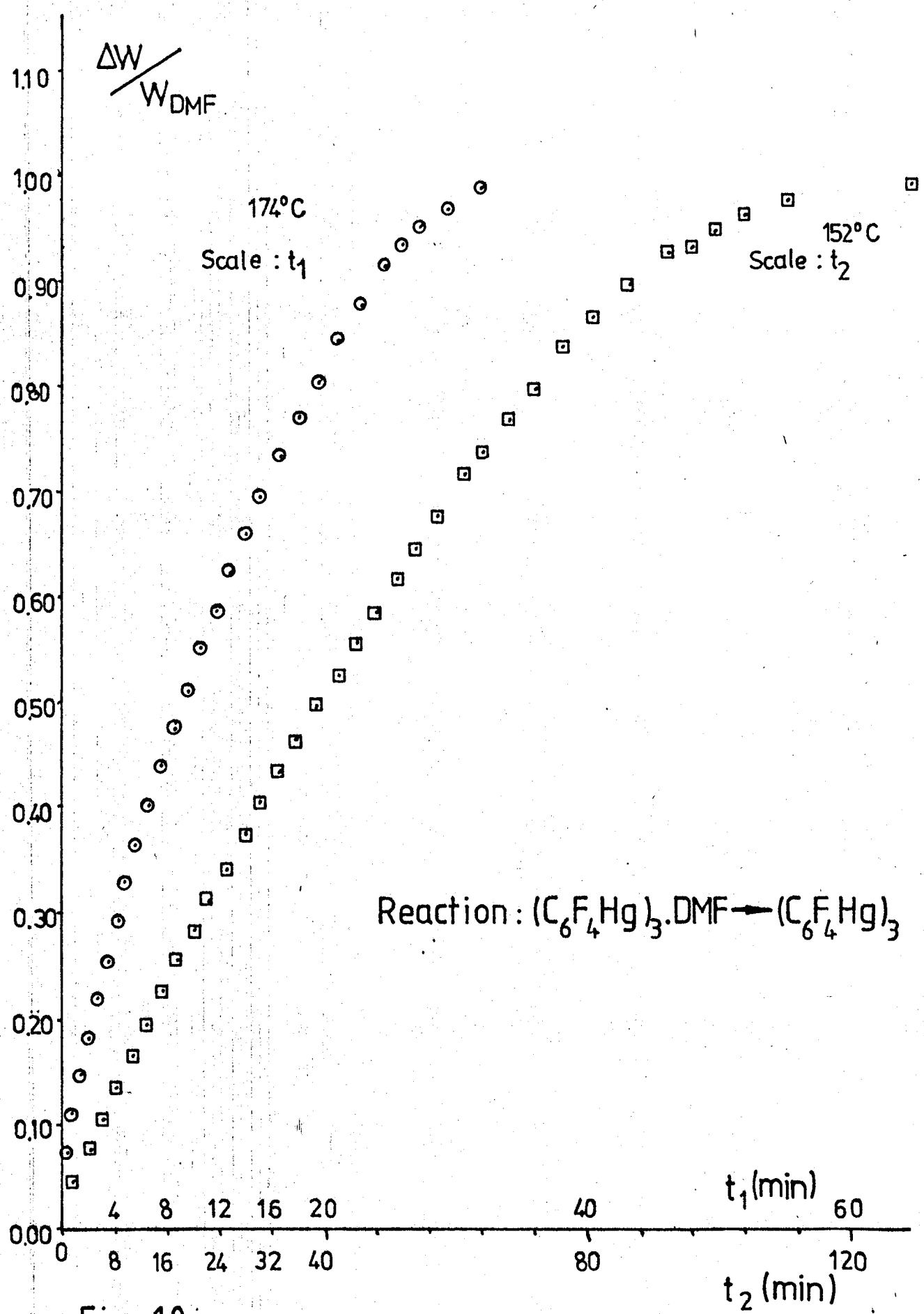


Fig. 10

Normalised weight-loss curves used to find $t_{1/2}$

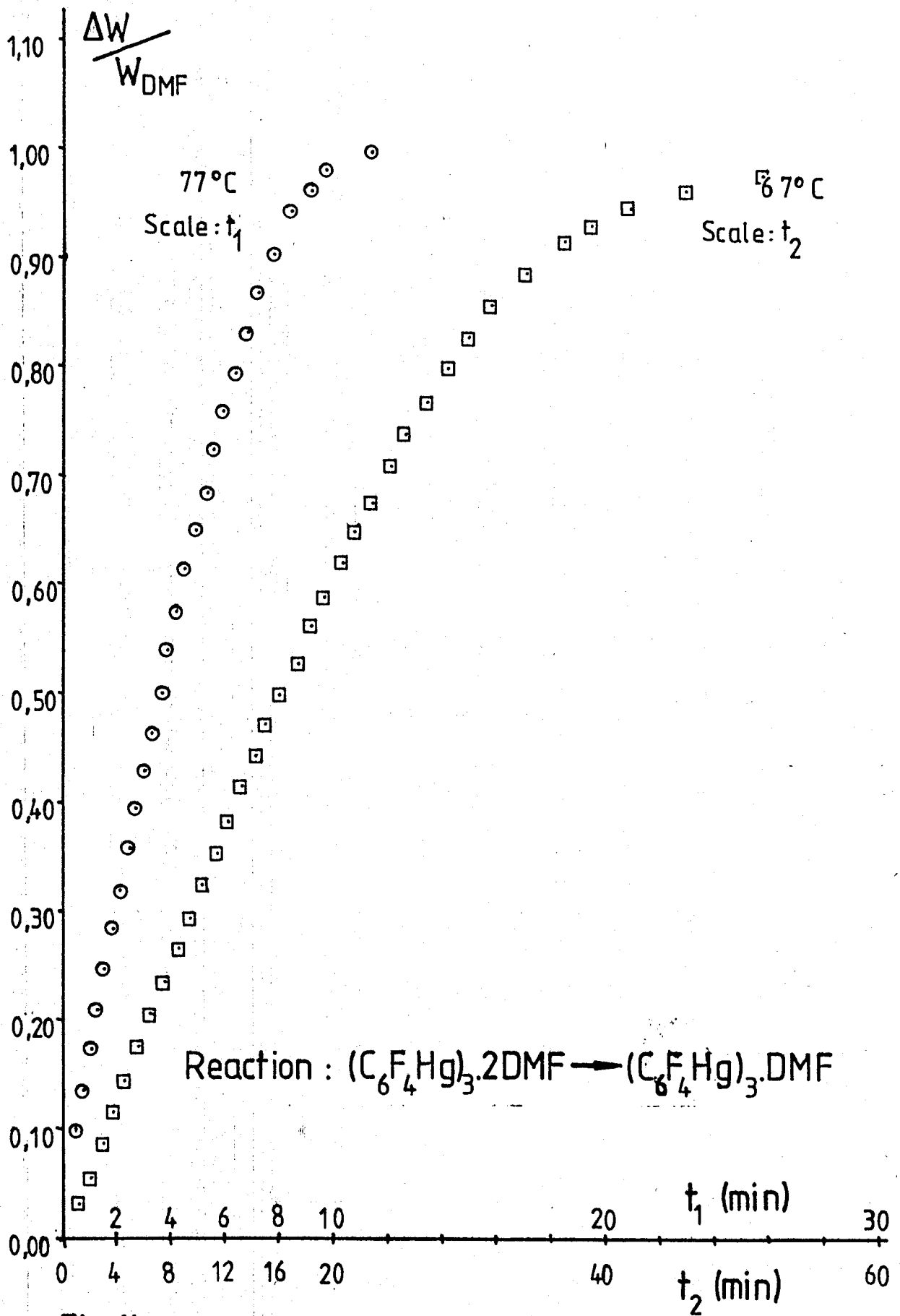
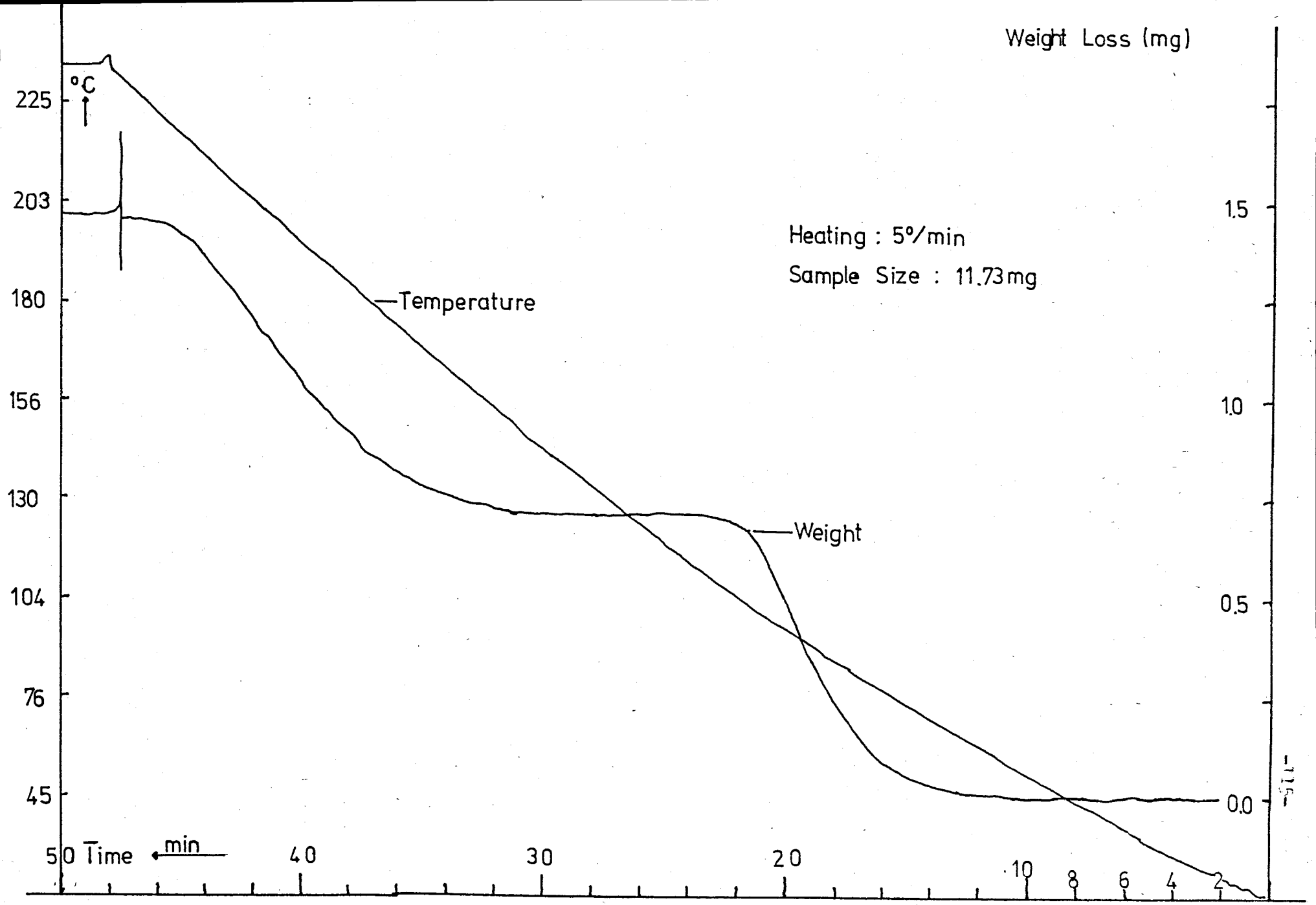


Fig.11

Normalised weight-loss curves used to find $t_{1/2}$

Fig.12 Thermogravimetric analysis curve : $(C_6F_4Hg)_3 2DMF$



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Technique

Probably the optimal procedure for TG is as follows: a temperature-programmed run is performed at a fairly high heating-rate (say 15°/min) and, from the results of this, temperatures for one or more isothermal runs are chosen. In the isothermal case the sample is heated at the maximum possible rate to the chosen temperature and then maintained at that value. Finally a temperature-programmed run is performed at the slowest reasonable heating rate (say 1° or 2° per minute) with rapid heating to about 20° below the lowest reaction temperature if this is high. The first run can be set up to give the total sample weight as full scale deflection, whereas subsequent analyses are best performed to give the weight loss as close as possible to full scale in the interests of precision. It might seem that the exploratory initial TGA is unnecessary as its purpose could be served as effectively by the final programmed analysis, but it is useful (a) to give an idea of proportional weight loss so that all later runs can have this near full scale, (b) to give an idea of the maximum temperatures to use, (c) to relate to thermal analysis results and (d) to investigate rapidly whether a given sample is amenable to TG methods.

TGA can give mechanistic data and reasonable approximations for the activation energy and frequency factor of the rate-determining step in a reaction sequence. Graphically this is achieved as follows: a graph is

plotted of normalised weight loss against normalised time and the curve compared with theoretical values.[156] Examples of this technique are shown in Figures 13 and 14; the symbols used for theoretical curves are given in Table 14 together with the kinetic equation they represent. It can be seen that the line of best fit gives the most probable mechanism, but the geometrical approximations (e.g. cubes or spheres for 3-dimensional kinetics) in the mathematics may make the correlation imperfect. The activation energy and frequency factor may be obtained from a temperature-programmed analysis by the method of Satava and Skvara.[157] Using their symbols a plot of log $g(\alpha)$ against temperature is made: they give tables of log $g(\alpha)$ for values of normalised weight loss calculated for a variety of mechanisms. Curve matching against standard curves of log p(x) for various activation energies yields this datum and the frequency factor can be calculated from the equation

$$\log \frac{ZE}{Rq} = \log g(\alpha) - \log p(x)$$

Z is the frequency factor

E is the activation energy

R is the gas constant

q is the rate of heating

log $g(\alpha)$ and log p(x) are complex integrals: the numerical value corresponding to their difference is obtained from the standard log p(x) curves referred to above.

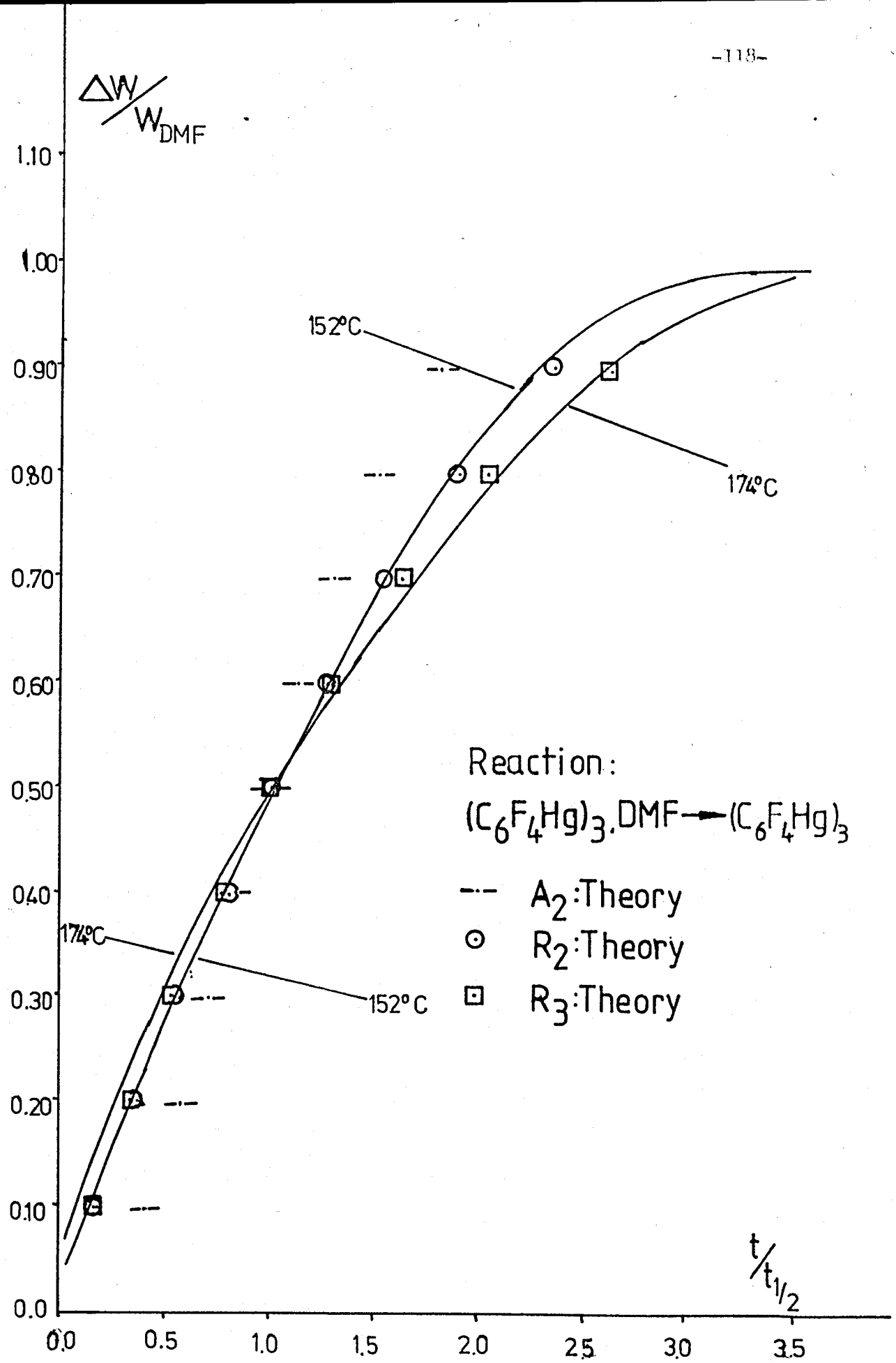


Fig.13

Isothermal TGA curves

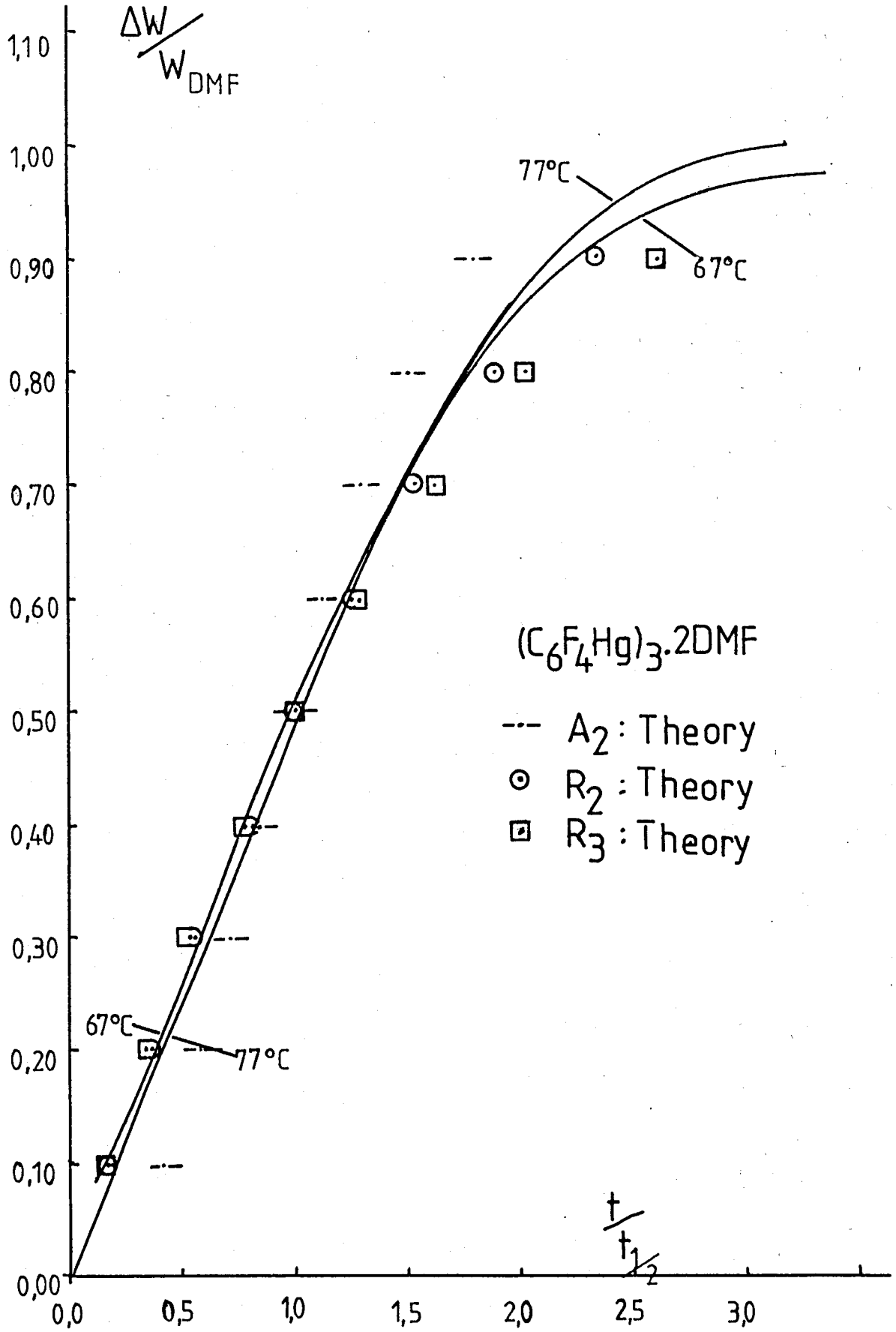


Fig. 14
Isothermal TGA curves

Table 14

Explanation of kinetic symbols

Symbol	Equation*	Rate-Controlling Process
D_1	$\alpha^2=kt$	One dimensional diffusion
D_2	$\alpha+(1-\alpha)\ln(1-\alpha)=kt$	Two dimensional diffusion (Disc)
F_1	$-\ln(1-\alpha)=kt$	Random nucleation, one nucleus per particle
R_2	$1-(1-\alpha)^{\frac{1}{2}}=kt$	Phase boundary reaction (Disc)
R_3	$1-(1-\alpha)^{\frac{1}{3}}=kt$	Phase boundary reaction (Sphere)
A_2	$(-\ln(1-\alpha)^{\frac{1}{2}}=kt$	Random Nucleation, Avrami Equation

* k is a numerical constant

t is time

α is normallised weight loss

p117 ▷

Thermal Analysis

Two methods of scanning thermal analysis exist: differential thermal analysis (DTA) and differential scanning calorimetry (DSC). The former technique heats a sample and a reference (normally an empty sample pan) and monitors the difference in temperature between them. The latter process also heats a sample and a reference, but adjusts the heating to the sample and reference probes so that there is no net temperature difference between them. The output from DSC is the energy needed to do this: the disadvantage of this technique relative to DTA is its cost. DTA results have to be calibrated by specific heats: if a substance of known specific heat is analysed by DTA then a difference in temperature can be related to energy. The heats of fusion of metals or the specific heat of α-alumina are commonly used. A base-line is provided by analysis of two empty pans and reversibility of reaction can be shown by iteration of analysis on a single sample. If the change or reaction monitored involves loss of a volatile product then a closed pan will produce different results from an open pan due to the product being retained in the atmosphere over the sample. Typically this results in removal of peaks to higher temperatures and in resolution of shoulders. All these aspects of DTA are illustrated in Figure 15 together with use of a substance which suffers a sharp energy change at a known temperature to calibrate this scale.

A note of caution must be sounded about DTA and DSC

▷ p123

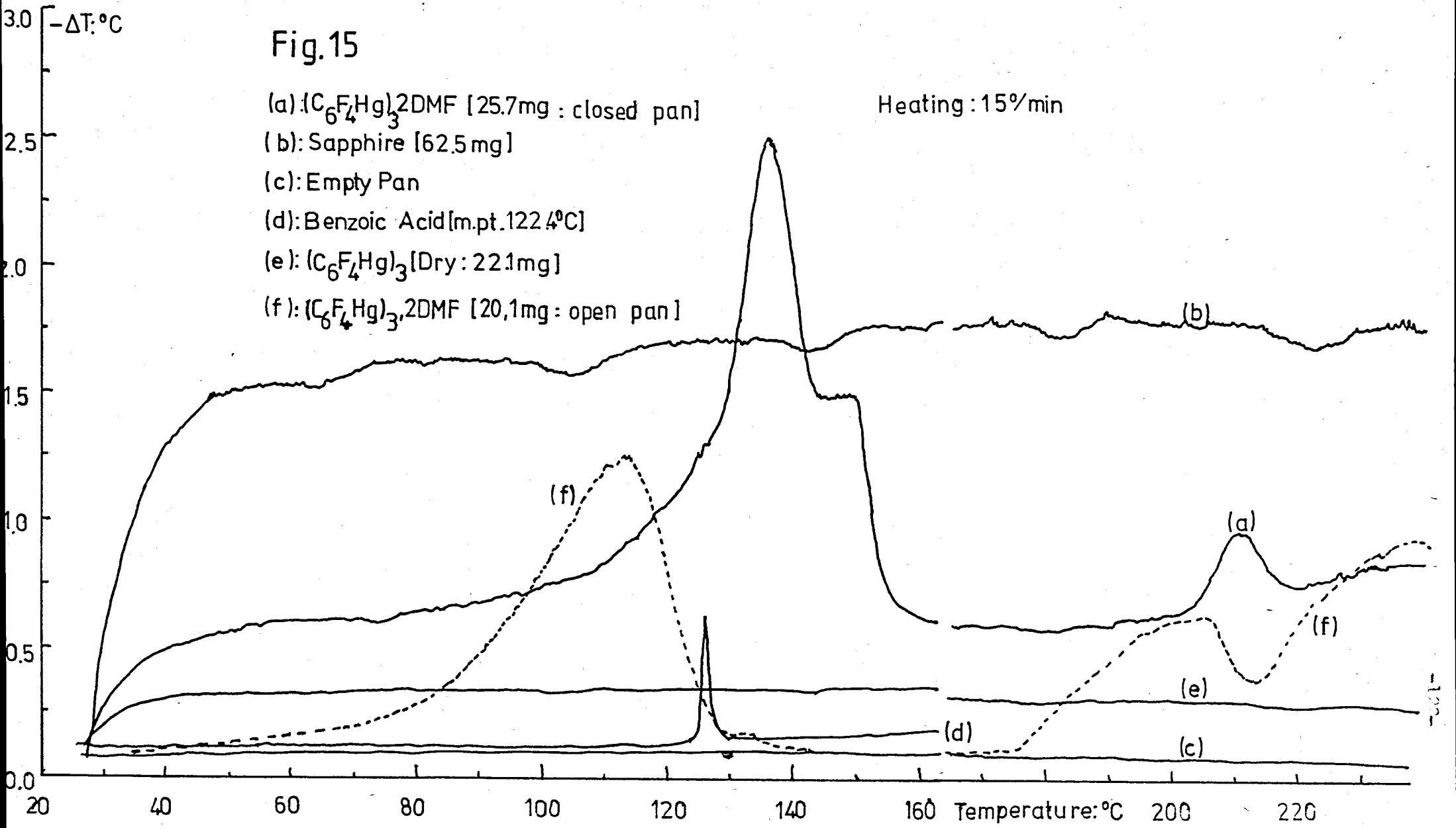


Fig. 15
(a): $(C_6F_4Hg)_3$2DMF [25.7mg : closed pan]
(b): Sapphire [62.5 mg]
(c): Empty Pan
(d): Benzoic Acid [m.pt. 122.4°C]
(e): $(C_6F_4Hg)_3$ [Dry : 22.1mg]
(f): $(C_6F_4Hg)_3$,2DMF [20,1mg : open pan]
Heating : 15°/min
-ΔT: °C
3.0
2.5
2.0
1.5
1.0
0.5
0.0
20
40
60
80
100
120
140
160
Temperature: °C
200
220
(a)
(b)
(c)
(d)
(e)
(f)

p121 ▷

results: all they measure is energy change. They give no information about the reactions causing the changes and in a process

$$AB(s) \longrightarrow A(s) + B(g)$$

several steps are involved: vapourisation of B, cleavage of A-B bonds, diffusion of B out of the residual solid, and rearrangement of the crystal lattice. This multiplicity of causes for DTA peaks explains why a single reaction (as monitored by TG) may have a more complex thermogram (Figure 16).

Experimental

TGA was performed on a Stanton-Redcroft TG750 Thermal Balance, temperature referenced against the triple point of water. Sample size was normally 1.5 - 12mg. A flowing atmosphere of dry nitrogen was maintained over the sample.

DTA was performed on a DuPont 900 Thermal Analyser, temperature referenced against the triple point of water. Sample size was normally 15-25mg. α-Alumina was used in an attempt to calibrate the temperature-difference scale.

Samples were prepared by recrystallisation of a solid starting material (e.g. perfluoro-o-phenylenemercury) from neat solvent where the resulting product would contain solvent of crystallisation; where the organic molecule desired to form an adduct was solid recrystallisation was

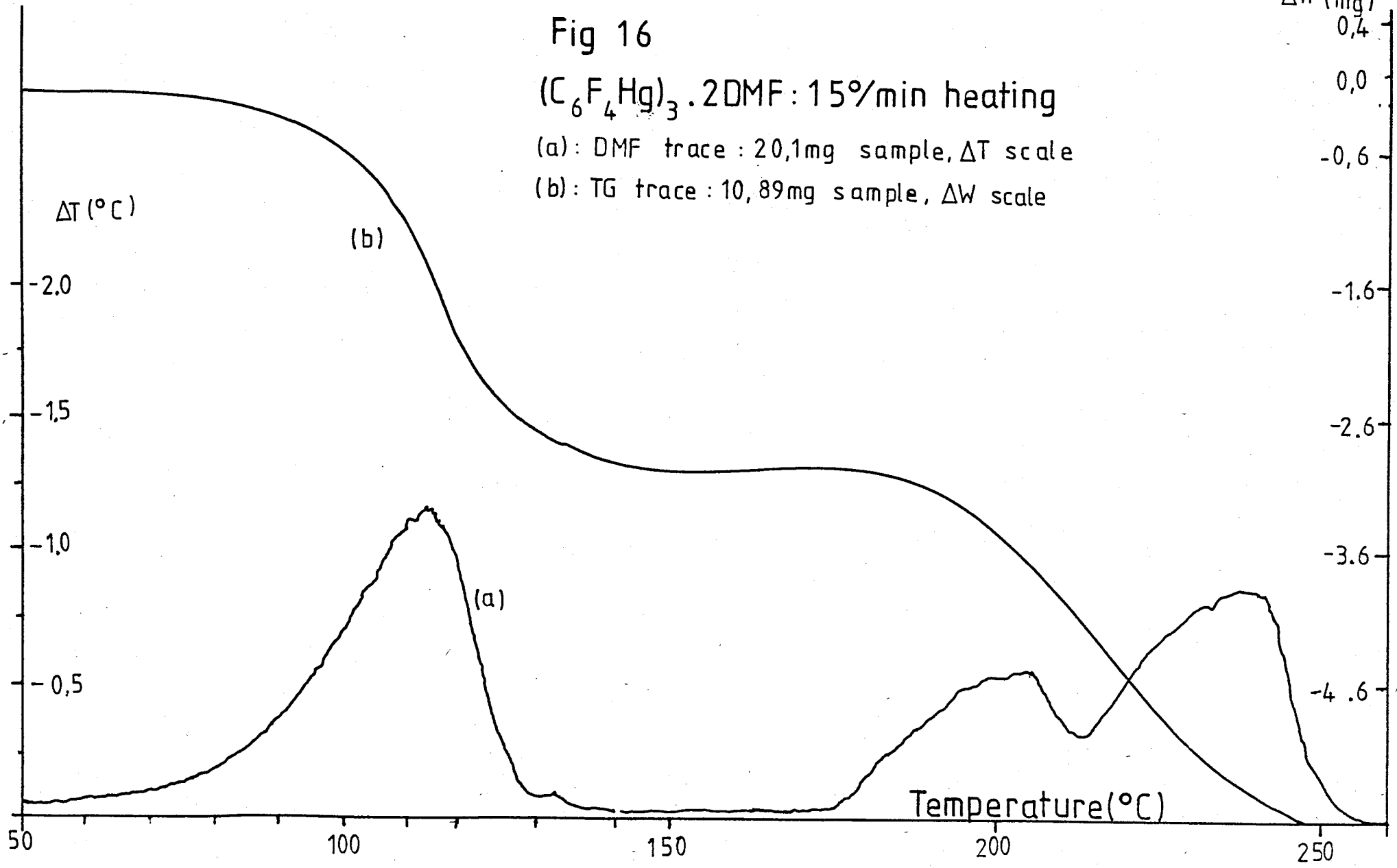
▷ p125

Fig 16

$(C_6F_4Hg)_3 . 2DMF$: 15°/min heating

(a) : DMF trace : 20,1mg sample, ΔT scale

(b) : TG trace : 10,89mg sample, ΔW scale



p123 ▷

of stoichiometric quantitites from ethanol. Samples were then removed from the mother liquor, dried on a filter paper, rapidly weighed and analysed.

Results

Reaction mechanism data obtained from the TG work is summarised in Table 15, activation energies and frequency factors are given in Table 16. Microanalytical results for some of the adducts are given in Table 17. To provide data from a complex of known structure the thermal decomposition of dichlorotetrapyridinecobalt(II) was investigated, and these results are also quoted. Direct comparison with mercury complexes was not possible as mercuric chloride- and bromide-pyridine complexes gave poor data because of the volatility of the metal halide; the mercuric iodide-pyridine complex did not give clear-cut mechanistic data. Bis(pentafluorophenyl)mercury also was too volatile, and bis(pentachlorophenyl)mercury did not give adducts stable enough to study. Thermal analysis results were not converted into free energy values as attempts to do this for dichlorodipyridinecobalt(II) gave values differing from those in the literature [158,159,160,161,162] by a factor of two.

Discussion

The failure of the thermal analysis performed was probably due to the sample size used, and this was determined by the need for a favourable signal/noise ratio. The

▷ p130

Table 15

Reaction mechanisms for the loss of solvent from adducts of perfluoro-o-phenylenemercury, I, and for $CoCl_2py_4$ and HgI_2py_2

Reaction	Temperature(S)(K)	Mechanism(s)*
2DMF.I→1DMF.I	340, 350	R_2
1DMF.I→I	425	R_2
	447, 459	R_3
3DMA.I→2DMA.I	288	A_2 or R_2
2DMA.I→1DMA.I	351	A_2 or R_2
	377,379,382,392,410	R_2
1DMA.I→I	437	R_2
	467,482,493	R_3
3DEF.I→2DEF.I	316,319,331,340	A_2 of R_2
	312	R_3
	314	R_2
2DEF.I→1DEF.I	354,370,397	R_2
	386,393	R_3
	404	D_1 or F_1
1DEF.I→I	427	R_3 or F_1
	433	R_3 or F_1 or D_1
	440	R_3
	442	D_2
	458,463	D_1

3py.I→1py.I	311,320,325,332	R_2
1py.I→I	356	R_2 or R_3
	360	R_2
	375	R_3
	406	R_3 or D_1
3(2-pic).I→2(2-pic).I	291	A_2
2(2-pic).I→I	318	R_3
	325	R_2 or R_3
1(4-phenylpyridine).I→I	384,406	R_3
2(triphenylphosphine).I→I	421,434	R_2
$CoCl_2py_4 \rightarrow CoCl_2py_2$	318,334,345,346	A_2 or R_2
$CoCl_2py_2 \rightarrow CoCl_2py$	381,391,399,402,407,417	R_2
$CoCl_2py \rightarrow CoCl_2py_{2/3}$	469	R_3
	486	D_1
$CoCl_2py_{2/3} \rightarrow CoCl_2$	521	R_2
	559	R_3
$HgI_2py_2 \rightarrow HgI_2$	326	A_2 or R_2
	334	R_3

* The mechanism symbols are explained in Table 14

Table 16

Activation energies and frequency factors for the loss of solvent from adducts of perfluoro-o-phenylenemercury, I, and for $Co\,py_4Cl_2$

Reaction	Activation Energy (kcal/mole)*	Frequency Factor
2DMF.I→1DMF.I	22	1.4×10^{14}
1DMF.I→I	26	9.7×10^{13}
2DMA.I→1DMA.I	26	1.9×10^{12}
1DMA.I→I	30	6.7×10^{11}
2DEF.I→1DEF.I	30	6.7×10^{17}
3py.I →1py.I	22	7.2×10^{13}
1py.I →I	26	9.7×10^{13}
1(4-phenylpyridine).I→I	30	2.1×10^{15}
2(triphenylphosphine).I→I	34	1.9×10^{15}
α-$CoCl_2py_2$→$CoCl_2py$	22	1.1×10^{10}
$CoCl_2py$→$CoCl_2py_{2/3}$	34	2.3×10^{14}
$CoCl_2py_{2/3}$→$CoCl_2$	38	1.3×10^{14}

* Results are ± 4 kcal/mole

Table 17

Micro-Analysis Results (%)

Complex	C		H		N		F	
	obs	calc	obs	calc	obs	calc	obs	calc
I	21.1	21.2	0.2?	0.0	0.0	0.0	22.2	22.4
I.DMF	22.5	22.4	0. 6	0.65	1.3	1.29	21.0	21.1
I.2DMF	24.2	24.17	1. 1	1.17	2.1	2.35	19.4	19.14
I.2DEF	27.2	26.8	1. 8	1.76	2.2	2.2		
I.2DMA	25.8	25.6	1. 5	1.47	2.5	2.3		
I.py	26.0	24.5	0. 5	0.4	1.4	1.2		
I.1(2-pic)	22.4	25.2	0. 5	0.6	0.9	1.2		
I.2(3-pic)	30.1	29.2	1. 3	1.1	2.7	2.3		
I.2(4-pic)	27.5	29.2	0. 9	1.1	1.9	2.3		
I.(2,6-lut)	25.8	26.0	1. 0	0.8	1.5	1.2		
I.(4-Ph-py)	30.6	28.9	1. 0	0.7	1.6	1.2		
I.2(DMSO)	21.4	21.9	1. 0	1.0	0.0	0.0		
I.C_5H_8O	24.4	24.4	0. 7	0.7	0.0	0.0		

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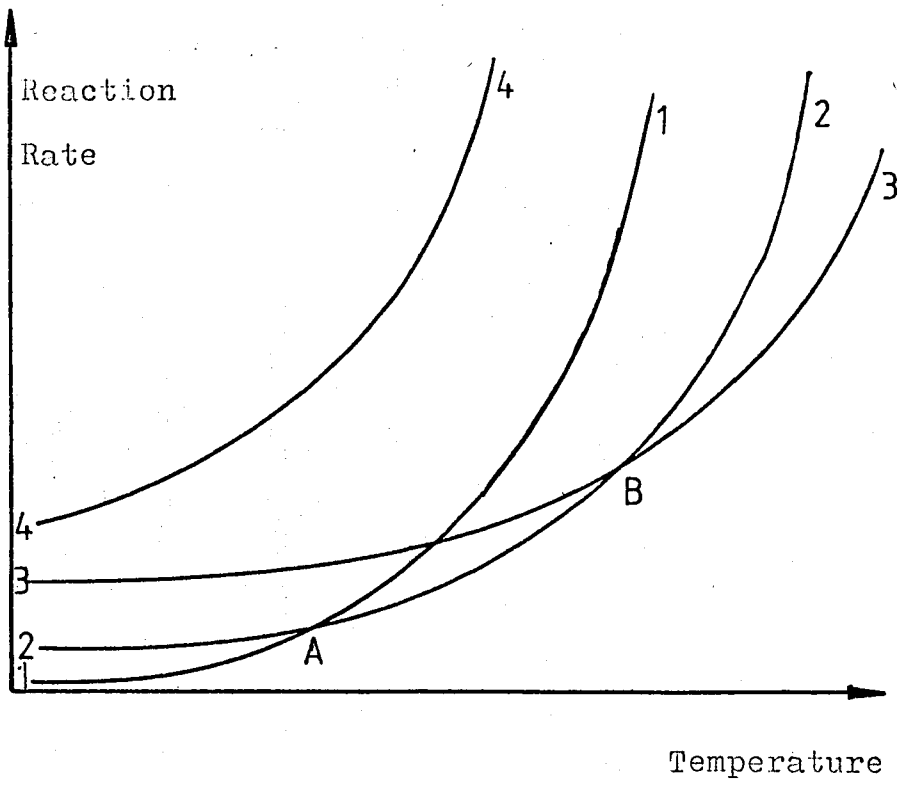
basis of thermal analysis is the assumption that the total effect of any change is measured (this is obviously much less problematical in TGA) and the larger the sample used the more effects of such tings as sample packing will be appreciable. On the wholely empirical basis the energy changes seemed to be about half those found in dichlorodipyridinecobalt (II).

The TGA results form an homogenous whole in which a variety of trends can be discerned. One of these is that the data for the adducts with most solvent present is often too poor for reliable determination of activation energies or even, in some cases, mechanistic data. The reasons for this are two-fold: the efflorescence reaction can be too rapid for the substance analysed to be of the original stoichiometry (this makes calculation of normalised weight curves valueless), and the mathematics on which the activation energies are calculated assumes that the substance is analysed over a range of temperature which covers indefinite stability through to completion of reaction. For these reasons activation energies were not evaluated for adducts very unstable at room temperature or for those which gave no clear-cut mechanism. This included all the mercuric halide-pyridine complexes analysed and the loss of the final molecule of DEF from the adduct with perfluoro-o-phenylenemercury.

As would be expected there was a correlation between thermal stability and activation energy, but the values

do not distinguish between the chemical types of solvent used. The somewhat higher values for the cobalt complexes are probably a reflection of stronger bonding in these compounds. Another aspect of this is the reaction temperature needed to decompose the compounds studied: the classical complexes were stable toward final degradation at temperatures considerably above the boiling point of the ligand. The most stable organo-mercury adducts decomposed within 10°C of that value. The frequency factors for the adducts were sufficiently similar to those from the cobalt complexes to show them to be uninformative.

Whilst some adducts decomposed by a single mechanism over a wide range of temperature (e.g. the 1:3 adduct with pyridine) others had several stages and in general these can be associated with the rapidity of the reaction. Typically at the lowest temperatures reactions would comply with the R_2 model or be intermediate between R_2 and A_2 kinetics. As the temperature was raised the kinetic model of best fit would change to R_3, then F_1 or even D_1. This sequence, best illustrated by the decomposition of the 1:1 adduct with DEF, does not cast doubt on the analytical technique, but merely shows that a "single" reaction may consist of many steps. At different temperatures different steps may be rate-determining, and hence the kinetics may change.



In the diagram step 1 would be rate determining from low temperature to A, step 2 from A to B and step 3 from B to high temperature. At no time would step 4 be rate-determining; at A and B the kinetic data would not be clear-cut. A delicate balance between activationenergy and frequency factor determines the relative rates for the various steps.

The actual data implies that substantial molecular forces, whose order of magnitude is that of weak chemical bonds, are in play but do not "prove" the substances analysed to be "complexes". The structure determination of the 4-phenylpyridine adduct makes the data from it of particular interest: it is in no way outstanding, both the activation energy and reaction mechanism of the

decomposition being typical. This strong inference that all the adducts are of the same type, however, still does not constitute proof.

Chapter 4

Radiochemistry

Summary: the elimination of lithium fluoride was studied by radio-tracer techniques: experimental results are presented and discussed in the light of extant theories covering this reaction.

The Addition of $Li^{80m}Br$ to Polyhalogenoarynes

Introduction

The elimination of lithium fluoride from pentafluorophenyllithium generates a species best formulated as tetrafluorobenzyne, C_6F_4: . The addition of inorganic lithium salts to this reactive intermediate has been established [66] but not studied in detail: it was only careful analysis of some unexpected reaction products that indicated the reaction sequence below at all.

$$C_6F_5Br + 2Li \longrightarrow C_6F_5Li + LiBr$$

$$C_6F_5Li \longrightarrow C_6F_4: + LiF$$

$$C_6F_4: + LiBr \longrightarrow C_6F_4BrLi$$

$$C_6F_4BrLi + C_6F_5Br \longrightarrow C_6F_4Br_2 + C_6F_5Li$$

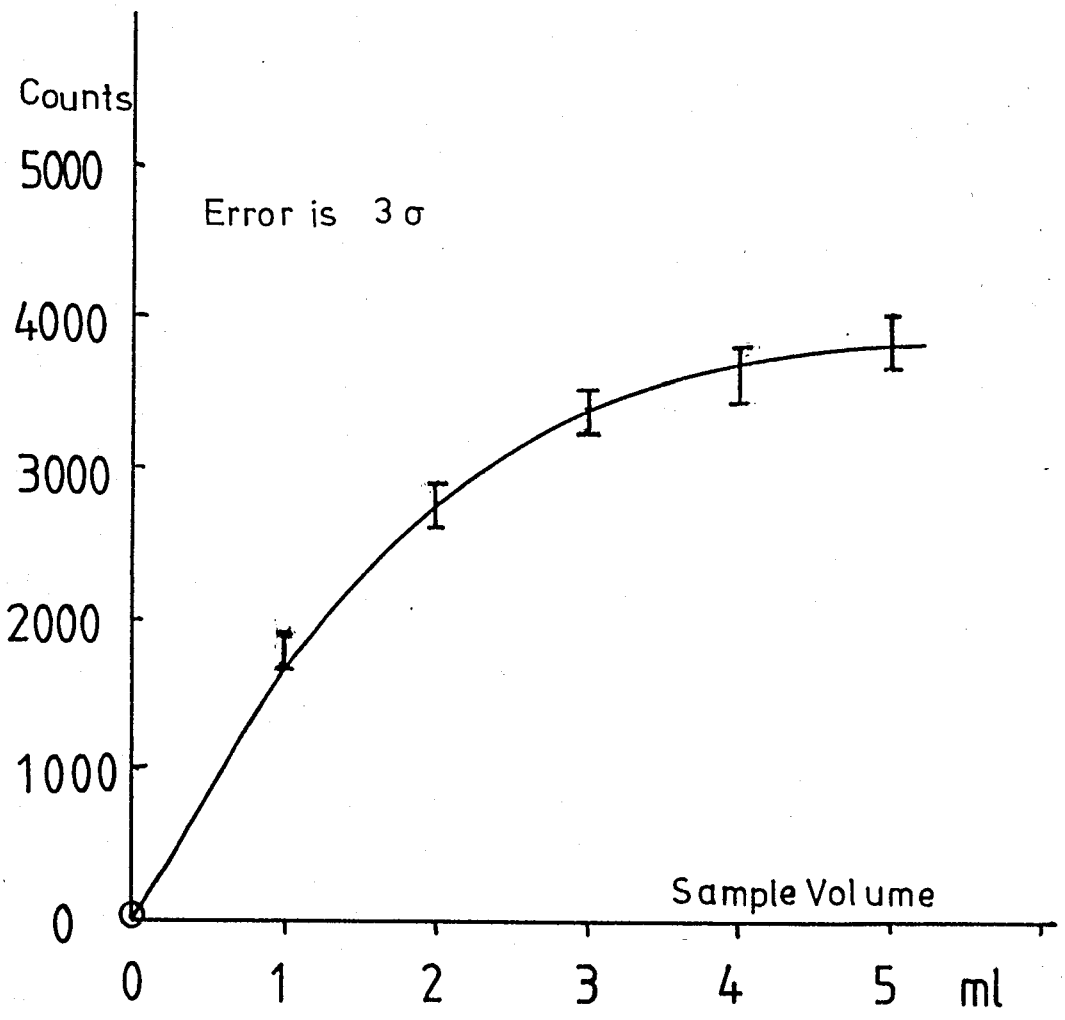
Analogous reactions based on iodopentafluorobenzene and giving rise to 1,2-diidotetrafluorobenzene were also performed [66] but chloropentafluorobenzene did not yield 1,2-dichlorotetrafluorobenzene. As lithium bromide is easily dried without decomposition (in contrast to lithium iodide) and as ^{80m}Br has the reasonably long half-life of 4.5hr it was decided to investigate the elimination reaction using radiobromine as a tracer.

Experimental

$Li^{80m}Br$ was generated by fast neutron (~14MeV) irradiation of powdered anhydrous LiBr(dried at 150°C and stored over phosphorus pentoxide) in a stoppered polypropylene tube. A solution of polyhalogenoarene in ether (10mMole in 125ml) was thermostatically cooled to the desired temperature in a jacketed two-necked flask and active lithium bromide (2.4gm, 27.6mMole) added. Irradiation times varied as did neutron fluxes, but expression of the final results in terms of the radiochemical yields overcame these problems. The active suspension was magnetically stirred and n-butyllithium (5ml; 1.3 molar in hexane) added under nitrogen. The experiment times were measured from this addition. Reactions were quenched by addition of 5 (or 10ml) of approximately molar sulphuric acid, which caused less emulsion formation than water. The resulting mixture was then distilled at 60°C (water bath) to reduce its volume and a full sample-tube of each phase counted for 1000 sec in a γ-scintillation counter. Initial measurements showed the distillate to be free from detectable activity. The effect of sample volume on the detected count-rate was investigated and a full tube used as small variations in sample volume affect the measurements least (Figure 17). The results were corrected for the volumes of bulk liquid present and for the elapsed time between sample measurement. This latter correction was necessary as the counting time used is an

p138

Fig. 17


Counts
5000
4000
3000
2000
1000
0
Error is 3 σ
Sample Volume
0
1
2
3
4
5
ml

p136 ▷

appreciable fraction of the half-life. Some initial high-energy γ counting was performed to detect the decay

$$^{80}Br \xrightarrow[\gamma]{\beta} {}^{80}Se \qquad t_{\frac{1}{2}} = 17 \text{ min}$$

Sample counts were comparable but higher background count-rates for the high-energy technique led to use of the low-energy counter to minimise statistical fluctuations.

In an attempt to obtain kinetic data from a single run for calculation of kinetic parameters (leading to activation energy and frequency factor values) a series of experiments was performed using $Li^{82}Br$. This was prepared by addition of an aqueous carrier-free $Na^{82}Br$ (25μl ; obtained from the Radiochemical Centre, Amersham) to anhydrous THF (25ml) containing lithium bromide, added as a 50% w/w aqueous solution (0.4ml). 1ml aliquots of this solution were then added, together with inactive lithium bromide, and the experiment started as described above. Aliquot samples (2ml) were taken at appropriate intervals, quenched with acid (5ml) and diluted with hexane (3ml). The technique was modified by successive extraction with acid, alkali, and acid in later experiments.

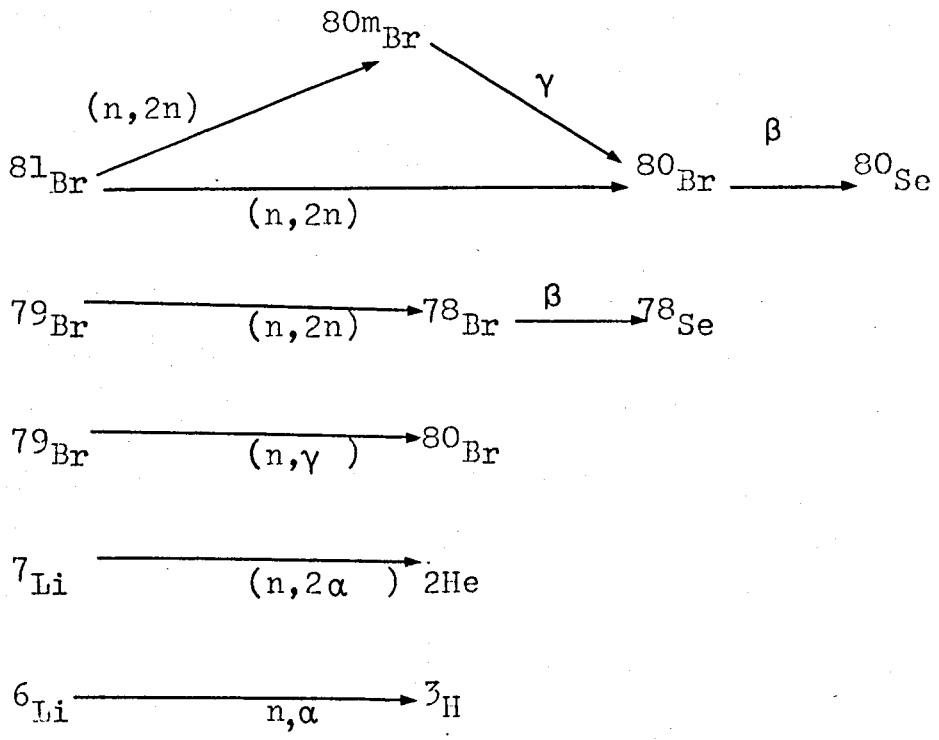
Results

Numerical results from the first technique are given in Table 18, from the second technique in Table 19, and

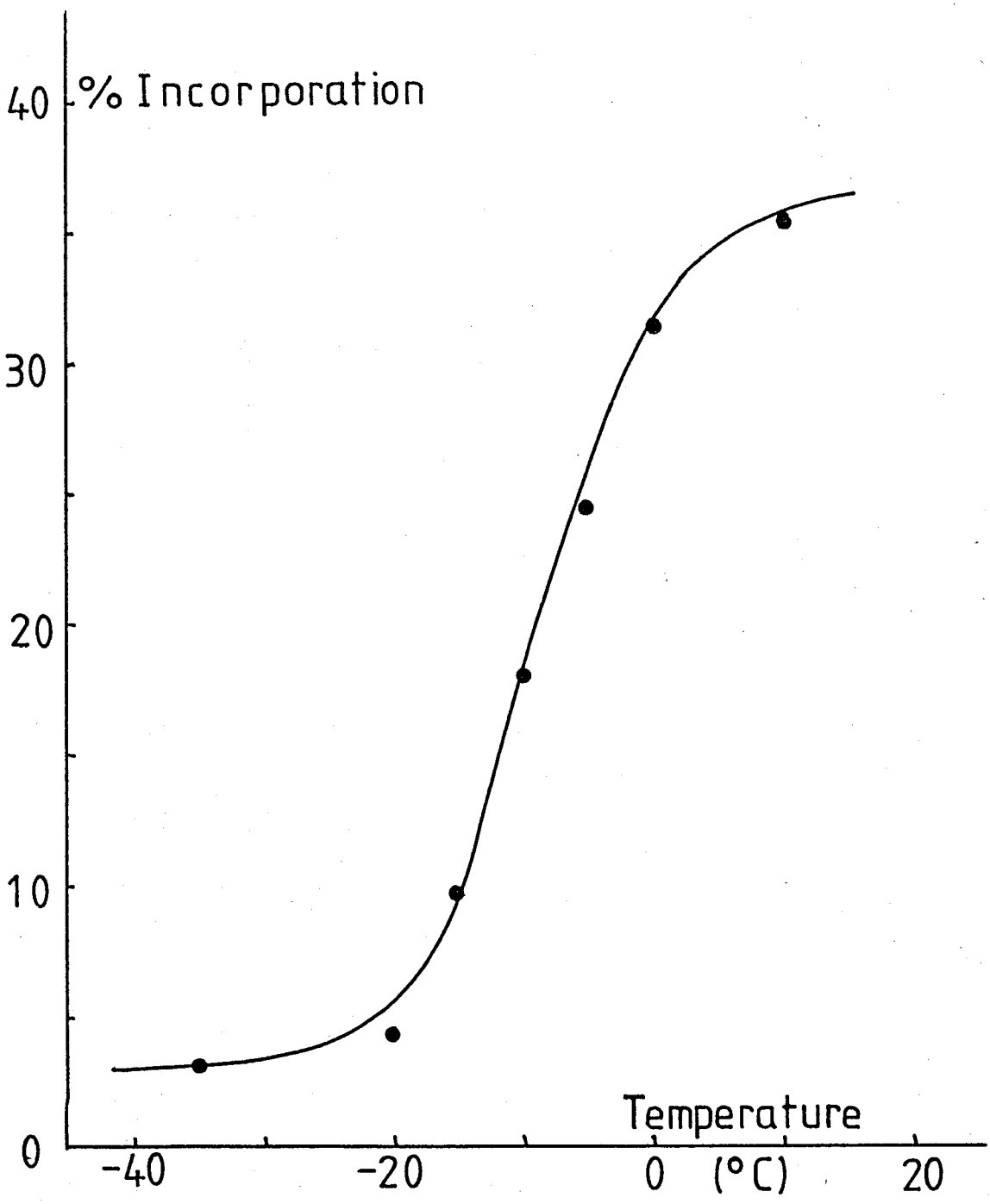
from the modified second technique in Table 20. Figure 18 shows the variation of incorporation with temperature.

Discussion

The reactions possible during the nuclear irradiation are as follows:



Other theoretically possible reactions are of such low probability that they may be neglected. Nuclear reactions involve atoms in transitions where the available energy vastly exceeds that holding a crystal lattice together, so neutron bombardment and the "hot" atoms produced produce many lattice defects. A "new" nucleus, when most of its energy has been lost by collision processes, may either react chemically or lodge elsewhere



Reaction time : 16 hr.

Solvent : ether/hexane (25:1)

Reagents : C_6F_5I, C_4H_9Li, Li Br (10 : 6.5 : 27.6 m Mole)

Fig. 18

Table 18

Incorporation (with standard deviations from counting statistics in parentheses) for the reaction of lithiated polyhaloaromatics

Reagent	Temperature	Reaction Time	Extra Conditions	% Incorporation
C_6F_5Cl	0°C	16 hr		49.21(58); 50.85(82) 51.44(99); 48.72(1.18) 44.50(50); 51.72(91) 52.42(59); 52.50(27)
C_6F_5Cl	0°C	16 hr	LiBr*stood for 1 hour	40.21(27)
C_6F_5I	0°C	24 hr		45.70(94)
C_6F_5I	-10°C	24 hr		17.34(62)
C_6F_5I	0°C	6 hr		20.12(19); 32.14(33) 12.60(10); 15.15(15
C_6F_5I	0°C	6 hr	25gm benzene added	23.99(30)
C_6F_5I	0°C	6 hr	20m Mole naphthalene added	20.85(24)
C_6F_5I	0°C	6 hr	20m Mole anthracene added	11.27(23)
C_6F_5I	0°C	6 hr	No n-butyllithium	2.74(10)
C_6F_5I	0°C	6 hr	20gm TMED added	3.90(12); 4.16(18)
C_6F_5I	0°C	6 hr	Hexane as solvent	1.28(10); 2.73(15)

C_6F_5I	0°C	6 hr	$Na^{80m}Br$ used	4.04(12)
C_6F_5I	10°C	16 hr		35.90(40)
C_6F_5I	0°C	16 hr		31.48(20)
C_6F_5I	-5°C	16 hr		24.41(51)
C_6F_5I	-10°C	16 hr		18.47(32)
C_6F_5I	-15°C	16 hr		9.76(22)
C_6F_5I	-20°C	16 hr		4.44(13)
C_6F_5I	-35°C	16 hr		3.10(14)
C_6Cl_5H	0°C	6 hr		19.01(19)
C_6Cl_5H	0°C	6 hr	No n-butyllithium	2.13(10)
$C_6F_4Br_2$	0°C	4 hr		10.17(17);11.11(21)
$C_6F_4Br_2$	0°C	6 hr		25.49(36);23.22(37) 15.91(20);16.33(18)
$C_6F_4Br_2$	25°C	16 hr		0.88(9)
$C_6F_4Br_2$	0°C	2 hr		8.09(13); 10.76(32)
$C_6F_4Br_2$	0°C	6 hr	slow addition n-butyllithium	17.75(15)
$C_6F_4Br_2$	0°C	16 hr	20mMole anthracene added	6.56(38)

Table 19

Incorporation (with standard deviations from counting statistics in parentheses) for the reaction of lithiated C_6F_5Cl (1) and $C_6F_4Br_2$ (2) with $Li^{82}Br$ at 0°C, single acid extraction.

Time (minutes)	% Incorporation (1)	(2)
15	3.00(6)	1.95(6)
40	3.86(6)	4.00(7)
130	8.26(9)	4.36(7)
180	10.41(11)	4.71(7)
240	21.21(15)	24.25(15)
305	17.07(13)	21.25(15)
370	21.02(14)	29.80(18)
415	17.95(14)	9.04(11)
475	19.63(14)	14.49(12)
540	13.18(11)	15.48(13)
595	12.12(12)	12.54(10)
780	-	5.06(10)

Table 20

Incorporation (with standard deviations from counting statistics in parentheses) for the reaction of lithiated $C_6F_4Br_2$ with $Li^{82}Br$ at -5°C, the organic phase (1) being successively extracted with approx M H_2SO_4(2), approx M NaOH (3) and approx M H_2SO_4 (4)

Time (min)	Uncorrected Counts				% Incorporation
	1	2	3	4	
30	1172	75430	6378	1241	0.85(6)
90	1514	61247	12877	2701	1.49(8)
150	1541	73211	4353	852	1.56(8)
210	1941	72172	4535	963	2.02(8)
270	3941	67865	9511	3405	4.40(10)
340	7493	37384	37511	4459	8.17(12)
575	2635	60401	4006	1646	3.38(10)
1090	2905	55968	3100	982	4.21(12)
1330	2653	53114	3825	677	3.89(12)

.. Background: 366(19)

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in the lattice. Possible chemical reactions for the active bromine atoms are:

(1) $Li + Br^* \longrightarrow LiBr^*$ (re-formation of the crystal lattice)

(2) $Br^* + Br \longrightarrow Br\text{-}Br^*$

Reaction between two active species or between an active atom and one produced by nuclear decay is very unlikely because of the very small numbers involved compared with the quantity of starting material. These two possible reactions would give different results on addition of n-butyllithium:

(3) $Br - Br^* + n\text{-}C_4H_9Li \longrightarrow LiBr + n\text{-}C_4H_9Br^*$

(4) $LiBr^* + n\text{-}C_4H_9Li \longrightarrow$ No reaction

On lithiation, reaction (3) would put half of the activity into 1-bromobutane, and thence it would end up in the organic phase. Experimentally very little blank incorporation was detected so reaction (2) must be of very low probability.

The half-lives and energies of the isotopes produced are such that (a) tritium activity can be discounted, (b) after about two hours ^{78}Br activity is negligable and (c) the best way to detect the ^{80m}Br activity is by low-energy γ scintillation counting.

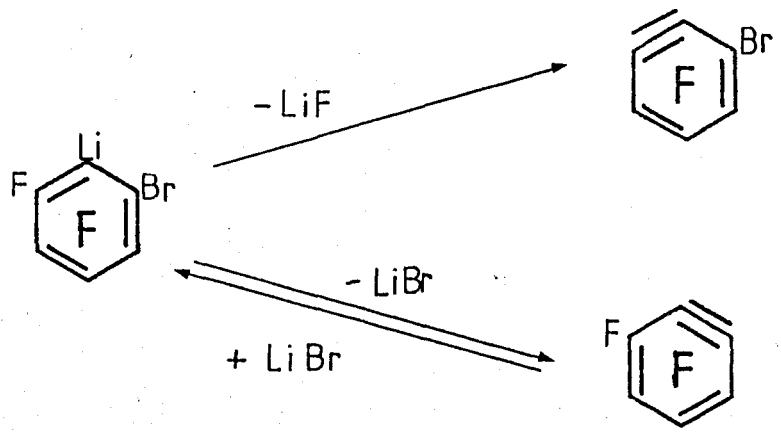
It can be seen that the values from experiments run

for longer times are less variable than those obtained from shorter intervals for the ^{80m}Br work, and that the ^{82}Br work produced very low quality data, both before and after variation of the extraction procedure. It was not, therefore, possible to produce thermodynamic data from the work performed. The ^{80m}Br results were reasonably reliable as is shown in the incorporation/temperature graph (Figure 18). The inference that benzyne formation occurs above about $-20^{o}C$ agrees with previous workers.[66]

No significant difference can be seen between the results from iodopentafluorobenzene, chloropentafluorobenzene and 1,2-dibromotetrafluorobenzene. Bromopentafluorobenzene was not investigated as the possibility of halogen exchange

$$C_6F_5Br + LiBr^{*} \longrightarrow C_6F_5Br^{*} + LiBr$$

could not be totally discounted and pentafluorobenzene was neglected because of doubts about the speed of metallation. The suggestion of Tamborski [163] who explained the apparently anomalous elimination of lithium fluoride from 2-bromotetrafluorophenyllithium on the basis of the reaction scheme below does not appear to fit these unanimous results.



This scheme rationalised the preference for elimination of lithium fluoride over lithium bromide (as judged by the great preponderance of reaction products arising from bromotrifluorobenzyne) towards agreement with work on 2-halophenyllithium compounds. The ease of expulsion of lithium halide in these is I > Br > Cl > F[68]. Were the reversible elimination of lithium bromide from 2-bromotetrafluorophenyllithium to take place the lithium bromide should be incorporated much more efficiently into that than pentafluorophenyllithium. This is particularly pertinent as the benzyne-trap competition reactions show there to be an association in solution between the lithium bromide and the polyhalophenyllithium. Charge transfer complexes are known to exist between benzene (and its methylated analogues) and hexafluorobenzene,[164] albeit the benzene complex has been shown to be weakly bound.[165] Organic benzyne products would be expected, were the lithium bromide not more strongly attached, in systems containing benzene, naphthalene etc. Only the results from the anthracene experiments show any significant reduction in incorporation and anthracene strongly favours

1,4-addition.

Two further investigations into the reaction were carried out: tetramethylethylenediamine (TMED) was added to the reaction mixture to increase the ionic nature of the organolithium species. The amount of incorporation was drastically reduced, possibly because the loose association between the lithium bromide and the organolithium compound was destroyed, possibly because nucleophilic reactions are more favourable in this system. Secondly, the addition of active lithium bromide was shown to take place in solution rather than on the surface of the solid present by two separate experiments. Hexane was used as the sole solvent present in one, and sodium bromide was substituted for lithium bromide in the other. In neither case was incorporation observed; presumably this is related to the finding that a molecule of solvent is present in the activated complex for the elimination of lithium halide from 2-halophenyl-lithium.[68]

Chapter 5

Computing

Summary: the computing quoted during the course of this work was performed as a tool rather than as an end in itself and so most calculations were carried out using standard program packages. The GINO-F package was manipulated to produce drawings based on the atomic co-ordinates produced during X-ray structure analyses (Chapter 2) and the GAUSSIAN 70 package in an unsuccessful attempt to calculate thermodynamic energy values for pentafluorophenyllithium.

Computing

The following computer packages were used during the course of this work: XRAY 72,[155] MULTAN 74,[154] SHELX,[152] ORTEP,[166] the Cambridge Data File,[167] GINO-F[168] and GAUSSIAN 70.[169] All are Fortran based and all but the last two were used in their normal applications and so no details of these will be given. Calculations were performed on the University of Manchester Regional Computing Centre CDC 7600, and the Loughborough University ICL 1904A or Primos machines.

GINO-F is a package for drawing pictures and it was used to produce views of the X-ray structures determined: Figures 3 and 6 (Chapter 2) are amongst those produced in this way. Drawing was performed as a batch operation: rotations, for example, were carried out as a series of steps. The job that produced Figure 6 (Chapter 2) is given as Table 21. The logic of the program is as follows: initial viewing and scaling is performed, then a unit box is drawn with the origin and axes marked. A small, quite primitive loop uses a single set of atomic co-ordinates to produce several views of the asymmetric unit, then the program terminates. The scaling and shifting transformations are performed in a cumulative manner and unit cell translations are used to ensure that all points are within the unit cell. Probably the simplest example of this would be space group $P\bar{1}$: it has two general equivalent positions at x,y,z and -x,-y,-z.

Table 21

GINO-F program to draw Figure 6

```
      CALL T4010
      CALL DEVSPE (1200)
      CALL UNITS (7.0)
      CALL WINDOW  (3)
      CALL PICCLE
      CALL SHIFT 3(-5.893,0.0, - 6.557)
      CALL AXON 3(0.0,19.484,0.0)
      CALL SHIFT 3(5,893,0.0,6.557)
      CALL SHEAR 3(1,3,0.7648)
      CALL SCALE 3(9.36,13.114,4.871)
      CALL SHIFT 3(1.5,0.0,-4.0)
      CALL ROTAT 3(1,5.0)
      CALL ROTAT 3(3,5.0)
      CALL MOVTO 3(0.0,0.0,0.0)
      CALL SYMBOL (8)
      CALL LINTO 3(1.0,0.0,0.0)
      CALL LINTO 3(1.0,1.0,0.0)
      CALL LINTO 3(0.0,1.0,0.0)
      CALL LINTO 3(0.0,0.0,0.0)
      CALL LINTO 3(0.0,0.0,1.0)
      CALL LINTO 3(1.0,0.0,1.0)
      CALL LINTO 3(1.0,1.0,1.0)
      CALL LINTO 3(0.0,1.0,1.0)
      CALL LINTO 3(0.0,0.0,1.0)
      CALL MOVTO 3(0.0,1.0,0.0)
```

```
      CALL LINTO 3(1.0,1.0,1.0)
      CALL MOVTO 3(1.0,0.0,0.0)
      CALL LINTO 3(1.0,0.0,1.0)
      CALL MOVTO 3(1.1,0.0,0.0)
      CALL CHACEN (1HA)
      CALL MOVTO 3(0.0,1.1,0.0)
      CALL CHACEN (1HB)
      CALL MOVTO 3(0.0,0.0,1.15)
      CALL CHACEN (1HC)
      I = 0
      CALL SHIFT 3(0.0,1.0,0.0)
10    I = I + 1
      IF (I.LT.2) GO TO 20
      IF (I.LT.3) GO TO 30
      IF (I.LT.4) GO TO 40
      IF (I.LT.5) GO TO 50
      IF (I.LT.6) GO TO 110
30    CALL SCALE 3(-1.0,-1.0,-1.0)
      CALL SHIFT 3(-1.0,-1.0,-1.0)
      GO TO 20
40    CALL SHIFT 3(0.0,0.5,0.5)
      CALL SCALE 3(1.0,-1.0,1.0)
      GO TO 20
50    CALL SHIFT 3(1.0,0.0,0.0)
      CALL SCALE 3(-1.0,-1.0,-1.0)
20    CONTINUE
      CALL MOVTO 3(0.0,-0.5,0.5)
      CALL DOT (0.5)
```

```
      CALL LINTO 3(0.148,-0.233,0.517)
      CALL LINTO 3(0.155,-0.225,0.422)
      CALL LINTO 3(0.251,-0.033,0.428)
      CALL LINTO 3(0.326,0.147,0.529)
      CALL LINTO 3(0.222,-0.067,0.618)
      CALL LINTO 3(0.148,-0.233,0.517)
      CALL MOVTO 3(0.326,0.131,0.632)
      CALL LINTO 3(0.406,0.297,0.733)
      CALL MOVTO 3(0.326,0.147,0.529)
      CALL LINTO 3(0.423,0.351,0.537)
      CALL MOVTO 3(0.251,-0.033,0.428)
      CALL LINTO 3(0.253,0.031,0.326)
      CALL MOVTO 3(0.155,-0.225,0.422)
      CALL LINTO 3(0.082,-0.342,0.317)
      GO TO 10
110   CONTINUE
      CALL CHAMOD
      CALL DEVEND
      CALL EXIT
      END
```

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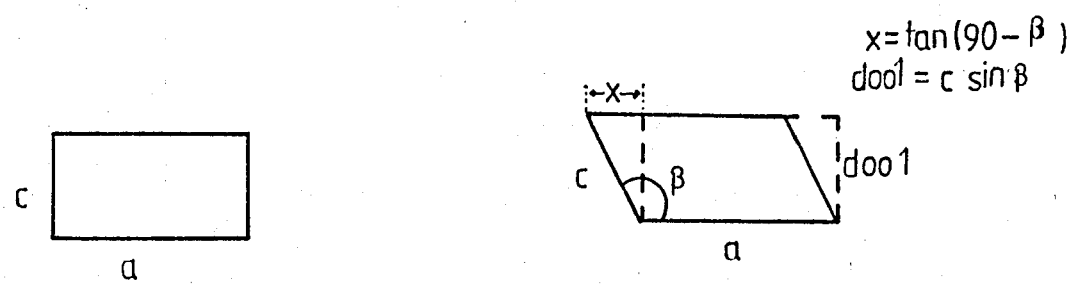
To locate the two asymmetric units within the unit cell the positions x,y,z and 1-x, 1-y, 1-z would have to be used. Equivalent positions are normally quoted in the first manner as this emphasises the symmetry concerned rather than a single unit cell contents.

Parallel projection was used, and the transforms on either side of this cell (AXON 3) together with the numerical values produce a simple axial projection. More general views can be produced by using rotations. The monoclinic unit cell shown in Figures 3 and 6 (Chapter 2) were achieved using the SHEAR3 call: this requires (a) that the d-spacing be used rather than the axis value and (b) that the shear parameter be tan(90-β).



(i) unsheared cell (projection) (ii) sheared cell (projection)

In the job shown the cell is sheared to define β before it is scaled to produce a and c thus there is no dependance of the shear parameter, x, on the unit cell values.

The advantages of GINO-F over the more usual packages lie in its semi-interactive availability. The Prime machine in conjunction with a Tektronix T4010 visual display terminal means that drawing programs could be run, debugged, and the angle of viewing optimised quite rapidly: job turn-round was often as low as 30 seconds. A hard-

copy device was used in conjunction with the terminal. Apart from specialised problems where the relative orientation of two parts of a molecule is desired and rapid job turn-round is a great advantage, GINO-F is probably best employed in the production of views of an entire unit cell. ORTEP, for example, is a much more sophisticated program and produces molecular drawings with much more information on them (Figure 7, Chapter 2) but this sort of detail is at best wasted and at worst confusing when several molecules are viewed. It is the simplicity of GINO-F that makes the rapid job turn-round possible.

GAUSSIAN 70 is a program to calculate energy values based on SCF MO considerations. It was used to perform the calculations cited in reference 24 and on the lithiation of trifluorobenzene, but most effort was expended in an attempt to obtain a theoretical value for the activation energy of the loss of lithium fluoride from pentafluorophenyllithium. Since use of the program is not always obvious from the manual an example of a geometry optimisation job is given as Table 22. The atomic numbering scheme adopted is shown in Figure 19. As an internal check on the program no attempt was made to produce a symmetrical pattern in defining the atoms: if equivalent atoms defined "illogically" produce the same electron populations within the molecule then at least nothing too obvious can be invalid. The main points where the quoted job differs from a standard route calculation

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Table 22

(a) Instruction cards for a geometry optimisation conserving calculated orbitals and suppressing most of the output listing.

OVERLAY	OPTIONS AND SEGMENTS	JUMP
2	0000000000000000000000000000000000000000000000000000	0
3	0000000000000000000000000000000000000000000000000000	0
4	1000000000000000000000000000000000000000000000000000	0
5	0000000000000000000000000000000000000000000000000000	0
6	1100000000000000000000000000000000000000000000000000	0
2	1000000000000000000000000000000000000000000000000000	0
3	0000000000000000000000000000000000000000000000000000	0
4	0000000000000000000000000000000000000000000000000000	0
2	1000000000000000000000000000000000000000000000000000	-2
3	0000000000000000000000000000000000000000000000000000	0
4	1100000000000000000000000000000000000000000000000000	0

(b) Data cards to define pentafluorophenyllithium as in Figure 19. Numbers in parentheses are "variable" numbers allocated by the program.

```
6
0    1   1.000000     (  1)
6    1   1.385000     (  2)     2   240.0000     ( 15)
6    1   1.385000     (  3)     2   120.0000     ( 16)     3   180.0000     ( 28)     0
6    4   1.385000     (  4)     1   240.0000     ( 17)     3   180.0000     ( 29)     0
6    3   1.385000     (  5)     3   240.0000     ( 18)     4   180.0000     ( 30)     0
6    5   1.385000     (  6)     4   240.0000     ( 19)     6   180.0000     ( 31)     0
9    7   1.344000     (  7)     5   120.0000     ( 20)     3   180.0000     ( 32)     0
9    5   1.344000     (  8)     5   120.0000     ( 21)     6   180.0000     ( 33)     0
9    3   1.344000     (  9)     6   120.0000     ( 22)     4   180.0000     ( 34)     0
9    6  -1.344000     ( 10)     2   120.0000     ( 23)     1   180.0000     ( 35)     0
0    1   .6925000     ( 11)     2   240.0000     ( 24)     4   180.0000     ( 36)     0
0   12   1.450000     ( 12)     1   270.0000     ( 25)     2   180.0000     ( 37)     0
6   13   1.116300     ( 13)    12   270.0000     ( 26)     5   180.0000     ( 38)     0
5   13   .4214000     ( 14)    12   180.0000     ( 27)     5   180.0000     ( 39)     0
```

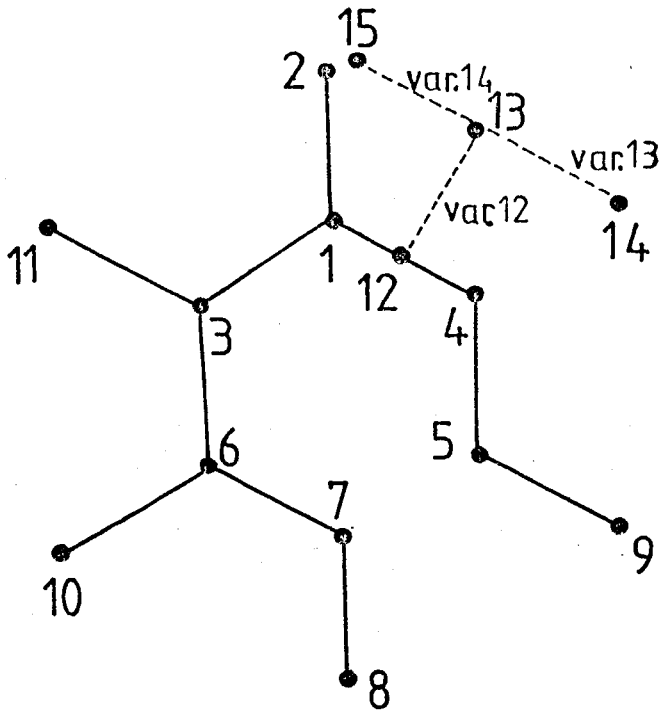

Fig. 19
Numbering scheme adopted for pentafluorophenyllithium.
Broken lines: parameters varied
Heavy lines : parameters fixed
1,3,4,5,6&7 : Carbon atoms
2,12&13 : Zero-weight "atoms"
8,9,10,11&14 : Fluorine atoms
15 : Lithium atom

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are that it re-uses the initial orbitals after the first cycle. The "initial guess" built into the program calculates values based on Hückel molecular orbitals for the first cycle. Since many parameters could be varied some assumptions were made and the results presented are in the nature of a preliminary study. Amongst the more obvious approximations made are non-refinement of the planarity of the molecule or of bonds involving atoms other than those expelled. An apparently peculiar system was used to define the molecule to make meaningful calculations possible: for the purposes of the program, zero atomic number "atoms" can be used to fix points in space, and the distance of the two "real" atoms eliminated from the ring was varied using two such zero-weight "atoms". In terms of the Figure these are atoms 12 and 13. The separations of the eliminated atoms from the second non-atom (13) were optimised for a series of values for the distance between the two non-atoms. The figure shows these as variables 13,14 and 12 respectively. Final results from this are given in Table 23 and the variation of optimised energy value with intermolecular separation is shown in Figure 20. Optimisation involved several stages and normally four or five individual calculations were needed for each of the two variables before convergence on the lowest energy arrangement was achieved. It proved to be impossible to perform similar refinement on the angles involved as well: in the Figure these are 12-13-14 and 12-13-15 and

▷p161

Table 23

Optimised values of energy and variables 13 and 14 over a range of values for variable 12

Variable 12(Å)*	Variable 13(Å)	Variable 14(Å)	Energy (a.u.)
1.350	1.3059	0.2595	-721.72327
1.400	1.2430	0.3563	-721.83781
1.425	1.2161	0.3977	-721.84345
1.450	1.1965	0.4241	-721.84817
1.475	1.1870	0.4298	-721.85182
1.500	1.1142	0.5750	-721.85385
1.525	1.1196	0.5478	-721.85596
1.550	1.0916	0.5988	-721.85658
1.575	1.0876	0.5942	-721.85640
1.600	1.0810	0.5967	-721.85523
1.650	1.0467	0.6545	-721.85051
1.750	1.0190	0.6753	-721.83369
1.850	1.0218	0.6357	-721.81150
1.950	1.0278	0.5740	-721.78802

* For notation used see Figure 19

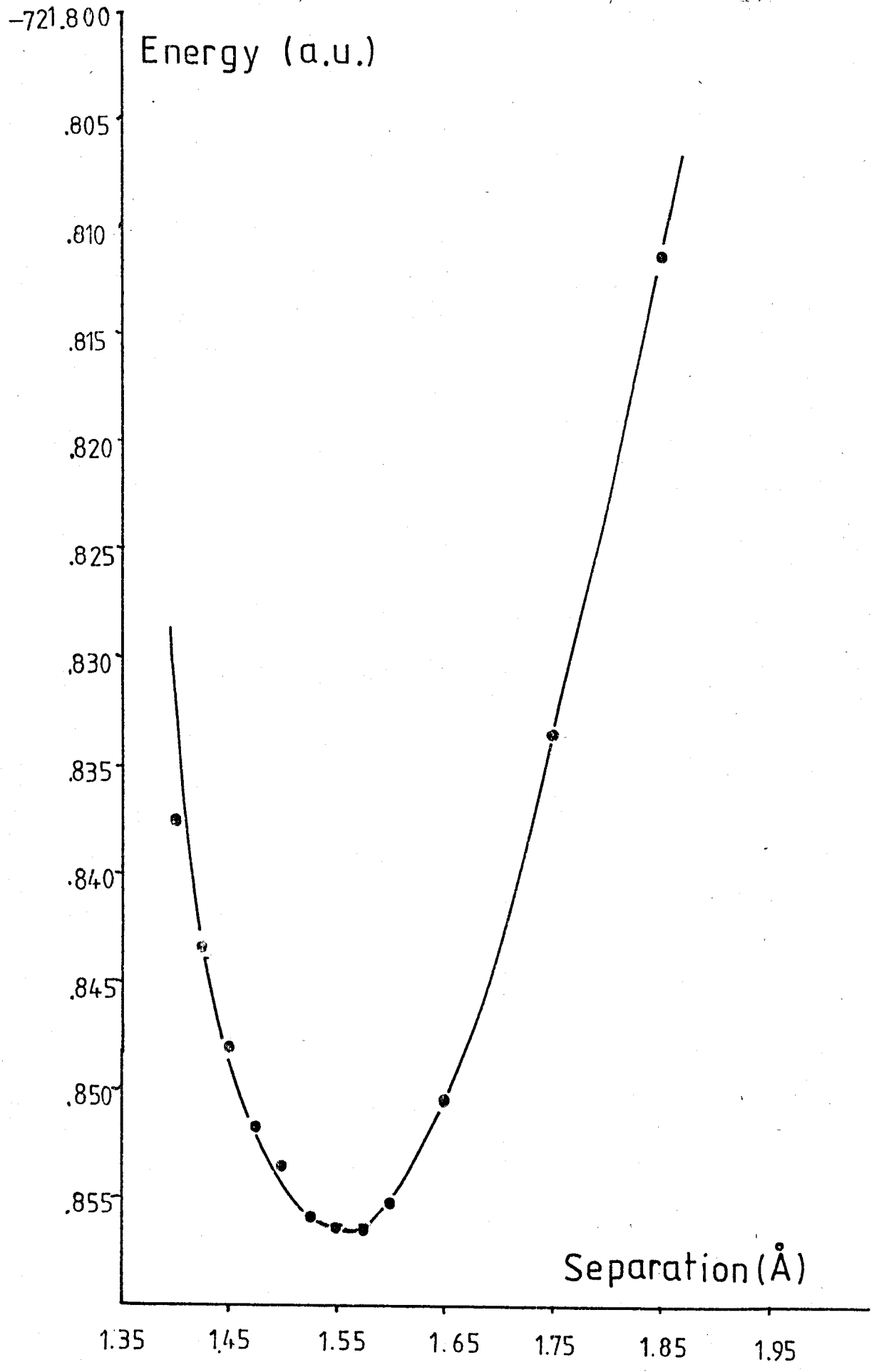

Fig. 20

Energy curve for the reaction $C_6F_5Li \rightarrow C_6F_4 + LiF$

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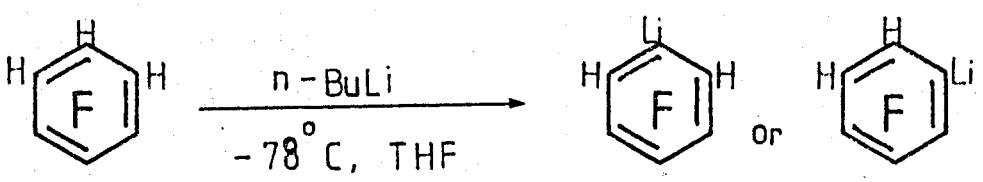
are defined as 90°. Attempts to optimise the molecular arrangement with these two angles variable as well as the distances mentioned above ended in failure: the greater the values used for variable 12 then the greater became the distances between the expelled atoms and atom 13, together with correspondingly more acute angles. In empirical terms this meant that a single conformation of lowest energy overall was possible and the atoms were refining towards it. Figure 20 shows the reason for this: no maximum exists for overall energy thus at no point does refinement tend towards infinite separation of the lithium fluoride from the tetrafluorophenyl fragment.

The optimised energy values show that a meaningful activation energy calculation is almost certainly not possible: the simplifications involved in omitting solvation from consideration are too great for extrapolation from the gas phase to be valid. Two experimental facts pinpoint solvation as the crucial difference: the presence of a molecule of solvent in the activated complex when lithium halides are eliminated from 2-halophenyllithium [68], and the appreciable difference in thermal stability between ether and THF solutions of pentafluorophenyllithium. It is always possible to criticise all-theoretical calculations on real systems: the single-molecule assumption built into the computation is a considerable approximation even for most gas reactions (let alone liquid phase studies) but until the calculations

are tried the validity remains problematical. A truer theoretical value could be obtained, but only after a considerably longer series of calculations with many more parameters varied.

During the course of the computational work outlined above a chemical system was devised to check the relevance of GAUSSIAN 70 to polyfluoroaryl compounds. The internal check built into the program is a dipole moment calculation. This is of dubious use for activation energy work, and polyfluoroarenes themselves are very non-polar, yet to measure the dipole moment of pentafluorophenyllithium would be a major exercise. 1,2,3-Trifluorobenzene has two possible chemically distinct sites for lithiation and calculations were performed upon it and upon the two isomers of 1,2,3-trifluorophenyllithium:



The results from the calculations on trifluorobenzene are given in Table 24; they show no pronounced difference between the two proton sites. The calculations on the two organolithium compounds showed the asymmetric isomer to be favoured by c. 20 KJ/mole. Chemically the isomeric analysis was performed by preparation of a mercurial: this method was chosen as it seemed probable that separation of organomercury compounds from the rest of the reaction

▷p164

Table 24

Atomic electron population 1,2,3-trifluoro-4,5,6-trihydrobenzene*

Atom(s)*	Electronic Population
Carbon 1, Carbon 3	5.8708
Carbon 2	5.9015
Carbon 4, Carbon 6	6.0825
Carbon 5	6.0497
Fluorine 1, Fluorine 3	9.1228
Fluorine 2	9.1210
Hydrogen 4, Hydrogen 6	0.9240
Hydrogen 5	0.9273

*Atoms are numbered as in this name, rather than as in Figure.

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mixture would be quite straightforward, and that the "purification" involved would not resolve the bis(trifluorophenyl) mercury isomers. ^{19}F nmr was then performed to establish which isomer was formed: the asymmetric isomer having three chemically non-equivalent fluorine sites and the symmetric isomer but two. Mass spectral data was also obtained as a check on the formula weight and chemical composition of the compound produced. X-ray studies (as further and conclusive evidence) were not possible, as detailed in Chapter 2. The isomer produced was the asymmetric possibility, bis(2,3-dihydro-trifluorophenyl)mercury, and this fact together with the data given in Table 24 show that GAUSSIAN 70 is capable of handling highly fluorinated aromatic systems. The activation energy results show also that the calculations are only as good as the molecular model used as input for the program: this implies that any approximations introduced are common in the case of the 1,2,3-trifluoro-phenyllithium isomers (and cancel) but invalidate theoretical data from pentafluorophenyllithium.

GAUSSIAN 70 has several drawbacks: it cannot compute d orbitals, it has fairly low limits on the number of atoms and orbitals usable and it is not always reliable in its handling of data calculated during intermediate stages of computation. These lattermost pitfalls can be quite subtle: the program has a default value of 20 stages for convergence of its SCF energy calculations and does not fail if all steps have been used. Oscillations

of 10-20 a.u. are possible if atoms are too close and these would not be detected by the program. Three energy values are needed to calculate the optimum, and the assumption is made that these points define a parabola whose minimum is at the numerical value sought. Whilst this makes interpolation reasonable, extrapolation can produce dubious or grossly incorrect results. Similarly the parameters varied will not give valid optima unless appreciably different energy values are produced by the intermediate calculations and the program has no inbuilt check that the "optimised" variable in fact gives a more favourable energy value than the preliminary stages.

The option in the program of simultaneous variation of more than one parameter was a blind alley as far as pentafluorophenyllithium was concerned. The parabolic assumption has limitations where the only parameters concerned are one variable and the energy, but extreme care would be needed before it could be used with two independent variables. In physical terms this would involve fitting a two-dimensional line onto points on a three-dimensional surface.

Parenthetically it can be remarked that the program is a heavy consumer of computer time: geometry optimisation jobs for a single parameter were typically of the order of 500 seconds.

Chapter 6

Experimental

Summary: Experimental details of the preparative chemistry performed are presented.

Experimental

Infra-red spectra were recorded on a Perkin-Elmer 457 machine using KBr discs or mulls between CsI plates. Raman spectra were recorded on a Cary 81 machine, ^{1}H nmr on a Nuclear Magnetic Resonance EM 360A machine and ^{19}F nmr on a Perkin-Elmer R32. Far infra-red spectra were recorded by Dr. R.E. Humphries, University of Windsor, Ontario, on a Perkin-Elmer 180 machine using polyethylene plates. Micro-analyses were by the University of Manchester Micro-analytical service. n-Butyllithium was used in hexane solution.

Preparations

1. Tribenzo[b,e,h][1,4,7]trimercuronin was prepared by vigorous agitation of a solution of 1,2-dibromobenzene in an ether solvent with an alkali metal amalgam. A variety of ethers and of metals was employed. Product was extracted with boiling DMF from the insoluble residue and collected by filtration after the solvent had cooled. Yields: 20-40% M.pt. 325-328°C (decomp.)

2. Perfluorotribenzo[b,e,h][1,4,7]trimercuronin was prepared by the method of Sartori[80] modified as follows: mercuric acetate was dissolved in warm dilute acetic acid and this liquid was filtered into a warm aqueous solution of tetrafluorophthallic acid (Bristol Organics Ltd.). The filtered precipitate was dried at 110°C in a fume cupboard then heated in a sand-bath under vacuum. Crude product

was collected on a water-cooled probe set immediately above the mercuric tetrafluorophthallate and purified by filtration of a DMF solution followed by heating to 220°C in a fume cupboard of the solid from a vapour diffusion crystallisation. Yields: 30-65% m.pt. c 340°C (subl.)

3. Bis(2,3-dihydrotrifluorophenyl)mercury was prepared by lithiation of 1,2,3-trifluorobenzene (1.32gm,10mMole, Imperial Smelting Co.) in anhydrous THF (100ml) at -60°C with n-butyllithium (7.5ml,10mMole). The resulting mixture was stirred for 2 hr, then mercuric chloride (1.35gm, 5mMole) was added in THF solution (5ml). The reaction mixture immediately darkened with a grey precipitate of colloidal mercury and was allowed to reach ambient temperature overnight before filtration. The solvent was removed and the resulting flakey crystals were washed twice with water (100ml) and twice with hexane (50ml). The product was recrystallised by boiling a methanol/THF/water solution until precipitation just commenced; on cooling the solid was filtered off and allowed to evaporate dry. Yield: 1.6gm (70%)m.pt. 152-155°(subl.). Shown to be $(C_6F_3H_2)_2Hg$ by m.s. and to be the 2,3-dihydro-isomer by ^{19}Fnmr.

4. 4,4'-Dimethoxy-3,3',5,5'-tetramethyl-o-biphenylenemercury was prepared by lithiation of 2,2'-diiodo-4,4'-dimethoxy-3,3',5,5'-tetramethylbiphenyl (5.2gm,10mMole) in anhydrous THF (100ml) at 60°C with n-butyllithium (15ml,20mMole)

over 30 minutes. The solution went immediately yellow, then cloudy. Ten minutes after the final n-butyllithium addition, mercuric chloride (2.71gm, 10mMole) was added in THF(10ml): the bulk liquid went immediately orange, then cloudy and grey with colloidal mercury. After being allowed to attain room temperature the solution was filtered, the THF was removed and the solid extracted with water and hexane. Yield 4.32gm (90%) mpt > 310°C.

5. Bis(pentamethylphenyl)mercury was prepared by lithiation of bromopentamethylbenzene (4.44gm,20mMole) in anhydrous THF(100ml) with n-butyllithium (15ml,20mMole) at -60°C added over 1 hr. The solution was allowed to warm to 0°C then solid mercuric chloride (27gm,10mMole) was added. The immediate grey/white ppt. was filtered, washed with water then extracted with boiling DMF. Yield: 4.5gm (80%).

6. 1,2-dibromotetramethylbenzene was prepared by bromination of 1,2-dihydrotetramethylbenzene (20gm) in glacial acetic acid (60ml) with bromine (50gm) in the same solvent (40ml). After stirring for 1 hr. the excess bromine was destroyed with 60% aqueous sodium hydroxide and 100ml of water added. The solid product was filtered; then recrystallised by addition of ethanol to a boiling solution in chloroform until precipitation just occured. Yield: 17.7gm (30%) mpt 108-110°.

7. 1,2-diiodotetramethylbenzene was prepared by fusion of 1,2-dihydrotetramethylbenzene (1.34gm,10mMole) with mercuric trifluoroacetate (11.0gm,30mMole) followed by heating until the mixture solidified. 150ml of DMF was used to wash this into a solution of 30gm each of iodine and potassium iodide in 75 ml of DMF. The mixture was stirred for 3 days, then diluted with 250ml of water and extracted with toluene. Yield: 1.9gm (45%) m.pt.182-186°C.

8. 2-Hydro-1-iodotetramethylbenzene was prepared by refluxing 1,2-dihydrotetramethylbenzene (10gm) with iodine (16gm) in glacial acetic acid (150ml). Iodic acid (8gm) in water (8ml) was added dropwise to the boiling solution which was then refluxed for 5 hr. After dilution with an equal volume of water and removal of the bulk of the aqueous layer by decantation the excess iodine was destroyed with 60% aqueous sodium hydroxide. The organic phase was extracted with chloroform then vacuum distilled. The fraction which came over at c.120°C and solidified in the condenser was shown by nmr to be 2-hydro-1-iodotetramethylbenzene. Yield: 3.6gm. (18%) m.pt. 28-30°C.

9. Bromopentamethylbenzene was prepared by bromination of pentamethylbenzene (10gm) in glacial acetic acid (50ml) with bromine (10gm) in the same solvent (20ml). The product precipitated out immediately and after dilution of the reaction mixture with 70ml of water excess bromine was destroyed with 60% aqueous sodium hydroxide. The

product was washed with water, glacial acetic acid, alkali, and water; then recrystallised by addition of methanol to a boiling carbon tetrachloride solution. Yield 12.7gm (85%)

10. The reaction of 1,2-diiodotetramethylbenzene with mercury. 1gm and 8gm respectively of the starting materials were heated at 200°C over night in a sealed tube then for 3hr at 250°C. No reaction was observed at 200°C and ether extraction of the final (charred) residue produced only hexamethylbenzene(?), a solid fluorescent in solution.

11. Reaction of 1,2-dibromotetramethylbenzene with 1.5% sodium amalgam. 2.2gm and 20gm respectively of the starting materials were heated slowly to 200°C in a sealed tube. The residue was extracted with 100-120 pet.ether, followed by water then boiling DMF. The insoluble residue had a melting point of 260-270°C (decomp.) Yield 50mgm. (2%)

12. Reactions of 2,3-dibromonaphthalene with alkali metal amalgams. 2,3-dibromonaphthalene (1gm) was reacted (1) in THF solution with 0.5% potassium amalgam (200gm), (2) in ether solution then 4:1 ether/THF solution with 3.3% potassium amalgam (50gm), and (3) in freshly distilled diglyme with 1% sodium amalgam. In no instance could any organomercury products be detected.

13. Permethyl-o-phenylenemercury was prepared by agitation of a refluxing solution of 1,2-dibromotetramethylbenzene (5.8gm,20mMole) in tetralin (200ml) with 3.3% sodium amalgam (100gm). The resulting solid was extracted with chloroform, water, hexane, boiling DMF, DMSO and quinoline. The residue was proved to contain mercury by x-ray fluorescence and to be permethyl-o-phenylenemercury by preparation of 1,2-diiodotetramethylbenzene on reaction with triiodide ions in DMF solution. Yield: 4.6gm (65%) m.pt. 260-270°C (decomp.)

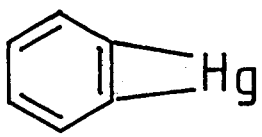
Chapter 7

Discussion

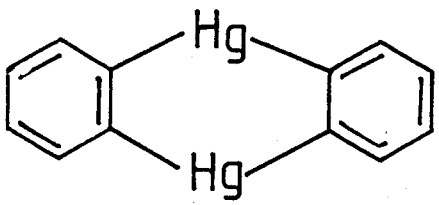
Summary: The work presented in separate sections is discussed, wherever possible, in a unified manner.

Discussion

o-Phenylenemercury is a troublesome compound to study as it is quite insoluble in all solvents in the cold and in most boiling solvents, is high melting (325-328° with decomposition [72]) and is not particularly easy to prepare. It has the advantages, however, of the stability to heat, light and moisture typical of mercurials. As it contains a di-substituted phenyl ring a variety of oligomeric structures are possible, but a monomer and a dimer are ruled out on the principle that bicoordinate mercury must be linear to be a good approximation.



monomer



dimer

Early studies of mercurials quite often postulated structures like those above and one reason for this is the dipole moments possessed by many mercurials which are now believed to arise from the polarisation of the metal atom rather than from any asymmetry of the overall molecules.[144] Infra-red spectral studies have shown diphenylmercury to have the same conformation in solution as in the solid state,[105] where an X-ray structure

analysis has shown it to be linear about the metal atom with the rings coplanar.[146] The outer electronic configuration of mercury ($4f^{14}5d^{10}6s^2$) with the full f and d shells make the atom polarisable and in a bi-coordinate system only two atomic orbitals would be used, to give a pair of co-linear sp hybrid orbitals.

Higher oligomers of o-phenylenemercury $(C_6H_4Hg)_n$ having C-Hg-C angles of 180° are possible for n = 3 or any even number other than 2. The trimer is planar but the other oligomers - the limiting case is a polymer of formula $(C_6H_4Hg)_{2n}$ - are not. Molecular point-groups are given in Table 26 for some of the lower oligomers. Group theory can be used to predict, on the basis of the point group, which vibrations should be active in the infra-red and which in the Raman, but it also predicts that the total number of modes is (3N-6) for a non-linear molecule where N is the number of atoms present. For a trimer ($C_{18}H_{12}Hg_3$) this amounts to 93 bands, many of them being degenerate because the vibrational coupling is not great enough to lift the degeneracy arising from molecular symmetry. The portions of the infra-red spectrum of o-phenylenemercury shown in Figures 21 and 22 show that the compound is remarkable for its lack of absorbtion rather than the contrary. Attempts were made to obtain Raman spectra but both crystal modifications studied exhibited broad-band fluorescence and thus point-group analysis proved impossible. Comparison of the monoclinic and orthorhombic forms of o-phenylenemercury

p177

Table 26

Molecular point-groups for selected mercurials

Molecule	Oligomer	Point Group
Bis(2-hydrotetrafluorophenyl)mercury*	-	C_{2n}
Bis(pentafluorophenyl)mercury•	-	C_1
o-Phenylenemercury*	Trimer	D_{3h}
o-Phenylenemercury•	Tetramer	D_{2d}
o-Phenylenemercury•	Hexamer	D_{3d}
o-Phenylenemercury•	Polymer	C_s^2
o-Biphenylenemercury•	Trimer	C_3
o-Terphenylenemercury•	Dimer	C_{2h}

* Planar molecule

• Non-planar molecule

p175 ▷

by spectral techniques revealed no major differences: small variations occur in the i-r band at c. 750cm^{-1} (Figure 21) and the broad band at 150-250cm^{-1} (Figure 22) appears to be more intense in the orthorhombic form. These differences can probably be attributed to differing inter-molecular contacts in the solid state: the orthorhombic form has metal-metal contacts but the monoclinic has not (Chapter 2). Additionally the orthorhombic form fluoresces somewhat more strongly under laser Raman conditions.

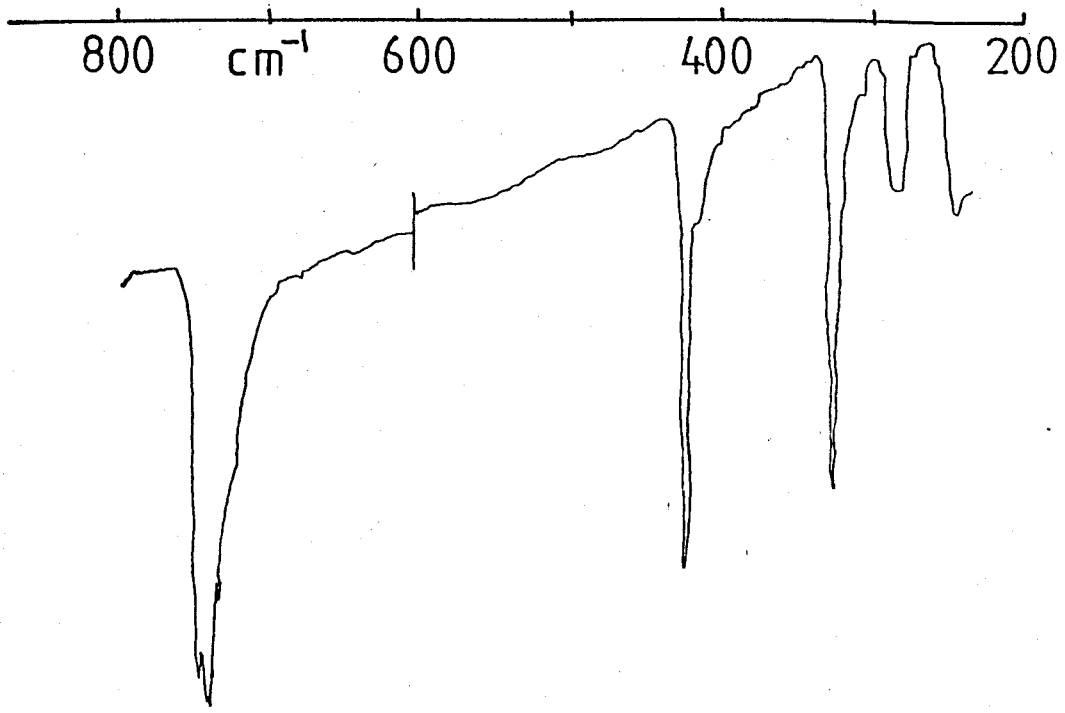
Low resolution microwave spectroscopy can resolve oligomers by measurement of the molecular moment of inertia, but only[170] if the molecule is a good approximation of a symmetrical rotor, has an appreciable dipole moment and a vapour pressure ≥ c.20m Torr. o-Phenylenemercury is ineligible for such a study on both of the last two counts.

Mass spectrometry should be able to show the empirical formula of a compound by a display of the parent ion peak(s) and by detection only of ions derived from it. However, the conditions (10^{-6} Torr, heat) needed for the technique are such that some doubt must always remain that the spectra are artefacts: the mass cut-off at Hg_3 species shown by o-phenylenemercury[93] is by no means rigorous proof that the parent compound is trimeric.

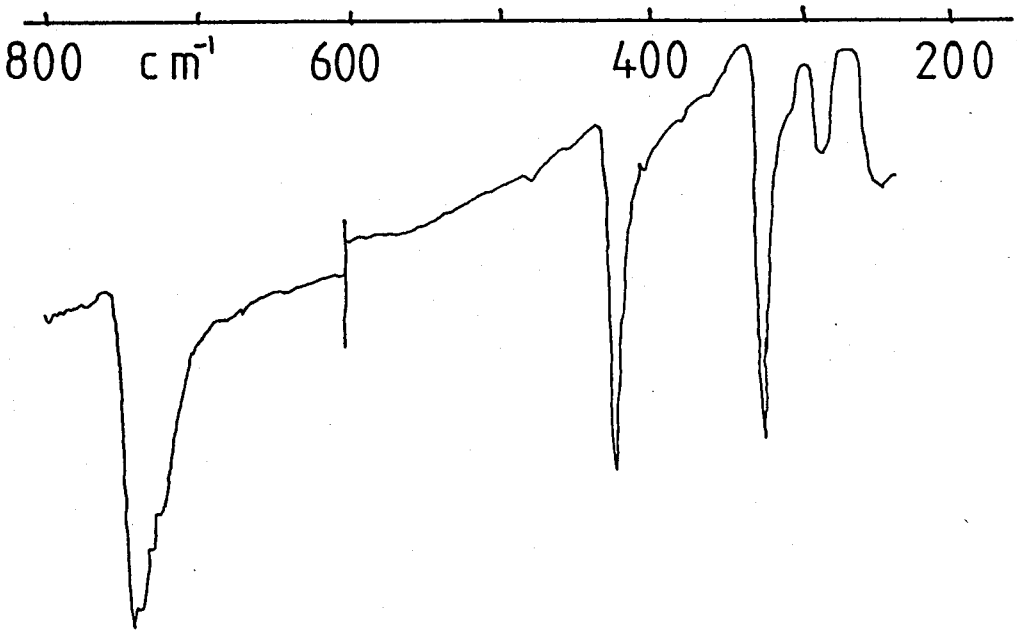
o-Phenylenemercury can be prepared only by metal amalgam reactions, typically

$$1,2\text{-}C_6H_4Br_2 \xrightarrow{Na/Hg} (C_6H_4Hg)$$

▷ p180



$(C_6H_4Hg)_3$; $P2_1/c$



$(C_6H_4Hg)_3$; $P2_12_12_1$

Fig. 21

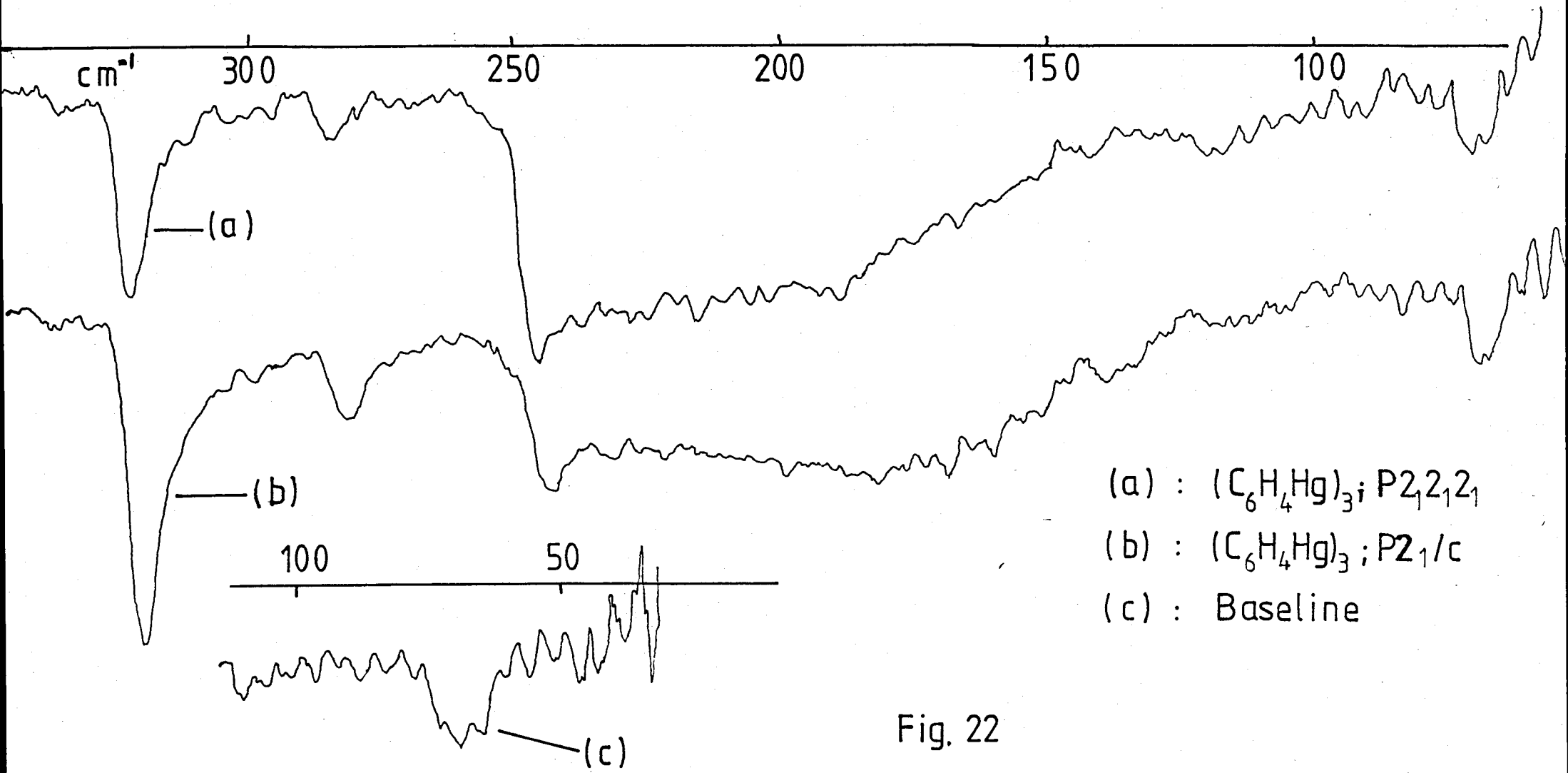

cm⁻¹
300
250
200
150
100
(a)
(b)
100
50
(c)
(a) : $(C_6H_4Hg)_3$; $P2_12_12_1$
(b) : $(C_6H_4Hg)_3$; $P2_1/c$
(c) : Baseline

Fig. 22

p177 ▷

The alternate methods of mercurial synthesis discussed in Chapter 1 are not available since both 1,2-dilithiobenzene and the ortho-diGrignard Reagent[172] are both prepared from the mercurial; furthermore, 1,2-diaminobenzene diazotises abnormally[173] and mercuric phthallate monodecarboxylates only.[82] Other halogens can be substituted for bromine and 1-bromo-2-fluorobenzene, 1,2-diiodobenzene and 1,2-dichlorobenzene have all been used, the lattermost reagent giving very poor yields.[93] The dihalides are dispersed in an inert (etherial solvent) and shaken with the amalgam for about an hour.

The most likely mechanism for the reaction invokes free radicals:

$$NaHg\bullet + 1,2\text{-}C_6H_4Br_2 \rightarrow 1,2\text{-}C_6H_4BrHg\bullet + NaBr$$

$$Na\bullet + 1,2\text{-}C_6H_4Br_2 \rightarrow 2\text{-}BrC_6H_4\bullet + NaBr$$

$$Hg + 2\text{-}BrC_6H_4\bullet \rightarrow 1,2\text{-}C_6H_4BrHg\bullet$$

The subsequent combination of radicals would eliminate mercury and quantities of grey colloidal mercury are indeed observed.

$$2(1,2\text{-}C_6H_4BrHg\bullet) \rightarrow (2\text{-}BrC_6H_4)_2Hg + Hg$$

No other experimental evidence is available to support this theory, but any other mechanism seems even less

probable: metallation by the alkali metal would produce benzynes from 1,2-dihalobenzenes, and insertion of mercury into the carbon-halogen bond followed by reductive symmetrisation fails on two counts.

$$1,2\text{-}C_6H_4Br_2 + Hg \rightarrow 2\text{-}BrC_6H_4HgBr$$

$$2(\ 2\text{-}BrC_6H_4HgBr) + 2Na \rightarrow (2\text{-}BrC_6H_4)_2Hg + Hg + 2NaBr$$

The first of these is that the reaction works well with 1-bromo-2-fluorobenzene and mercury insertion into a carbon-fluorine bond is not a reasonable postulate. The second is the formation of o-terphenylenemercury, $\left[(C_6H_4)_3Hg\ \right]_2$, with more basic ethers.[73] The free-radical mechanism can account for this by solvation effects changing which of the two radicals is favoured. Coupling of the o-bromophenyl radical to give a biphenyl (and hence a terphenyl) is quite possible:

$$2(2\text{-}BrC_6H_4\cdot) \rightarrow 2,2'\text{-}Br_2C_{12}H_8$$

Single crystal X-ray and neutron diffraction are the only remaining techniques to distinguish between oligomers and in 1959 Grdenic published a partial structure determination on data he interpreted as proof for a hexameric structure.[141] Closer examination of his published work, however, reveals that he was using a twinned crystal and basing his conclusions solely on a

projection Patterson map. In mitigation it must be said that to obtain any results at all from a twinned crystal using the data collection and unautomated calculation techniques available at that time was something of a tour de force.

After several attempts using various solvents it finally proved possible to isolate single crystals of o-phenylenemercury from DMF by slow cooling. The structure was solved in space group $P2_12_12_1$ (Chapter 2) and in that space group only a trimer is possible given the density of 3.5Mg m^{-3}. Grdenic had found the compound to crystallise in the monoclinic space group $P2_1/n$ and no possibility exists of reconciliation between this and our orthorhombic system. In the centrosymmetric $P2_1/n$ a hexamer is possible with one half of the molecule as the asymmetric unit since the hexamer is itself centrosymmetric. Further crystallisation attempts eventually produced a monoclinic crystal modification on a unit cell diagonal to the unit used by Grdenic, giving the space group as $P2_1/c$. The trimer was finally proved to be the only oligomer by determination of the monoclinic structure (Chapter 2) and by interconversion of the two forms.

As both recrystallisations of o-phenylenemercury that had given suitable crystals for X-ray structure analysis had used DMF as solvent it was chosen again to purify a sample of perfluoro-o-phenylenemercury. The discovery and solid state kinetics of decomposition of

the adducts of perfluoro-o-phenylenemercury are given in Chapter 3 and the X-ray structure of the 1:1 adduct with 4-phenylpyridine is given in Chapter 2. This structure analysis proved that perfluoro-o-phenylene-mercury is trimeric as originally proposed[80] and completes the cycle of evidence about these compounds. $(C_6H_4Hg)_n$ was investigated because n was stated to be 6 compared with 3 for $(C_6F_4Hg)_3$ and in the end both compounds were shown to be trimers. The only evidence for polymorphism in the fluorinated case is indirect: an ethanol recrystallisation gave a DTA peak at c.200-220°C yet the compound showed no weight change on TGA, thus indicating a phase transition of some sort.

The adducts of perfluoro-o-phenylenemercury are interesting in that the metal atoms in the mercurial are held in a rigid electron-withdrawing matrix. This restricts the ability of the mercury atom to complex (models showed that tetrahedral coordination was sterically impossible) whilst at the same time the electron-with-drawing groups make formation of donor/acceptor complexes at least theoretically possible. The recrystallisation of o-phenylenemercury from quinoline which converted the monoclinic modification into the orthorhombic was performed, in part, to investigate the ability of this compound to form adducts: the perfluoro mercurial had been shown to form an adduct with this solvent. The word "adduct" has been used to describe the compounds containing perfluoro-o-phenylenemercury and solvent

molecules since it does not define a specific type of bonding just as the trivial name for the mercurial does not state that any particular oligomeric state is present. Five "bonding" types are possible: clathrates, charge-transfer complexes, coordination complexes and packing involving hydrogen/fluorine bonding or van der Waals forces.

Clathrates are relatively rare and their decomposition kinetics would be predicted to be diffusion-controlled. It is also difficult to visualise a clathrate that (a) has up to three separate sites and (b) will accept molecules as diverse in size as acetone and triphenyl-phosphine. The most convincing evidence against clathrate formation, however, came from X-ray powder pictures. In any molecular array containing some very heavy atoms amongst other quite light atoms the greatest part of the X-ray diffraction patterns are determined by the heavy atoms. In a clathrate the relative positions of these atoms would be unchanged, yet the patterns from the original mercurial and its 1:1 and 1:2 adducts with DMF were all completely distinct.

Charge-transfer complexes are usually coloured and as stable in solution as in the solid state. The adducts examined, in contrast, were all colourless and the 1:1 pyridine compound in solution gave no extra band in the U-V region (Figure 23).

Hydrogen-fluorine bonding cannot be disproved on solely spectroscopic evidence, but the C-D stretching

p186

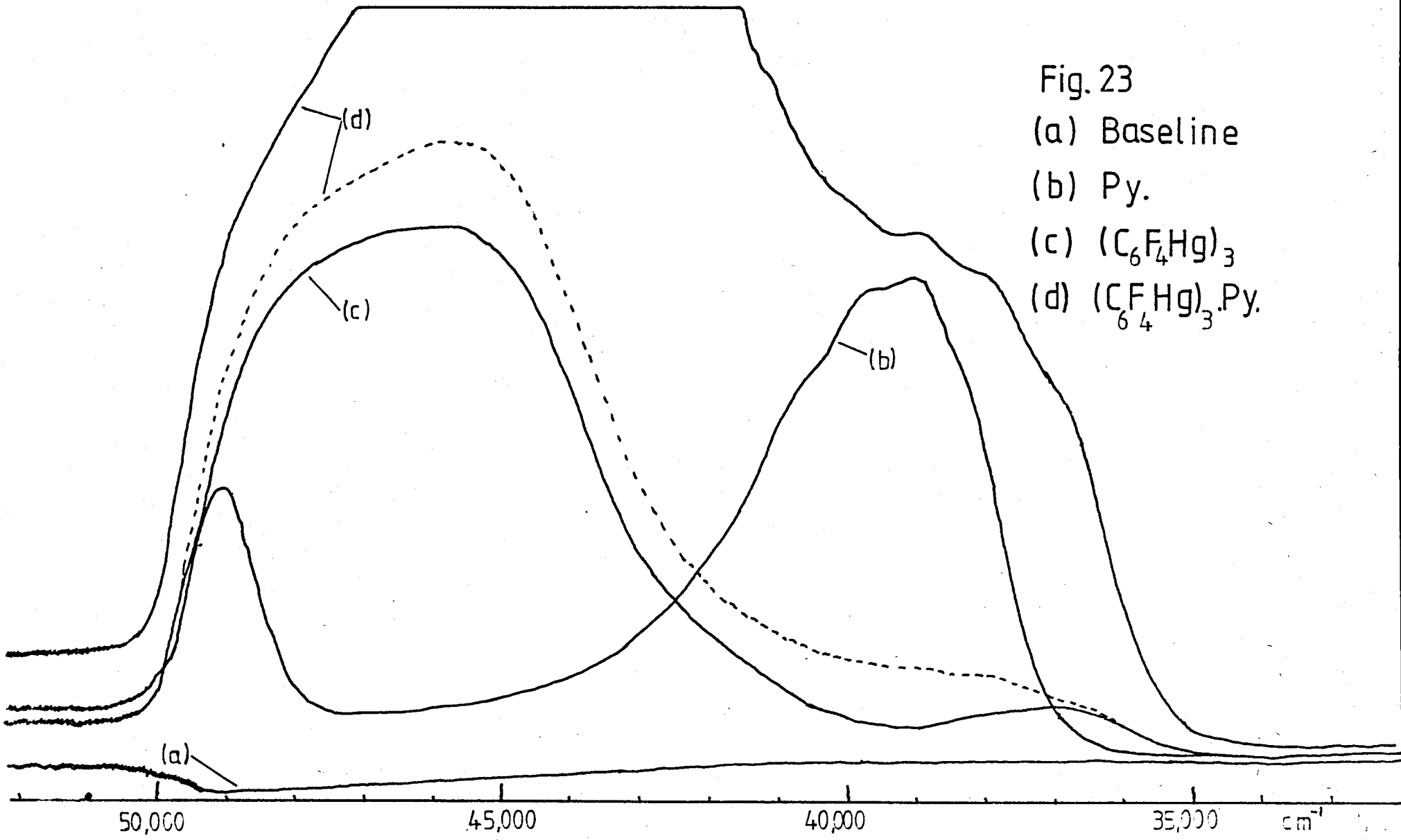


Fig. 23

(a) Baseline

(b) Py.

(c) $(C_6F_4Hg)_3$

(d) $(C_6F_4Hg)_3.Py.$

p184 ▷

frequency in the 1:1 and 1:3 perdunteriopyridine adducts appeared to be unaltered in position, although the low intensity of the absorbtion would make slightly shifted bands difficult to detect. Additionally ^{19}F nmr spectra were recorded on samples dissolved in pyridine, DMF and ethanol, which last named solvent does not form adducts. It can be seen (Figure 24), in spite of the poor signal/noise ratio, that no major changes in the chemical environments of the fluorine atoms have taken place. ^{19}F nmr is prone to solvent shifts and the variations displayed are normal in this context: it is more important that no broadening of the peaks or major changes in coupling constants (which would also show as changes in peak shape) have occured.

Most spectral data is obtained from solutions and thus it would appear that some explanation for the general lack of liquid phase spectra of the adducts should be forthcoming. Empirically the 2-methylpyridine adduct was shown to decompose in solution on the basis of vapour pressure. This was insufficient in the 1:2 adduct in the solid state for it to smell greatly of the solvent, but an ethanol solution of the same compound smelt very strongly of 2-methylpyridine. The ^{19}F nmr spectra and also the U-V spectra mentioned previously also imply decomposition but the clearest proof comes from the solution i-r spectra of the DPF adduct (Figure 25). There is no shift in the carbonyl band of the DPF in polar solvents and there is evidence of decomposition

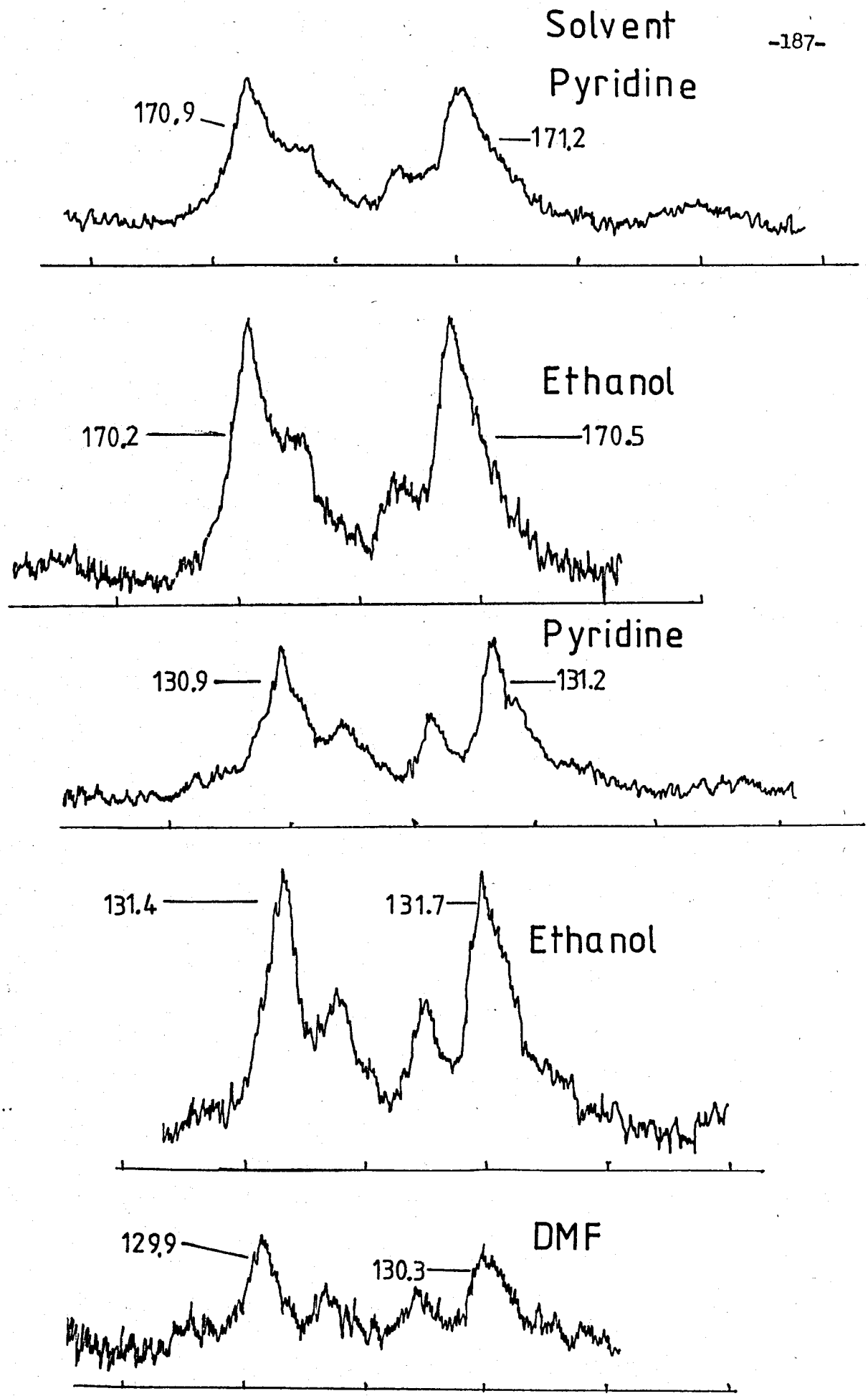


Fig 24

^{19}F nmr spectra of $(C_6F_4Hg)_3$; values in ppm

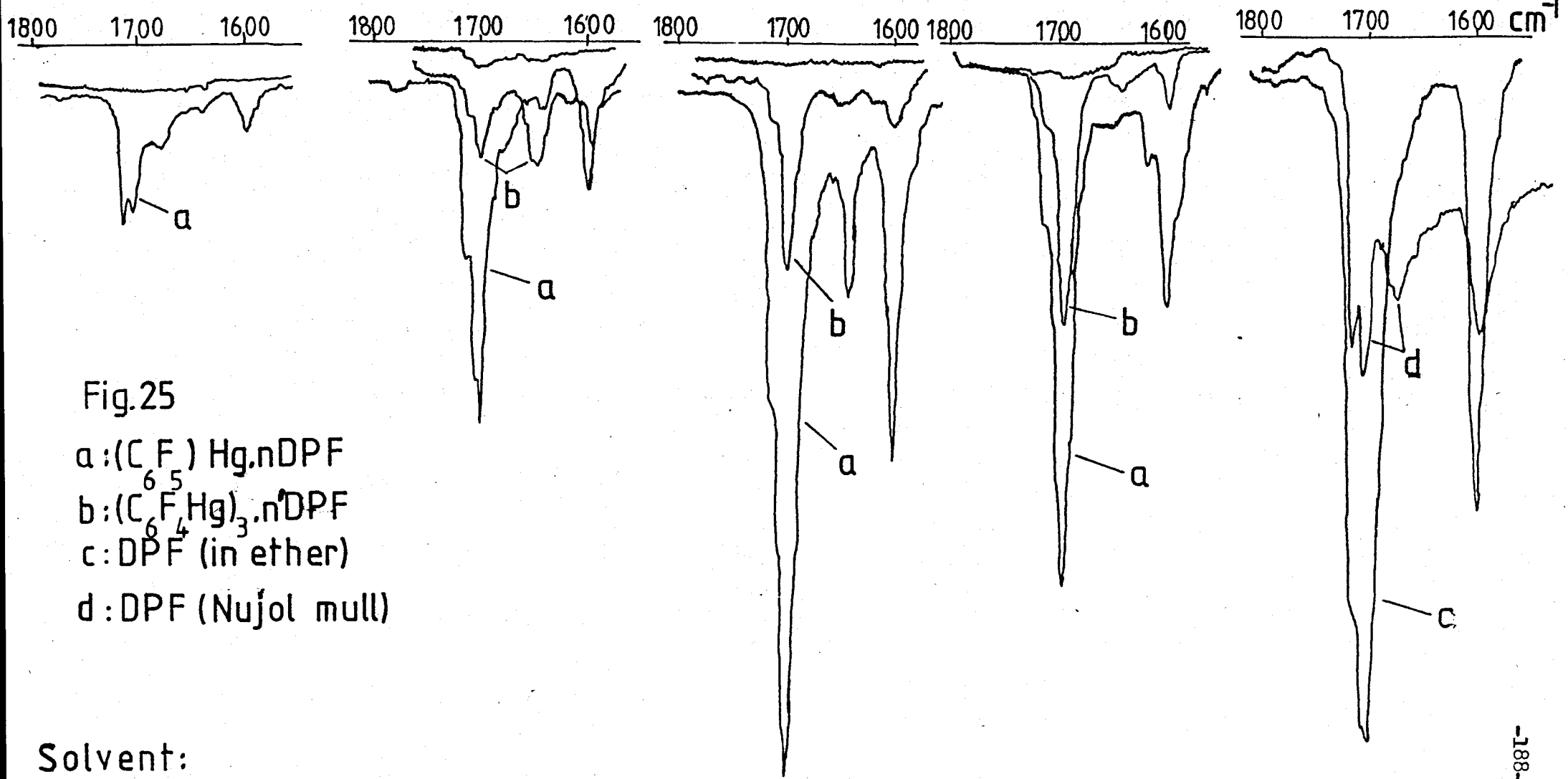


Fig. 25

a : $(C_6F_5)_2Hg$, nDPF

b : $(C_6F_4Hg)_3$, nDPF

c : DPF (in ether)

d : DPF (Nujol mull)

Solvent:

Hexane | Ether | THF | 1,2-Dimethoxyethane | —

p186 ▷

even in ether solution. The carbonyl stretching mode is the only solvent band to show even slight shifts on adduct formation (Figure 26), and some values are presented in Table 25. The absorbtion attributed to (carbonyl) C-N bending, at 653cm^{-1} in DMF,[174,175] is unaffected both in DMF and DEF adducts: these results are in sharp contrast to transition metal complexes where quite substantial shifts of this band are reported.[175] Similarly the "umbrella" mode in pyridine at 703cm^{-1} is unchanged in its 1:1 and 1:3 adducts despite reports of its sensitivity to complexation.[176]

Infra-red spectra were recorded on mulls (in Nujol or hexachlorobutadiene) to avoid the possibility that the 18 ton/in^2 applied to sinter KBr into discs also changes the nature of the compounds studied. Far infra-red examination was made of the parent mercurial and of four of its adducts (Figures 27,28) since conclusive proof of coordination-complex bonding would have been supplied by the presence of an absorbtion band in this region absent in the separate spectra. These occur at about 120-140cm^{-1} for mercury-pyridine complexes.[177] As an extra check the 1:1 adduct with perdeuteriopyridine was also investigated as an isotopic shift would show up an absorbtion which was pyridine-sensitive. No extra bands are visible in any of the 1:1 adduct spectra. The extra peaks in the 1:2 adduct with DMF are thus impossible to attribute to a mercury-nitrogen vibration as DMF has eight modes which absorb[174] below 200cm^{-1}. Pyridine

▷ p194

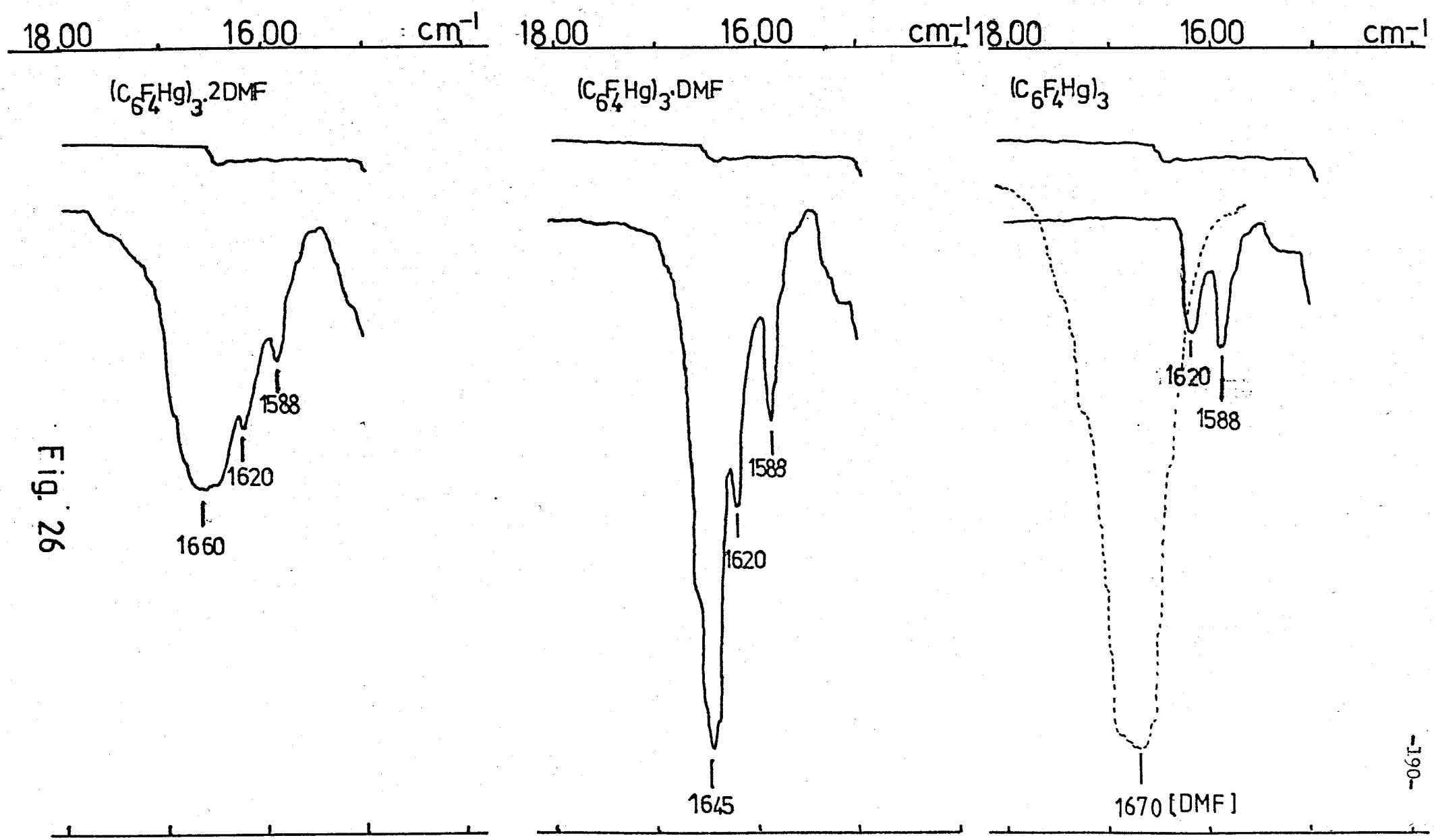

18,00
16,00
cm⁻¹
(C6F4Hg)3.2DMF
1588
1620
1660
(C6F4Hg)3.DMF
1588
1620
1645
(C6F4Hg)3
1620
1588
1670 [DMF]

Fig. 26

Table 25

(a) Position of C = O stretching mode (cm^{-1}) in adducts $(C_6F_4Hg)_3\ L_n$

L	"Free"	n = 1	n = 2	n = 3
DMF	1670	1645	1660	-
DEF	1675	1630	1643;1630	1660
DPF	1718; 1706	1650	-	-
DMA	1640	1593	1604	1614
Acetone*	1712	1682	-	-
Cyclopentanone*	1750;1740	1780	-	-

* stoichiometry of adduct not established

(b) Position of O = C - N bending mode (cm^{-1}) in adducts $(C_6F_4Hg)_3\ L_n$

L	"Free"	n = 1	n = 2	n = 3
DMF	660	665	661	-
DEF	647	645	642	645

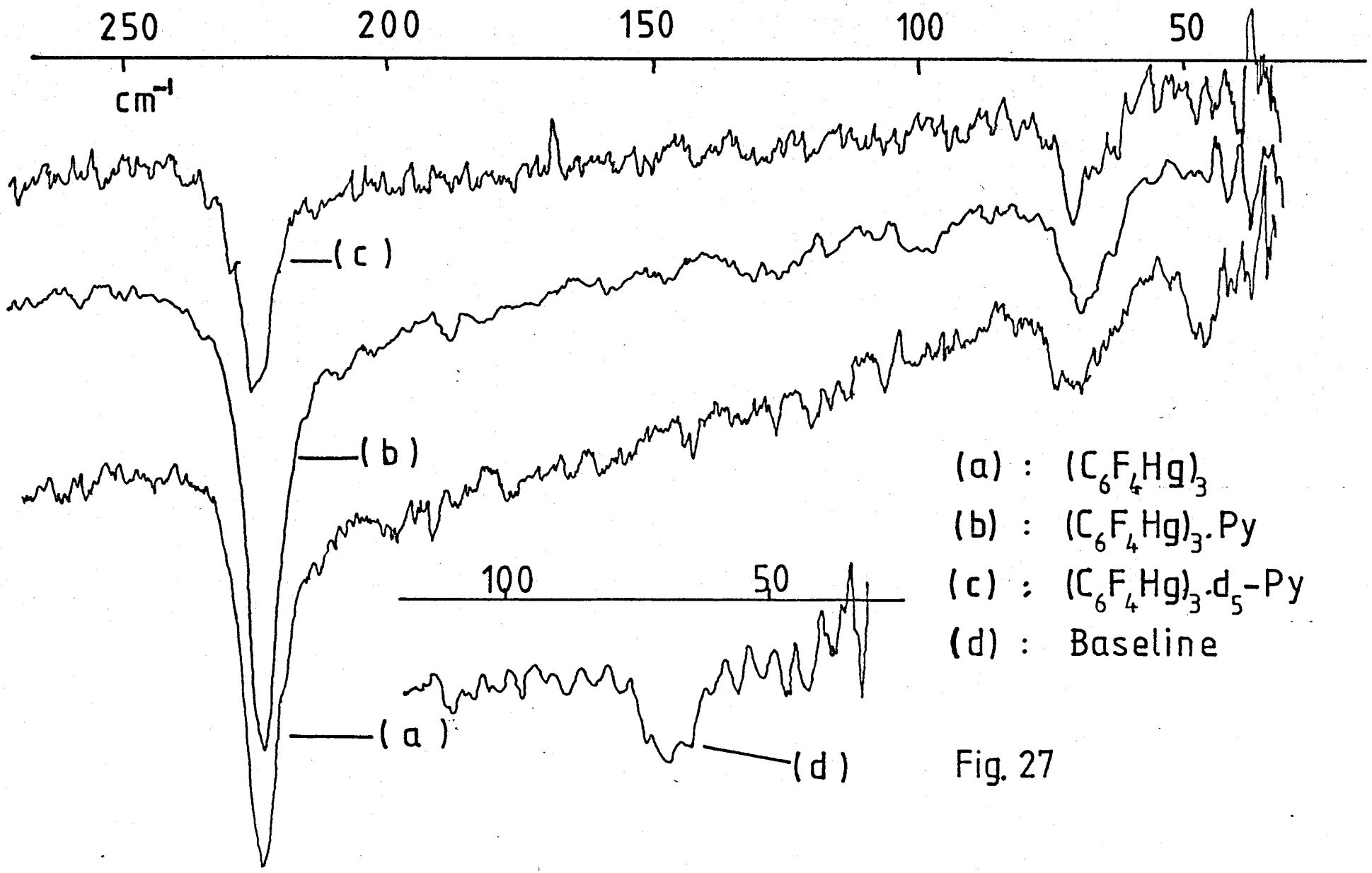

250
200
150
100
50
cm⁻¹
(c)
(b)
(a)
100
50
(d)
(a) : $(C_6F_4Hg)_3$
(b) : $(C_6F_4Hg)_3.Py$
(c) : $(C_6F_4Hg)_3.d_5$-Py
(d) : Baseline

Fig. 27

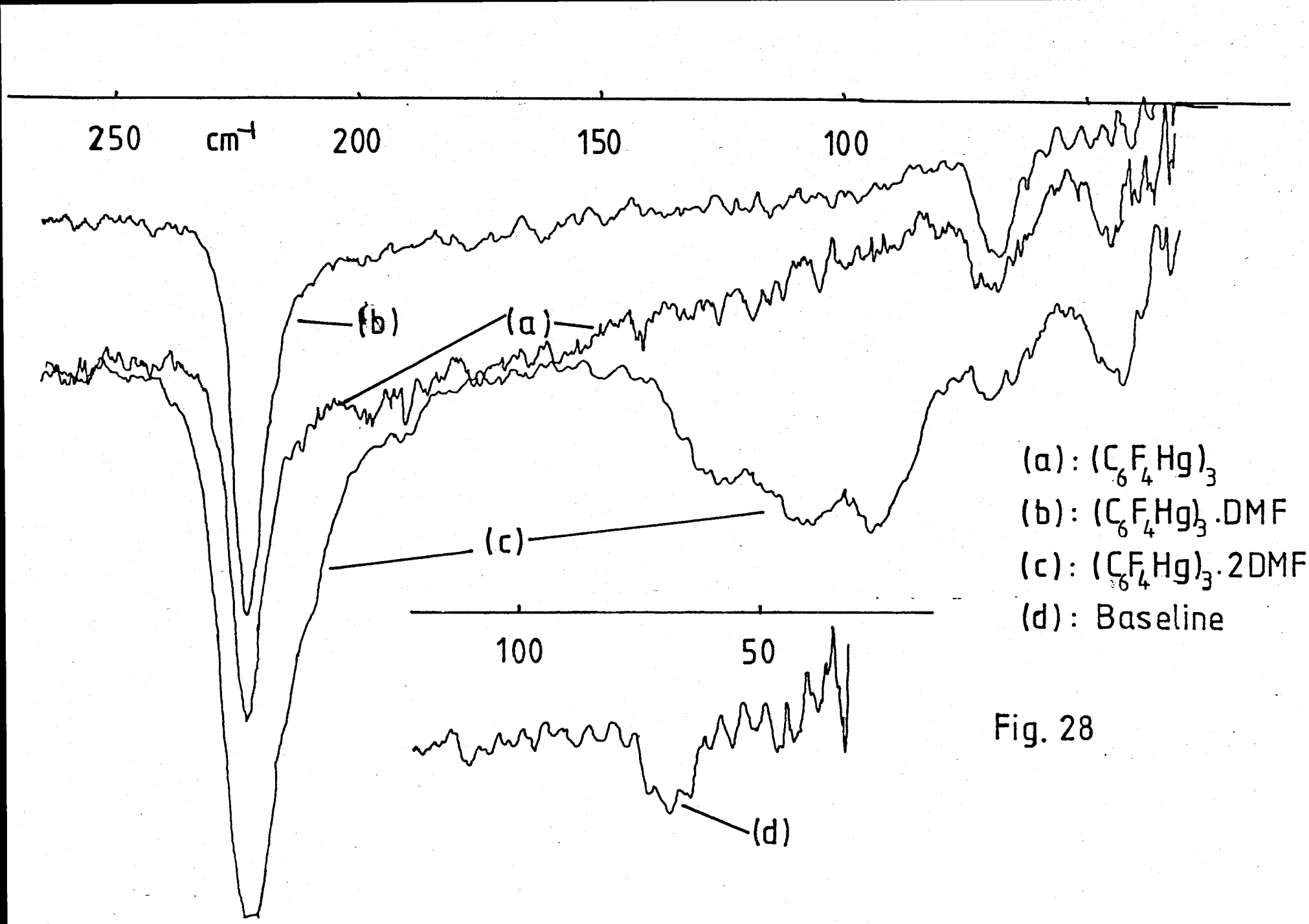

250
cm⁻¹
200
150
100
(b)
(a)
(c)
100
50
(d)
(a): $(C_6F_4Hg)_3$
(b): $(C_6F_4Hg)_3$.DMF
(c): $(C_6F_4Hg)_3$.2DMF
(d): Baseline

Fig. 28

p189 ▷

does not absorb[177] in the infra-red below 400cm^{-1}. The structure of the adduct with 4-phenylpyridine revealed that this adduct, at least, is not a coordination complex and would not be expected to reveal a mercury-nitrogen infra-red absorbtion.

The only real change in the mercurial component of the i-r spectra is the splitting of the band at c.1098cm^{-1}. This absorbtion is also moved to lower energy (Figure 29); error on the numbers quoted in the Figure is about $\pm$3cm^{-1}. This splitting is probably due to a slight change in the molecular geometry, expected when extra molecules are co-crystallised: the slight nature of the difference between the new values would indicate that any deviation from D_{3h} point symmetry is small. Just as with o-phenylenemercury the complicated nature of the molecule combined with broad-band fluorescence under laser Raman conditions makes detailed analysis of the spectra (to find which oligomer occurs) impossible.

The 4-phenylpyridine adduct was shown (Chapter 2) to be bound together solely by van der Waals forces and the strength of these forces were shown by the kinetic studies (Chapter 3). It is, however, anomalous in some respects. The free organic molecule is a solid and it is the only adduct studied whose crystallisation gave a monoclinic system: all the others were triclinic. In line with the other pyridine and substituted pyridine adducts it shows little change in the i-r between "complexed" and "free" spectral values. It is thus not

▷ p196

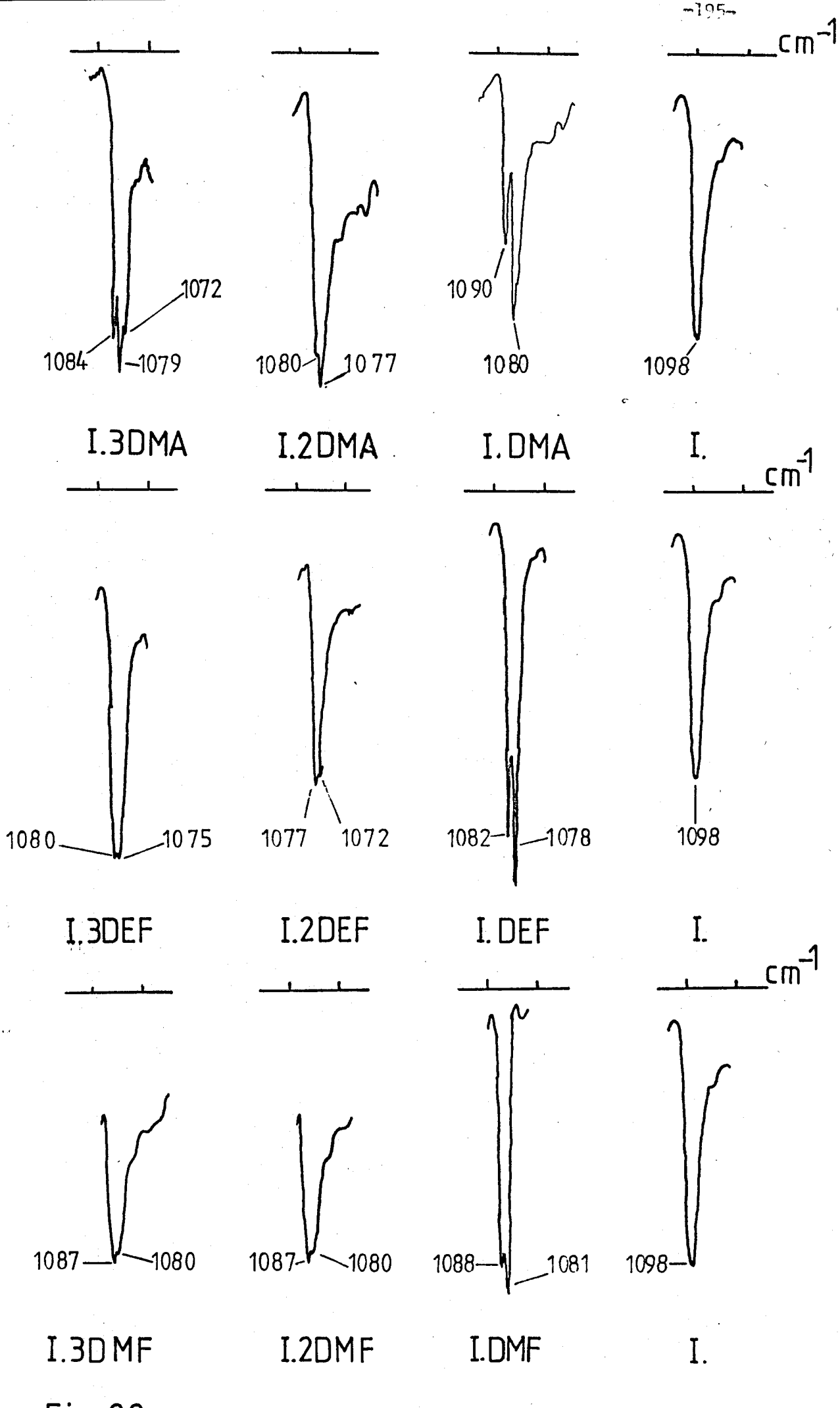

cm-1
1072
1084
1079
1080
1077
1090
1080
1098
I.3DMA
I.2DMA
I.DMA
I.
cm-1
1080
1075
1077
1072
1082
1078
1098
I.3DEF
I.2DEF
I.DEF
I.
cm-1
1087
1080
1087
1080
1088
1081
1098
I.3DMF
I.2DMF
I.DMF
I.

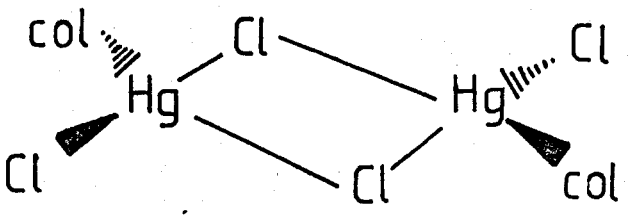
Fig. 29

p194 ▷

possible on spectral evidence to state whether it is typical or atypical of the series of adducts examined. The kinetic data from the 4-phenylpyridine adduct - which show it to be wholely uniform with the other adducts - does not form conclusive proof that all the adducts are of the one type. It can be cogently argued that steric factors are very important in these adducts (this would be true irrespective of the type of bonding) and that the shape of 4-phenylpyridine may make a "solvent of crystallisation" adduct more favourable than a coordination complex solely for this molecule. Nevertheless all the molecules which formed adducts contain appreciable dipole moments and this appears to be their major physical or chemical property in common. The van der Waals forces between the dipole of the organic molecule(s) and the induced dipoles of the mercurial are considerably stronger than those between non-polar molecules and this may explain (in part) the weakness of the association between hexafluorobenzene and hexamethylbenzene.[165] Final proof that all the adducts form an homogenous series or, indeed, that they do not, must await further X-ray studies.

Discussion of the possible symmetry around a mercury atom in a compound is made difficult by the very extensive distortions found, and X-ray structure determinations have variously described coordinated mercury as tetrahedral[178], trigonal,[178] octahedral[179], trigonal bipyramidal[181], square-[181] and T-shaped[150]. With this

in mind the description in this work of a mercury adduct as "non-complexed" requires some justification. In the complex $[HgCl_2py_2]$ the Hg-N separation of 2.60Å was initially thought to disprove coordination[183] but later spectroscopic work showed an interaction to exist.[177] In contrast the complex $[HgCl_2col]$ gave the Hg-N separation as 2.18Å in a dimer[180]:



col = collidine(2,4,6-trimethylpyridine)

This incidentally shows the preference of mercury for tetrahedral coordination(albeit the bridging halogen atoms are not equidistant from the two metal atoms: there is one short and one long bond) rather than T-shaped. This latter form of co-ordination has been shown, by X-ray methods, to occur in the 2:1 complex between bis(pentafluorophenyl)mercury and bis(diphenylarsino)-methane,[150] and indicated by thermodynamic results[184] for the 1:1 pyridine complex. ^{199}Hg nmr also indicates T-shaped mercury co-ordination in solutions of methyl-mercuric chloride in the presence of excess chloride ions.[185] Presumably bonding is dative to an empty mercury p orbital.[184]

Trigonal bipyramidal co-ordination, an alternative formulation for the collidine complex above,[180] is

strongly disfavoured to the point that a mercury-phenyl interation is proposed to complete an octahedral mercury environment in the 1:1 complex between mercuric chloride and diphenylsulphoxide.[179] Mercury complexes have been proved by X-ray methods both where the donor molecule is nitrogen and where it is oxygen: 1,10-phenanthroline[186], 2,2'-bipyridyl[187,188], dioxan[189], THF[190], methanol[191], cyclononanone[181] and cyclohexa-1,4-dione[192] complexes have all been studied.

Organomercury complexes are found only where the fragment is strongly electron-withdrawing as in the bis(pentafluorophenyl)mercury complex[150] mentioned above, and in the complex between bis(phenylethynyl)mercury and 1,10-phenanthroline.[193]

Recrystallisation of bis(pentafluorophenyl)mercury either from, or in the presence of, donor/acceptor complexing solvents gives[194] complexes (as shown by spectral, analytical and molecular weight data) but similar treatment of the analogous non-fluorinated compounds yields only unchanged starting materials. An early report[195] of hexa-coordinate mercury in 1:2 adducts between diphenylmercury and 1,10-phenanthroline (or substituted phenantholines) were later shown by a crystal structure analysis to be false.[149] The compounds were formed of an organic matrix supporting an uncomplexed mercurial.

Perfluoro-o-phenylenemercury is thus interesting as it is a compound where the metal atoms are held in a rigid,

organically-bridged system. The tetrafluorophenyl moiety is electron-withdrawing but, unlike halide ions, it cannot provide bridging between molecules. Similar limitations apply to "donor" molecules such as pyridine, but oxygen in such ligands as cyclononanone[181] and DMSO[196] can bridge between metal atoms. In contrast to bis(pentafluorophenyl)mercury, perfluoro-o-phenylenemercury is involatile enough to make thermochemical analyses possible at temperatures up to about 250°C. The rough idea of "bond-strengths" obtained from these studies is quite revealing about the nature of the bonding: in this case showing the adducts to be only slightly less strongly attached than in transition metal complexes. It is, nevertheless, a truism that TGA and DTA results cannot prove a particular type of bonding to be present: any interpretation of thermochemical data is at best intelligent guesswork in the absence of unambiguous structural information. Since mercury(II) complexes are less stable than the corresponding cobalt(II) complexes - $[HgCl_2py_2]$ decomposes at room temperature but $[CoCl_2py_2]$ does not - this implies that the adducts of perfluoro-o-phenylenemercury have some form of bonding more favourable than in mercury coordination complexes, either alone or in addition to electron donation. It is quite possible that rigid planar molecules such as pyridine or DMF[174] can form only "solvent of crystallisation" adducts whereas molecules which contain atoms capable of forming inter-molecular bridges can form adducts which

involve coordination to the metal as well. The planar nature of perfluoro-o-phenylenemercury is a contributing factor to the stability of its amide adducts as judged by the position of the carbonyl band in the i-r: it is at 1650cm^{-1} in the DPF adduct of this compound compared with 1669cm^{-1} in the "adduct" with bis(pentafluorophenyl)-mercury. There appears also to be a correlation between this parameter and the stability of the adducts: Table 25 shows that the more thermally stable adducts with few organic molecules to each molecule of mercurial, also exhibit greater shifts of the carbonyl stretching frequency. Were the DPF adduct a simple coordination complex then the more electron-withdrawing pentafluoro-phenyl groups would give greater stability to the bis(pentafluorophenyl)mercury adduct.

The properties of perfluoroaromatic compounds of metals and metalloids are quite well established and hence it was decided to investigate the analogous compounds where the aromatic system was substituted with methyl groups. Two mercurials were investigated as the initial stage of this study: bis(pentamethylphenyl)-mercury and permethyl-o-phenylenemercury. These per-substituted compounds were chosen as considerable data was available about the properties of both the "parent" phenyl- and phenylene-mercurials and also their per-fluorinated analogues. Additionally, per-substitution eliminates the chance of formation of structural isomers, if not of a variety of reaction products.

The synthetic starting points for all permethyl studies were the appropriate hydrocarbons: 1,2-dihydrotetramethylbenzene and pentamethylbenzene. Bromination of these compounds was extremely facile by the method of Smith[133] and iodination by the method of Deacon.[37] Bis(pentamethylphenyl)mercury was then prepared by the reaction sequence:

$$2(CH_3)_5\ C_6Br + 2C_4H9Li \longrightarrow 2(CH_3)_5\ C_6Li + 2C_4H9Br$$

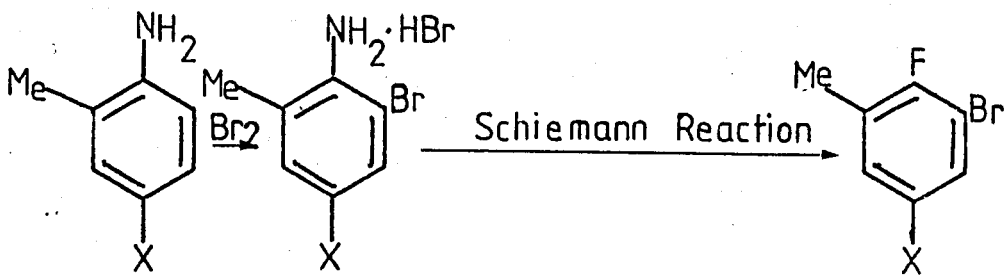
$$2(CH_3)_5\ C_6Li + HgCl_2 \longrightarrow (\ (CH_3)_5C_6)_2\ Hg + 2LiCl.$$

These reactions were also extremely straightforward, the mercurial precipitating out at the speed of mixing on addition of the mercuric chloride. In contrast to diphenylmercury, which is somewhat soluble in polar organic solvents, bis(pentamethylphenyl)mercury proved to be freely soluble only in boiling DMF.

Permethyl-o-phenylenemercury was prepared only under vigorous conditions using amalgam reactions similar to those discussed for o-phenylenemercury itself. After initial reaction mixtures at room temperature had failed to yield mercurials a sealed tube reaction at 220°C and a preparation in refluxing tetralin were both tried. As indicated by melting point and i-r spectra the two preparations gave the same product which was insoluble in all solvents tried. These included hexane, chloroform, water, and the following boiling solvents: DMF, DMSO

and quinoline. The presence of mercury and the absence of bromine in the residual fawn-coloured dust was proved by X-ray fluorescence: it was assumed to be permethyl-o-phenylenemercury. Further evidence for this postulation was obtained by cleavage of the carbon-mercury bonds by triiodide ions: 1,2-diiodotetramethylbenzene was extracted in 60% yield from the final reaction mixture and identified by comparison with an authentic sample.

Attempts to prepare the permethyl mercurials, described above, by mercuration reactions came to nothing: the method of Smith[197] was followed but gave only unreacted starting materials. Also unsuccessful were attempts to prepare dihalo derivatives of partially methylated benzenes. The reaction sequence chosen was:



X = H, Me

Wittig used this route starting with 2,4,5-trimethylaniline (pseudocumidine) to prepare 1-bromo-2-fluoro-5-hydrotri-

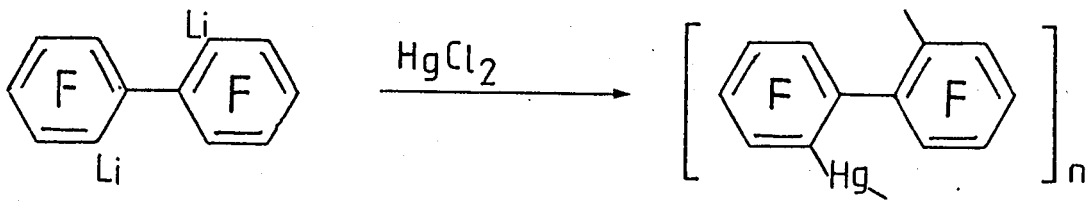
methylbenzene and thence a mercurial.[198] However, all attempts to prepare diazonium salts from either 2-bromo-6-methylaniline or 2-bromo-4,6-dimethylaniline ended only in elimination of nitrogen as the nitrite solution was added. The most extreme experimental conditions used in these attempts involved the use of aqueous tetrafluoroboric acid as solvent with diazotisation at -15° to $-20^{\circ}C$.

In summary, then, the preparation of methylated aromatic organometallic compounds, at least of mercury, has been shown to be far from straightforward: the volatility, solubility and thermal stability of the permethyl derivatives, crucial to the preparation of pure compounds, are considerably less favourable than those of the "parent" unmethylated species. It was therefore not possible, for example, to extend the crystal structure determinations performed to include a study of the oligomeric nature of permethyl-o-phenylene-mercury.

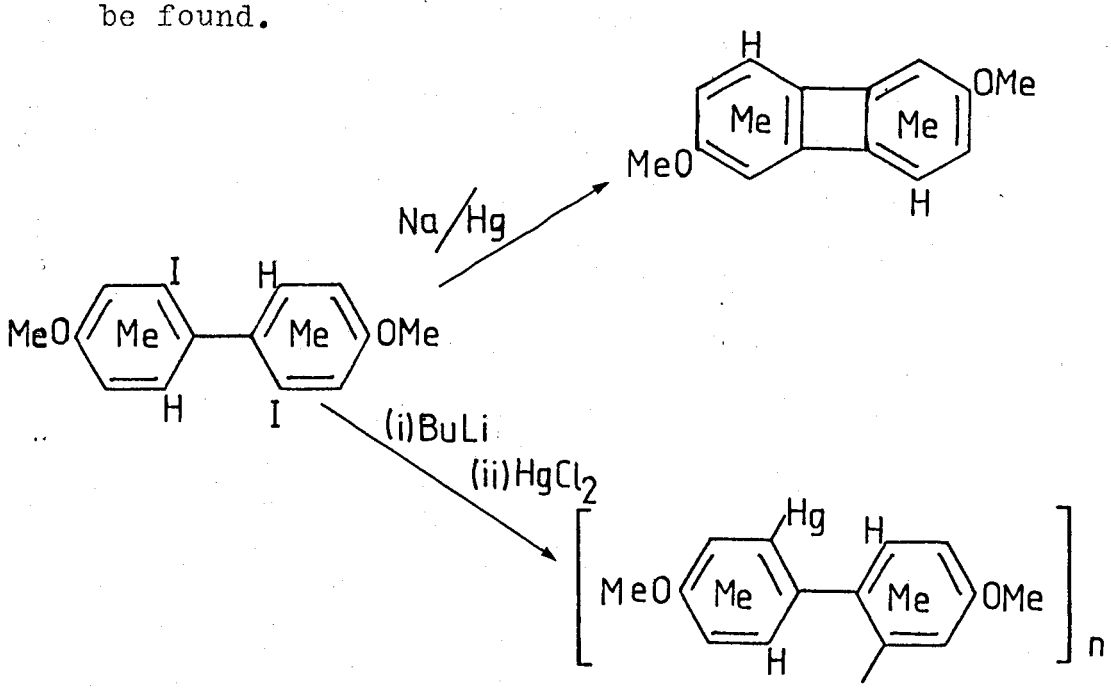
Further Work

In the nature of things, solution of one problem only leads to another and several further studies could be made. The oligomeric nature of o-biphenylenemercurials has not been determined by X-ray methods and all the reasons that necessitated studies of o-phenylenemercurials by this technique apply also to these compounds. Some unpublished mass spectral data from perfluoro-o-biphenyl-

enemercury have indicated that the reaction



produces both trimeric and tetrameric species. The preparation of one o-biphenylenemercurial was attempted as part of this work: reaction of 2,2'-diiodo-4,4'-dimethoxy-3,3',5,5'-tetramethylbiphenyl in refluxing ethyl acetate with sodium amalgam gave only the biphenylene but lithiation followed by addition of mercuric chloride gave a mercury-containing compound. However, no crystals suitable for an X-ray study could be found.



Further X-ray studies would also clear up the problem of the amide adducts of perfluoro-o-phenylenemercury by showing how the molecular packing affects the carbonyl function: this would then show how typical the 4-phenylpyridine adduct is.

E.s.r. studies could be used to examine the reactive intermediate produced by the elimination of lithium fluoride from pentafluorophenyllithium to show whether it is a singlet or a triplet (i.e. a benzyne or a diradical). An investigation of the degree of solvation during this reaction would also be of interest.

Spectra

Infra-red Spectra: 4000-250cm^{-1} or 4000-625cm^{-1} ( )
Spectra were run as mulls in Nujol or as KBr discs (*);
values are ±3cm^{-1} Bis(pentamethylphenyl)mercury; $C_{22}H_{30}Hg$
1410, 1287, 1068, 818, 728, 574, 506, 350

* Bromopentamethylbenzene; $C_{11}H_{15}Br$
3010(sh), 2930, 2870(sh),1430(br), 1385(br), 1210, 1068,
1020(sh), 1005, 920, 818(w), 724, 506; all bands weak.

* Pentamethylbenzene; $C_{11}H_{16}$
3020(sh), 2960(br), 2880(sh), 2745, 1485(br), 1455(sh),
1395, 1085(w), 1025(w), 871(w).

* Tetramethyl-o-phenylenemercury; $(C_{10}H_{12}Hg)n$
2980(sh), 2925, 2880(sh), 1445(br), 1388, 1237, 1206, 1085(w),
1070(w), 1025(w), 1008(w), 778, 697.

1,2-dihydrotetramethylbenzene; $C_{10}H_{14}$ (liquid film)
1471(br), 1450(sh), 1370, 1175(w), 1018, 813(str)

* 1,2-dibromotetramethylbenzene; $C_{10}H_{12}Br_2$
1440(br), 1404, 1380, 1260, 1198, 995(br), 955, 892, 775,
717(w), 580.

* 1,2-diiodotetramethylbenzene; $C_{10}H_{12}I_2$
2940(br), 1450(br), 1392(br), 1194, 1088, 1005, 951, 887,757.

* 1-iodo-2-hydrotetramethylbenzene: $C_{10}H_{13}I$

1582, 1560, 1460(br), 1386, 1270(w), 1261(w), 1232(w), 1203, 1073, 1020(br), 940, 867, 749, 711, 521, 290.

3,3',5,5'-Tetramethyl-4-4'-dimethoxy-2,2'-biphenylenemercury; $(C_{18}H_{20})_2Hg)_n$

1262, 1211, 1176, 1147, 1027(br), 872, 771(w), 727, 595(w,br), 540(w), 522, 502, 340.

* Bis(2,3-dihydrotrifluorophenyl)mercury; $C_{12}H_4F_6Hg$

2960, 2925, 2875(sh), 2860, 1890(w), 1760(w), 1638(sh), 1621, 1607, 1590, 1562(w) 1500(br), 1448, 1440, 1338(w) 1313(sh), 1293, 1279, 1270(sh), 1228, 1220(sh), 1180(w) 1114, 1092(w), 1082(w,sh), 1020, 879, 820, 788(w), 706, 686, 628, 590, 547(w), 340, 324, 285.

* Bis(2,3-dihydrotrifluorophenyl)mercury.1,10-phenanthroline; $C_{24}H_{12}F_6N_2Hg$

2970, 2930, 2860, 1620, 1590, 1523, 1490, 1445, 1440(sh), 1435(sh), 1348(w), 1290, 1288(sh), 1229, 1212, 1152, 1112, 1109(sh), 1020, 1015, 1013, 906(w), 870, 850, 842, 812, 778(w), 769(w), 730, 705, 683(w), 645(w), 620, 587, 548(w), 540(w), 477(w), 424(w), 338(w), 320(w).

Bis(pentafluorophenyl)mercury.diphenylformamide

1718(sh), 1705(sh), 1669, 1599, 1517, 1500, 1419, 1397(w), 1356, 1338(w) 1308, 1289(sh), 1278, 1144, 1138(sh), 1088, 1079, 1071, 1008, 969, 915, 849, 810, 788(w), 770, 750, 702, 680, 578, 530, 461, 443(w), 400(w), 342(w), 292(w).

$CoCl_2py_4$

1610, 1490, 1225, 1160, 1080, 1050, 1020, 941, 752, 726, 691, 657(w), 641, 425.

$CoCl_2py_2$ (α-form)

1607, 1578, 1420, 1243, 1222, 1156, 1086, 1045, 1016, 960(w), 880(w), 760, 691, 636, 434.

$CoCl_2py_2$ (β-form)

1609, 1488, 1448, 1280, 1219(sh), 1162, 1084, 1070, 1048, 1018, 762, 752, 700, 691, 645, 637(w), 432, 428, 348(w), 310.

$CoCl_2py_{2/3}$

1610, 1490, 1228, 1153, 1070, 1050, 1020, 942, 750, 724 690, 655(w), 643, 427.

Miscellaneous Organic Compounds

4,4'-dimethoxy-3,3',5,5'-tetramethylbiphenylene

1274. 1226, 1178, 1101, 1029, 980(w,br), 893, 870, 730, 662(w), 495(w), 323(w).

4,4'-Dimethoxy-3,3',5,5'-tetramethyl-o-biphenylenemercury

1630(br), 1263, 1212, 1180, 1149, 1030, 882, 870, 840(w), 729(br), 527(w), 505(w), 342(w,br).

Complexes of Perfluoro-o-phenylenemercury (I), 2500cm^{-1}-250cm^{-1} and of the ligands involved.

I

1620, 1588, 1420, 1370, 1330, 1313(w), 1290, 1252, 1098, 1055(w,br), 1010, 820, 777, 725, 643, 475, 370.

I.DMF

1645, 1620, 1588, 1418, 1366(w), 1359(w), 1328, 1310, 1290, 1252, 1109, 1088(sh), 1081, 1062(w,br), 1008, 819, 775, 725(w), 665, 642, 474, 412(w), 376, 336.

I.2DMF

1660(br), 1620, 1588, 1415, 1355, 1320, 1308, 1285, 1248, 1100, 1000, 812, 770, 661, 640, 472, 415(w), 370, 325.

DMF (liquid film)

1670(br), 1500, 1440, 1409(sh), 1390, 1259, 1254, 1094, 1067, 869, 660, 409(w), 353, 320.

I.1DEF

1630, 1595(w), 1582,1420(sh), 1415, 1396, 1366(w), 1351(w), 1321, 1304, 1285, 1250, 1213(w), 1123, 1110(w), 1082, 1078, 1006, 815, 771, 722, 645, 639, 471, 369.

I.2DEF

1643, 1630, 1413, 1398, 1392, 1365, 1350(w), 1320, 1304, 1284, 1265, 1241, 1211, 1120, 1103, 1077, 1072(sh), 1000, 824(sh), 819, 810, 768, 722, 642, 638(sh), 518, 470, 365, 345.

I.3DEF

1660(br), 1618, 1588, 1416, 1400, 1386, 1368, 1351, 1319, 1305, 1295, 1285(sh), 1268, 1245, 1218, 1120, 1107, 1077, 1000, 946, 826, 810, 769, 645, 640(sh), 520, 472, 361, 280.

DEF (liquid film)

1675(br), 1465, 1435, 1401, 1385, 1369, 1352, 1310, 1264, 1220, 1115, 1075(sh), 1005, 946, 826, 793, 647, 508, 353, 323, 285.

I. 1DMA

1593, 1418, 1322, 1308, 1285, 1250, 1090, 1080, 1077(sh), 1005, 814, 770, 739(sh), 720, 640, 586, 479, 470, 371.

I.2DMA

1600(br), 1415, 1321, 1305, 1285, 1245, 1188, 1080(sh), 1077, 1002(sh), 999, 810, 769, 739, 721, 639, 586, 478, 470, 367.

I.3DMA

1620(br), 1415, 1322, 1308, 1288, 1245, 1190, 1078, 1000, 812, 770, 742, 642, 590, 480(sh), 475, 370.

DMA (liquid film)

1640(br), 1507(br), 1418, 1400, 1360, 1270, 1194, 1065(sh), 1020, 740(w), 590, 477, 427(w), 340(w,br).

I.n(DPF)

1650, 1620, 1599, 1502, 1420, 1360, 1323, 1308, 1284,

1250(w), 1147(w), 1128, 1079, 1006, 961(w), 813, 770(sh), 762, 759(sh), 746, 700, 678, 639(w), 578, 471(w), 461(w), 414(w), 365, 290(w,br).

DPF

1718, 1706, 1676, 1597, 1500, 1417(w), 1392, 1256, 1168, 1139, 1080, 787, 761, 748, 698, 579, 530, 441, 410, 393, 325, 290, 267.

I. 2DMSO

1618, 1585, 1417, 1356(w), 1349(w), 1319, 1305, 1294, 1243, 1218, 1076, 1030(br), 1000, 951, 808, 765, 725, 680, 636, 471, 382, 360, 339.

DMSO

1437, 1405, 1312, 1045, 1030, 954, 700, 669, 382, 335.

I.n (Acetone)

1710(sh), 1682, 1620, 1588, 1420, 1327, 1310, 1290, 1255, 1240, 1092, 1082, 1008, 820, 785, 725, 642, 536, 475, 374.

Acetone (liquid film)

1750(sh), 1712, 1465, 1420, 1365, 1225, 1000

I.1 (cyclopentanone)

1701(br), 1620, 1583, 1420, 1355, 1325, 1310, 1290, 1252, 1168, 1088, 1082, 1009, 960, 838, 820, 775, 726, 642, 590, 562, 475, 376.

I.3 (cyclopentanone)

1750(sh), 1730, 1617, 1588, 1420, 1365, 1318, 1303, 1292, 1213, 1160, 1078, 1014(w), 1000, 961, 913(w), 891, 808, 768, 724, 639, 582(w), 472, 361.

Cyclopentanone (liquid film)

1740(br), 1625(sh), 1471, 1455, 1410, 1365, 1280, 1270, 1232, 1155, 1025, 960, 916, 892(w), 835, 810, 712(w), 580, 472.

I.(4-phenylpyridine)

1620, 1595, 1552, 1422, 1411, 1323, 1308, 1285, 1250, 1085, 1072, 1044, 1008, 832, 813, 769, 760(sh), 750, 735, 697, 640, 612, 561, 470, 370.

4-Phenylpyridine

1611, 1595, 1554, 1486, 1411, 1344(w), 1074, 1048, 1008, 994, 923, 830, 761, 751(w), 738, 699, 611, 561, 442(br), 368(w).

I.n (Quinoline)

1622, 1599, 1578, 1573(sh), 1505, 1435(w) 1470, 1396, 1350(w) 1317, 1303, 1292, 1285(sh), 1245, 1220(w), 1145, 1125, 1078, 1041, 1000, 958(w), 947, 944(sh), 807, 788, 768, 740, 638, 631(sh), 620(sh), 616, 525, 480, 395, 380,362.

Quinoline (liquid film)

1622, 1598, 1573, 1503, 1472, 1433, 1395, 1374, 1316, 1142,

1121, 1036, 1018, 983, 942, 809, 789, 762, 740, 632, 615, 525, 481, 396, 380.

I.3(3-pic)
1618, 1600, 1578, 1418, 1320, 1306, 1285, 1250, 1192, 1129, 1105, 1075(br), 1048, 1030, 1000, 815, 782, 770, 722, 711, 638, 630(sh), 535, 471, 458, 400, 369.

3-pic (liquid film)
1599(sh), 1580, 1481, 1460(br), 1417, 1388, 1230, 1194, 1130, 1109, 1047, 1032, 790, 715, 634, 404.

I.3(2-pic)
1615(sh), 1610, 1588, 1418, 1319, 1305, 1079, 1071, 1044, 998, 802, 798, 769, 728, 641, 638, 522, 487, 364.

2-pic (liquid film)
1595, 1572, 1480, 1435, 1380, 1298, 1240, 1153, 1106, 1054, 1001, 756, 733, 632, 548, 424, 408, 362.

I.1py
1617, 1592, 1582, 1420, 1323, 1310, 1290, 1255, 1226(w), 1220(w), 1090, 1085, 1010, 997(sh), 857, 820, 774, 750, 724, 700, 659, 640, 612, 475, 411, 375.

I.3py
1615, 1588, 1580, 1440, 1418, 1321, 1308(w), 1288, 1248, 1218, 1150, 1082, 1080(sh), 1064, 1032, 1004, 995(sh),

815, 770, 751, 725, 700, 639, 612, 471, 405, 377.

py (liquid film)
1635, 1600, 1580, 1483, 1440, 1219, 1149, 1070, 1031, 995, 942(w), 749, 705, 605, 408.

I.3(d_5-py)
2285, 2255, 1620, 1588, 1551(sh), 1540, 1418, 1312, 1250(w), 1165(w), 1072(br), 999, 970, 890, 825, 809, 768, 725, 639, 588, 528, 472, 370.

I.1(d_5-py)
2280, 2265, 1620, 1585, 1550, 1540, 1420, 1328, 1310, 1292, 1256, 1090, 1085, 1010, 968, 830, 820, 765, 726, 642, 588, 549, 527, 473, 376.

d_5-py
2292(sh), 2270(sh), 2250, 1650, 1552(sh), 1539, 1465, 1417, 1369, 1322(sh), 1301, 1230, 1043, 1011(br), 966, 910, 889, 815, 770, 692, 627, 579, 530(s), 370.

Inorganic pyridine complexes (2000-250cm^{-1})
$HgBr_2py$
1599, 1482, 1447, 1242(w), 1215, 1210, 1154, 1068, 1033, 1010, 748, 692, 636, 628, 411.

$HgBr_2py_2$
1600, 1245(w), 1217, 1152, 1070, 1037, 1010, 950(w), 750,

703, 695(sh), 679(sh), 630, 420, 413.

$HgCl_2py_{2/3}$

1610, 1489, 1220, 1162, 1072, 1046, 1020, 753, 725, 690, 645, 418, 355, 295.

$HgCl_2py$

1608, 1598(sh), 1570, 1560, 1489, 1418, 1244, 1222, 1163(sh), 1160, 1075, 1046, 1020, 800, 789, 751, 725(w), 702(w), 690, 656, 644, 425, 293.

$HgCl_2py_2$

1604, 1579, 1247, 1225, 1160, 1082, 1040, 1019, 759, 726, 696, 640, 422.

HgI_2py_2

1595, 1581, 1215, 1150, 1068, 1032, 1009, 745, 723, 701, 626, 600, 418, 410.

Far Infra-red Spectra: 400-32cm^{-1}

Spectra were run as mulls in Nujol; values are $\pm$2cm^{-1}

I

374, 224.

I.1DMF

374, 330(w), 224.

I.2DMF

375, 320, 276, 224, 126(br), 108(br), 95, 43.

I.py

396, 371, 364, 352(sh), 224.

I.d_5-py

372, 226.

$(C_6H_4Hg)_3$; $P2_I/c$ form

320, 281, 240-150(br)

$(C_6H_4Hg)_3$; $P2_12_12_1$ form

320, 281, 240-150(br)

$(C_6F_5)_2Hg$

366, 362, 356, 342, 315(sh), 310, 282, 230, 198, 121, 100

Raman Spectra: 4000-c.100cm^{-1}

Spectra were taken from powder samples, some of them exhibited slight broad-band fluorescence (*) and in others this was severe (**). Values are ± 1cm^{-1}.

** I

1615, 1252, 1055(w), 770, 596(w), 470, 410, 180.

** I.2DMF

1645, 1618, 1588, 1579, 1499(w), 1473, 1443, 1416, 1385, 1295, 1249, 1105, 1077, 1000, 866, 815, 769, 698(w), 663, 635(w), 599, 475, 410, 344, 185.

* I.2DEF

1640, 1630, 1612, 1462(sh), 1455, 1440(sh), 1395, 1260, 1239, 1120, 1078, 1055, 995, 820(sh), 807, 760, 640(w), 596(w), 469, 435(w), 407, 330, 280, 179.

Bis(2,3-dihydrotrifluorophenyl)mercury: $(C_6F_3H_2)_2Hg$

3080(w,br), 2930(w,br), 2860(w,br), 1603(w), 1443(w), 1298, 1151,1105(w), 1020, 884(w), 867(w,sh), 699, 616, 585(w) 491(w,br), 317, 287, 235, 172, 155(w), 111.

$(C_6H_4Hg)_3$ $P2_1/c$ form

1025, 641, 272, 155, 86.

Bis(pentafluorophenyl)mercury; spectrum run on a Spectra Physics 700 instrument

($\pm$5cm^{-1}) 139, 153(sh), 157(sh), 166, 233, 287, 297, 333, 353, 383(w), 400, 444, 494, 572, 633, 803(w), 872(w); ($\pm$10cm^{-1}) 1094, 1133, 1367, 1420, 1620.

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Appendix 1

Temperature Factors for the structures analysed in Chapter 2.

Anisotropic parameters refer to the equation $\exp\left[-2\pi^2 (U_{11}a^{*2}h^2 + \ldots\ldots\ 2\,U_{23}b^*c^*kl + \ldots\ldots)\right]$

Isotropic parameters refer to the equation $\exp\left[-8\pi^2 U \sin^2(\vartheta/\lambda)\right]$

All values have been multiplied by 10^3; standard deviations are given in parentheses.

(a) Orthorhombic Tribenzo[b,e,h][1,4,7] trimercuronin

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Hg(1)	42.6(9)	36.5(7)	39.2(8)	-6.0(10)	3.0(10)	0.6(7)
Hg(2)	40.7(8)	34.0(7)	40.6(7)	6.0(9)	4.4(10)	-1.2(7)
Hg(3)	39.8(8)	39.3(8)	33.6(7)	-3.2(8)	-6.5(9)	1.9(8)

	U		U		U
C(1)	64.8(15.6)	C(7)	35.9(9.7)	C(13)	69.0(16.9)
C(2)	43.7(11.1)	C(8)	35.9(9.2)	C(14)	54.3(13.8)
C(3)	30.2(8.6)	C(9)	36.7(9.8)	C(15)	40.2(11.9)
C(4)	34.8(9.7)	C(10)	41.8(11.4)	C(16)	60.9(15.9)
C(5)	38.4(10.6)	C(11)	41.9(11.4)	C(17)	31.7(9.4)
C(6)	40.4(9.6)	C(12)	44.5(9.8)	C(18)	34.3(8.6)

(b) Monoclinic Tribenzo[b,e,h][1,4,7] trimercuronin

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Hg(1)	74.6(8)	51.4(6)	31.7(5)	3.2(6)	19.0(4)	1.5(4)
Hg(2)	73.5(8)	56.8(7)	32.3(5)	3.6(6)	15.9(4)	-1.8(4)
Hg(3)	66.0(7)	52.0(6)	31.9(4)	0.0(5)	10.8(4)	-4.0(4)

	U		U		U
C(1)	60.4(9.2)	C(7)	44.6(5.7)	C(13)	63.5(8.2)
C(2)	47.1(7.4)	C(8)	55.9(7.1)	C(14)	45.4(8.1)
C(3)	64.3(8.7)	C(9)	45.5(5.3)	C(15)	63.1(7.4)
C(4)	55.7(10.9)	C(10)	59.7(6.0)	C(16)	48.2(7.1)
C(5)	57.1(7.4)	C(11)	57.2(6.4)	C(17)	51.3(6.3)
C(6)	86.4(11.4)	C(12)	59.7(7.1)	C(18)	39.1(5.4)

(c) Bis(2-hydrotetrafluorophenyl)mercury

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Hg(1)	41.7(5)	47.5(5)	65.1(6)	9.1(8)	30.9(4)	0.7(8)

	U		U
C(1)	58.7(4.8)	C(6)	44.8(3.5)
C(2)	47.4(3.7)	F(2)	76.5(3.2)
C(3)	55.5(4.3)	F(3)	79.4(3.3)
C(4)	49.6(3.3)	F(4)	83.3(3.0)
C(5)	53.4(4.1)	F(5)	72.9(3.1)

(d) Perfluorotribenzo[b,e,h][1,4,7]trimercuronin.. 4-phenylpyridine

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Hg(1)	43.0(7)	34.6(5)	50.0(6)	-0.5(5)	9.1(5)	-1.7(5)
Hg(2)	41.7(7)	39.2(6)	50.8(6)	-1.4(5)	9.7(5)	0.0(5)
Hg(3)	41.0(7)	39.3(5)	50.6(6)	-0.2(5)	8.0(5)	1.2(5)

	U		U		U
C(1)	44.0(6.4)	C(11)	43.1(6.1)	C(21)	45.7(6.6)
C(2)	41.0(6.0)	C(12)	50.7(7.1)	C(22)	39.9(5.9)
C(3)	55.2(7.6)	C(13)	52.5(7.3)	C(23)	55.6(7.6)
C(4)	57.2(7.8)	C(14)	58.1(7.9)	C(24)	56.4(7.7)
C(5)	62.6(8.4)	C(15)	50.0(6.9)	C(25)	55.8(7.6)
C(6)	51.8(7.2)	C(16)	45.1(6.5)	C(26)	52.7(7.2)
F(3)	60.3(4.4)	F(13)	68.0(4.9)	F(23)	60.1(4.3)
F(4)	73.5(5.2)	F(14)	69.4(4.9)	F(24)	69.2(4.9)
F(5)	82.9(5.8)	F(15)	70.9(5.0)	F(25)	70.5(5.0)
F(6)	73.2(5.2)	F(16)	63.5(4.6)	F(26)	62.4(4.5)
C(31)	53.2(7.3)	C(41)	54.9(7.4)		
C(32)	54.3(7.5)	C(42)	61.0(8.2)		
C(33)	63.3(8.6)	C(43)	72.7(9.7)		
N(34)	68.2(7.5)	C(44)	70.6(9.4)		
C(35)	66.2(8.8)	C(45)	72.3(9.6)		
C(36)	54.0(7.3)	C(46)	52.9(7.2)		

Structure Factor Tables for

Orthorhombic Tribenzo(b,e,h)(1,4,7)trimercuronin.

0,K,0

6	6229	6071
8	6827	6542
10	3766	3598
12	2308	2262
14	4579	4392
16	4605	4459
18	1351	1204
20	945	872
22	2585	2527
24	1823	1842
26	524	499
28	583	683
30	934	1059
32	436	603

0,K,1

3	1591	1624
4	347	296
5	1732	1686
6	1547	1592
7	709	701
8	0*	141
9	2437	2333
10	546	546
11	1315	1256
12	934	951
13	986	939
14	1270	1262
15	495	519
16	465	182
17	1684	1694
18	366	218
19	266*	267
20	657	686
21	0*	327
22	853	790
23	731	635
24	0*	74
25	897	1019
26	373	213
27	0*	200
28	391	572
29	0*	157
30	258*	312
31	462	391
32	103*	52

0,K,2

0	2636	2860
1	3653	3861
2	1075	1151
3	414	403
4	0*	122
5	735	762
6	1451	1524
7	3822	3761
8	2286	2325
9	2345	2302
10	672	584
11	0*	138
12	0*	183
13	1115	991
14	1141	1143
15	2640	2575
16	1086	1097
17	1366	1351
18	0*	184
19	203*	199
20	0*	18
21	735	733
22	724	706
23	1440	1360
24	0*	376
25	395	346
26	0*	202
27	354	65
28	177*	77
29	631	572
30	0*	224
31	558	556
32	284*	36

0,K,3

1	218	142
2	997	1059
3	487	502
4	425	365
5	565	537
6	2832	2674
7	738	790
8	934	870
9	1253	1229
10	2452	2412
11	1178	1152
12	1119	1073
13	1093	1065
14	1436	1359
15	1211	1177
16	683	655
17	1359	1283
18	362	499
19	1152	1146
20	746	691
21	1045	980
22	369	465
23	1012	1018
24	458	534
25	916	935
26	0*	271
27	580	746
28	421	529
29	521	681
30	325*	202
31	591	638
32	587	298

0,K,4

0	107*	187
1	964	1031
2	1307	1436
3	4424	4453
4	2097	2199
5	3571	3564
6	886	948
7	609	564
8	0*	163
9	1606	1601
10	993	1041
11	3393	3391
12	1429	1429
13	1983	1958
14	277	295
15	255*	277
16	0*	175
17	1082	1135
18	871	830
19	2057	2067
20	425	492
21	979	926
22	0*	65
23	0*	112
24	207*	5
26	0*	296
27	735	919
28	0*	206
29	0*	228
30	203*	91
31	0*	102

0,K,5

1	1311	1312
2	1303	1363
3	945	974
4	126*	103
5	1625	1625
6	897	979
7	1067	1179
8	550	533
9	908	942
10	1012	993
11	281	157
12	258	380
13	1518	1559
14	410	429
15	613	576
16	668	677
17	414	487
18	594	564
19	495	408
20	118*	196
21	967	1028
22	63*	51
23	0*	284
24	583	466
25	306*	238
26	473	250
27	369	325
28	0*	126
29	388	561
30	384	82
31	0*	57

0,K,6

0	2068	1936
1	140*	309
2	4154	4100
3	498	590
4	5546	5452
5	498	482
6	3231	3190
7	233*	306

0,K,6

8	2249	2180
9	343	281
10	3512	3539
11	484	436
12	3718	3718
13	373	326
14	1739	1757
15	177*	108
16	1182	1198
17	270*	213
18	2518	2471
19	63*	246
20	2108	2092
21	177*	121
22	753	652
23	288*	66
24	786	748
25	288*	113
26	1178	1255
27	0*	115
28	384	759
29	0*	24
30	314*	219

0,K,7

1	1307	1262
2	779	841
3	953	1000
4	100*	114
5	1610	1609
6	196*	347
7	1104	1103
8	561	618
9	1008	1047
10	809	869
11	207*	113
12	225*	130
13	1577	1617
14	358	138
15	539	605
16	805	758
17	561	609
18	757	745
19	539	365
20	92*	231
21	1119	1076
22	284*	266
23	81*	218
24	565	585
25	377	198
26	473	425
27	0*	370
28	0*	176
29	476	528
30	295*	264

0,K,8

0	517	514
1	155*	228
2	591	680
3	1783	1789
4	1562	1592
5	1267	1322
6	314	219
8	402	388
9	247*	157
10	727	782
11	1462	1514
12	1019	983
13	746	776
14	74*	64
15	0*	342
16	144*	239
17	343	367
18	495	541
19	927	1021
20	432	469
21	303*	244
24	0*	122
25	425	379
26	354	282
27	528	509
28	174*	92
29	140*	92

0,K,9

1	159*	166
2	1846	1785
3	0*	18
4	0*	171
5	487	579
6	1381	1376
7	628	550
8	476	508
9	166*	322
10	1285	1262
11	502	583
12	465	432
13	790	803
14	750	769
15	598	616
16	738	730
17	421	513
18	676	783
19	683	715
20	432	395
21	724	740
22	417	306
23	484	521
24	417	522
25	454	445
26	162*	318
27	0*	487
28	0*	248

0,K,10

0	1012	989
1	2352	2337
2	524	513
3	639	681
4	0*	138
5	1008	942
6	609	651
7	2426	2440
8	823	876
9	1806	1795
10	273*	287
11	340	296
12	207*	23
13	894	907
14	473	406
15	1754	1748
16	528	553
17	809	862
18	0*	133
19	78*	201
20	0*	37
21	738	732
22	199*	227
23	1052	968
24	0*	190
25	303*	335
26	395	49

0,K,11

1	565	575
2	757	784
3	550	572
4	170*	140
5	528	547
6	665	685
7	37*	262
8	0*	247
9	864	812
10	484	647
11	325	309
12	0*	282
13	395	445
14	613	464
15	81*	93
16	332	327
17	606	631
18	295*	291
19	380	260
20	340*	281
21	203*	211
22	0*	151
23	277*	135
24	417	229
25	517	355

0,K,12

0	2343	2304
1	406	473
2	1540	1469
3	100*	192
4	646	645
5	0*	271
6	1776	1698
7	465	563
8	2308	2306
9	177*	328
10	853	914
11	155*	39
12	428	423
13	166*	237
14	1292	1361
15	281*	376
16	1263	1318
17	273*	195
18	462	476

0,K,12

19	399	63
20	251*	436
21	343*	140
22	820	866
23	321*	164

0,K,13

1	631	645
2	288*	170
4	78*	77
5	506	515
6	399	359
7	0*	162
8	0*	233
9	646	637
10	0*	45
11	410	258
12	410	279
13	325*	329
14	510	384
15	377	91
16	0*	176
17	510	635
18	354	208
19	0*	166
20	273*	350
21	447	232

0,K,14

0	650	640
1	358	408
2	521	97
3	0*	306
4	546	361
5	188*	137
6	318*	177
7	299*	445
8	314*	449
9	343	274
10	0*	86
11	410	231
12	255*	203
13	0*	52
14	0*	265
15	354	374
16	0*	240
17	380	117
18	33*	181
19	118*	168

0,K,15

1	306*	166
2	495	588
3	240*	176
4	0*	116
5	210*	8
6	292*	440
7	0*	74
8	199*	80
9	233*	244
10	0*	208
11	37*	241
12	0*	263
13	218*	130
14	550	371
15	425	234
16	0*	143

0,K,16

0	0*	54
1	343*	358
2	236*	171
3	1078	983
4	0*	239
5	975	882
6	0*	90
7	310*	139
8	0*	68
9	369	329
10	262*	176
11	905	954
12	0*	164

0,K,17

1	256*	194
2	318*	272
3	0*	175
4	535	104
5	428	236

1,K,0

3	2160	2119
4	694	683
5	1809	1692
6	1521	1437
7	2068	1958
8	768	763
9	654	597
10	679	644
11	2289	2196
12	1591	1479
13	646	627
14	1606	1538
15	1385	1277
16	1093	1043
17	218*	21
18	1060	1034
19	1211	1250
20	1248	1306
21	0*	54
22	1196	1172
23	517	686
25	18*	267
26	657	812
27	380	526
28	772	878
29	0*	150
30	661	697
31	177*	257
32	609	498

1,K,1

3	1662	1786
4	2234	2218
5	1894	1889
6	3297	3276
7	931	970
8	2747	2587
9	1473	1382
10	2799	2659
11	1551	1448
12	1676	1652
13	1108	1087
14	2035	1987
16	1654	1657
17	750	746
18	1207	1202
19	572	609
20	1060	1012
21	476	381
22	1089	1007
23	358	162
24	842	892
25	510	420
26	469	540
27	214*	177
28	554	611
29	270*	218
30	473	435
31	30*	94
32	0*	427

1,K,2

0	3131	3153
1	1296	1429
2	510	520
3	1466	1559
4	2419	2455
5	1004	1061
6	694	708
7	838	911
8	1300	1286
9	0*	45
10	594	651
11	897	942
12	1370	1354
13	779	683
14	1041	991
15	1056	890
16	1093	987
17	347	104
18	931	865
19	727	829
20	853	784
21	576	590
22	827	815
23	469	452
24	495	444
25	0*	213
26	465	519
27	332*	369
28	447	380
29	435	299
30	354*	362
31	52*	179
32	0*	161

1,K,3

1	6418	6341
2	473	455
4	399	450
5	4774	4738
6	402	477
7	4689	4625
8	657	707
9	4328	4309
10	199*	32
11	3508	3522
12	0*	223
13	3471	3428
14	473	460
15	2939	2863
16	406	389
17	2659	2694
18	0*	169
19	1758	1760
20	0*	174
21	1780	1804
22	292*	288
23	1425	1441
24	258*	147
25	1159	1271
26	148*	108
27	716	860
28	0*	84
29	683	803
30	196*	142
31	620	567
32	0*	36

1,K,4

0	2633	2587
1	1078	1135
2	303	246
3	790	838
4	2016	1944
5	480	483
6	484	526
7	786	845
8	1591	1557
9	772	799
10	750	726
11	738	750
12	1171	1169
13	244*	161
14	696	862
15	816	899
16	1178	1196
17	834	818
18	742	785
19	591	619
20	713	700
21	299*	252
22	690	748
23	694	654
24	354	546
25	414	527
26	532	538
27	281*	299
28	255*	255
29	395	265
30	432	374
31	329*	349

1,K,5

0	820	872
1	1204	1319
2	1950	2087
3	849	924
4	1617	1634
5	1104	1184
6	1946	2003
7	1270	1345
8	967	935
9	1274	1355
10	1717	1745
11	395	373
12	1329	1364
13	927	981
14	1156	1187
15	683	700
16	838	878
17	646	606
18	982	1053
19	174*	123
20	657	740
21	528	560
22	447	519
23	0*	270
24	572	568
25	0*	300
26	583	487
27	0*	122
28	377	488
29	0*	255
30	487	219
31	0*	83

1,K,6

0	0*	50
1	1639	1752
2	480	591
3	1436	1332
4	310	328
5	698	797
6	229*	158
7	1713	1792
8	764	926
9	912	805
10	1141	1202
11	1211	1234
12	716	681
13	343	191
14	676	631
15	1263	1255
16	1086	1059
17	498	457
18	1063	1094
19	805	774
21	0*	157
22	580	706
23	498	701
24	820	884
25	159*	166
26	565	695
27	373	371
28	465	471
29	0*	191
30	380	519

1,K,7

0	1780	1840
1	1370	1247
2	2611	2617
3	665	637
4	2212	2210
5	816	797
6	2378	2364
7	1108	1230
8	1780	1820
9	879	946
10	2049	2110
11	236*	315
12	1599	1618
13	665	657
14	1514	1581
15	720	736
16	1174	1240
17	513	530
18	1108	1161
19	107*	55
20	1027	1106
21	255*	314
22	801	799
23	325*	297
24	716	713
25	0*	199
26	295*	559
27	0*	53
28	580	502
29	0*	216

1,K,8

0	1182	1167
1	735	717
2	166*	326
3	668	655
4	1078	1051
5	399	368
6	0*	359
7	772	795
8	975	1131
9	491	447
10	535	546
11	561	586
12	668	794
13	0*	132
14	329	429
15	521	644
16	635	704
17	0*	184
18	587	539
19	473	368
20	325	377
21	208*	114
22	402	407
23	495	354
24	414	361
25	0*	129
26	402	335

1,K,8

27	391	184
28	0*	155

1,K,9

0	155*	69
1	2648	2629
2	528	512
3	2577	2539
4	609	717
5	2511	2468
6	0*	396
7	2585	2616
8	0*	171
9	2511	2480
10	218*	414
11	1639	1622
12	465	489
13	1872	1869
14	244*	181
15	1551	1592
16	0*	157
17	1451	1492
18	354	376
19	1145	1139
20	233*	259
21	1082	1121
22	70*	33
23	698	814
24	0*	129
25	631	743
26	244*	144
27	0*	464

1,K,10

0	1012	1031
1	181*	284
2	480	154
3	358	355
4	1137	1129
5	491	466
6	63*	396
7	561	489
8	927	911
9	92*	161
10	255*	493
11	318	335
12	831	807
13	439	555
14	443	534
15	358	432
16	583	532
17	292*	264
18	432	478
19	417	469
20	473	456
21	506	497
22	273*	426
23	512	337
24	0*	254
25	0*	198
26	288*	346

1,K,11

0	373	502
1	646	628
2	908	920
3	698	573
4	0*	138
5	613	631
6	687	721
7	292*	240
8	447	407
9	559	517
10	635	528
11	358	327
12	126*	303
13	502	490
14	521	515
15	329	22
16	362	439
17	517	477
18	543	366
19	366	183
20	388	299
21	384	324
22	402	315
23	281*	101
24	222*	280

1,K,12

0	174*	161
1	388	497
2	44*	160
3	676	818
4	414	333
5	502	500
6	528	466
7	535	620
8	373	231
9	222*	247
10	0*	179
11	554	752
12	255*	508
13	89*	246
14	491	518
15	462	511
16	314*	311
17	0*	71
18	321*	351
19	233*	508
20	572	459
21	0*	127
22	373*	415
23	299*	309

1,K,13

0	1045	1061
1	358	236
2	1278	1261
3	539	475
4	1004	1006
5	358	400
6	1222	1167
7	0*	134
8	853	890
9	366	302
10	1052	1001
11	402	377
12	897	843
13	480	249
14	927	824
15	354	41
16	738	692
17	210*	203
18	569	619
19	0*	211
20	546	522
21	0*	100

1,K,14

0	495	361
1	229*	194
2	347	137
3	414	376
4	277*	459
5	0*	278
6	347	239
7	414	417
8	66*	463
9	306*	217
10	210*	201
11	539	480
12	391	403
13	0*	136
14	229*	230
15	0*	272
16	155*	227
17	0*	102
18	188*	149

1,K,15

0	192*	375
1	812	857
2	244*	263
3	942	926
4	0*	151
5	964	924
6	0*	284
7	635	714
8	0*	314
9	897	790
10	233*	165
11	720	734
12	0*	122
13	679	701
14	137*	238
15	569	467

1,K,16

0	465	454
1	225*	134
2	170*	2
3	0*	147
4	402	413
5	63*	74
6	321*	130
7	107*	110
8	395	423
9	247*	260

1,K,16

10	162*	138
11	528	192

1,K,17

0	0*	115
1	0*	261
2	292*	287
3	332*	188

1,K,3

3	4416	4377

2,K,0

3	753	655
4	6126	5982
5	731	652
7	284	213
8	2932	2849
9	746	749
10	4025	3989
11	303	280
12	4147	4115
13	624	460
14	2201	2117
15	288	75
16	1617	1593
17	646	721
18	2747	2680
19	369	153
20	2215	2211
21	347	306
22	919	902
23	329	194
24	834	899
25	251*	349
26	1237	1316
27	299*	3
28	687	853
29	236*	53
30	0*	239
31	199*	204

2,K,1

3	1204	1192
4	713	663
5	1730	1778
6	794	760
7	1226	1223
8	1257	1243
9	938	905
10	1034	1003
11	572	507
12	561	478
13	1658	1620
14	532	525
15	831	746
16	894	893
17	491	421
18	735	768
19	432	508
20	0*	112
21	1012	1078
22	336	468
23	436	366
24	550	622
25	299*	169
26	469	389
27	639	410
28	188*	61
29	343*	570
30	310*	292
31	0*	121

2,K,2

0	306	249
1	938	834
2	1215	1273
3	2991	3100
4	1831	1913
5	2489	2590
6	1063	1071
7	377	341
8	255	378
9	1050	1066
10	1374	1317
11	2455	2419
12	1329	1278
13	1433	1455
14	214*	347
15	284	67
16	517	425
17	883	816
18	764	656
19	1591	1590
20	580	536
21	628	733
22	207*	59
23	92*	53
24	214*	317
25	484	621
26	495	319
27	546	698
28	255*	189
29	0*	214
30	0*	133
31	310*	78

2,K,3

0	1015	931
1	594	670
2	1964	1955
3	908	931
4	303	366
5	801	832
6	1920	1943
7	1130	1168
8	809	844
9	820	812
10	1721	1690
11	1296	1342
12	738	705
13	1012	1056
14	1111	1054
15	1233	1180
16	805	760
17	1041	1014
18	764	761
19	986	1080
20	657	555
21	905	940
22	0*	439
23	871	901
24	609	564
25	820	780
26	270*	325
27	532	732
28	185*	328
30	0*	124
31	572	547

2,K,4

0	1983	2117
1	3050	3220
2	1322	1441
3	894	950
4	318	192
5	1252	1257
6	1285	1396
7	3128	3197
8	1377	1484
9	2348	2383
10	724	748
11	436	451
12	469	475
13	1130	1187
14	979	1014
15	2223	2257
16	868	873
17	1134	1146
18	491	435
19	0*	221
20	380	320
21	868	909
22	587	554
23	1159	1201
24	0*	341
25	510	462
26	0*	99
27	284*	112
28	0*	268
29	502	499
30	521*	168

2,K,5

0	1012	1001
1	853	980
2	1189	1207
3	879	815
4	1086	1141
5	860	904
6	905	883
7	783	860
8	388	269
9	1425	1490
10	613	674
11	764	942
12	609	665
13	602	607
14	757	744

2,K,5

15	366	500
16	118*	378
17	1075	1017
18	447	515
19	281*	254
20	646	693
21	273*	178
22	347	393
23	428	413
24	336	136
25	550	653
26	277*	251
27	170*	199
28	0*	304
29	0*	119

2,K,6

0	5114	5108
1	894	930
2	3139	3073
3	628	583
4	1477	1474
5	709	824
6	3320	3390
7	502	652
8	4032	4170
9	606	636
10	1983	2051
11	340	170
12	1226	1222
13	687	730
14	2559	2592
15	343	352
16	2500	2590
17	454	385
18	1001	994
19	395	209
20	886	755
21	414	493
22	1495	1553
23	0*	145
24	1156	1177
25	0*	155
26	402	345
27	181*	151
28	284*	436
29	273*	246

2,K,7

0	532	502
1	1082	1097
2	428	424
3	971	894
4	716	769
5	713	772
6	609	799
7	321	287
8	587	611
9	1219	1200
10	362	276
11	517	524
12	750	821
13	329	466
14	831	740
15	155*	370
16	384	266
17	971	1042
18	487	454
19	421	387
20	484	552
21	473	229
22	524	595
23	447	399
24	450	236
25	495	592
26	0*	304
27	37*	82
28	421	403

2,K,8

0	953	1043
1	1388	1483
2	521	559
3	458	467
4	233*	259
5	473	362
6	757	819
7	1219	1243
8	1049	1110
9	794	739
10	613	513
11	0*	130
13	414	356
14	698	675
15	953	1019
16	450	498
17	631	620
18	425	82
19	262*	208
20	343	233
21	473	370
22	325*	318
23	587	625
24	480	189
25	0*	207
26	362*	199
27	0*	64

2,K,9

0	0*	57
1	414	438
2	949	974
3	166*	440
4	517	463
5	247*	220
6	890	931
7	524	637
8	258*	244
9	569	604
10	583	669
11	539	655
12	594	548
13	362	470
14	672	663
15	742	696
16	0*	307
17	617	662
18	277*	353
19	532	584
20	465	473
21	388	458
22	74*	329
23	583	577
24	0*	182
25	476	496
26	0*	148

2,K,10

0	170*	108
1	738	796
2	742	784
3	2057	2069
4	727	788
5	1761	1775
6	462	527
7	454	485
8	377	325
9	853	816
10	453	589
11	1754	1779
12	587	587
13	1196	1192
15	462	303
16	325*	251
17	635	726
18	506	415
19	1152	1070
20	377	277
22	0*	88
23	406	152
24	0*	196
25	487	440

2,K,11

0	487	534
1	266*	436
2	476	547
3	550	476
4	0*	211
5	661	644
6	524	449
7	569	589
8	247*	232
9	443	483
10	277*	321
11	0*	438
12	0*	150
13	580	643
14	247*	360
15	236*	317
16	122*	317
17	0*	226
18	207*	198
19	0*	210
20	517	228
21	521	401
22	155*	205
23	181*	144

2,K,12

1	0*	348
2	1455	1409
3	528	472
4	1942	1982
5	310*	441
6	1078	1073
7	277*	261
8	609	553
9	0*	426
10	1337	1341
11	281*	387
12	1444	1470
13	0*	310
14	650	651
15	0*	105
16	587	449
17	524	330
18	923	937
19	288*	183
20	646	826
21	155*	161
22	262*	250

2,K,13

0	602	405
1	439	473
2	114*	255
3	222*	382
4	33*	340
5	550	558
6	277*	138
7	292*	365
8	288*	406
9	369	355
10	443	394
11	0*	47
12	402	271
13	757	583
14	292*	204
15	207*	212
16	369	390
17	454	254
18	351*	345
19	0*	151

2,K,14

0	0*	287
1	476	303
2	89*	206
3	458	447
4	377	452
5	587	353
6	214*	184
8	351	269
9	306*	202
10	318*	293
11	366	370
12	458	302
13	417	237
14	414	151
15	399	198
16	0*	181
17	185*	160

2,K,15

0	199*	238
1	332*	154
2	340*	530
3	266*	248
4	0*	42
5	391	269
6	395	400
7	258*	207
8	347*	251
9	185*	66
10	439	423
11	0*	261
12	148*	110
13	203*	273

2,K,16

0	0*	254
1	853	785
2	207*	230
3	233*	290
4	0*	44
5	388	361
6	251*	254
7	698	812
8	277*	203

2,K,0

6	4028	3962

3,K,0

3	491	490
4	203	142
5	251	180
6	650	651
7	1717	1666
8	1111	1082
9	975	1006
10	1780	1749
11	521	425
12	247*	335
13	122*	236
14	266*	160
15	1248	1181
16	1455	1441
17	543	411
18	1333	1352
19	450	359
20	439	402
21	270*	272
22	502	537
23	642	689
24	1093	1088
25	0*	119
26	919	780
27	432	177
28	303*	287
29	314*	167
30	388	468

3,K,1

3	406	513
4	2263	2276
5	687	697
6	1843	1785
7	1750	1762
8	1255	1066
9	1182	1123
10	1765	1745
11	362	282
12	1662	1617
13	705	666
14	1141	1109
15	1182	1187
16	687	737
17	395	469
18	1148	1139
19	380	320
20	1115	1064
21	450	498
22	366	533
23	233*	535
24	458	528
25	177*	139
26	577	590
27	295*	239
28	377	423
29	52*	260
30	181*	221

3,K,2

0	1034	1104
1	823	882
2	576	634
3	617	672
4	742	730
5	606	650
6	554	557
7	772	773
8	1255	1275
9	1134	1157
10	871	865
11	450	420
12	738	717
13	495	498
14	602	476
15	594	600
16	927	935
17	805	747
18	617	607
19	262*	245
20	0*	272
21	0*	276
23	491	432
24	594	526
25	351*	460
26	299*	377
27	0*	70
28	0*	140
29	0*	117
30	377	270

3,K,3

0	890	937

3,K,3

1	3390	3466
2	258	328
4	1189	1283
5	3164	3139
6	362	322
7	3323	3436
8	798	835
9	3080	3105
10	598	495
11	2197	2181
12	831	898
13	2297	2242
14	391	357
15	2083	2083
16	340	432
17	1876	1848
18	694	593
19	1396	1395
20	362	420
21	1303	1313
22	329*	371
23	1067	1068
24	380	214
25	901	868
26	406	321
27	450	583
28	314*	174
29	642	577

3,K,4

0	753	810
1	657	726
2	428	421
3	779	857
4	1182	1231
5	1082	1082
6	709	729
7	713	813
8	690	734
9	484	520
10	594	629
11	576	526
12	886	937
13	997	1079
14	713	675
15	450	397
16	373	424
17	0*	205
18	454	466
19	432	593
20	598	619
21	716	767
22	332*	466
23	414	280
24	0*	215
25	358	137
26	469	332
27	266*	372
28	0*	325
29	391	424

3,K,5

0	1588	1611
1	439	438
2	1248	1273
3	1244	1301
4	103*	257
5	986	1008
6	1159	1261
7	0*	177
8	1289	1306
9	473	563
10	886	800
11	960	927
12	524	436
13	510	561
14	890	961
15	247*	219
16	853	862
17	399	463
18	528	473
19	620	580
20	140*	403
21	107*	156
22	598	671
23	133*	225
25	295*	261
26	229*	157
27	299*	183
28	199*	246

3,K,6

0	314	328
1	281	354
2	679	760
3	1281	1249
4	347	477
5	945	967
6	1171	1240
7	126*	316
8	281*	283
9	347	258
10	133*	217
11	1015	1121
12	927	1091
13	713	531
14	1119	1203
15	391	349
16	351	352
17	306*	210
18	52*	307
19	694	749
20	883	924
21	310*	256
22	746	811
23	210*	215
24	425	294
25	166*	211
26	436	423
27	196*	367
28	639	691

3,K,7

0	1854	1873
1	0*	282
2	1651	1685
3	1163	1283
4	1119	1205
5	883	918
6	1603	1637
7	181*	242
8	1359	1453
9	428	514
10	1167	1276
11	971	1081
12	1123	1012
13	406	551
14	1215	1227
15	0*	266
16	1075	1102
17	192*	299
18	746	725
19	594	607
20	687	617
21	151*	90
22	705	686
23	321*	195
24	535	539
25	0*	275
26	380	349
27	0*	202

3,K,8

0	628	613
1	609	552
2	624	589
3	794	805
4	783	847
5	702	697
6	558	678
7	332	378
8	439	569
9	476	489
10	384	399
11	642	576
12	761	749
13	524	573
14	558	595
15	0*	207
16	203*	306
17	510	368
18	122*	296
19	277*	391
20	550	444
21	225*	325
22	222*	389
23	354*	87
24	0*	125
25	199*	206
26	432	200

3,K,9

0	1052	1128
1	1972	1966
2	92*	310
3	1891	1893
4	251*	450
5	1835	1871
6	443	419
7	1374	1433
8	720	857

3,K,9

9	1606	1533
10	428	222
11	1603	1651
12	369	268
13	1370	1400
14	480	502
15	1019	1053
16	495	492
17	1030	1115
18	299*	205
19	805	830
20	270*	192
21	594	737
22	439	401
23	546	559
24	329*	216
25	244*	581

3,K,10

0	694	776
1	535	615
2	0*	166
3	491	556
4	469	495
7	354	328
8	594	648
9	757	741
10	199*	336
11	329*	423
12	469	334
13	0*	186
14	299*	334
15	321*	391
16	318*	485
17	683	671
18	0*	259
19	281*	263
20	222*	256
21	325*	25
22	0*	276
23	362*	367

3,K,11

0	174*	215
1	443	440
2	210*	540
3	240*	190
4	606	629
5	432	274
6	454	463
7	594	514
8	44*	232
9	373	353
10	480	519
11	0*	188
12	561	520
13	388	302
14	358	318
15	185*	330
16	303*	188
17	362	150
18	399	410
19	358*	161
20	181*	274

3,K,12

0	0*	36
1	510	663
2	406	483
3	177*	271
4	377	106
5	0*	159
6	177*	273
7	598	617
8	258*	419
9	402	418
10	558	608
11	0*	227
12	303*	85
13	0*	85
14	199*	102
15	425	491
16	395	462
17	454	314
18	458	486
19	0*	182

3,K,13

1	650	521
2	960	876
3	240*	154
4	879	831
5	0*	134
6	654	811
7	439	553
8	646	648
9	0*	333
10	665	715
11	0*	181
12	654	665
13	162*	180
14	580	598
15	284*	410
16	617	456
17	0*	130

3,K,14

0	576	352
1	399	303
2	377	302
3	0*	136
4	111*	258
5	292*	167
6	414	224
7	0*	258
8	402	305
9	0*	185
10	432	231
11	0*	54
13	273*	171
14	0*	146

3,K,15

0	321*	105
1	713	730
2	0*	227
3	672	551
4	295*	439
5	572	565
6	318*	99
7	576	686
8	0*	70
9	690	635
10	133*	251

3,K,3

3	3179	3190

4,K,0

3	690	630
4	1953	1885
5	1185	1111
7	901	841
8	3216	3147
9	1215	1129
10	1931	1865
11	258*	198
12	1241	1174
13	1167	1154
14	1990	1916
15	0*	207
16	1953	1942
17	535	382
18	1108	1086
19	0*	286
20	883	869
21	654	616
22	1148	1116
23	144*	92
24	868	906
25	126*	216
26	258*	424
27	240*	235
28	89*	378

4,K,1

3	506	486
4	1318	1288
5	229*	311
6	465	532
7	679	607
8	620	610
9	631	676
10	709	628
11	528	480
12	916	902
13	203*	159
14	447	452
15	454	524
16	137*	345
17	661	691
18	428	561
19	303*	417
20	569	628
21	0*	141
22	417	394
23	417	374
24	0*	117

4,K,1

25	465	397
26	462	391
27	236*	166
28	281*	274

4,K,2

0	923	971
1	1385	1526
2	1075	1084
3	561	702
4	103*	266
5	727	740
6	1204	1204
7	1396	1367
8	897	900
9	1134	1137
10	798	750
11	510	416
12	447	487
13	809	766
14	805	835
15	1004	971
16	502	528
17	668	718
18	92*	215
19	70*	230
20	469	468
21	532	537
22	528	385
23	642	622
24	292*	224
25	443	341
26	199*	120
27	343*	135

4,K,3

0	535	535
1	908	982
2	979	997
3	1082	1009
4	665	630
5	447	494
6	801	813
7	871	883
8	343	500
9	676	586
10	528	627
11	794	853
12	543	562
13	661	606
14	569	507
15	1019	1012
16	306*	389
17	750	689
18	321	451
19	805	845
20	340	386
21	790	581
22	255*	332
23	642	712
24	159*	231
25	594	520
26	255*	218
27	277*	504

4,K,4

0	151*	272
1	916	994
2	1012	1120
3	1614	1738
4	709	797
5	1595	1635
6	783	868
7	713	723
8	495	505
9	779	880
10	879	925
11	1444	1441
12	561	643
13	1241	1172
14	554	458
15	439	476
16	391	523
17	786	712
18	513	502
19	894	916
20	218*	353
21	558	568
22	325*	65
23	0*	230
24	410	357
25	447	393
26	0*	194
27	318*	498

4,K,5

0	1041	1031
1	524	419
2	299	364
3	676	751
4	329	447
5	679	751
6	447	412
7	657	679
8	809	786
9	225*	334
10	63*	182
11	661	628
12	255*	234
13	742	713
14	521	492
15	292*	468
16	624	595
17	0*	94
18	388	254
19	340	386
20	229*	101
21	443	435
22	406	408
23	332*	283
25	0*	94
26	0*	144

4,K,5

0	1536	1509
1	635	626
2	2012	2038
3	495	611
4	2341	2399
5	628	628
6	1647	1687
7	332	442
8	1200	1256
9	838	903
10	1795	1776
11	299*	403
12	1798	1827
14	1086	1125
15	0*	197
16	860	877
17	580	642
18	1111	1140
19	0*	124
20	1004	1005
21	140*	238
22	569	556
23	262*	215
24	532	490
25	351*	432

4,K,7

0	938	971
1	318	348
2	321	314
3	402	477
4	631	686
5	521	570
6	421	369
7	343	360
8	820	897
9	218*	152
10	395	533
11	373	325
12	414	463
13	377	549
14	299*	423
15	340	331
16	532	591
17	299*	109
18	295*	446
19	251*	282
20	0*	225
21	465	428
22	484	409
23	251*	214
24	469	406

4,K,8

0	255*	155
1	388	414
2	591	602
3	757	825
4	314	428
5	598	723
6	513	537
7	0*	256
8	417	270
9	210*	451
10	535	615
11	535	617

4,K,8

12	174*	361
13	646	557
14	137*	237
15	210*	52
16	458	305
17	92*	366
19	495	499
20	332*	141
21	399	339
22	0*	67
23	0*	30

4,K,9

0	532	558
1	225*	366
2	528	582
3	528	665
4	310	173
5	473	485
6	524	566
7	487	554
8	598	509
9	66*	315
10	506	531
11	654	749
12	0*	172
14	354	399
15	535	545
16	373	387
17	399	384
18	0*	291
19	546	564
20	288*	149
21	329*	345
22	0*	214

4,K,10

0	0*	594
1	1100	1125
2	594	704
3	613	637
4	0*	124
5	668	703
6	554	634
7	1063	1086
8	425	436
9	616	897
10	550	418
11	487	461
12	391	308
13	543	597
14	354	492
15	638	803
16	351*	311
17	358*	511
18	133*	244
19	366	277
20	373	287

4,K,11

0	133*	314
1	421	364
2	347	347
3	314*	302
4	602	550
5	0*	206
6	0*	168
7	476	405
8	244*	184
9	395	360
10	277*	284
11	336*	316
12	373	400
13	318*	96
14	0*	99
15	0*	310
16	0*	153
17	266*	224
18	338	294

4,K,12

0	1311	1239
1	469	455
2	897	869
3	321*	323
4	513	512
5	377	438
6	838	859
7	225*	252
8	1049	1004
9	439	314
10	524	629
11	126*	173
12	602	466
13	0*	405
14	702	698
15	0*	164
16	517	711

4,K,13

0	0*	511
1	258*	226
2	0*	105
3	114*	153
4	181*	431
5	0*	139
6	0*	213
7	288*	140
8	502	352
9	0*	278
10	410	188
11	0*	176
12	0*	381
13	0*	80

4,K,14

0	0*	106
1	380	285
2	0*	181
3	292*	202
4	107*	50
5	63*	255
6	399	225
7	0*	241
8	0*	126
9	0*	277

4,K,0

6	2780	2745

5,K,0

3	786	777
4	447	339
5	794	769
6	1071	1052
7	318	302
8	122*	126
9	192*	334
10	144*	213
11	694	628
12	849	795
13	510	481
14	1004	1003
15	310	228
16	0*	142
17	262*	297
18	0*	141
19	414	458
20	853	802
21	0*	236
22	757	673
23	0*	56
24	0*	153
25	0*	171

5,K,1

2	823	880
3	993	1099
4	450	408
5	801	737
6	993	971
7	181*	191
8	971	991
9	0*	235
10	565	571
11	757	757
12	565	524
13	454	372
14	816	775
15	347	330
16	798	787
17	247*	256
18	428	353
19	484	589
20	373	239
21	266*	69
22	687	534
23	0*	262
24	270*	358
25	399	160

5,K,2

0	111*	39
1	539	498
2	428	487
3	665	562
4	436	446

5,K,2

5	879	788
6	609	723
8	181*	103
9	753	718
10	362	412
11	410	334
12	469	534
13	801	772
14	587	537
15	310	208
16	0*	103
17	240*	326
18	0*	167
19	196*	260
20	502	421
21	439	448
22	373	291
23	166*	63
24	181*	34

5,K,3

0	849	957
1	1654	1720
2	0*	74
4	720	792
5	1599	1672
6	222*	342
7	1507	1514
8	831	898
9	1462	1494
10	107*	303
11	1396	1354
12	594	585
13	1159	1201
14	469	439
15	1097	1081
16	388	510
19	868	815
20	546	296
21	694	684
22	340*	380
23	583	559
24	0*	251

5,K,4

0	373	354
1	480	603
2	399	348
3	303	520
4	0*	27
5	484	548
6	340	339
7	432	388
8	362	463
9	864	917
10	550	568
11	0*	390
12	0*	90
13	177*	444
14	0*	137
15	299*	268
17	624	655
18	222*	301
19	366	183
20	122*	78
21	0*	184
22	0*	172
23	410	287
24	310*	304

5,K,5

0	0*	131
1	772	815
2	447	594
3	0*	350
4	971	976
5	0*	138
6	336	415
7	709	795
8	0*	64
9	539	425
10	650	624
11	343	306
12	687	714
13	0*	174
14	0*	214
15	665	598
16	96*	53
17	233*	119
18	569	495
19	262*	344
20	262*	475
21	252*	161
22	107*	123
23	292*	317

5,K,6

0	0*	37
1	650	636
2	831	890
3	70*	264
4	210*	148
5	185*	280
6	351	505
7	513	593
8	0*	467
9	554	516
10	879	904
11	240*	205
12	181*	154
13	162*	252
14	0*	75
15	273*	434
16	746	712
17	421	336
18	750	693
19	151*	93
20	0*	111
21	0*	162
22	229*	166

5,K,7

0	591	550
1	724	827
2	846	868
3	0*	281
4	1045	1076
5	366	204
6	646	767
7	786	834
8	528	536
9	332	464
10	761	753
11	222*	285
12	805	810
13	207*	206
14	351	526
15	650	612
16	0*	356
17	362	150
18	395	547
19	0*	293
20	491	518
21	318*	204

5,K,8

0	421	336
1	458	369
2	473	415
3	314	325
4	0*	93
5	366	361
6	266*	288
7	0*	264
8	362	328
9	454	387
10	391	361
11	277*	196
12	0*	79
13	395	340
14	118*	165
15	329*	163
16	0*	342
17	0*	308
18	510	259
19	0*	106
20	0*	94

5,K,9

0	0*	380
1	1104	1111
2	0*	235
3	919	889
4	624	682
5	820	857
6	0*	110
7	1012	1027
8	0*	312
9	934	923
10	0*	324
11	690	678
12	580	499
13	679	714
14	295*	170
15	779	722
16	0*	201
17	447	558
18	0*	293

5,K,10

1	406	349
2	380	180
3	459	287
4	281*	249
5	233*	482
6	114*	230
7	362	303
8	114*	42
9	384	260
10	148*	122
11	314*	186
12	92*	255
13	650	519
14	210*	209
15	0*	207
16	0*	81

5,K,11

0	306*	368
1	236*	113
2	295*	161
3	262*	306
4	0*	210
5	336*	237
6	388	253
7	166*	230
8	258*	457
9	354	118
10	144*	168
11	366	328
12	0*	159
13	0*	96
14	0*	268

5,K,12

0	273*	149
1	0*	143
2	480	364
3	0*	329
4	0*	115
5	0*	317
6	469	467
7	63*	100
8	358	126
9	162*	146
10	229*	184

5,K,13

0	657	512
1	0*	144
2	0*	450
3	484	403
4	432	393

5,K,3

3	1684	1752

6,K,0

3	450	397
4	1248	1187
5	572	515
7	306	270
8	1100	1074
9	853	781
10	1078	985
11	539	367
12	982	945
13	524	384
14	982	878
15	218*	71
16	783	688
17	661	487
18	598	587
19	129*	122
20	746	570
21	366	124

6,K,1

2	214*	150
3	414	431
4	391	399
5	273	338
6	251*	310
7	314	199
8	650	619
9	185*	120
10	199*	117
11	281*	400
12	329	242
13	318	270
14	318	392
15	240*	260
16	521	460
17	0*	174
18	0*	175
19	273*	272
20	0*	154
21	0*	152

6,K,2

0	207*	295
1	506	512
2	543	578
3	465	543
4	126*	156
5	620	620
6	510	508
7	358	390
8	402	328
9	506	410
10	502	502
11	454	455
12	399	156
13	587	504
14	329	299
15	358	327
16	351	335
17	343	332
18	425	287
19	0*	283
20	395	108

6,K,3

0	436	468
1	458	502
2	284	426
3	628	614
4	325	421
5	336	398
6	384	420
7	447	449
8	273*	393
9	214*	369
10	417	348
11	694	533
12	458	290
13	284*	265
14	377	322
15	583	510
16	299*	308
17	196*	356
18	318*	231
19	624	539

6,K,4

0	310	312
1	646	667
2	591	615
3	594	640
4	225*	191
5	569	637
6	620	648
7	450	558
8	0*	333
9	594	537
10	332	418
11	628	562
12	373	268
13	469	496
14	380	440
15	373	385
16	443	217
17	436	442
18	380	144
19	0*	325

6,K,5

0	0*	347
1	414	383
2	37*	234
3	0*	140
4	646	663
5	255*	115
6	0*	41
7	436	406
8	0*	222
9	384	216
10	295*	346
11	33*	193
12	0*	470
13	0*	125
14	126*	51
15	306	298
16	0*	136
17	288*	182
18	0*	310

6,K,6

1	414	347
2	967	943
3	126*	293
4	871	866
5	510	515
6	871	857
7	410	314
8	849	880
9	196*	407
10	738	791
11	181*	102
12	694	650
13	583	539
14	713	627
15	247*	169
16	594	607
17	192*	198

6,K,7

0	310	361
1	299	256
2	432	162
3	0*	41
4	476	541
5	369	111
6	0*	132
7	384	303
8	377	334
9	391	208
10	0*	291
11	318*	184
12	303*	443
13	0*	124
14	380	201
15	0*	233
16	0*	217

6,K,8

0	0*	124
1	452	301
2	203*	357
3	0*	212
4	192*	114
5	137*	288
6	255*	394
7	325	264
8	0*	43
9	366	354
10	329*	262
11	336	141
12	0*	236
13	0*	249
14	0*	275

6,K,9

0	0*	196
1	340	367
2	343	285
3	181*	262
4	310*	340
5	306*	221
6	292*	225
7	550	451
8	244*	182
9	0*	244
10	0*	273
11	0*	279
12	310*	264

6,K,10

0	288*	66
1	388	448
2	325*	414
3	351	464
4	203*	214
5	432	465
6	406	320
7	517	460
8	229*	127

6,K,11

0	354	368
1	0*	162
2	244*	147

6,K,0

0	1097	1086

Structure Factor Tables for

Bis(2-hydrotetrafluorophenyl)mercury.

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
-16	0	8	19	18	-11	0	6	46	49	-7	0	8	94	90	-2	0	6	63	58	5	0	0	105	103
-16	0	10	19	20	-11	0	8	22	25	-7	0	10	31	35	-2	0	8	69	64	5	0	2	108	87
-16	0	12	15	16	-11	0	10	25	27	-7	0	12	40	43	-2	0	10	40	38	5	0	4	55	53
-16	0	14	16	14	-11	0	12	32	32	-7	0	14	20	21	-2	0	12	23	25	5	0	6	30	32
-15	0	4	20	20	-11	0	14	18	21	6	0	0	58	55	-1	0	4	123	117	5	0	8	24	26
-15	0	6	22	24	10	0	0	31	31	-6	0	2	136	131	-1	0	6	103	97	6	0	0	60	55
-15	0	8	28	24	-10	0	2	47	50	-6	0	4	87	86	-1	0	8	52	55	6	0	2	79	76
-15	0	10	21	22	-10	0	4	66	59	-6	0	6	81	76	-1	0	10	66	71	6	0	4	54	44
-15	0	12	21	19	-10	0	6	59	59	-6	0	8	86	82	-1	0	12	22	27	6	0	6	33	31
-15	0	14	13	16	-10	0	8	70	68	-6	0	10	54	52	0	0	4	128	123	6	0	8	17	22
-14	0	2	16	18	-10	0	10	48	49	-6	0	12	24	26	0	0	6	91	89	7	0	0	76	77
-14	0	4	21	24	-10	0	12	30	30	-6	0	14	21	23	0	0	8	48	47	7	0	2	52	52
-14	0	6	21	25	-10	0	14	15	17	5	0	0	104	103	0	0	10	30	30	7	0	4	41	42
-14	0	8	26	28	-10	0	16	12	13	-5	0	2	97	89	0	0	12	19	17	7	0	6	19	21
-14	0	10	22	28	9	0	0	49	49	-5	0	4	167	160	1	0	4	70	60	8	0	0	53	56
-14	0	12	18	22	-9	0	2	55	55	-5	0	6	52	53	1	0	6	87	86	8	0	2	45	45
13	0	0	18	19	-9	0	4	51	51	-5	0	8	70	70	1	0	8	31	32	8	0	4	29	32
-13	0	2	26	23	-9	0	6	65	67	-5	0	10	55	49	1	0	10	15	15	8	0	6	13	14
-13	0	4	22	26	-9	0	8	68	68	-5	0	12	25	25	1	0	12	15	15	9	0	0	47	49
-13	0	6	38	32	-9	0	10	48	43	-5	0	14	17	17	2	0	0	89	86	9	0	2	37	40
-13	0	8	35	34	-9	0	12	30	31	4	0	0	95	95	2	0	2	154	151	9	0	4	20	22
-13	0	10	39	41	-9	0	14	17	17	-4	0	2	101	98	2	0	4	116	112	10	0	0	30	31
-13	0	12	23	24	-9	0	16	16	14	-4	0	4	99	94	2	0	6	71	74	-7	5	3	22	25
-13	0	14	19	19	8	0	0	54	56	-4	0	6	76	72	2	0	8	32	37	-7	5	5	23	25
-13	0	16	15	13	-8	0	2	63	63	-4	0	8	55	57	2	0	10	20	22	-7	5	7	20	21
12	0	0	27	29	-8	0	4	63	61	-4	0	10	47	46	3	0	0	129	126	-7	5	9	16	19
-12	0	2	25	29	-8	0	6	96	93	-4	0	12	27	27	3	0	2	88	82	-7	5	11	13	14
-12	0	4	37	38	-8	0	8	62	62	-4	0	14	15	16	3	0	4	61	64	-6	5	1	23	26
-12	0	6	41	42	-8	0	10	58	56	3	0	0	128	126	3	0	6	44	41	-6	5	3	23	23
-12	0	8	34	32	-8	0	12	44	47	-3	0	6	149	143	3	0	8	33	32	-6	5	5	27	27
-12	0	10	25	24	-8	0	14	23	29	-3	0	8	81	80	3	0	10	17	16	-6	5	7	24	25
-12	0	12	26	28	-8	0	16	12	11	-3	0	10	39	42	4	0	0	97	95	-6	5	9	21	19
-12	0	14	18	18	7	0	0	75	77	-3	0	12	17	16	4	0	2	94	93	-6	5	11	14	16
11	0	0	21	23	-7	0	2	147	115	-3	0	14	17	17	4	0	4	35	40	-5	5	1	33	31
-11	0	2	34	38	-7	0	4	109	104	2	0	0	87	86	4	0	6	47	50	-5	5	3	28	30
-11	0	4	41	39	-7	0	6	79	73	-2	0	2	53	59	4	0	8	25	23	-5	5	5	30	33

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
-5	5	7	26	27	2	5	7	14	14	-7	1	6	14	15	-8	5	3	16	22	-11	1	9	50	47
-5	5	9	20	20	3	5	1	34	35	-7	1	7	63	68	-8	5	5	22	26	-11	1	11	37	37
-5	5	11	13	14	3	5	3	27	29	-7	1	9	65	60	-8	5	7	19	20	-11	1	13	21	21
-4	5	1	31	31	3	5	5	16	18	-7	1	11	38	35	-8	5	9	14	17	-11	1	15	17	17
-4	5	3	32	35	3	5	7	15	14	-7	1	13	22	23	-16	1	9	19	17	-10	1	1	41	44
-4	5	5	26	26	4	5	1	33	29	-7	1	15	15	14	-16	1	11	15	15	-10	1	3	43	42
-4	5	7	26	28	4	5	3	22	25	-6	1	1	77	78	-15	1	5	18	18	-10	1	4	14	8
-4	5	9	19	21	4	5	5	19	19	-6	1	3	79	78	-15	1	7	18	20	-10	1	5	59	59
-4	5	11	15	15	5	5	1	26	24	-6	1	5	87	83	-15	1	9	21	24	-10	1	7	52	54
-3	5	1	36	39	5	5	3	20	20	-6	1	6	28	27	-15	1	11	19	21	-10	1	9	36	36
-3	5	3	30	31	6	5	1	21	22	-6	1	7	79	75	-15	1	13	15	16	-10	1	11	36	37
-3	5	5	29	32	6	5	3	17	16	-6	1	8	11	9	-15	1	15	15	13	-10	1	13	29	30
-3	5	7	22	24	7	5	1	17	18	-6	1	9	54	54	-14	1	3	16	20	-10	1	15	13	16
-3	5	9	18	20	-9	1	4	12	-10	-6	1	11	45	45	-14	1	5	22	25	9	1	0	12	8
-3	5	11	15	13	-9	1	5	59	58	-6	1	13	28	29	-14	1	7	34	25	-9	1	1	46	53
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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
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Structure Factor Tables for

Monoclinic Tribenzo(b,e,h)(1, 4,7)trimercuronin.

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2	4874
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10	2882
12	980
14	1081
16	1114
18	861
20	840
22	806

0,1,L

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2	736
3	1460
4	1304
5	1703
6	2090
7	1447
8	531
9	1102
10	3123
11	719
12	1938
13	212
14	1172
15	380
16	2065
17	791
18	208
19	863
20	1248
21	532
22	875
23	395

0,2,L

0	665
1	225
2	535
3	1238
4	5751
5	115
6	4865
7	1161
8	558
9	1591
10	1971
11	933
12	909
13	225
14	369
18	759
19	222
20	481
21	334
22	236
23	182

0,3,L

1	949
2	603
3	1940
4	1218
5	2653
6	2422
7	2521
8	953
9	910
10	1259
11	711
12	798
13	1140
14	1423
15	472
16	1895
18	474
20	830
21	389
22	506

0,4,L

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1	1100
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3	2387
4	1088
5	1421
6	1199
7	44*
8	1353
9	385
10	1991
11	290
12	281
13	915
14	867
15	1161
16	604
17	669
20	327
21	244
22	550

0,5,L

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2	1322
3	1409
4	912
5	367
6	689
7	726
8	295
9	51*
10	1836
11	1054
12	1592
13	889
14	59*
16	487
17	860
19	749
20	629

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1	754
2	541
3	1022
4	1964
5	134
6	1248
7	1358
8	408
9	1780
10	712
11	1045
12	254
13	60*
14	475
18	609
19	231

0,7,L

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2	922
3	305
5	957
6	1153
7	1024
8	1297
9	315
10	279
11	427
13	602
14	493
16	714
17	310

0,8,L

0	536
1	517
2	288
3	1026
4	321
5	631
8	655
10	443
11	309
12	303
13	583
14	590
15	534

0,9,L

1	381
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3	221
4	765
5	176
6	189
7	330
8	178
10	315
11	317
12	586

0,10,L

3	254
7	408

1,0,L

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-6	3637
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-8	1633
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-10	4536
12	1392
-12	3562
14	1782
-14	1280
16	940
-16	217
18	619
-18	626
20	612
-20	495
22	310

1,1,L

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-2	23*
3	1262
-3	503
4	1902
-4	892
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-5	1099
6	1857
-6	2217
7	2912
-7	1226
8	1473
-8	844
9	1829
-9	2204
10	2966
-10	2096
11	1314
-11	1868
12	999
-12	2053
13	1079
-13	2164
14	2053
-14	549
15	1011
-15	1403
16	1996
-16	2194
17	930
-17	648
-18	799
19	527
-19	454
20	1192
-20	1098
-21	272
22	427
-22	1186
-23	208

1,2,L

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-2	2946
3	745
-3	2519
4	2313
-4	3365
5	118
-5	1239
6	507
-6	5467
7	1085
-7	37*
8	3179
-8	2644
9	789
-9	963
10	3285
-10	669
11	201
-11	307
12	1522
-12	47*

1,2,L

13	261
-13	49*
14	393
-14	1770
15	711
-15	389
16	667
-16	1740
17	399
18	585
-18	803
-19	327
-20	375
-21	469
22	212
-22	344
-23	304

1,3,L

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3	900
-3	487
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6	2676
-6	639
7	553
-7	2696
8	213
-8	226
9	1389
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-10	1844
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-11	677
12	938
-12	1747
13	1767
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15	880
-15	750
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-16	1889
-17	1216
18	503
-18	924
-19	1085
20	1180
-20	537
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-21	344
22	549
-22	632

1,4,L

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3	2232
-3	676
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-5	563
6	2333
-6	1886
7	540
-7	1343
4	3343
8	47*
-8	1127
9	914
-9	1748
10	50*
-10	3101
11	464
-11	1083
12	1018
-12	1965
13	524
-13	425
14	1077
-14	55*
15	391
-15	661
16	373
-16	180
-17	711
-18	562
19	484
-19	242
20	257
-20	493
21	575

1,5,L

1	530
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-3	693
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-4	357
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6	588
-6	1751
7	1985
-7	699
8	305
-8	1516
9	835
-9	287
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-10	209
11	195
-11	1618
12	298
-12	1434
13	342
-13	1567
14	921
-14	162
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-16	623
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19	509
-19	255
20	308
-20	729

1,6,L

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-3	2285
4	928
-4	1103
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6	323
-6	1581
7	1126
-7	52*
8	1638
-8	302
9	1165
-9	737
10	1192
-10	362
11	58*
-11	204
12	60*
-12	391
13	365
-13	258
14	63*
-14	986
15	723
-15	653
16	445
-16	638
17	528
18	548
19	188
-19	306
-20	189

1,7,L

0	163
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-2	1560
3	265
4	480
-4	1602
5	445
-5	714
6	1246
-6	244
7	480
-7	1101
8	544
-8	466
9	332
-9	670
10	480
-10	276
11	851
-11	197
12	595
-12	541
13	744
-13	488
-16	563
17	317
-17	618
-18	484

1,8,L

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-2	319
3	1096
-3	253
4	579
-4	335
5	505
-6	217
7	201
-7	761
8	426
-8	538
9	223
-9	815
-10	705
-11	374
12	619
-13	262
14	556
-14	439
-15	348

1,9,L

0	319
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-4	287
5	379
-5	218
6	282
-6	569
7	415
-7	307
8	266
-8	917
9	196
10	209
-10	327
11	312
-11	270
-12	300

1,10,L

-1	312
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6	264
-8	307

2,0,L

0	299
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-6	6651
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-8	3858
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-10	1428
12	215
-12	2300
14	341
-14	234
16	880
-16	747
18	659

2,0,L

-20	809
22	303
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-24	335

2,1,L

0	378
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3	1942
-3	1281
4	2764
-4	735
5	1844
-5	2530
6	1677
-6	1258
7	1456
-7	2523
8	1827
-8	1209
9	204
-9	1997
10	2661
-10	891
11	668
-11	566
12	49*
-12	1816
13	771
-13	197
14	2217
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15	613
-15	368
16	1325
-16	2148
17	471
-17	225
18	623
-18	1458
19	463
-19	293
20	1026
-20	542
21	497
-21	436
-22	1176
-23	570
-24	271

2,2,L

1	934
-1	972
2	757
3	1102
-3	1117
4	2181
-4	1045
5	612
-5	1442
6	218
-6	2542
7	41*
-7	175
8	1750
-8	381
9	161
-9	411
10	1121
-10	2877
11	328
-11	278
12	553
-12	2535
13	742
-13	463
14	764
-14	50*
15	602
-15	825
16	468
-16	1346
17	385
-17	632
18	693
-18	878
-19	173
20	851
-20	468
21	204
22	512
-22	455
-23	202
-24	445

2,3,L

2	725
-2	122
3	1219
-3	1933
4	1413
-4	120
5	342
-5	620
6	820
-6	39*
7	210
-7	141
8	1940
-8	285
9	478
-9	549
10	2736
-10	1595
11	755
-11	1129
12	580
-12	2327
13	290
-13	1172
14	1273
-14	777
15	623
-15	255
16	725
-16	852
17	1034
-17	784
18	683
-18	676
19	732
-19	1044
20	871
-20	649
21	309
-21	563
-22	1011
-23	179

2,4,L

0	289
1	465
-1	40*
2	1804
-2	427
3	552
-3	1426
4	2668
-4	1928
5	489
-5	746
6	868
-6	3722
7	1686
-7	911
8	970
-8	1920
9	1659
-9	2134
10	608
-10	897
11	834
-11	1583
12	55*
-12	1078
13	57*
-13	360
14	59*
-14	374
15	300
16	760
-16	569
18	547
-18	219
19	280
-19	324
-20	656
-21	453
-22	298

2,5,L

0	269
1	46*
-1	45*
2	46*
-2	122
3	848
-3	595
4	1432
-4	655
5	1518
-5	1546
6	1654
-6	822
7	1243
-7	1988
8	229
-8	1666
9	53*
-9	1167
10	512
-10	802
11	1038
-11	200
12	402
-12	358
13	810
-13	893
14	1310
-14	155
-15	529
16	805
-16	1274
17	260
-17	212
18	239
-18	987
-19	388

2,6,L

1	717
-1	50*
2	148
-2	1354
3	1379
-3	1197
4	596
-4	390
5	616
-5	1311
6	486
-6	658
7	55*
-7	53*
8	1121
-8	186
9	57*
-9	371
10	177
-10	1205
11	432
-11	197
12	691
-12	731
13	744
-13	789
14	521
-14	512
15	735
-15	1126
-16	645
17	433
-17	750
-19	273
-20	237

2,7,L

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-2	380
-3	571
4	182
-4	1156
5	511
6	190
-6	380
7	549
-7	520
8	622
-8	449
9	173
-9	211
10	1013
-10	222
11	656
-11	562
12	545
-12	1071
13	308
-13	862
-14	901
15	317
-15	330
-16	182
-17	357

2,8,L

2	450
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3	264
-3	566
4	433
-4	387
5	344
-5	222
6	339
-6	623
7	921
-7	541
8	580
9	807
-9	1065
-10	356
11	386
-11	767
12	562
-13	282
14	186
-14	448
-16	277

2,9,L

2	255
-2	302
4	277
-4	641
5	375
-5	235
6	750
-6	187
7	329
-7	371
8	497
-8	900
-9	275
-10	743
-11	196
-13	350

2,10,L

1	143
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3	286
-3	294
-5	278

3,0,L

2	327
4	1220
-4	183
6	1597
-6	4630
8	3015
-8	4334
10	2079
-10	356
12	579
-12	1247
14	974
-14	591
16	744
-16	2277
-18	1809
20	458
-20	682
-22	164

3,1,L

0	365
1	772
-1	636
2	1084
-2	523
3	870
-3	156
4	2846
-4	598
5	974
-5	913
6	777
-6	35*
7	1411
-7	1465
8	2544
-8	339
9	1919
-9	1964
10	2452
-10	622
11	1595
-11	1468
12	676
-12	2082
13	1214
-13	1087
14	1760
-14	444
15	603
-15	924
16	559
-16	1499
17	204
-17	1192
18	965
-18	1559
-19	1059
20	830
-21	617
-22	1104
-24	491

3,2,L

0	562
1	625
-1	450
3	842
-3	315
4	3351
-4	459
5	275
-5	450
6	1827
-6	2888
7	374
-7	344
8	243
-8	1538
9	696
-9	1173
10	915
-10	2751
11	51*
-11	1064
12	919
-12	4017
13	339
-13	216
14	631
-14	1829
-15	670
16	173
-16	201
-17	315
18	454
19	313
-19	230
20	511
-20	681
21	328
-22	494

3,3,L

1	125
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3	1052
-3	588
4	1284
-4	554
5	2106
-5	39*
6	138
-6	507
7	1999
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8	1776
-8	1550
9	845
-9	473
10	1406
-10	46*
11	240
-11	1545
12	569
-12	899
13	278
-13	1830
14	1925
-14	987
15	825
-15	1356
16	726
-16	862
17	734
-17	516
18	491
-18	1051
19	201
20	436
-20	329
-22	1089
-23	387

3,4,L

1	295
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2	448
3	481
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4	527
-4	338
5	399
-5	1943
6	1407
-6	2394
7	878
-7	456
8	1798
-8	2241
9	590
-9	658
10	954
-10	134
11	55*
-11	490
12	57*
-12	502
13	618
-13	296
14	460
-14	652
15	802
-15	585
16	659
-16	1667
17	446
-17	457
-18	866
-19	250
-21	615
-23	575

3,5,L

0	187
1	634
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2	392
-2	439
3	219
-3	384
4	1499
-4	1521
5	340
-5	777
6	962
-6	867
7	52*
-7	1533
8	836
-8	50*
9	947
-9	1234
10	1052
-10	52*
11	1442
-11	298
12	60*
-12	1046
13	831
-13	424
14	615
-14	544
-15	59*
-16	539
17	310
-17	781
18	744
-18	947
-19	1034
-20	248
-21	559

3,6,L

0	51*
1	823
-1	472
2	839
-2	680
3	994
-3	130
4	865
-4	200
5	282
-5	315

3,6,L

6	55*
-6	741
7	526
-7	675
8	221
-8	308
9	534
-9	1452
10	592
-10	1062
11	199
-11	1053
12	908
-12	1225
13	64*
-13	60*
14	205
-14	174
-15	545
16	200
-16	303
-17	535
-18	201
-20	533

3,7,L

0	701
-1	307
2	581
-2	399
3	321
-3	166
4	144
-4	208
5	934
-5	272
6	257
-6	209
7	764
-7	490
8	269
-8	1240
9	158
-9	228
10	375
-10	959
11	448
-11	402
12	284
-13	968
14	573
-14	578
15	282
-15	656

3,8,L

0	144
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3	159
-3	814
-4	176
5	278
-5	969
6	670
-6	379
7	467
-7	352
8	664
-8	270
9	305
-9	257
10	189
-10	208
-11	253
12	356
13	361
-13	247
-14	433
-15	358
-16	359

3,9,L

-1	162
-2	357
4	352
-4	927
5	232
6	382
-6	629
7	245
-7	266
9	202
-9	267
-10	356
-12	177

3,10,L

-1	189
1	195
2	167
3	170
-7	296

4,0,L

2	699
4	1081
-4	3037
6	675
-6	1140
8	972
-8	2165
10	183
-10	1490
12	409
-12	3643
14	280
-14	1958
16	473
-16	751
18	1046
-18	1436
20	871
-20	666
-22	206
-24	321

4,1,L

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-2	981
3	507
-3	1589
4	1978
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-5	1842
6	489
-6	377
7	116
-7	1089
8	2777
-8	107
9	49*
-9	1256
10	1556
-10	405
11	174
-11	1121
12	984
-12	1440
13	523
-13	852
14	1537
-14	1107
15	746
-15	361
-16	643
17	758
-17	375
18	848
-18	1251
19	416
-19	565
20	447
-20	163
-21	598
-22	1031
-23	290
-24	767

4,2,L

0	366
1	142
-1	114
-2	774
3	170
-3	337
4	1694
-4	469
5	477
-5	851
6	45*
-6	3712
7	930
-7	266
8	767
-8	4143
9	760
-9	1010
10	238
-10	913
11	217
-11	1073
12	262
-12	1815
13	202
-13	384
14	928
-14	852
15	220
-15	219
16	753
-16	760
-17	174
-18	728
19	245
-20	322
-21	319
-22	655
-23	264
-24	478

4,3,L

0	152
1	323
-1	41*
2	1083
-2	755
3	876
-3	661
4	1848
-4	358
5	1353
-5	1313
6	360
-6	291
7	567
-7	1992
8	1319
-8	703
9	462
-9	1832
10	600
-10	905
11	1016
-11	677
12	1256
-12	257
13	658
-13	335
14	1396
-14	315
-15	365
-16	954
17	158
18	672
-18	1507
19	246
-19	372
-20	519
-22	604
-23	374

4,4,L

0	608
1	786
-1	299
2	444
3	1030
-3	1025
4	412
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5	448
-5	1089
6	771
-6	441
7	51*
-7	547
8	549
-8	902
9	54*
-9	518
10	452
-10	999
11	385
-11	368
12	654
-12	1940
13	674
-13	476
14	63*
-14	808
15	637
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17	208

4,4,L

-17	1035
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-18	777
-19	410
-20	172
-23	222

4,5,L

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1	605
-1	943
2	50*
-2	534
3	51*
-3	1028
4	510
-4	410
5	626
-5	199
6	432
-6	660
7	366
-7	263
8	1456
-8	51*
9	319
-9	52*
10	1051
-10	53*
11	533
-11	682
12	218
-12	907
-13	1104
14	499
-14	1190
15	578
-15	734
16	199
-16	430
17	653
-17	207
-18	248
-19	751
-21	590

4,6,L

0	291
1	324
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2	698
-2	241
3	55*
-3	447
4	285
-4	141
5	595
-5	839
6	525
-6	1034
7	1084
-7	155
8	374
-8	1321
9	887
-9	1203
10	325
-10	196
11	421
-11	1308
12	288
-12	513
-13	513
14	357
-15	201
16	478
-16	583
-18	287
-19	288
-20	375

4,7,L

0	191
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3	336
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-4	493
5	644
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6	625
-6	394
7	330
-7	802
-8	698
9	422
-9	668
-10	1147
11	589
12	519
-12	481
13	266
-13	428
14	424
-15	453
-16	204
-18	616

4,8,L

1	379
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-2	273
3	397
-3	332
-4	340
5	217
-5	553
6	549
-7	259
8	254
-9	227
10	409
-10	342
11	274
-12	446
-13	418
-15	582
-16	305

4,9,L

0	397
1	137
-1	204
2	249
-4	426
5	278
-6	507
8	319
-10	312

4,10,L

0	145
-3	172
-5	206

5,0,L

0	867
4	1823
-4	1339
6	740
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8	937
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10	617
-10	381
12	303
-12	3515
-14	3343
16	262
-16	517
18	635
-18	159
-20	265
-22	694
-24	514

5,1,L

0	264
1	526
-1	245
2	1312
-2	1255
3	828
-3	171
4	1318
-4	872
5	1406
-5	154
6	953
-6	40*
7	1338
-7	126
8	2178
-8	42*
9	1094
-9	632
10	474
-10	206
11	391
-11	1058
12	1393
-12	558
13	707
-13	1572
14	1231
-14	862
15	399
-15	931
16	173
-16	239
17	207
-17	836
18	644
-18	1202
-19	633
-20	443
-21	451
-22	769
-23	359
-24	875

5,2,L

0	551
1	275
-1	172
2	331
3	185
-3	668
4	413
-4	1545
5	187
-5	1046
6	1502
-6	1284
7	422
-7	456
8	1291
-8	2956
9	228
-9	187
10	362
-10	1503
11	56*
-11	471
12	605
-12	887
13	427
-13	225
14	834
-14	489
15	392
-15	381
16	275
-16	1201
-17	541
18	444
-18	2004
-20	983
-21	283
-23	368

5,3,L

0	108
1	710
-1	1050
2	1175
-2	448
3	227
-3	662
4	1334
-4	151
5	153
-5	203
6	568
-6	1069
7	573
-7	998
8	1637
-8	615
9	1186
-9	1205
10	548
11	1036
-11	763
12	870
-12	605
13	541
-13	181
14	617
-14	834
16	451
-16	195
-17	762
18	701
-18	983
-19	1047
-20	604

5,3,L

-21	849
-22	320
-23	296

5,4,L

0	546
1	836
-1	653
2	1121
-2	594
3	587
-3	110
4	762
-4	886
5	52*
-5	357
6	164
-6	623
7	614
-7	232
8	437
-8	1441
9	472
-9	1287
10	909
-10	208
11	154
-11	1249
12	445
-12	1955
-13	496
14	208
-14	1593
-15	511
-16	291
17	193
-17	629
-18	252
-19	275
-20	295
-22	566

5,5,L

0	566
1	52*
-1	334
2	228
-2	884
3	798
-3	272
4	454
-4	314
5	1224
-5	227
6	322
-6	51*
7	700
-7	500
8	841
-8	515
9	60*
-9	299
10	61*
-10	1092
11	224
-11	513
12	899
-12	320
-13	1054
14	604
-14	349
15	436
-15	1080
-16	195
-17	446
-18	407
-20	250
-21	188

5,6,L

0	181
1	233
-1	183
2	253
-2	486
3	57*
-3	874
4	414
-4	772
5	287
-5	1286
6	844
-6	194
7	353
-7	752
8	309
-8	937
9	263
-9	57*
10	202
-10	376
11	251
-11	524
12	67*
-12	345
13	519
14	314
-15	535
-16	679
-17	354
-18	606
-20	181

5,7,L

1	281
-1	400
2	295
-3	304
4	524
-4	633
5	230
-6	933
-7	520
8	422
-8	318
9	472
-9	511
-10	225
11	566
12	191
-13	300
-14	594
-15	238
-16	344
-18	258

5,8,L

0	347
1	386
-1	338
2	296
3	208
-4	207
6	349
7	230
9	196
-9	712
10	452
-11	686
-12	293
-13	180
-14	174
-15	192

5,9,L

0	395
-1	152
-2	283
3	149
5	269
6	165
-6	194
-7	159
-8	303
-10	727

6,0,L

0	1271
2	1075
-2	448
4	463
-4	625
6	335
-6	1802
8	182
-8	3451
10	243
-10	2459
12	835
-12	570
14	954
-14	1481
16	271
-16	178
18	291
-18	1126
-20	614
-22	495
-24	627

6,1,L

0	406
1	519
-1	688
2	1569
-2	1034
3	424
-3	636
4	861
-4	928
5	347
-5	1284
6	1055
-6	44*
7	52*
-7	1479
8	1415
-8	456
9	518
-9	1352
10	56*
-10	47*
11	531
-11	1040
12	1334
-12	50*
13	580
-13	511
14	666
-14	411
15	383
16	388
17	298
18	492
-18	951
-20	708
-23	302

6,2,L

0	204
1	660
-1	341
2	505
-2	1742
3	394
-3	44*
4	147
-4	2237
5	139
-5	541
6	332

7,2,L

-7	49*
8	730
-8	1462
9	375
-9	529
10	357
-10	1094
-11	765
-12	1150
-13	419
14	165
-14	2398
-15	189
16	396
-16	1177
-17	273
-19	257
-20	167
-22	391
-23	219

7,3,L

0	387
1	464
-1	51*
2	1035
-2	951
3	867
-3	144
4	54*
-4	1029
5	912
-5	264
6	982
-6	170
7	527
-7	453
8	731
-8	181
9	61*
-9	341
10	513
-10	272

7,3,L

-11	375
12	818
-12	430
-13	874
14	257
15	229
-15	1119
-17	630
-18	358
-19	272
-20	425

7,4,L

0	184
1	305
-1	53*
2	174
-2	527
3	56*
-3	570
4	626
-4	950
5	170
-5	892
6	601
-6	399
7	343
-7	817
8	129
-8	949
9	63*
-9	55*
10	64*
-10	1150
11	245
-11	372
12	420
13	444
-13	208
14	358
-14	693
-15	436
-17	635
-18	948
-20	829
-21	253

7,5,L

0	433
1	352
-1	765
2	770
-2	188
3	135
-3	601
4	222
-4	56*
5	60*
-5	56*
6	608
-6	606
7	286
-7	397
8	487
-8	783
9	591
-9	556
10	66*
-10	272
11	418
-11	330
12	281
-14	343
-15	188
-16	485
-17	166
-19	587
-20	429

7,6,L

0	691
1	504
-1	514
2	324
-2	292
3	183
-3	194
4	152
-4	249
5	179
-5	177
6	65*
-6	170
7	308
-7	60*
8	434
-8	359
9	265
-9	578
10	329
-10	399
-11	954
-12	334
-13	506
-14	687
-16	281
-17	400
-19	220

7,7,L

0	179
-1	276
-2	577
3	446
-3	182
-4	331
5	411
6	196
-7	304
8	155
-9	227
-10	572
-12	644
-13	323
-14	186
-15	416
-16	293

7,8,L

0	321
-3	271
4	327
-4	255
-5	540
-6	278
-7	476
-10	241

7,9,L

-4	180
-6	436

8,0,L

0	146
2	114
-2	806
4	55*
-4	1781
6	248
-6	1237
8	523
-8	294
10	63*
-10	738
-12	825
14	165
-14	2089
-16	1209
-18	369
-20	1003
-22	316

8,1,L

0	1051
1	224
-1	634
2	1113
-2	523
3	54*
-3	872
4	303
-4	1331
5	187
-5	711
6	1080
-6	371
7	183
-7	611
8	557
-8	605
9	159
-9	557
10	519
-10	573
11	248
-11	738
12	561
-12	132
13	288
-13	810
-15	580
-17	328
-18	182
-20	450
-21	190

6,2,L

-6	803
7	53*
-7	367
8	228
-8	1281
9	56*
-9	313
10	435
-10	250
11	169
-11	417
-12	2082
13	358
-14	2265
15	252
-15	629
16	538
-16	364
-17	602
-18	1102
-19	325
-20	766
-23	104

6,3,L

0	48*
1	563
-1	1184
2	845
-2	1150
3	157
-3	1157
4	322
-4	703
5	478
-5	651
6	1266
-6	370
7	294
-7	310
8	1504
-8	619
9	57*
-9	293
10	59*
-10	164
11	61*
-11	811
12	755
-12	351
13	370
-13	1089
14	283
-14	867
15	574
-15	883
16	369
-16	501
17	478
-17	161
-18	372
-19	494
-20	280
-21	582
-22	412
-23	237

6,4,L

0	749
1	321
-1	159
2	731
-2	50*
3	53*
-3	370
4	53*
-4	373
5	611
-5	651
6	417
-6	718
7	829
-7	261
8	58*
-8	2061
9	582
-9	695
10	168
-10	1457

6,4,L

-11	1205
12	432
-12	350
13	180
-13	658
14	627
-14	830
16	256
-16	160
-17	212
-18	740
-20	176
-21	433
-22	451

6,5,L

0	172
1	54*
-1	226
2	903
-2	178
3	525
-3	53*
4	659
-4	137
5	568
-5	453
6	59*
-6	569
7	60*
-7	974
8	427
-8	55*
9	595
-9	1017
10	357
-10	706
11	633
-11	516
12	729
-12	743
13	202
-13	188
14	291
-15	405
-18	591
-19	365
-20	770
-21	298

6,6,L

0	338
1	637
-1	469
2	227
-2	363
3	465
-3	198
4	291
-4	877
5	222
-5	695
6	392
-6	419
7	63*
-7	417
8	192
-8	249
9	65*
-9	192
10	535
-10	60*
11	279
-11	416
12	171
-12	733
13	424
-14	650
-15	715
-17	772
-18	377
-19	378

6,7,L

0	361
1	190
-1	520
-2	565
3	241
-3	406
5	360
-5	155
6	442
-6	384
-7	215
8	523
-8	288
9	237
-10	236
-11	170
-13	476
-14	565
-15	491
-16	705

6,8,L

0	404
2	194
-2	162
3	159
-3	223
4	267
-4	153
5	290
-5	366
6	289
7	422
-7	176
-8	292
-9	349
-10	285
-11	617
-13	420

6,9,L

-1	174
2	176
-4	157
-6	326
-7	175
-9	208
-10	510

7,0,L

0	223
2	159
-2	1269
4	776
-4	1685
6	739
-6	377
8	349
-8	1739
10	313
-10	1912
12	863
14	446
-14	865
16	281
-18	1767
-20	1623
-22	486
-24	224

7,1,L

0	902
1	604
-1	831
2	1447
-2	819
3	425
-3	607
4	232
-4	1030
5	523
-5	264
6	1136
-6	47*
7	758
-7	335
8	969
-8	768
9	603
-9	447
10	346
-10	455
11	533
-11	607
12	939
-12	188
13	215
-13	491
14	162
-14	331
-15	530
16	461
-16	203
-17	390
-18	512
-19	803
-20	667
-21	674
-23	422
-24	572

7,2,L

0	1209
1	488
-1	565
2	1050
-2	48*
3	170
-3	180
4	497
-4	900
5	195
-5	163
6	527
-6	48*
7	278

8,1,L

-23	294

8,2,L

0	771
1	53*
-1	235
2	287
-2	317
3	55*
-3	238
4	144
-4	340
5	278
-5	395
6	58*
-6	52*
7	307
-7	188
-8	1531
8	61*
9	210
-9	53*
10	331
-10	1961
-11	474
12	665
-12	671
-13	458
14	411
-14	789
-16	495
-18	695
-20	817
-21	236
-23	254

8,3,L

0	1081
1	245
-1	54*
2	1119
-2	266
3	415
-3	253
4	58*
-4	557
5	59*
-5	457
6	617
-6	237
7	266
-7	973
8	63*
-8	476
9	493
-9	1000
10	533
-10	215
11	468
-11	711
12	541
-12	357
13	177
-13	234
-14	310
-15	147
-18	277
-19	211
-20	530
-21	251
-22	288

8,4,L

1	630
-1	494
2	58*
-2	148
3	361
-3	157
4	276
-4	917
-5	396
-6	778
-7	447
8	386
-8	57*
-9	57*
10	162
-10	460
-11	524
-12	439
-13	232
-14	1252
-15	446
-16	742
-17	771
-18	234
-19	457
-20	460

8,5,L

0	196
1	60*
-1	634
2	319
-2	559
3	402
-3	779
4	385
-4	679
5	372
-5	318
6	721
-6	130
-7	59*
8	347
-8	471
-9	60*
-10	202
-11	218
-13	569
-14	201
-15	644
-16	561
-17	318
-18	366
-19	204

8,6,L

0	483
1	63*
-1	62*
2	64*
-2	411
3	65*
-3	245
4	352
-4	143
5	395
-5	411
6	67*
-6	176
-7	372
8	164
-8	402
-12	302
-13	564
-14	235
-18	243

8,7,L

0	363
-1	223
2	391
3	314
-3	255
5	155
-6	240
-7	316
-8	279
-9	374
-11	274
-12	523
-14	331
-15	190

8,8,L

0	225
1	314
-1	366
-2	268
-3	151
-4	163
-5	175
-6	343
-7	226
-11	196

9,0,L

0	924
2	606
-2	527
4	584
-4	380
6	627
-6	397
8	473
-8	504
-10	1178
12	301
-14	1309
-16	1489
-18	289
-20	403

9,1,L

0	1233
1	598
-1	422
2	830
3	658
-3	376
4	495
-4	1160
5	468
-5	360
6	864
-6	692
7	265
-7	345
-8	323
10	538
-10	531
-11	157
12	344
-13	503
-15	572
-17	499
-18	251
-19	366
-20	320
-21	281

9,2,L

0	202
1	190
-1	144
2	579
-2	381
-3	207
4	568
-4	922
-5	497
-6	793
-7	424
-8	326
-9	187
10	405
-10	1053
12	446
-12	555
-14	599
-16	436
-17	350
-18	612
-19	181
-20	1147
-21	179
-22	646

9,3,L

0	1025
1	208
-1	713
2	660
-3	786
4	419
-4	645
5	233
-5	326
6	657
-6	204
7	333
8	153
-8	542
9	380
-9	353
10	356
-10	650
11	232
-11	275
-12	231
-16	172
-19	354
-20	272
-21	611

9,4,L

0	636
1	368
-1	503
2	163
-2	670
-3	235
5	243
6	404
-6	284
7	362
-7	143
8	316
-8	222
9	210
-9	272
-10	713
-11	717
-13	631
-14	749
-16	910
-17	230
-19	264
-20	262

9,5,L

0	453
1	406
2	322
-2	289
3	596
-3	201
4	214
-4	768
5	423
-5	141
6	372
-6	381
-7	360
8	159
-9	406
-12	432
-13	299
-14	369
-15	521
-17	369

9,6,L

2	384
-2	183
-3	199
4	368
-4	260
-5	486
-6	428
-7	559
-9	231
-10	345
-12	290
-15	193
-16	211

9,7,L

0	276
-1	339
2	172
3	164
-3	396
-5	157
-6	232
-8	446
-9	163
-10	228

10,0,L

0	257
-2	334
-8	484
10	460
-10	1374

10,0,L

-12	1038
-16	664
-20	773

10,1,L

0	1272
-1	141
2	478
-2	415
4	587
-4	758
-5	598
6	584
-6	740
7	234
-7	468
-8	176
9	268
-9	593
10	341
-10	640
-11	556
-12	271
-13	393
-14	216
-15	263
-16	223
-19	196
-20	269

10,2,L

1	332
-1	330
2	160
3	174
-4	704
6	447
-6	881
-7	272
8	253
-8	328
10	163
-10	292
-11	207
-13	180
-14	914
-16	1111
-17	255
-18	265
-19	332
-20	473

10,3,L

0	718
1	167
-1	365
2	158
-2	141
3	353
-3	669
4	670
-4	922
5	229
-5	541
6	584
-6	692
-7	183
-10	507
-11	224
-12	257
-13	485
-15	575
-17	340
-18	166

10,4,L

0	167
2	217
-2	470
3	211
5	237
-5	417
6	164
-6	175
7	288
-7	360
-8	270
-10	743
-11	286
-12	683
-13	462
-15	218
-16	342

10,5,L

0	746
1	160
2	341
-2	298
3	234
-3	237
4	179
-4	303
-6	188
-7	421
-8	166
-9	532
-10	195
-11	329
-12	156
-14	363
-16	186

10,6,L

1	357
-1	408
2	228
-2	261
3	196
-3	242
-6	405
-7	165
-8	319
-11	220
-13	200
-14	238

10,7,L

-3	311
-4	320
-5	162
-8	178

11,0,L

0	522
2	559
-2	229
-4	485
-6	589
8	198
-8	242
-10	529
-12	536
-16	623
-20	696

11,1,L

0	909
1	310
-1	465
-2	626
3	276
-3	538
4	651
-4	475
5	215
-5	484
6	360
-6	752
7	202
-7	219
-10	584
-12	431
-16	177
-17	188
-19	329

11,2,L

0	303
1	206
-1	229
2	252
-2	513
4	460
-4	298
6	402
-7	149
-10	480
-11	252
-12	419
-13	307
-14	321
-16	823
-18	459

11,3,L

0	694
1	495
-1	212
-2	384
3	511
4	452
-4	564
5	270
6	201
-6	830
-7	330
-8	164
-9	320
-10	295
-11	162
-14	263
-15	324
-16	285
-17	322

11,4,L

0	298
1	192
2	424
-4	188
-5	361
-6	509
-7	488
-8	299
-9	231
-10	162
-12	352
-16	294

11,5,L

0	416
-1	350
-2	343
-3	559
-4	213
-5	328
-6	237
-8	219
-9	211
-10	402
-12	232

11,6,L

-2	368
-3	232
-4	346
-10	159

12,0,L

0	173
4	408
-6	544
-8	346
-12	196
-14	340
-16	806

12,1,L

0	569
2	212
-2	625
3	231
-3	227
4	564
-4	287
-5	350
-6	790
-7	296
-8	297
-9	175
-10	356
-11	223
-12	467
-13	321
-15	257
-16	211
-17	243

12,2,L

0	207
-2	160
-5	177
-7	183
-10	433
-12	670
-13	199
-14	282
-15	166
-16	201

12,3,L		12,4,L		13,0,L		-7	227	-12	234
						-8	476		
0	553	-1	355	-4	349	-9	260	13,3,L	
-2	660	-3	244	-10	242	-10	171		
-6	571	-6	294	-12	357	-12	372	-5	416
-7	297	-7	175					-6	408
-9	416	-8	392	13,1,L		13,2,L		-7	256
-10	295	-13	220					-10	279
-11	328			0	363	-2	319		
-12	290	12,5,L		-1	184	-4	189		
-13	181			-2	632	-6	264		
		-5	261	-5	204	-7	197		
		-6	441	-6	672	-8	292		

Structure Factor Tables for

Perfluorotribenzo(b,e,h)(1,4,7)trimercuronin.4-phenylpyridine.

H	K	L	FO	FC
0	2	0	63	-36
0	4	0	152	-133
0	8	0	425	-460
0	10	0	467	-463
0	12	0	196	217
0	1	1	216	191
0	2	1	501	-558
0	3	1	118	-91
0	4	1	19	-16
0	5	1	123	138
0	6	1	178	-165
0	7	1	30	9
0	8	1	384	-390
0	9	1	278	-276
0	10	1	488	436
0	11	1	118	118
0	12	1	160	160
0	0	2	375	-400
0	1	2	340	-350
0	2	2	88	-32
0	3	2	161	-165
0	4	2	51	-25
0	5	2	76	96
0	6	2	111	-111
0	7	2	324	-315
0	8	2	186	198
0	9	2	63	51
0	10	2	300	331
0	11	2	287	224
0	12	2	52	-35
0	1	3	164	-162
0	2	3	108	85
0	3	3	50	48
0	4	3	110	111
0	5	3	91	-90
0	6	3	35	37
0	7	3	126	112
0	8	3	59	51
0	9	3	276	260
0	10	3	36	-40
0	11	3	38	31
0	12	3	156	-148
0	0	4	58	51
0	1	4	29	17
0	3	4	123	112
0	4	4	113	-108
0	5	4	200	201
0	6	4	22	-26
0	7	4	150	140
0	9	4	55	47
0	10	4	137	-127
0	11	4	106	-111
0	12	4	58	59
0	1	5	64	69
0	2	5	83	-95
0	3	5	137	180
0	4	5	115	110
0	5	5	96	-98
0	6	5	35	49
0	7	5	192	-187
0	8	5	137	-137
0	9	5	61	-62
0	10	5	110	99
0	11	5	262	-269
0	0	6	143	-139
0	2	6	154	157
0	3	6	127	-134
0	4	6	101	95
0	5	6	154	-151
0	6	6	228	-224
0	7	6	36	-37
0	8	6	49	52
0	9	6	28	-26
0	11	6	58	56
0	12	6	175	-167
0	1	7	104	-101
0	2	7	121	115
0	3	7	34	25
0	4	7	236	-235
0	6	7	51	-36
0	8	7	140	136
0	9	7	115	116
0	10	7	149	-148
0	11	7	47	41
0	12	7	85	83
0	0	8	59	62
0	1	8	119	121
0	2	8	124	-123
0	4	8	79	-85
0	5	8	61	-60
0	6	8	159	160
0	7	8	123	122
0	11	8	86	-89
0	12	8	131	126
0	1	9	53	53
0	3	9	99	-106
0	4	9	86	94
0	5	9	51	50
0	6	9	52	53
0	7	9	27	32
0	9	9	93	-96
0	11	9	51	9
0	12	9	31	-31
0	0	10	40	48
0	2	10	26	31
0	5	10	44	51
0	7	10	36	-41
0	8	10	49	-45
0	10	10	21	-24
0	11	10	27	32
0	1	11	17	18
0	14	0	162	-164
0	16	0	37	-52
0	18	0	415	441
0	20	0	98	-89
0	24	0	133	131
0	26	0	181	-179
0	28	0	118	-122
0	30	0	66	71
0	32	0	43	-54
0	13	1	43	50
0	14	1	70	-64
0	15	1	111	-111
0	16	1	350	358
0	17	1	166	166
0	18	1	23	17
0	19	1	36	36
0	20	1	280	-273
0	21	1	61	-57
0	22	1	22	23
0	23	1	21	-18
0	24	1	88	-94
0	25	1	35	-41
0	26	1	167	-166
0	27	1	82	-80
0	28	1	99	107
0	29	1	29	33
0	30	1	49	50
0	31	1	17	-20
0	13	2	74	-67
0	14	2	31	23
0	15	2	168	167
0	16	2	36	31
0	17	2	157	152
0	18	2	211	-218
0	19	2	183	-187
0	20	2	85	-84
0	22	2	20	19
0	23	2	21	-17
0	24	2	31	-37
0	25	2	117	-117
0	26	2	51	51
0	27	2	56	56
0	28	2	111	126
0	29	2	37	43
0	30	2	26	-27
0	31	2	20	-22
0	32	2	15	-15
0	13	3	25	-18
0	14	3	29	-23
0	15	3	72	61
0	17	3	178	-179
0	18	3	96	-97
0	19	3	106	-103
0	20	3	105	101
0	21	3	34	32
0	22	3	80	84
0	24	3	34	-36
0	25	3	41	42
0	26	3	99	103
0	27	3	103	112
0	29	3	27	26
0	30	3	89	-94
0	31	3	14	11
0	13	4	200	-175
0	15	4	93	87
0	15	4	133	-114
0	16	4	71	-64
0	17	4	54	-55
0	18	4	65	59

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
0	21	4	97	100	0	27	6	31	-40	-1	7	8	44	45	-1	4	6	73	-68	-1	24	5	24	-17
0	22	4	77	-75	0	14	7	185	182	-1	8	8	92	91	-1	6	6	23	28	-1	25	5	77	77
0	23	4	75	75	0	16	7	96	-96	-1	9	8	104	106	-1	7	6	80	-71	-1	26	5	21	19
0	25	4	25	25	0	17	7	66	-64	-1	10	8	110	-101	-1	9	6	148	-129	-1	28	5	71	-82
0	26	4	44	44	0	18	7	28	20	-1	11	8	91	81	-1	10	6	25	-4	-1	29	5	55	-66
0	27	4	33	35	0	19	7	69	-71	-1	12	8	66	64	-1	11	6	115	-103	-1	1	4	278	-268
0	28	4	71	-83	0	20	7	56	57	-1	14	8	94	88	-1	13	6	38	26	-1	2	4	190	167
0	29	4	34	-44	0	22	7	108	-123	-1	16	8	73	-62	-1	16	6	43	-40	-1	3	4	204	187
0	13	5	26	12	0	24	7	19	-22	-1	17	8	31	-28	-1	17	6	53	50	-1	4	4	121	118
0	14	5	126	-108	0	13	8	56	55	-1	19	8	83	-88	-1	18	6	76	57	-1	5	4	126	-124
0	15	5	125	112	0	14	8	63	-54	-1	20	8	41	42	-1	19	6	133	116	-1	6	4	81	90
0	16	5	73	59	0	15	8	40	-39	-1	22	8	58	-68	-1	20	6	34	-31	-1	7	4	30	-24
0	18	5	58	47	0	16	8	78	-77	-1	23	8	17	27	-1	22	6	40	-42	-1	8	4	105	104
0	19	5	137	125	0	17	8	64	-67	-1	0	7	71	-70	-1	23	6	47	-41	-1	9	4	385	376
0	20	5	96	-86	0	18	8	22	26	-1	2	7	51	53	-1	24	6	23	23	-1	10	4	88	-93
0	21	5	90	87	0	19	8	61	68	-1	3	7	92	-93	-1	26	6	36	-42	-1	11	4	99	-101
0	22	5	43	40	0	20	8	60	-71	-1	4	7	78	70	-1	27	6	63	-76	-1	12	4	170	-158
0	23	5	70	-71	0	22	8	29	-35	-1	5	7	102	-104	-1	0	5	49	54	-1	13	4	94	-89
0	24	5	44	46	0	13	9	32	34	-1	6	7	51	-45	-1	1	5	206	202	-1	14	4	73	-65
0	26	5	45	-51	0	14	9	71	-77	-1	7	7	65	-64	-1	2	5	129	132	-1	15	4	199	169
0	27	5	22	-24	0	15	9	55	-59	-1	9	7	55	-50	-1	3	5	143	136	-1	16	4	121	-104
0	28	5	20	23	-1	4	9	46	-48	-1	10	7	39	27	-1	4	5	98	79	-1	17	4	237	-196
0	29	5	71	-86	-1	6	9	107	112	-1	11	7	101	95	-1	6	5	72	-63	-1	18	4	71	-67
0	13	6	151	148	-1	7	9	90	90	-1	12	7	78	-68	-1	7	5	208	197	-1	19	4	141	-127
0	14	6	88	84	-1	11	9	74	-74	-1	13	7	138	116	-1	8	5	26	-6	-1	20	4	148	133
0	15	6	40	41	-1	12	9	94	97	-1	15	7	41	33	-1	9	5	24	14	-1	21	4	119	106
0	16	6	120	114	-1	14	9	52	-54	-1	16	7	45	43	-1	10	5	112	-107	-1	22	4	49	48
0	17	6	44	38	-1	15	9	29	-26	-1	17	7	65	61	-1	11	5	224	-207	-1	23	4	32	-30
0	18	6	101	-92	-1	16	9	49	-49	-1	18	7	54	-45	-1	12	5	85	-86	-1	24	4	47	47
0	19	6	34	29	-1	17	9	58	-66	-1	21	7	97	-98	-1	14	5	79	73	-1	26	4	87	86
0	20	6	80	77	-1	18	9	26	28	-1	22	7	30	32	-1	15	5	112	-94	-1	27	4	124	129
0	21	6	92	-93	-1	19	9	30	39	-1	23	7	25	-27	-1	17	5	149	-124	-1	28	4	17	-18
0	22	6	53	57	-1	1	8	72	-74	-1	24	7	30	-35	-1	19	5	114	100	-1	29	4	18	-24
0	23	6	30	-35	-1	2	8	78	76	-1	1	6	103	110	-1	20	5	140	120	-1	30	4	61	-68
0	24	6	76	-85	-1	4	8	132	-133	-1	2	6	22	-28	-1	21	5	47	47	-1	0	3	1041	-1135
0	26	6	16	20	-1	6	8	29	-34	-1	3	6	47	39	-1	22	5	24	-21	-1	1	3	609	-626

H	K	L	FO	FC
1	28	2	22	22
1	29	2	73	74
1	30	2	75	-81
1	31	2	21	24
1	0	3	100	78
1	1	3	145	-146
1	2	3	96	-95
1	3	3	267	261
1	4	3	80	-51
1	5	3	418	391
1	6	3	171	152
1	7	3	68	-60
1	9	3	68	65
1	10	3	51	-44
1	12	3	67	72
1	13	3	348	-327
1	15	3	117	-104
1	16	3	155	-141
1	17	3	63	56
1	18	3	69	67
1	19	3	116	-115
1	20	3	27	18
1	21	3	118	120
1	22	3	100	-99
1	23	3	131	128
1	24	3	51	50
1	25	3	40	-42
1	26	3	31	30
1	27	3	44	48
1	28	3	49	-50
1	30	3	33	37
1	31	3	80	-95
1	1	4	89	84
1	2	4	175	-172
1	3	4	228	232
1	4	4	294	286
1	5	4	150	-138
1	6	4	59	58
1	7	4	157	-153
1	8	4	232	-215
1	9	4	57	43
1	10	4	214	189
1	11	4	282	-253
1	12	4	108	-97
1	13	4	78	-70
1	14	4	259	-234
1	15	4	210	180
1	16	4	149	132
1	19	4	83	81
1	20	4	110	-98
1	21	4	136	129
1	22	4	150	146
1	23	4	61	-64
1	24	4	42	42
1	25	4	35	-38
1	26	4	70	-71
1	28	4	53	58
1	29	4	78	-89
1	0	5	239	-247
1	1	5	20	9
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1	4	5	169	178
1	5	5	145	-139
1	6	5	359	-350
1	7	5	34	-27
1	8	5	82	76
1	10	5	74	75
1	12	5	303	-275
1	13	5	92	90
1	14	5	158	140
1	15	5	75	71
1	16	5	167	142
1	18	5	120	-110
1	20	5	154	146
1	21	5	53	-48
1	22	5	66	65
1	23	5	50	-50
1	24	5	134	-142
1	26	5	25	27
1	1	6	76	-76
1	2	6	124	119
1	3	6	90	82
1	4	6	321	-321
1	5	6	28	-18
1	6	6	101	-88
1	8	6	145	140
1	9	6	105	103
1	10	6	159	-158
1	11	6	27	-18
1	12	6	86	80
1	14	6	226	212
1	16	6	79	-71
1	17	6	89	-87
1	19	6	29	-23
1	20	6	76	77
1	22	6	145	-148
1	23	6	35	-38
1	24	6	40	-39
1	25	6	21	21
1	26	6	38	43
1	1	7	96	96
1	2	7	118	-118
1	4	7	83	-87
1	5	7	72	-73
1	6	7	143	141
1	7	7	119	122
1	8	7	65	68
1	11	7	62	-67
1	12	7	115	110
1	13	7	77	81
1	14	7	26	-23
1	15	7	31	-23
1	16	7	101	-94
1	17	7	40	-34
1	19	7	61	64
1	20	7	55	-57
1	21	7	31	-29
1	22	7	45	-51
1	23	7	18	-17
1	24	7	48	60
1	2	8	52	46
1	3	8	66	-72
1	4	8	79	83
1	5	8	37	39
1	6	8	79	83
1	7	8	35	30
1	9	8	33	-30
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1	12	8	23	-19
1	13	8	28	24
1	14	8	88	-83
1	15	8	42	-40
1	16	8	37	-33
1	18	8	33	34
1	21	8	24	-31
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1	7	9	31	30
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1	11	9	27	-21
1	12	9	26	-30
1	15	9	29	-26
1	16	9	49	55
1	1	10	56	55
1	4	10	40	-49
1	6	10	32	-34
1	9	10	61	-66
1	3	0	128	-113
-2	1	11	40	50
-2	3	11	33	-41
-2	4	11	43	56
-2	1	10	34	42
-2	2	10	36	-43
-2	3	10	33	40
-2	6	10	41	41
-2	7	10	48	50
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-2	14	10	26	-25
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-2	3	8	83	-89
-2	4	8	41	-44
-2	5	8	61	-68
-2	6	8	49	42
-2	7	8	59	-62
-2	9	8	39	-30
-2	11	8	87	82

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
-2	12	8	60	55	-2	12	6	85	-85	-2	26	5	58	55	-2	5	3	88	76	-2	13	2	94	90
-2	13	8	75	68	-2	13	6	124	101	-2	27	5	106	110	-2	6	3	193	-195	-2	15	2	228	230
-2	14	8	48	-43	-2	14	6	43	31	-2	28	5	33	-37	-2	7	3	106	116	-2	16	2	38	43
-2	17	8	58	54	-2	15	6	70	-57	-2	29	5	32	-37	-2	8	3	246	-258	-2	18	2	187	185
-2	19	8	22	-8	-2	16	6	53	46	-2	1	4	235	-245	-2	10	3	317	312	-2	19	2	53	-56
-2	20	8	51	-53	-2	17	6	186	-159	-2	3	4	19	21	-2	11	3	66	57	-2	20	2	30	24
-2	21	8	59	-66	-2	18	6	51	40	-2	4	4	103	88	-2	12	3	71	68	-2	21	2	38	40
-2	1	7	140	151	-2	19	6	173	154	-2	5	4	214	215	-2	13	3	93	82	-2	23	2	108	-108
-2	3	7	54	-55	-2	20	6	89	78	-2	6	4	171	-176	-2	14	3	53	-44	-2	25	2	78	-79
-2	4	7	143	-136	-2	23	6	32	-33	-2	7	4	164	-169	-2	15	3	103	-83	-2	26	2	62	-65
-2	5	7	34	29	-2	24	6	32	-29	-2	8	4	278	296	-2	16	3	294	282	-2	27	2	82	86
-2	8	7	28	31	-2	25	6	95	103	-2	9	4	47	-47	-2	17	3	85	-77	-2	28	2	74	-82
-2	9	7	204	-184	-2	1	5	221	-219	-2	10	4	267	263	-2	18	3	37	-38	-2	29	2	29	-29
-2	10	7	63	-56	-2	2	5	215	219	-2	11	4	160	151	-2	19	3	49	41	-2	1	1	58	71
-2	12	7	90	83	-2	3	5	295	287	-2	12	4	89	-97	-2	20	3	179	-178	-2	2	1	13	-34
-2	13	7	63	54	-2	4	5	124	112	-2	13	4	166	-159	-2	21	3	35	-37	-2	3	1	146	144
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2	16	7	52	-52	2	6	10	65	78	-3	8	8	55	55	-3	2	6	122	130	-3	13	5	114	-105
2	17	7	54	-54	2	7	10	47	-53	-3	9	8	195	-181	-3	3	6	156	147	-3	14	5	55	53
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5	3	0	148	-150
5	4	0	47	49
5	5	0	20	13
5	6	0	118	127
5	8	0	179	182
5	9	0	57	56
5	10	0	191	-194

H	K	L	FO	FC
5	11	0	119	119
5	12	0	143	-147
5	13	0	53	-49
5	14	0	32	-31
5	16	0	163	-172
5	17	0	41	38
5	19	0	109	-111
5	20	0	144	149
5	22	0	22	13
5	23	0	98	98
5	24	0	83	82
5	25	0	47	-48
5	26	0	85	80
5	27	0	29	29
5	28	0	51	-49
5	29	0	64	68
5	30	0	44	-46
5	1	1	101	91
5	2	1	55	40
5	3	1	168	-149
5	4	1	73	-76
5	5	1	48	51
5	6	1	192	193
5	7	1	129	145
5	8	1	308	-312
5	9	1	32	30
5	10	1	212	-216
5	11	1	165	-177
5	12	1	148	145
5	13	1	84	-74
5	14	1	145	-146
5	15	1	42	-36
5	17	1	107	-116
5	18	1	228	231
5	19	1	46	40
5	21	1	104	112

H	K	L	FO	FC
5	24	1	86	86
5	25	1	41	38
5	26	1	102	-107
5	27	1	42	38
5	28	1	48	-51
5	29	1	55	-60
5	30	1	29	37
5	1	2	235	253
5	2	2	230	-241
5	3	2	154	-159
5	4	2	158	152
5	5	2	95	85
5	6	2	144	-129
5	7	2	37	-28
5	8	2	197	-192
5	9	2	344	-344
5	10	2	209	209
5	13	2	57	52
5	14	2	81	-63
5	15	2	116	-100
5	16	2	196	187
5	17	2	162	161
5	18	2	25	-17
5	19	2	139	138
5	20	2	100	-103
5	21	2	84	-81
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5	23	2	33	34
5	24	2	73	-71
5	26	2	62	-64
5	27	2	118	-123
5	28	2	58	62
5	0	3	87	-97
5	1	3	264	-276
5	3	3	103	-113
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H	K	L	FO	FC
5	5	3	129	122
5	6	3	98	-84
5	7	3	353	-340
5	8	3	56	55
5	10	3	85	76
5	11	3	302	288
5	12	3	98	-90
5	13	3	68	-67
5	14	3	36	27
5	15	3	136	129
5	17	3	187	175
5	18	3	69	-61
5	19	3	165	-162
5	21	3	57	-49
5	23	3	23	26
5	24	3	42	-40
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5	2	4	50	-42
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5	5	4	98	-102
5	6	4	31	-28
5	8	4	34	-27
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5	11	4	28	14
5	13	4	50	-48
5	15	4	100	102
5	16	4	36	34
5	17	4	168	-153
5	18	4	31	-30
5	19	4	133	-133
5	21	4	81	75
5	23	4	52	-51
5	24	4	43	-44

H	K	L	FO	FC
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5	3	5	93	98
5	6	5	40	-42
5	7	5	129	128
5	8	5	98	106
5	10	5	67	67
5	11	5	128	-121
5	12	5	53	-49
5	13	5	57	-58
5	14	5	55	54
5	15	5	38	-36
5	16	5	47	-39
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5	18	5	67	-68
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5	14	6	58	-62
5	16	6	52	-48
5	19	6	73	76
5	20	6	19	22
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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
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5	4	7	27	28	-6	15	10	25	27	-6	2	7	182	193	-6	23	6	54	-59	-6	13	4	56	-45
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5	9	7	50	-55	-6	2	9	44	-46	-6	4	7	127	-130	-6	25	6	17	14	-6	18	4	99	95
5	11	7	26	23	-6	3	9	42	-43	-6	6	7	38	27	-6	26	6	42	49	-6	20	4	116	124
5	12	7	53	-52	-6	4	9	65	69	-6	7	7	71	68	-6	2	5	88	-92	-6	21	4	24	26
5	13	7	31	30	-6	5	9	37	36	-6	8	7	183	186	-6	3	5	136	141	-6	22	4	46	-49
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5	16	7	37	39	-6	9	9	124	-123	-6	10	7	164	-151	-6	5	5	116	-114	-6	28	4	94	-104
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5	10	8	30	-30	-6	2	8	86	-93	-6	22	7	69	-71	-6	14	5	31	29	-6	9	3	62	57
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-6	6	2	94	-94	-6	19	1	93	-91	6	1	1	236	238	6	17	2	135	127	6	12	4	35	30
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-6	22	2	43	39	6	4	0	160	-154	6	16	1	120	119	6	7	3	26	23	6	10	5	46	42
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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
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6	20	6	71	84	-7	4	6	129	-124	-7	9	4	81	79	-7	25	3	19	-22	-7	7	1	208	-209
6	2	7	33	39	-7	6	6	86	-80	-7	10	4	115	-114	-7	26	3	74	80	-7	8	1	92	-97
6	3	7	70	81	-7	8	6	39	-35	-7	11	4	134	-125	-7	27	3	25	22	-7	10	1	129	-125
6	4	7	136	-141	-7	9	6	45	-38	-7	12	4	110	-100	-7	28	3	55	63	-7	11	1	181	182
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6	8	7	36	31	-7	20	6	72	-70	-7	17	4	53	-46	-7	4	2	226	213	-7	15	1	141	145
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6	10	7	48	-51	-7	0	5	141	146	-7	20	4	109	110	-7	6	2	101	-80	-7	17	1	71	76
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6	3	8	31	-32	-7	11	5	55	-52	-7	4	3	82	92	-7	15	2	57	-58	-7	27	1	26	25
6	5	8	92	-99	-7	12	5	51	-51	-7	5	3	185	202	-7	16	2	191	195	-7	28	1	40	-41
-7	21	8	21	-27	-7	13	5	103	100	-7	6	3	203	-207	-7	17	2	93	-96	7	1	0	271	243
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-7	8	7	78	70	-7	20	5	105	103	-7	12	3	186	-167	-7	24	2	46	-51	7	6	0	65	64
-7	9	7	44	-43	-7	22	5	29	-53	-7	13	3	205	-196	-7	25	2	42	45	7	7	0	70	-67
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-7	21	7	55	-58	-7	3	4	177	189	-7	19	3	41	-45	-7	1	1	158	-154	7	13	0	33	-26
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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
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7	18	0	34	36	7	3	2	123	-113	7	23	3	22	25	7	5	6	50	-52	-9	15	8	63	-84
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-8	6	7	41	-45	-8	9	5	71	74	-8	7	3	121	121	-8	26	2	18	16	8	24	0	24	-29
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-8	9	7	73	-68	-8	11	5	152	-136	-8	9	3	180	157	-8	3	1	73	69	8	1	1	49	45
-8	11	7	50	45	-8	12	5	51	-51	-8	10	3	171	145	-8	4	1	49	-57	8	2	1	25	-14
-8	12	7	89	80	-8	13	5	91	-79	-8	11	3	63	52	-8	6	1	108	-110	8	3	1	197	-189
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-1	8	2	396	-401	-1	14	1	143	-145	1	10	0	226	243	1	15	1	239	231	1	25	2	73	73
-1	9	2	180	-174	-1	17	1	34	18	1	11	0	28	34	1	16	1	34	28	1	26	2	54	55
-1	10	2	517	479	-1	18	1	386	390	1	12	0	136	134	1	17	1	35	41	1	27	2	24	22

H	K	L	FO	FC
8	13	2	112	-98
8	14	2	90	-85
8	16	2	121	-118
8	17	2	49	51
8	18	2	33	32
8	19	2	74	-74
8	20	2	98	-98
8	22	2	50	-51
8	23	2	29	31
8	24	2	78	85
8	1	3	45	-46
8	2	3	98	-101
8	4	3	245	248
8	6	3	74	71
8	8	3	109	-108
8	9	3	62	62
8	10	3	114	108
8	12	3	101	-96
8	14	3	193	-187
8	16	3	67	69
8	17	3	25	-29
8	18	3	21	-20
8	19	3	27	-28
8	20	3	53	-54
8	22	3	107	118
8	0	4	72	-79
8	1	4	26	-30
8	2	4	113	118
8	3	4	35	38
8	4	4	67	77
8	5	4	75	83
8	6	4	138	-143
8	12	4	149	-144
8	13	4	93	-95
8	14	4	50	53
8	16	4	75	75
8	18	4	40	-41
8	20	4	56	67
8	21	4	41	47
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8	4	5	63	-64
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8	15	5	59	65
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8	13	6	53	64
8	1	7	46	-59
8	7	7	24	30
-8	3	2	94	-92
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-7	3	1	122	-123
-7	1	11	52	-66
8	11	6	21	22
2	8	10	37	-48
-2	0	4	498	-499
3	12	9	47	58
4	5	0	244	267
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-7	5	10	24	25
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-7	9	10	89	-95
-7	10	10	52	52
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-7	12	8	32	-28
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-7	16	8	94	-85
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