STRUCTURAL STUDIES OF NITRATO COBALT COMPLEXES, YLIDES AND TWO RELATED ORGANIC MOLECULES BY X-RAY ANALYSIS.

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SUMMARY

In this thesis the techniques of crystal structure analysis are applied to the study of bonding and molecular conformations in three classes of compounds. The contents are divided into four parts ; in PART I historical and theoretical aspects of structure determination are surveyed, with particular emphasis being placed on those techniques which were used in the present studies.

PART II is concerned with the study of five nitrato-cobalt complexes. In an introduction, aspects of the co-ordinated nitrato group are surveyed, with particular emphasis being placed on the rationalization of the distortions observed in co-ordinated nitrato groups relative to the symmetrical (D_{3h}) structure of the free nitrate ion. This is followed by a description of the analyses of three novel cobalt complexes of formula $[CoA_2(NO_3)Cl]_2$, [A = pyridine, acetonitrile and tetrahydrofuran]. The three complexes are found to be centrosymmetric dimers, with asymmetrically bridging chlorine atoms. The monomeric units are described as octahedra and as sharing a meridional edge. The octahedra exhibit grossly distorted geometries, the distortions being accountable in terms of the severe constraint imposed by the short 'bite' of the nitrato group on two cis octahedral sites.

Many physical techniques have been used in attempts to rationalize the structures of series of nitrato-metal complexes. In particular, spectroscopic evidence suggested that complexes

of formula $MA_2(NO_3)_2$ [A = amine, M = Co(II), Ni(II), Cu(II) and Zn(II)] have structures which are similar to that observed for $Co(Me_3PO)_2(NO_3)_2$, ie six co-ordinate with cis-bidentate nitrato groups. However no previous analyses had revealed this stereochemistry.. Thus it was of interest to investigate the structures of $CoA_2(NO_3)_2$ [A = pyridine, acetonitrile], the results of which are reported in the final section of PART II. Both analyses have revealed monomeric molecular structures having quasi C_2 symmetry, and with geometries in accord with the above mentioned prediction.

PART III is devoted to a study of ylides. In an introduction, some aspects of the chemistry of ylides containing second-row 'onium species are surveyed, with particular reference to their marked stability relative to their first-row analogues. In view of the paucity of data on S(VI) 'onium ylides, the crystal and molecular structures of three dimethylsulphoxonium ylides were undertaken. The results are presented in the following three sections, and compared with their sulphur(IV) analogues and other related systems. The final section of PART III is devoted to a discussion of aspects of these analyses that are of overall relevance to the study of such systems. The literature is surveyed in tabular form, and the competition of 'onium and stabilizing groups to delocalize the negative charge on the anionic atom is discussed. Finally the conformations of ylide structures are discussed in terms of the steric requirements for electron delocalization and the minimization of non-bonding interactions.

Accounts of the structure analyses of two xanthene-9-spiro-4'-piperidine derivatives are contained in PART IV. These are the first of a series of related compounds which it is proposed to study in this laboratory. The observed geometries of the two molecules are accountable in terms of the theory of isovalent hybridization and also in terms of intramolecular non-bonded interactions.

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PART I

ASPECTS OF CRYSTAL STRUCTURE ANALYSIS

1.1 HISTORICAL

The beauty of crystals has aroused the curiosity of man from earliest times and, as early as 1665, the regular external forms of native crystals had evoked speculation regarding their ultimate structure(1). Subsequent work spread over a period of about 200 years led to the development of a geometrical theory of crystallography(2).

In 1784, Abbe R J Haüy discovered the fundamental law of rational indices from observations on cleavage directions in calcite, and this led him to envisage a model of the crystalline state as a lattice of crystal units(3). Interest soon became focussed on this geometrical abstraction and by 1848 Auguste Bravais had demonstrated that only 14 distinct types of space lattice are possible(4). Combination of the lattice operation with the symmetry operations of the 32 point groups led the German mathematician Schönflies to derive the 230 possible space groups. The same results were achieved independently and almost simultaneously by Federov and Barlow(5). However, although these theories were complete by 1894, they aroused little interest until 1919, when Niggli(6) showed how the space groups of crystals could be determined by X-ray studies.

X-rays were discovered by Röntgen in 1895, but until 1912 the nature of this very penetrating radiation was unknown. However, in 1912, the experiments of von Laue, Friedrich and Knipping showed that a crystal could act as a three-dimensional diffraction grating for X-rays(7). This discovery, besides establishing the nature of X-rays, provided a powerful physical means of examining crystals on the atomic scale. This technique was immediately taken up and developed by the Braggs(8), who realised that the resulting intensity-weighted diffraction pattern could be used in the elucidation of crystal structures.

Initially, due to limited knowledge and the enormous labour of computation involved, this technique could only be applied to the study of simple inorganic structures. However, with the advent of fast electronic computers and highly sophisticated methods of analysis, it has become possible to solve increasingly complex structures such as proteins and nucleic acids(9).

The remainder of this section is devoted to a survey of the theory and techniques used in the structure analysis of the compounds which are the subject of this thesis.

1.2 THE BRAGG EQUATION

After the discovery of the diffraction of X-rays by crystals, von Laue described the crystalline state as a three-dimensional diffraction grating and showed that the phenomenon of diffraction could be described in terms of a set of equations :

$$\underline{a}.(\underline{S} - \underline{S}_0) = h\lambda$$
$$\underline{b}.(\underline{S} - \underline{S}_0) = k\lambda$$
$$\underline{c}.(\underline{S} - \underline{S}_0) = l\lambda$$

where,

$\underline{a}$, $\underline{b}$ and $\underline{c}$ are the vectors which define the unit cell,

$\underline{S}$ and $\underline{S}_0$ are unit vectors in the directions of the incident and diffracted rays,

λ is the X-ray wavelength,

and h, k, l are integers, called Laue orders(10).

However, these Laue conditions were not in a suitable mathematical form for the interpretation of experimental results(11). But, if a lattice array of atoms scatters in the Laue orders h, k, l, this requires all points on the crystallographic plane (hkl) to scatter in phase, which is geometrically equivalent to reflection of the X-rays by atoms in the crystallographic plane (hkl)(12). This provides an alternative description of diffraction as reflection from stacks of parallel, equally-spaced planes (hkl). The condition for constructive interference becomes

$$2d(hkl)\sin\theta = n\lambda$$

where,

d(hkl) is the interplanar spacing,

λ is the wavelength of the radiation,

θ is the grazing angle of incidence, and

n is an integer

This is the Bragg equation(13).

1.3 THE RECIPROCAL LATTICE

From Bragg's law it follows that sin θ is inversely proportional to d(hkl). However it is advantageous to substitute this inverse relationship by a direct one and introduce the concept of the reciprocal lattice defined by $\underline{a}^*$, $\underline{b}^*$ and $\underline{c}^*$, where

$$\underline{a}^* = \frac{\underline{b} \cdot \underline{c}}{\underline{a} \cdot \underline{b} \times \underline{c}}$$

with similar expressions for $\underline{b}^*$ and $\underline{c}^*$, and $\underline{a}$, $\underline{b}$ and $\underline{c}$ are the crystal lattice vectors. In the reciprocal space defined by these relationships each crystal lattice plane (hkl) is transformed into a point the co-ordinates of which (measured in units of a^*, b^* and c^*) are h,k,l.

1.4 THE STRUCTURE FACTOR

The structure factor F(hkl) may be defined by

$$F(hkl) = \int_V \rho(xyz)\exp\left[2\pi i(hx + ky + lz)\right] dV$$

where $\rho(xyz)$ is the electron density at the point (x,y,z), in a unit cell of volume V. F(hkl) thus represents the ratio of the total radiation scattered by the contents of the unit cell in the order hkl relative to that of a single electron at the origin of the unit cell. However it is more convenient to consider the electron density as the superposition of N 'atomic' electron densities(14). The structure-factor is then given by

$$F(hkl) = \sum_j f_j(hkl)\exp\left[2\pi i(hx_j + ky_j + lz_j)\right]$$

where x_j, y_j and z_j are the fractional co-ordinates of the jth atom, and where

$$f_j(hkl) = V\iiint_{-\infty}^{\infty}\rho_j(uvw)\exp\left[2\pi i(hu + kv + lw)\right]dudvdw$$

is the scattering factor of atom j whose electron density is $\rho_j(uvw)$, (uvw) being the co-ordinates referred to (x_j, y_j, z_j) as origin(15).

The scattering factor is thus the Fourier transform of the atomic electron-density, and represents the amplitude of the wave scattered by the atom relative to that which would be scattered by an electron at rest. As sin θ increases, the X-rays scattered from different parts of the atom will be increasingly out of phase and will therefore interfere destructively with each other. Thus, due to the finite size of the atom, f attenuates with increase of sin θ (where θ is the Bragg angle).

Since the duration of the scattering experiment is much greater than the period of thermal vibration, thermal motion effectively increases the volume occupied by the electrons scattering the X-rays. This smearing may be allowed for by using the expression

$$f = f_o\exp\left[-8\pi^2U(\sin\theta/\lambda)^2\right]$$

where f_o is the scattering factor of an atom at rest (and is taken to be independent of the environment of the atom in the unit cell and of the radiation used for the experiment), and U is the mean square amplitude of isotropic vibration. Anisotropic thermal vibration can be allowed for by the more general expression

$$f = f_o\exp\left[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)\right]$$

where $U_{ij}(i,j = 1,2,3)$ are the components of the symmetric tensor, $\underline{U}$, describing the ellipsoid of mean-square vibration with reference to the reciprocal axes.

A further complication arises from the phenomenon of Anomalous Dispersion. Scattered radiation arises from modulation of the natural oscillation of the atomic electrons induced by the electromagnetic field of the incident X-rays. The electrons thus become a source of radiation, scattering X-rays with a phase lag of π (Thomson scattering). However, when the X-ray frequency approaches an absorption edge of a diffracting atom, resonance effects set in and the phase lag decreases to $\pi/2$ at resonance, and to 0 for a photon of much lower energy than the binding energy of the electron (Rayliegh scattering). It follows that near the absorption edge the scattering factor becomes a complex quantity expressible as

$$f = f_o + \Delta f' + i\Delta f''$$

where f_o is the normal scattering factor and $\Delta f'$ and $\Delta f''$ are the correction terms required to allow for this anomalous dispersion effect(16,17). In the case of non-centrosymmetric space groups this effect may lead to the breakdown of Friedel's law and has been used to distinguish between enantiomorphic structures(18).

1.5 GEOMETRIC AND INTENSITY DATA MEASUREMENTS

Preliminary unit-cell parameters for the compounds described in this thesis were determined from oscillation and Weissenberg photographs taken with Cu-K_α radiation, and from precession photographs taken with Mo-K_α radiation. Space-group identification was based on the systematically absent reflections. The crystal under investigation was then transferred to a Hilger and Watts' Y290 diffractometer. The crystal was always in an offset position on χ to prevent multiple reflections(19).

The various photographs and initial unit-cell parameters enabled the location and indexing of two strong, low-order reflections. The angular settings were optimised by means of 2θ, ϕ and χ scans and incorporated, together with the approximate cell dimensions, in an orientation matrix which was used to check the indexing of the reflections and to locate twelve well-defined reflections with a wide spread of ϕ and χ values and with θ values in the typical range 12° to 17°. The angular settings of each of the reflections and their Friedel partners (to a maximum total of 23) were optimised and used in the refinement of the unit-cell parameters by least-squares methods and thence to calculate an accurate orientation matrix.

Intensity measurements were made exposing the crystal to graphite-monochromated or Zr-filtered Mo-K_α radiation and using the $\theta,2\theta$ scan procedure with each reflection being scanned typically over 40 equal steps between the limits $(2\theta_{calc.} - 0.40^\circ)$ and $(2\theta_{calc.} + 0.40^\circ)$. Each scan-step was counted for one second and stationary-crystal/stationary-counter background counts were made at each extreme of the scan for a total time equal to the total peak-scan time.

The intensities of three standard reflections were monitored at regular intervals both as a check on diffrectometer-stability and crystal deterioration, and also to enable scaling of all reflections to a common scale. In most cases, weak reflections were not measured, those reflections with $I \leqslant 2\sigma_I$ (where σ_I was obtained from counting statistics) being automatically identified and omitted from the counting procedure.

1.6 DATA REDUCTION

The data thus obtained consists of a set of 'integrated intensities' I(hkl), which are a measure of the total amount of energy diffracted by the crystal from the planes (hkl) as the crystal rotates in the X-ray beam. The integrated intensity is defined$^{(20)}$ by the relationship

$$I(hkl) = E\omega I_o^{-1} = \lambda^3 N^2 r_e^2 |F(hkl)|^2 LpV$$

where E is the energy diffracted by the crystal of volume V (assumed to be small), rotating with an angular velocity, ω, in an X-ray beam of wavelgnth λ and intensity I_o;
$r_e = e^2m^{-1}c^{-2}$ is the classical radius of the electron;
N is the number of unit cells per unit volume; F(hkl) is the structure-factor of the plane (hkl) and L and p are respectively the Lorentz and polarisation factors which are known functions of θ. Thus in a particular experiment,

$$|F(hkl)| = \left[I(hkl)K^{-1}L^{-1}p^{-1}\right]^{\frac{1}{2}}$$

The polarisation factor, p, allows for the partial polarisation of the reflected beam, and, for an unpolarised incident beam

$$p = \tfrac{1}{2}(1 + \cos^2 2\theta)$$

where θ is the Bragg angle of the reflection (hkl). However if the X-ray beam has been reflected from a crystal monochrometer, the incident beam is also partially polarised and the modified equation becomes(21)

$$p = (1 + \cos^2 2\theta_m . \cos^2 2\theta)(1 + \cos^2 2\theta_m)^{-1}$$

where θ_m is the Bragg angle of the stack of reflecting planes of the crystal monochromator. This expression is valid when the primary beam, the beam reflected by the monochromator, and the diffracted beam are coplanar, the general expression being much more complex(22). For the graphite monochromator utilized in the present studies $\cos^2 2\theta_m$ has the value of 0.965.

The Lorentz factor, L, allows for the relative time each plane is in the reflecting condition. This may be easily envisaged in terms of the reciprocal lattice/reflecting sphere concept, the reflecting condition being the interval for which the finite reciprocal lattice point is in contact with the sphere of reflection. Therefore the duration of the reflecting condition is dependent on the individual reflection and on the method of data collection. In the present studies the Lorentz factor is given by the expression

$$L = (\sin 2\theta)^{-1}$$

The quantity K is a constant for a particular experiment and may be calculated from diffraction theory(23).

1.6.1 THE RELATIVE STRUCTURE-FACTOR

In practice it is usual to assume K = 1 and to calculate relative structure-factor moduli $|F_{rel}|$. These may then be put on an approximate absolute scale by means of the Wilson-Plot method(24). It has been shown that by dividing reciprocal space into concentric shells, each thin enough that the change of f with sin θ/λ within each shell is negligible, and averaging the variables over each shell, then

$$\ln\left[\left\langle |F_{rel.}|^2 \right\rangle \Big/ \sum_j f_{oj}\right] = -2(\ln K + B\langle s\rangle^2)$$

where K is the scaling factor such that

$$K\sum|F_{rel}| = \sum|F(hkl)| \quad ,$$

$s = \sin\theta/\lambda$ and B is an overall thermal parameter. A best-line fit to a plot of the left hand side of the above expression against $\langle s\rangle^2$ gives adequate preliminary working values of K and B.

When a part-structure is known the scale factor may be obtained by correlating $k\sum|F_{rel}|$ with $\sum|F_{calc}|$. Once the structure is solved, the scale factor is included as a variable parameter in the subsequent least-squares refinement.

1.6.2 ABSORPTION

X-rays are absorbed by crystals to varying extents leading to a reduced intensity given by the expression

$$I = I_o\exp[-\mu t]$$

where I_o is the incident intensity, t is the distance traversed in the crystal by the beam, and μ, the linear absorption coefficient, is a function of the elemental composition and of the wavelength of the X-rays.

Failure to correct for high absorption manifests itself in physically meaningless values of isotropic temperature factors (even negative values in very serious cases) and to large errors in the positional parameters of the atoms. However in the present work the low linear absorption coefficients of the compounds and the small crystals used were together considered to justify neglect of absorption effects.

1.6.3 EXTINCTION

Extinction is the attenuation of the incident beam, when a crystal is in the reflecting position, thereby reducing the intensity of the diffracted beam. This may arise in two ways.

a) PRIMARY EXTINCTION

When an X-ray beam is reflected at the Bragg angle by a set of planes, it follows that the reflected beam is at the correct angle to be reflected by other planes in the stack. The phase change of $\pi/2$ that accompanies reflection, leads to destructive interference of the n-tuply (n even) diffracted beam with the incident beam, and of the n-tuply (n odd) diffracted beams with each other. This only occurs with crystals of very low mosaicity, and so is a rare phenomenon.

b) SECONDARY EXTINCTION

This arises for reflections of such intensity that an appreciable amount of the incident radiation is reflected by the first planes encountered by the beam. Thus the deeper planes receive an attenuated beam and therefore reflect less. Secondary extinction is therefore a function of the scattering power and relative alignment of the individual mosaic blocks, and is most pronounced for reflections occurring at low sin θ/λ. Zachariasen(25) has shown how the effects of secondary extinction can be allowed for during the least-squares refinement. However, since it is a function of the crystal perfection, it was not a problem in the cases reported in this thesis, and was ignored.

1.7 FOURIER SYNTHESIS AND THE PHASE PROBLEM

A crystal is a tri-periodic structure and as such may be described by a three-dimensional Fourier series. This was first suggested by W L Bragg in 1915(26). It can be shown that a general expression for a Fourier synthesis may be written as

$$\rho(xyz) = V^{-1}\sum_{h}\sum_{k}\sum_{l} F(hkl)\exp\left[-2\pi i(hx + ky + lz)\right],$$

whe$\rho(xyz) = V^{-1}\sum\sum\sum F(hkl)\exp\left[-2\pi i(hx + ky + lz)\right]$,finite number of terms. The above expression may be written as

$$\rho(xyz) = V^{-1}\sum_{h}\sum_{k}\sum_{l}|F(hkl)|\exp\left[i\alpha(hkl) - 2\pi i(hx + ky + lz)\right]$$

where $\alpha(hkl)$ is the argument or phase of the complex quantity F(hkl).

The above expression indicates that knowledge of the unobservable phases is a pre-requisite to the calculation of the electron distribution. This constitutes the Phase Problem. However, although the structure-factor moduli are the only directly obtainable quantities, a considerable amount of extra information may be derived from the observed data by employing rather elegant mathematical techniques. Two such methods, which were used in the present work, will now be surveyed.

1.8 THE PATTERSON FUNCTION AND THE HEAVY ATOM METHOD

Although it is not possible to determine the atomic positions in a straight-forward manner from the intensity data, it is possible, at least in principle, to determine the inter-atomic vectors. This approach was first introduced by A L Patterson in 1934-35$^{(27)}$, who realised that the self-convolution of a unit cell containing N atoms, and defined by

$$P(uvw) = V\int_0^1\int_0^1\int_0^1 \rho(xyz).\rho(x + u,\ y + v,\ z + w)dxdydx$$

would consist of a set of N(N - 1) peaks, corresponding to the interatomic vectors (uvw), together with N null-vectors superimposed at the origin. This follows from P(uvw) having appreciable magnitude only when $\rho(xyz)$ and $\rho(x + u,\ y + v,\ z + u)$ both correspond to atomic sites.

The elegance of this approach becomes clear when one substitutes the electron-density by the Fourier transform of the structure-factor. The function one obtains may be shown to lead to a vector-map defined by

$$P(uvw) = V^{-1} \sum_{h}\sum_{k}\sum_{l} |F(hkl)|^2 \exp\left[2\pi i(hu + kv + lw)\right]$$

and so may be computed directly from the phaseless structure-factor moduli. The resulting vector-map consists of a set of maxima with peak-heights proportional to the product of the scattering factors of the atoms involved. Thus the presence of heavy atoms (i.e atoms of high atomic number relative to the other atoms) will give rise to heavy atom-heavy atom vectors that stand out strongly against a background of heavy-light and light-light atom vectors. Identification of the heavy atom-heavy atom vectors allows the determination of the heavy atom co-ordinates. Once the heavy atom is located, it may be used to phase the observed structure-factor moduli in a Fourier synthesis. The error in such a phasing moduli has been shown$\sum Z^2_{heavy} / \sum Z$elated to

$$r = \sum Z^2_{heavy} / \sum Z^2_{light}$$

when $r \sim 1$, the phasing is generally likely to be reliable enough to allow resolution of the structure to proceed without undue difficulty. As r decreases, the phasing becomes less reliable and an iterative procedure of phasing and electron-density calculations may become necessary for complete resolution. On the other hand, when r is much greater than unity, the heavy atom tends to dominate the phases and intensities to such an extent that the comparison of $|F_o|$ and $|F_c|$ becomes insensitive to the lighter atoms, rendering it difficult to deduce an accurate model.

1.9 DIRECT METHODS

In 'direct methods' the resolution of a structure is formulated as a sequence of purely mathematical operations on the observed data. Direct methods owe their inception to the derivation of inequality relationships between structure factors by Harker and Kasper(29). However, the requirements for inequalities to hold are so severe as to restrict their application to small structures. Inequalities in fact represent the limiting cases of the more general probability approach(30) and present day methods are based on strategies which estimate a phase together with its associated probability of being correct.

Procedures of phase determination are usually expressed in terms of the normalised structure factor $E_{\underline{h}}$(31), the modulus of which being defined by

$$|E_{\underline{h}}|^2 = |F_{\underline{h}}|^2 / \varepsilon \sum_i f_i^2$$

where ε is a symmetry dependent integer introduced to correct for space-group extinctions and $\underline{h}$ is the vector (hkl).

Since the $|E_{\underline{h}}|$ are uniquely determined by the crystal structure and are independent of the choice of origin(32), the strategy used in direct methods is to obtain relationships between phases which are also origin-independent, the so called structure invariants. It can be shown that $\sum_{\underline{h}} A_{\underline{h}} \phi_{\underline{h}}$ is a structure invariant if $\sum_{\underline{h}} A_{\underline{h}} \underline{h} = 0$, for integral $A_{\underline{h}}$. At present the most widely used structure invariants are the triplets $\phi_{\underline{h}_1} + \phi_{\underline{h}_2} + \phi_{\underline{h}_3}$ where $\underline{h}_1 + \underline{h}_2 + \underline{h}_3 = 0$, though more powerful methods involving quartets are being developed.

From the triplet structure invariant it follows that the phase of $E_{\underline{h}}$ is correlated to the phases of $E_{\underline{h}-\underline{k}}$ and $E_{\underline{k}}$, and it may be shown that

$$\phi_{\underline{h}} \simeq \left\langle \phi_{\underline{k}} + \phi_{\underline{h}-\underline{k}} \right\rangle_{\underline{k}}$$

holds for phases associated with large $|E|$ values(33). In practice the more efficient Tangent formula(33)

$$\tan \phi_{\underline{h}} = \frac{\sum_{\underline{k}} |E_{\underline{k}} \cdot E_{\underline{h}-\underline{k}}| \sin(\phi_{\underline{k}} + \phi_{\underline{h}-\underline{k}})}{\sum_{\underline{k}} |E_{\underline{k}} \cdot E_{\underline{h}-\underline{k}}| \cos(\phi_{\underline{k}} + \phi_{\underline{h}-\underline{k}})}$$

is used for phase determination. The reliability and variance of an estimated phase may also be determined using formulae derived by Karle and Karle(33) and in general are dependent on the magnitude of the $|E|$'s.

The above relationships form the basis of the symbolic addition method of Karle and Karle(33). In this method one choses a basic set of phases necessary to specify an origin and, in the case of non-centrosymmetric space-groups, an enantiomorph together with a small number of phases denoted by symbols(33,34). The choice is usually a balance between large $|E|$ values, which increase the reliability of a phase estimation, and the number of triple-phase relationships ($\sum_2$ interactions) in which the phase is involved. The latter lead to multiple indications for unknown phases, thus increasing the reliability of phase determination during the initial crucial stages. The symbols are then assigned values (all possible combinations of $\pm\pi/4$, $\pm 3\pi/4$ or in the case of centric reflections, the values 0 or π) yielding a series of alternative self-consistent phase sets. Each phase set may be used with the observed $|E|$'s in a Fourier synthesis (E-map), one of which may reveal the correct structure. The above procedure has been automated in the suite of computer programmes MULTAN by Germain, Main and Wolfson(35) and modifications of the procedure are available as links of the X-RAY'72 suite of crystallographic programmes(36).

1.10 ACCURACY AND LEAST SQUARES REFINEMENT

The atomic parameters obtained from a Fourier synthesis are in error.due to termination of series effects. To overcome this problem and to produce a model which is a best-fit to the experimental data, one uses Legendre's method of least-squares(37), first introduced into crystallography by Hughes(38). The function which is usually minimised is

$$M = \sum_{r=1}^{m} w_r (|F_o| - |F_c|)^2 = \sum_{r=1}^{m} w_r \Delta_r^2$$

where the summation is over the set of m crystallographically independent data and w_r is a weighting factor associated with each term.

For a minimum

$$\frac{\partial M}{\partial p_j} = \sum_{r=1}^{m} w_r \Delta_r \frac{\partial |F_c|}{\partial p_j} = 0, \text{ for all } p_j, \qquad .....(A)$$

where p_j are the $n(\ll m)$ structural parameters.

For the trial set of values, p_j ($j = 1,2,...,n$), close to their optimum values, Δ can be expanded as a function of the parameters by a Taylor series to the first order giving

$$(\underline{P} + \underline{\epsilon}) = (\underline{P}) - \sum_{i=1}^{m} \epsilon_i \frac{\partial |F_c|}{\partial p_i} \qquad .....(B)$$

where $\underline{P}$ and $\underline{\epsilon}$ represent the whole set of n parameters and changes, and ϵ_i is a small change in p_i.

Substituting (B) in (A) gives

$$\sum_{i=1}^{n} \sum_{r=1}^{m} w_r \frac{\partial |F_c|}{\partial p_i} \frac{\partial |F_c|}{\partial p_j} \epsilon_i = \sum_{r=1}^{m} w_r \Delta \frac{\partial |F_c|}{\partial p_j}$$

which is a set of n equations in n unknowns called the normal equations. These normal equations may be expressed in matrix notation as

$$A.X = B$$

where,

A is an nxn symmetric matrix with $a_{ij} = \sum_{r=1}^{m} w_r \frac{\partial |F_c|}{\partial p_i} \frac{\partial |F_c|}{\partial p_j}$

X is a vector of order n with $x_j = \epsilon_i$

B is a vector of order n with $b_j = \sum_{r=1}^{m} w_r \Delta \frac{\partial |F_c|}{\partial p_j}$

The set of parameter shifts is therefore given by $X = A^{-1}.B$. Although the refinement of structural parameters is a non-linear process, the non-linearities are known to be negligible when the parameter shifts are small. Nevertheless, the calculated shifts will not be exact and structural refinement has to be carried out by an iterative process.

In the least-squares refinement each observation was given an associated weight w. Absolute weights reflect the precision of measurements of $|F_o|$ and are given by the reciprocal of the variance, σ^2, of the observation due to random experimental errors. However it is not practical to measure each reflection a sufficient number of times to obtain reliable estimates of the variance. Instead, relative weights may be assigned by expressions of the type

$$w = (a + b|F_o| + c|F_o|^2 + d \sin \theta)^{-1}$$

where the coefficients are chosen to give approximately constant averages of $w\Delta^2$ when the set of $w\Delta^2$ values is analysed in a systematic manner. Weights chosen in this way, besides allowing for random errors, also allow for such systematic experimental errors not paralleled in the calculated model and such defects in the model not paralleled in the data(40).

It is customary to test the final refined model, obtained by least-squares methods, by a Fourier synthesis with $\Delta F = (|F_o| - |F_c|)$ as coefficients, ie

$$\Delta\rho(xyz) = V^{-1} \sum_h \sum_k \sum_l (|F_o| - |F_c|)\exp[i\alpha - 2\pi i(hx + ky + lz)]$$

where α is the phase of F_c as obtained from the model.

This 'Difference Map' will indicate any gross errors in the model. The method is free from series-termination errors and has been used to locate hydrogen atoms from X-ray data.

1.11 ANALYSIS OF RESULTS

a) Standard Deviations of Parameters

The estimated standard deviation σ of a parameter p_i, when using relative weights, is given by :

$$\sigma^2 = (a_{ii}^{-1}\sum_{r=1}^{m} w\Delta^2)/(m - n)$$

where a_{ii}^{-1} is the i^{th} diagonal element of the inverse matrix A^{-1}.

The estimated standard deviations derived in this way are sometimes underestimated, particularly if block-diagonal least-squares methods are employed. The reliability of the estimated standard deviations (esd's) may sometimes be assessed by an examination of the bond lengths and angles and their associated esd's in a part of the molecule of known geometry such as a phenyl ring.

b) The Standard Deviations of Bond-lengths and Angles$^{(41)}$

The standard deviation $\sigma(l)$ of a bond, of length l, between two independent atoms A and B is given by

$$\sigma^2(l) = \sigma^2(A) + \sigma^2(B)$$

where $\sigma^2(A)$ and $\sigma^2(B)$ are the variances of the co-ordinates of A and B in the direction AB. If the atoms A, B and C are independent, the standard deviation $\sigma(\theta)$, of the angle θ subtended at B is given by

$$\sigma^2(\theta) = \sigma^2(A)/AB^2 + \sigma^2(B)\left[(1/AB^2) - (2\cos\theta/AB.AC) + (1/BC^2)\right] + \sigma^2(C)/BC^2$$

where $\sigma^2(A)$ and $\sigma^2(C)$ are the variances of A and C in the ABC plane and perpendicular to AB and BC respectively, and $\sigma^2(B)$ is the variance of B in the direction tangential to the circle through ABC. This expression is only valid for orthogonal axes, the general expression being much more complex.

c) Least-Squares Planes and the χ^2 test

It is often desirable to know whether a set of four or more atoms are coplanar within experimental error. Besides being an interesting aspect of the molecular structure, the significance of deviations from co-planarity may also provide a means of judging the accuracy of a structure when a particular set of atoms (eg a phenyl ring) are expected to be co-planar. It is usual to discuss planarity in terms of the least-squares plane through the set of atoms and the deviations of the atoms from the least-squares plane$^{(42)}$. The estimated standard deviation, σ_p of the atoms from the least-squares plane is given by

$$\sigma_p^2 = \left[\sum_m d_m^2\right]/(m - 3)$$

where d_m are the perpendicular distances of the m atoms to the plane. If the positional estimated standard deviations of the atoms do not differ greatly so that their mean variance σ_r^2 is comparable to the individual variances then, the ratio

$$\left[(m - 3)\sigma_p^2\right]/\sigma_r^2 = \left[\sum_m d_m^2\right]/\sigma_r^2$$

follows the χ^2 distribution so that

$$\chi^2 = \left[\sum_m d_m^2\right]/\sigma_r^2$$

for (m - 3) degrees of freedom.

The probability of the deviation from planarity due to random experimental errors can be examined from the χ^2 tables(43). If the probability that the plane is a good fit is less than 0.01 it may be assumed that the atoms are not coplanar, or equivalently, that at least one atom included in the mean-plane calculation deviates significantly from planarity.

d) Comparison of Bond-lengths and Angles

Although it is impossible to know the true value of experimentally derived quantities, it is possible to specify the probability that two measurements of equal quantities agree within certain limits if only random errors are present, since such errors should show a normal Gaussian distribution and so may be treated analytically. If two quantities with standard deviations σ_1 and σ_2 differ by an amount of Δq, the standard deviation of their difference is $\sigma = (\sigma_1^2 + \sigma_2^2)^{\frac{1}{2}}$. The probability P that the observed difference is due to chance is given(44) by the following limits :

If

$$\Delta q \leqslant 1.96\sigma \text{ then } P \geqslant 5\%$$

$$1.96\sigma \leqslant \Delta q \leqslant 2.58\sigma \text{ then } 5\% \geqslant P \geqslant 1\%$$

$$2.58\sigma \leqslant \Delta q \leqslant 3.29\sigma \text{ then } 1\% \geqslant P \geqslant 0.1\%$$

$$\Delta q > 3.29\sigma \text{ then } P < 0.1\%$$

The limits of significance are arbitrary but if $P > 0.05$ the difference is commonly considered <u>not</u> significant. If $0.05 > P > 0.01$ the difference is possibly significant. But if $P < 0.01$ the difference is generally accepted as significant.

PART II

STRUCTURAL STUDIES OF NITRATO-COBALT COMPLEXES

INTRODUCTION

The nitrate group is a versatile ligand(1) which can in principle be ionic, covalent-monodentate, covalent-bidentate, or may act as a bridging ligand in a polynuclear molecule. Examples of all these types of behaviour are known to occur in simple and complexed nitrates(2). Complex transition metal nitrates which include other ligands in addition to covalent nitrato groups have become the subject of increased structural studies, particularly by X-ray diffraction methods(3). Five such studies form the basis of the present report.

The nitrate ion in an isotropic environment has a symmetrical (D_{3h}) planar structure with bonds of length 1.245(10)Å(1) (1.241(2)Å in $NaNO_3$(4)), and is geometrically similar to the ions BO_3^{3-} and CO_3^{2-} with which it is isoelectronic. It has been suggested(5) that the nitrate ion be considered a disc of van der Waal's radius 2.31Å and thickness 2.2Å, and hence of volume 24.8Å^3. This illustrates the compact nature of the nitrate ion since the volume of the spherical chloride ion is also 24.8Å^3. On co-ordination, however, it is observed(3) that the dimensions of the nitrato group are distorted from those of the free ion and that the degree of distortion is dependent on the mode of bonding and the strength of the metal-nitrate interaction(6).

From a survey of the literature(7) it is apparent that the vast majority of the structures which have been investigated by diffraction techniques contain bidentate nitrato groups with varying degrees of asymmetry. It has been suggested(1) that the nitrato group be considered symmetrically bidentate when the difference in the metal-oxygen bonded distances, $\Delta(M-O)$, is less than 0.2Å, asymmetrically bidentate when $0.2Å < \Delta(M-O) < 0.7Å$ and asymmetric monodentate when $\Delta(M-O) > 0.7Å$. This is an arbitrary classification and not necessary for the following discussion, in which asymmetry is taken to mean $\Delta(M-O)$ is significantly greater than zero.

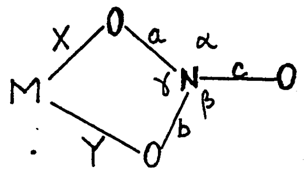
In an asymmetrically bidentate co-ordinated nitrato group, it is generally observed (eg see Table 2.0.1) that :

i) The terminal N-O bond (ie involving an unco-ordinated oxygen) is shorter, and the N-O bonds, involving the co-ordinated oxygen atoms, longer than those in the free ion.

ii) The O-N-O interbond angle, α, opposite the shorter metal-oxygen bond is systematically increased from 120°, the O-N-O interbond angle, γ, subtended by both co-ordinated oxygen atoms is decreased from 120° and the third angle, β, is of intermediate value such that $\beta = 360 - (\alpha + \gamma)$, presumably to preserve the planarity of the nitrato group.

The contraction of the O-N-O interbond angle, γ, defined by both the co-ordinated oxygen atoms, might be considered as a consequence of the attraction of the electron clouds of these atoms by the metal cation. However the O-N-O angle is also reduced for bridging nitrato groups between copper nuclei (Figure 2.0.1, A and B),

Table 2.0.1



$X < Y$

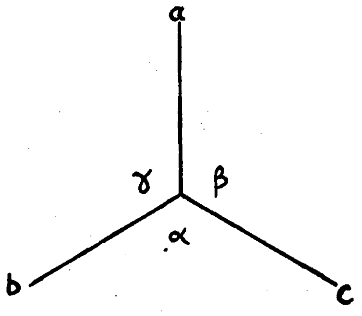
Ref.	X	Y	a	b	c	α	β	γ
58*	2.059(5)	2.292(6)	1.268(9)	1.255(9)	1.232(9)	122.5(7)	120.7(7)	116.8(6)
	2.076(6)	2.282(6)	1.270(9)	1.245(9)	1.224(11)	123.1(8)	121.2(8)	115.7(7)
**	2.054(3)	2.204(3)	1.276(5)	1.259(5)	1.207(5)	123.6(4)	122.2(4)	114.2(3)
	2.055(3)	2.197(3)	1.290(4)	1.239(5)	1.209(5)	124.3(4)	120.4(4)	115.3(3)
**	2.061(4)	2.273(5)	1.272(6)	1.261(8)	1.223(7)	124.3(5)	120.3(6)	115.4(5)
	2.074(4)	2.264(4)	1.282(6)	1.243(7)	1.226(7)	122.6(5)	121.0(5)	116.5(5)
56	2.207(9)	2.311(9)	1.287(13)	1.235(13)	1.223(13)	125.0(11)	121.0(10)	114.0(9)
**	2.154(2)	2.204(2)	1.261(2)	1.260(2)	1.219(3)	123.0(2)	121.7(2)	115.3(2)
**	2.118(5)	2.171(5)	1.265(9)	1.263(9)	1.202(9)	123.5(7)	122.0(7)	114.6(6)
70	2.010(4)	2.490(5)	1.287(7)	1.249(7)	1.214(7)	124.0(6)	119.3(5)	116.7(5)
9	1.992(2)	2.653(2)	1.281(3)	1.238(3)	1.241(3)	122.1(1)	119.2(1)	118.6(1)

* Calculated from reported fractional co-ordinates and e.s.d.'s

** Indicates this work.

where the attraction would be expected to increase the angle. An alternative interpretation consistent with the observed distortions is given by the valence-shell electron-pair-repulsion model of Gillespie and Nyholm(10). With this model, as the electron-pairs in the O-N-O bonds are polarised towards the oxygen atoms, it is expected that the repulsion between these electron-pairs is diminished and thus the angle subtended at the nitrogen atom is reduced. This is apparent when one compares the two nitrato groups, B and C, given in Figure 2.0.1, in which the absence of a bridge involving O(2) in C, and hence a lower polarization of the N-O(2) bond, leads to the observed O(1)-N-O(2) angle in C being closer to the trigonal value of 120°, than it is in B.

As a third explanation for the observed distortions in the geometry co-ordinated nitrato groups it may be considered that since the O-N-O interbond angles are not all equal to 120°, the hybridization of the σ-orbitals of the nitrogen atom no longer constitute three equivalent sp^2 hybrids(11). It has been shown(11) that in the case of a planar molecule



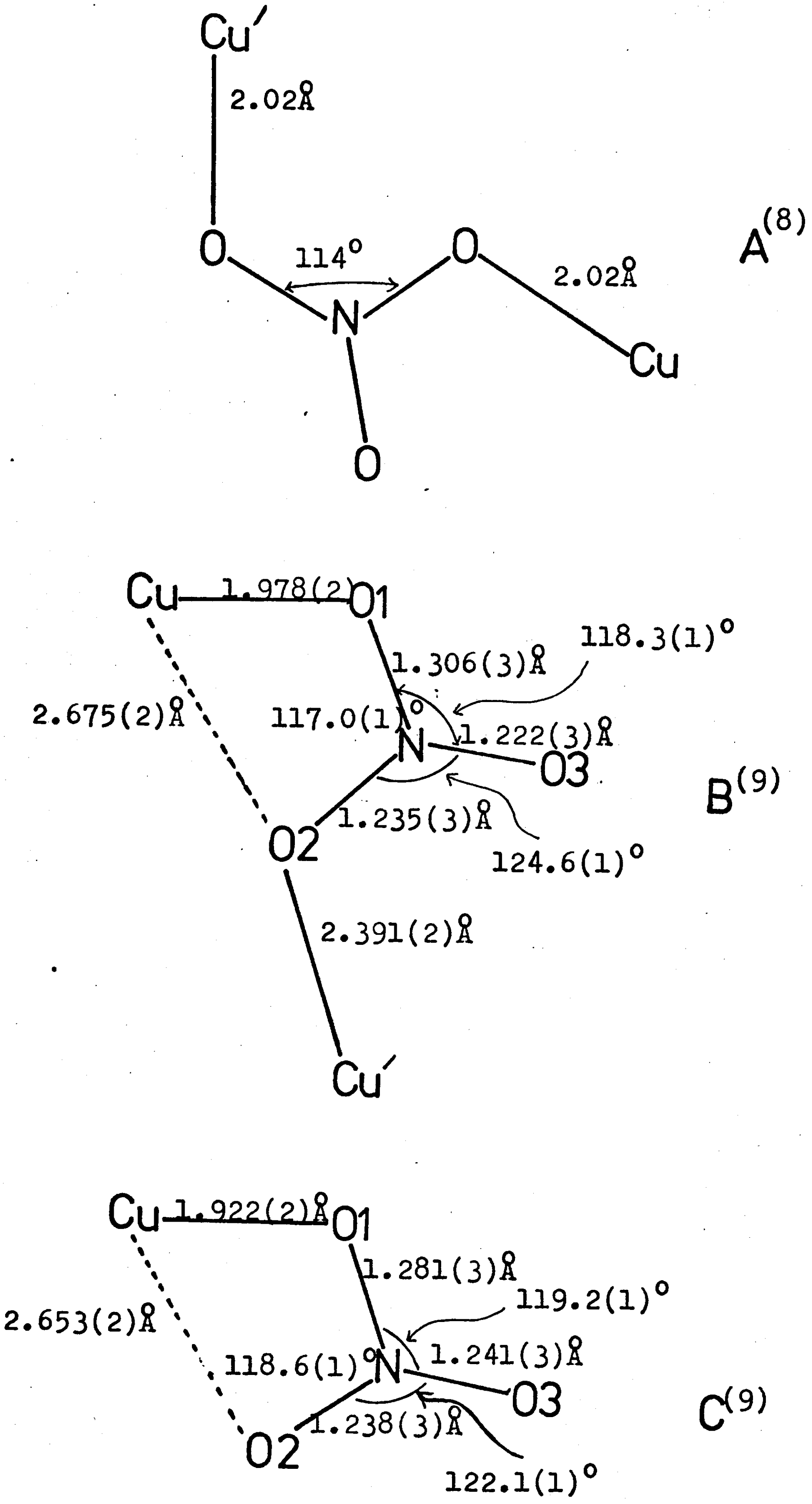

Cu′
2.02Å
O
114°
O
2.02Å
N
Cu
O
A(8)
Cu
1.978(2)
O1
1.306(3)Å
118.3(1)°
2.675(2)Å
117.0(1)°
N
1.222(3)Å
O3
B(9)
1.235(3)Å
O2
124.6(1)°
2.391(2)Å
Cu′
Cu
1.922(2)Å
O1
1.281(3)Å
119.2(1)°
2.653(2)Å
118.6(1)°
N
1.241(3)Å
O3
C(9)
1.238(3)Å
O2
122.1(1)°

Figure 2.0.1

the hybridization ratio, in a hybrid orbital of the form $s + \lambda p_{\sigma}$ is

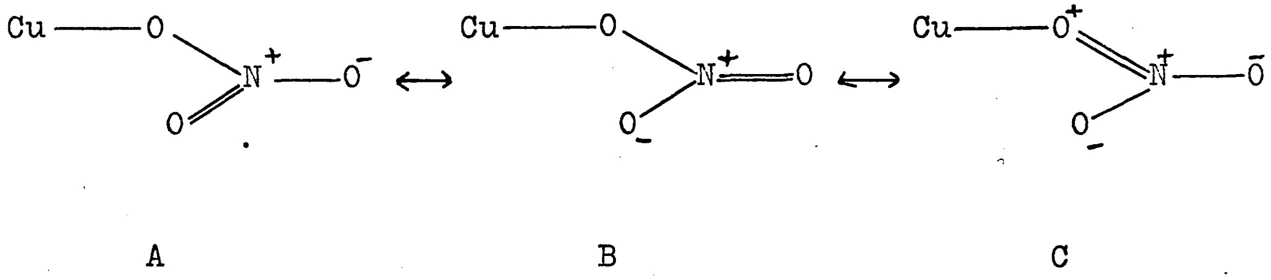
$$\lambda_a = \left[-\cos\alpha/(\cos\beta\cos\gamma)\right]^{\frac{1}{2}}$$

and similarly for λ_b and λ_c.

It follows, therefore, that as the O-N-O angle opposite a particular bond increases then the amount of p-character (λ) in the nitrogen σ-orbital involved in that bond increases. Furthermore, the covalent radius of an atom varies with hybridization such that it decreases with increasing s-character(12) (in an sp^n-type hybrid, $n \leqslant 3$, this is equivalent to saying that the covalent radius increases with increasing p-character ie $r_{sp^3} > r_{sp^2} > r_{sp}$). Hence the longest N-O bond is predicted (on the basis of the perturbation of the σ-bonds) to be opposite the largest O-N-O interbond angles. Furthermore since the polarization of the oxygen-nitrogen bond towards the oxygen is expected to increase with decreasing metal-oxygen (M-O) distances, the largest angle should be opposite the shortest M-O bond. This is in agreement with the experimental observations.

However, though the predicted order of bond lengths and angles agree with experiment, the observed changes in bond-lengths appear to be too great(13) to be solely accountable in terms of polarization of the nitrato group and rehybridization of the nitrogen atom. The effect of co-ordination on the π-system within the nitrato group must also be expected to affect the bond lengths. A valence-bond consideration of the changes in π-bonding that occur on co-ordination (Figure 2.0.2) suggests the same order ie the N-O bond lengths are expected to be in the order a>b>c. Though, in general, this trend is exhibited by most structures, in some cases the differences may not be statistically significant.

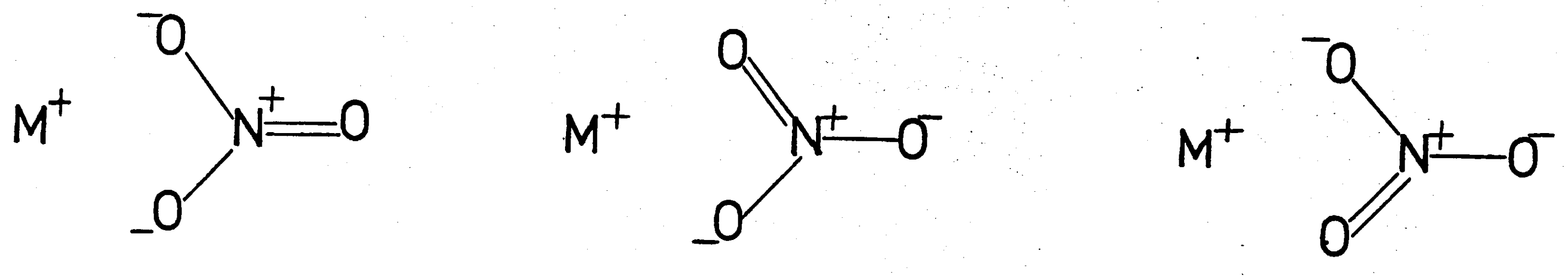
One exception to the above observations results from the analysis of $(Ph_2MeP)_3Cu(NO_3)^{(14)}$ in which the order of the N-O bonds is reported to be a<b<c. In this case, the reverse order has been explained in terms of a larger than expected contribution from a resonance-form of type c in order to minimize the charge build-up on the copper atom



Such a canonical form is usually considered negligible due to the adjacency of like charge, and may suggest the absence of any covalent interaction. Furthermore the total (valence) bond order estimated from the dimensions of the nitrato group is 4.6 which exceeds the value of 4.0 of a free nitrate ion and contrasts with the usual values of~4.0 (Table 2.0.2). There does not appear to be a satisfactory explanation for this discrepancy.

The asymmetric monodentate co-ordination and symmetric

Ionic interaction



Covalent interaction

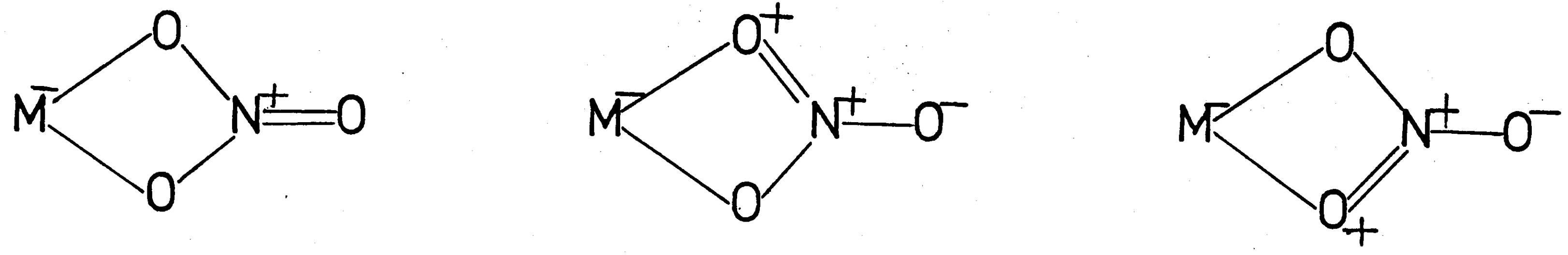


Figure 2.0.2

Table 2.0.2

Compound	Total (valence) bond-order*
$Co(C_{11}H_{12}ON_2)_2(NO_3)_2$	4.0
	4.0
$Co(CH_3CN)_2(NO_3)_2$	4.0
	4.0
$Co(C_5H_5N)_2(NO_3)_2$	4.1
	3.9
$Co(C_5H_5N)_3(NO_3)_2$	4.0
$Co(C_5H_5N)_2Cl(NO_3)$	3.9
$Co(CH_3CN)_2Cl(NO_3)$	4.0
$Cu(C_4H_4N_2)(NO_3)_2$	3.9
$Cu(H_2O)_2(NO_3)_2.0.5H_2O$	4.0
$Cu(C_5H_5N)_3(NO_3)_2$	3.9
$Cu(C_{11}H_{12}ON_2)_2(NO_3)$	3.9
	3.8
$Cu[(CH_3)(C_6H_5)_2P]_3(NO_3)$	4.6

* estimated from the data in original paper (see text) and Figure 2.0.3

Figure 2.0.3

A plot of N-O bond length(Å) (ordinate) against valence bond order (abscissa), after Addison(1).

The following data(4,26) were used in the plot:

	N-O(Å)	Bond order
HONO	1.46	1.00
NO_3^-	1.241	1.33
NOCl	1.140	2.00
NO^+	1.060	3.00

The polynomial fit to the curve is given by

$$y = 3.459 - 3.310x + 1.552x^2 - 0.2385x^3$$

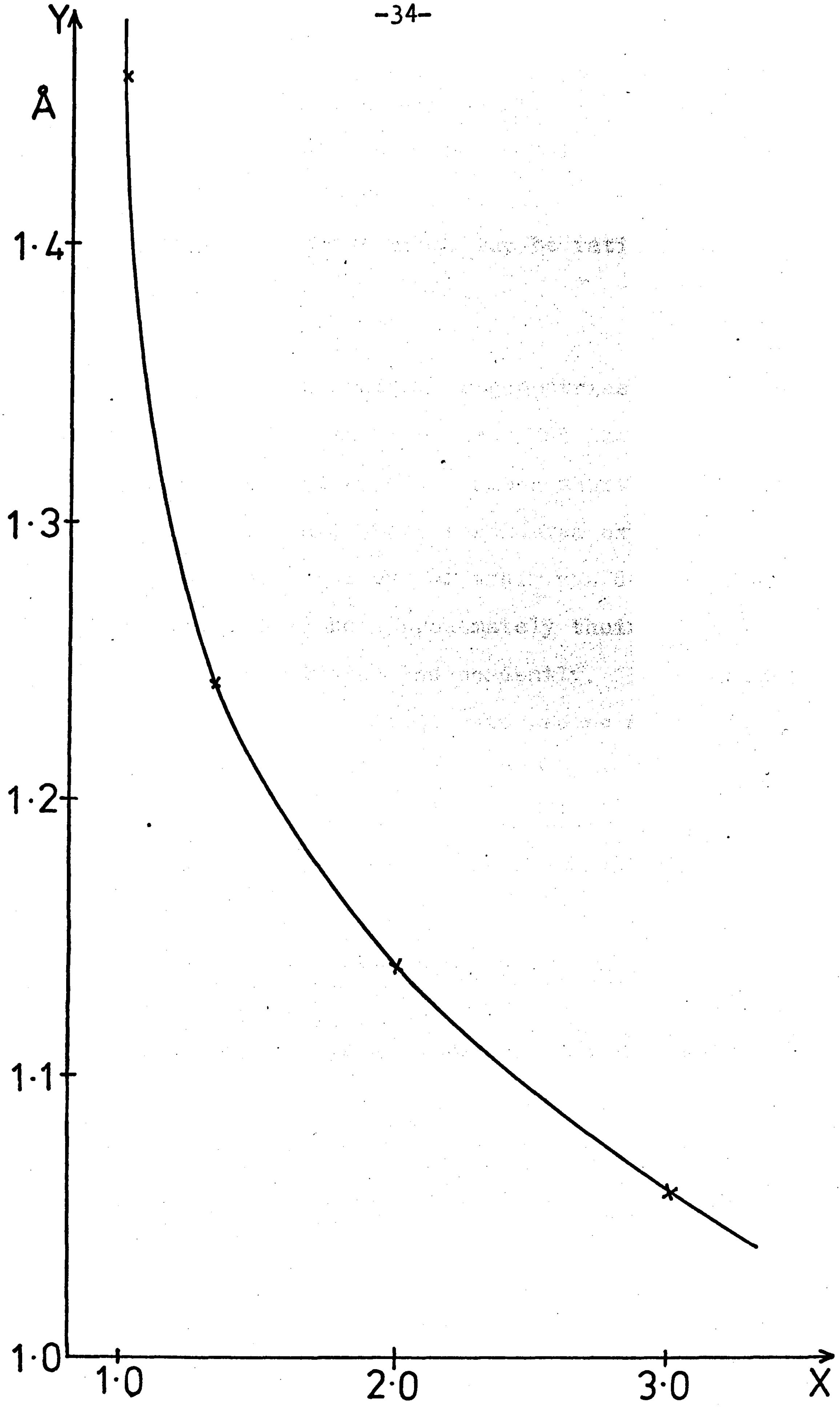


Figure 2.0.3

bidentate co-ordination modes may be considered the limiting cases of increased and decreased asymmetry, respectively, of the asymmetric bidentate mode of co-ordination. Thus the distortion observed in these cases may be rationalised in similar terms.

A discussion of the molecular geometries expected of nitrato complexes is dominated by the fact that the nitrato group is a very compact ligand and has a short 'bite' of approximately 2.1Å. Thus, the co-ordinated oxygens have a smaller separation than the sum of their van der Waal's radii [2.80Å(16)], which would be approximately their closest approach if they co-ordinated independently. In view of this, complexes containing bidentate nitrato groups may attain unusually high co-ordination numbers(17). Thus Ti(IV)(18), Mn(II)(19), Fe(III)(20) Co(II)(21) and Sn(IV)(22) are all eight co-ordinate in their tetranitrato species, whilst Ce(III)(23), Ce(IV)(24) and Th(IV)(25) are all twelve co-ordinate in their hexanitrato anions.

The stereochemistries of many of these complexes may be correlated with those containing simple ligands. Thus, all the tetranitrato species have four nitrato groups located at the vertices of somewhat distorted tetrahedra which may be compared with their tetrachloro analogues. Such stereochemistries may be rationalized by the radius-ratio rules(26), assuming a disc of van der Waal's radius 2.31Å for the nitrato group(5) and the values for the radii of the cations as listed by Pauling(27).

A natural extension of these structural correlations has been the suggestion(17,28) that the nitrato ligands be viewed as occupying only one co-ordination site, situated along the line joining the central atom to the 'centroid' of the chelating oxygens, and that the geometry be discussed in terms of a polyhedron appropriate to the lower co-ordination number which then results. This concept has been used by several other workers(18,21,29-35) in the interpretation of the magnetic and spectroscopic properties of complexes, and also to describe an otherwise grossly-distorted co-ordination polyhedron. However, apart from the description of the overall geometries under consideration, it may be better to consider the bidentate nitrato group as occupying two co-ordination sites, particularly in the analysis of the perturbation of d-orbitals in an asymmetric ligand field(36).

In the following sections, the results of studies on five novel nitrato-cobalt complexes are reported and discussed.

2.1 THE CRYSTAL AND MOLECULAR STRUCTURES OF THREE COMPLEXES OF THE FORM $Co(L)_2Cl(NO_3)$.

I L = PYRIDINE

II L = ACETONITRILE

III L = TETRAHYDROFURAN

2.1 Experimental and results for I

Bis(pyridine)chloronitratocobalt(II) dimer

Di-μ-chloro-tetrakis-(pyridine)dinitratodicobalt(II)

Crystal data

Monomer formula	$C_{10}H_{10}N_3O_3ClCo$
Formula weight	$M = 314.6$
Crystal system	Triclinic
Unit cell dimensions	$a = 7.586(1)$Å
	$b = 11.503(1)$Å
	$c = 8.028(8)$Å
	$\alpha = 99.43(6)^\circ$
	$\beta = 72.68(3)^\circ$
	$\gamma = 107.50(2)^\circ$
Unit cell volume	$U = 635.8$Å^3
Measured density	$D_m = 1.63$ g cm^{-3}
Number of monomers per unit cell	$Z = 2$
Calculated density	$D_c = 1.64$ g cm^{-3}
Number of electrons per unit cell	$F(000) = 318$
Linear absorption coefficient	$\mu(\text{Mo-K}_\alpha) = 16.1$ cm^{-1}
Space group	$P\bar{1}$ (C_i^1, No. 2)

Data collection

Radiation used	Mo-K$_\alpha$, $\lambda = 0.71069$Å
Filter	Graphite monochromator, $\cos^2 2\theta_m = 0.965$
Upper limit for data collection	$2\theta_{max} = 54^\circ$
Number of independent reflections	$m = 2201$
Unobserved cut-off	$2\sigma_I$
Number of parameters refined	$n = 203$
Number of reflections per parameter	$m/n = 10.8$

Structure Determination

The unit cell dimensions and the absence of any symmetry or systematic absences in the diffraction data suggested the possible space groups P1 or $P\bar{1}$. The low frequency i.r. spectrum indicated that the complex contained bridging chlorine atoms, and was hence a dimer(37). The space-group was therefore assumed to be $P\bar{1}$, a choice which was subsequently vindicated by successful refinement of the model with no anomalous effects.

The structure was resolved by a combination of Patterson and Fourier techniques. The co-ordinates of the cobalt and chlorine atoms were obtained from an analysis of the peaks in a sharpened, origin-removed vector map. The atoms were assigned isotropic thermal parameters equal to the overall thermal parameter ($U = 0.035Å^2$), obtained from a Wilson plot, and used to phase the observed structure factor moduli in a calculation of the electron density distribution, which revealed the sites of all non-hydrogen atoms.

Structure Refinement

Prior to least-squares refinement all atoms were assigned isotropic thermal parameters ($U_{iso} = 0.06Å^2$).The full-matrix least-squares refinement of positional, thermal and scale parameters converged after 19 cycles when R was 0.024 and $R'(=\sum w\Delta^2/\sum wF_o^2)$ was 0.00096. Full details of the course of refinement are given in Table 2.1.1. Initially unit weights were applied to all reflections. In later stages weights given by the expression

$$w = (0.2446 - 0.03074\,|F_o| + 0.00179\,|F_o|^2)^{-1}$$

were applied. The coefficients of the quadratic expression were obtained from a least-squares fit of $a + b\,|F_o| + c\,|F_o|^2$ to the distribution of $\langle w\Delta^2 \rangle$ with $\langle |F| \rangle$ obtained from an analysis of $w\Delta^2$ with increasing $|F|$. This weighting scheme leads to an approximately constant $\langle w\Delta^2 \rangle$ with increasing $|F_o|$ and sin θ.

A difference synthesis after cycle 5 revealed residual electron density peaks in positions which were stereochemically acceptable for hydrogen atoms. Hydrogen atoms were therefore introduced at those sites and assigned thermal parameters equal to those of the adjoining carbon atom after cycle 5. In the later stages of refinement corrections for the anomalous dispersion of cobalt and chlorine were applied, but did not contribute to any significant changes in the model.

The refinement was assumed complete when the parameter-shifts calculated by a cycle of least-squares refinement were insignificant compared to the corresponding estimated standard deviations. A final difference synthesis showed no errors in the model, the highest peak in the residual electron-density distribution being 0.3e/Å^3. In all structure-factor calculations the atomic scattering factors for cobalt were taken from 'International Tables for X-Ray Crystallography, Vol III$^{(66)}$, those for chlorine, nitrogen, oxygen and carbon were computed from numerical Hartree-Fock wave functions(67), whilst the scattering factors for hydrogen were those given by Stewart(68). Observed and final calculated structure factors are listed in Appendix I.

A general view of the dimer illustrating the thermal ellipsoids(69) and giving the atomic numbering scheme is given in Figure 2.1.1. A view of the unit cell contents along $\underline{a}$ is given in Figure 2.1.2. The final fractional co-ordinates and thermal parameters of all atoms are given in Table 2.1.2. The values of U_{ij} refer to the anisotropic temperature factor expression given in Part I. Bond lengths, valence angles and other relevant intra- and intermolecular data are given in Table 2.1.3 and Table 2.1.4.

TABLE 2.1.1

COURSE OF REFINEMENT

CYCLES	PARAMETERS REFINED	FINAL R	FINAL R'
1 - 5	X,Y,Z,U(ISO) FOR CO,CL,O,N,C. SCALE FACTOR. FULL MATRIX, UNIT WEIGHTS.	0.077	0.0058
6 - 7	AS ABOVE. HYDROGEN ATOMS INCLUDED BUT NOT REFINED.	0.071	0.0048
8 - 11	X,Y,Z,UIJ FOR CO,CL,O,N,C. SCALE FACTOR. FULL MATRIX, UNIT WEIGHTS. HYDROGEN ATOMS INCLUDED BUT NOT REFINED.	0.028	0.0012
12 - 13	AS ABOVE, BUT WITH WEIGHTING SCHEME APPLIED	0.026	0.0010
14 - 15	AS ABOVE,BUT WITH CORRECTIONS FOR ANOMALOUS DISPERSION OF CO,CL INCLUDED.	0.026	0.0010
16 - 19	AS FOR CYCLES 12-13, BUT WITH X,Y,Z,U(ISO) FOR H-ATOMS ALSO REFINED.	0.024	0.00096

TABLE 2.1.2

A. FRACTIONAL CO-ORDINATES($\times 10^5$) OF NON-HYDROGEN ATOMS

ATOM	X/A	Y/B	Z/C
CO	97742(3)	84108(2)	94232(3)
CL	80104(7)	97703(4)	93521(7)
N(3)	95663(25)	70661(16)	117757(23)
O(1)	108703(22)	71409(14)	103615(20)
O(2)	84964(22)	77614(15)	119952(20)
O(3)	93459(28)	63800(18)	128718(27)
N(1)	78312(23)	68437(14)	84835(22)
C(11)	84663(32)	59162(19)	75166(32)
C(12)	72923(36)	48967(21)	68526(36)
C(13)	53812(37)	48225(21)	71860(35)
C(14)	46912(34)	57546(21)	82147(35)
C(15)	59517(30)	67421(18)	88352(30)
N(2)	118264(22)	84971(14)	70199(20)
C(21)	135308(30)	83358(20)	68904(29)
C(22)	149083(35)	83143(21)	53245(33)
C(23)	145545(37)	85092(21)	38419(31)
C(24)	128226(40)	86928(23)	39488(31)
C(25)	114802(34)	86748(21)	55527(29)

TABLE 2.1.2(CONT'D)

B. FRACTIONAL CO-ORDINATES($\times 10^3$) AND THERMAL PARAMETERS($Å^2 \times 10^3$) OF HYDROGEN ATOMS.

ATOM	X/A	Y/B	Z/C	U(ISO)
H(11)	983(4)	560(2)	729(3)	72(8)
H(12)	789(4)	429(3)	607(4)	68(7)
H(13)	457(4)	418(3)	680(3)	69(8)
H(14)	345(4)	575(3)	850(4)	80(8)
H(15)	551(4)	746(2)	961(3)	64(7)
H(21)	1378(3)	826(2)	793(3)	56(6)
H(22)	1606(4)	819(3)	530(4)	80(8)
H(23)	1548(4)	850(2)	277(4)	67(7)
H(24)	1245(4)	889(3)	306(4)	84(9)
H(25)	1034(3)	878(2)	567(3)	49(6)

TABLE 2.1.2(CONT'D)

C. ANISOTROPIC THERMAL PARAMETERS($Å^2 \times 10^4$) OF NON-H ATOMS

ATOM	U11	U22	U33	U12	U13	U23
CO	374(1)	362(1)	432(1)	116(1)	-77(1)	32(1)
CL	462(3)	377(2)	627(3)	139(2)	-240(2)	-6(2)
N(3)	470(9)	466(9)	573(10)	42(7)	-192(8)	116(7)
O(1)	519(8)	609(9)	597(9)	222(7)	-103(7)	83(7)
O(2)	529(8)	613(9)	545(8)	176(7)	-49(7)	82(7)
O(3)	799(13)	810(13)	889(13)	37(10)	-308(10)	447(11)
N(1)	430(8)	379(8)	512(9)	96(6)	-128(7)	14(6)
C(11)	453(11)	452(11)	707(14)	116(9)	-83(10)	-49(10)
C(12)	609(14)	459(12)	773(16)	105(10)	-111(12)	-111(11)
C(13)	628(14)	419(11)	756(15)	-7(10)	-253(12)	-3(10)
C(14)	450(12)	508(12)	831(16)	82(9)	-244(11)	66(11)
C(15)	450(11)	422(10)	654(13)	132(8)	-162(9)	14(9)
N(2)	399(8)	417(8)	439(8)	79(6)	-99(6)	36(6)
C(21)	466(11)	540(11)	509(11)	173(9)	-82(9)	56(9)
C(22)	506(12)	560(12)	643(14)	178(10)	-2(10)	39(10)
C(23)	646(14)	518(12)	500(12)	56(10)	19(11)	-10(9)
C(24)	787(17)	599(13)	467(12)	0(11)	-218(11)	69(10)
C(25)	505(12)	582(12)	519(12)	61(10)	-196(9)	76(9)

TABLE 2.1.3

INTERATOMIC DISTANCES(Å) AND ANGLES(°) WITH ESTIMATED STANDARD DEVIATIONS IN PARANTHESIS.

A. BONDED DISTANCES

CO -CL	2.361(1)	CO -CL'	2.523(1)	CO -O(1)	2.204(2)
CO -O(2)	2.154(2)	CO -N(1)	2.147(2)	CO -N(2)	2.083(2)
N(3) -O(1)	1.260(2)	N(3) -O(2)	1.261(2)	N(3) -O(3)	1.219(3)
N(1) -C(11)	1.337(3)	N(1) -C(15)	1.341(3)	C(11)-C(12)	1.379(3)
C(12)-C(13)	1.372(4)	C(13)-C(14)	1.377(3)	C(14)-C(15)	1.378(3)
N(2) -C(21)	1.332(3)	N(2) -C(25)	1.339(3)	C(21)-C(22)	1.377(3)
C(22)-C(23)	1.361(3)	C(23)-C(24)	1.368(4)	C(24)-C(25)	1.382(3)
MEAN C-H	0.94				

B. INTERBOND ANGLES

CL -CO -CL'	86.46(1)	CL -CO -O(1)	161.72(5)
CL -CO -O(2)	103.38(5)	CL' -CO -O(1)	91.10(4)
CL' -CO -O(2)	90.14(3)	O(1) -CO -O(2)	58.48(6)
CL -CO -N(1)	93.79(6)	CL -CO -N(2)	105.00(5)
CL' -CO -N(1)	177.8(5)	CL' -CO -N(2)	89.64(4)
O(1) -CO -N(1)	87.96(6)	O(1) -CO -N(2)	93.09(6)
O(2) -CO -N(1)	87.63(6)	O(2) -CO -N(2)	151.55(8)
N(1) -CO -N(2)	92.45(6)	CO -O(1) -N(3)	91.8(1)
CO -O(2) -N(3)	94.1(1)	O(1) -N(3) -O(2)	115.3(2)
O(1) -N(3) -O(3)	123.0(2)	O(2) -N(3) -O(3)	121.7(2)
C(15)-N(1) -C(11)	117.1(2)	N(1) -C(11)-C(12)	123.1(2)
C(11)-C(12)-C(13)	119.0(2)	C(12)-C(13)-C(14)	118.8(2)
C(13)-C(14)-C(15)	118.9(2)	C(14)-C(15)-N(1)	123.1(2)
C(25)-N(2) -C(21)	117.6(2)	N(2) -C(21)-C(22)	123.0(2)
C(21)-C(22)-C(23)	119.0(2)	C(22)-C(23)-C(24)	118.9(2)
C(23)-C(24)-C(25)	119.3(2)	C(24)-C(25)-N(2)	122.1(2)
CO -N(1) -C(11)	120.5(1)	CO -N(1) -C(15)	122.3(1)
CO -N(2) -C(21)	120.2(1)	CO -N(2) -C(25)	122.2(1)
CL -CO -G	132.63(4)	N(2) -CO -G	122.36(6)

TABLE 2.1.3(CONT'D)

D. SELECTED INTRAMOLECULAR DISTANCES <3.6Å

CO ...N(3)	2.57	O(1) ...O(2)	2.13	O(1) ...O(3)	2.18
O(2) ...O(3)	2.17	CO ...CO'	3.56	CL ...CL'	3.35
N(2) ...CL	3.53	N(1) ...O(1)	3.02	N(2) ...CL'	3.26
N(1) ...O(2)	2.98	N(2) ...O(1)	3.11	N(1) ...CL	3.29
N(2) ...N(1)	3.05	N(1) ...N(3)	3.23	O(2) ...CL	3.54
O(1) ...CL'	3.38	O(2) ...CL'	3.32	O(2) ...C(15)	3.48
CO ...C(11)	3.05	CO ...C(21)	2.98	CO ...C(15)	3.08
CO ...C(25)	3.02	O(1) ...C(11)	3.23	N(1) ...C(25)	3.45
O(1) ...C(21)	3.16	N(2) ...C(11)	3.27	C(15)...CL	3.37
C(21)...CL'	3.53				

' INDICATES THE CENTROSYMMETRICALLY RELATED ATOM OF DIMER

D. INTERMOLECULAR DISTANCES ⩽ 3.6Å

O(1) ...C(14^{I})	3.58	C(22)...O(2^{II})	3.33	C(23)...O(2^{II})	3.22
O(3) ...C(12^{III})	3.57	N(3) ...C(24^{III})	3.37	O(1) ...C(24^{III})	3.60
O(3) ...C(24^{III})	3.34	O(3) ...C(25^{III})	3.44	O(3) ...C(11^{IV})	3.45
O(3) ...C(12^{IV})	3.38	O(3) ...C(13^{V})	3.45	O(3) ...C(14^{V})	3.54

ROMAN NUMERALS AS SUPERSCRIPTS REFER TO THE FOLLOWING EQUIVALENT POSITIONS RELATIVE TO THE REFERENCE MOLECULE AT X,Y,Z :

I	1+X, Y, Z	IV	2-X, 1-Y, 2-Z
II	1+X, Y, -1+Z	V	1-X, 1-Y, 2-Z
III	X, Y, 1+Z		

TABLE 2.1.4

LEAST-SQUARES PLANES

X,Y,Z ARE ORTHOGONAL CO-ORDINATES IN ANGSTROMS
AN ASTERISK(*) INDICATES ATOM USED IN DEFINING THE PLANE

1. EQUATION: $-0.2101X + 0.5263Y - 0.8240Z + 2.8538 = 0$

DISTANCES(Å) OF ATOMS FROM THE PLANE:-

N(1)*	0.012(2)	C(11)*	-0.004(2)	C(12)*	-0.007(3)
C(13)*	0.012(3)	C(14)*	-0.005(2)	C(15)*	-0.006(2)
CO	0.0507(2)	N(2)	1.492(2)		

2. EQUATION: $0.1480X + 0.9755Y + 0.1627Z - 10.6831 = 0$

DISTANCES(Å) OF ATOMS FROM THE PLANE:-

N(2)*	-0.003(2)	C(21)*	0.011(2)	C(22)*	-0.011(2)
C(23)*	0.002(2)	C(24)*	0.006(3)	C(25)*	-0.005(2)
CO	-0.0845(2)	N(1)	-1.992(2)		

3. EQUATION: $0.5824X + 0.6822Y + 0.4421Z - 13.2067 = 0$

DISTANCES(Å) OF ATOMS FROM THE PLANE:-

N(3)*	-0.002(2)	O(1)*	0.001(2)	O(2)*	0.001(2)
O(3)*	0.001(2)	CO	-0.1961(2)	CL	-0.262(1)
N(2)	-0.286(2)	C(21)	0.323(2)	C(22)	0.240(2)
C(23)	-0.453(2)	C(24)	-1.072(3)	C(25)	-0.978(2)
N(1)	-2.320(2)				

TABLE 2.1.4(CONT'D)

4\. EQUATION: $-0.5660X - 0.7337Y - 0.3761Z + 12.9061 = 0$

DISTANCES(Å) OF ATOMS FROM THE PLANE:-

CL*	-0.007(1)	O(1)*	-0.013(2)	O(2)*	0.012(2)
N(2)*	-0.008(2)	CO	0.0369(2)	N(3)	0.059(2)
O(3)	0.159(2)	N(1)	2.180(2)		

5\. EQUATION: $-0.5503X - 0.7488Y - 0.3694Z + 12.8461 = 0$

DISTANCES(Å) OF ATOMS FROM THE PLANE:-

O(1)*	0.000(2)	O(2)*	0.000(2)	CO*	0.0000(2)
CL	0.073(2)	N(2)	-0.030(2)		

6\. EQUATION: $-0.5657X - 0.7341Y - 0.3755Z + 12.8970 = 0$

DISTANCES(Å) OF ATOMS FROM THE PLANE:-

CL*	-0.016(1)	G*	-0.007(2)	N(2)*	0.000(2)
CO*	0.0293(2)				

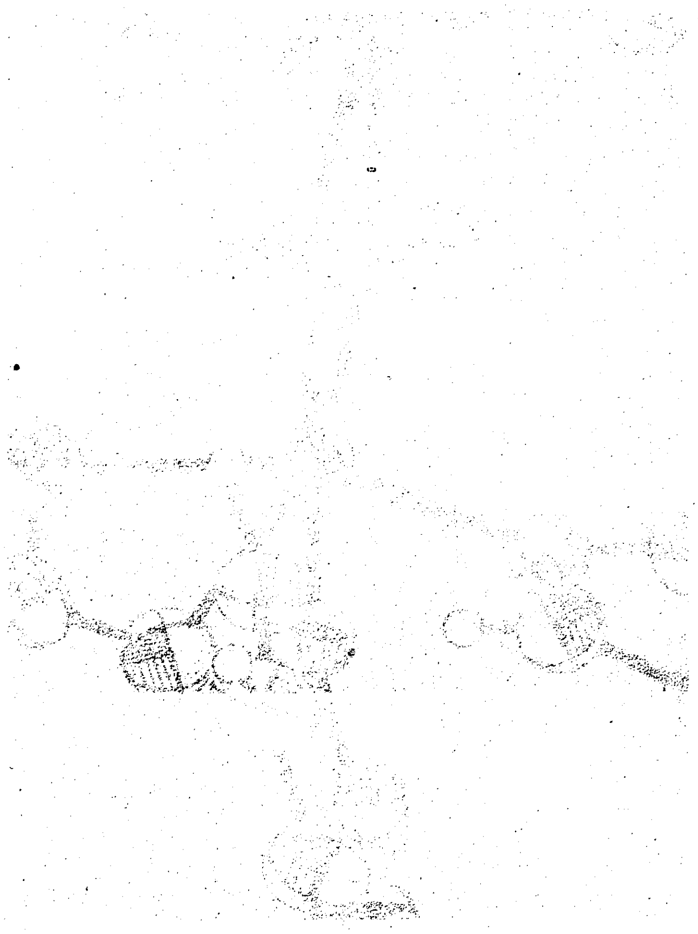
(G IS THE CENTROID OF O(1) AND O(2))

DIHEDRAL ANGLES(°) BETWEEN PLANES

1 AND 2	69.6	1 AND 3	97.3	2 AND 3	34.6
3 AND 5	174.1				

Figure 2.1.1

A general view of I giving the atomic numbering scheme. Hydrogen atoms are numbered as the atoms to which they are bonded.



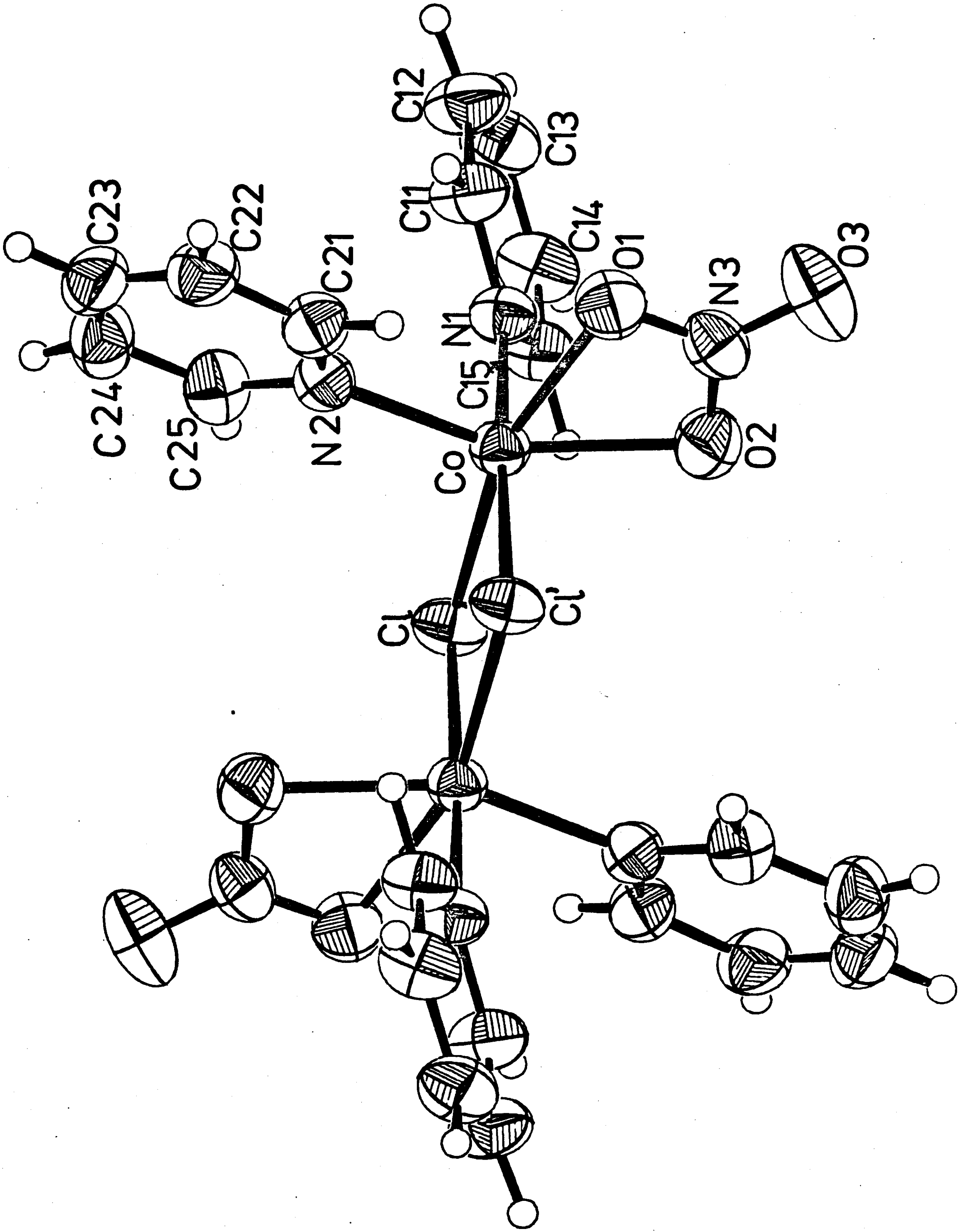
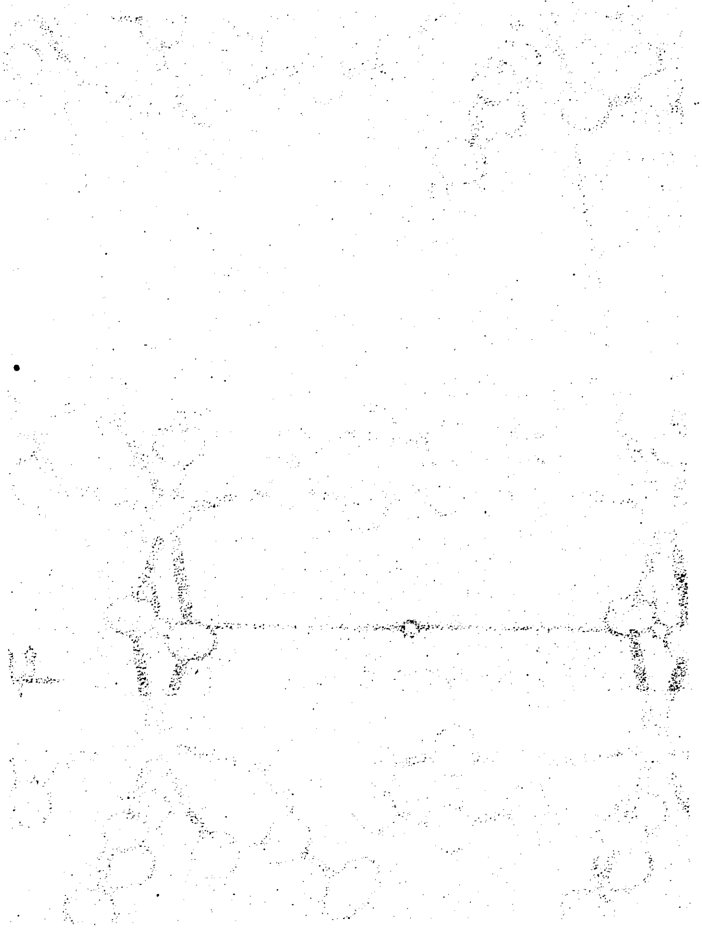
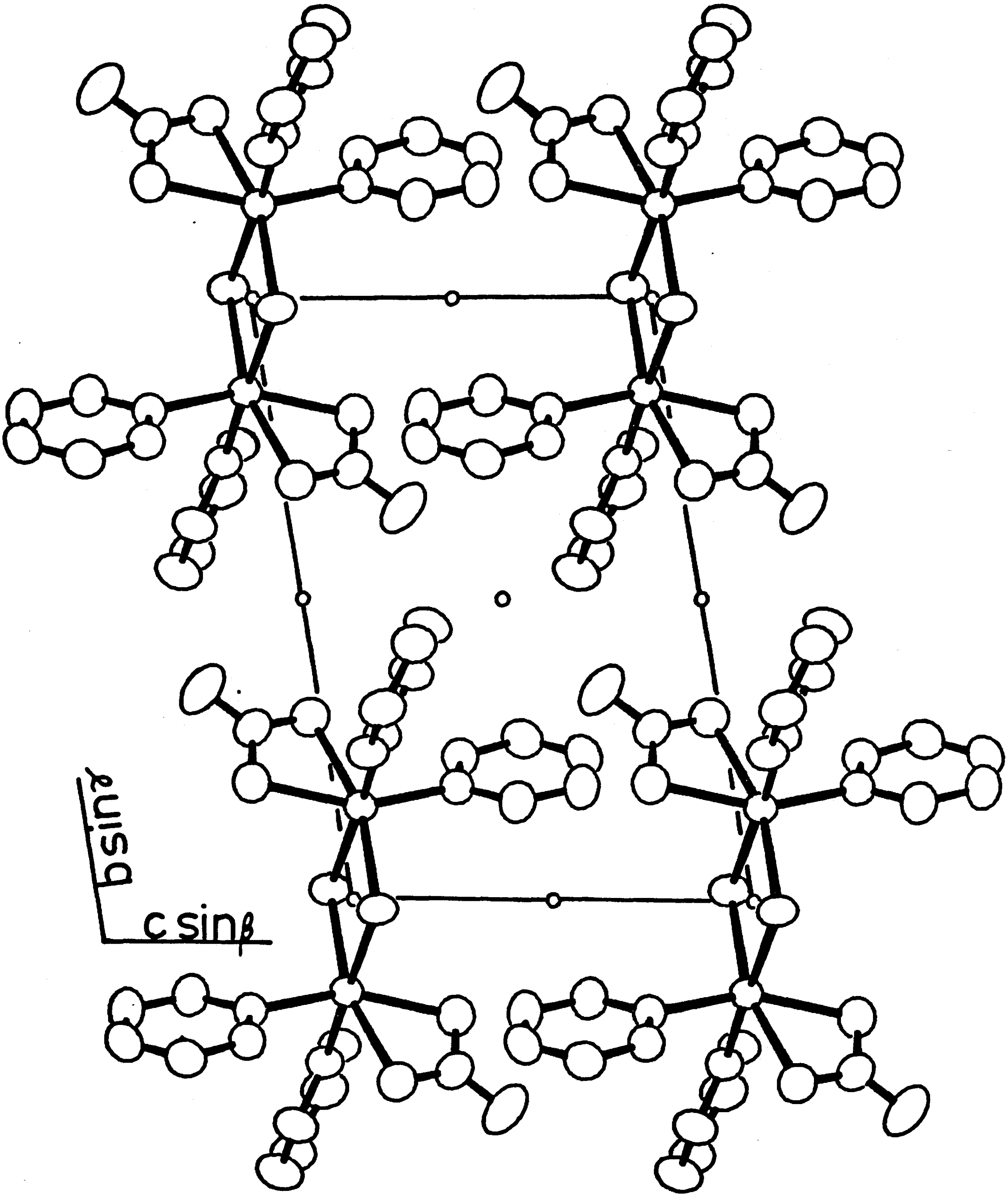

C23
C22
C21
C24
C25
N2
Co
C15
N1
C11
C12
C13
C14
O1
N3
O3
O2
Cl
Cl'

Figure 2.1.2

The molecular packing of I viewed along the a axis.




b sin α
c sin β

2.2 Experimental and results for II

Bis(acetonitrile)chloronitratocobalt(II) dimer

Di-μ-chloro-tetrakis-(acetonitrile)dinitratodicobalt(II)

Crystal data

Monomer formula	$C_4H_6N_3O_3ClCo$
Formula weight	$M = 238.5$
Crystal system	Monoclinic
Unit cell dimensions	$a = 10.222(1)$Å
	$b = 8.218(1)$Å
	$c = 11.118(1)$Å
	$\beta = 95.945(6)^\circ$
Unit cell volume	$U = 928.9$Å^3
Measured density	$D_m = 1.70$ g cm^{-3}
Number of monomers per unit cell	$Z = 4$
Calculated density	$D_c = 1.705$ g cm^{-3}
Number of electrons per unit cell	$F(000) = 476$
Linear absorption coefficient	$\mu(\text{Mo-K}_\alpha) = 21.8$ cm^{-1}
Space group	$P2_1/n$
Equivalent positions	X, Y, Z
	$\frac{1}{2} + X, \frac{1}{2} - Y, \frac{1}{2} + Z$
	$-X, -Y, -Z$
	$\frac{1}{2} - X, \frac{1}{2} + Y, \frac{1}{2} - Z$

Data collection

Radiation used	Mo-K_α $\lambda = 0.71069$Å
Filter	Zirconium
Upper limit for data collection	$2\theta_{max} = 50^\circ$
Number of independent reflections	$m = 1038$
Unobserved cut-off	$2\sigma_I$
Number of parameters refined	$n = 109$
Number of reflections per parameter	$m/n = 9.5$

Structure Determination

The space group is uniquely determined by its systematic absences ($h0l$ when $h + l$ is odd and $0k0$ when k is odd).

The structure was resolved by a combination of Patterson and Fourier techniques. The co-ordinates of the cobalt and chlorine atoms were obtained from an analysis of the peaks in a sharpened, origin-removed vector map. The atoms were assigned isotropic thermal parameters equal to the overall thermal parameter ($U = 0.039 Å^2$), obtained from a Wilson plot, and used to phase the observed structure factor moduli in a calculation of the electron density distribution, which revealed the sites for the acetonitrile atoms. Two further electron density calculations revealed the sites of all the non-hydrogen atoms.

Structure Refinement

Prior to least-squares refinement all atoms were assigned isotropic thermal parameters ($U_{iso} = 0.05 Å^2$). The full matrix least-squares refinement of positional, thermal and scale parameters converged after 16 cycles when R was 0.049 and R' was 0.0024. Full details of the course of refinement are given in Table 2.2.1. Initially unit weights were applied to all reflections. In later stages weights given by the expression

$$w = (a + b|F_o| + c|F_o|^2 + 3\sin\theta)^{-1}$$

were applied, where the coefficients were obtained from an analysis of the distribution of $\langle w\Delta^2\rangle$ with $\langle|F|\rangle$ and sin θ. The final values for the coefficients were a = 5.713, b = -0.2419, c = 0.0032. This weighting scheme leads to an approximately constant $\langle w\Delta^2\rangle$ with increasing $|F_o|$ and sin θ. A difference synthesis after cycle 9 revealed residual electron density peaks in positions which were stereochemically acceptable for hydrogen atoms. Hydrogen atoms were introduced at these sites and assigned isotropic thermal parameters equal to those of the adjoining carbon atom after cycle 5. The hydrogen atom parameters would not refine in a satisfactory manner, and after cycle 12 new positional co-ordinates for hydrogen atoms were calculated, and H atoms were introduced at these sites with isotropic temperature factors of 0.06Å^2, but not refined. In the later stages of refinement corrections for the anomalous dispersion of cobalt and chlorine were applied, but the corrections did not lead to any significant changes in the model.

The refinement was assumed complete when the parameter-shifts calculated by a cycle of least-squares refinement were insignificant compared to the corresponding estimated standard deviations. A final difference synthesis showed no errors in the model the highest peak in the residual electron density distribution being 0.4e/Å^3. In all structure factor calculations the atomic scattering factors for cobalt were taken from 'International Tables for X-Ray Crystallography,Vol III(66), those for chlorine, nitrogen, oxygen and carbon were computed from numerical Hartree-Fock wave functions(67), whilst the scattering factors for hydrogen were those given by Stewart(68).

Observed and final calculated structure factors are listed in Appendix II.

A general view of the dimer illustrating the thermal ellipsoids(69) and giving the atomic numbering scheme is given in Figure 2.2.1. The crystal packing arrangement viewed along b is given in Figure 2.2.2. The final fractional co-ordinates and thermal parameters of all atoms are given in Table 2.2.2. The values of U_{ij} refer to the anisotropic temperature factor expression given in Part I. Bond lengths valence angles and other relevant intra- and intermolecular data are given in Table 2.2.3 and Table 2.2.4.

TABLE 2.2.1

COURSE OF REFINEMENT

CYCLES	PARAMETERS REFINED	FINAL R	FINAL R'
1 - 3	X,Y,Z,U(ISO) FOR CO,CL,O,N,C. SCALE FACTOR. FULL MATRIX, UNIT WEIGHTS.	0.076	0.0071
3 - 5	X,Y,Z,UIJ FOR CO,CL,O,N,C(11),C(21). X,Y,Z,U(ISO) FOR C(22),C(12). SCALE FACTOR. FULL MATRIX, UNIT WEIGHTS.	0.060	0.0050
6 - 7	X,Y,Z,UIJ FOR CO,CL,O,N,C. SCALE FACTOR. FULL MATRIX, UNIT WEIGHTS.	0.057	0.0046
8 - 9	AS ABOVE, BUT WITH WEIGHTING SCHEME APPLIED	0.056	0.0041
10 - 16*	AS ABOVE, BUT WITH CORRECTIONS FOR ANOMALOUS DISPERSION OF CO,CL INCLUDED. HYDROGEN ATOMS INCLUDED BUT NOT REFINED.	0.049	0.0024

* PRIOR TO CYCLE 13, NEW CO-ORDINATES FOR H-ATOMS WERE CALCULATED, AND FOUR REFLECTIONS, FOR WHICH $|\Delta F| > 20$, WERE REMOVED FROM THE DATA SET.

TABLE 2.2.2

A. FRACTIONAL CO-ORDINATES($\times 10^4$) OF ALL ATOMS.

ATOM	X/A	Y/B	Z/C
CO	6080(1)	5023(1)	3925(1)
CL	6231(2)	5779(2)	5986(2)
N(2)	6656(6)	2605(8)	4252(6)
C(21)	6944(7)	1396(10)	4635(7)
C(22)	7329(9)	-0187(12)	5160(9)
N(3)	5337(6)	6622(8)	2015(6)
O(1)	5662(5)	5137(7)	2021(4)
O(2)	5419(5)	7280(6)	3047(5)
O(3)	4971(6)	7330(8)	1095(6)
N(1)	8023(6)	5672(8)	3719(6)
C(11)	9088(7)	5946(9)	3565(6)
C(12)	10454(7)	6247(11)	3372(7)
H(11)	10565	6833	2656
H(12)	10890	5168	3311
H(13)	10883	6824	4068
H(21)	7093	-0292	5990
H(22)	8313	-0293	5133
H(23)	6925	-1043	4610

TABLE 2.2.2(CONT'D)

B. THERMAL PARAMETERS($Å^2 \times 10^4$)

ATOM	U11	U22	U33	U12	U13	U23
CO	379(5)	331(5)	432(5)	14(5)	55(3)	9(5)
CL	351(9)	469(11)	445(10)	-50(8)	32(7)	-61(9)
N(2)	471(36)	318(37)	536(40)	71(30)	-36(30)	11(32)
C(21)	408(42)	467(52)	486(47)	-10(37)	-18(34)	-15(40)
C(22)	919(64)	474(61)	989(74)	101(54)	145(54)	191(56)
O(1)	650(31)	404(31)	504(31)	-86(32)	58(24)	20(31)
O(2)	604(34)	357(31)	575(36)	-14(25)	-49(27)	-25(27)
O(3)	865(45)	709(46)	676(41)	-164(34)	-214(34)	342(35)
N(1)	367(35)	527(41)	531(40)	3(29)	47(31)	83(32)
C(11)	473(45)	407(47)	353(40)	13(37)	-11(33)	55(34)
C(12)	364(41)	708(63)	627(54)	-78(39)	100(38)	40(45)

H-ATOMS WERE ASSIGNED U(ISO) OF $0.06 Å^2$

TABLE 2.2.3

INTERATOMIC DISTANCES(Å) AND ANGLES(°) WITH ESTIMATED STANDARD DEVIATIONS IN PARANTHESIS.

A. BONDED DISTANCES

CO	-CL	2.363(2)	CO	-CL'	2.464(2)	CO	-O(1)	2.118(5)
CO	-O(2)	2.171(5)	CO	-N(1)	2.092(6)	CO	-N(2)	2.094(6)
N(3)	-O(1)	1.265(9)	N(3)	-O(2)	1.263(9)	N(3)	-O(3)	1.202(9)
N(1)	-C(11)	1.142(10)	C(11)	-C(12)	1.455(10)			
N(2)	-C(21)	1.109(10)	C(21)	-C(22)	1.463(13)			

B. INTERBOND ANGLES

CL	-CO	-CL'	89.9(1)	CL	-CO	-O(1)	160.7(2)
CL	-CO	-O(2)	101.4(2)	CL'	-CO	-O(1)	87.6(1)
CL'	-CO	-O(2)	89.5(1)	O(1)	-CO	-O(2)	59.4(2)
CL	-CO	-N(1)	94.1(2)	CL	-CO	-N(2)	95.3(2)
CL'	-CO	-N(1)	176.0(3)	CL'	-CO	-N(2)	89.6(2)
O(1)	-CO	-N(1)	86.5(2)	O(1)	-CO	-N(2)	103.8(2)
O(2)	-CO	-N(1)	89.3(2)	O(2)	-CO	-N(2)	163.3(3)
N(1)	-CO	-N(2)	90.4(2)	CO	-O(1)	-N(3)	94.2(4)
CO	-O(2)	-N(3)	91.8(4)	O(1)	-N(3)	-O(2)	114.6(6)
O(1)	-N(3)	-O(3)	122.0(7)	O(2)	-N(3)	-O(3)	123.5(7)
CO	-N(1)	-C(11)	176.0(6)	N(1)	-C(11)	-C(12)	178.4(8)
CO	-N(2)	-C(21)	167.4(6)	N(2)	-C(21)	-C(22)	179.0(9)
CL	-CO	-G	134.1(2)	O(21)	-CO	-G	126.0(3)

C. SELECTED INTRAMOLECULAR DISTANCES <3.6Å

CO ...N(3)	2.55	O(1) ...O(2)	2.13	O(1) ...O(3)	2.16
N(2) ...CL	3.30	N(1) ...O(1)	2.94	N(2) ...CL'	3.22
O(2) ...O(3)	2.17	CO ...CO'	3.42	CL ...CL'	3.41
N(1) ...O(2)	3.00	N(2) ...O(1)	3.32	N(1) ...CL	3.27
N(2) ...N(1)	2.97	N(1) ...N(3)	3.26	O(2) ...CL	3.51
O(1) ...CL'	3.18	O(2) ...CL'	3.27		

' INDICATES THE CENTROSYMMETRICALLY RELATED ATOM OF DIMER

TABLE 2.2.3(CONT'D)

D. INTERMOLECULAR DISTANCES $\leqslant$ 3.6Å

N(3) ...N(2^{I})	3.60	N(3) ...C(21^{I})	3.49	O(1) ...C(21^{I})	3.37
O(1) ...C(22^{I})	3.35	O(2) ...C(11^{I})	3.57	O(3) ...N(2^{I})	3.52
O(3) ...C(21^{I})	3.42	O(3) ...N(1^{I})	3.42	O(3) ...C(12^{I})	3.31
N(2) ...C(11^{I})	3.42	C(11)...O(1^{I})	3.52	C(12)...O(1^{I})	3.41
N(1) ...O(3^{II})	3.54	C(11)...O(3^{II})	3.19	O(3) ...C(12^{II})	3.33
O(2) ...C(22^{III})	3.57	C(22)...O(3^{IV})	3.30		

ROMAN NUMERALS AS SUPERSCRIPTS REFER TO THE FOLLOWING EQUIVALENT POSITIONS RELATIVE TO THE REFERENCE MOLECULE AT X,Y,Z :

I	3/2-X,	1/2+Y,	1/2-Z	III	X,	1+Y,	Z
II	1/2+X,	3/2-Y,	1/2+Z	IV	1/2+X,	1/2-Y,	1/2+Z

TABLE 2.2.4

LEAST-SQUARES PLANES

X,Y,Z ARE ORTHOGONAL CO-ORDINATES IN ANGSTROMS
AN ASTERISK(*) INDICATES ATOM USED IN DEFINING THE PLANE

1. EQUATION: $-0.9597X - 0.2634Y + 0.0984Z + 6.2239 = 0$

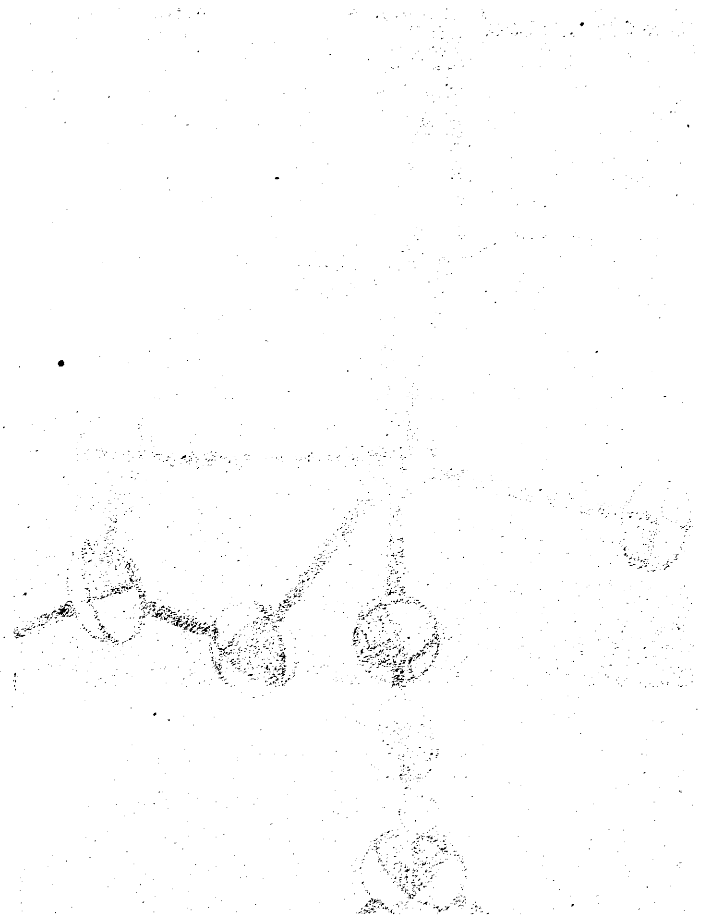
DISTANCES(Å) OF ATOMS FROM THE PLANE:-

N(3)*	-0.002(6)	O(1)*	0.001(5)	O(2)*	0.001(5)
O(3)*	0.001(6)	CO	0.034(1)	CL	0.174(2)
N(2)	0.063(6)	C(21)	0.127(7)	C(22)	0.207(10)

```
                          TABLE 2.2.4(CONT'D)

2.    EQUATION:  -0.9627X - 0.2644Y + 0.0571Z + 6.3612 = 0

      DISTANCES(Å) OF ATOMS FROM THE PLANE:-

      CL*       0.015(2)    O(1)*     0.024(5)    O(2)*   -0.023(5)
      N(2)*    -0.016(6)    CO       -0.030(1)    N(3)     0.021(6)
      O(3)      0.067(6)    N(1)     -2.120(6)

3.    EQUATION:  -0.9626X - 0.2648Y + 0.0573Z + 6.3675 = 0

      DISTANCES(Å) OF ATOMS FROM THE PLANE:-

      CL*       0.021(2)    G*        0.006(5)    N(2)*   -0.009(6)
      CO*      -0.024(1)
      (G IS THE CENTROID OF O(1) AND O(2))

4.    EQUATION:   0.9636X + 0.2546Y - 0.0835Z - 6.2405 = 0

      DISTANCES(Å) OF ATOMS FROM THE PLANE:-

      O(1)*     0.000(5)    O(2)*     0.000(5)    CO*      0.000(1)
      CL       -0.112(2)    N(2)     -0.004(6)


      DIHEDRAL ANGLES(°) BETWEEN PLANES
         1 AND 4   179.0      1 AND 2      0.1      1 AND 3      2.4
```

Figure 2.2.1

A general view of II showing the atomic numbering scheme. Hydrogen atoms are numbered as the atoms to which they are bonded.



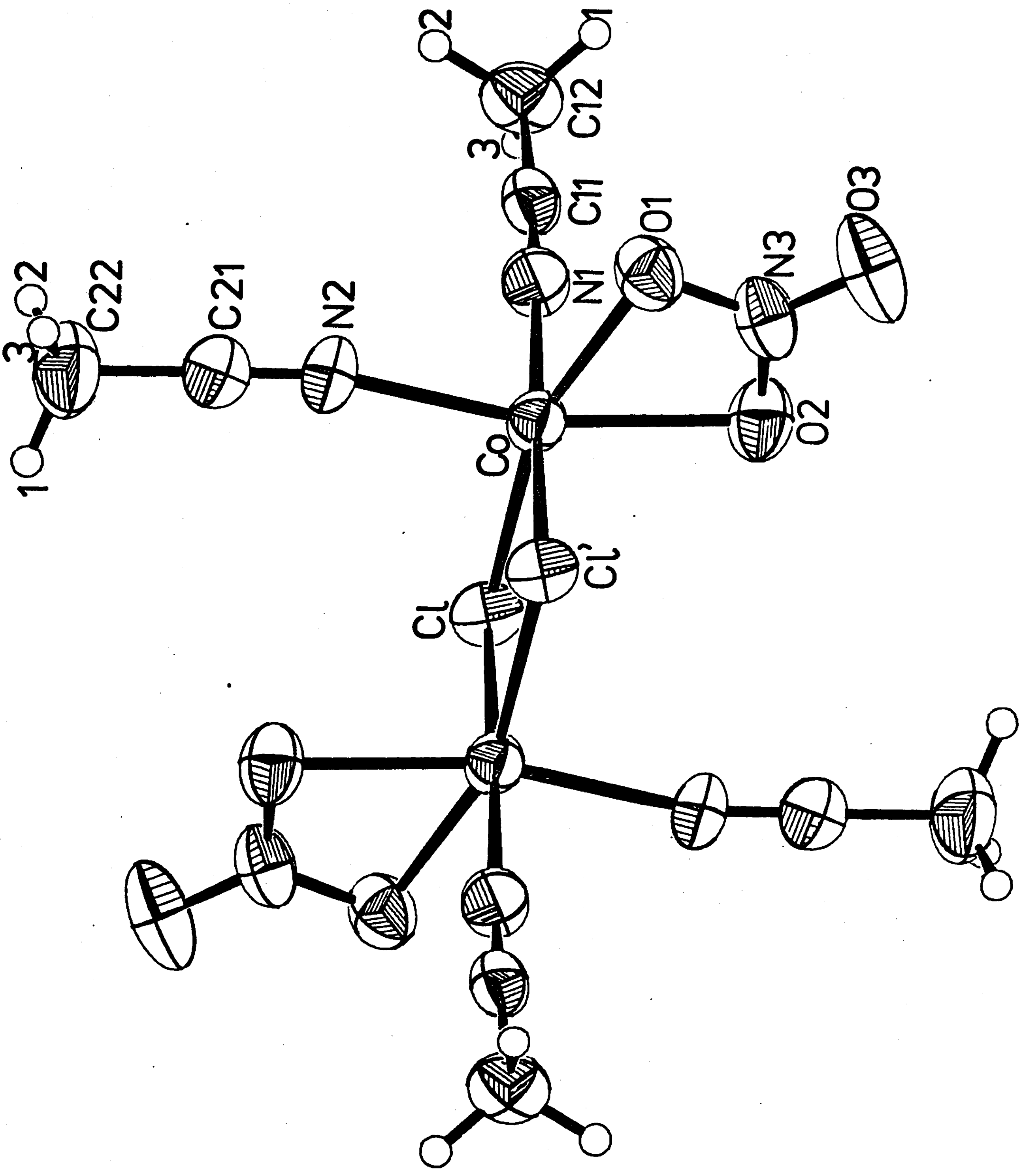
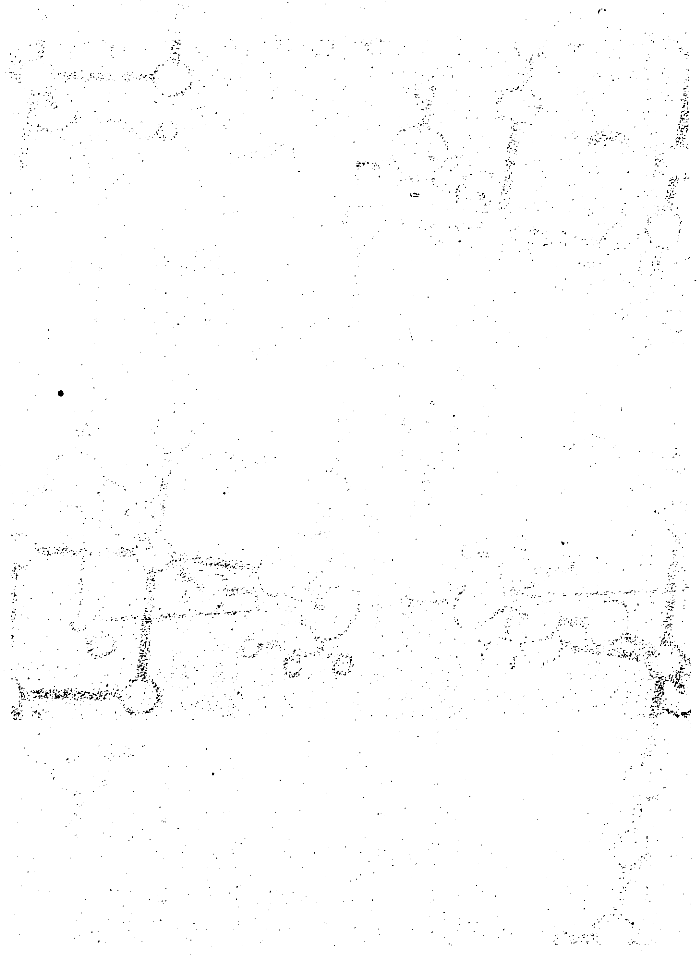
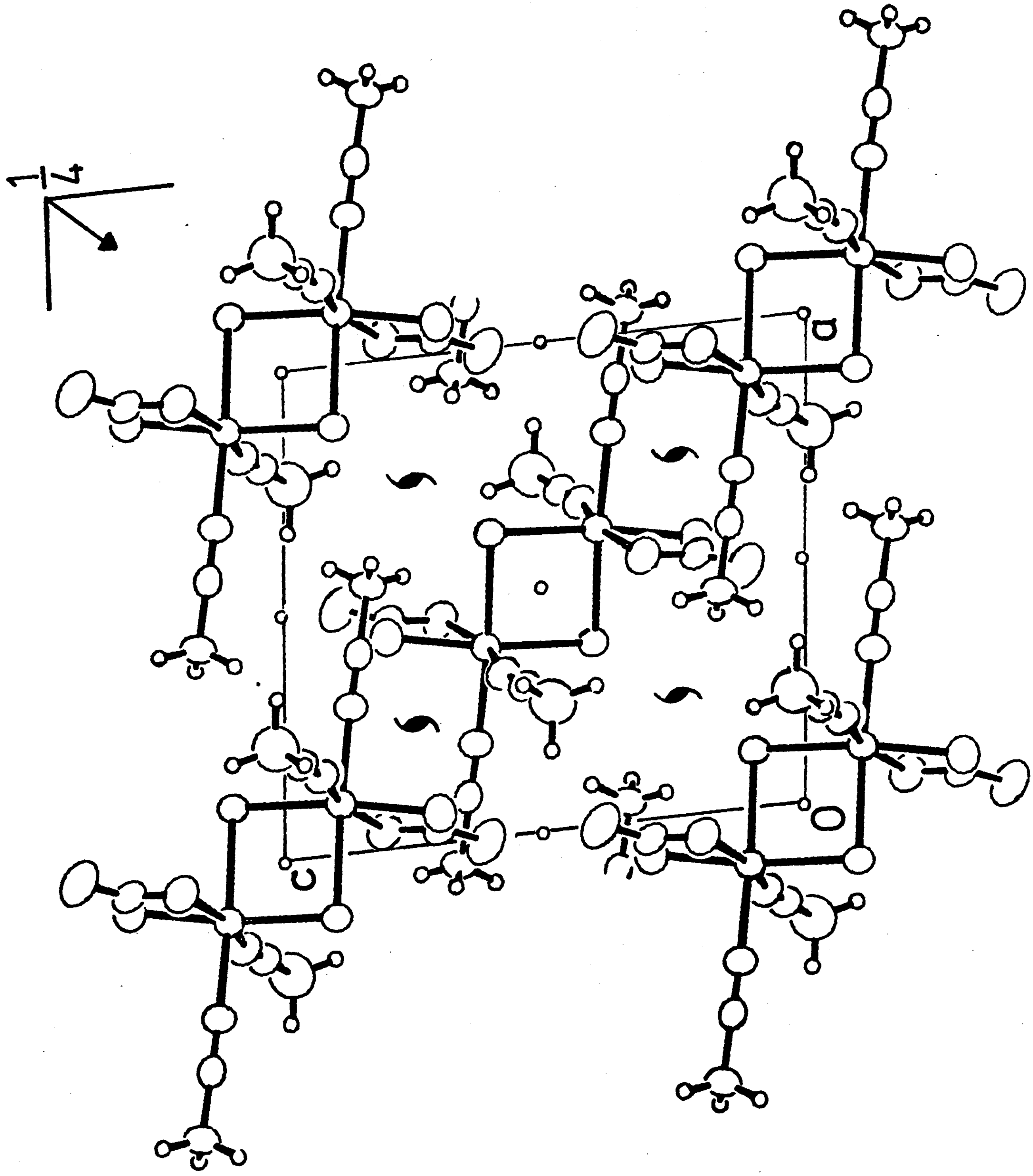

1
2
3
C22
C21
N2
Co
2
1
3
C12
C11
N1
O1
N3
O3
O2
Cl
Cl'
2
3
1

Figure 2.2.2

The molecular packing of II viewed along the b axis.





2.3 Experimental and results for III

Bis(tetrahydrofuran)chloronitratocobalt(II) dimer

Di-μ-chloro-tetrakis-(tetrahydrofuran)dinitratodicobalt(II)

Crystal data

Monomer formula	$C_8H_{16}O_5NClCo$
Formula weight	M = 300.6
Crystal system	Monoclinic
Unit cell dimensions	a = 9.529(4)Å
	b = 8.028(2)Å
	c = 17.347(3)Å
	β = 100.84(3)°
Unit cell volume	U = 1303.3Å^3
Measured density	D_m = 1.52 g cm^{-3}
Number of monomers per unit cell	Z = 4
Calculated density	D_c = 1.53 g cm^{-3}
Number of electrons per unit cell	F(000) = 620
Linear absorption coefficient	μ(Mo-K$_\alpha$) = 15.8 cm^{-1}
Space group	$P2_1/n$
Equivalent positions	X, Y, Z
	$\frac{1}{2}$ + X, $\frac{1}{2}$ - Y, $\frac{1}{2}$ + Z
	-X, -Y, -Z
	$\frac{1}{2}$ - X, $\frac{1}{2}$ + Y, $\frac{1}{2}$ - Z

Data collection

Radiation used	Mo-K_α, $\lambda = 0.71069$Å
Filter	Zirconium
Upper limit for data collection	$2\theta_{max} = 50^\circ$
Number of independent reflections	$m = 1267$
Unobserved cut-off	$2\sigma_I$
Number of parameters refined	$n = 145$
Number of reflections per parameter	$m/n = 8.7$

Structure Determination

The space group is uniquely determined by its systematic absences (h0l when h + l is odd and 0k0 when k is odd).

The structure was resolved by a combination of Patterson and Fourier techniques. The co-ordinates of the cobalt and chlorine atoms were obtained from an analysis of the peaks in a sharpened, origin-removed vector map. The atoms were assigned isotropic thermal parameters equal to the overall thermal parameter ($U = 0.03\text{Å}^2$), obtained from a Wilson plot, and used to phase the observed structure factor moduli in a calculation of the electron density distribution, which revealed sites for all non-hydrogen atoms.

Structure Refinement

Prior to least-squares refinement all atoms were assigned isotropic thermal parameters ($U_{iso} = 0.05\text{Å}^2$). The full matrix least-squares refinement of positional, thermal and scale parameters converged after 15 cycles when R was 0.057 and R' was 0.0044. Full details of the course of refinement are given in Table 2.3.1. Initially unit weights were applied to all reflections. In later stages weights given by the expression

$$w = (2.801 - 0.1314|F_o| + 0.0029|F_o|^2)^{-1}$$

were applied. The coefficients of the quadratic expression were obtained from a least-squares fit of $a + b|F_o| + c|F_o|^2$ to the distribution of $\langle w\Delta^2 \rangle$ with $\langle |F_o| \rangle$ obtained from an analysis of $w\Delta^2$ with increasing $|F_o|$. This weighting scheme leads to an approximately constant $\langle w\Delta^2 \rangle$ with increasing $|F_o|$ and $\sin\theta$.

A difference synthesis after cycle 4 did not reveal any residual electron density in positions which would be stereochemically acceptable for hydrogen atoms. Therefore positions for the hydrogen atoms were calculated and their calculated co-ordinates, together with isotropic thermal parameters equal to those of the adjoining carbon atom after cycle 4, were used as fixed contributors to the structure factors. These co-ordinates were re-calculated in later stages of refinement. In the later stages of refinement corrections for the anomalous dispersion of cobalt and chlorine were applied, but the corrections did not lead to any significant changes in the model.

The refinement was assumed complete when the parameter-shifts calculated by a cycle of least-squares refinement were insignificant compared to the corresponding estimated standard deviations. A final difference synthesis showed no errors in the model, the highest peak in the residual electron density distribution being $0.35 e\text{Å}^{-3}$. In all structure factor calculations the atomic scattering factors were taken from 'International Tables for X-Ray Crystallography, Vol 111'(66), those for chlorine, nitrogen, oxygen and carbon were computed from numerical Hartree-Fock wave functions(67), whilst the scattering factors for hydrogen were those given by Stewart(68). Observed and final calculated structure factors are listed in

Appendix III.

A general view of the dimer illustrating the thermal ellipsoids(69) and giving the atomic numbering scheme is given in Figure 2.3.1. The crystal packing arrangement viewed along b is given in Figure 2.3.2. The final fractional co-ordinates and thermal parameters of all atoms are given in Table 2.3.2. The values of U_{ij} refer to the anisotropic temperature factor expression given in Part I. Bond lengths, valence angles and other relevant intra- and intermolecular data are given in Table 2.3.3 and Table 2.3.4.

TABLE 2.3.1

COURSE OF REFINEMENT

CYCLES	PARAMETERS REFINED	FINAL R	FINAL R'
1 - 4	X,Y,Z,U(ISO) FOR CO,CL,O,N,C. SCALE FACTOR. FULL MATRIX, UNIT WEIGHTS.	0.139	0.0213
5 - 10*	X,Y,Z,UIJ FOR CO,CL,O,N,C. H-ATOMS INCLUDED BUT NOT REFINED. SCALE FACTOR. FULL MATRIX, UNIT WEIGHTS.	0.058	0.0035
11 - 12	AS ABOVE, BUT WITH WEIGHTING SCHEME APPLIED	0.058	0.0044
13 - 15	AS ABOVE, BUT WITH CORRECTIONS FOR ANOMALOUS DISPERSION OF CO,CL INCLUDED.	0.057	0.0044

* PRIOR TO CYCLE 8, THE CO-ORDINATES FOR H-ATOMS WERE RE-CALCULATED, AND FOUR REFLECTIONS, FOR WHICH $|\Delta F| > 10$, WERE REMOVED FROM THE DATA SET.

TABLE 2.3.2

A. FRACTIONAL CO-ORDINATES($\times 10^4$) OF NON-HYDROGEN ATOMS.

ATOM	X/A	Y/B	Z/C
CO	6049(1)	4797(1)	4289(1)
CL	6232(2)	3905(3)	5608(1)
N	6814(9)	7386(11)	3653(6)
O(1)	6134(7)	6244(8)	3262(3)
O(2)	7094(7)	7160(8)	4381(4)
O(3)	7169(10)	8628(10)	3334(5)
O(11)	8015(6)	3704(8)	4193(3)
C(12)	8565(14)	2213(16)	4557(9)
C(13)	9761(13)	1674(16)	4188(9)
C(14)	10112(14)	3042(21)	3760(8)
C(15)	8938(16)	4300(20)	3712(8)
O(21)	5064(6)	2752(7)	3712(3)
C(22)	4663(18)	2647(16)	2889(6)
C(23)	3663(18)	1333(18)	2687(7)
C(24)	3487(13)	0513(15)	3391(8)
C(25)	4389(14)	1375(14)	4025(6)

TABLE 2.3.2(CONT'D)

B. CALCULATED FRACTIONAL CO-ORDINATES($\times 10^4$) AND ASSIGNED THERMAL PARAMETERS($Å^2 \times 10^2$) OF H-ATOMS.

ATOM	X/A	Y/B	Z/C	U(ISO)
H(121)	8984	2411	5135	12
H(122)	7880	1334	4523	12
H(131)	10620	1236	4590	12
H(132)	9482	0702	3847	12
H(141)	11069	3496	4000	12
H(142)	10199	2666	3215	12
H(151)	9473	5319	3924	14
H(121)	8550	4410	3176	14
H(221)	4121	3717	2687	13
H(222)	5406	2473	2621	13
H(231)	2686	1811	2442	13
H(232)	3962	0585	2339	13
H(241)	2450	0521	3450	11
H(242)	3767	-0659	3366	11
H(251)	3755	1817	4393	11
H(252	5062	0612	4321	11

TABLE 2.3.2(CONT'D)

C. ANISOTROPIC THERMAL PARAMETERS($\mathring{A}^2 \times 10^4$ FOR CO,CL; $\mathring{A}^2 \times 10^3$ FOR OTHER ATOMS)

ATOM	U11	U22	U33	U12	U13	U23
CO	828(7)	701(7)	503(5)	8(6)	86(4)	3(5)
CL	823(14)	974(16)	513(10)	158(12)	42(9)	103(10)
N	111(6)	71(5)	112(7)	0(5)	48(5)	-2(5)
O(1)	127(5)	75(4)	62(3)	0(4)	21(3)	11(3)
O(2)	126(5)	92(4)	73(4)	-17(4)	20(4)	-10(3)
O(3)	207(9)	92(5)	146(7)	-18(6)	67(6)	28(5)
O(11)	96(4)	90(4)	85(4)	21(4)	35(3)	15(3)
C(12)	147(11)	117(9)	195(13)	35(7)	82(10)	49(9)
C(13)	105(9)	119(10)	212(14)	25(8)	57(9)	17(10)
C(14)	130(11)	192(14)	155(11)	65(11)	69(9)	53(11)
C(15)	166(12)	193(14)	162(12)	63(12)	98(10)	55(11)
O(21)	118(5)	74(4)	51(3)	-12(3)	8(3)	-2(3)
C(22)	252(16)	149(11)	59(6)	-58(11)	-3(7)	-3(7)
C(23)	250(17)	138(11)	99(9)	-73(12)	-65(10)	-12(8)
C(24)	136(10)	100(8)	131(10)	-19(7)	8(8)	-25(8)
C(25)	183(11)	100(8)	77(6)	-38(8)	21(7)	-10(6)

TABLE 2.3.3

INTERATOMIC DISTANCES(Å) AND ANGLES(°) WITH ESTIMATED STANDARD DEVIATIONS IN PARANTHESIS.

```
A.   BONDED DISTANCES

     CO    -CL       2.372(2)    CO    -CL'      2.447(2)    CO    -O(1)     2.141(6)
     CO    -O(2)     2.135(6)    CO    -O(11)    2.104(6)    CO    -O(21)    2.056(5)
     N     -O(1)     1.247(10)   N     -O(2)     1.255(12)   N     -O(3)     1.218(13)
     O(11)-C(12)     1.408(14)   O(11)-C(15)     1.405(17)   C(12)-C(13)     1.474(21)
     C(13)-C(14)     1.401(22)   C(14)-C(15)     1.498(22)
     O(21)-C(22)     1.409(11)   O(21)-C(25)     1.436(13)   C(22)-C(23)     1.421(21)
     C(23)-C(24)     1.423(10)   C(24)-C(25)     1.439(16)

B.   INTERBOND ANGLES

     CL    -CO    -CL'      87.9(1)           CL    -CO    -O(1)    163.5(2)
     CL    -CO    -O(2)    104.4(2)           CL'   -CO    -O(1)     90.2(2)
     CL'   -CO    -O(2)     91.4(2)           O(1)  -CO    -O(2)     59.3(2)
     CL    -CO    -O(11)    92.6(2)           CL    -CO    -O(21)    99.9(2)
     CL'   -CO    -O(11)   179.3(13)          CL'   -CO    -O(21)    92.6(2)
     O(1)  -CO    -O(11)    89.2(2)           O(1)  -CO    -O(21)    96.5(2)
     O(2)  -CO    -O(11)    88.1(3)           O(2)  -CO    -O(21)   155.5(2)
     O(11)-CO     -O(21)    87.7(2)           CO    -O(1)  -N        92.6(5)
     CO    -O(2)  -N        92.6(5)           O(1)  -N     -O(2)    115.5(8)
     O(1)  -N     -O(3)    121.1(9)           O(2)  -N     -O(3)    123.4(8)
     C(15)-O(11)-C(12)     109.6(10)          O(11)-C(12)-C(13)     107.9(11)
     C(12)-C(13)-C(14)     106.4(11)          C(13)-C(14)-C(15)     107.9(12)
     C(14)-C(15)-O(11)     106.4(12)
     C(25)-O(21)-C(22)     106.4(8)           O(21)-C(22)-C(23)     109.6(11)
     C(22)-C(23)-C(24)     108.2(10)          C(23)-C(24)-C(25)     106.4(11)
     C(24)-C(25)-O(21)     109.1(8)
     CO    -O(11)-C(12)    125.5(7)           CO    -O(11)-C(15)    124.9(7)
     CO    -O(21)-C(22)    123.6(6)           CO    -O(21)-C(25)    128.8(5)
     CL    -CO    -G       131.1(2)           N(2)  -CO    -G       133.5(2)
```

TABLE 2.3.3(CONT'D)

C. SELECTED TORSION ANGLES

C(15)-O(11)-C(12)-C(13)	-10.2	O(11)-C(12)-C(13)-C(14)	14.2
C(12)-C(13)-C(14)-C(15)	-12.5	C(13)0C(14)-C(15)-O(11)	6.6
C(14)-C(15)-O(11)-C(12)	2.5	C(24)-O(21)-C(22)-C(23)	5.0
O(21)-C(22)-C(23)-C(24)	-3.6	C(22)-C(23)-C(24)-C(25)	0.8
C(23)-C(24)-C(25)-O(21)	2.3	C(24)-C(25)-O(21)-C(22)	-4.5

MEAN E.S.D. 1.4

D. SELECTED INTRAMOLECULAR DISTANCES ≤3.65Å

CO ...N	2.53	O(1) ...O(2)	2.12	O(1) ...O(3)	2.15
O(2) ...O(3)	2.18	CO ...CO'	3.47	CL ...CL'	3.35
O(21)...CL	3.40	O(11)...O(1)	2.98	O(21)...CL'	3.27
O(11)...O(2)	2.95	O(21)...O(1)	3.13	O(11)...CL	3.24
O(21)...O(11)	2.88	O(11)...N	3.24	O(2) ...CL	3.56
O(2) ...CL	3.56	O(1) ...CL'	3.26	O(2) ...CL'	3.29
O(2) ...C(15)	3.24	CO ...C(12)	3.14	CO ...C(22)	3.07
CO ...C(15)	3.13	CO ...C(25)	3.16	O(1) ...C(15)	3.07
O(11)...C(22)	3.65	O(1) ...C(22)	3.22	O(21)...C(12)	3.41
C(12)...CL	3.41	C(21)...CL'	3.27		

' INDICATES THE CENTROSYMMETRICALLY RELATED ATOM OF DIMER

E. INTERMOLECULAR DISTANCES(A) < 3.7Å

O(3)...C(12^{I})	3.67	O(3)...C(13^{I})	3.59	O(3)...C(15^{II})	3.55
O(2)...C(13^{III})	3.63				

ROMAN NUMERALS AS SUPERSCRIPTS REFER TO THE FOLLOWING EQUIVALENT POSITIONS RELATIVE TO THE REFERENCE MOLECULE AT X,Y,Z :

I X, 1+Y, Z   II 3/2-X, 1/2+Y, 1/2-Z   III 2-X, 1-Y, 1-Z

TABLE 2.3.4

```
                          LEAST-SQUARES PLANES

   X,Y,Z ARE ORTHOGONAL CO-ORDINATES IN ANGSTROMS
   AN ASTERISK(*) INDICATES ATOM USED IN DEFINING THE PLANE

1.    EQUATION:  -0.4270X - 0.4586Y - 0.7793Z + 9.6447 = 0

      DISTANCES(Å) OF ATOMS FROM THE PLANE:-

      O(11)*   0.037(6)     C(12)*  -0.071(14)    C(13)*   0.079(15)
      C(14)*  -0.058(14)    C(15)*   0.013(15)    CO       0.320(1)
      CL      -0.993(2)     N       -0.189(9)     O(1)     0.973(6)
      O(2)    -1.085(7)

2.    EQUATION:   0.7913X - 0.6080Y - 0.0652Z + 1.1314 = 0

      DISTANCES(Å) OF ATOMS FROM THE PLANE:-

      O(21)*  -0.028(6)     C(22)*   0.025(15)    C(23)*  -0.013(16)
      C(24)*  -0.005(12)    C(25)*   0.020(12)    CO      -0.496(1)
      CL      -0.409(2)

3.    EQUATION:   0.8924X - 0.4429Y - 0.0866Z - 1.5651 = 0

      DISTANCES(Å) OF ATOMS FROM THE PLANE:-

      N*       0.001(9)     O(1)*    0.000(7)     O(2)*    0.000(7)
      O(3)*    0.000(9)     CO      -0.009(1)     CL       0.114(2)
```

```
                              TABLE 2.3.4(CONT'D)

4.     EQUATION:    0.9057X - 0.4221Y - 0.0397Z - 2.0521 = 0

       DISTANCES(Å) OF ATOMS FROM THE PLANE:-

       CL*      -0.033(2)     O(1)*    -0.058(7)     O(2)*     0.054(7)
       O(21)*    0.038(6)     CO       -0.015(1)     N         0.000(9)
       O(3)      0.000(9)     O(11)     2.088(6)

5.     EQUATION:    0.9056X - 0.4223Y - 0.0396Z - 2.0484 = 0

       DISTANCES(Å) OF ATOMS FROM THE PLANE:-
       CL*      -0.030(2)     G*        0.000(7)     O(21)*    0.041(6)
       CO*      -0.012(1)
       (G IS THE CENTROID OF O(1) AND O(2))


       DIHEDRAL ANGLES(°) BETWEEN PLANES

          1 AND 2     90.5       1 AND 3     96.3       2 AND 3     11.2
```

Figure 2.3.1

A general view of III showing the atomic numbering scheme. Hydrogen atoms are numbered as the atoms to which they are bonded.

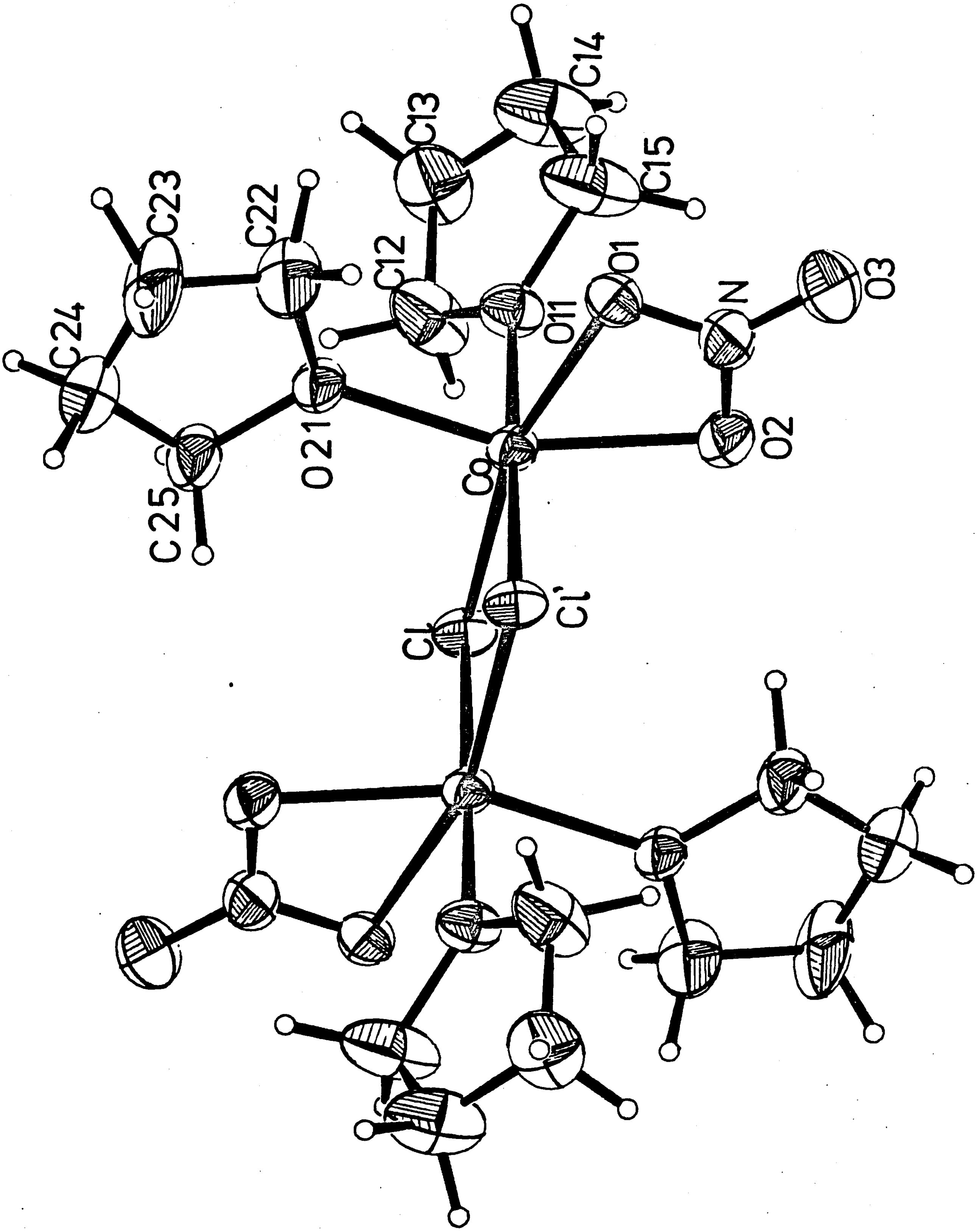
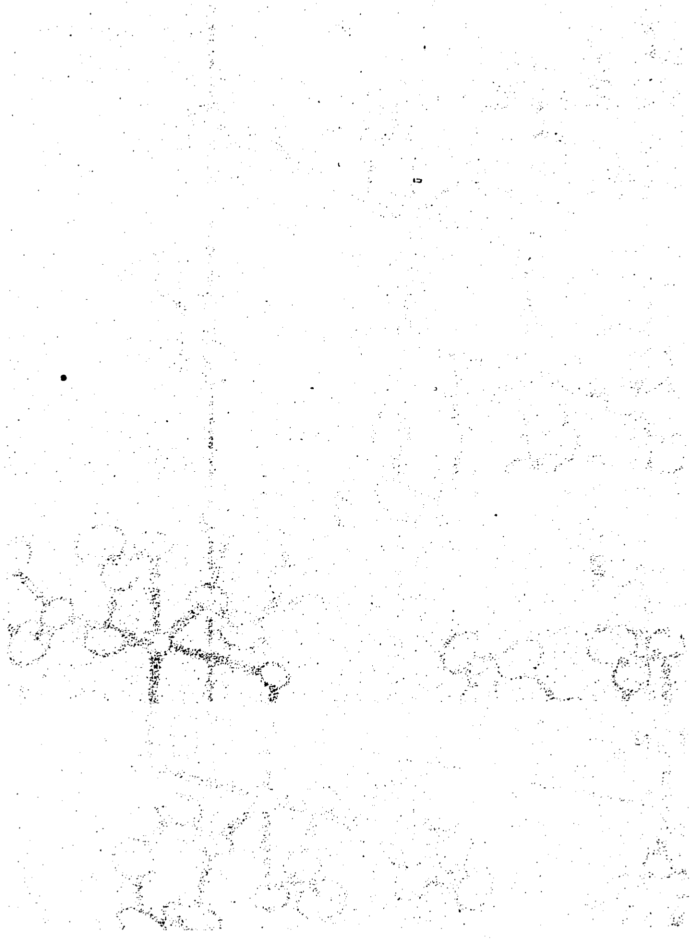
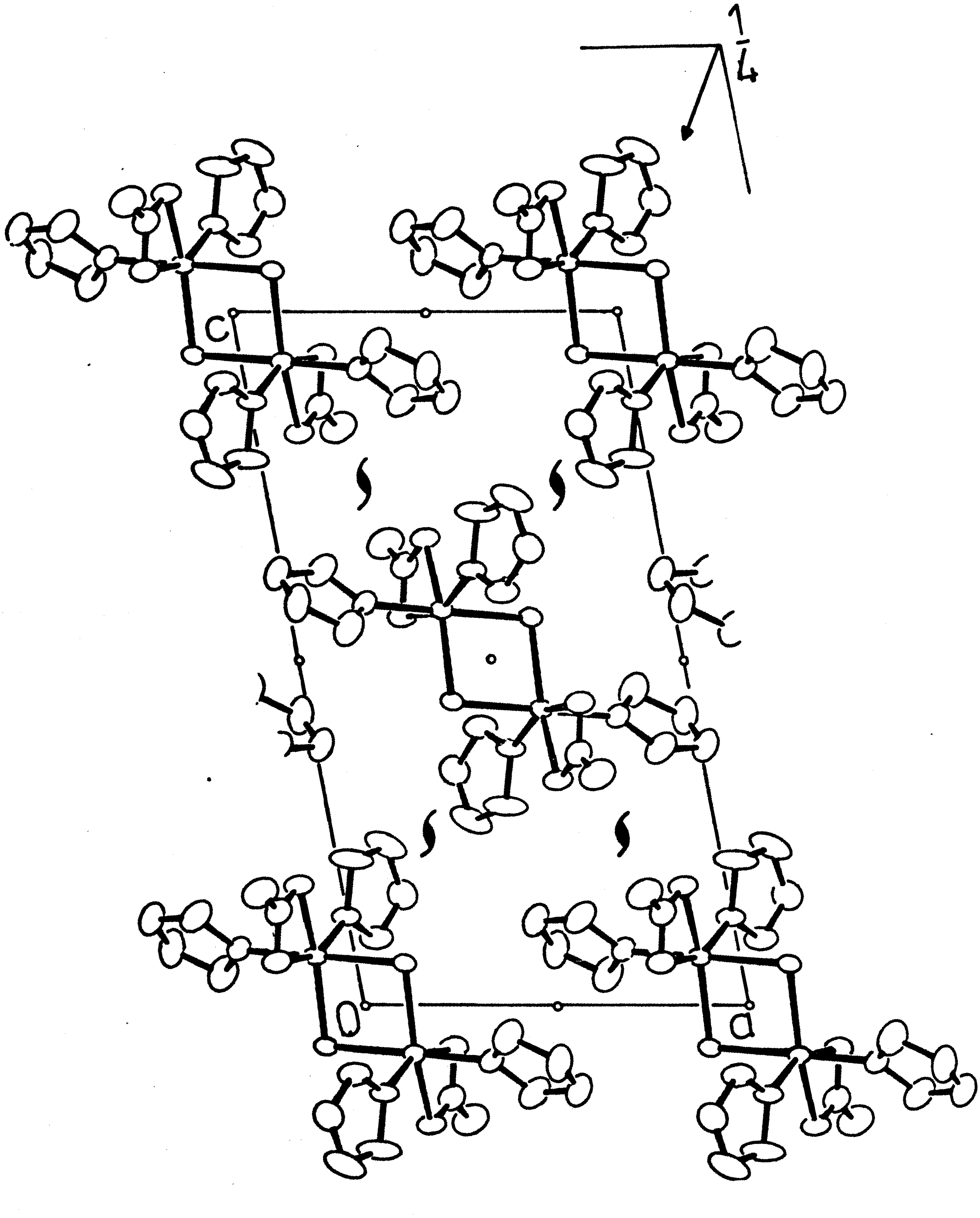

C14
C13
C15
C23
C22
C12
C24
O1
O11
N
O3
O21
O2
Co
C25
Cl
Cl'

Figure 2.3.2

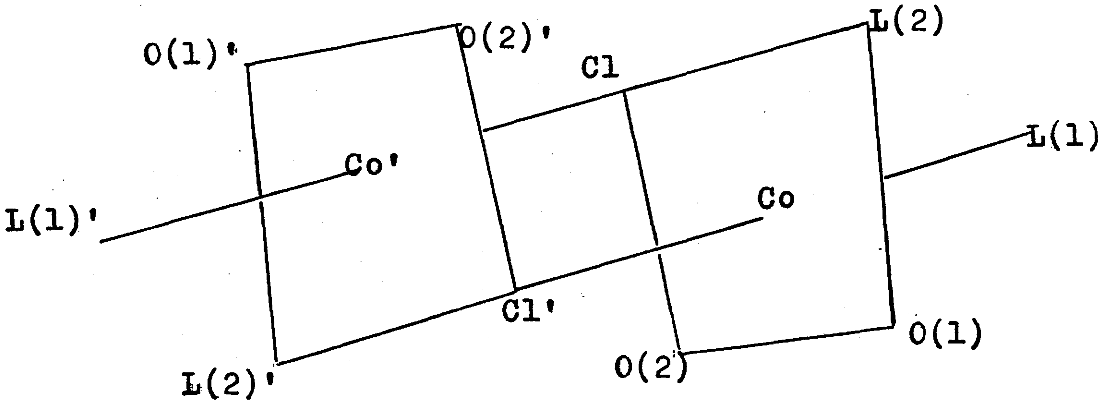
The molecular packing of III viewed along the **b** axis.




1/4
c
0
a

2.I Discussion of I, II and III

The three analyses have revealed that the complexes possess dimeric structures with crystallographic C_i symmetry. The dimers consist of two octahedral monomeric units sharing a meridional edge defined by the two bridging chlorine atoms.



The two monodentate ligands (L) are cis, occupying an axial and an equatorial site, the remaining two equatorial sites being occupied in each case by a bidentate nitrato group. The presence of bridging chlorine atoms is in accordance with the predictions made from infra-red studies(37).

The present description of the dimer as two octahedra sharing a meridional edge (ie an axial and an equatorial site) is suggested by various considerations. Firstly, of the three possible choices for the equatorial plane, only the set of atoms consisting of Cl, L(2), O(1) and O(2) are seen to be quasi-planar (Tables 2.1.4, 2.2.4 and 2.3.4). Thus the sum of the valence angles subtended at the cobalt atom is 360.0°, 359.9° and 360.1° in I, II and III respectively.

Secondly, such a choice immediately suggests that the larger angular distortions (4° - 30°) from ideal octahedral geometry are associated with the short 'bite' of the nitrato group(1). Thus the Cl-Co-O(2) valence angles, 103.38(5)°, 101.4(2)° and 104.4(4)° in I, II and II respectively, are not markedly different, the steric requirements of the associated ligands being the same in the three complexes, and yet are considerably greater than 90°. The Cl-Co-L(2) valence angles, 105.00(5)°, 95.3(2)° and 99.9(2)° in I, II and III respectively, however, differ markedly from the octahedral values and significantly from each other, presumably due to the different steric requirements of the respective ligands for occupying the extra space around the central atom made available through the 'bite' of the nitrato group(1).

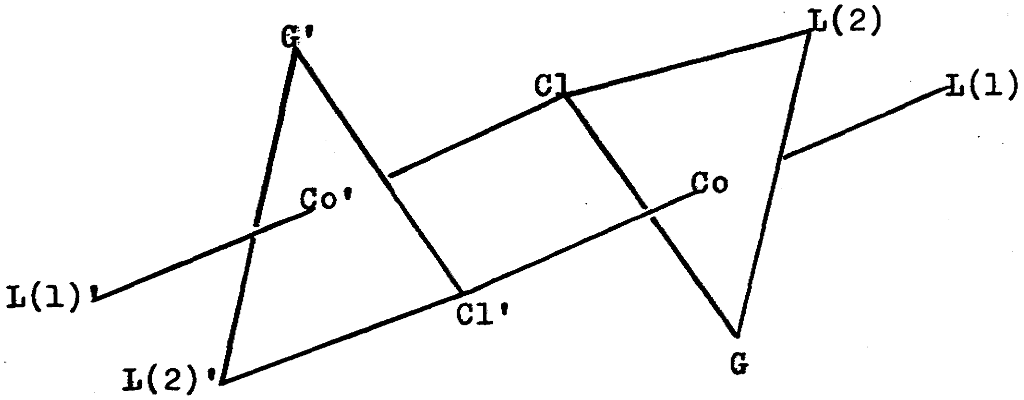
Although the cobalt atom is 6 co-ordinate in each complex, the co-ordination geometries are severely distorted from octahedral, particularly in the equatorial planes. It has been suggested(18,21,28-35) that for complexes containing a bidentate group the description of the molecular geometry is simplified by considering the bidentate group as occupying only one co-ordination site (situated at the 'centroid' of the chelating atoms) about the metal ion. Although such a concept has its limitations(1), and may perhaps even be unnecessary(31) this assumption of a geometry based on a lower co-ordination number is known to correlate well with the observed spectral and magnetic properties(30). Furthermore applying this concept to the molecules under discussion provides an alternative interpretation of the observed stereochemistries. If the 'centroid', G, of the chelating oxygens is taken as lying along the Co-N vector (where N is the central atom of the nitrato group) then Co, G, Cl and L(2) are found to be quasi-planar (Tables 2.1.4, 2.2.4 and 2.3.4), the maximum deviation from the plane being 0.0293(2), 0.024(1) and 0.041(6)Å in I, II and III respectively, with Cl' and L(1) above and below the plane thus leading to a geometry which is very close to that of a trigonal bipyramid. The angles within the plane for I, II and III are :

Cl-Co-G 132.63(4)°, 131.1(2)°, 134.1(2)° ;
Cl-Co-L(2) 105.00(5)°, 95.3(2)°, 99.9)° ;
L(2)-Co-G 122.36(6)°, 133.5(2)°, 126.0(3)° ; the sum of which add up to 360° in all three cases.

The equatorial Co-Cl bonds do not differ significantly from each other being 2.361(1), 2.363(2) and 2.372(2)Å in I, II and III respectively. They are, however, relatively short compared to the Co-Cl bonds, 2.405(6)Å, in $Co(C_4H_4N_2)_2Cl_2$ (octahedral, tetramer, Cl non-bridging)(38) and even more so when compared to the Co-Cl bonds, 2.50(1)Å, in α-$Co(py)_2Cl_2$ (octahedral, polymer, Cl bridging)(39). The axial Co-Cl' bonds are, however, significantly different being 2.523(1), 2.464(2) and 2.447(2)Å respectively, and are also significantly longer than the respective equatorial bonds, the difference between the Co-Cl' (axial) and the Co-Cl (equatorial) bonds being 0.16, 0.10 and 0.08Å in I, II and III respectively. Thus the bridging chlorine atoms are markedly asymmetric with respect to the cobalt atoms in the dimer. This contrasts with the symmetric chlorine bridges in β-dichloro-bis

(4-vinylpyridine) cobalt(II)(40) and α-dichloro-bis (pyridine) cobalt(II)(39), in which the Co-Cl bond lengths are 2.51(2) and 2.50(1)Å respectively. However γ-dichloro bis (pyridine) cobalt(II)(39), which is related to the α-form <u>via</u> a reversible solid-state phase transformation at about 150K, exhibits asymmetric bridging (2.435(5) and 2.507(5)Å). That the phase-change results in a significant increase in density (ca. 4.4%) and is accompanied by shortening of intermolecular contacts by up to 0.9Å suggests that the asymmetry may arise partly as a result of intermolecular interactions. It may be significant that the least asymmetric of the chloronitrato complexes being discussed (<u>ie</u> III) has no intermolecular contacts less than 3.55Å.

In so far as the trigonal bipyramidal model is geometrically plausible, it is of interest that the distortions of the cobalt ligand bond lengths may then be considered as axial elongations in this model.



Thus besides the above mentioned bonds, the axial Co-N(1) bond in I, 2.147(2)Å, is significantly longer than the equatorial Co-N(2) bond, 2.083(2)Å. Similarly in III the axial Co-O(11) bond, 2.104(6)Å is significantly longer than the equatorial Co-O(21) bond, 2.056(5)Å. Such a distortion was the mechanism suggested by Zemann(41,42) for minimizing ligand-ligand repulsions in a trigonal bipyramid. The significance of the steric requirements of the pyridine ligands in I and the tetrahydrofuran ligands in III is emphasised by the cobalt-acetonitrile Co-N bonds in II. Thus the steric requirements of a linear acetonitrile group in the immediate neighbourhood of the cobalt atom are no more than that of a sharp (narrow) cone, and the two Co-N bond lengths, 2.092(6) and 2.094(6)Å are experimentally equal. It is also significant that in bis(pyridine) dinitratocobalt(II)(43) and bis(acetonitrile) dinitratocobalt(II)(43), in which the presence of two bidentate nitrato groups leads to two pairs of octahedral sites being constrained to subtend an angle less than 60° at the cobalt, and hence to make available to the monodentate ligands a greater region of the co-ordination sphere, the four Co-N bond lengths, 2.054(4), 2.053(4), 2.054(3), 2.049(3)Å, are experimentally identical.

The nitrato groups in I, II and III are virtually planar (Tables 2.1.4, 2.2.4 and 2.3.4) and their relative internal geometries do not show any statistically significant differences. As is often found in nitrato complexes(1), the nitrato groups show slight but significant polarisation effects as a result of cobalt-oxygen co-ordination. This is most clearly evident in I, and to a less significant extent in II where the N-O bonds associated with co-ordinate oxygen atoms [N(3)-O(1) 1.260(2) and 1.265(9)Å respectively and N(3)-O(2) 1.261(2) and 1.263(9)Å respectively] are significantly longer than the terminal N(3)-O(3) bonds [1.219(3) and 1.202(9)Å respectively]. Moreover, the O-N-O valency angles differ from the ideal value of 120° in the expected manner, with the largest angle opposite the shortest cobalt-oxygen bond. The Co-O-N angles are also markedly less than the value of 110°(44) obtained for normal unidentate co-ordination, and hardly differ from a value of 92.5° which would be expected for symmetrical bi-dentate co-ordination to cobalt. The bond legnths and valency angles within the two crystallographically independent pyridine rings of I are experimentally equal (Table 2.1.3) and are in agreement with the corresponding values found in other complexes(43,45) and those reported for free pyridine(46). Although the rings are planar within the limits of the accuracy of the analyses, the cobalt atom is removed from the planes of the pyridine rings by 0.051Å (in the direction of N(2)) from the mean plane through the N(1)-C(15) ring and by 0.085Å (in the direction of N(1)) from the mean plane through the N(2)-C(25) ring (Table 2.1.4). This may well result from crystal packing effects(47). The dihedral angle between the mean planes through the pyridine rings is 69.6°.

The geometries and dimensions of the two acetonitrile groups in II are in agreement with the values found in other co-ordination compounds(48) and with those reported for free acetonitrile(49). The ligands are linear within experimental error but the Co-N-C angles differ from each other, 176.0(6)° and 167.4(6)°, the latter indicating a geometrically significant distortion from co-linearity of the cobalt and ligand moiety. Such distortions have often been noted(43,50) and have been attributed to intermolecular crystal packing effects(51).

The atoms constituting the two tetrahydrofuran ligands in III are characterised by very high anisotropic thermal parameters with the major axis of the thermal ellipsoids approximately perpendicular to the planes defined by the pair of bonds from each atom to the adjoining non-hydrogen atoms. Moreover, the atoms in both rings do not deviate significantly from their mean plane (Table 2.3.4) and the sums of the endocyclic angles are 538.2° and 539.7°. These results contrast with the geometries and internal dimensions observed in other complexes with THF ligands(52) and are suggestive of disorder. The conformation of THF has been extensively studied and it is known that there are two principal conformations, an envelope conformer (C_s symmetry) and a twist or half-chair conformer (C_2 symmetry). The latter possesses the lower energy, but by only 0.1kcal.mol^{-1}(53), and the two conformations are interconvertible by a dynamic process of "pseudorotation". This gives rise to two possibilities for the crystal of III. Firstly, that a dynamic equilibrium between conformers still exists in the crystal or secondly, that the crystal contains a statistical distribution of both conformers and/or of different orientations of a conformer. Both these hypotheses are revealed as disorder in an X-ray diffraction experiment and are thus indistinguishable. However, vibrational (infra red and Raman)spectroscopy may and usually does allow such a distinction to be made(54).

In I the plane of the bidentate nitrato group is inclined at 174.1° to the O(1), O(2), Co plane; the folding about the O(1)...O(2) line of 5.9° being towards N(1). Inspection of the intermolecular contacts (Table 2.1.3) shows that the nitrato group is involved in four close contacts 3.4Å with the pyridine (N(2)-C(25)) ligand of an adjacent dimer, which is on the side of the nitrato group remote from N(1). In the absence of such folding, presumably the C...O contacts would be too short. This sterically induced folding would account for the cobalt atom being displaced in the direction of N(1) by 0.1961(2)Å from the mean plane through the nitrato group. In II the short intermolecular contacts involving the nitrato group are such that the interactions are practically co-planar with the nitrato group (Table 2.2.3 see also Figure 2.2.2). The observed fold about the O(1)...O(2) line is 1.0° (Table 2.2.4) which is hardly significant. It is of interest that in III, in which there are no short contacts, the cobalt atom is coplanar with the nitrato group (Table 2.3.4).

In the molecular structures, all the groups are arranged so as to minimize steric interactions. Apart from those intermolecular distances already mentioned, all other separations are greater than or equal to the sum of the relevant van der Waal's radii.

2.II THE CRYSTAL AND MOLECULAR STRUCTURES OF TWO COMPLEXES OF THE FORM $Co(L)_2(NO_3)_2$.

IV L = ACETONITRILE

V L = PYRIDINE

2.4 Experimental and results for IV

Bis(acetonitrile)dinitratocobalt(II)

Crystal data

Molecular formula	$C_4H_6O_6N_4Co$
Molecular weight	$M = 265.0$
Crystal system	Orthorhombic
Unit cell dimensions	$a = 15.291(1)Å$
	$b = 16.539(2)Å$
	$c = 8.085(3)Å$
Unit cell volume	$U = 2044.6Å^3$
Measured density	$D_m = 1.73$ g cm^{-3}
Number of molecules per unit cell	$Z = 8$
Calculated density	$D_c = 1.722$ g cm^{-3}
Number of electrons per unit cell	$F(000) = 1064$
Linear absorption coefficient	$\mu(\text{Mo-K}_\alpha) = 17.6$ cm^{-1}
Space group	Pbca (D_{2h}^{15}, No. 61)

Data collection

Radiation used	Mo-K_α, $\lambda = 0.71069Å$
Filter	Graphite monochromator, $\cos^2 2\theta_m = 0.965$
Upper limit for data collection	$2\theta_{max} = 54°$
Number of independent reflections	$m = 1228$
Unobserved cut-off	$2\sigma_I$
Number of parameters refined	$n = 160$
Number of reflections per parameter	$m/n = 7.7$

Structure Determination

The space group is uniquely determined by its systematic absences (0kl when k is odd, h0l when l is odd and hk0 when h is odd).

The structure was resolved by a combination of Patterson and Fourier techniques. The co-ordinates of the cobalt atom were obtained from the Harker sections in a sharpened, origin-removed vector map. The cobalt atom was assigned an isotropic thermal parameter equal to the overall thermal parameter ($U = 0.028Å^2$), obtained from a Wilson plot, and used to phase the observed structure factor moduli in a calculation of the electron density distribution, which revealed sites for the atoms making up one nitrate group. A further electron-density calculation, with the phasing appropriate to the known partial structure, revealed sites for all non-hydrogen atoms.

Structure Refinement

Prior to least-squares refinement all atoms were assigned isotropic thermal parameters ($U_{iso} = 0.04Å^2$). The full matrix least-squares refinement of positional, thermal and scale parameters converged after 16 cycles when R was 0.031 and R' was 0.0015. Full details of the course of refinement are given in Table 2.4.1. Initially unit weights were applied to all reflections. In later stages weights given by the expression

$$w = (3.686 - 0.2076|F_o| + 0.0045|F_o|^2)^{-1}$$

were applied. The coefficients of the quadratic expression were obtained from a least-squares fit of $a + b|F_o| + c|F_o|^2$ to the distribution of $\langle w\Delta^2 \rangle$ with $\langle |F_o| \rangle$ obtained from an analysis of $w\Delta^2$ with increasing $|F_o|$. This weighting scheme leads to an approximately constant $\langle w\Delta^2 \rangle$ with increasing $|F_o|$ and sin θ.

A difference synthesis after cycle 11 revealed residual electron density peaks in positions which were stereochemically acceptable for hydrogen atoms. Hydrogen atoms were introduced at these sites and assigned isotropic thermal parameters equal to those of the adjoining carbon atom after cycle 6. In the later stages of refinement a correction for the anomalous dispersion of cobalt was applied, but did not lead to any significant changes in the model.

The refinement was assumed complete when the parameter-shifts calculated by a cycle of least-squares refinement were insignificant compared to the corresponding estimated standard deviations. A final difference synthesis showed no errors in the model, the highest peak in residual electron density distribution being 0.26e/Å^3. In all structure factor calculations the atomic scattering factors were taken from 'International Tables for X-Ray Crystallography,Vol 111'(66). Observed and final calculated structure factors are listed in Appendix IV.

A general view of the molecule illustrating the thermal ellipsoids(69) and giving the atomic numbering scheme is given in Figure 2.4.1. The crystal packing arrangement viewed along <u>c</u> is given in Figure 2.4.2. The final fractional co-ordinates and thermal parameters of all atoms are given in Table 2.4.2. The values of U_{ij} refer to the anisotropic temperature factor expression given in Part I. Bond lengths, valence angles and other relevant intra- and intermolecular data are given in Table 2.4.3 and Table 2.4.4.

TABLE 2.4.1

COURSE OF REFINEMENT

CYCLES	PARAMETERS REFINED	FINAL R	FIN1L R'
1 - 3	X,Y,Z,U(ISO) FOR CO,O,N,C. SCALE FACTOR. FULL MATRIX, UNIT WEIGHTS.	0.081	0.0072
4 - 6	X,Y,Z,UIJ FOR CO,O,N,C(11),C(21). X,Y,Z,U(ISO) FOR C(22),C(12). SCALE FACTOR. FULL MATRIX, UNIT WEIGHTS.	0.046	0.0029
7 - 8	X,Y,Z,UIJ FOR CO,O,N,C. SCALE FACTOR. FULL MATRIX, UNIT WEIGHTS.	0.041	0.0025
9 - 10	AS ABOVE, BUT WITH WEIGHTING SCHEME APPLIED	0.038	0.0023
11	AS ABOVE,BUT WITH CORRECTIONS FOR ANOMALOUS DISPERSION OF CO INCLUDED.	0.038	0.0023
12 - 16	AS ABOVE, TOGETHER WITH X,Y,Z,U(ISO) FOR H.	0.031	0.0015

TABLE 2.4.2

A. FRACTIONAL CO-ORDINATES($\times 10^5$ FOR NON-HYDROGEN ATOMS, $\times 10^3$ FOR HYDROGEN ATOMS)

ATOM	X/A	Y/B	Z/C
CO	83611(3)	40765(3)	19741(5)
N(3)	68763(23)	38385(18)	06762(47)
O(31)	70284(19)	39712(18)	22041(33)
O(32)	75518(21)	38042(19)	-02112(36)
O(33)	61435(21)	37632(20)	01440(46)
N(4)	94200(25)	29311(21)	15600(45)
O(42)	87039(21)	27921(17)	22179(42)
O(41)	95351(18)	36656(16)	10682(37)
O(43)	99829(23)	24288(21)	13465(56)
N(2)	87279(23)	42394(21)	43892(39)
C(21)	89908(24)	43062(22)	56822(44)
C(22)	93388(42)	44041(46)	73303(60)
N(1)	84003(21)	52721(19)	12931(40)
C(11)	83618(24)	59509(23)	11366(45)
C(12)	83052(49)	68202(27)	09479(75)
H(21)	913(5)	403(5)	785(10)
H(22)	916(5)	482(5)	771(9)
H(23)	994(9)	467(7)	731(13)
H(11)	788(5)	690(5)	036(9)
H(12)	871(5)	698(5)	026(10)
H(13)	851(4)	706(5)	185(9)

TABLE 2.4.2(CONT'D)

B. THERMAL PARAMETERS($Å^2 \times 10^4$ FOR NON-HYDROGEN ATOMS, $Å^2 \times 10^3$ FOR HYDROGEN ATOMS)

ATOM	U11/U(ISO)	U22	U33	U12	U13	U23
CO	544(3)	448(3)	427(2)	32(2)	-37(2)	22(2)
N(3)	637(21)	373(15)	710(22)	-34(13)	-180(18)	20(15)
O(31)	582(14)	791(20)	550(18)	-36(14)	-41(13)	27(15)
O(32)	723(18)	730(19)	544(15)	44(15)	-80(15)	-151(15)
O(33)	662(17)	717(19)	1069(25)	-144(16)	-338(19)	34(19)
N(4)	733(23)	510(19)	749(24)	133(18)	33(19)	13(17)
O(42)	663(16)	508(15)	953(23)	9(13)	103(17)	70(16)
O(41)	672(16)	540(16)	660(17)	100(14)	99(14)	93(14)
O(43)	914(21)	702(20)	1495(33)	338(20)	227(25)	69(22)
N(2)	672(20)	622(21)	441(17)	85(16)	-46(15)	31(15)
C(21)	475(19)	523(20)	487(21)	37(15)	5(17)	49(16)
C(22)	871(38)	904(37)	431(24)	78(33)	-141(24)	-46(25)
N(1)	646(19)	449(18)	528(16)	26(16)	-101(16)	25(14)
C(11)	562(19)	495(21)	494(18)	7(20)	-69(18)	7(17)
C(12)	951(36)	440(21)	770(31)	-57(26)	-85(36)	27(23)
H(21)	112(34)					
H(22)	98(29)					
H(23)	182(44)					
H(11)	101(29)					
H(12)	101(28)					
H(13)	94(26)					

TABLE 2.4.3

INTERATOMIC DISTANCES(Å) AND ANGLES(°) WITH ESTIMATED STANDARD DEVIATIONS IN PARANTHESIS.

A. BONDED DISTANCES

CO -N(1)	2.053(3)	CO -N(2)	2.049(3)	CO -O(31)	2.054(3)
CO -O(32)	2.204(3)	CO -O(41)	2.055(3)	CO -O(42)	2.197(3)
N(3) -O(31)	1.276(5)	N(3) -O(32)	1.259(5)	N(3) -O(33)	1.207(5)
N(4) -O(41)	1.290(4)	N(4) -O(42)	1.239(5)	N(4) -O(43)	1.209(5)
N(1) -C(11)	1.131(5)	C(11)-C(12)	1.448(6)		
N(2) -C(21)	1.125(5)	C(21)-C(22)	1.444(6)		
MEAN C-H	0.87				

B. INTERBOND ANGLES

N(1) -CO -N(2)	96.9(1)	N(1) -CO -O(31)	97.8(1)
N(1) -CO -O(32)	89.9(1)	N(1) -CO -O(41)	101.4(1)
N(1) -CO -O(42)	161.5(1)	N(2) -CO -O(31)	101.3(1)
N(2) -CO -O(32)	160.8(1)	N(2) -CO -O(41)	98.3(1)
N(2) -CO -O(42)	88.6(1)	O(31)-CO -O(32)	59.9(1)
O(31)-CO -O(41)	150.6(1)	O(31)-CO -O(42)	98.4(1)
O(32)-CO -O(41)	97.9(1)	O(32)-CO -O(42)	90.5(1)
O(41)-CO -O(42)	60.2(1)		
CO -O(31)-N(3)	96.2(2)	CO -O(32)-N(3)	89.7(2)
CO -O(41)-N(4)	94.7(2)	CO -O(42)-N(4)	89.6(2)
O(31)-N(3) -O(32)	114.2(3)	O(31)-N(3) -O(33)	122.2(4)
O(32)-N(3) -O(33)	123.6(4)	O(41)-N(4) -O(42)	115.3(3)
O(41)-N(4) -O(43)	120.4(4)	O(42)-N(4) -O(43)	124.3(4)
CO -N(1) -C(11)	169.8(3)	N(1) -C(11)-C(12)	179.4(11)
CO -N(2) -C(21)	174.7(3)	N(2) -C(21)-C(22)	178.9(9)

TABLE 2.4.3(CONT'D)

C. SELECTED INTRAMOLECULAR DISTANCES <3.6Å

CO ...N(3)	2.53	CO ...N(4)	2.51	O(31)...O(32)	2.13
O(41)...O(42)	2.14	O(31)...O(33)	2.17	O(41)...O(43)	2.17
O(32)...O(33)	2.17	O(42)...O(43)	2.16	N(2) ...O(41)	3.10
N(1) ...O(31)	3.09	N(2) ...O(42)	2.97	N(1) ...O(32)	3.01
N(2) ...O(31)	3.17	N(1) ...O(41)	3.18	N(2) ...N(4)	3.32
N(1) ...N(3)	3.36	O(32)...N(4)	3.51	O(42)...N(3)	3.52
O(32)...O(41)	3.21	O(42)...O(31)	3.22	N(2) ...N(1)	3.07
O(32)...O(42)	3.12				

D. INTERMOLECULAR DISTANCES ≤ 3.6Å

O(31)...N(1')	3.60	C(11)...O(32')	3.29	O(31)...C(11')	3.24
C(11)...O(33')	3.36	O(31)...C(12')	3.24	C(12)...O(32')	3.53
N(1) ...O(32')	3.53	C(21)...O(31')	3.47	N(1) ...O(33')	3.57
C(21)...O(33')	3.23	N(2) ...N(3')	3.47	C(21)...N(3')	3.34
N(2) ...O(33')	3.37	C(22)...O(31')	3.41	N(2) ...C(11')	3.51
C(22)...O(33')	3.59	C(22)...O(32'')	3.52	C(22)...O(41'')	3.27
C(12)...N(3''')	3.36	C(12)...O(33''')	3.38	C(21)...O(43^{IV})	3.29
C(22)...O(43^{IV})	3.29	C(21)...O(33^{V})	3.48	C(22)...O(33^{V})	3.57
O(43)...O(33^{VI})	2.91				

ROMAN NUMERALS AS SUPERSCRIPTS REFER TO THE FOLLOWING EQUIVALENT POSITIONS RELATIVE TO THE REFERENCE MOLECULE AT X,Y,Z :

I. 3/2-X, 1-Y, 1/2+Z; II. X, Y, 1+Z; III. 3/2-X, 1/2+Y, Z;
IV. X, 1/2-Y, 1/2+Z; V. 1/2+X, Y, 1/2-Z; VI. 1/2+X, 1/2-Y, -Z;

TABLE 2.4.4

LEAST-SQUARES PLANES

```
X,Y,Z ARE ORTHOGONAL CO-ORDINATES IN ANGSTROMS
AN ASTERISK(*) INDICATES ATOM USED IN DEFINING THE PLANE

1.    EQUATION:   0.0526X - 0.9856Y + 0.1610Z + 5.6200 = 0

      DISTANCES(Å) OF ATOMS FROM THE PLANE:-

      N(3)*     0.004(3)     O(31)*  -0.001(3)     O(32)*  -0.001(3)
      O(33)*   -0.002(3)     CO      -0.096(1)     N(2)    -0.017(4)
      C(21)     0.063(4)     C(22)    0.063(4)     N(1)    -2.130(3)

2.    EQUATION:  -0.3914X - 0.2292Y - 0.8912Z + 7.8673 = 0
      DISTANCES(Å) OF ATOMS FROM THE PLANE:-

      N(4)*    -0.005(4)     O(41)*   0.002(3)     O(42)*   0.002(3)
      O(43)*    0.002(4)     CO      -0.104(1)     N(1)    -0.090(3)
      C(11)    -0.212(4)     C(12)   -0.371(6)     N(2)    -2.126(3)

      THE DIHEDRAL ANGLE BETWEEN PLANES 1 AND 2 IS 86.5 DEGREES.
```

Figure 2.4.1

A general view of IV showing the atomic numbering scheme. Hydrogen atoms (not shown) are numbered as the atoms to which they are bonded.

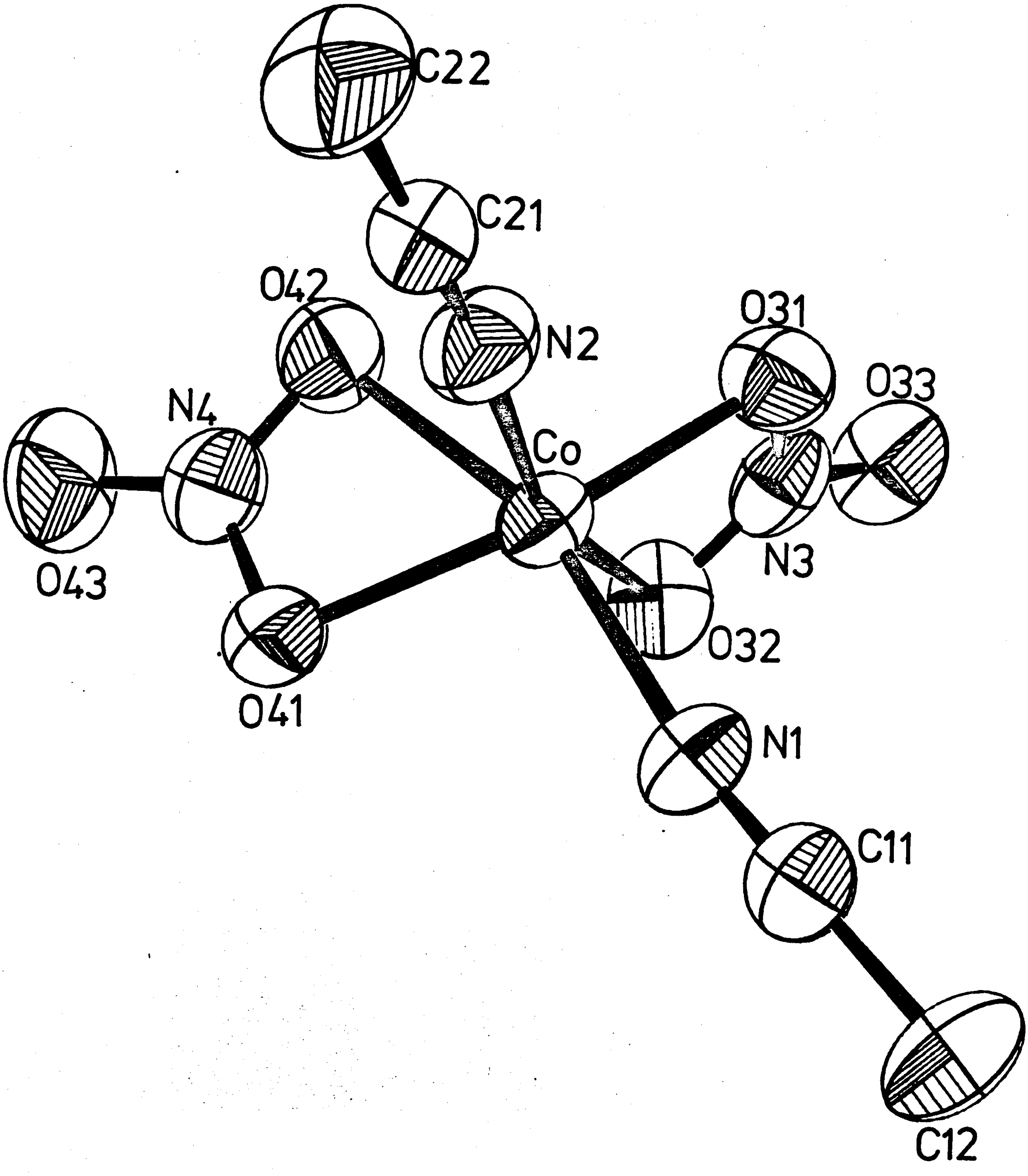
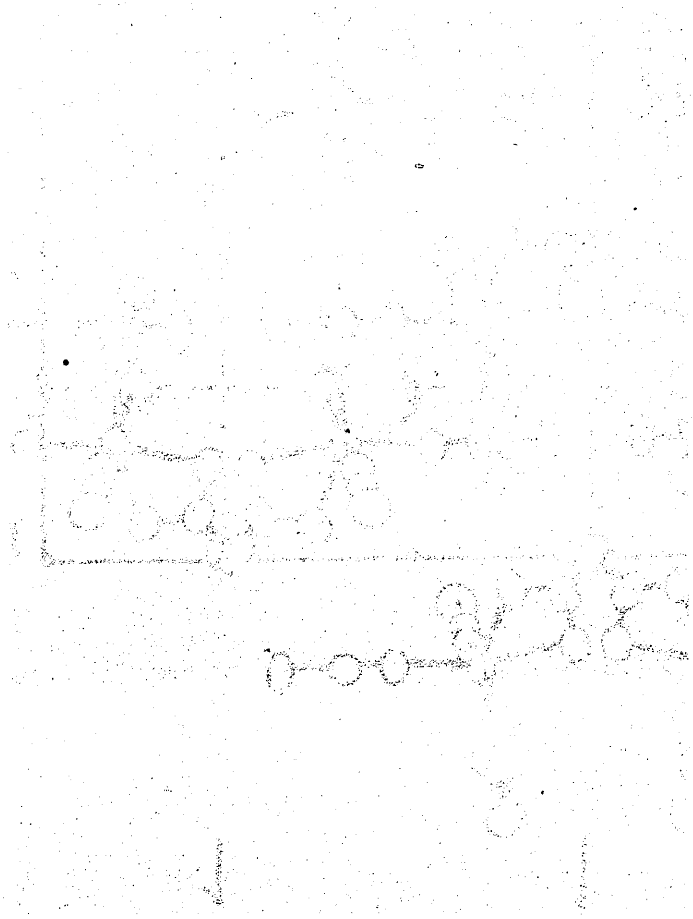
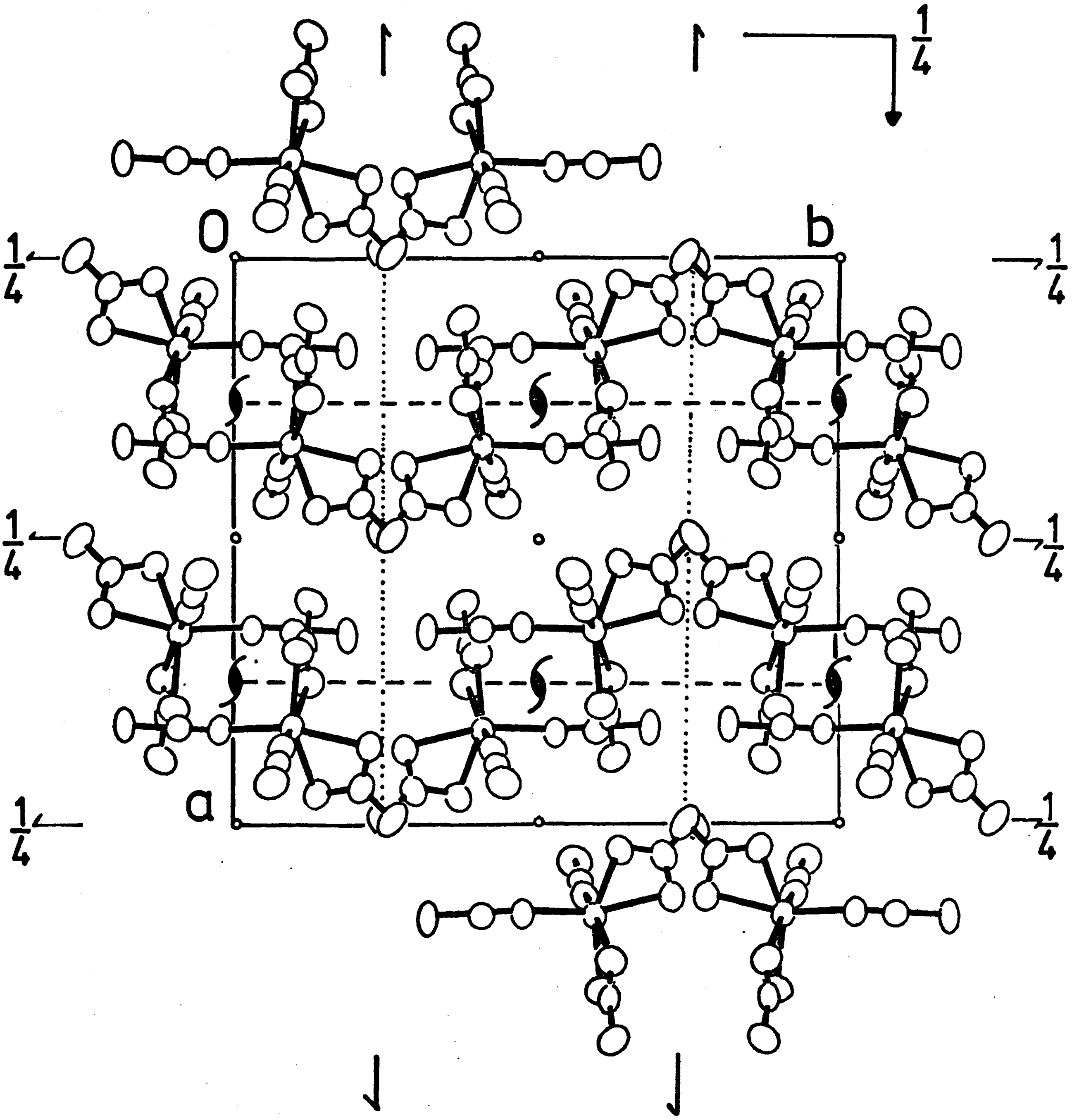

C22
C21
O42
N2
O31
O33
N4
Co
O43
N3
O32
O41
N1
C11
C12

Figure 2.4.2

The molecular packing of IV viewed along the c axis.




1/4
0
b
a
1/4
1/4
1/4
1/4
1/4
1/4

2.5 Experimental and results for V

Bis(pyridine)dinitratocobalt(II)

Crystal data

Molecular formula	$C_{10}H_{10}O_6N_4Co$
Molecular weight	M = 341.1
Crystal system	Monoclinic
Unit cell dimensions	a = 12.082(1)Å
	b = 8.036(6)Å
	c = 14.498(2)Å
	β = 90.134(8)°
Unit cell volume	U = 1407.7$Å^3$
Measured density	D_m= 1.61 g cm^{-3}
Number of molecules per unit cell	Z = 4
Calculated density	D_c= 1.609 g cm^{-3}
Number of electrons per unit cell	F(000) = 692
Linear absorption coefficient	μ(Mo-K_α) = 13.0 cm^{-1}
Space group	$P2_1/c$ (C^5_{2h}, No. 14)

Data collection

Radiation used	Mo-K_α, λ = 0.71069Å
Filter	Graphite monochromator,
	$\cos^2 2\theta_m$ = 0.965
Upper limit for data collection	$2\theta_{max}$ = 54°
Number of independent reflections	m = 1237
Unobserved cut-off	$2\sigma_I$
Number of parameters refined	n = 231
Number of reflections per parameter	m/n = 5.4

Structure Determination

The space group is uniquely determined by its systematic absences (h0l when l is odd and 0k0 when k is odd).

The structure was resolved by a combination of Patterson and Fourier techniques. The co-ordinates of the cobalt atom were obtained from the Harker sections in a sharpened, origin-removed vector map. The cobalt atom was assigned an isotropic thermal parameter equal to the overall thermal parameter ($U = 0.03Å^2$), obtained from a Wilson plot, and used to phase the observed structure factor moduli in a calculation of the electron density distribution, which revealed sites for all non-hydrogen atoms.

Structure Refinement

Prior to least-squares refinement all atoms were assigned isotropic thermal parameters ($U_{iso} = 0.05Å^2$). The least-squares refinement of positional, thermal and scale parameters converged after 20 cycles when R was 0.034 and R' was 0.0014. Full details of the course of refinement are given in Table 2.5.1. The refinement of H atom parameters necessitated the use of the block diagonal approximation to the normal equation matrix because of computer-store limitations. Two blocks were used. Initially unit weights were applied to all reflections. In later stages weights given by the expression

$$w = (1.913 - 0.0642|F_o| + 0.0012|F_o|^2)^{-1}$$

were applied. The coefficients of the quadratic expression were obtained from a least-squares fit of $a + b|F_o| + c|F_o|^2$ to the distribution of $\langle w\Delta^2 \rangle$ with $\langle |F_o| \rangle$ obtained from an analysis of $w\Delta^2$ with increasing $|F_o|$. The weighting scheme leads to an approximately constant $\langle w\Delta^2 \rangle$ with increasing $|F_o|$ and sin θ.

A difference synthesis after cycle 5 revealed residual electron density peaks in positions which were stereochemically acceptable for hydrogen atoms. Hydrogen atoms were introduced at these sites and assigned isotropic thermal parameters of 0.05Å^2. In the later stages of refinement a correction for the anomalous dispersion of cobalt was applied, but did not lead to any significant changes in the model.

The refinement was assumed complete when the parameter-shifts calculated by a cycle of least-squares refinement were insignificant compared to the corresponding estimated standard deviations. A final difference synthesis showed no errors in the model, the highest peak in the residual electron density distribution being 0.22e/Å^3. In all structure factor calculations the atomic scattering factors were taken from 'International Tables for X-Ray Crystallography,Vol 111'(66). Observed and final calculated structure factors are listed in Appendix V.

A general view of the molecule illustrating the thermal ellipsoids(69) and giving the atomic numbering scheme is given in Figure 2.5.1. The crystal packing arrangement viewed along b is given in Figure 2.5.2. The final fractional co-ordinates and thermal parameters of all atoms are given in Table 2.5.2. The values of U_{ij} refer to the anisotropic temperature factor expression given in Part I. Bond lenths, valence angles and other relevant intra- and intermolecular data are given in Table 2.5.3 and Table 2.5.4.

TABLE 2.5.1

COURSE OF REFINEMENT

CYCLES	PARAMETERS REFINED	FINAL R	FIN1L R'
1 - 5	X,Y,Z,U(ISO) FOR CO,O,N,C. SCALE FACTOR. FULL MATRIX, UNIT WEIGHTS.	0.088	0.0077
6 - 8	X,Y,Z,UIJ FOR CO,O,N,C. H-ATOMS INCLUDED BUT NOT REFINED. SCALE FACTOR. FULL MATRIX, UNIT WEIGHTS.	0.039	0.0015
9	AS ABOVE, BUT WITH WEIGHTING SCHEME APPLIED	0.039	0.0020
10	X,Y,Z,UIJ FOR CO,O,N,C, X,Y,Z FOR H. SCALE FACTOR, OVERALL TEMPERATURE, BLOCKED MATRIX, WEIGHTING SCHEME APPLIED.	0.036	0.0017
11 - 15	AS ABOVE,BUT WITH CORRECTIONS FOR ANOMALOUS DISPERSION OF CO INCLUDED.	0.034	0.0015
16 - 20	AS ABOVE, TOGETHER WITH U(ISO) FOR H.	0.034	0.0014

TABLE 2.5.2

A. FRACTIONAL CO-ORDINATES($\times10^4$) FOR NON-HYDROGEN ATOMS.

ATOM	X/A	Y/B	Z/C
CO	7504(1)	6687(1)	4364(1)
N(1)	8896(3)	7951(5)	3955(3)
C(11)	8923(5)	8948(8)	3214(4)
C(12)	9870(6)	9798(9)	2957(5)
C(13)	10801(5)	9595(9)	3471(6)
C(14)	10807(5)	8570(10)	4208(5)
C(15)	9838(4)	7769(7)	4433(4)
N(2)	6236(3)	8287(6)	4040(3)
C(21)	6293(4)	9934(8)	4101(4)
C(22)	5448(5)	10992(7)	3850(4)
C(23)	4501(5)	10302(9)	3495(4)
C(24)	4411(4)	8627(8)	3435(4)
C(25)	5284(4)	7653(7)	3709(4)
N(3)	7889(4)	3909(6)	3564(4)
O(32)	8468(4)	4266(6)	4261(4)
O(33)	7961(4)	2603(5)	3135(4)
O(31)	7216(3)	5032(5)	3304(3)
N(4)	6886(4)	5886(6)	5985(4)
O(41)	7703(3)	6836(5)	5783(2)
O(42)	6347(3)	5315(6)	5326(3)
O(43)	6645(4)	5600(7)	6791(3)

TABLE 2.5.2(CONT'D)

B. FRACTIONAL CO-ORDINATES($\times 10^3$) AND THERMAL PARAMETERS ($Å^2 \times 10^3$) OF HYDROGEN ATOMS

ATOM	X/A	Y/B	Z/C	U(ISO)
H(11)	827(4)	900(6)	290(3)	33(14)
H(12)	981(5)	1049(7)	239(4)	68(19)
H(13)	1127(4)	1027(7)	335(3)	43(15)
H(14)	1152(5)	827(8)	456(4)	85(21)
H(15)	980(4)	712(6)	494(4)	45(16)
H(21)	696(4)	1033(6)	435(3)	31(13)
H(22)	558(4)	1214(7)	392(4)	53(16)
H(23)	396(4)	1098(6)	337(3)	35(14)
H(24)	390(4)	810(6)	312(3)	42(15)
H(25)	528(3)	656(5)	363(3)	11(10)

TABLE 2.5.2(CONT'D)

C. ANISOTROPIC THERMAL PARAMETERS($\mathrm{\AA}^2 \times 10^4$) FOR NON-HYDROGEN ATOMS

ATOM	U11	U22	U33	U12	U13	U23
CO	460(6)	615(6)	615(6)	-12(4)	-69(3)	74(5)
N(1)	431(23)	575(31)	583(28)	15(20)	6(19)	42(23)
C(11)	551(32)	820(43)	723(39)	75(30)	-30(28)	149(35)
C(12)	787(45)	925(51)	927(48)	28(39)	197(38)	301(41)
C(13)	636(40)	817(48)	1227(61)	-248(37)	214(40)	-8(46)
C(14)	539(34)	1053(57)	952(48)	-139(37)	-77(32)	20(46)
C(15)	524(32)	771(43)	655(36)	-61(29)	-89(27)	23(30)
N(2)	453(22)	536(26)	598(25)	17(23)	7(17)	3(24)
C(21)	556(31)	652(42)	591(35)	-56(29)	-7(25)	37(30)
C(22)	751(40)	583(35)	666(38)	27(32)	129(31)	17(30)
C(23)	635(36)	774(45)	683(40)	221(34)	36(30)	95(34)
C(24)	529(31)	817(49)	638(36)	68(32)	-124(26)	-71(32)
C(25)	534(33)	557(33)	649(36)	-2(26)	-61(26)	-4(28)
N(3)	653(33)	553(32)	1248(49)	-74(25)	162(32)	92(31)
O(32)	860(33)	884(36)	1255(41)	215(27)	-183(29)	322(32)
O(33)	1071(36)	534(26)	1996(56)	-18(27)	341(35)	-226(32)
O(31)	639(22)	652(25)	953(29)	121(20)	-136(21)	-148(23)
N(4)	713(33)	740(34)	701(36)	-29(28)	-109(29)	161(30)
O(41)	641(23)	889(29)	638(24)	-245(23)	-105(18)	73(23)
O(42)	803(26)	911(32)	700(26)	-292(25)	-158(22)	183(24)
O(43)	1070(35)	1268(41)	597(28)	-232(31)	5(24)	215(29)

TABLE 2.5.3

INTERATOMIC DISTANCES(Å) AND ANGLES(°) WITH ESTIMATED STANDARD DEVIATIONS IN PARANTHESIS.

A. BONDED DISTANCES

CO -N(1)	2.054(4)	CO -N(2)	2.053(4)	CO -O(31)	2.062(4)
CO -O(32)	2.273(5)	CO -O(41)	2.074(4)	CO -O(42)	2.264(4)
N(3) -O(31)	1.272(6)	N(3) -O(32)	1.261(8)	N(3) -O(33)	1.223(7)
N(4) -O(41)	1.282(6)	N(4) -O(42)	1.243(7)	N(4) -O(43)	1.226(7)
N(1) -C(11)	1.341(8)	N(1) -C(15)	1.339(7)	C(11)-C(12)	1.385(9)
C(12)-C(13)	1.358(10)	C(13)-C(14)	1.348(11)	C(14)-C(15)	1.376(8)
N(2) -C(21)	1.329(8)	N(2) -C(25)	1.345(6)	C(21)-C(22)	1.377(8)
C(22)-C(23)	1.370(9)	C(23)-C(24)	1.354(9)	C(24)-C(25)	1.373(8)
MEAN C-H	0.92				

TABLE 2.5.3(CONT'D)

B. INTERBOND ANGLES

N(1) -CO -N(2)	103.6(2)	N(1) -CO -O(31)	104.0(2)
N(1) -CO -O(32)	89.1(2)	N(1) -CO -O(41)	99.5(2)
N(1) -CO -O(42)	157.8(2)	N(2) -CO -O(31)	96.3(2)
N(2) -CO -O(32)	154.6(2)	N(2) -CO -O(41)	106.0(2)
N(2) -CO -O(42)	89.1(2)	O(31)-CO -O(32)	59.0(2)
O(31)-CO -O(41)	142.7(2)	O(31)-CO -O(42)	92.4(2)
O(32)-CO -O(41)	93.2(2)	O(32)-CO -O(42)	86.6(2)
O(41)-CO -O(42)	59.1(2)		
CO -O(31)-N(3)	97.5(3)	CO -O(32)-N(3)	87.9(3)
CO -O(41)-N(4)	96.1(3)	CO -O(42)-N(4)	88.4(3)
O(31)-N(3) -O(32)	115.4(5)	O(31)-N(3) -O(33)	120.3(6)
O(32)-N(3) -O(33)	124.3(5)	O(41)-N(4) -O(42)	116.5(5)
O(41)-N(4) -O(43)	121.0(5)	O(42)-N(4) -O(43)	122.6(5)
CO -N(1) -C(11)	123.2(3)	CO -N(1) -C(15)	119.5(4)
CO -N(2) -C(21)	124.7(3)	CO -N(2) -C(25)	118.7(4)
C(15)-N(1) -C(11)	117.3(4)	N(1) -C(11)-C(12)	122.1(5)
C(11)-C(12)-C(13)	116.5(6)	C(12)-C(13)-C(14)	120.7(6)
C(13)-C(14)-C(15)	118.1(5)	C(14)-C(15)-N(1)	123.3(5)
C(25)-N(2) -C(21)	116.5(4)	N(2) -C(21)-C(22)	124.0(5)
C(21)-C(22)-C(23)	117.9(5)	C(22)-C(23)-C(24)	119.6(5)
C(23)-C(24)-C(25)	119.2(5)	C(24)-C(25)-N(2)	122.8(5)

TABLE 2.5.3(CONT'D)

C. SELECTED INTRAMOLECULAR DISTANCES <3.6Å

CO ...N(3)	2.56	CO ...N(4)	2.55	O(31)...O(32)	2.14
O(41)...O(42)	2.15	O(31)...O(33)	2.16	O(41)...O(43)	2.18
O(32)...O(33)	2.20	O(42)...O(43)	2.16	N(2) ...O(41)	3.30
N(1) ...O(31)	3.24	N(2) ...O(42)	3.03	N(1) ...O(32)	3.04
N(2) ...O(31)	3.06	N(1) ...O(41)	3.15	N(2) ...N(4)	3.51
N(1) ...N(3)	3.51	O(32)...N(4)	3.41	O(42)...N(3)	3.36
O(32)...O(41)	3.16	O(42)...O(31)	3.13	N(2) ...N(1)	3.23
O(32)...O(42)	3.11	N(1) ...C(21)	3.53	C(11)...C(21)	3.52
CO ...C(11)	3.01	CO ...C(21)	3.01	CO ...C(15)	2.95
CO ...C(25)	2.95	O(32)...C(15)	3.27	O(42)...C(25)	3.27
O(31)...C(25)	3.20	O(41)...C(15)	3.30		

D. INTERMOLECULAR DISTANCES ≤ 3.6Å

O(43)...C(11')	3.45	O(43)...N(2')	3.42	O(43)...C(21')	3.40
O(43)...C(22')	3.56	O(43)...C(25')	3.53	O(33)...C(11$^{\mathrm{II}}$)	3.16
O(33)...C(12$^{\mathrm{II}}$)	3.24	O(33)...C(21$^{\mathrm{II}}$)	3.26	O(33)...C(22$^{\mathrm{II}}$)	3.46
O(42)...C(25$^{\mathrm{III}}$)	3.40	O(43)...C(25$^{\mathrm{III}}$)	3.58	O(42)...O(42$^{\mathrm{III}}$)	3.43
O(31)...C(23$^{\mathrm{IV}}$)	3.34	O(31)...C(24$^{\mathrm{IV}}$)	3.39	O(43)...O(33$^{\mathrm{V}}$)	3.60

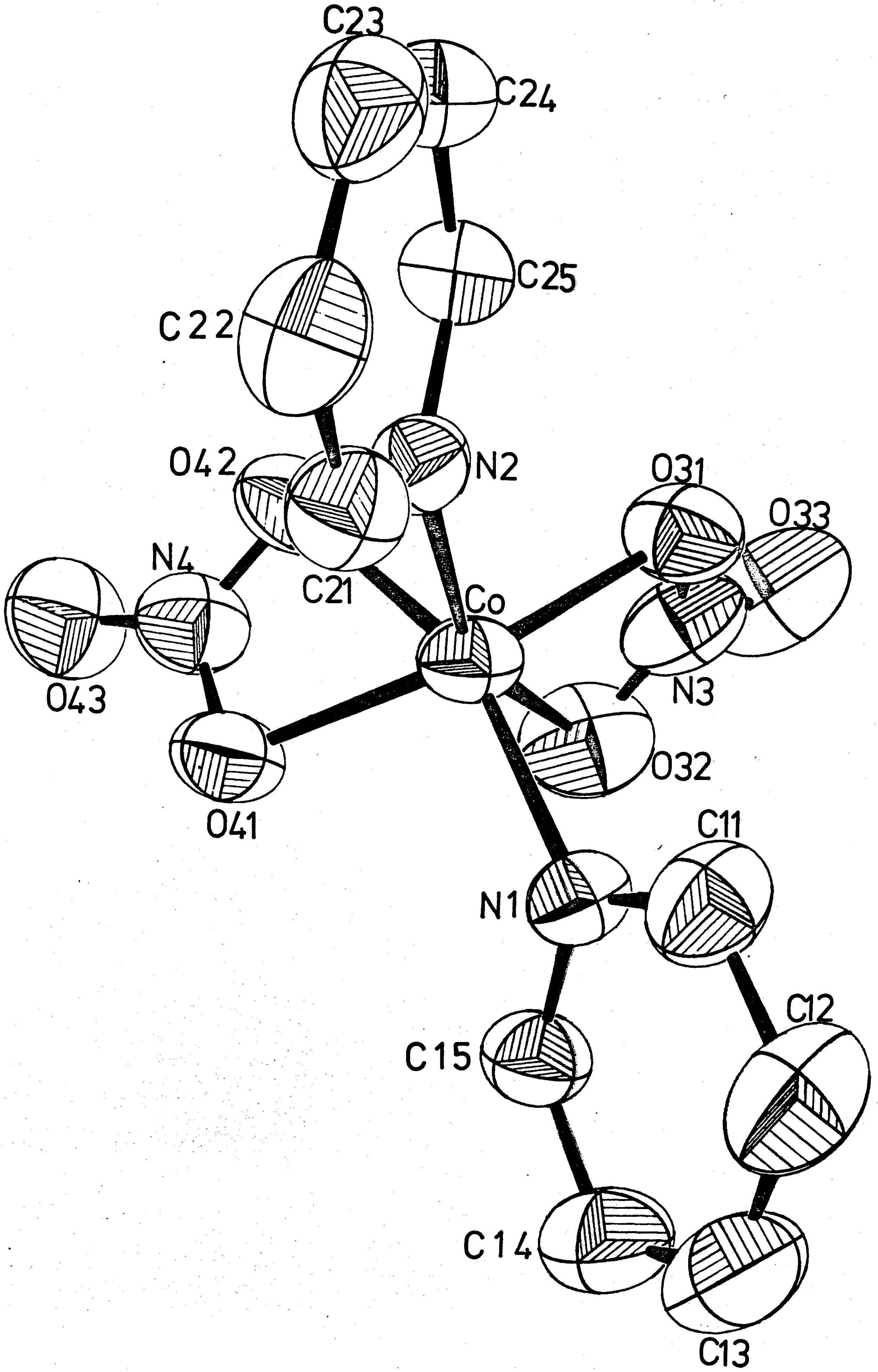
ROMAN NUMERALS AS SUPERSCRIPTS REFER TO THE FOLLOWING EQUIVALENT POSITIONS RELATIVE TO THE REFERENCE MOLECULE AT X,Y,Z :

I. X, 3/2-Y, 1/2+Z; II. X, -1+Y, Z; III. 1-X, 1-Y, 1-Z;
IV. 1-X,-1/2+Y, 1/2+Z; V. X, 1/2-Y, 1/2+Z;

```
                         TABLE 2.5.4

                    LEAST-SQUARES PLANES

    X,Y,Z ARE ORTHOGONAL CO-ORDINATES IN ANGSTROMS
    AN ASTERISK(*) INDICATES ATOM USED IN DEFINING THE PLANE

1.    EQUATION:  -0.7034X - 0.3981Y + 0.5889Z + 4.9109 = 0
      DISTANCES(Å) OF ATOMS FROM THE PLANE:-
      N(3)*     0.007(6)    O(31)*  -0.002(4)    O(32)*  -0.002(5)
      O(33)*   -0.003(5)    CO       0.131(1)    N(2)     0.419(4)
      C(21)    -0.104(5)    C(22)    0.061(6)    N(1)    -1.807(4)

2.    EQUATION:  -0.6022X + 0.7982Y + 0.0149Z + 4.9109 = 0
      DISTANCES(Å) OF ATOMS FROM THE PLANE:-
      N(4)*    -0.008(5)    O(41)*   0.002(4)    O(42)*   0.003(4)
      O(43)*    0.003(5)    CO       0.018(1)    N(1)    -0.194(4)
      C(11)     0.409(6)    C(12)    0.256(7)    N(2)     1.959(4)

3.    EQUATION:   0.2648X - 0.7698Y - 0.5807Z + 5.3975 = 0
      DISTANCES(Å) OF ATOMS FROM THE PLANE:-
      N(1)*    -0.009(4)    C(11)*   0.007(6)    C(12)*   0.001(7)
      C(13)*   -0.009(8)    C(14)*   0.007(7)    C(15)*   0.002(6)
      CO       -0.017(1)    N(2)    -1.139(4)    N(3)     2.500(5)
      N(4)     -1.086(5)

4.    EQUATION:  -0.3772X - 0.0408Y + 0.9252Z - 2.3158 = 0
      DISTANCES(Å) OF ATOMS FROM THE PLANE:-
      N(2)*    -0.005(4)    C(21)*  -0.003(5)    C(22)*   0.011(6)
      C(23)*   -0.011(6)    C(24)*   0.004(5)    C(25)*   0.005(5)
      CO       -0.095(1)    N(1)    -1.320(4)    N(4)     2.390(5)
      N(3)     -1.254(6)

     DIHEDRAL ANGLES(°) BETWEEN PLANES
      1 AND 2     83.4;  3 AND 4    127.3;  1 AND 3     102.8;
      2 AND 4     78.0;  1 AND 4     34.3;  2 AND 3     141.5;
```

Figure 2.5.1

A general view of V showing the atomic numbering scheme. Hydrogen atoms (not shown) are numbered as the atoms to which they are bonded.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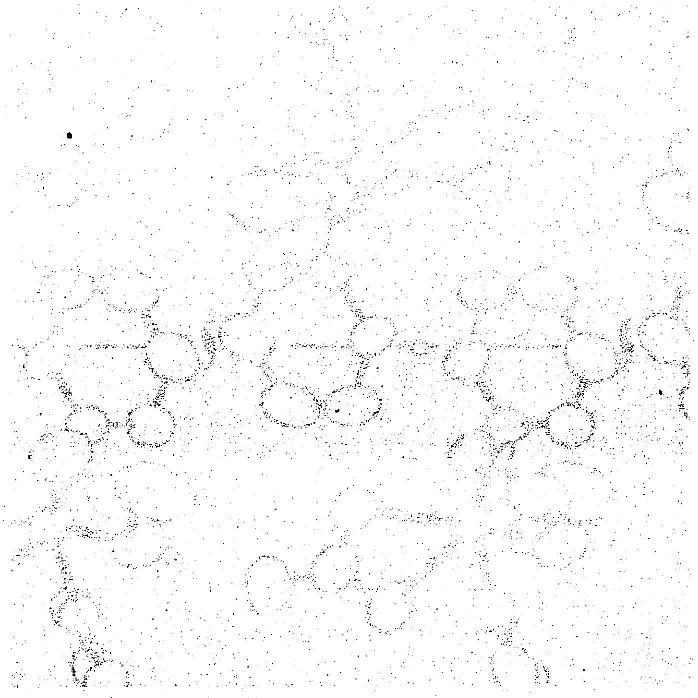
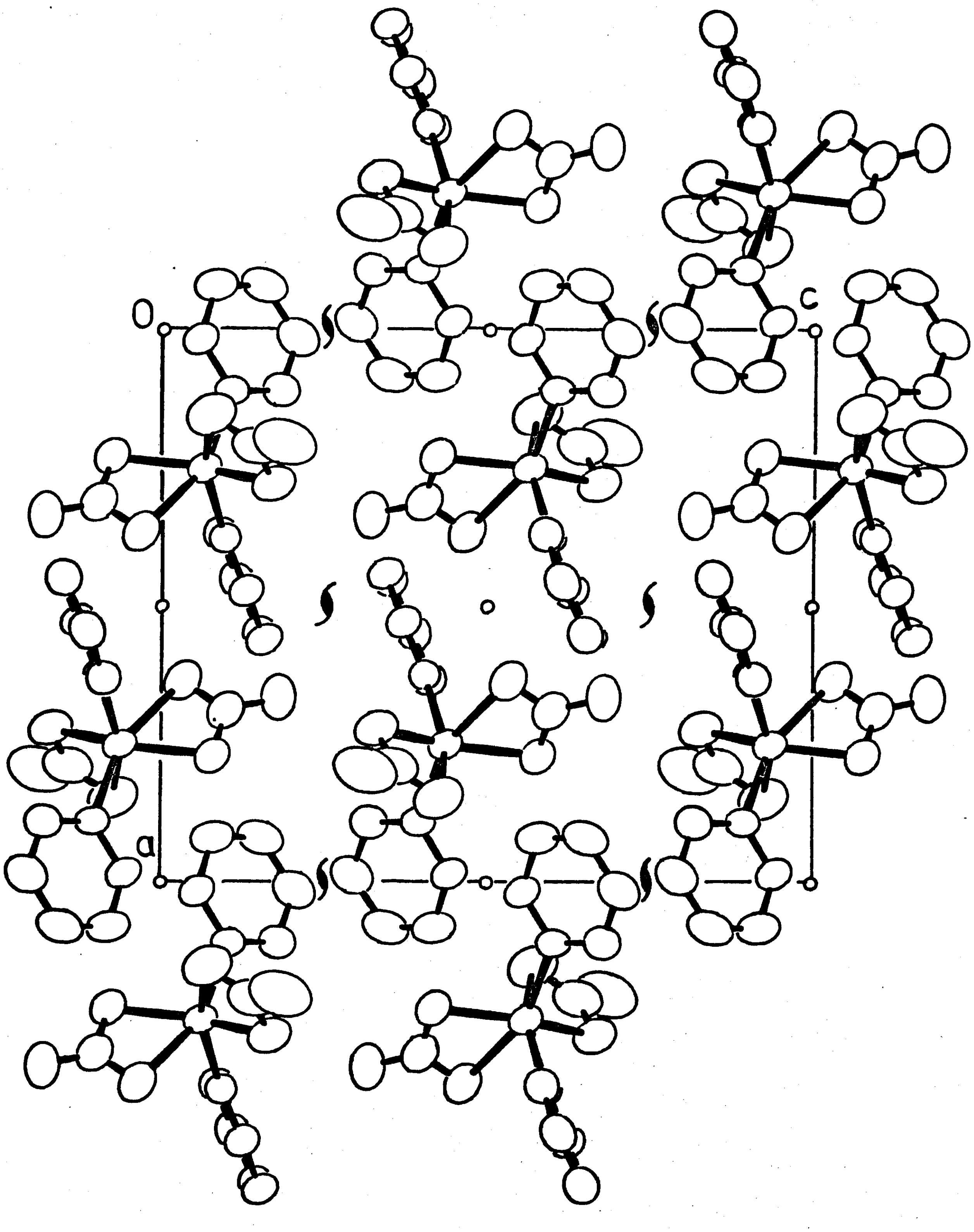
C24
C25
C22
N2
O42
O31
O33
N4
C21
Co
O43
N3
O32
O41
C11
N1
C12
C15
C14
C13

Figure 2.5.2

The molecular packing of V viewed along the b axis.




0
c
a

2.II Discussion of IV and V

The analyses of IV and V reveal that the complexes possess monomeric structures in which the cobalt atom is 6 co-ordinate. Both nitrato groups are bidentate ligands, and are equally asymmetric with respect to the cobalt atom. The overall molecular features of the complexes are very similar to those of $Co(MePO)_2(NO_3)_2$(34), as had been proposed by Lever(31).

The cobalt-nitrogen (amine) distances [2.054(3) and 2.049(3)Å in IV and 2.054(4) and 2.053(4)Å in V] are all experimentally equal. This contrasts with the expectation that Co-N(sp) bond lengths would be significantly shorter than Co-N(sp^2) bond lengths, particularly in view of the greater steric requirements of a pyridine ligand relative to an acetonitrile ligand. The Co-N (acetonitrile) distances in IV [2.054(3) and 2.049(3)Å] are significantly longer than the Co(11)-N(sp) distance of 1.952(5)Å in the tetrahedral $[Co(NCS)_4]^{2-}$complex-ion(55), and is in agreement with the $[Co(NCS)_4]$on that metal-ligand distances increase with co-ordination number(56), presumably due to steric requirements of the extra ligands. The Co-N(py) distances in V [2.054(4) and 2.053(4)Å] are significantly shorter than the corresponding distances in $Co(py)_3(NO_3)_2$ [2.152(9) and 2.124(11)Å] , which is 7 co-ordinate(56), again suggesting a bond-length dependence on co-ordination number.

The nitrato groups in IV are both equally asymmetric with respect to the cobalt atom. Thus the short Co-O bonds [2.054(3) and 2.055(3)Å] and the longer Co-O bonds [2.204(3) and 2.197(3)Å] are respectively experimentally equal. The asymmetric disposition of the N(4)-nitrato group is paralleled by an asymmetric distortion of the nitrato group which is in agreement with the theory outlined in the introductory discussion. Thus the longest N-O bond [N(4)-O(41), 1.290(4)Å] involves the oxygen atom which exhibits the shorter co-ordination distance to cobalt [Co-O(41) 2.055(3)Å] , and is also opposite the largest O-N-O interbond angle [O(42)-N(4)-O(43), 124.3(4)°]. The N(4)-O(42) is significantly shorter [1.239(5)Å] and is opposite the intermediate angle [O(41)-N(4)-O(43), 120.4(4)°]. The shortest N-O bond [N(4)-O(43) 1.209(5)Å] involves the unco-ordinated oxygen atom, and is also opposite the smallest angle [O(41)-N(4)-O(42) 115.3(3)°]. A similar trend is exhibited by the N(3)-nitrato group, but the estimated standard deviations renders the differences less significant.

In V the nitrato groups are also asymmetrically disposed with respect to the cobalt atom, but to an extent which is more marked than in IV. Thus the differences in the chelating Co-O bonds are 0.15 and 0.14Å in IV, but are 0.21 and 0.21Å in V. Since the steric requirements of pyridine ligands are greater than for acetonitrile ligands, and since it is known(57) that an amine-ligand co-ordinates more effectively than the oxygen of a nitrato group, it is not unexpected that the degree of asymmetry in V is greater than it is in IV. As in IV, the asymmetric disposition of the nitrato groups in V is paralleled by an asymmetric distortion of the nitrato groups, with the largest O-N-O interbond angles [O(32)-N(3)-O(33) 124.3(5)°, O(42)-N(4)-O(43) 122.6(5)°] opposite the shorter cobalt-oxygen distance [Co-O(31) 2.062(4)Å, Co-O(41) 2.074(4)Å]; the terminal N-O bonds [N(3)-O(33) 1.223(7)Å, N(4)-O(43) 1.226(7)Å] being generally shorter than the N-O bonds involving co-ordinated oxygens. However the estimated standard deviations render the individual differences insignificant.

In both complexes the nitrato groups are experimentally planar, with the cobalt atom deviating significantly from the mean planes [0.096(1) and 0.101(1)Å in IV and 0.131(1) and 0.018(1)Å in V], (Tables 2.4.4 and 2.5.4). This is similar to the cases in most nitrato complexes and is attributable to a folding about the line joining the co-ordinating oxygens, presumably due to intermolecular non-bonding interactions (see discussion of I, II and III). The dihedral angles between the mean planes through the nitrato groups are 86.5° and 83.4° in IV and V, which are comparable to the analogous values for other cis 6 co-ordinate complexes of the form $ML_2(NO_3)_2$ eg 80.1° in $Co(Me_3PO)_2(NO_3)_2$(34), 80.0° in $Co(C_{11}H_{12}N_2O)_2(NO_3)_2$(58), and 80.7° in $Zn(C_{11}H_{12}N_2O)_2(NO_3)_2$(59).

The geometries of the two pyridine rings in V are experimentally identical to each other (Table 2.5.4) and are in agreement with the geometries found for pyridine ligands in other complexes(43,45) and for free pyridine (46). The cobalt also deviates significantly from the mean planes through the pyridine rings [0.017(1) and 0.095(1)Å], presumably due to crystal packing effects(47). Similar deviations [0.07 and 0.10Å] have been observed in $Zn(py)_2(NO_3)_2$(60). The pyridine and nitrate groups are approximately staggered such that steric effects within the molecule are minimised.

The dimensions of the acetonitrile ligands in IV are experimentally identical to the corresponding values observed in $BF_3.NCCH_3$ and $BCl_3.NCCH_3$(48). Comparison of the C-N bond distances in the co-ordinated acetonitrile groups (1.131(5) and 1.125(5)Å) with the corresponding C-N distance [r_e,1.155(2)Å] observed in free acetonitrile(49) may indicate that a small and possibly significant(48,61) C-N bond shortening has occurred on co-ordination. This observation is possibly relevant to the origin of the general increase(62) in C≡N stretching frequencies which occur when nitriles serve as donors, as it suggests an increase in the C≡N force-constant in agreement with the conclusions of Purcell and Drago(63). Both acetonitrile ligands are linear within experimental error [N(1)-C(11)-C(12) 179.4(11)°, N(2)-C(21)-C(22) 178.9(9)°] but deviate from collinearity with the central cobalt atom [Co-N(1)-C(11) 169.8(3), Co-N(2)-C(21) 174.7(3)°] to differing extents. Such distortions have often been noted(50) and have been attributed to the effects of crystal packing(51).

Although the space group imposes no symmetry on the molecule of IV, the arrangement of the six co-ordinated atoms is such that there is a quasi two-fold rotation axis collinear with the bisector of the N(1)-Co-N(2) angle. This is clearly seen from Table 2.II.IV. The presence of C_2 symmetry is to be

Table 2.II.IV

Quasi two-fold symmetry of IV

Co-ordinates(Å) of atoms relative to orthogonal axes such that the xy-plane is the mean plane through N(1), N(2), O(32), O(42) and Co.

Atom	x	y	z
N(1)	-1.50	1.44	-0.34
N(2)	1.49	1.43	0.35
O(32)	-1.52	-1.49	0.34
O(42)	1.53	-1.46	-0.34
Co	-0.01	0.08	0.00
O(31)	-0.54	-0.45	1.91
O(41)	0.51	-0.44	-1.92
N(3)	-1.41	-1.32	1.58
N(4)	1.42	-1.28	-1.56
O(33)	-2.08	-1.90	2.40
O(43)	2.09	-1.86	-2.39

The quasi two-fold axis is along the y-axis and corresponds, approximately, to the internal bisector of the angle: N(1)-Co-N(2).

Table 2.II.V

Quasi two-fold symmetry of V

Co-ordinates(Å) of atoms relative to orthogonal axes such that the xy-plane is the mean plane through N(1), N(2), O(32), O(42) and Co.

Atom	x	y	z
N(1)	1.63	1.36	0.40
N(2)	-1.50	1.48	-0.41
O(32)	1.43	-1.56	-0.43
O(42)	-1.56	-1.43	0.42
Co	0.00	0.15	0.03
O(31)	0.30	-0.50	-1.91
O(41)	-0.37	-0.52	1.96
N(3)	1.10	-1.46	-1.64
N(4)	-1.28	-1.36	1.63
O(33)	1.50	-2.19	-2.53
O(43)	-1.86	-2.02	2.48

The quasi two-fold axis is along the y-axis and corresponds, approximately, to the internal bisector of the angle: N(1)-Co-N(2).

expected for an ideal octahedral geometry of a gaseous molecule of the form cis-MA_2B_4, A and B being rigid uniconformational ligands. This suggests that the severe distortion, imposed by the constraining 'bite' of the nitrato ligands on adjacent (cis) pairs of co-ordination sites, is also quasi-symmetrical, the observed deviations from C_2 symmetry being attributable to crystal packing effects on the ligands. The geometry of V is similar, the deviations from C_2 symmetry, however, being more marked (Table 2.II.V). It is in the presence of this quasi C_2 symmetry that IV and V are so similar to $Co(Me_3PO)_2(NO_3)_2$, and conform to the suggestion(31) that complexes of the form $ML_2(NO_3)_2$ (L = amine and the nitrato groups are bidentate), would exhibit moderately distorted forms of the approximately C_2 <u>cis</u> 6 co-ordinate $Co(Me_3PO)_2(NO_3)_2$. Such geometries are not restricted to bis-amine complexes, as originally proposed, since structures of the form $M(Ap)_2(NO_3)_2$ M = Co(58), Cu(64), Zn(59); Ap = Antipyrine exhibit analogous structures.

If the nitrato groups in the above mentioned complexes are viewed as occupying one co-ordination site situated at the centroid of the chelating oxygens as was suggested by Cotton and co-workers(17,28), then the immediate environment of the central atom may be regarded as having, in a sense, distorted tetrahedral geometry. The extent of the distortion is considerable, but by no means beyond comparison to the distortion found in some other (strictly four co-ordinate) 'tetrahedral' complexes, <u>eg</u> bis(imidazole) di-acetato cobalt(II)(65), in which the bond angles vary between 95° and 120°.

In the molecular structures the ligands are arranged so as to minimize intramolecular steric interactions. Since there are no unusually short intermolecular contacts, it may be assumed that the crystal packing has been determined by van der Waal's forces.

PART III

STRUCTURAL STUDIES OF YLIDES

INTRODUCTION

The term "ylide", first introduced by Wittig(1), is now taken to refer to a class of compounds which may be represented as formal vicinal zwitterions, $X^+ - Y^-$.

Though the history of ylides reaches as far back as 1894(2), ylide chemistry remained a field of only sporadic activity until 1953(3), when Wittig and Geissler discovered the synthetic use of methylenetriphenylphosphorane. Since then ylides have ceased to be chemical curiosities and are now subject to increasing synthetic, structural and theoretical investigations(4,5). A monograph by Johnson, published in 1966(6), has provided extensive coverage of the preparation, structural and physical properties, and reactions of ylides in general.

Ylides have been described as stabilized anions(7), and indeed the major chemical characteristic of ylides is their nucleophilicity(8). The nature of the stabilization is complex and may be attributed to several, not necessarily independent factors.

A qualitative comparison of the stability of ylides may be made from the relative ease of their preparation and isolation, and it is well known that ylides formed from second- and higher-row elements (X = P, As, Sb; S, Se; Br, I) possess greater stability than their first-row analogues (X = N, O, F)(5-9). This contrast is illustrated by the following observations :

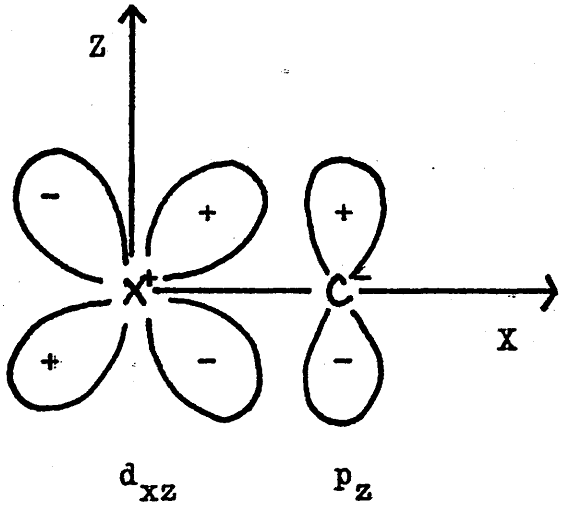
(i) Methylenetrimethylphosphorane is easily prepared(10) and tetramethylphosphonium iodide undergoes base-catalyzed hydrogen-deuterium exchange to the extent of 74 atom-percent after 3 hours at 62°C(11). The implied acidity of the phosphonium ion reflects the extent of stabilization of its conjugate base ie the ylide.

(ii) The nitrogen analogue has only been prepared as the LiBr complex(12). The free ylide decomposes rapidly to trimethylamine and methylene(13). Tetramethylammonium iodide does not incorporate deuterium to any measurable extent under the same conditions as for the phosphonium salt (see above) even after 504 hours(11). The acidity of $(Me)_4N^+$ has been estimated to be between that of benzene and toluene(12).

This enhanced stability of ylides containing second-row 'onium species (X^+) relative to the first-row analogues has been attributed to the possibility of a π-interaction of vacant 3d orbitals on the 'onium species with the lone-pairs of electrons on the anionic atom (Y^-)(6,8,14). Such valence-shell expansion is not possible for first-row elements(15) since the energy gap to the next vacant orbitals is sufficiently large to preclude their involvement in any appreciable bonding. A critical review of the evidence for, and the theory behind, the involvement of d-orbitals in the bonding of second-row elements has been given by Mitchell(16), and it seems that the postulate of d-orbital involvement in

π-interactions is justified in the consideration of compounds containing phosphorus and sulphur in their higher oxidation states.

In carbanionic ylides of second-row elements where the carbanion moiety exhibits trigonal (sp^2) geometry$^{(17)}$, the lone-pair of electrons may be assumed to occupy a p-orbital perpendicular to the plane defined by the σ-bonds in the $\overset{+}{X} - \overset{-}{C}\langle$ moiety. Clearly, such an arrangement is ideally suited to $d_\pi - p_\pi$ overlap with a suitable d-orbital of the 'onium species.

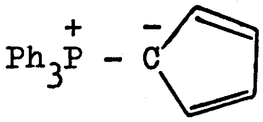


However, in the case of 'onium imines, a similar general inference is difficult to justify since the valence angle subtended at the nitrogen is observed to range from 110° to 146°$^{(18)}$. It follows that the nature and orientation of the two lone-pairs of electrons on the nitrogen are indeterminate, and therefore apparently indistinguishable. It has been suggested$^{(19)}$ that the two lone-pairs of electrons on the imine nitrogen should be considered to occupy two equivalent orbitals, possibly of an sp^3-hybrid nature, perturbed into non-equivalence to an extent depending on the nature of π-interactions with the 'onium and stabilizing groups$^{(18)}$. The π-bonding interactions of both lone-pairs of electrons may then be resolved into two mutually perpendicular components, one perpendicular to the plane defined by the σ-bonds (π-bonding) and one in the said plane (π'-bonding). This approach is theoretically valid and, although somewhat detached from a geometric model of orbital interactions, it has been used to account for the bonding in phosphonitrilic compounds$^{(20)}$ and P-O-P, S-O-S and S-N-S bridged systems$^{(21)}$.

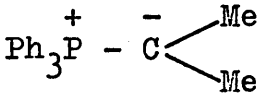
In the case of first-row ylides no such π-interaction is possible between the 'onium species and the lone-pair/s of electrons of the anionic moiety. Some stabilization by the 'onium species can take place by an inductive effect through the σ-bond, but such an effect is known to be very small$^{(5)}$. Apart from N-oxides, the free or "unstabilized" ylides are not isolable. Therefore the stability of ammonium ylides$^{(5)}$ must be attributed, at least principally, to the delocalization of the anionic charge by the electron-withdrawing substituents on the Y^- atom. Even second-row ylides (apart from oxides) only show marked stability (low chemical reactivity$^{(8)}$) when they possess electron-withdrawing (delocalizing) substituents on the Y^- atom, and then the stability of the ylide is directly related to the electron-withdrawing nature of the substituents$^{(8)}$. Thus whereas the ylide (A) is moderately reactive and decomposes slowly in air, ylide (C) is stable to hot alkali. Ylide (B) exhibits intermediate reactivity. In marked contrast, ylide (D), in which the substituents on C^- are a source of electrons, reacts violently with air and moisture(8).

$$Ph_3\overset{+}{P} - \overset{-}{C}H_2 \qquad (A)$$

$$Ph_3\overset{+}{P} - \overset{-}{C}H - CH = CH_2 \qquad (B)$$



(C)



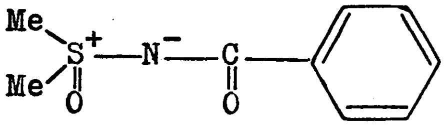
(D)

The anionic properties and stability of ylides might also be expected to vary with the electronegativity of the negative atom ie the extent to which the net negative charge can be borne by the atom. The trend in ylide stability of isoelectronic systems (Y = C, N, O) bears this out, and parallels the trend in electronegativity ($C < N < O$), eg $Me_3\overset{+}{N} - \overset{-}{C}H_2$, $Me_3\overset{+}{N} - \overset{-}{N}H$, $Me_3\overset{+}{N} - \overset{-}{O}$(4).

The bonding and conformational characteristics of ylides have, in recent years, become subjects of considerable interest, and a systematic study by A F Cameron and coworkers, using the techniques of X-ray crystal-structure analysis, has been in operation in Glasgow for several years. The work presented in this part was undertaken with the aim of obtaining information regarding the previously undiscussed dimethylsulphoxonium ylides. Accordingly, the crystal structures of three such ylides have been determined. The results are presented and discussed in the first three sections. Section four is an overall discussion of aspects of these analyses that are of overall relevance to the study of ylidic systems already carried out in this department and elsewhere.

3.1 . THE CRYSTAL AND MOLECULAR STRUCTURE OF N-BENZOYLIMINODIMETHYLOXYSULPHURANE

3.1.1. Experimental and results



I

N-benzoyliminodimethyloxysulphurane

Preparation of crystals

Dimethylsulphoximine was prepared by the method of Johnson and Rogers(32).

The title compound was prepared by shaking dimethylsulphoximine (0.06 mol) with benzoyl chloride (0.03 mol) in freshly distilled chloroform (100 ml) for two hours. After filtration, the chloroform was removed under vacuum and the resulting oil washed with petroleum ether. Recrystallization from water and, finally, n-pentane yielded sharp,flat needles (m.p. 107.5°, lit. 107-108°(33)).

A suitable crystal for data collection was obtained by allowing a solution of the ylide in 1,2-dichloroethane to evaporate on a watch-glass.

Crystal data

Molecular formula	$C_9H_{11}NO_2S$
Molecular weight	M = 197.3
Crystal system	Monoclinic
Unit cell dimensions	a = 5.735(4)Å
	b = 11.450(1)Å
	c = 8.476(1)Å
	β = 117.49(2)°
Unit cell volume	U = 493.8Å^3
Measured density	D_m = 1.32 g cm^{-3}
Number of molecules per unit cell	Z = 2
Calculated density	D_c = 1.33 g cm^{-3}
Number of electrons per unit cell	F(000) = 208
Linear absorption coefficient	μ(Mo-K$_\alpha$) = 2.92 cm^{-1}
Space group	Pc (C_s^2, No. 7)

Data collection

Radiation used	Mo-K$_\alpha$, λ = 0.71069Å
Filter	Graphite monochromator,
	$\cos^2 2\theta_m$ = 0.965
Upper limit for data collection	$2\theta_{max}$ = 50°
Number of independent reflections	m = 957
Unobserved cut-off	$2\sigma_I$
Number of parameters refined	n = 116
Number of reflections per parameter	m/n = 8.2

Structure Determination

Systematic absences in the diffraction data (h0l absent when l odd) suggested the possible space groups Pc or P2/c. A statistical analysis of the data suggested space group Pc, a choice which was subsequently vindicated by successful refinement of the model with no anamolous effects.

The structure was resolved by evaluation and analysis of the Patterson function and subsequent calculations of the electron-density distribution. The y - co-ordinate of the sulphur atom was determined from the Harker plane (0, 2Y, 0.5) in a sharpened, origin-removed vector map. The indeterminate x and z co-ordinates were assigned values of 0.5 and 0.25 respectively in order to define an origin. The sulphur atom was then used to phase the observed structure-factor moduli in an evaluation of the electron density distribution (R = 0.41). From the resulting pseudo-symmetric distribution five atomic sites, belonging to one asymmetric unit, were chosen. These were assigned isotropic thermal parameters of 0.03Å^2 and one cycle of least-squares refinement (R = 0.29) followed by two structure-factor and electron-density calculations revealed the sites of all non-hydrogen atoms.

Structure Refinement

Prior to least-squares refinement all atoms were assigned isotropic thermal parameters ($U_{iso} = 0.05Å^2$). The full-matrix least-squares refinement of positional, thermal and scale parameters (other than the x and z co-ordinates of the sulphur atom) converged after 12 cycles when R was 0.032 and R' was 0.0016. Full details of the course of refinement are given in Table 3.1.2. Initially unit weights were applied to all reflections. In later stages weights given by the expression

$$w = (0.4198 - 0.1127|F_o| + 0.0087|F_o|^2)^{-1}$$

were applied. The coefficients of the quadratic expression were obtained from a least-squares fit of $a + b|F_o| + c|F_o|^2$ to the distribution of $\langle w\Delta^2\rangle$ with $\langle |F_o|\rangle$ obtained from an analysis of $w\Delta^2$ with increasing $|F_o|$. This weighting scheme leads to approximately constant $\langle w\Delta^2\rangle$ with increasing $|F_o|$ and $\sin\theta$.

A 'difference' synthesis after cycle 3 did not reveal any residual electron density in positions which would be stereochemically acceptable for hydrogen atoms. Therefore positions for the hydrogen atoms were calculated and their calculated co-ordinates together with an isotropic thermal parameter ($U_{iso} = 0.076Å^2$) were used as fixed contributors to the structure factors. These co-ordinates were re-calculated in later stages of refinement.

The refinement was assumed complete when the parameter-shifts calculated by a cycle of least-squares were insignificant compared to the corresponding estimated standard deviations. A final difference synthesis showed no errors in the model, the highest peak in the residual electron-density map being 0.13e/Å^3. In all structure-factor calculations the atomic scattering factors for sulphur were taken from ref.22, those for oxygen, nitrogen and carbon were computed from numerical Hartree-Fock wave functions$^{(23)}$, whilst the scattering factors for hydrogen were those given by Stewart$^{(24)}$. Observed and final calculated structure factors are listed in Appendix VI.

The final fractional co-ordinates and thermal parameters of all atoms are given in Table 3.1.3. The values of U_{ij} refer to the anisotropic temperature factor expression given in PART I. Bond lengths, valence angles and other relevant intra- and intermolecular data are given in Table 3.1.4 and Table 3.1.5. A general view of the molecule illustrating the thermal ellipsoids$^{(25)}$ and giving the atomic numbering scheme is given in Figure 3.1.1. The molecular packing arrangement viewed down the $\underline{c}$ axis is given in Figure 3.1.2.

TABLE 3.1.1

STATISTICAL ANALYSIS OF DATA

	THEORETICAL		EXPERIMENTAL
	CENTRIC	ACENTRIC	
AVERAGE |E|	0.798	0.886	0.920
AVERAGE |E|**2	1.000	1.000	1.000
AVERAGE |E**2-1|	0.968	0.736	0.622
|E| >1.0 (PERCENT)	31.73	36.79	39.20
|E| >1.8 (PERCENT)	7.19	3.92	2.81
|E| >2.0 (PERCENT)	4.55	1.83	0.92

TABLE 3.1.2

COURSE OF REFINEMENT

CYCLES	PARAMETERS REFINED	FINAL R	FINAL R'
1 - 3	Y,U(ISO) FOR S. X,Y,Z,U(ISO) FOR O,N,C. SCALE FACTOR. FULL MATRIX, UNIT WEIGHTS.	0.102	0.0220
4 - 5	AS ABOVE BUT WITH CALCULATED HYDROGEN ATOMS INCLUDED AS FIXED CONTRIBUTORS.	0.089	0.0185
6 - 7	Y,U(IJ) FOR S. X,Y,Z,U(IJ) FOR O,N,C. SCALE FACTOR. FULL MATRIX, UNIT WEIGHTS. CALCULATED H ATOM CONTRIBUTIONS INCLUDED BUT NOT REFINED.	0.069	0.0159
8 -11	AS ABOVE*, BUT WITH WEIGHTING SCHEME APPLIED.	0.032	0.0016

* H-ATOM POSITIONS WERE RECALCULATED AFTER CYCLE 8, AND TWO DESCREPANT REFLECTIONS, FOR WHICH |F(OBS)| < 0.05|F(CALC)|, WERE REMOVED FROM THE DATA SET.

TABLE 3.1.3

A. FRACTIONAL CO-ORDINATES(x10^4) OF NON-HYDROGEN ATOMS

ATOM	X/A	Y/B	Z/C
S	5000	0880(1)	2500
O(1)	2956(5)	0004(2)	1977(4)
O(2)	1534(5)	2482(2)	2848(4)
N	5634(6)	1620(3)	4198(4)
C(1)	4458(6)	3044(3)	5800(4)
C(2)	2572(8)	3721(4)	5957(6)
C(3)	3233(9)	4397(3)	7473(6)
C(4)	5752(9)	4403(3)	8822(6)
C(5)	7682(9)	3729(4)	8672(6)
C(6)	7024(7)	3049(3)	7171(4)
C(7)	4445(11)	1784(5)	0693(6)
C(8)	7991(7)	0204(4)	3010(5)
C(9)	3697(6)	2349(3)	4128(4)

B. CALCULATED FRACTIONAL CO-ORDINATES(x10^4) AND ASSIGNED THERMAL PARAMETERS(Å^{2}x10^4) OF HYDROGEN ATOMS

ATOM	X/A	Y/B	Z/C	U(ISO)
H(21)	0595	3749	4849	760
H(31)	1662	4903	7605	760
H(41)	6268	4904	10104	760
H(51)	9742	3752	9726	760
H(61)	8560	2562	6990	760
H(71)	4076	1293	-0533	760
H(72)	6296	2331	0979	760
H(73)	2880	2419	0350	760
H(81)	7808	-0331	1840	760
H(82)	8709	-0332	4151	760
H(83)	9519	0884	3189	760

TABLE 3.1.3(CONT'D)

C. ANISOTROPIC THERMAL PARAMETERS($\mathring{A}^2 x10^4$) OF NON-H ATOMS

ATOM	U11	U22	U33	U12	U13	U23
S	335(3)	456(3)	325(3)	-6(5)	139(2)	-13(5)
O(1)	479(14)	594(14)	595(15)	-143(13)	250(12)	-123(13)
O(2)	448(13)	671(17)	472(13)	88(12)	106(11)	-23(12)
N	395(15)	504(17)	354(14)	60(14)	148(12)	-12(13)
C(1)	416(17)	364(15)	404(15)	4(12)	220(13)	12(12)
C(2)	511(23)	552(22)	539(23)	86(18)	271(18)	-12(17)
C(3)	663(23)	615(24)	665(24)	86(20)	391(20)	-98(19)
C(4)	729(26)	491(21)	566(21)	51(18)	317(19)	-115(16)
C(5)	593(24)	494(22)	545(23)	26(18)	206(19)	-112(18)
C(6)	439(17)	429(17)	448(17)	22(14)	185(14)	-48(14)
C(7)	1056(40)	703(28)	502(24)	217(29)	486(26)	224(22)
C(8)	407(17)	649(24)	538(20)	58(17)	204(16)	-114(18)
C(9)	336(14)	470(17)	398(15)	1(13)	152(12)	26(12)

TABLE 3.1.4

INTERATOMIC DISTANCES(Å) AND ANGLES(°) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

A. BONDED DISTANCES

S -C(8)	1.744(4)	S -C(7)	1.752(5)	S -O(1)	1.448(3)
S -N	1.561(3)	N -C(9)	1.369(5)	C(9)-C(1)	1.503(5)
C(1)-C(2)	1.386(5)	C(2)-C(3)	1.395(6)	C(3)-C(4)	1.367(6)
C(4)-C(5)	1.403(6)	C(5)-C(6)	1.387(6)	C(6)-C(1)	1.392(5)
C(9)-O(2)	1.223(4)				

B. INTERBOND ANGLES

C(7)-S -C(8)	103.9(2)	C(7)-S -O(1)	110.3(2)
C(7)-S -N	110.8(2)	C(8)-S -O(1)	109.5(2)
C(8)-S -N	103.2(2)	O(1)-S -N	118.0(2)
S -N -C(9)	116.9(2)	N -C(9)-O(2)	125.7(3)
N -C(9)-C(1)	113.9(3)	O(2)-C(9)-C(1)	120.3(3)
C(9)-C(1)-C(2)	119.1(3)	C(9)-C(1)-C(6)	121.6(3)
C(2)-C(1)-C(6)	119.2(3)	C(1)-C(2)-C(3)	120.5(4)
C(2)-C(3)-C(4)	120.4(4)	C(3)-C(4)-C(5)	119.7(4)
C(4)-C(5)-C(6)	120.0(4)	C(5)-C(6)-C(1)	120.2(3)

C. INTRAMOLECULAR NON-BONDED DISTANCES

O(2)...S	2.82	C(9)...O(1)	3.16	O(2)...O(1)	3.13
C(9)...C(7)	3.20	O(2)...C(8)	4.48	C(9)...C(8)	3.89
O(2)...C(7)	3.10	N ...C(6)	2.80	O(2)...C(2)	2.80
N ...C(2)	3.68	O(2)...C(6)	3.62		

TABLE 3.1.4(CONT'D)

D. INTERMOLECULAR DISTANCES <4.0Å

C(5)...O(2^{I})	3.50	C(6)...C(3^{II})	3.78	C(7)...O(2^{II})	3.69
C(8)...C(9^{II})	3.84	C(8)...O(1^{II})	3.35	C(8)...O(2^{II})	3.35
C(6)...C(2^{II})	3.85	C(5)...C(3^{II})	3.84	C(5)...C(7^{III})	3.80
C(3)...C(7^{III})	3.89	C(4)...C(7^{III})	3.63	C(5)...C(2^{IV})	3.89
C(5)...C(3^{IV})	3.97	C(8)...O(1^{V})	3.26	C(4)...C(1^{VI})	3.61
C(3)...C(2^{VI})	3.81	C(4)...C(2^{VI})	3.78	C(4)...C(6^{VI})	3.90
C(3)...C(9^{VI})	3.95	C(3)...O(2^{VI})	3.76	C(3)...C(1^{VI})	3.90
C(4)...C(9^{VI})	3.95	C(1)...O(1^{VII})	3.83	C(9)...O(1^{VII})	3.77
O(1)...C(7^{VII})	3.52	C(6)...C(8^{VII})	3.79	N ...C(8^{VII})	3.55
N ...O(1^{VII})	3.83				

ROMAN NUMERALS AS SUPERSCRIPTS REFER TO THE FOLLOWING EQUIVALENT POSITIONS RELATIVE TO THE REFERENCE MOLECULE AT X,Y,Z :

I	1+X, Y, 1+Z
II	1+X, Y, Z
III	X, Y, 1+Z
IV	1+X, 1-Y, 1/2+Z
V	1+X, -Y, 1/2+Z
VI	X, 1-Y, 1/2+Z
VII	X, -Y, 1/2+Z

E. SELECTED TORSION ANGLES

C(7)-S -N -C(9)	63.2(3)	O(1)-S -N -C(9)	-65.3(3)
C(8)-S -N -C(9)	173.9(3)	S -N -C(9)-O(2)	-1.0(5)
N -C(9)-C(1)-C(6)	8.5(5)	N -C(9)-C(1)-C(2)	-173.4(3)
O(2)-C(9)-C(1)-C(2)	8.2(5)		

TABLE 3.1.5

LEAST-SQUARES PLANES

1. PLANE DEFINED BY: C(1),C(2),C(3),C(4),C(5),C(6).

EQUATION: 0.4724X + 0.7667Y - 0.4347Z = 0.9131

DISTANCES(Å) OF ATOMS FROM THE PLANE:-

C(1)	-0.001(3)	C(9)	0.039(3)
C(2)	0.002(4)	O(2)	0.224(3)
C(3)	0.000(4)	N	-0.112(3)
C(4)	-0.004(4)	S	-0.065(1)
C(5)	0.005(4)	O(1)	-1.120(3)
C(6)	-0.002(3)	C(7)	1.503(5)
		C(8)	-0.108(4)

2. PLANE DEFINED BY: N,C(9),O(2),C(1).

EQUATION: 0.5889X + 0.7286Y - 0.3500Z = 1.1801

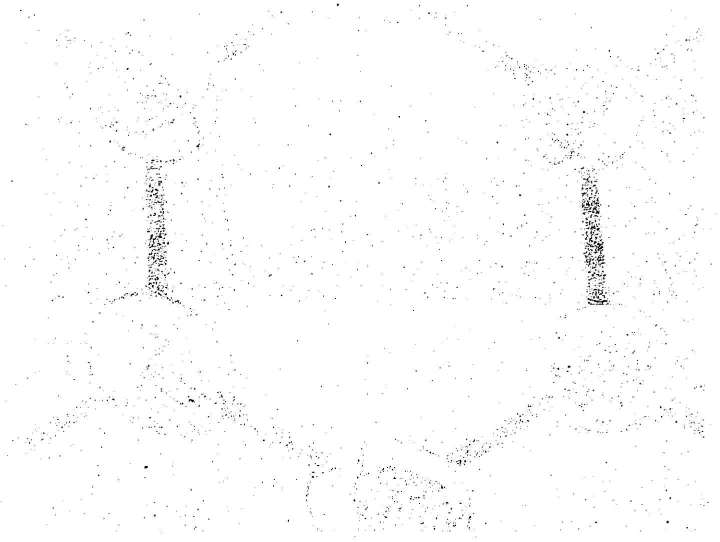
DISTANCES(Å) OF ATOMS TO THE PLANE:-

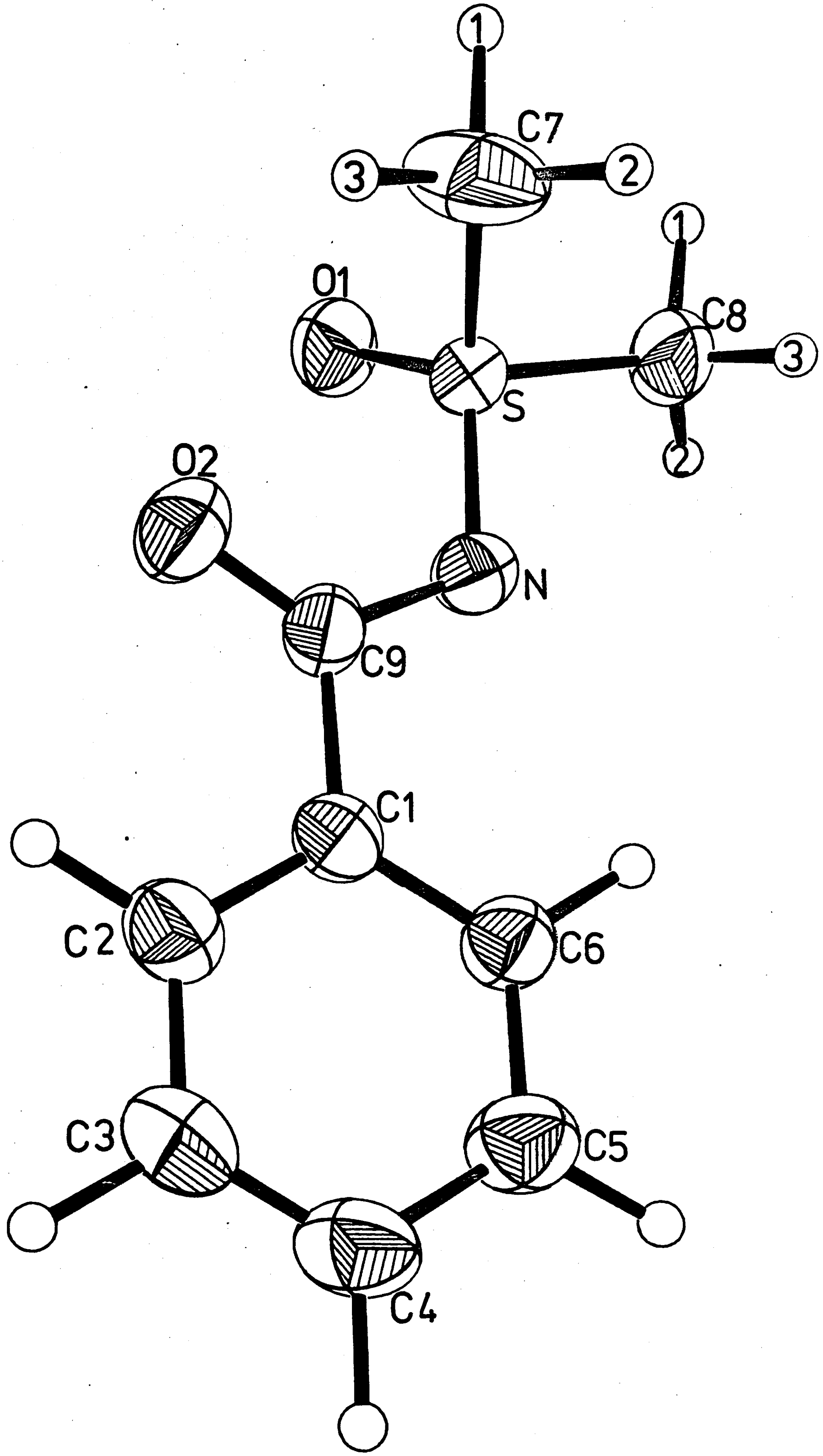
N	0.003(3)	S	0.009(1)
C(9)	-0.008(3)	O(1)	-1.154(3)
O(2)	0.003(3)	C(7)	1.468(5)
C(1)	0.002(3)	C(8)	0.205(4)

THE DIHEDRAL ANGLE BETWEEN PLANE 1 AND PLANE 2 IS 8.5 DEGREES

Figure 3.1.1

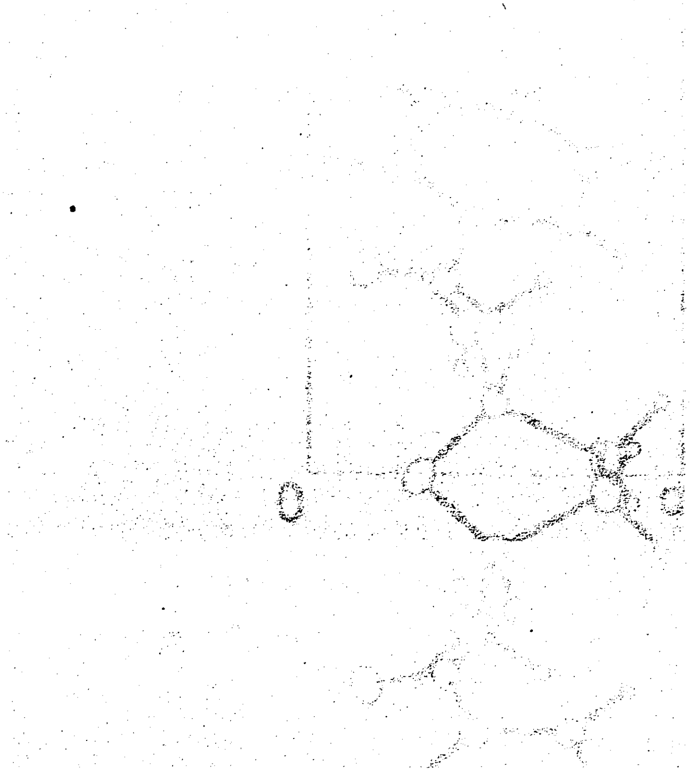
A general view of I showing the atomic numbering scheme. Hydrogen atoms are numbered as the atoms atoms to which they are bonded.

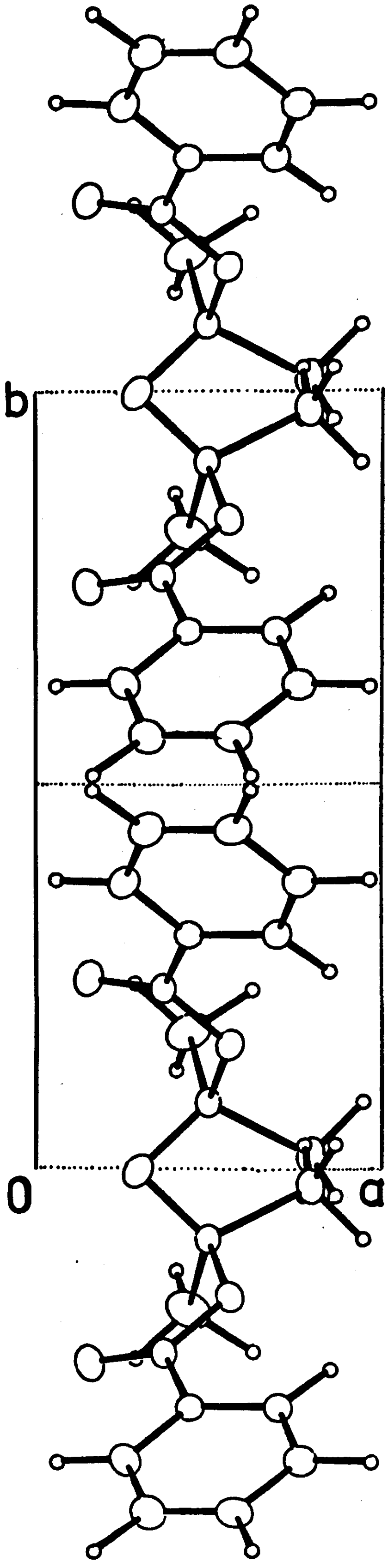


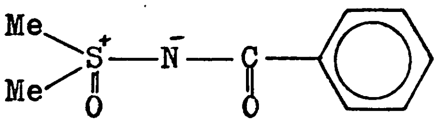

1
C7
3
2
1
O1
C8
3
S
2
O2
N
C9
C1
C2
C6
C3
C5
C4

<u>Figure 3.1.2</u>

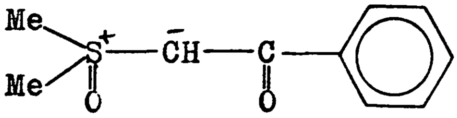
The molecular packing of I viewed along the <u>c</u> axis.



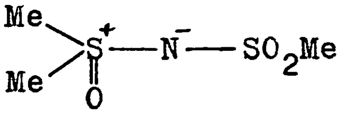

b
0
a



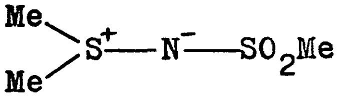
I(*)



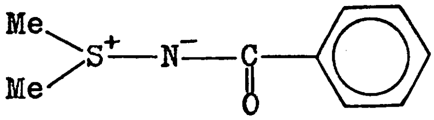
II(*)



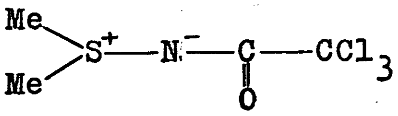
III(*)



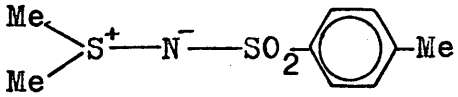
IV(39)



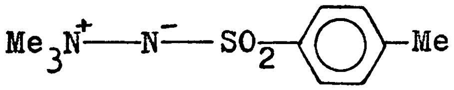
V(18)



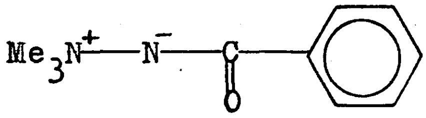
VI(26)



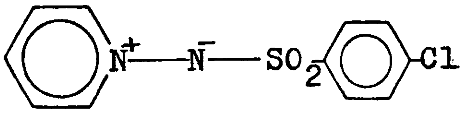
VII(40)



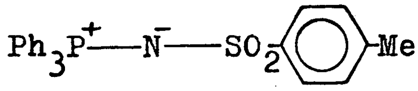
VIII(18)



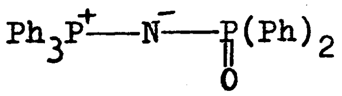
IX(31)



X(18)



XI(52)



XII(38)

(*) indicates this work.

3.1.2 Discussion of I

Comparison of the molecular geometry of I with that of V and VI is of interest. As in the iminosulphuranes(18,19), clear evidence of charge delocalization from the negative nitrogen atom to the 'onium group in I, by $d_{\pi}-p_{\pi}$ interaction, is provided by the shortness of the S-N bond, 1.561(3)Å, relative to the single bond in sulphamic acid, 1.772(1)Å(18), and to the value of 1.74Å from Pauling's covalent radii(27). This S-N length is similar to the corresponding value observed in III, 1.552(2)Å, but is significantly shorter than the value in V, 1.659(2)Å, and other S(IV) imino sulphuranes(18).

It is of interest to note that the S-N bond contraction of 0.098(5)Å from V (a sulphur(IV) compound) to I (a sulphur(VI)) is similar to the difference in the proposed covalent radii of 1.19Å and 1.08Å for sulphur(IV) and sulphur(VI) respectively(28). However it is unlikely that the observed contraction is due solely to a change in effective covalent radius with oxidation number as the change in the corresponding sulphur-methyl distances [1.748(4)Å (mean) in I and 1.777(3)Å (mean) in V] is less marked.

Consideration of the N-C(O) bond length in I, 1.369(5)Å, indicates that the N-C bond has considerable double-bond character comparable to that in pyridine, 1.340(5)Å(29). The C=O bond length shows no difference from the normal value of 1.215(5)Å(30). In contrast, in V, the corresponding values are 1.344(3)Å and 1.246(3)Å, and in IX, in which d_{π}-p_{π} delocalization to the 'onium is not possible(15), the values are 1.313(6)Å and 1.243(5)Å. Thus, relative to I, the dimensions of V and IX suggest greater delocalization to the carbonyl moiety.

It may plausibly be concluded that the dimethylsulphoxonium group in I is thus more effective in delocalizing the anionic charge than is the dimethylsulphonium group in V. This is in keeping with the observation that whereas $(Me)_2S(O)(NH)$ is a stable, isolable solid(32), $(Me)_2S(NH)$ is an unstable, but characterizable oil, while $(Me)_3N(NH)$ has only been postulated as a non-isolable intermediate(6). This trend in stability is paralleled by the iso-electronic methylene analogues. The extra stability of sulphur(VI) compounds relative to sulphur(IV) compounds is reflected throughout the chemistry of sulphur, and has been attributed to the destabilization that results from the presence of the lone-pair on the sulphur(IV) atom(34).

An interesting feature of I is the value of the valency angle N-C(9)-O(2), 125.7(3)°, which, in common with other benzoyl-stabilized ylides, eg II,V,VI,IX, is greater than the ideal trigonal value. Though intra-molecular non-bonded interactions cannot be completely discounted, it is unlikely that these are the principal causative factors since angles of comparable magnitude have been observed in acetamide(35) and in a carbamoyl chloride(36). Furthermore, in spite of the extra O(1)...O(2) interaction in I, the corresponding angle in V is identical to that in I. Even intermolecular interactions may be partially discounted since there are no unduly short intermolecular contacts in the present structure. Furthermore, similar values have been observed for pairs of similar molecules in different crystal environments eg I and V, VI and IX. However there appears to be an underlying feature which is common to the examples cited above, ie the apparent correlation between the magnitude of the angle and the nature of the opposite bond. Thus the smallest angle in the carbonyl moiety is always opposite the carbonyl bond, which is a formal double bond and, even in cases with appreciable enolate character, still has considerable π-character. The intermediate angle is always opposite the bond from the ylide's anionic atom to the carbonyl carbon atom, the length of which, at the least, indicates incipient π-character. Finally the largest angle is always opposite a formal single bond. The angles observed in I, $113.9(3)^\circ$, $120.3(3)^\circ$ and $125.7(3)^\circ$ are identical to those in V. The above comments parallel the observations made on the dimensions of the complexed nitrato group (see PART II) and is in keeping with the theory of Coulson$^{(37)}$. The discussion may have been expressed alternatively in terms of the mutual repulsion of bonds, the degree of repulsion being governed by the extent of the localized charge or double-bond character in a pair of bonds. It is intuitively plausible that the greater the double-bond character in such bonds, then the greater will be the angle subtended by these bonds.

Interatomic non-bonded interactions were partially discounted solely to simplify the discussion and to bring out an underlying feature. However, since angle bending is a low-energy process, non-bonded interactions may also be significant, although difficult to quantify. Furthermore other factors, such as the electronegativity of the atoms bonded to the carbonyl carbon, may also have a bearing on the situation(18).

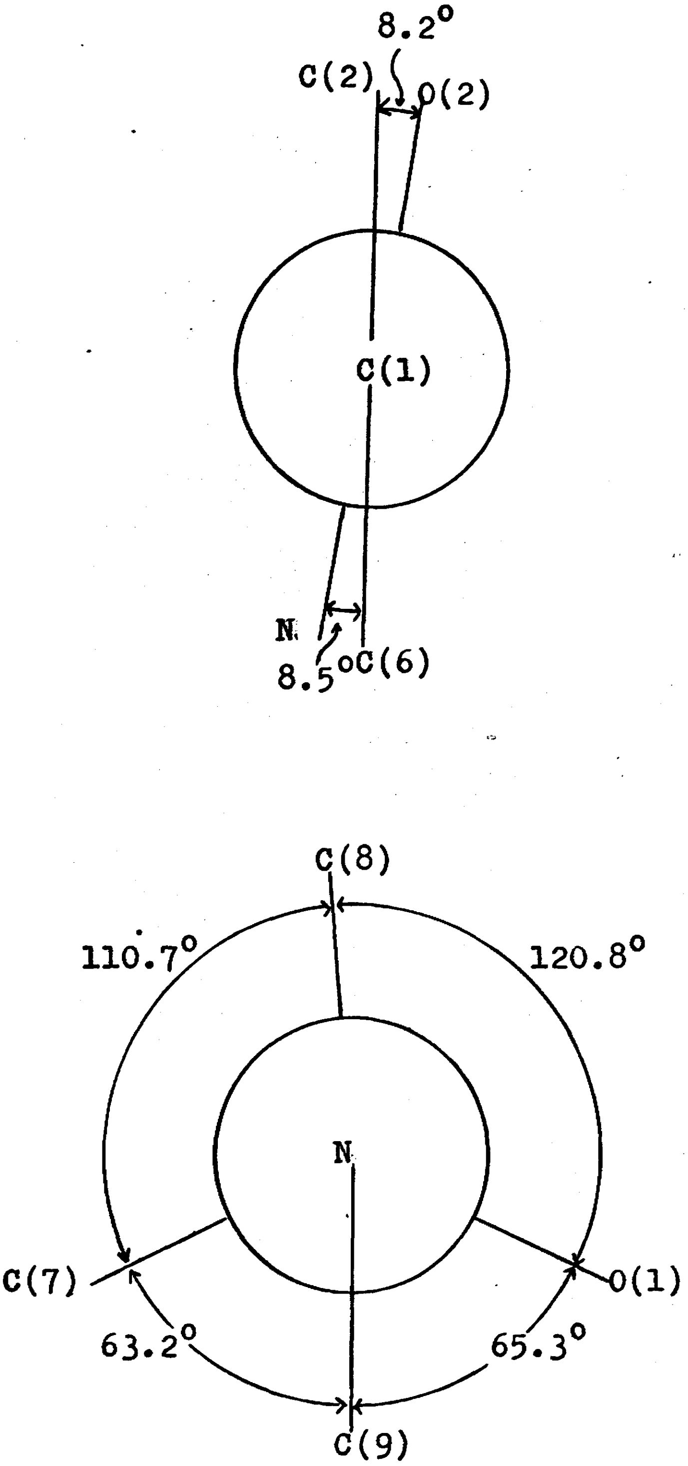
The angle subtended at the anionic nitrogen atom may also be discussed in similar terms. The angle in I, 116.9(2)°, is significantly greater than the corresponding angle in V, 110.4(1)°, and may thus reflect the greater π-character (increased $d_{\pi}-p_{\pi}$ bonding) in the S-N bond in I relative to that in V. Therefore, to the extent that the converse is valid, the angle of 120.2(1)° in III and of 146.0(2)° in XII may reflect the increased $d_{\pi}-p_{\pi}$ interaction in going from sulphur(IV) to sulphur(VI) and finally to phosphorus(V). This trend is the same as that observed in the stability of the free imines.

However the variation of the angle subtended at the imino nitrogen atom also correlates with changes in the size of the 'onium and stabilizing moieties. Thus the angle in the carbonyl-stabilized ylide, I, is smaller than that in the corresponding sulphonyl-stabilized ylide, III (116.9(2)° and 120.2(1)° respectively). This trend is followed in the dimethyliminosulphuranes, V and IV, in which the angles are 110.4(1)° and 116.2(6)° respectively, and also in the trimethylammoniumimines, IX and VIII, in which the angles are 114.2(3)° and 118.0(1)° respectively. The correlation of this angle and the size of the 'onium moiety may also be implied by the trend observed in going along the following series of sulphonyl imines : X, VII, VIII, III, XI, in which the steric requirements of the 'onium moiety increase in the given order, and the corresponding angles are 111.9(1)°, 113.4(5)°, 118.0(1)°, 120.2(1)° and 126.4(2)° respectively. Furthermore the possible sensitivity of this angle to intramolecular non-bonded interactions may also imply that intermolecular interactions could also play a significant role. However in view of the many apparently plausible factors, which are inherently difficult to quantify, and the small number of suitably related crystal-structure analyses, the above rationalization is at best tentative.

The 'onium moiety in I exhibits distorted tetrahedral geometry which is similar to that observed in III. The S-O bond length, 1.448(3)Å, is also normal and similar to values observed in sulphonyl groups. There is no evidence that the considerable delocalization into the carbonyl moiety extends also to the benzene ring, since the C(9)-C(1) bond, 1.503(5)Å, is typical of $C(sp^2)-C(sp^2)$ single bond lengths, and no significant deviations from normal geometry occur in the benzene ring. The torsion angle O(2)-C(9)-C(1)-C(6) of 8.2(5)° is similar to the values observed in V, 9.5(2)°, and II, 8.4(4)°. This twisting may arise from the need to minimise the O(2)... C(2) and N...C(6) close contacts, 2.80 and 2.80Å respectively.

The comparable values in V are 2.81 and 2.79Å respectively. Also the co-planarity of the S-N-C(9)-O(2) moiety, with a torsion angle of -1.0(5)° is experimentally identical to the value of -0.5(2)° observed in V. In fact the solid-state of conformations of I and V are remarkably similar. They both adopt a more or less extended conformation, with the sulphonium lone-pair in V being replaced by an oxygen atom in I.

The asymmetric disposition of the distorted tetrahedral dimethylsulphoxonium group relative to the C(9)-N bond is illustrated in Figure 3.1.3 by the Newman projection along the N-S bond. This reveals the staggered arrangement of the dimethylsulphoxonium group relative to the imine moiety, which may be attributed to a minimizing of non-bonded interactions.



C(1) - C(9)
Projection

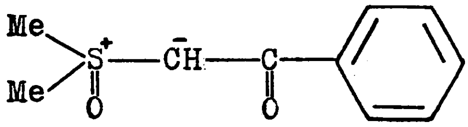
N - S
Projection

Newman projections illustrating
the solid-state conformation of I

Figure 3.1.3

3.2 . THE CRYSTAL AND MOLECULAR STRUCTURE OF PHENACYLIDINEDIMETHYLOXYSULPHURANE

3.2.1. Experimental and results



II

Phenacylidinedimethyloxysulphurane

Preparation of crystals

The title compound was prepared by the method of Corey and Chaykovsky(41).

A suitable crystal for data collection was obtained by allowing a solution of the ylide in a mixture of ether and pentane to evaporate slowly.

Crystal data

Molecular formula	$C_{10}H_{12}O_2S$
Molecular weight	M = 196.3
Crystal system	Orthorhombic
Unit cell dimensions	a = 21.138(2)Å
	b = 5.740(2)Å
	c = 8.200(1)Å
Unit cell volume	$U = 994.9Å^3$
Measured density	$D_m = 1.29$ g cm^{-3}
Number of molecules per unit cell	Z = 4
Calculated density	$D_c = 1.31$ g cm^{-3}
Number of electrons per unit cell	F(000) = 416
Linear absorption coefficient	$\mu(Mo-K_\alpha) = 2.86$ cm^{-1}
Space group	$Pna2_1$ (C^9_{2v}, No. 33)

Data collection

Radiation used	$Mo-K_\alpha$, $\lambda = 0.71069$Å
Filter	Graphite monochromator,
	$\cos^2 2\theta_m = 0.965$
Upper limit for data collection	$2\theta_{max} = 60^\circ$
Number of independent reflections	m = 1080
Unobserved cut-off	$2\sigma_I$
Number of parameters refined	n = 165
Number of reflections per parameter	m/n = 6.5

Structure Determination

Systematic absences in the diffraction data (h0l absent when h odd and 0kl when k + l odd) suggested the possible space groups $Pna2_1$ or Pnma (with an interchange of the axes b and c). A statistical analysis of the data suggested space group $Pna2_1$, a choice which was subsequently vindicated by successful refinement of the model with no anomalous effects.

The crystal structure was resolved by a combination of non-centrosymmetric direct methods(42), using the multisolution program (MULTAN) developed by Germain, Main and Woolfson(43), and conventional structure-factor and electron-density calculations. Those 130 reflections with $|E| > 1.40$ were used in 1500 unique $\sum_2$ relationships. Origin and enantiomorph definition was carried out automatically and a further three reflections were included in the starting set (Table 3.2.2). Of the 32 generated phase sets, the one with the highest combined figure of merit(43) was used to compute an E-map, from which a chemically-sensible 8-atom partial structure was located. The atoms were assigned isotropic thermal parameters equal to the overall thermal parameter ($U = 0.033Å^2$), obtained from a Wilson plot, and were refined by two cycles of isotropic least-squares calculations. A subsequent calculation of the electron-density distribution ($R = 0.25$) revealed sites for all the non-hydrogen atoms.

Structure Refinement

Prior to least-squares refinement all atoms were assigned isotropic thermal parameters ($U_{iso} = 0.03Å^2$). The full-matrix least-squares refinement of positional, thermal and scale parameters (other than the z co-ordinate of the sulphur atom) converged after 15 cycles when R was 0.028 and R' was 0.0012. Full details of the course of refinement are given in Table 3.2.3.

Initially unit weights were applied to all reflections. In later stages weights given by the expression

$$w = (0.1308 - 0.0152|F_o| + 0.0015|F_o|^2)^{-1}$$

were applied. The coefficients of the quadratic expression were obtained from a least-squares fit of $a + b|F_o| + c|F_o|^2$ to the distribution of $\langle w\Delta^2\rangle$ with $\langle |F_o|\rangle$ obtained from an analysis of $w\Delta^2$ with increasing $|F_o|$. This weighting scheme leads to an approximately constant $\langle w\Delta^2\rangle$ with increasing $|F_o|$ and $\sin\theta$.

A difference synthesis after cycle 4 revealed electron density in positions which were stereochemically acceptable for hydrogen atoms. Hydrogen atoms were introduced at these locations and assigned isotropic thermal parameters of $0.05Å^2$. After cycle 7 a difference synthesis yielded improved co-ordinates for the hydrogen atoms which were then assigned thermal parameters identical to those of the adjoining carbon atom after cycle 4.

The refinement was assumed complete when the parameter-shifts calculated by a cycle of least-squares were insignificant compared to the corresponding estimated standard deviations. A final difference synthesis showed no errors in the model, the highest peak in the residual electron-density map being 0.16e/Å^3.

In all structure-factor calculations the atomic scattering factors for sulphur, oxygen and carbon were computed from numerical Hartree-Fock wave functions(23), whilst the scattering factors for hydrogen were those given by Stewart(24). Observed and final calculated structure factors are listed in Appendix VII.

The final fractional co-ordinates and thermal parameters of all atoms are given in Table 3.2.4. The values of U_{ij} refer to the anisotropic temperature factor expression given in PART I. Bond lengths, valence angles and other relevant intra- and intermolecular data are given in Table 3.2.5 and Table 3.2.6. A general view of the molecule illustrating the thermal ellipsoids(25) and giving the numbering scheme is given in Figure 3.2.1. The molecular packing arrangement viewed down the <u>b</u> axis is given in Figure 3.2.2.

TABLE 3.2.1

STATISTICAL ANALYSIS OF DATA

	THEORETICAL		EXPERIMENTAL
	CENTRIC	ACENTRIC	
AVERAGE |E|	0.798	0.886	0.912
AVERAGE |E| **2	1.000	1.000	1.000
AVERAGE |E**2-1|	0.968	0.736	0.653
|E| >1.0 (PERCENT)	31.73	36.79	38.95
|E| >1.6 (PERCENT)	10.96	7.73	5.73
|E| >2.0 (PERCENT)	4.55	1.83	1.05

TABLE 3.2.2

A. ORIGIN- AND ENANTIOMORPH-DEFINING REFLECTIONS

H	K	L	PHASE	E
11	2	1	$\pi/4$	1.99
5	1	3	0	1.84
5	2	0	0	1.57

B. VARIABLE REFLECTIONS USED IN STARTING SET

H	K	L	PHASE	E
4	1	0	$0, \pi$	2.35
6	4	3	$\pm\pi/4, \pm3\pi/4$	2.02
5	2	2	$\pm\pi/4, \pm3\pi/4$	1.65

C. CORRECT SOLUTION

H	K	L	PHASE
4	1	0	π
6	4	3	$3\pi/4$
5	2	2	$-3\pi/4$

TABLE 3.2.3

COURSE OF REFINEMENT

CYCLES	PARAMETERS REFINED	FINAL R	FINAL R'
1 - 3	X.Y.U(ISO) FOR S. X,Y,Z,U(ISO) FOR O,C. SCALE FACTOR. FULL MATRIX. UNIT WEIGHTS.	0.087	0.0104
3 - 4	X,Y.UIJ FOR S. X,Y,Z,UIJ FOR O(1),O(2), C(9),C(1). X,Y,Z,U(ISO) FOR C(2)-C(6),C(7), C(8).C(10). SCALE FACTOR. FULL MATRIX. UNIT WEIGHTS.	0.073	0.0085
5 - 6	X,Y,UIJ FOR S. X,Y,Z,UIJ FOR O.C. HYDROGEN ATOMS INCLUDED BUT NOT REFUNED. SCALE FACTOR. FULL MATRIX, UNIT WEIGHTS.	0.049	0.0045
7 - 9	AS ABOVE* BUT WITH WEIGHTING SCHEME APPLIED.	0.032	0.0018
10 - 12	AS ABOVE, AND X,Y,Z FOR H-ATOMS.	0.029	0.0014
13 - 15	AS ABOVE. AND U(ISO) FOR H-ATOMS.	0.028	0.0012

* PRIOR TO CYCLE 7, THE MORE INTENSE REFLECTIONS WERE CORRECTED FOR DEAD-TIME LOSSES INHERENT IN THE ELECTRONIC COUNTER. HOWEVER THE CORRECTIONS FOR FOUR REFLECTIONS (0.1.-1; 3,1.0; 4,0,-1; 4,1.0) WERE NOT SUFFICIENT TO GET GOOD AGREEMENT BETWEEN |F(OBS)| AND |F(CALC)| AND THESE REFLECTIONS WERE THEREFORE DELETED FROM THE DATA SET, THIS STRATEGY YIELDING IMPROVED H-ATOM POSITIONS FROM A SUBSEQUENT DIFFERENCE SYNTHESIS.

TABLE 3.2.4

A. FRACTIONAL CO-ORDINATES(x10^4) OF NON-HYDROGEN ATOMS

ATOM	X/A	Y/B	Z/C
S	4526(1)	8757(1)	3481
C(7)	4853(2)	6495(7)	2289(5)
C(8)	3947(2)	9954(6)	2192(4)
O(1)	5004(1)	10502(4)	3825(3)
C(10)	4200(1)	7687(5)	5186(4)
C(9)	3759(1)	5882(4)	5046(3)
O(2)	3601(1)	5047(3)	3693(3)
C(1)	3474(1)	4900(5)	6571(4)
C(2)	3108(1)	2897(6)	6436(4)
C(3)	2838(2)	1900(6)	7814(5)
C(4)	2928(2)	2878(7)	9328(4)
C(5)	3290(2)	4856(7)	9471(4)
C(6)	3559(1)	5874(6)	8108(3)

B. FRACTIONAL CO-ORDINATES(x10^4) AND THERMAL PARAMETERS(Å^{2}x10^3) OH HYDROGEN ATOMS.

ATOM	X/A	Y/B	Z/C	U(ISO)
H(71)	4518(22)	5335(92)	1973(60)	82(14)
H(72)	5183(24)	5944(89)	2898(72)	94(16)
H(73)	4970(22)	7147(81)	1453(73)	85(14)
H(81)	3616(19)	8951(70)	2091(48)	58(11)
H(82)	3812(19)	11251(76)	2683(62)	69(11)
H(83)	4153(18)	10162(74)	1103(69)	73(12)
H(10)	4337(18)	8229(65)	5994(55)	57(11)
H(2)	3042(18)	2128(65)	5347(51)	61(10)
H(3)	2561(21)	0700(80)	7609(65)	76(12)
H(4)	2758(18)	2405(66)	10231(56)	61(10)
H(5)	3347(17)	5477(70)	10449(56)	62(11)
H(6)	3798(17)	7311(66)	8210(54)	66(10)

TABLE 3.2.4(CONT'D)

C. ANISOTROPIC THERMAL PARAMETERS($\mathring{A}^2 \times 10^4$) OF NON-H ATOMS

ATOM	U11	U22	U33	U12	U13	U23
S	460(3)	406(3)	361(2)	-64(3)	5(3)	9(3)
C(7)	637(20)	573(20)	569(18)	109(17)	173(16)	56(16)
C(8)	649(17)	453(16)	452(15)	52(15)	-43(14)	-12(13)
O(1)	688(12)	699(14)	514(15)	-322(11)	-17(10)	43(10)
C(10)	526(14)	486(15)	320(10)	-103(11)	-23(11)	-12(12)
C(9)	372(11)	367(11)	371(11)	13(9)	-3(9)	-22(10)
O(2)	564(10)	451(9)	378(11)	-56(8)	-7(8)	-56(8)
C(1)	349(11)	378(12)	407(11)	20(10)	0(9)	-11(11)
C(2)	532(15)	488(15)	467(15)	-111(12)	33(13)	-35(13)
C(3)	569(17)	552(17)	613(18)	-161(17)	75(15)	41(17)
C(4)	570(18)	693(22)	463(17)	-86(16)	106(14)	74(16)
C(5)	682(19)	773(23)	386(15)	-157(18)	54(14)	-70(16)
C(6)	531(14)	548(15)	420(15)	-122(13)	49(10)	-62(11)

TABLE 3.2.5

INTERATOMIC DISTANCES(Å) AND ANGLES(°) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

A. BONDED DISTANCES

S -C(8)	1.757(4)	S -C(7)	1.766(4)	S -O(1)	1.451(3)
S -C(10)	1.675(3)	C(9)-C(10)	1.398(4)	C(9)-C(1)	1.499(4)
C(1)-C(2)	1.390(4)	C(2)-C(3)	1.389(5)	C(3)-C(4)	1.376(6)
C(4)-C(5)	1.375(6)	C(5)-C(6)	1.384(5)	C(6)-C(1)	1.391(4)
C(9)-O(2)	1.254(3)				
MEAN C-H(METHYL)	0.92(5)				
MEAN C-H(ARYL)	0.93(4)				

B. INTERBOND ANGLES

C(7)-S -C(8)	103.2(2)	C(9)-C(1)-C(2)	118.0(3)
C(7)-S -O(1)	110.0(2)	C(9)-C(1)-C(6)	123.6(2)
C(7)-S -C(10)	110.7(2)	C(2)-C(1)-C(6)	118.5(3)
C(8)-S -O(1)	109.4(1)	C(1)-C(2)-C(3)	120.3(3)
C(8)-S -C(10)	111.1(2)	C(2)-C(3)-C(4)	120.6(3)
O(1)-S -C(10)	112.2(1)	C(3)-C(4)-C(5)	119.4(3)
O(2)-C(9)-C(10)	122.3(2)	C(4)-C(5)-C(6)	120.6(3)
C(1)-C(9)-C(10)	118.6(2)	C(5)-C(6)-C(1)	120.6(3)
S -C(10)-C(9)	118.6(2)	O(2)-C(9)-C(1)	119.1(2)

C. INTRAMOLECULAR NON-BONDED DISTANCES

O(2)...S	2.90	C(9)...O(1)	3.87	O(2)...O(1)	4.32
C(9)...C(7)	3.25	O(2)...C(8)	3.16	C(9)...C(8)	3.33
O(2)...C(7)	3.00	C(6)...C(10)	2.94	O(2)...C(2)	2.77
C(2)...C(10)	3.73	O(2)...C(6)	3.65		

TABLE 3.2.5(CONT'D)

D. INTERMOLECULAR DISTANCES <4.0A

O(1)...C(7^{I})	3.68	C(8)...O(2^{I})	3.25	C(10)...C(2^{I})	3.92
O(1)...O(2^{I})	3.95	C(6)...C(3^{I})	3.79	C(8)...C(4^{II})	3.60
C(8)...C(5^{II})	3.85	C(5)...O(2^{III})	3.53	C(5)...C(8^{III})	3.93
O(1)...S^{IV}	3.97	C(10)...O(1^{IV})	3.58	O(1)...C(8^{IV})	3.55
C(6)...O(1^{IV})	3.73	O(1)...C(7^{IV})	3.34	C(10)...C(7^{V})	3.57
C(6)...C(7^{V})	3.68	C(9)...C(7^{V})	3.72	C(1)...C(7^{V})	3.67
C(5)...C(2^{VI})	3.79	C(5)...C(3^{VI})	3.82	O(2)...C(4^{VII})	3.65
C(9)...C(3^{VII})	3.88	C(1)...C(4^{VII})	3.88	O(2)...C(3^{VII})	3.30
C(9)...C(4^{VII})	3.79	C(2)...C(4^{VII})	3.99		

ROMAN NUMERALS AS SUPERSCRIPTS REFER TO THE FOLLOWING EQUIVALENT POSITIONS RELATIVE TO THE REFERENCE MOLECULE AT X,Y,Z :

I	X,	1+Y,	Z
II	X,	1+Y,	-1+Z
III	X,	Y,	1+Z
IV	1-X,	2-Y,	1/2+Z
V	1-X,	1-Y,	1/2+Z
VI	1/2-X,	1/2+Y,	1/2+Z
VII	1/2-X,	1/2+Y,	1/2-Z

E. SELECTED TORSION ANGLES

C(7)-S -C(10)-C(9)	-52.8(3)	C(10)-C(9)-C(1)-C(2)	-170.9(3)
C(8)-S -C(10)-C(9)	61.2(3)	C(10)-C(9)-C(1)-C(6)	8.6(4)
O(1)-S -C(10)-C(9)	-176.0(2)	O(2) -C(9)-C(1)-C(2)	8.4(4)
O(2)-C(9)-C(10)-S	-0.1(4)		

TABLE 3.2.6

LEAST-SQUARES PLANES

1. PLANE DEFINED BY: C(1),C(2),C(3),C(4),C(5),C(6).

EQUATION: $-0.8177X + 0.5612Y - 0.1280Z = -5.1137$

DISTANCES(Å) OF ATOMS FROM THE PLANE:-

C(1)	-0.001(2)	C(9)	-0.019(2)
C(2)	-0.000(3)	O(2)	0.128(2)
C(3)	0.000(4)	C(10)	-0.214(3)
C(4)	0.001(4)	S	-0.254(1)
C(5)	-0.003(4)	O(1)	-0.555(3)
C(6)	0.003(3)	C(7)	-1.423(4)
		C(8)	1.268(4)

2. PLANE DEFINED BY: C(10),C(9),O(2),C(1).

EQUATION: $0.7412X - 0.6686Y + 0.0606Z = 3.8868$

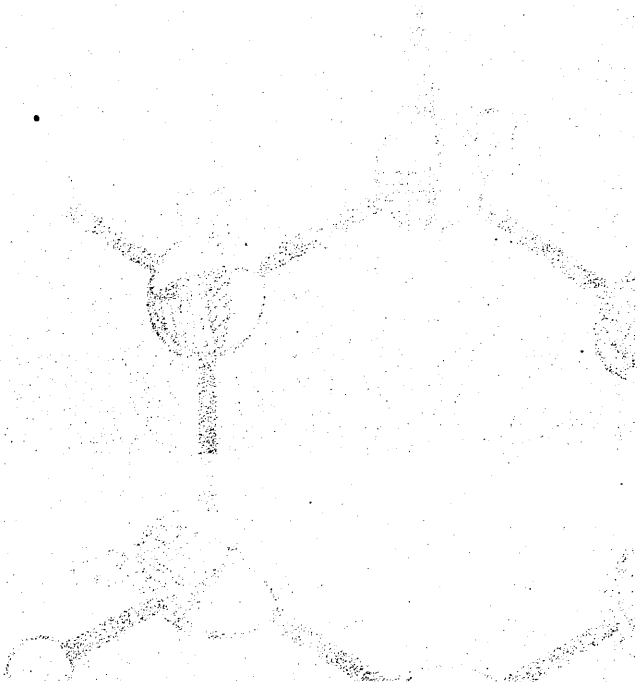
DISTANCES(Å) OF ATOMS FROM THE PLANE:-

C(10)	0.001(3)	S	0.016(1)
C(9)	-0.004(2)	O(1)	0.113(3)
O(2)	0.001(2)	C(7)	1.337(4)
C(1)	0.001(2)	C(8)	-1.415(4)

THE DIHEDRAL ANGLE BETWEEN PLANE 1 AND PLANE 2 IS 171.5 DEGREES

Figure 3.2.1

A general view of II showing the atomic numbering scheme. Hydrogen atoms are numbered as the atoms to which they are bonded.



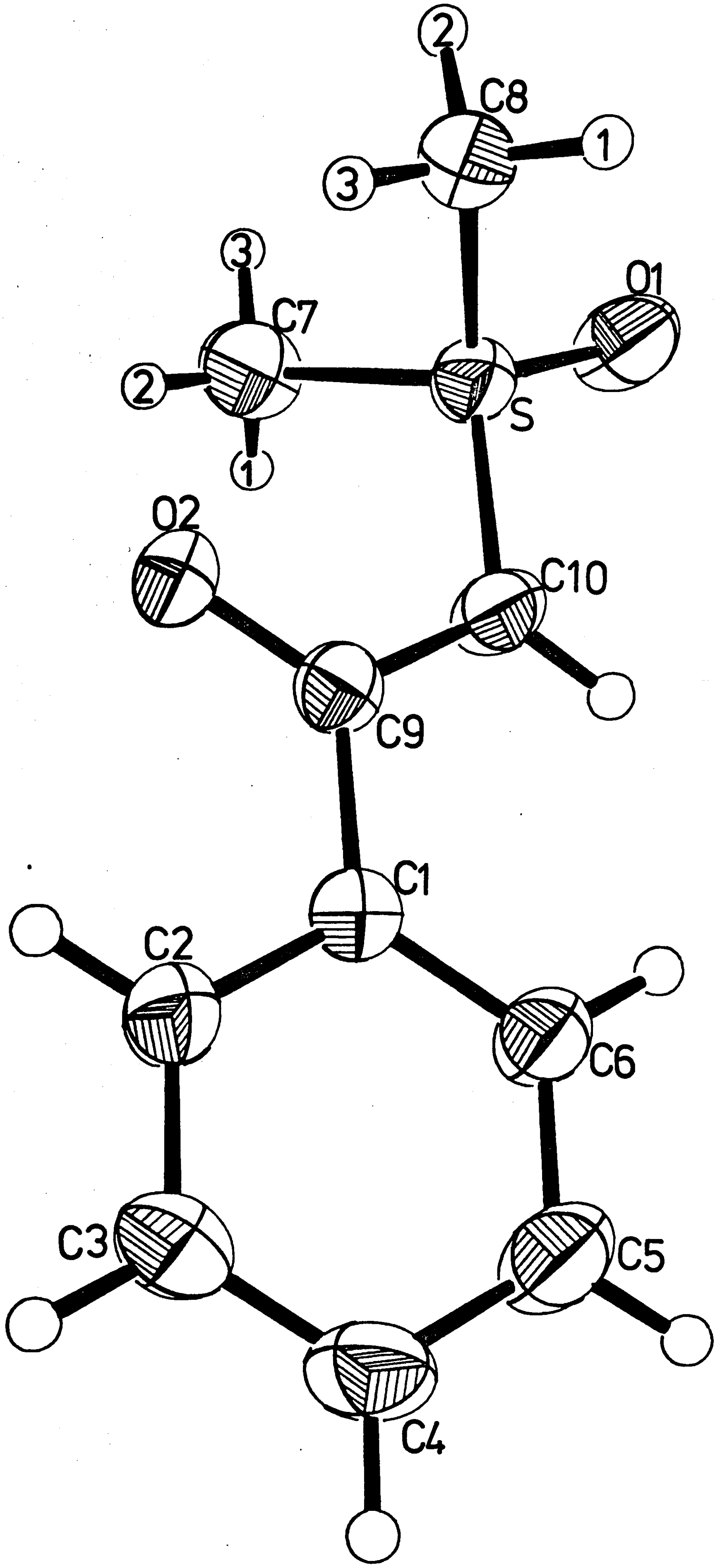
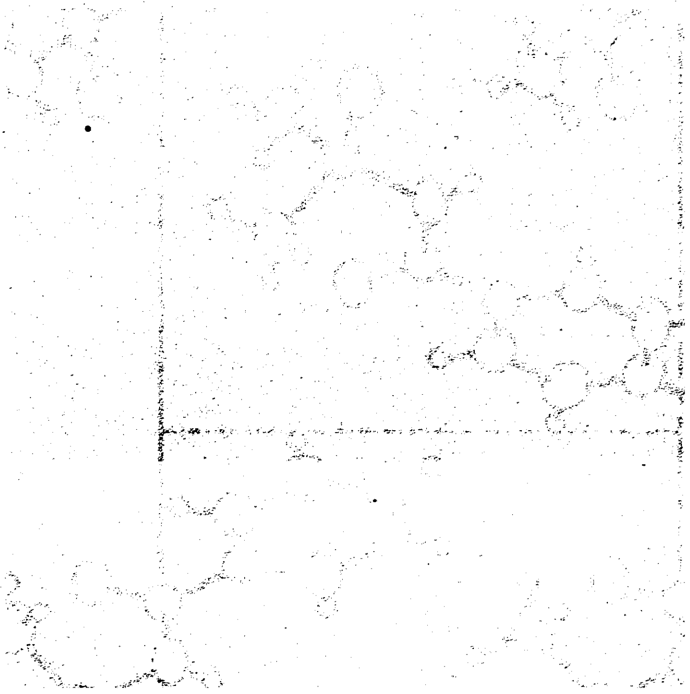
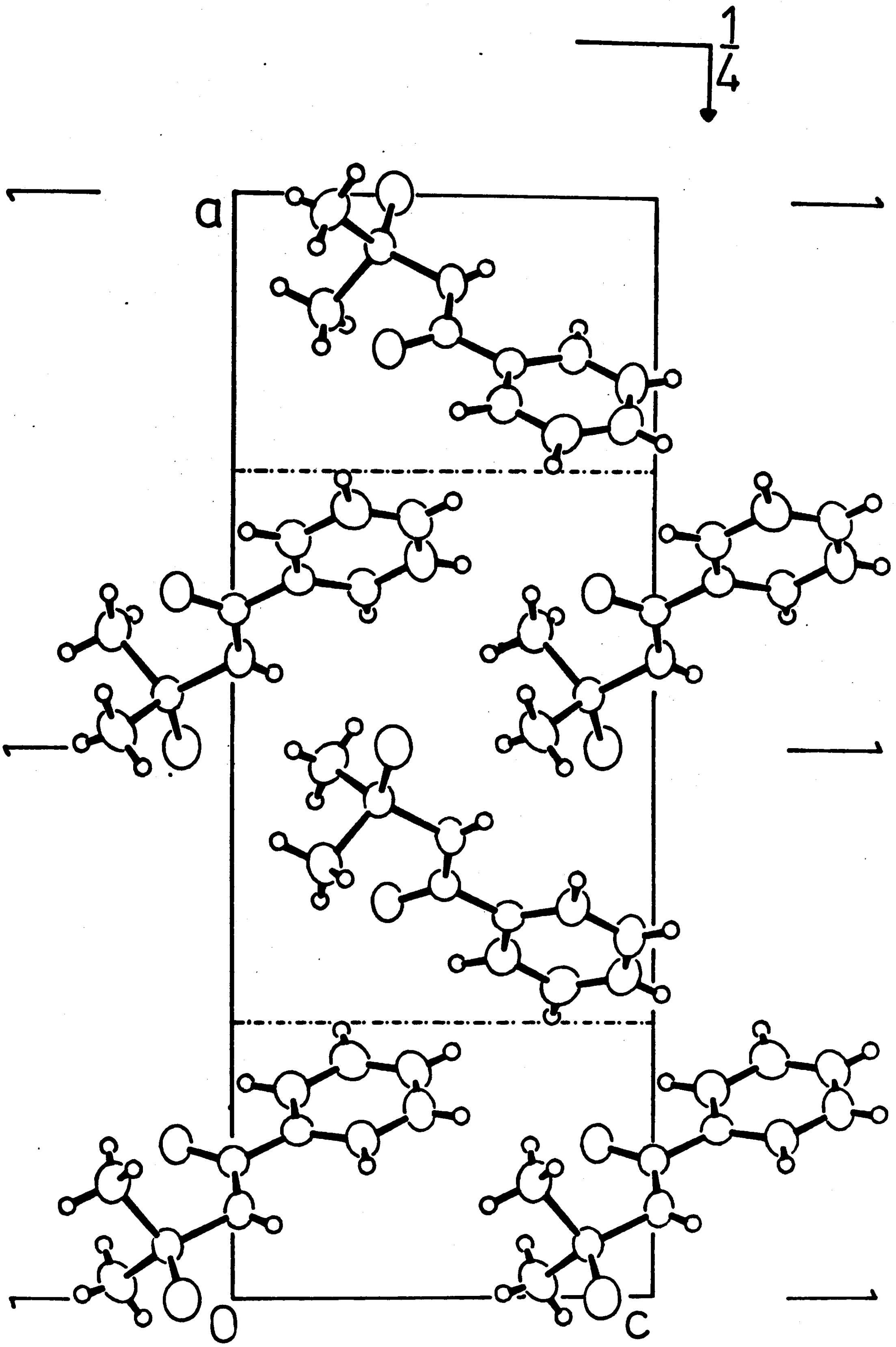

2
C8
1
3
3
C7
O1
2
S
1
O2
C10
C9
C1
C2
C6
C3
C5
C4

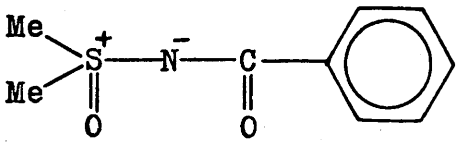
Figure 3.2.2

The molecular packing of II viewed along the b axis.

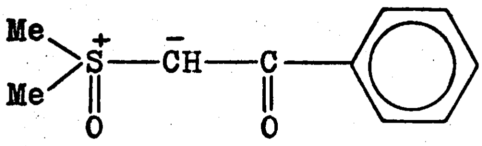




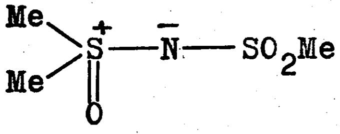
1/4
a
0
c



I(*)



II(*)



III(*)

(*) indicates this work.

3.2.2 Discussion of II

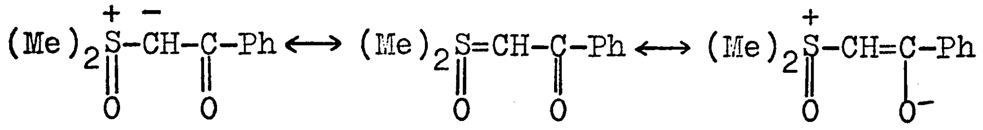
Compound II is formally iso-electronic to I, and so their molecular structures were expected to be very similar. It is thus of interest to compare and contrast the results obtained in the structure analysis of II with those of I.

As in I, and other sulphonium ylides(18,19), charge delocalization from the carbanionic moiety to the 'onium group is indicated by shortness of the S-C(10) bond, 1.675(3)Å, which is comparable to, and probably shorter than, the C-S bond in thioacetamide(44), 1.713(6)Å. The difference in oxidation state increases the validity of the comparison, since the covalent radius of a sulphur (II) atom is considered to be shorter, than that of a sulphur (VI) atom, by 0.05Å(28). However, the difference of 0.114Å, between the S-C(10) bond length in II and the corresponding S-N bond length in I, is larger than the differences of 0.07Å, in the Pauling covalent radii for C(sp^2) and N(sp^2)(27), and of 0.059Å in the C-C and C-N bond lengths in benzene(45) and pyridine(29) respectively. Thus it appears that delocalization of the anionic charge to the 'onium moiety in II is less effective than in I. This observation is strengthened by comparing the carbonyl moieties in II and I. Whilst in I the N-C(O) bond, 1.369(5)Å, is possibly longer than the N-C bond, 1.340(1)Å, in pyridine, in II the C-C(O) bond, 1.398(4)Å, is experimentally identical to that in benzene, 1.399(1)Å(45), 1.394(5)Å(30). Furthermore, the carbonyl C=O bond in I, 1.223(4)Å, is equal to the normal value, 1.215(5)Å(30), whilst in II it is significantly longer (1.254(3)Å).

The above observation is in keeping with the fact that whereas $(Me)_2S(O)NH$ is a stable, isolable solid(32), $(Me)_2S(O)CH_2$ is a characterizable, but non-isolable, compound(41). It does not seem likely that this difference may be accounted for by invoking π'-bonding of the in-plane component of the lone-pairs of electrons on the nitrogen with the 'onium group, since it has been shown that N-alkylation, which effectively removes the in-plane component does not produce any discernible effect on the S^+-N bond(40).

The lower degree of delocalisation in II relative to the delocalisation I may be rationalized in terms of the lower electronegativity of carbon relative to nitrogen. Since the electronegativity difference between S^+ and N^- in I is greater than between S^+ and C^-in II, it follows that a greater inductive withdrawal, via the σ-bond framework, will be present in I. This presents a better opportunity for back-donation(16) of the nitrogen p_z lone-pair of electrons into vacant d-orbitals of the sulphur via a π-overlap relative to that of the carbon in II. Such an effect may plausibly explain the larger relative contraction of the $X^+ - Y^-$ bond in I, and may also account for the greater chemical stability of the free dimethylsulphoximine relative to the iso-electronic methylide.

From the molecular dimensions and the above discussion, it appears that the major contributing canonical forms are



$$(Me)_2\underset{O}{\underset{\|}{\overset{+}{S}}}-\overset{-}{C}H-\underset{O}{\underset{\|}{C}}-Ph \longleftrightarrow (Me)_2\underset{O}{\underset{\|}{S}}=CH-\underset{O}{\underset{\|}{C}}-Ph \longleftrightarrow (Me)_2\underset{O}{\underset{\|}{\overset{+}{S}}}-CH=\underset{O^-}{\underset{|}{C}}-Ph$$

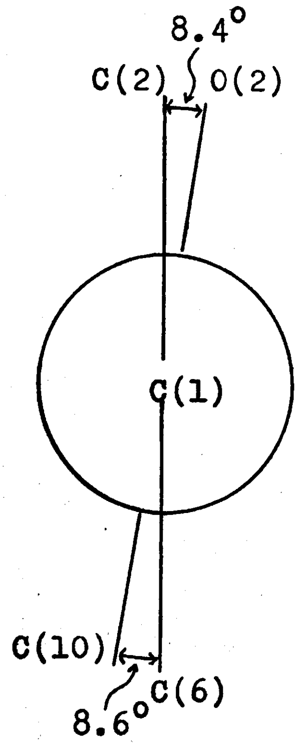
IIa IIb IIc

with IIa and IIc having greater weight relative to similar resonance structures for I. The greater contribution from IIc, relative to the contribution from a similar resonance structure for I, is also reflected in valence angles of the carbonyl moiety (see section 3.1.2). The decrease in π-character of the C-O bond is accompanied by a considerable increase in the C(10)-C(9)-C(1) angle, 118.6(2)^{o}, in II, compared to 113.9(3)^{o}, for the corresponding angle in I. The slight increase in π-character of the C(10)-C(9) bond compared to the N-C(9) bond in I is accompanied by a possibly significant decrease in the angle O(2)-C(9)-C(1), 119.1(2)^{o}, compared to the corresponding value, 120.3(3)^{o} in I. However, the lower electronegativity of carbon, in II, relative to nitrogen may also be a contributing factor. The angle subtended at the anionic carbon, 118.5(2)^{o}, is possibly significantly greater than the corresponding angle, 116.9(2)^{o}, subtended at the nitrogen in I. This may be attributed to the smaller space requirement of the C-H bonded pair of electrons in II, relative to the corresponding lone-pair on the nitrogen in I (compare the increasing H-A-H valence angle in progressing along the series H_2O, NH_3, CH_4). However, it has also been argued (see section 3.1.2) that this angle is also sensitive to steric factors.

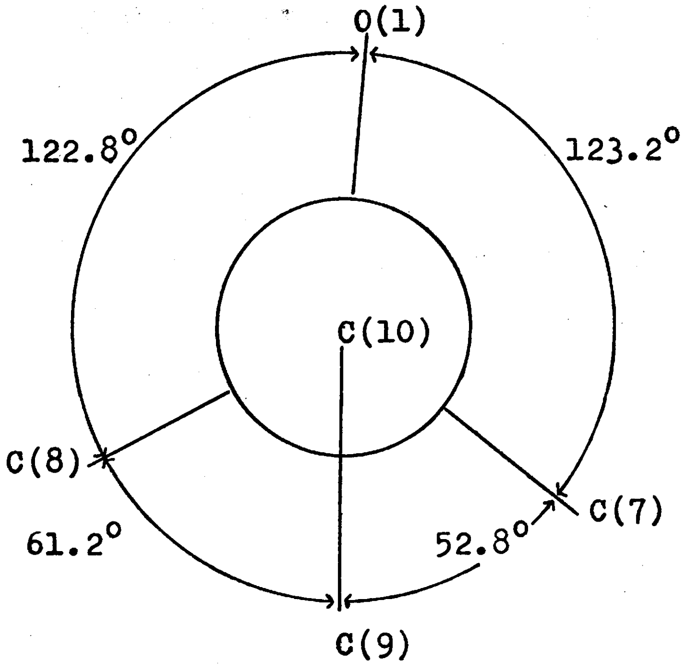
The 'onium moiety in II exhibits distorted tetrahedral geometry which is similar to that observed in I, except that it is rotated through 120° about the C(10)-S bond. This is illustrated in Figure 3.2.3 by the Newman projection along the C(10)-S bond. This reveals the quasi-symmetric disposition of the dimethylsulphoxonium group, which is a marked departure from the conformation observed in I and III and other iminosulphuranes(18,19). The staggered arrangement (disregarding the eclipsed H(10)) may be attributed to a minimizing of non-bonded interactions.

As in the case I there is no evidence that the delocalization into the carbonyl moiety extends to the benzene ring in II, since the C(9)-C(1) bond, 1.499(4)Å, is experimentally identical to the corresponding value, 1.503(5)Å, in I, and is typical of $C(sp^2)-C(sp^2)$ single bond lengths(30), and no anomalous deviations from normal geometry occur in the benzene ring.

Other features of the geometry of II are similar to the corresponding ones in I. There are no abnormally short intermolecular contacts.



C(1) - C(9)
Projection



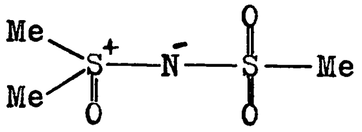
C(10) - S
Projection

Newman projections illustrating
the solid-state conformation of II

Figure 3.2.3

3.3 THE CRYSTAL AND MOLECULAR STRUCTURE OF N-METHANESULPHONYLIMINODIMETHYLOXYSULPHURANE

3.3.1. Experimental and results



III

N-methanesulphonyliminodimethyloxysulphurane

Preparation of crystals

Dimethylsulphoximine was prepared by the method of Johnson and Rogers(32).

The title compound was prepared by shaking dimethylsulphoximine (0.11 mol) with methanesulphonyl chloride (0.05 mol) in freshly distilled chloroform (50 ml) for three hours.. After filtration, the chloroform was removed under vacuum. The resulting oil was washed with diethyl ether, leaving a white powder. Recrystallization from methanol yielded sharp, needle-like crystals [m.p. 124°; anal. Calculated for $C_3H_9O_3NS_2$: C, 21.04; H, 5.30; N, 8.18; S, 37.50. Found : C, 21.13; H, 5.37; N, 8.17; S, 37.62. M^+, 171].

A suitable crystal for data collection was obtained by allowing a hot solution of the ylide in methanol to cool very slowly.

Crystal data

Molecular formula	$C_3H_9NO_3S_2$
Molcular weight	M = 171.2
Crystal system	Monoclinic
Unit cell dimensions	a = 7.701(1)Å
	b = 16.561(1)Å
	c = 5.920(3)Å
	β = 103.13(1)°
Unit cell volume	U = 735.3$Å^3$
Measured density	D_m= 1.55 g cm^{-3}
Number of molecules per unit cell	Z = 4
Calculated density	D_c= 1.55 g cm^{-3}
Number of electrons per unit cell	F(000) = 360
Linear absorption coefficient	μ(Mo-K_α) = 6.45 cm^{-1}
Space group	$P2_1/n$
Equivalent positions	X, Y, Z
	$\frac{1}{2}$ + X, $\frac{1}{2}$ - Y, $\frac{1}{2}$ + Z
	-X, -Y, -Z
	$\frac{1}{2}$ - X, $\frac{1}{2}$ + Y, $\frac{1}{2}$ - Z

Data collection

Radiation used	Mo-K_α, λ= 0.71069Å
Filter	Graphite monochromator,
	$\cos^2 2\theta$ = 0.965
Upper limit for data collection	$2\theta_{max}$ = 54°
Number of independent reflections	m = 1433
Unobserved cut-off	$2\sigma_I$
Number of parameters refined	n = 82
Number of reflections per parameter	m/n = 17.5

Structure Determination

The space group is uniquely determined by its systematic absences ($h0l$ when $h + l$ is odd and $0k0$ when k is odd).

The structure was resolved by an evaluation of the Patterson function and subsequent structure-factor and electron-density calculations. The co-ordinates of both sulphur atoms were obtained from the Harker sections in a sharpened, origin-removed, vector map. The sulphur atoms were assigned isotropic thermal parameters equal to the overall thermal parameter ($U = 0.03\,\text{Å}^2$), and were used to phase the observed structure-factor moduli in a calculation of the electron-density distribution ($R = 0.42$) which revealed sites for all non-hydrogen atoms.

Structure Refinement

Prior to least-squares refinement all atoms were assigned isotropic thermal parameters ($U_{iso} = 0.038\,\text{Å}^2$). The full-matrix least-squares refinement of positional, thermal and scale parameters converged after 10 cycles when R was 0.034 and R' was 0.0029. Full details of the course of refinement are given in Table 3.3.1. Initially unit weights were applied to all reflections. In later stages weights given by the expression

$$w = \left[1 + \left(\overline{|F_o| - A}\,/B\right)^2\right]^{-1}$$

were applied. The values of the constants A and B were

$v\langle w\Delta^2\rangle$ with increasing $|F_o|$ lead to an approximately constant $\langle w\Delta^2\rangle$ with increasing $|F_o|$. The final values were A = 4.0 and B = 8.0.

A difference synthesis after cycle 3 revealed residual electron-density peaks in positions which were stereochemically acceptable for hydrogen atoms. Hydrogen atoms were introduced at these sites and assigned isotropic thermal parameters of 0.076Å^2. After cycle 7 a difference synthesis yielded improved co-ordinates for the hydrogen atoms which were then assigned thermal parameters equal to those of the adjoining carbon atom after cycle 5. The hydrogen-atom parameters would not refine in a satisfactory manner and so were included as fixed contributors to the structure factors.

The refinement was assumed complete when the parameter-shifts calculated by a cycle of least-squares were insignificant compared to the corresponding estimated standard deviations. A final difference synthesis showed no errors in the model, the highest peak in the residual electron-density distribution being 0.27e/Å^3.

In all structure-factor calculations, the atomic scattering factors were taken from ref.22. Observed and final calculated structure factors are listed in Appendix VIII.

The final fractional co-ordinates and thermal parameters of all atoms are given in Table 3.3.2. The values of U_{ij} refer to the anisotropic temperature factor expression given in PART I. Bond lengths, valence angles and other relevant intra- and intermolecular data are given in Table 3.3.3 and Table 3.3.4.

A general view of the molecule illustrating the thermal ellipsoids(25) and giving the numbering scheme is given in Figure 3.3.1. The molecular packing arrangement viewed down the c axis is given in Figure 3.3.2.

TABLE 3.3.1

COURSE OF REFINEMENT

CYCLES	PARAMETERS REFINED	FINAL R	FINAL R'
1 - 2	X,Y,Z,U(ISO) FOR S,O,N,C. SCALE FACTOR. FULL MATRIX, UNIT WEIGHTS.	0.121	0.0204
3 - 4	AS ABOVE, AND H-ATOM CONTRIBUTIONS INCLUDED BUT NOT REFINED.	0.110	0.0166
5 - 6	X,Y,Z,UIJ FOR S,O,N,C. SCALE FACTOR. FULL MATRIX, UNIT WEIGHTS. H-ATOM CONTRIBUTIONS INCLUDED BUT NOT REFINED	0.067	0.0108
7 - 8*	AS ABOVE, BUT WEIGHTING SCHEME APPLIED.	0.044	0.0042
9 -10	AS ABOVE**, AND CORRECTION FOR THE ANOMALOUS DISPERSION OF S APPLIED.	0.034	0.0029

* NEW CO-ORDINATES FOR H-ATOMS OBTAINED FROM A DIFFERENCE SYNTHESIS AFTER CYCLE 7.

** PRIOR TO CYCLE 9, THE MORE INTENSE REFLECTIONS WERE CORRECTED FOR DEAD-TIME LOSSES INHERENT IN THE ELECTRONIC COUNTER. HOWEVER THE CORRECTIONS APPLIED TO 17 REFLECTIONS WERE INSUFFICIENT TO GIVE GOOD AGREEMENT (THE LOW-VOLTAGE PEAK COUNTS ALSO SUFFERED FROM DEAD-TIME LOSSES) BETWEEN |F(OBS)| AND F|(CALC)| AND SO THESE REFLECTIONS WERE REMOVED FROM THE DATA SET.

TABLE 3.3.2

A. FRACTIONAL CO-ORDINATES($\times 10^4$) OF NON-HYDROGEN ATOMS

ATOM	X/A	Y/B	Z/C
S(1)	4262(1)	3469(1)	7001(1)
S(2)	7288(1)	4389(1)	8396(1)
N	5143(2)	4306(1)	7682(3)
O(1)	4729(3)	2811(1)	8620(3)
O(2)	7676(2)	5227(1)	8165(3)
O(3)	8150(2)	3819(1)	7165(3)
C(1)	4549(4)	3153(2)	4269(4)
C(2)	1993(3)	3705(1)	6579(4)
C(3)	7894(3)	4155(2)	11348(4)

B. FRACTIONAL CO-ORDINATES($\times 10^4$) AND ASSIGNED THERMAL PARAMETERS(Å$^2\times 10^4$) OF H-ATOMS.

ATOM	X/A	Y/B	Z/C	U(ISO)
H(11)	3990	2592	3964	625
H(12)	5773	3075	4351	625
H(13)	3894	3532	3013	625
H(21)	1373	3268	5988	220
H(22)	1589	4019	5265	220
H(23)	1934	3932	8302	220
H(31)	9159	4072	11862	377
H(32)	7468	3572	11667	377
H(33)	7136	4483	12187	377

TABLE 3.3.2(CONT'D)

C. ANISOTROPIC THERMAL PARAMETERS($\AA^2$x10^4) OF NON-H ATOMS

ATOM	U11	U22	U33	U12	U13	U23
S(1)	347(3)	302(3)	321(3)	-26(2)	42(2)	7(2)
S(2)	254(3)	428(3)	368(3)	-22(2)	45(2)	43(2)
N	267(8)	327(8)	435(9)	-2(7)	22(7)	-40(7)
O(1)	679(12)	415(9)	490(10)	-10(8)	24(8)	140(7)
O(2)	457(9)	524(10)	575(10)	-173(8)	2(8)	162(8)
O(3)	385(9)	847(14)	591(11)	106(9)	165(8)	-124(10)
C(1)	643(16)	517(14)	417(12)	-45(12)	145(11)	-121(10)
C(2)	297(10)	516(13)	535(13)	-112(10)	22(9)	-35(11)
C(3)	418(12)	513(13)	395(11)	-38(11)	-19(9)	82(10)

TABLE 3.3.3

INTERATOMIC DISTANCES(Å) AND ANGLES(°) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

A. BONDED DISTANCES

S(1)-C(1)	1.761(3)	S(1)-C(2)	1.752(2)	S(1)-O(1)	1.443(2)
S(2)-C(3)	1.747(2)	S(2)-O(2)	1.433(2)	S(2)-O(3)	1.443(2)
S(1)-N	1.555(2)	S(2)-N	1.616(2)		
MEAN C-H	0.99				

B. INTERBOND ANGLES

C(1)-S(1)-C(2)	105.4(1)	C(3)-S(2)-O(2)	107.2(1)
C(1)-S(1)-O(1)	108.7(1)	C(3)-S(2)-O(3)	108.1(1)
C(1)-S(1)-N	111.4(1)	C(3)-S(2)-N	105.5(1)
C(2)-S(1)-O(1)	110.7(1)	O(2)-S(2)-O(3)	117.2(1)
C(2)-S(1)-N	101.6(1)	O(2)-S(2)-N	106.3(1)
O(1)-S(1)-N	118.2(1)	O(3)-S(2)-N	111.9(1)
S(1)-N -S(2)	120.2(1)		

C. INTRAMOLECULAR NON-BONDED DISTANCES

O(2)...S(1)	3.88	C(3)...S(1)	3.53	C(3)...O(1)	3.42
O(3)...S(1)	3.03	S(2)...S(1)	2.75	O(3)...O(1)	3.39
S(2)...O(1)	3.30	O(3)...C(1)	3.11	S(2)...C(1)	3.50
O(2)...O(1)	>4.00	O(2)...C(1)	>4.00	C(3)...C(1)	>4.00
O(2)...C(2)	>4.00	C(3)...C(2)	>4.00	O(3)...C(2)	>4.00
S(2)...C(2)	>4.00				

TABLE 3.3.3(CONT'D)

D. INTERMOLECULAR DISTANCES <4.0Å

$C(3)...C(2^{I})$	3.96	$O(3)...C(2^{II})$	3.06	$C(3)...O(3^{III})$	3.45
$O(1)...C(1^{III})$	3.43	$C(3)...C(1^{III})$	3.80	$O(2)...O(2^{IV})$	3.82
$O(2)...C(3^{IV})$	3.51	$O(2)...N^{V}$	3.71	$C(2)...C(3^{V})$	3.75
$N\ ...S(2^{V})$	3.94	$C(3)...N^{V}$	3.59	$C(2)...O(2^{V})$	3.54
$N\ ...N^{V}$	3.62	$N\ ...N^{VI}$	3.89	$S(1)...O(2^{VI})$	3.76
$N\ ...O(2^{VI})$	3.73	$C(1)...O(2^{VI})$	3.33	$C(2)...O(2^{VI})$	3.38
$C(3)...O(1^{VII})$	3.68	$O(1)...C(1^{VII})$	3.98	$O(1)...C(2^{VII})$	3.32
$O(3)...C(1^{VII})$	3.57	$O(3)...O(1^{VIII})$	3.78		

ROMAN NUMERALS AS SUPERSCRIPTS REFER TO THE FOLLOWING EQUIVALENT POSITIONS RELATIVE TO THE REFERENCE MOLECULE AT X,Y,Z :

I	1+X,	Y,	1+Z
II	1+X,	Y,	Z
III	X,	Y,	1+Z
IV	2-X,	1-Y,	2-Z
V	1-X,	1-Y,	2-Z
VI	1-X,	1-Y,	1-Z
VII	1/2+X,	1/2-Y,	1/2+Z
VIII	1/2+X,	1/2-Y,	-1/2+Z

E. SELECTED TORSION ANGLES

C(1)-S(1)-N -S(2)	-71.7(2)	C(2)-S(1)-N -S(2)	176.6(1)
O(1)-S(1)-N -S(2)	55.3(2)	S(1)-N -S(2)-O(2)	161.1(1)
S(1)-N -S(2)-O(3)	32.2(2)	S(1)-N -S(2)-C(3)	-85.1(1)

TABLE 3.3.4

LEAST-SQUARES PLANE

PLANE DEFINED BY: S(1),N,S(2).

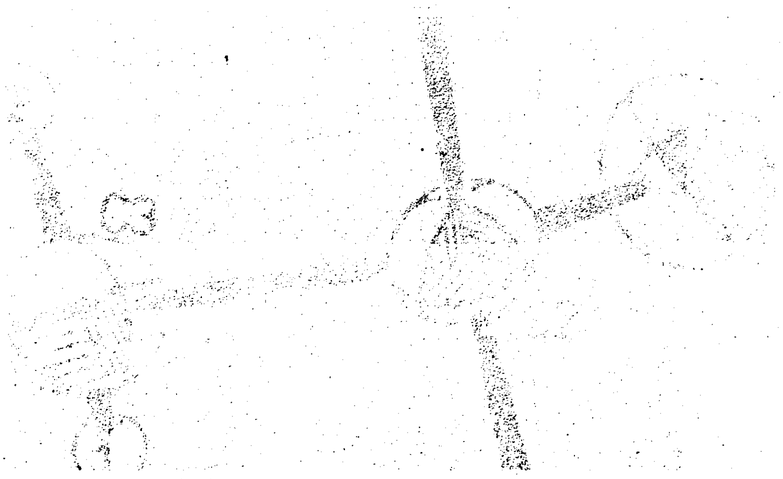
EQUATION: $-0.2376X - 0.1708Y + 0.9562Z = 2.3213$

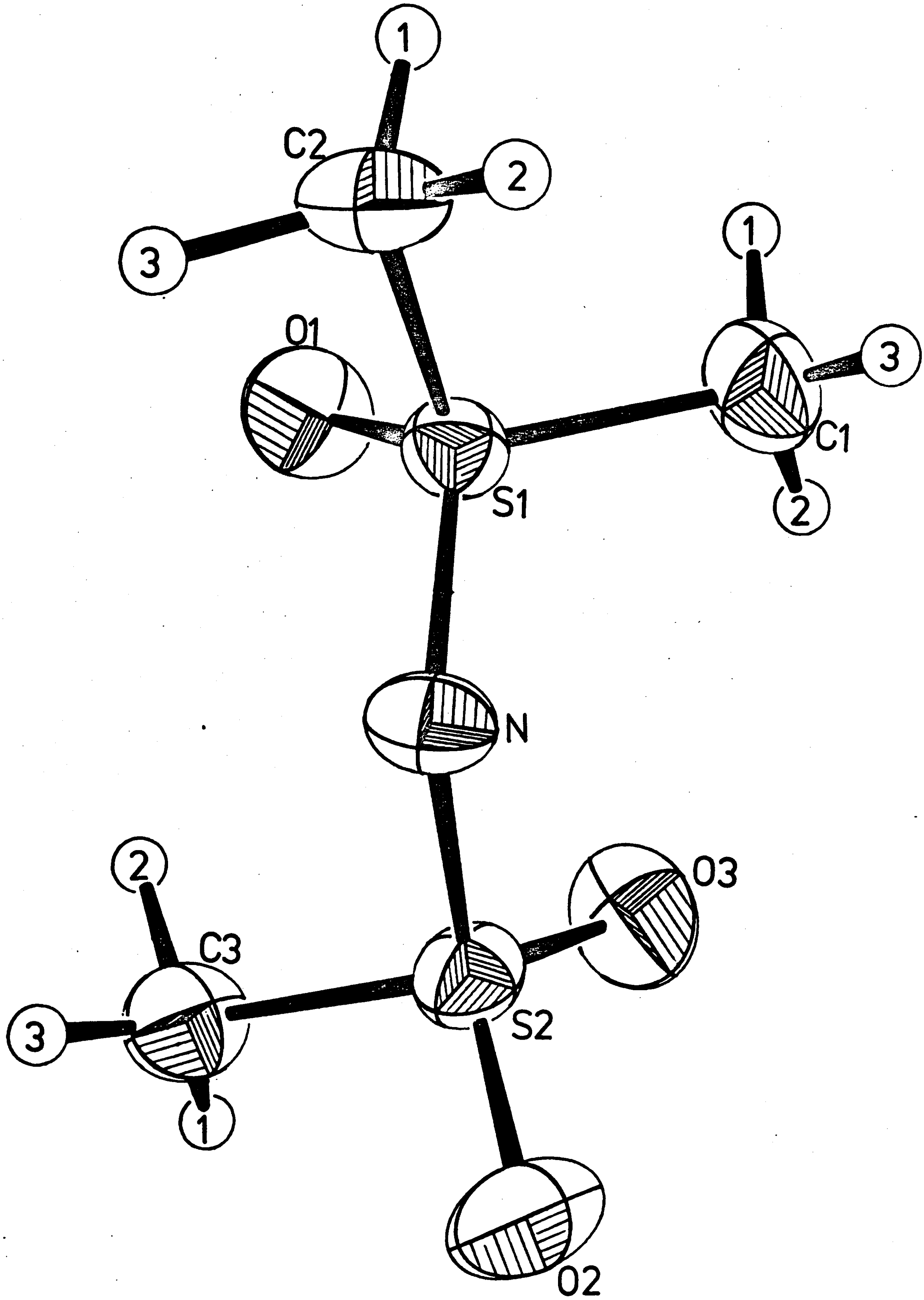
DISTANCES(Å) OF ATOMS FROM THE PLANE:-

O(1)	1.049	C(1)	-1.556
O(2)	-0.444	C(2)	0.101
O(3)	-0.714	C(3)	1.674

Figure 3.3.1

A general view of III showing the atomic numbering scheme. Hydrogen atoms are numbered as the atoms to which they are bonded.




1
C2
2
3
1
O1
3
S1
C1
2
N
2
O3
C3
3
S2
1
O2

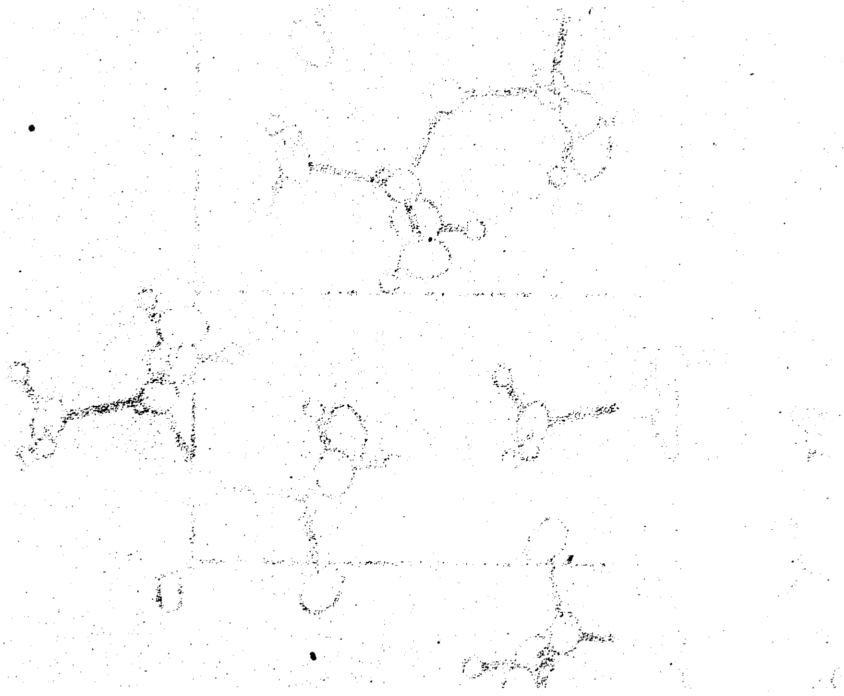
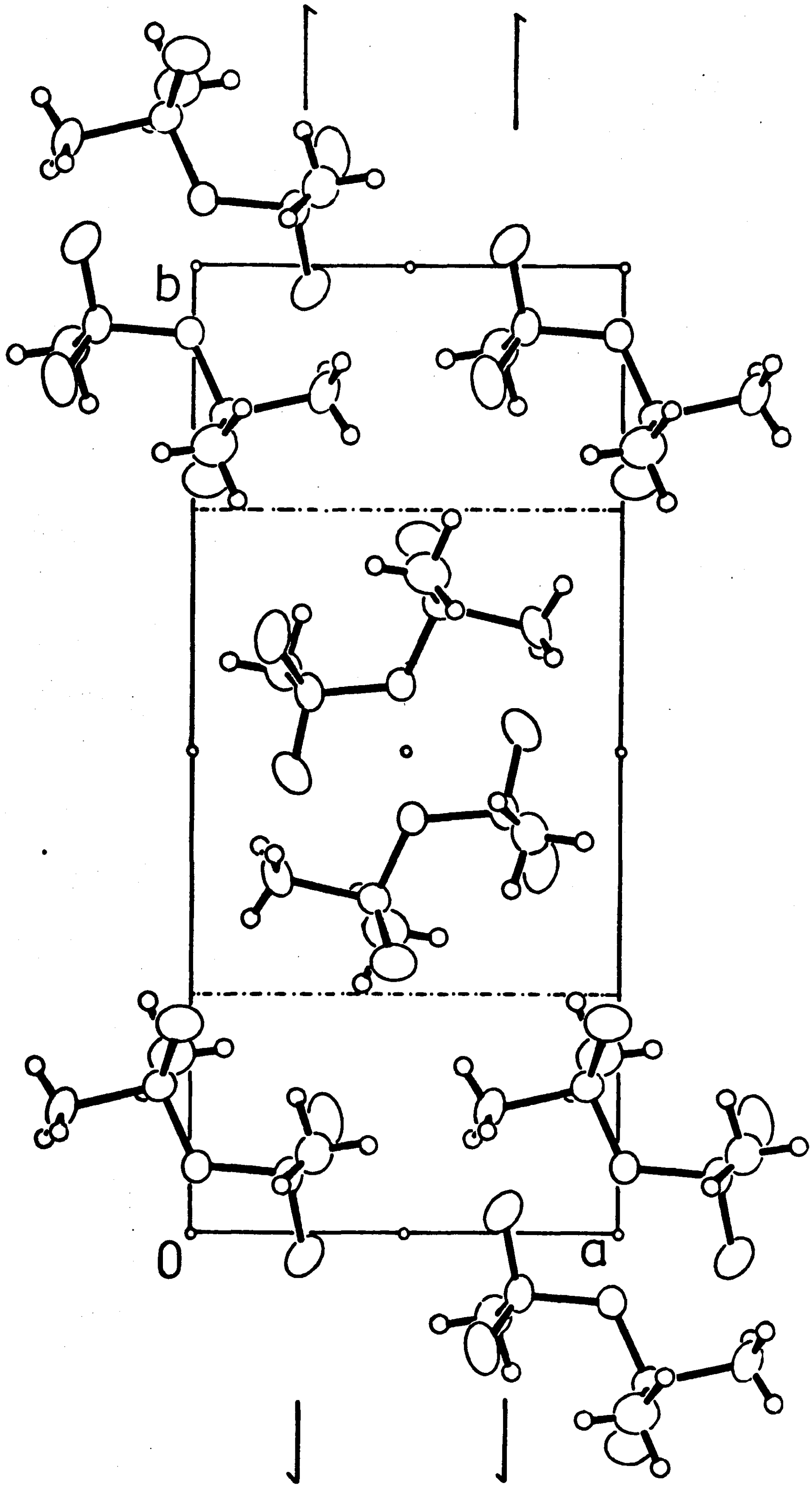
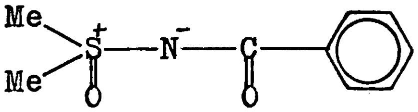


Figure 3.3.2

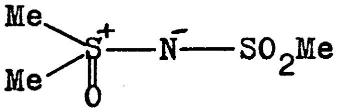
The molecular packing of III viewed along the c axis.



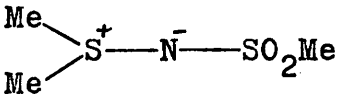
b
0
a



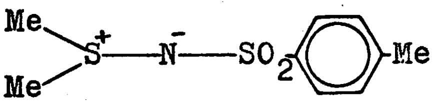
I(*)



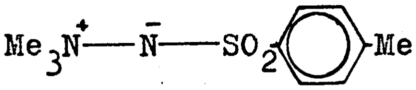
III(*)



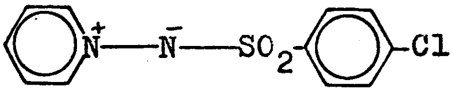
IV(39)



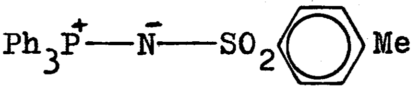
VII(40)



VIII(18)



X(18)



XI(52)

(*) indicates this work.

3.3.2 Discussion of III

The structure analysis of the ylide, III, has provided further evidence supporting the involvement of d-orbitals in the ylidic bond system of second-row ylides. Furthermore, the results obtained allow comparisons to be made with bond systems in similar molecules.

As in the iminosulphuranes(18,19), evidence of charge delocalisation from the negative nitrogen to the 'onium group in III, by $d_{\pi}-p_{\pi}$ interaction, is provided by the shortness of the S(1)-N bond, 1.552(2)Å, relative to the single bond in sulphamic acid, 1.772(1)Å(18), and to the value of 1.74Å from Pauling's covalent radii(27). This S(1)-N length is similar to the corresponding value observed in I, 1.561(3)Å, but is significantly shorter than the value in IV, 1.633(9)Å, and other sulphur (IV) ylides(18,19). Furthermore, the sulphonium-nitrogen bond, S(1)-N 1.552(2)Å, is significantly shorter than the sulphonyl-nitrogen bond, S(2)-N 1.616(2)Å. This is the reverse order to that observed in IV and other sulphonyl-stabilized dialkyl- and diarylsulphilimines (18,19). This suggests that the dimethylsulphoxonium group is more effective in delocalizing the anionic charge than is the dimethylsulphonium group. This is in agreement with the observations made in Section 3.1.2.

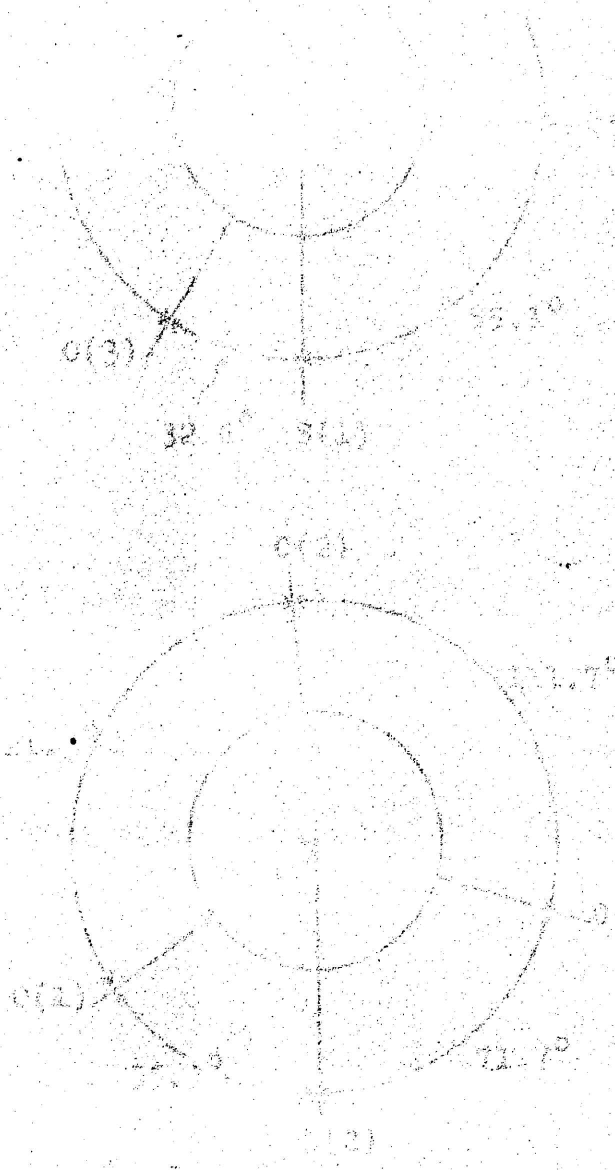
Comparison of the S(1)-N bond, 1.552(2)Å, with the S-N bond lengths in $Me_2S(NH)_2$, 1.533(2)Å(46), 1.536(6)Å(47), and in $Me_2S(O)NH$, 1.521(3)Å$^{(48)}$, indicates considerable lengthening of the 'onium-nitrogen bond in III relative to that in an "unstabilized" sulphur (VI) imine. This suggests a significant degree of delocalization towards the sulphonyl moiety in III. It is of interest that the (interpolated) valence bond-orders$^{(49)}$ of the S(1)-N and S(2)-N bonds in III are 1.6 and 1.4 respectively, possibly indicating that the equivalent of one lone-pair is delocalized over the S-N-S system.

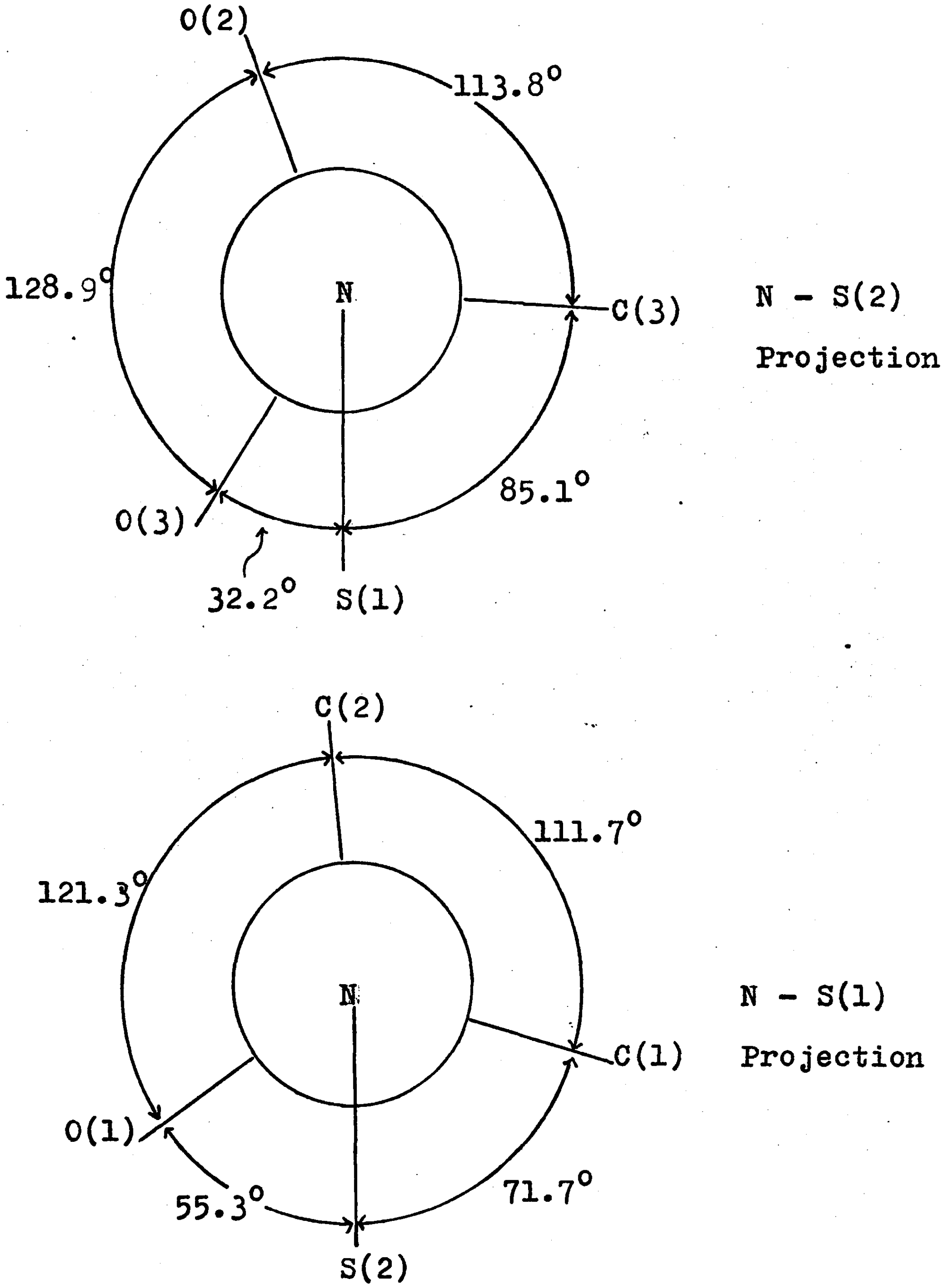
Comparison of the interbond angles in the 'onium group of III with those of the unsubstituted sulphoximine, $Me_2S(O)NH$, provides further indication of delocalization to the sulphonyl group. Thus the O-S-N angle in $Me_2S(O)NH$ of $132.6(9)^{o(48)}$, whilst comparable to the N-S-N angle in $Me_2S(NH)_2$, $135(1)^{o(46)}$, is considerably greater than the corresponding angle, 118.2(1)°, in III. This may be attributed to a lower electron density localised in the O-S(1)-N moiety in III relative to $Me_2S(O)NH$. The decrease in the O-S(1)-N angle in III relative to $Me_2S(O)NH$, presumably due to less interbond repulsion, is accompanied by a redistribution of the other angles subtended at S(1) with values closer to the ideal tetrahedral values (Table 3.3.3).

The geometry about S(2) in III is similar to that observed for other sulphonyl-stabilized ylides$^{(18,19)}$ and the interbond angles are similar to those observed in sulphones. Thus, in III, O(2)-S(2)-O(3), 117.2(1)°, is similar to the O-S-O angle in dimethyl sulphone(50), 117.9(8)°, and in 4,5-dihydrothiepin-1,1-dioxide(51), 116.9(1)°. Furthermore, the sulphonyl S-O bond lengths in III, 1.433(2)Å and 1.443(2)Å, are experimentally identical to the values observed in IV, VII, VIII, X, XI, and the two cited sulphones. Thus there is no evidence that the delocalisation to the sulphonyl group extends beyond the sulphur atom. This is in agreement with the observation that conjugative effects are not relayed onto oxygen atoms attached to sulphur in sulphonyl groups(53).

One other feature of the geometry about S(2) is the marked difference between the angles O(3)-S(2)-N, 111.9(1)°, and O(2)-S(2)-N, 106.3(1)°. This feature is paralleled in IV, VII, VIII, X and XI. Observation of the Newman projection along the N-S(2) bond (Figure 3.3.3) shows that the larger angle is associated with the syn (gauche to S(1)) oxygen, O(3). Furthermore the O(3)...S(1) intramolecular contact, 3.03Å, is shorter than the sum of the van der Waals' radii(54). Observation of the respective Newman projections for the ylides cited above reveals that the larger angle is associated with the syn oxygen (to X^+), which also has a close contact with the 'onium central atom. This suggests that the larger angle may be due to intramolecular steric effects. The shortest intermolecular contact, 3.06Å, involves the O(3)...C(2) interaction and may also be a contributing factor.

Other features of the geometry of III are covered in the overall discussion which follows.





N - S(2) Projection

N - S(1) Projection

Newman projections illustrating the solid-state conformation of III

<u>Figure 3.3.3</u>

3.4 OVERALL ASPECTS OF YLIDE STRUCTURES

3.4 Overall Discussion

Two aspects of ylides are considered here. Firstly, Hair's postulate(19) on the competition of 'onium and stabilizing groups to delocalize the negative charge on the anionic atom is discussed in the light of the more extensive data now available. Secondly, the conformations of ylide structures are discussed in terms of the steric requirements for electron delocalization and the minimization of non-bonding interactions.

In a review of the various structural studies of ylides(19) it was concluded that there is competition, between the 'onium and stabilizing groups, to delocalize the negative charge on the anionic atom. The data that is available is summarized in Tables 3.4.1-4. Table 3.4.1 clearly shows the interdependence of the two partially-multiple-bonds, P^+-C^- and C^--Z, in methylenetriphenylphosphoranes; ie the increase in the P^+-C^- bond-length in going along the series : 1,2,3,4a,4c; parallels the delocalizing ability of the substituents.

This trend is also exhibited by $S^+(IV)-N^-$ ylides (Table 3.4.2;1-6) in which the more effective delocalization to a carbonyl group relative to a sulphonyl group(69) is accompanied by a longer S^+-N^- bond-length. However $S^+(VI)-N^-$ ylides are dissimilar in that the S^+-N^- bond length, although apparently sensitive to the presence of a substituent, shows no variation (within the accuracy of the data) with changes in the nature of the substituent (see Table 3.4.2;7-10). This contrasting behaviour between otherwise analogous compounds appears to correlate with the increased positive charge on the sulphur atom in S(VI)-ylides. This suggestion appears more plausible in the light of the data available for bis-ylides (Table 3.4.2; 11-16) in which the sulphur atom carries two formal positive charges, and in which the $S^{2+}-N^-$ bond lengths are even shorter and show no sensitivity to the presence or nature of the substituents. The trend in S^+-N^- bond lengths parallels the decrease in S-O bond lengths in progressing along the series : Me_2SO(70)(1.513(5)Å), SO(71)(1.481Å), F_2SO(72)(1.412Å), which was attributed(73) to a contraction of d-orbitals resulting from an increase of the effective nuclear charge (Z_{eff}) on the sulphur atom leading to a more efficient orbital-overlap.

It is plausible that the apparent insensitivity to substituents of the S^+-N^- bond length in the quoted S(VI)-ylides and bis-ylides is due to a relatively small difference in perturbing influence of the different substituents. However competition between 'onium and stabilizing groups to delocalize the anionic charge should manifest itself in an interdependence of the π-interactions between the groups and the negatively charged atom separating these groups. Therefore a large enough change in the nature of the 'onium group should influence the bond between the negative atom and a common stabilizing group, and possibly be observable. This interdependence is evident in the following N-sulphonyl systems :

System	Compound	S^+-N^-(Å)	N^--S(Å)
$S^+(IV)-N^--S$	1,2,3,4 (average)	1.630(4)	1.598(3)
$S^+(VI)-N^--S$	9	1.552(2)	1.616(2)
$S^{2+}-N^--S$	16 (mean)	1.523	1.685

The corresponding bond lengths in substituted methylenesulphuranes are in agreement with the above analysis. However the paucity of data and diversity of substituents diminishes the significance of this agreement. (See Table 3.4.3)

An examination of iminophosphoranes (Table 3.4.4) of which only a few examples are available, reveals a trend which is compatible with the above discussion. Competition between the phosphonium and stabilizing groups is clearly shown by the diphenylphosphinyl,3, and dichlorophosphinyl,4, pair of ylides. Chlorine substitution should lead to an increase in the effective nuclear charge on the phosphorus atom and the consequent d-orbital contraction(73) may lead to better orbital-overlap. However the decreased P^+-N^- interaction in ylide 4 is less apparent than the increased N^--phosphinyl interaction and suggests an apparently low sensitivity of the P^+-N^- bond to N-substitution. This case may be analogous to that discussed for sulphur ylides and warrants further study.

Besides the nature of the bonding in the $\rangle X^+-Y^--Z-$ moiety in ylides, the conformation adopted by the molecules is also of interest. A considerable amount of data has been accumulated and trends in the preferential conformations adopted by classes of ylides have been indicated(18,19).

It has been observed(19) that ylides stabilized by groups containing a single p π-orbital system adopted a conformation in which the X^+-Y^--Z(=O) moiety was planar. A recent study(18) broadly confirms this, and any deviations from planarity have been satisfactorily accounted for in terms of intramolecular non-bonded interactions and intramolecular hydrogen-bonding(18). The results reported in sections 3.1.1 and 3.2.1 are in agreement with the above observations. The observed conformations correspond to staggered, extended structures which, presumably, minimize steric interactions and maximize any potential delocalization of the anionic charge <u>via</u> p_π-p_π orbital overlap.

The solid state conformation of sulphonyl stabilized ylides has also evoked considerable interest, and on the basis of studies on five such ylides it was suggested(19) that in ylides stabilized by a multiple π-orbital system based on d-orbitals an X^+-Y^--Z(=O) moiety adopted a planar conformation if the anionic atom, Y, possessed one lone-pair of electrons and a conformation deviating from cis-coplanarity by 30° to 40° if Y carried two lone-pairs of electrons. However, in the light of further studies, it became apparent that this classification does not extend to ylides with other d-orbital-based stabilizing groups, and that it is not general for sulphonyl stabilized ylides(18).

A summary of the data is given in Table 3.4.5 and a representative Newman projection down the Y^--S bond is given in Fig 3.4.1. The variability of angle τ_1, given in Table 3.4.5

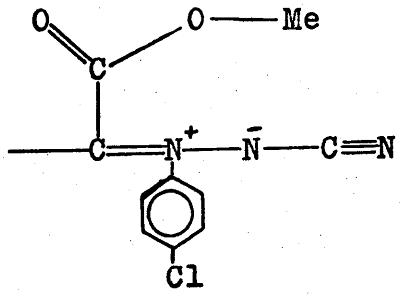
may be attributed to steric interactions, particularly the 'gauche' interactions between the 'onium moiety, X^+, and the alkyl or aryl substituent, A, on the sulphur atom, and possibly intermolecular interactions. The regularity with which such a conformation (or its mirror image) occurs is remarkable. Intuitively, if interactions were purely steric in origin one might expect the 'anti' conformation, Fig 3.4.2 to be adopted (81) particularly when A and X^+ are bulky groups. This is not observed in any of the quoted examples. If one assumes that the lone-pairs of electrons on an anionic nitrogen atom are approximately staggered with respect to the sulphonyl group, it is seen, in the Newman projection Fig 3.4.1, that the out-of-plane component (p_z-orbital type) of the lone-pairs is oriented approximately along the plane that bisects the O-S-O angle. This fits in with the 'gauche effect' ie the tendency of a molecule to adopt a conformation which has a maximum number of 'gauche' interactions between the adjacent electron pairs and/or polar bonds(82).

This preferentially adopted conformation of the sulphonyl-anion moiety is not restricted to imine-ylides. It is also adopted by the carbanionic ylides(57), N-Alkyl-N-sulphonyl-imines(38,80), α-sulphonyl carbanions(83), α-sulphinyl carbanions(84), benzene sulphonates(85) and sulphinates(86). It has been suggested that this conformation is adopted because it provides the opportunity for delocalization of the anion electrons into the (partially) vacant sulphur orbitals and follows from a rationale based on an sp^3d^2 model for the sulphur atom(87). However extensive ab initio MO calculations on the hypothetical models, $C^-H_2S(O)H$(88) and $C^-H_2S(O)_2H$(89), indicate that the most stable structure for the anions fits the context of the 'gauche effect' as a result of a balance of the attractive and repulsive terms which constitute the total energy of the system(90) without any significant contribution of the sulphur d-orbitals(82). However, in view of the wealth of chemical and physical data available, d-orbital participation seems justified, and these calculations simply show that the conformation adopted by a d_π-p_π system is insensitive to d-orbital participation. This is not surprising since in such a d_π-p_π system, ie X^+-Y^--SO_2R, the tetrahedral sulphur has (at least) two d-orbitals available for π-bonding and any torsion about the Y^--S bond, dictated by steric or electro-static factors, simply causes the $p\pi$-orbital of Y^- to be matched with a different d-orbital combination(73).

Table 3.4.1

Delocalization in $P^+ - C^- - Z$ systems

Compound	Ref.	$P^+ - C^-$ (Å)	$C^- - Z$ (Å)
1. $Ph_3\overset{+}{P}-\overset{-}{C}H_2$	55	1.661(8)	-
2. $Ph_3\overset{+}{P}-\overset{-}{C}H-CH=C(Me)_2$	56	1.677(3)	1.433(5)
3. $Ph_3\overset{+}{P}-\overset{-}{C}H-SO_2$-tol.	57	1.709(19)	1.686(19)
4. $Ph_3\overset{+}{P}-\overset{-}{C}R-CO_2Me$			
a. R = $-CH_2-CO_2H$	58	1.732(4)	1.392(6)
b. R = $-CH_2-CO_2Bu^t$	58	1.715(5)	1.415(7)
c. R = I	59	1.753(5)	1.441(8)
5. $Ph_3\overset{+}{P}-\overset{-}{C}(Cl)-CO-Ph$	60	1.736(14)	1.361(20)



I

Table 3.4.2

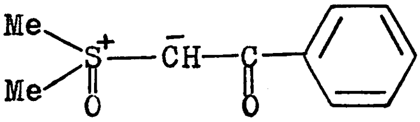
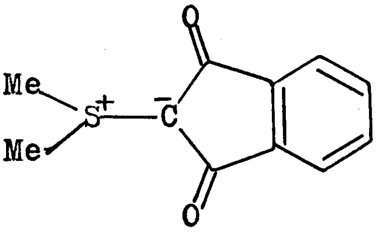
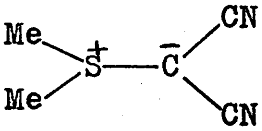
Delocalization in $S^{+}-N^{-}-Z$ systems

	Compound	Ref.	$S^{+}-N^{-}$ (Å)	$N^{-}-Z$ (Å)
1.	$Ph_2S^{+}-N^{-}-SO_2$-tol.	61	1.628(7)	1.598(5)
2.	$Me_2S^{+}-N^{-}-SO_2$-tol.	40	1.636(8)	1.591(8)
3.	$Ph.nPr.S^{+}-N^{-}-SO_2$-tol.	62	1.620(7)	1.618(7)
4.	$Me_2S^{+}-N^{-}-SO_2Me$	39	1.633(9)	1.581(10)
5.	$Me_2S^{+}-N^{-}-CO-Ph$	18	1.659(2)	1.344(3)
6.	$Me_2S^{+}-N^{-}-CO-CCl_3$	26	1.667(7)	1.320(10)
7.	$Me_2S^{+}(O)-\overline{N}H$	48	1.521(3)	-
8.	$(C_7H_7)_2\overset{+}{S}(O)-\overline{N}$-Phth. Phth = Phthalimido	63	1.561(6)	1.426(7)
9.	$Me_2\overset{+}{S}(O)-\overline{N}-SO_2Me$	*	1.552(2)	1.616(2)
10.	$Me_2\overset{+}{S}(O)-\overline{N}-CO-Ph$	*	1.561(3)	1.369(5)
11.	$Me_2\overset{2+}{S}(-\overline{N}H)$	47	1.536(6)	-
		46	1.533(2)	-
12.	$\overset{2+}{S}(-\overline{N}-Me)_2$	66	1.53(1)	-
13.	$\overset{2+}{S}(-\overline{N}-Ph)_2$	67	1.54	-
14.	$\overset{2+}{S}(-\overline{N}$-tol.$)_2$	64	$1.54^{\overset{*}{*}}$	-
15.	$\overset{2+}{S}(-\overline{N}-S-Ph)_2$	68	1.529(5)	1.659(5)
16.	$\overset{2+}{S}(-\overline{N}-SO_2$-tol.$)_2$	65	$1.523^{\overset{*}{*}}$	$1.685^{\overset{*}{*}}$

* indicates this work $\overset{*}{*}$ indicates mean value

Table 3.4.3

Delocalization in S^+- C^-- Z systems

Compound	Ref.	S^+- C^-(Å)	C^-- Z (Å)
1. 	*	1.675(3)	1.398(4)
2. 	74	1.707(4)	1.437(5) 1.420(5)
3. 	75	1.730(8)	1.388(15) 1.403(14)

(*) indicates this work.

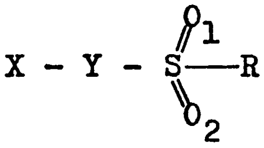
Table 3.4.4

Delocalization in $P^+ - N^- - Z$ systems

Compound	Ref.	$P^+ - N^-$ (Å)	$N^- - Z$ (Å)
1. $Ph_3\overset{+}{P}-\overset{-}{N}-\overset{+}{P}Ph_3$	76	1.56(2)	-
		1.59(2)	-
2. $Ph_3\overset{+}{P}-\overset{-}{N}-C_6H_4.Br$	77	1.567(6)	1.417(11)
3. $Ph_3\overset{+}{P}-\overset{-}{N}-P(O)Ph_2$	38	1.557(2)	1.604(2)
4. $Ph_3\overset{+}{P}-\overset{-}{N}-P(O)Cl_2$	38	1.582(2)	1.558(2)
5. $Ph_3\overset{+}{P}-\overset{-}{N}-SO_2$-tol.	52	1.579(4)	1.586(4)

Table 3.4.5

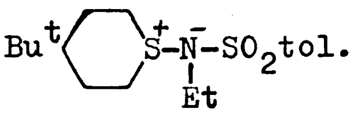
Conformations of some sulphonyl-stabilized ylides and related compounds.

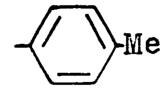


Torsion angles(^{o})

$\tau_1 = X - Y - S - O_1$

$\tau_2 = X - Y - S - O_2$

	Compound	Ref.	τ_1	τ_2
1.	$Me_3\overset{+}{N}-\overset{-}{N}-SO_2tol.$	18	-40.7	-168.6
2.	$Ph_3\overset{+}{P}-\overset{-}{N}-SO_2tol.$	52	37.6	167.7
3.	$Me_2\overset{+}{S}-\overset{-}{N}-SO_2tol.$	40	36.8	167.2
4.	$Ph_2\overset{+}{S}-\overset{-}{N}-SO_2tol.$	61	34.9	163.9
5.	$Me_2\overset{+}{S}-\overset{-}{N}-SO_2tol.$	39	31.7	160.5
6.	$Me_2\overset{+}{S}(O)-\overset{-}{N}-SO_2Me$	*	32.2	161.3
7.	$Ph.nPr.\overset{+}{S}-\overset{-}{N}-SO_2tol.$	62	35.3	163.7
8.	$Pyridinium\overset{+}{}-\overset{-}{N}-SO_2tol.$	18	54.4	-176.8
9.	$Penicillinium\overset{+}{}-\overset{-}{N}-SO_2tol.$	38	-5.3	126.3
10.	$\overset{-}{N}(-SO_2Ph)_2$	78	29.9	157.9
			-37.0	-165.0
11.	$NH(-SO_2Me)_2$	79	33.1	136.9
			36.7	164.6
12.	$Ph_3\overset{+}{P}-\overset{-}{C}H-SO_2tol.$	57	8.3	-122.8
13.	$Penicilliniu\overset{+}{m}-NR-SO_2tol.$	38	-9.2	-137.3
14.		80	-50.9	180.0

tol ≡ 

(*) indicates this work.

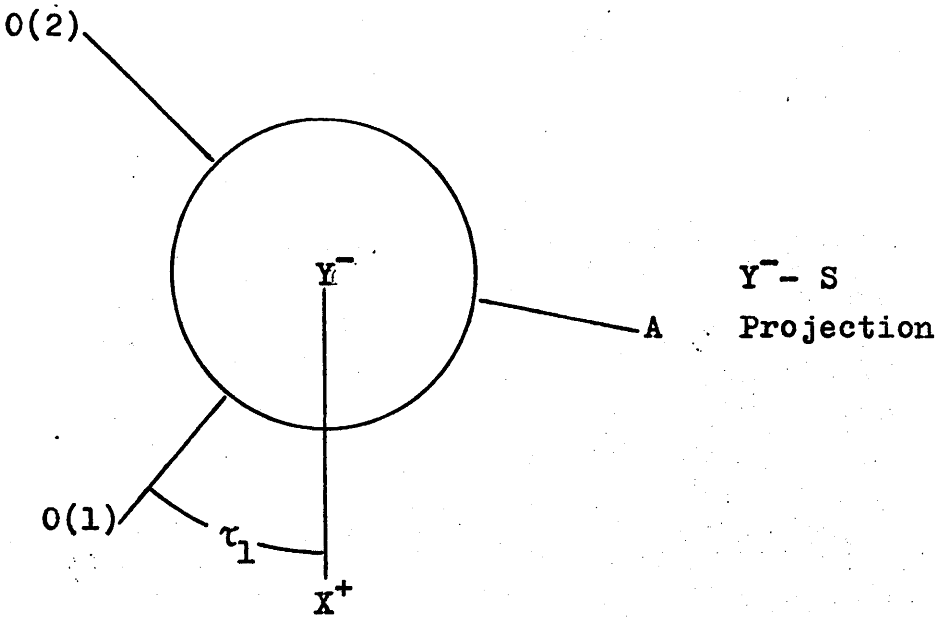


Figure 3.4.1

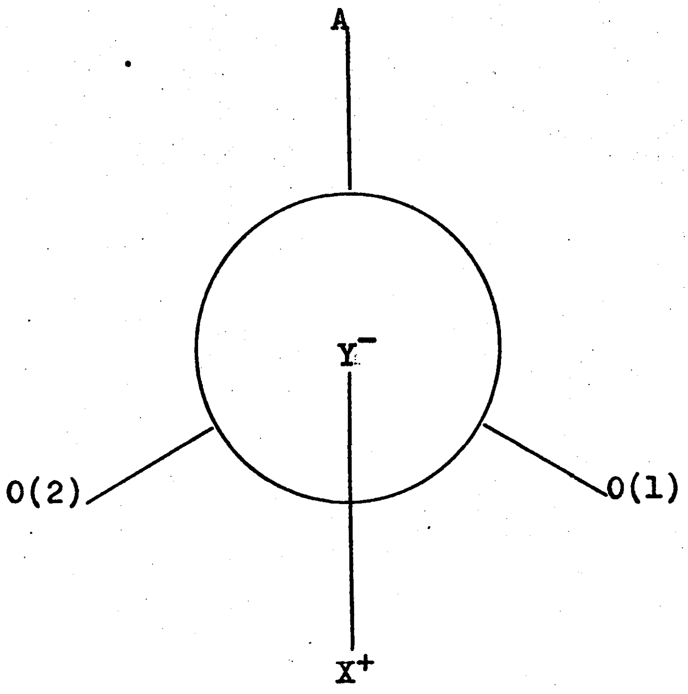


Figure 3.4.2

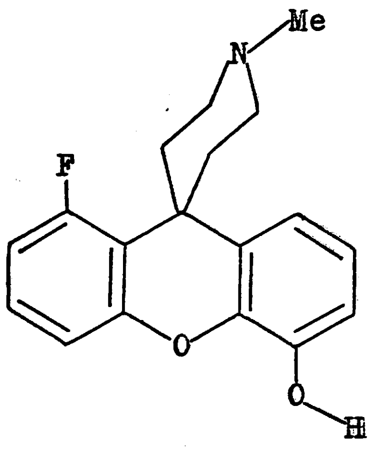
PART IV

THE CRYSTAL AND MOLECULAR STRUCTURES OF TWO RELATED ORGANIC MOLECULES

THE CRYSTAL AND MOLECULAR STRUCTURES OF 4-HYDROXYXANTHENE-9-SPIRO-4'-(N-METHYLPIPERIDINE) AND ITS 8-FLUORO DERIVATIVE

The title compounds are the first in a series of xanthene-9-spiro-4'-piperidine derivatives which it is proposed to study in this laboratory. The purpose of this investigation is to examine the detailed molecular geometries of derivatives with a range of pharmacological activities, and in which the flexibility of the parent system is modified to quasi-rigidity via substitution at certain key centres of the molecules. The additional possibility of correlating molecular geometry with pharmacological activity necessitates the future study of other suitable derivatives which will permit more detailed comparisons to be made. It is therefore not feasible to usefully discuss this aspect at this stage.

4.1 Experimental and results for I



I

8-Fluoro-4-hydroxyxanthene-9-spiro-4'-(N-methylpiperidine)

Crystal data

Molecular formula	$C_{18}H_{18}NO_2F$
Molecular weight	M = 299.3
Crystal system	Monoclinic
Unit cell dimensions	a = 26.179(3)Å
	b = 6.932(4)Å
	c = 17.351(2)Å
	β = 109.15(1)°
Unit cell volume	U = 2974.5$Å^3$
Measured density	D_m= 1.33 g cm^{-3}
Number of molecules per unit cell	Z = 8
Calculated density	D_c= 1.337 g cm^{-3}
Number of electrons per unit cell	F(000) = 1264
Linear absorption coefficient	μ(Mo-K_α) = 1.03 cm^{-1}

Space group	I2/c
Equivalent positions	X, Y, Z
	-X, Y, $\frac{1}{2}$ - Z
	$\frac{1}{2}$ + X, $\frac{1}{2}$ + Y, $\frac{1}{2}$ + Z
	$\frac{1}{2}$ - X, $\frac{1}{2}$ + Y, -Z
	-X, -Y, -Z
	X, -Y, $\frac{1}{2}$ + Z
	$\frac{1}{2}$ - X, $\frac{1}{2}$ - Y, $\frac{1}{2}$ - Z
	$\frac{1}{2}$ + X, $\frac{1}{2}$ - Y, Z

Data collection

Radiation used	Mo-K_α, $\lambda = 0.71069$Å
Filter	Graphite monochromator, $\cos^2 2\theta_m = 0.965$
Upper limit for data collection	$2\theta_{max} = 54^\circ$
Number of independent reflections	m = 1915
Unobserved cut-off	$2\sigma_I$
Number of parameters refined	n = 272
Number of reflections per parameter	m/n = 7.0

Structure Determination

Systematic absences in the diffraction data (hkl when $h+k+l = 2n + 1$ and h0l when $l = 2n+1$) suggested the possible space groups Ic or I2/c. A statistical analysis of the data (Table 4.1) suggested space group I2/c, a choice which was subsequently vindicated by successful refinement of the model, with no anomalous effects.

The phase problem was overcome by centrosymmetric direct phasing methods. Normalized structure factors were calculated and triplet relationships derived for the 382 reflections with $|E| \geqslant 1.20$. With a starting set of two origin-defining reflections, a solution for the 70 strongest reflections was obtained using relationships of probability $\geqslant 0.75$. A total of 318 reflections were then phased from this solution and an E-map, calculated with these reflections only, revealed clear sites for all the non-hydrogen atoms.

Structure Refinement

Prior to least-squares refinement all atoms were assigned isotropic thermal parameters equal to the overall thermal parameter ($U = 0.024\text{Å}^2$) obtained from a Wilson plot. The least-squares refinement of positional, thermal and scale parameters converged after 17 cycles when R was 0.038 and R' was 0.0029. Full details of the course of refinement are given in Table 4.2. Initially unit weights were applied to all reflections. In later stages weights given by the expression

$$w = (2.26 - 0.119|F_o| + 0.0039|F_o|^2)^{-1}$$

were applied. The coefficients of the quadratic expression were obtained from a least-squares fit of $a + b|F_o| + c|F_o|^2$ to the distribution of $\langle w\Delta^2\rangle$ with $\langle|F_o|\rangle$ obtained from an analysis of $w\Delta^2$ with increasing $|F_o|$. This weighting scheme leads to approximately constant $\langle w\Delta^2\rangle$ with increasing $|F_o|$ and $\sin\theta$.

A difference-synthesis after cycle 4 revealed residual electron-density in positions which were stereochemically acceptable for hydrogen atoms. Hydrogen atoms were introduced at these locations and assigned isotropic thermal parameters of 0.05Å^2.

The refinement was assumed complete when the parameter-shifts calculated by a cycle of least-squares were insignificant compared to the corresponding estimated standard deviations A final difference synthesis showed no errors in the model, the highest peak in the residual electron-density distribution being 0.16e/Å^3. In all structure-factor calculations the atomic scattering factors for carbon, oxygen and nitrogen were computed from numerical Hartree-Fock wave functions(1) those for fluorine were taken from ref.2, whilst the scattering factors for hydrogen were those given by Stewart(3). Observed and final calculated structure factors are listed in Appendix IX.

The final fractional co-ordinates and thermal parameters of all atoms are given in Table 4.3. The values of U_{ij} refer to the anisotropic temperature factor expression given in PART I. Bond lengths, valence angles and other relevant intra- and intermolecular data are given, together with the corresponding values for II, in Table 4.6 and Table 4.7. A general view of the molecule illustrating the thermal ellipsoids(4) and giving the numbering scheme is given in Figure 4.1. The molecular packing arrangement viewed along the b axis is given in Figure 4.2.

TABLE 4.1

STATISTICAL ANALYSIS OF DATA

	THEORETICAL		EXPERIMENTAL
	CENTRIC	ACENTRIC	
AVERAGE |E|	0.798	0.886	0.863
AVERAGE |E|**2	1.000	1.000	1.000
AVERAGE |E**2-1|	0.968	0.736	0.817
|E| >1.0 (PERCENT)	31.73	36.79	30.08
|E| >1.8 (PERCENT)	7.19	3.92	5.46
|E| >2.0 (PERCENT)	4.55	1.83	3.17
|E| >2.5 (PERCENT)	1.24	0.19	1.21

TABLE 4.2

COURSE OF REFINEMENT OF I

CYCLES	PARAMETERS REFINED	FINAL R	FINAL R'
1 - 4	X,Y,Z,U(ISO) FOR C,O,N,F. SCALE FACTOR. FULL MATRIX, UNIT WEIGHTS.	0.126	0.017
5 - 10*	X,Y,Z,UIJ FOR C,O,N,F. H-ATOM CONTRIBUTIONS INCLUDED BUT NOT REFINED. SCALE FACTOR. FULL MATRIX, UNIT WEIGHTS.	0.046	0.0027
11 - 12	AS ABOVE,BUT WITH WEIGHTING SCHEME APPLIED.	0.045	0.0041
13 - 14	AS ABOVE, AND X,Y,Z FOR H-ATOMS ALSO REFINED OVERALL THERMAL PARAMETER, BLOCKED MATRIX.	0.039	0.0030
15 - 17	AS ABOVE; U(ISO) FOR H-ATOMS ALSO REFINED.	0.038	0.0029

* PRIOR TO CYCLE 9, THE MORE INTENSE REFLECTIONS WERE CORRECTED FOR DEAD-TIME LOSSES INHERENT IN THE ELECTRONIC COUNTER.

TABLE 4.3

A. FRACTIONAL CO-ORDINATES($\times 10^4$) OF NON-HYDROGEN ATOMS

ATOM	X/A	Y/B	Z/C
C(1)	3943(1)	2240(3)	5608(1)
C(2)	4152(1)	2184(3)	6451(1)
C(3)	4218(1)	3846(3)	6912(1)
C(4)	4051(1)	5614(3)	6537(1)
O(4)	4060(1)	7298(2)	6931(1)
C(11)	3843(1)	5641(3)	5681(1)
C(10)	3179(1)	7256(3)	4662(1)
O(10)	3651(1)	7404(2)	5323(1)
C(5)	2794(1)	8683(4)	4587(1)
C(6)	2321(1)	8606(5)	3940(2)
C(7)	2229(1)	7113(5)	3391(2)
C(8)	2618(1)	5708(4)	3493(1)
F	2495(1)	4272(3)	2936(1)
C(9)	3114(1)	5714(3)	4121(1)
C(12)	3801(1)	3998(3)	5204(1)
C(13)	3595(1)	4319(3)	4276(1)
C(14)	3464(1)	2456(3)	3762(1)
C(15)	3952(1)	1257(3)	3774(1)
N	4363(1)	2383(2)	3561(1)
C(16)	4519(1)	4073(3)	4094(1)
C(17)	4043(1)	5372(3)	4027(1)
C(18)	4833(1)	1149(4)	3635(2)

TABLE 4.3(CONT'D)

B. FRACTIONAL CO-ORDINATES($\times 10^4$) AND THERMAL PARAMETERS($\AA^2 \times 10^3$) FOR H-ATOMS

ATOM	X/A	Y/B	Z/C	U(ISO)
H(1)	3917(8)	1048(32)	5311(12)	31(5)
H(2)	4234(10)	0934(39)	6676(15)	53(7)
H(3)	4368(10)	3826(35)	7546(15)	52(7)
H(4)	4156(12)	7221(41)	7525(19)	73(8)
H(5)	2859(10)	9633(39)	4946(16)	55(8)
H(6)	2054(12)	9528(41)	3882(17)	68(8)
H(7)	1899(13)	6990(45)	2919(19)	79(9)
H(141)	3299(10)	2811(35)	3209(16)	48(6)
H(142)	3230(11)	1605(37)	3930(15)	53(7)
H(151)	4128(9)	0655(35)	4298(15)	47(6)
H(152)	3829(11)	0165(40)	3405(16)	63(8)
H(161)	4681(9)	3675(34)	4654(15)	45(6)
H(162)	4793(10)	4726(33)	3968(14)	43(6)
H(171)	4180(9)	6545(33)	4357(13)	39(6)
H(172)	3889(8)	5789(32)	3463(14)	39(6)
H(181)	5008(12)	0712(40)	4217(18)	69(8)
H(182)	5099(12)	1916(42)	3428(16)	69(8)
H(183)	4709(10)	-0046(38)	3245(16)	56(7)

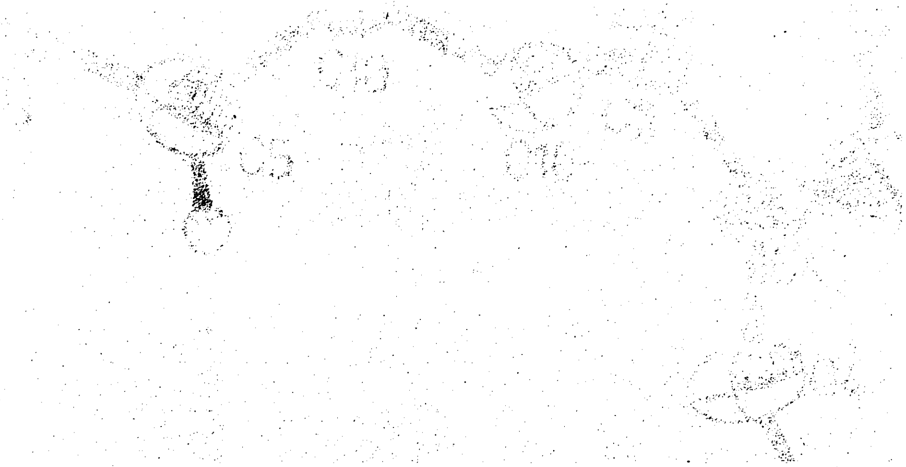
TABLE 4.3(CONT'D)

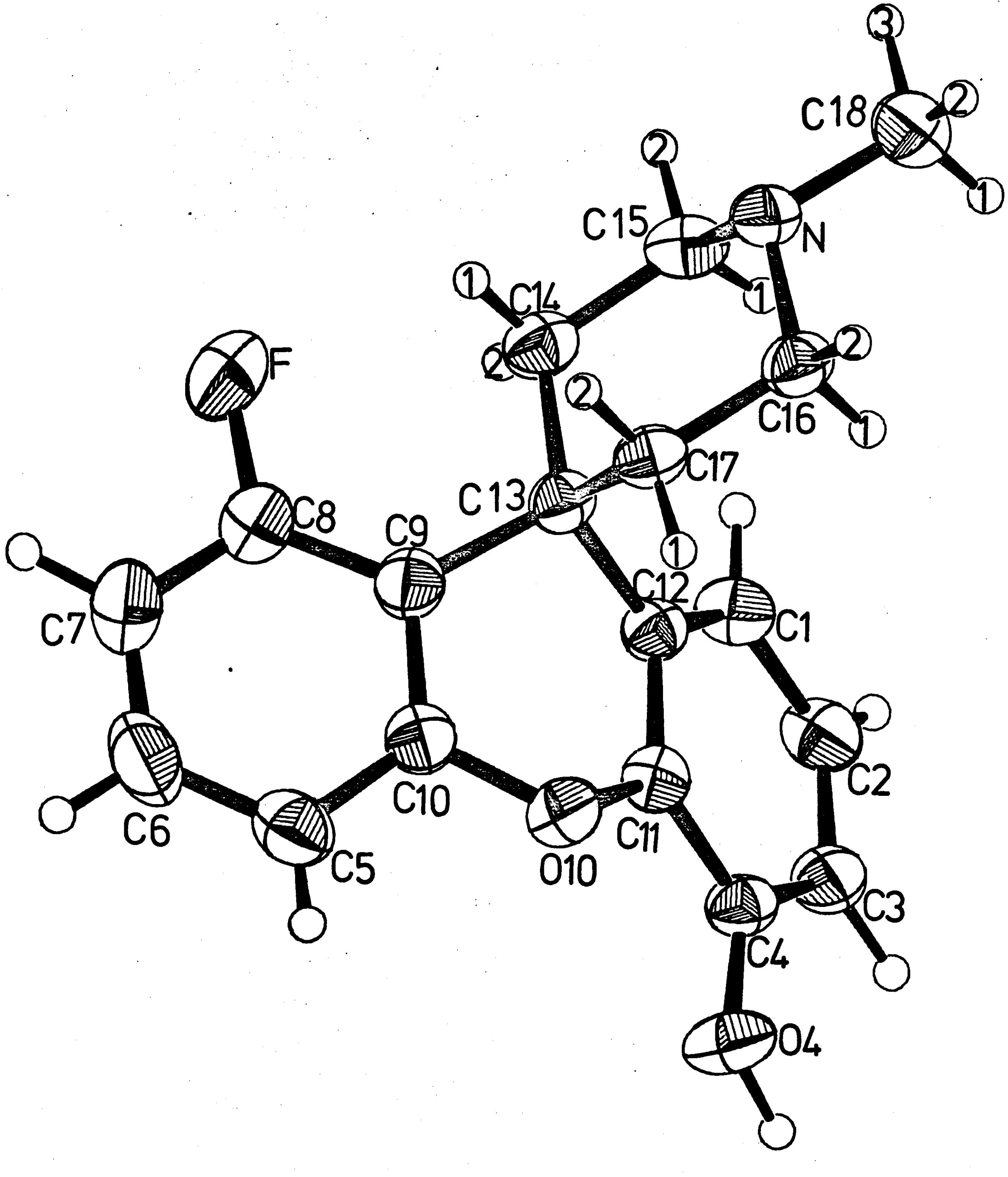
C. ANISOTROPIC THERMAL PARAMETERS($\mathring{A}^2 x 10^4$) OF NON-H ATOMS

ATOM	U11	U22	U33	U12	U13	U23
C(1)	510(12)	325(11)	385(11)	2(9)	199(9)	7(9)
C(2)	555(13)	415(13)	394(11)	113(11)	230(10)	99(10)
C(3)	470(11)	503(13)	296(10)	60(10)	150(9)	46(10)
C(4)	388(10)	391(11)	313(9)	-29(9)	150(8)	-22(9)
O(4)	728(11)	420(9)	307(7)	-18(8)	167(7)	-44(7)
C(11)	357(10)	329(10)	323(9)	-15(8)	139(8)	36(8)
C(10)	387(10)	407(11)	329(10)	11(9)	150(8)	54(9)
O(10)	484(8)	311(7)	338(7)	1(6)	98(6)	9(6)
C(5)	525(13)	508(14)	470(13)	95(12)	247(11)	36(12)
C(6)	445(13)	800(20)	649(16)	219(14)	226(12)	87(15)
C(7)	406(13)	959(22)	560(15)	111(14)	53(11)	-34(16)
C(8)	424(12)	704(17)	440(12)	25(11)	79(10)	-87(12)
F	588(9)	1059(14)	685(10)	127(9)	-120(8)	-377(10)
C(9)	372(10)	450(12)	337(10)	-2(9)	129(8)	19(9)
C(12)	326(9)	359(10)	304(9)	-38(8)	131(7)	-11(8)
C(13)	350(9)	362(10)	283(9)	-28(8)	108(7)	-18(8)
C(14)	422(11)	418(12)	359(11)	-90(10)	132(9)	-57(10)
C(15)	556(13)	363(11)	378(11)	-26(10)	186(10)	-66(10)
N	405(9)	407(10)	300(8)	24(8)	129(7)	-29(7)
C(16)	376(10)	464(12)	300(9)	-52(9)	121(8)	-35(9)
C(17)	432(11)	359(11)	283(9)	-41(9)	140(8)	-9(9)
C(18)	541(14)	602(16)	482(13)	146(13)	171(11)	-20(13)

Figure 4.1

A general view of I showing the atomic numbering scheme. Hydrogen atoms are numbered as the atoms to which they are bonded.

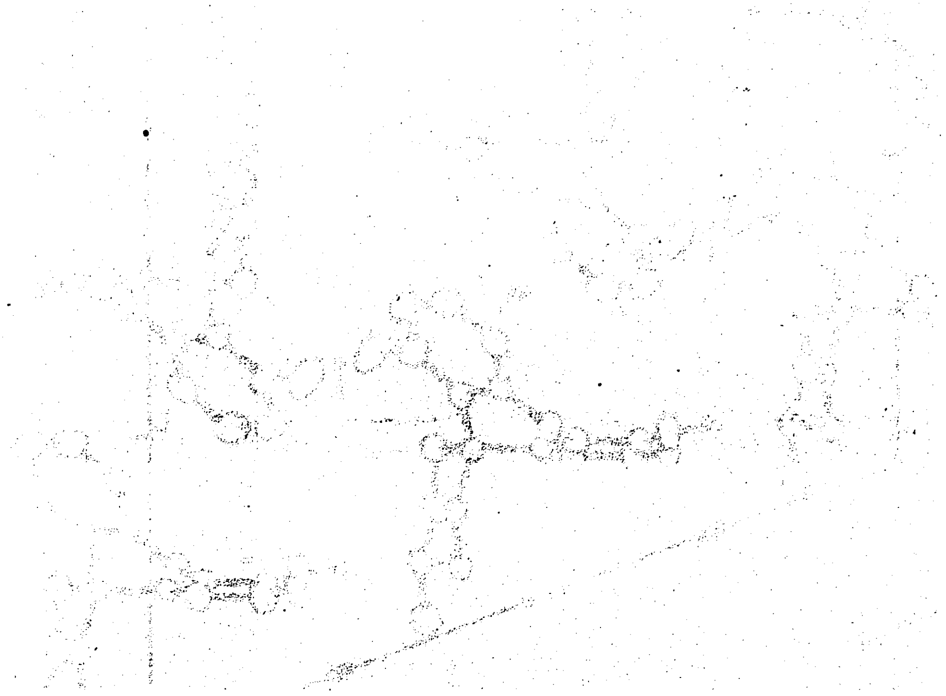


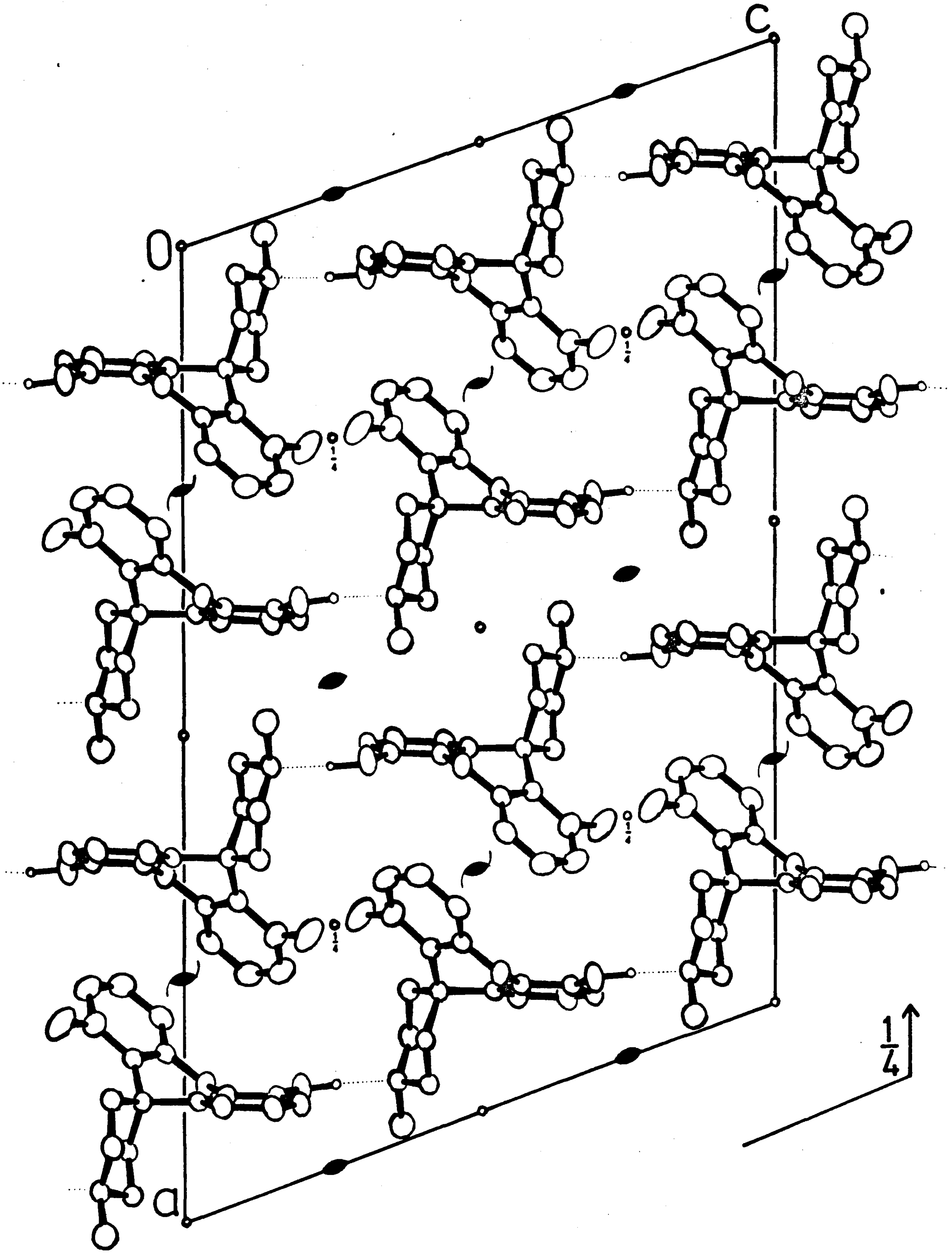


3
C18
2
1
2
C15
N
1
1
C14
2
F
2
C16
2
1
C17
C13
C8
C9
1
C12
C1
C7
C2
C6
C10
C5
O10
C11
C3
C4
O4

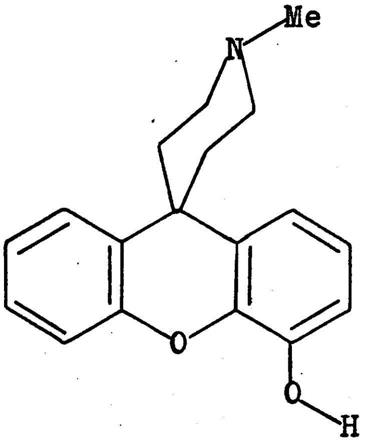
Figure 4.2

The molecular packing of I viewed along the b axis, and showing the hydrogen-bonding between molecules related by the c glide plane.




C
O
a
1/4
1/4
1/4
1/4
1/4

4.2 Experimental and results for II



II

4-Hydroxyxanthene-9-spiro-4'-(N-methylpiperidine)

Crystal data

Molecular formula	$C_{18}H_{19}NO_2$
Molecular weight	M = 281.4
Crystal system	Monoclinic
Unit cell dimensions	a = 26.277(3)Å
	b = 6.882(4)Å
	c = 17.296(2)Å
	β = 108.96(1)°
Unit cell volume	U = 2958.1Å^3
Measured density	D_m = 1.25 g cm^{-3}
Number of molecules per unit cell	Z = 8
Calculated density	D_c = 1.263 g cm^{-3}
Number of electrons per unit cell	F(000) = 1200
Linear absorption coefficient	μ(Mo-K_α) = 0.88 cm^{-1}

Space group	I2/c
Equivalent positions	X, Y, Z
	-X, Y, $\frac{1}{2}$ - Z
	$\frac{1}{2}$ + X, $\frac{1}{2}$ + Y, $\frac{1}{2}$ + Z
	$\frac{1}{2}$ - X, $\frac{1}{2}$ + Y, -Z
	-X, -Y, -Z
	X, -Y, $\frac{1}{2}$ + Z
	$\frac{1}{2}$ - X, $\frac{1}{2}$ - Y, $\frac{1}{2}$ - Z
	$\frac{1}{2}$ + X, $\frac{1}{2}$ - Y, Z

Data collection

Radiation used	Mo-K_α, $\lambda = 0.71069$Å
Filter	Graphite monochromator, $\cos^2 2\theta_m = 0.965$
Upper limit for data collection	$2\theta_{max} = 54^\circ$
Number of independent reflections	m = 1225
Unobserved cut-off	$2\sigma_I$
Number of parameters refined	n = 267
Number of reflections per parameter	m/n = 4.6

Structure Determination

The similarity between the cell parameters and diffraction patterns, together with the expected similarity in molecular structure, suggested that the crystals of II were isomorphous to and possibly quasi-isostructural with those of I. Therefore the fractional co-ordinates and isotropic thermal parameters (after cycle 4, ie at isotropic convergence) of the relevant non-hydrogen atoms of I were used in a trial refinement. The bond lengths of the isotropically refined model of II were experimentally identical to the corresponding parameters of I at the same stage of refinement.

This suggested that the trial model was acceptable, the acceptance of which being subsequently vindicated by successful refinement of the model, with no anomalous effects.

Structure Refinement

The least-squares refinement of positional, thermal and scale parameters converged after 19 cycles when R was 0.038 and R' was 0.0020. Full details of the course of refinement are given in Table 4.4. Initially unit weights were applied to all reflections. In later stages weights given by the expression

$$w = (8.063 - 0.2778|F_o| + 0.0038|F_o|^2)^{-1}$$

were applied. The coefficients of the quadratic expression were obtained from a least-squares fit of $a + b|F_o| + c|F_o|^2$ to the distribution of $\langle w\Delta^2 \rangle$ with $\langle |F_o| \rangle$ obtained from an analysis of $w\Delta^2$ with increasing $|F_o|$. This weighting scheme leads to approximately constant $\langle w\Delta^2 \rangle$ with increasing $|F_o|$ and $\sin\theta$.

A difference-synthesis after cycle 3 revealed residual electron-density in positions which were stereochemically acceptable for hydrogen atoms. Hydrogen atoms were introduced at these locations and assigned isotropic thermal parameters of 0.05Å^2.

The refinement was assumed complete when the parameter-shifts calculated by a cycle of least-squares were insignificant compared to the corresponding estimated standard deviations A final difference synthesis showed no errors in the model, the highest peak in the residual electron-density distribution being 0.16e/Å^3. In all structure-factor calculations the atomic scattering factors for carbon, oxygen and nitrogen were computed from numerical Hartree-Fock wave functions(1), whilst the scattering factors for hydrogen were those given by Stewart(3). Observed and final calculated structure factors are listed in Appendix X.

The final fractional co-ordinates and thermal parameters of all atoms are given in Table 4.5. The values of U_{ij} refer to the anisotropic temperature factor expression given in PART I. Bond lengths, valence angles and other relevant intra- and inter-molecular data are given, together with the corresponding values of I, in Table 4.6 and Table 4.7. A general view of the molecule illustrating the thermal ellipsoids(4) and giving the numbering scheme is given in Figure 4.3. The molecular packing arrangement viewed along the b axis is given in Figure 4.4.

TABLE 4.4

COURSE OF REFINEMENT OF II

CYCLES	PARAMETERS REFINED	FINAL R	FINAL R'
1 - 3	X,Y,Z,U(ISO) FOR C,O,N. SCALE FACTOR, FULL MATRIX, UNIT WEIGHTS.	0.143	0.0216
4 - 8	X,Y,Z,UIJ FOR C,O,N. H-ATOM CONTRIBUTIONS INCLUDED BUT NOT REFINED. SCALE FACTOR, FULL MATRIX, UNIT WEIGHTS.	0.051	0.0028
9 - 10	AS ABOVE,BUT WITH WEIGHTING SCHEME APPLIED.	0.050	0.0036
11 - 14	AS ABOVE, AND X,Y,Z FOR H-ATOMS ALSO REFINED OVERALL THERMAL PARAMETER, BLOCKED MATRIX.	0.039	0.0021
15 - 19	AS ABOVE; U(ISO) FOR H-ATOMS ALSO REFINED.	0.038	0.0020

TABLE 4.5

A. FRACTIONAL CO-ORDINATES($\times 10^4$) OF NON-HYDROGEN ATOMS

ATOM	X/A	Y/B	Z/C
C(1)	3959(2)	2220(6)	5645(2)
C(2)	4171(2)	2202(6)	6490(2)
C(3)	4227(2)	3902(6)	6937(2)
C(4)	4042(1)	5638(6)	6541(2)
O(4)	4043(1)	7360(4)	6932(2)
C(5)	2756(2)	8517(7)	4532(3)
C(6)	2300(2)	8313(9)	3878(3)
C(7)	2236(2)	6775(11)	3350(4)
C(8)	2645(2)	5416(8)	3470(3)
C(9)	3121(2)	5584(6)	4116(2)
C(10)	3162(2)	7153(6)	4639(2)
O(10)	3623(1)	7378(3)	5314(1)
C(11)	3833(1)	5637(5)	5686(2)
C(12)	3808(1)	3966(5)	5224(2)
C(13)	3605(1)	4244(5)	4294(2)
C(14)	3481(2)	2347(6)	3789(3)
C(15)	3965(2)	1151(6)	3789(3)
N	4367(1)	2298(4)	3570(2)
C(16)	4525(2)	3994(6)	4106(2)
C(17)	4048(2)	5289(6)	4038(2)
C(18)	4835(2)	1049(8)	3637(3)

TABLE 4.5(CONT'D)

B. FRACTIONAL CO-ORDINATES($\times 10^4$) AND THERMAL PARAMETERS($Å^2 \times 10^3$) OF H-ATOMS

ATOM	X/A	Y/B	Z/C	U(ISO)
H(1)	3926(15)	1095(59)	5371(21)	46(12)
H(2)	4254(17)	1035(63)	6782(25)	61(13)
H(3)	4368(14)	3853(52)	7560(23)	48(11)
H(4)	4173(20)	7230(76)	7688(33)	113(18)
H(5)	2803(13)	9576(49)	4920(20)	29(9)
H(6)	2034(20)	9147(64)	3775(26)	66(15)
H(7)	1946(23)	6698(77)	2884(32)	95(19)
H(8)	2624(17)	4471(60)	3095(25)	77(13)
H(141)	3297(14)	2795(54)	3216(23)	46(11)
H(142)	3231(15)	1573(55)	3927(22)	45(11)
H(151)	4155(14)	0526(51)	4340(22)	39(10)
H(152)	3846(15)	0055(55)	3385(23)	48(11)
H(161)	4711(14)	3578(51)	4721(23)	43(10)
H(162)	4787(16)	4707(56)	3955(22)	48(12)
H(171)	4180(14)	6429(56)	4390(22)	44(11)
H(172)	3879(13)	5700(46)	3436(21)	34(9)
H(181)	5000(18)	0588(65)	4311(29)	79(14)
H(182)	5062(18)	1731(64)	3529(26)	58(15)
H(183)	4675(21)	-0192(76)	3325(31)	97(18)

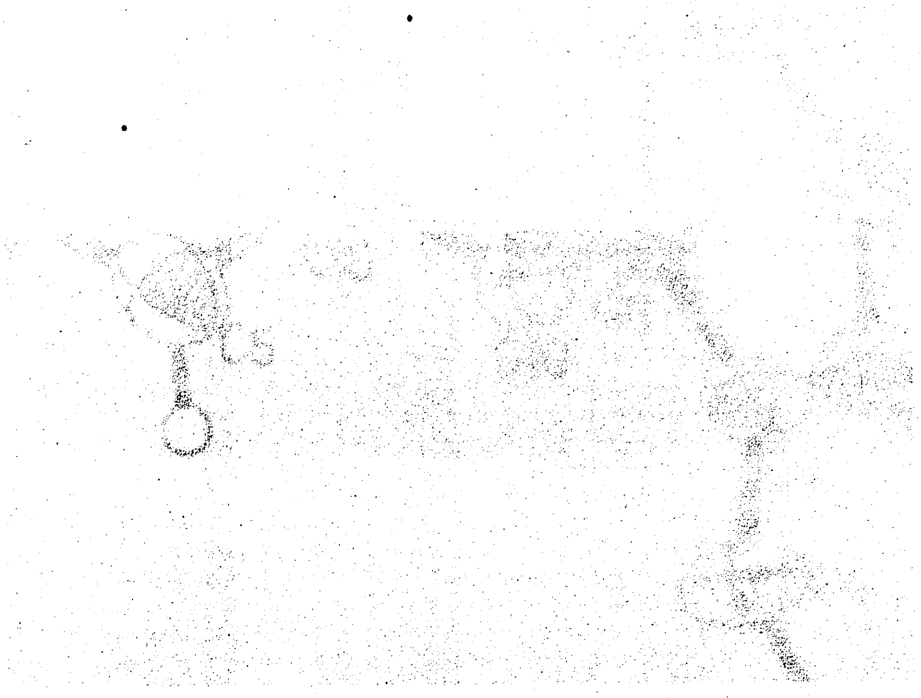
TABLE 4.5(CONT'D)

C. ANISOTROPIC THERMAL PARAMETERS($\AA^2 \times 10^3$) OF NON-H ATOMS

ATOM	U11	U22	U33	U12	U13	U23
C(1)	60(3)	32(2)	46(2)	3(2)	26(2)	-1(2)
C(2)	60(3)	40(3)	43(2)	10(2)	22(2)	7(2)
C(3)	55(3)	45(2)	32(2)	6(2)	16(2)	6(2)
C(4)	44(2)	42(2)	40(2)	-4(2)	20(2)	-3(2)
O(4)	84(2)	38(2)	40(1)	-1(2)	22(1)	-6(1)
C(5)	59(3)	61(3)	56(3)	13(3)	30(3)	10(2)
C(6)	50(3)	101(5)	77(4)	36(3)	23(3)	24(4)
C(7)	55(4)	131(6)	65(4)	24(4)	8(3)	-4(4)
C(8)	48(3)	90(4)	53(3)	9(3)	12(2)	-7(3)
C(9)	41(2)	54(3)	37(2)	4(2)	15(2)	6(2)
C(10)	45(2)	43(2)	44(2)	8(2)	22(2)	11(2)
O(10)	57(2)	31(1)	39(1)	4(1)	13(1)	6(1)
C(11)	45(2)	30(2)	39(2)	1(2)	20(2)	3(2)
C(12)	39(2)	33(2)	37(2)	-3(2)	17(2)	1(2)
C(13)	42(2)	34(2)	33(2)	-6(2)	13(2)	-3(2)
C(14)	49(3)	46(3)	45(2)	-12(2)	18(2)	-7(2)
C(15)	64(3)	35(2)	41(2)	-4(2)	20(2)	-9(2)
N	47(2)	39(2)	32(2)	3(2)	15(1)	-3(2)
C(16)	42(2)	42(2)	37(2)	-4(2)	13(2)	-4(2)
C(17)	46(2)	35(2)	35(2)	-2(2)	15(2)	0(2)
C(18)	59(3)	56(3)	58(3)	7(3)	24(3)	-3(3)

Figure 4.3

A general view of II showing the atomic numbering scheme. Hydrogen atoms are numbered as the atoms to which they are bonded.



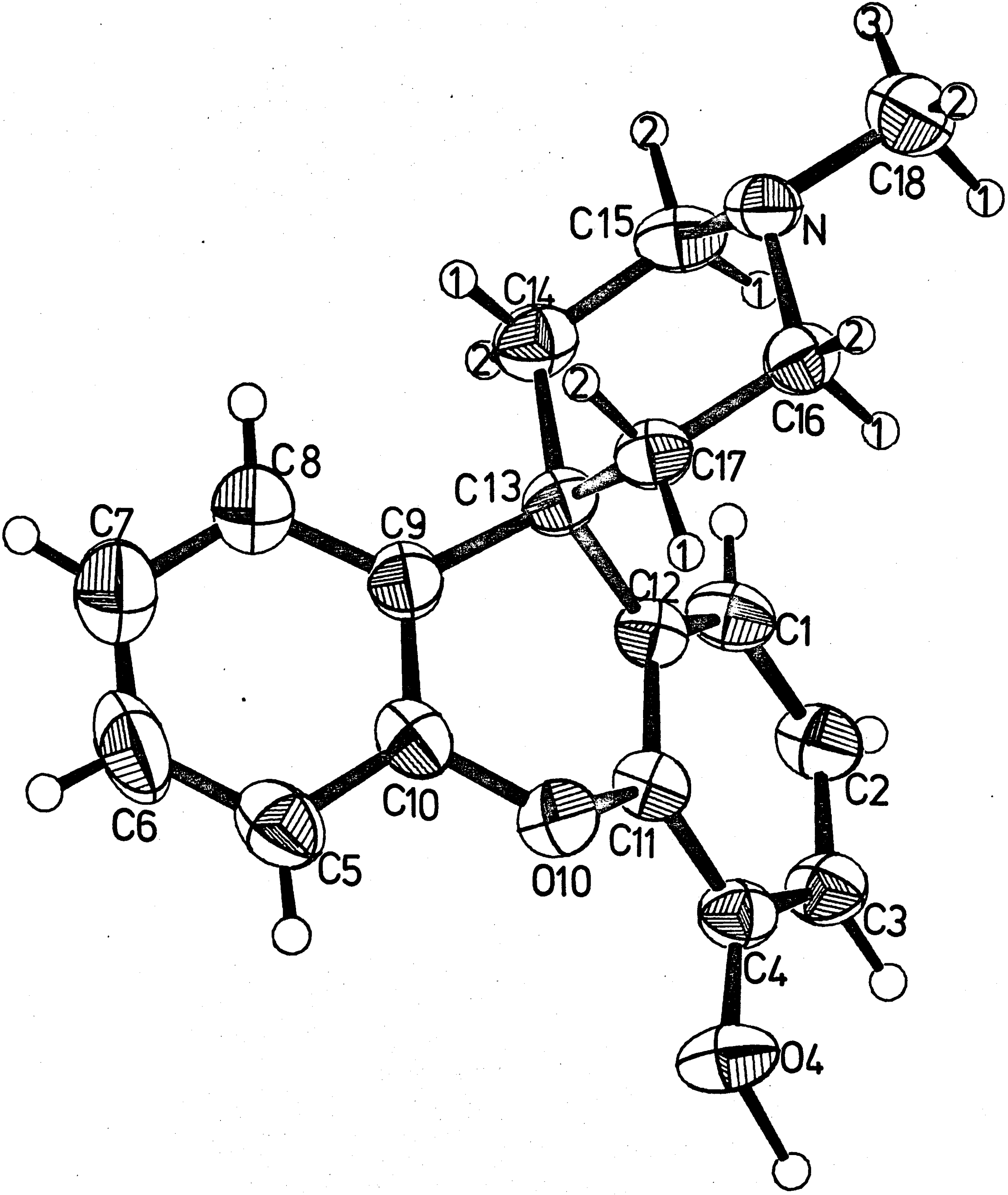
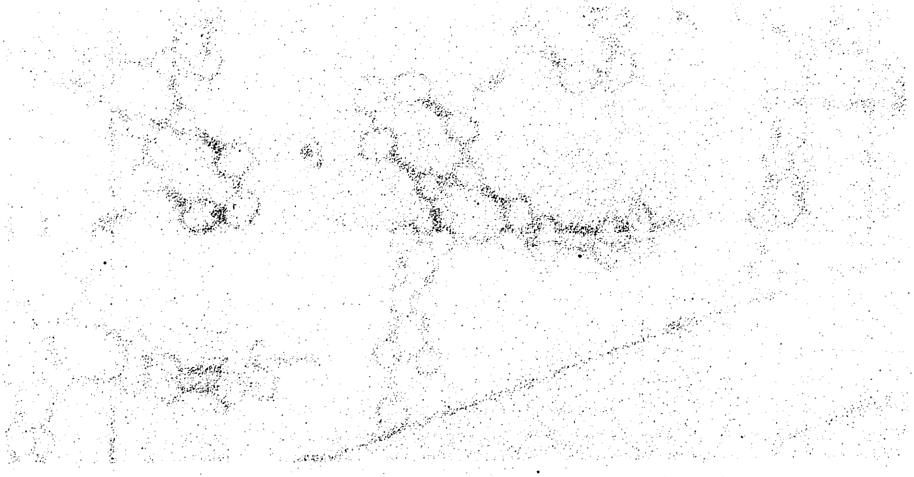
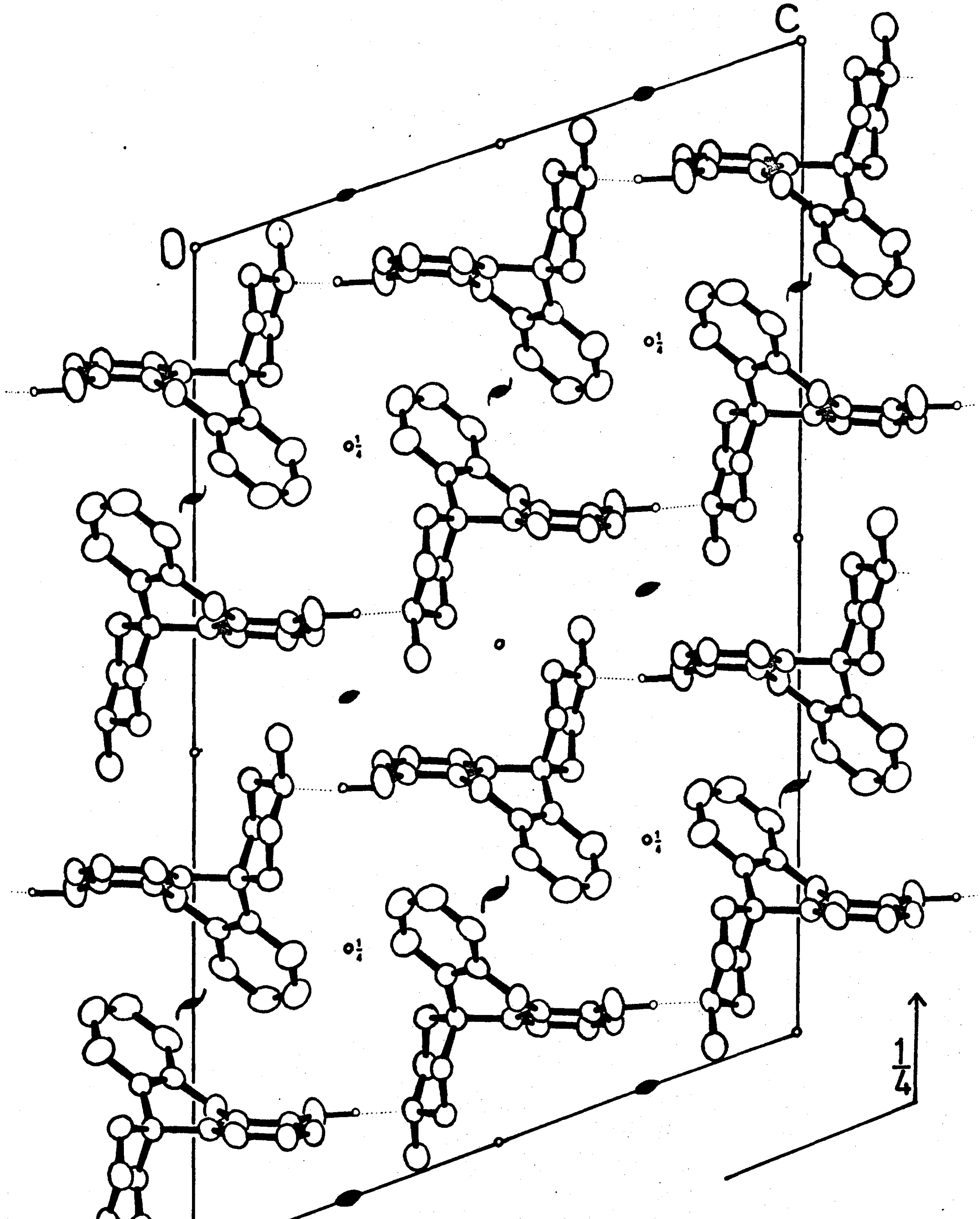

3
2
C18
1
2
C15
N
1
1
C14
2
2
C16
1
2
C17
C8
C13
C7
C9
1
C12
C1
C10
C2
C6
C5
C11
O10
C3
C4
O4

Figure 4.4

The molecular packing of II viewed along the *b* axis, and showing the hydrogen-bonding between molecules related by the *c* glide plane.




c
0
a
1/4
o ¼
o ¼
o ¼
o ¼
1/4

Tables 4.6 and 4.7

Interatomic distances, angles and mean planes for I and II

TABLE 4.6

INTERATOMIC DISTANCES(Å) AND ANGLES(°) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

A. BONDED DISTANCES

	I	II		I	II
C(1) -C(2)	1.385(2)	1.384(6)	C(2) -C(3)	1.381(3)	1.384(6)
C(3) -C(4)	1.390(3)	1.385(5)	C(4) -C(11)	1.404(3)	1.400(5)
C(11)-C(12)	1.390(3)	1.390(5)	C(12)-C(1)	1.394(3)	1.395(5)
C(4) -O(4)	1.349(3)	1.364(5)	C(5) -C(6)	1.373(3)	1.360(7)
C(6) -C(7)	1.373(5)	1.373(10)	C(7) -C(8)	1.378(4)	1.388(8)
C(8) -C(9)	1.394(3)	1.385(5)	C(9) -C(10)	1.396(3)	1.390(6)
C(10)-C(5)	1.387(3)	1.388(7)	C(8) -F	1.350(3)	-
C(9) -C(13)	1.539(3)	1.520(6)	C(12)-C(13)	1.539(3)	1.533(5)
C(10)-O(10)	1.387(2)	1.390(4)	C(11)-O(10)	1.388(2)	1.387(4)
C(13)-C(14)	1.542(3)	1.546(6)	C(13)-C(17)	1.558(3)	1.550(6)
C(14)-C(15)	1.518(4)	1.516(7)	C(17)-C(16)	1.511(3)	1.513(6)
C(15)-N	1.471(3)	1.464(6)	C(16)-N	1.466(3)	1.464(5)
N -C(18)	1.469(3)	1.475(7)			
			O(4) -H(4)	0.98(3)	1.24(5)
			MEAN C-H(ARYL)	0.96	1.09
			MEAN C-H(METHYL)	1.03	1.00
			MEAN C-H(METHYLENE)	0.96	1.00

TABLE 4.6(CONT'D)

B. INTERBOND ANGLES

	I	II		I	II
C(12)-C(1) -C(2)	120.2(2)	120.5(4)	C(1) -C(2) -C(3)	121.3(2)	121.0(4)
C(2) -C(3) -C(4)	120.3(2)	119.8(4)	C(3) -C(4) -C(11)	117.4(2)	118.4(3)
C(3) -C(4) -O(4)	125.1(2)	124.1(3)	O(4) -C(4) -C(11)	117.4(2)	117.5(3)
C(4) -C(11)-C(12)	123.1(2)	122.5(3)	C(11)-C(12)-C(1)	117.5(2)	117.4(3)
C(4) -C(11)-O(10)	116.2(2)	116.8(3)	O(10)-C(11)-C(12)	120.6(2)	120.6(3)
C(11)-O(10)-C(10)	113.5(2)	113.6(3)	O(10)-C(10)-C(9)	119.4(2)	119.7(3)
O(10)-C(10)-C(5)	116.6(2)	117.3(4)	C(5) -C(10)-C(9)	124.0(2)	123.0(3)
C(10)-C(5) -C(6)	118.7(2)	118.2(5)	C(5) -C(6) -C(7)	120.2(3)	121.1(6)
C(6) -C(7) -C(8)	119.4(2)	119.9(5)	C(7) -C(8) -C(9)	123.9(2)	121.1(5)
C(7) -C(8) -F	115.9(2)	-	C(9) -C(8) -F	120.2(2)	-
C(8) -C(9) -C(10)	113.8(2)	116.7(4)	C(8) -C(9) -C(13)	129.3(2)	126.1(4)
C(10)-C(9) -C(13)	116.9(2)	117.2(3)	C(13)-C(12)-C(1)	126.6(2)	126.8(3)
C(13)-C(12)-C(11)	115.9(2)	115.8(3)	C(9) -C(13)-C(12)	105.0(2)	105.7(3)
C(9) -C(13)-C(14)	114.3(2)	112.9(3)	C(12)-C(13)-C(14)	114.8(2)	115.2(3)
C(9) -C(13)-C(17)	107.7(2)	108.5(3)	C(12)-C(13)-C(17)	108.7(1)	108.6(3)
C(17)-C(13)-C(14)	106.1(2)	105.7(3)	C(13)-C(14)-C(15)	115.1(2)	115.8(3)
C(14)-C(15)-N	112.8(2)	112.5(3)	C(15)-N -C(18)	109.3(2)	108.6(3)
C(16)-N -C(18)	111.0(2)	110.9(3)	C(15)-N -C(16)	109.9(2)	110.3(3)
N -C(16)-C(17)	112.0(2)	111.2(3)	C(16)-C(17)-C(13)	112.1(2)	112.6(3)

TABLE 4.6(CONT'D)

C. SELECTED INTRAMOLECULAR NON-BONDED DISTANCES

	I	II		I	II
C(14)...C(17)	2.48	2.45	C(15)...C(16)	2.40	2.40
C(14)...C(16)	2.86	2.85	C(15)...C(17)	2.88	2.85
C(13)...N	3.00	3.00	C(9)...C(11)	2.75	2.75
C(10)...C(12)	2.76	2.76	C(13)...O(10)	2.78	2.78
C(14)...C(1)	3.04	3.04	C(15)...C(1)	3.26	3.30
N ...C(1)	4.05	4.07	C(16)...C(1)	3.66	3.66
C(17)...C(1)	3.57	3.57	C(17)...C(11)	3.09	3.09
C(14)...C(8)	3.09	2.97	C(15)...C(8)	4.56	4.44
N ...C(8)	5.08	4.96	C(17)...C(8)	3.54	3.49
F ...C(14)	2.77	-	C(8) ...C(13)	2.65	2.59
C(1) ...C(13)	2.62	2.62	C(5) ...O(10)	2.36	2.37
C(4) ...O(10)	2.37	2.37	C(9) ...C(6)	2.83	2.79
C(7) ...C(10)	2.73	2.73			

D. INTERMOLECULAR DISTANCES <3.6Å

	I	II		I	II
O(10)...C(1^{I})	3.44	3.45	O(4) ...C(2^{I})	3.51	3.46
C(16)...C(16^{II})	3.56	3.56	O(4) ...C18^{II})	3.52	3.57
C(2) ...C(18^{III})	3.56	3.50	O(4) ...C(15^{IV})	3.45	3.44
O(4) ...C(18^{IV})	3.17	3.20	O(4) ...N^{IV}	2.69	2.69
F ...F^{V}	2.89	-	F ...C(14^{V})	3.40	-

ROMAN NUMERALS AS SUPERSCRIPTS REFER TO THE FOLLOWING EQUIVALENT POSITIONS RELATIVE TO THE REFERENCE MOLECULE AT X,Y,Z :

I	X, 1+Y, Z	IV	X, 1-Y,1/2+Z
II	1-X, 1-Y, 1-Z	V	1/2-X,1/2-Y,1/2-Z
III	1-X, -Y, 1-Z		

TABLE 4.6(CONT'D)

E. SELECTED TORSION ANGLES

	I	II
C(17)-C(13)-C(14)-C(15)	49.6	48.5
C(13)-C(14)-C(15)-N	-52.7	-51.8
C(14)-C(15)-N -C(16)	54.6	54.8
C(15)-N -C(16)-C(17)	-59.3	-59.9
N -C(16)-C(17)-C(13)	60.7	61.2
C(16)-C(17)-C(13)-C(14)	-52.9	-52.5
C(14)-C(15)-N -C(18)	176.6	176.5
C(17)-C(16)-N -C(18)	179.8	179.7
C(8) -C(9) -C(13)-C(14)	-13.1	-12.8
C(8) -C(9) -C(13)-C(17)	104.5	104.0
C(1) -C(12)-C(13)-C(14)	8.8	9.4
C(1) -C(12)-C(13)-C(17)	-109.7	-108.9
C(5) -C(10)-O(10)-C(11)	141.0	141.3
C(4) -C(11)-O(10)-C(10)	-139.8	-141.7
MEAN E.S.D.	0.2	0.4
C(12)-C(1) -C(2) -C(3)	0.9	1.4
C(1) -C(2) -C(3) -C(4)	3.1	3.7
C(2) -C(3) -C(4) -C(11)	-3.3	-4.1
C(3) -C(4) -C(11)-C(12)	-0.2	-0.4
C(4) -C(11)-C(12)-C(1)	4.0	5.3
C(11)-C(12)-C(1) -C(2)	-4.3	-5.7
MEAN E.S.D.	0.3	0.6

TABLE 4.7

I. LEAST-SQUARES PLANES FOR I

A. EQUATIONS OF PLANES (X, Y, Z ARE ORTHOGONAL CO-ORDINATES IN Å)

1. $-0.9906X - 0.1310Y + 0.0382Z + 6.9332 = 0$
2. $0.6308X + 0.5373Y - 0.5599Z - 1.9998 = 0$
3. $0.6187X + 0.7780Y + 0.1091Z - 7.4110 = 0$
4. $0.4940X - 0.4879Y + 0.7196Z - 7.0293 = 0$
5. $0.5386X - 0.5345Y + 0.6514Z - 7.9788 = 0$
6. $-0.7841X + 0.1007Y + 0.6124Z - 0.7427 = 0$
7. $0.1470X + 0.1372Y - 0.9796Z + 4.7624 = 0$
8. $-0.8644X - 0.3725Y + 0.3378Z + 4.2025 = 0$

B. DEVIATIONS OF ATOMS FROM THE PLANE(Å).
ASTERISK(*) INDICATES ATOM USED TO DEFINE PLANE

1.	C(1)*	0.017(2)	C(2)*	0.009(2)	C(3)*	-0.024(2)
	C(4)*	0.013(2)	C(11)*	0.013(2)	C(12)*	-0.027(2)
	O(4)	0.083(2)	O(10)	0.128(1)	C(13)	-0.104(2)
2.	C(5)*	-0.009(3)	C(6)*	0.008(3)	C(7)*	0.001(3)
	C(8)*	-0.010(3)	C(9)*	0.009(2)	C(10)*	0.000(2)
	F	-0.037(2)	O(10)	-0.010(1)	C(13)	0.087(2)
3.	C(9)*	0.000(3)	C(13)*	0.000(2)	C(12)*	0.000(2)
	C(14)	-1.127(2)	C(17)	1.336(2)		
4.	C(13)*	0.000(2)	C(14)*	0.000(2)	C(17)*	0.000(2)
	C(9)	-1.233(2)	C(12)	1.210(2)		
5.	C(15)*	0.000(2)	N*	0.000(2)	C(16)*	0.000(2)
	C(14)	-1.141(2)	C(17)	-1.204(2)	C(18)	1.176(3)

TABLE 4.7(CONT'D)

6.	C(10)*	0.000(2)	O(10)*	0.000(1)	C(11)*	0.000(2)
7.	C(14)*	-0.026(2)	C(15)*	0.027(2)	C(16)*	-0.027(2)
	C(17)*	0.027(2)	C(13)	-0.666(2)	N	-0.653(2)
8.	C(9)*	-0.010(2)	C(10)*	0.011(2)	C(11)*	-0.011(2)
	C(12)	0.011(2)	C(13)	-0.577(2)	O(10)	-0.404(1)

C. DIHEDRAL ANGLE(°) BETWEEN PLANES:

1 AND 2	135.8;	6 AND 8	32.1;	8 AND 3	142.0;
4 AND 7	134.4;	7 AND 5	129.2;	3 AND 4	89.7;
4 AND 5	5.4;	3 AND 6	109.9;		

II. LEAST-SQUARES PLANES FOR II

A. EQUATIONS OF PLANES (X, Y, Z ARE ORTHOGONAL CO-ORDINATES IN Å)

1. $-0.9871X - 0.1528Y + 0.0477Z + 6.9543 = 0$
2. $0.6161X + 0.5477Y - 0.5661Z - 1.9143 = 0$
3. $0.6009X + 0.7937Y + 0.0947Z - 7.2253 = 0$
4. $0.4949X - 0.4763Y + 0.7268Z - 7.2075 = 0$
5. $0.5512X - 0.5350Y + 0.6396Z - 8.1161 = 0$
6. $-0.8018X + 0.0719Y + 0.5933Z - 0.2839 = 0$
7. $0.1378X + 0.1362Y - 0.9810Z + 4.8615 = 0$
8. $-0.8579X - 0.3889Y + 0.3359Z + 4.2705 = 0$

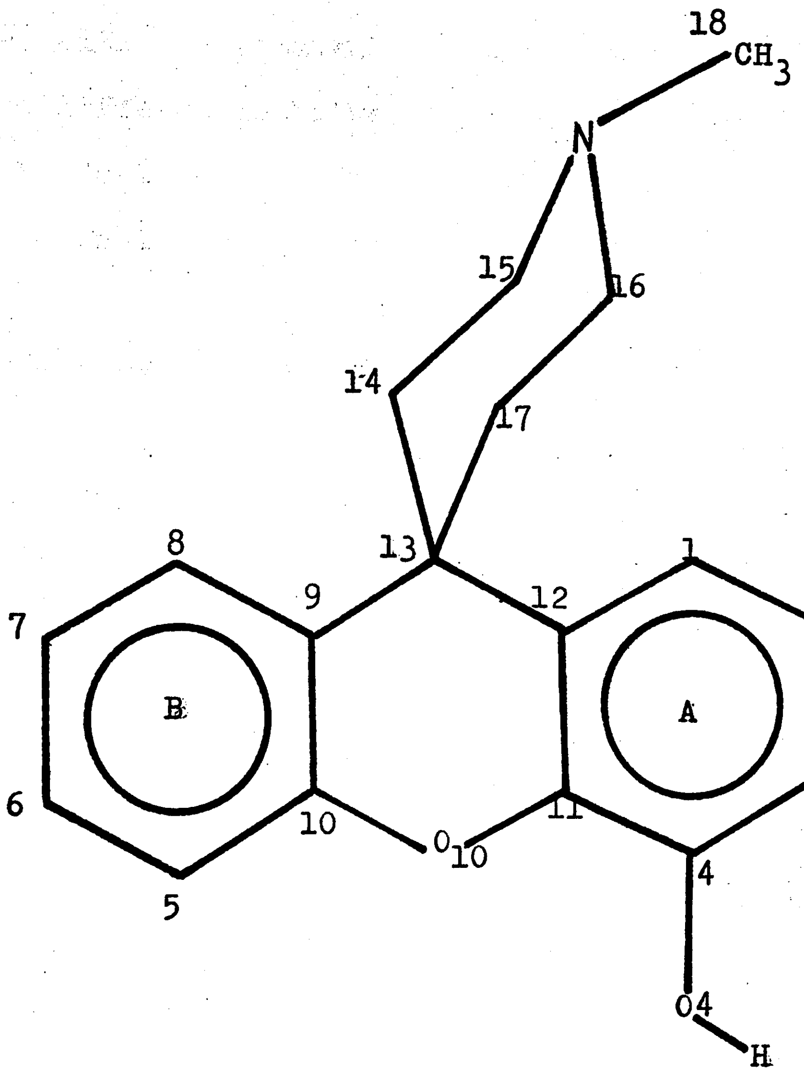
TABLE 4.7(CONT'D)

B. DEVIATIONS OF ATOMS FROM THE PLANE(Å). ASTERISK(*) INDICATES ATOM USED TO DEFINE PLANE

1.	C(1)*	0.023(4)	C(2)*	0.011(4)	C(3)*	-0.031(4)
	C(4)*	0.016(4)	C(11)*	0.017(4)	C(12)*	-0.036(4)
	O(4)	0.079(3)	O(10)	0.144(3)	C(13)	-0.126(4)
2.	C(5)*	-0.008(5)	C(6)*	0.009(6)	C(7)*	-0.002(7)
	C(8)*	-0.005(5)	C(9)*	0.006(4)	C(10)*	0.000(4)
			O(10)	-0.028(3)	C(13)	0.059(4)
3.	C(9)*	0.000(4)	C(13)*	0.000(4)	C(12)*	0.000(4)
	C(14)	-1.140(4)	C(17)	1.317(4)		
4.	C(13)*	0.000(4)	C(14)*	0.000(4)	C(17)*	0.000(4)
	C(9)	-1.231(4)	C(12)	1.202(4)		
5.	C(15)*	0.000(4)	N*	0.000(3)	C(16)*	0.000(4)
	C(14)	-1.143(4)	C(17)	-1.220(4)	C(18)	1.189(4)
6.	C(10)*	0.000(4)	O(10)*	0.000(3)	C(11)*	0.000(4)
7.	C(14)*	-0.031(4)	C(15)*	0.032(4)	C(16)*	-0.032(4)
	C(17)*	0.031(4)	C(13)	-0.658(3)	N	0.653(3)
8.	C(9)*	-0.013(4)	C(10)*	0.013(4)	C(11)*	-0.013(4)
	C(12)	0.013(4)	C(13)	-0.562(4)	O(10)	-0.389(3)

C. DIHEDRAL ANGLE(°) BETWEEN PLANES:

1 AND 2	136.0;	6 AND 8	30.8;	8 AND 3	142.4;
4 AND 7	135.2;	7 AND 5	128.6;	3 AND 4	90.7;
4 AND 5	6.9;	3 AND 6	111.6;		



II

I is the 8-fluoro derivative

4.3 Discussion

The structure analyses of I and II have confirmed the isomorphism that was indicated by the similarity of the cell parameters and diffraction patterns. The bond-lengths of the asymmetric units are remarkably similar in that there are no significant differences between the corresponding bond lengths in I and II (Table 4.6), both sets of bond lengths being comparable with literature values for similar bond types(5).

The relative differences that are observed between the molecules of I and II may be correlated to the direct effect on ring B of the 8-fluoro substituent in I. Thus the endocyclic valence angle subtended at C(8) in I, 123.9(2)°, is greater than the corresponding angle in II, 121.1(5)°, and compares with the value of 123.4(4)° observed in fluorobenzene(8) the latter value having been attributed to the rehybridization (so called isovalent hybridization) of the carbon atom under the influence of an electronegative substituent(9-10). The endocyclic valence angles (relative to ring B) subtended at C(10) in I and II, 124.0(2)° and 123.0(3)° respectively, do not differ significantly(11), are both larger than the normal trigonal values of 120° and are in agreement with the rehybridization of C(10) under the electronegative influence of the ether-type oxygen, O(10). The valence angle C(8)-C(9)-C(10) in I, 113.8(2)°, is more significantly deformed from the trigonal value than is the corresponding angle in II, 116.7(4)°, possibly to preserve the planarity of the ring(12) (the sum of the endocyclic valence angles of ring B is 720.0° in both I and II). The exocyclic angle subtended at C(9) in I, 129.3(2)°, is larger than that subtended at C(12), 126.6(2)°, and larger than both the corresponding angles in II, 126.1(4)° and 126.8(3)° respectively. This may arise from the marked deformation of the valence angle C(8)-C(9)-C(10), discussed above, and the sp^2 nature of C(9) (sum of valence angles is 360.0°). However it may also be attributed to the peri interactions between the fluorine atom and atom C(13) and its substituents. Thus, the short F...C(14) contact of 2.77Å in I may account for the observed widening of the C(9) exocyclic angle, and may also account for the F-C(8)-C(9) angle, 120.2(2)°, being larger than the F-C(8)-C(7) angle, 115.9(2)°. These observations are paralleled by 1,8 dimethylnaphthalene(13) in which the widening of the C(9) exocyclic angle, 125.2°, and the asymmetry of the C(8) (and C(1)) exocyclic angles, 124.8° and 116.2°, were attributed to the strong peri interactions resulting from the close methyl...methyl contact of 2.932Å.

Except for the angular distortions discussed above, ring B shows no further unusual features. The ring bond-lengths range from 1.373(5)Å to 1.396(3)Å in I and from 1.360(7)Å to 1.390(6)Å in II and are in agreement with usually observed values(5). The C-F bond-length in I, 1.350(3)Å is experimentally identical to the value, 1.354(6)Å, observed in fluorobenzene(8). Ring B is planar, within the experimental error of the analyses, in both I and II (Table 4.7).

Ring A also shows typical benzene-type bond-lengths, ranging from 1.381(3)Å to 1.404(3)Å in I and from 1.384(6)Å to 1.400(5)Å in II. The C(4)-O(4) bond-lengths, 1.349(3)Å and 1.364(5)Å in I and II respectively, do not differ significantly(11) and, although shorter than the values observed in some 2,3-disubstituted phenols(14), typically 1.402(4)Å, are comparable to the values observed in isovanillin(15) [1.358Å], p-hydroxybenzaldehyde(16) [1.357Å], and resorcinol(17) [1.364(4) and 1.353(5)Å (uncorrected for thermal motion)], all of which are involved in short O(H)...O hydrogen bonding. The angular deformations from ideal trigonal values, 117.4(2)° to 123.1(2)° for I and 117.4(3)° to 122.5(3)° for II, are not unusual for 1,2,3-trisubstituted benzene systems. Thus the corresponding values in I and II are experimentally identical and are similar to those in 2,6-xylenol(18), 2,3-xylenol(14), 3-bromo-2-methylphenol(14), and 2-hydroxy-3-methyl benzoic acid(19). However ring A exhibits a slight but significant boat-like distortion from planarity, suggested by the atomic deviations from the mean plane (Table 4.7) and by torsion angles of -4.3(3)° to +4.0(3)° for I and -5.7(6)° to +5.3(6)° for II. That the observed puckering is genuine is suggested by the fact that the observed distortions in I and II are experimentally identical and that rings B are planar within the accuracy of the respective analyses, thus acting as internal standards. There are no close intermolecular interactions that could account for this puckering, and although electronic conjugative effects within the phenolic moiety cannot be completely discounted there does not seem to be a clear causative factor.

The piperidine rings adopt a slightly skewed chair conformation with torsion angles in the range $|49.6^{o}|$ to $|60.7^{o}|$ for I and $|48.5^{o}|$ to $|61.2^{o}|$ for II. The corresponding torsion angles in I and II do not differ significantly from each other (Table 4.6) and are similar to the corresponding values observed in 3-benzoyl-3-ethyl-1-methylpiperidine bitartrate(20). The deviations for N $\left[0.65Å \text{ in I and II}\right]$ and for C(13) $\left[-0.67Å \text{ in I and } -0.66Å \text{ in II}\right]$ from the mean-plane through the central four atoms of the piperidine moiety are similar to the values observed in other piperidine derivatives(21). The N-methyl group adopts an equatorial orientation. This contrasts with unsubstituted piperidine and morpholine in which the N-proton is axial(22). Presumably this is due to the greater steric requirements of a methyl group relative to a lone-pair of electrons and the unfavourable steric interactions that would arise in the axial conformer(23).

The xanthene moiety is not planar, but is folded approximately about the C(13)-O(10) vector. The dihedral angle between the mean planes through the two phenylene rings is 135.8^{o} in I and 136.0^{o} in II. These values are similar to the angle of fold observed in thioxanthene(24), 135.3^{o}, and 9-sila-9,10-dihydroanthracene(25), 136.0^{o}, and do not differ markedly from a mean value of 138.9^{o} observed in some 9,10-heterocyclic analogues of 9,10-dihydroanthracene(26). Presumably this folding enables C(13) to retain sp^3 valency angles comparable with those found in non-cyclic compounds, since a planar conformation, together with the fact that C(Aryl)-C(sp^3) bond lengths are greater than C(Aryl)-O bond lengths, would lead to the pyran endocyclic angles being greatly distorted from trigonal and tetrahedral values. Furthermore, examination of a scale-model suggests that a planar xanthene system would lead to hard interactions between the C(14)- and C(17)- appended hydrogens and the C(8)- substituents. Any tilt of the piperidine ring to relieve such interactions would only serve to worsen the C(1)... piperidine interactions and to flatten the piperidine conformation. As a result of the folding, the pyran ring exhibits a boat conformation. O(10) lies 0.40Å in I and 0.39Å in II distant from the mean-plane through C(9), C(10), C(11) and C(12). The corresponding distances for C(13) are 0.58Å and 0.56Å respectively.

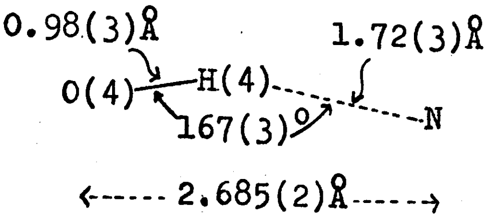
One aspect of this work was the investigation of the tilt, if any, of the piperidine ring towards the A ring which would possibly be induced by 8-substitution. However the conformation of the piperidine ring in I is unchanged relative to that in II, and the relevant intramolecular distances to the atoms of ring A show no significant differences. Thus the C(14)...C(13), C(14)...C(12), C(14)...C(1) distances are 1.54, 2.60 and 3.04Å in I, whilst the corresponding distances in II are 1.55, 2.60 and 3.05Å respectively. The intramolecular distances of the piperidine atoms to C(8), however, do show significant differences. Thus the C(8)...C(14) contact, 3.09Å, in I is longer than the corresponding contact, 2.97Å, in II. The C(8)...C(15) distances, 4.56 and 4.44Å respectively, and the C(8)...N distances, 5.08 and 4.96Å respectively, also show the same difference. However, these differences are correlated to the angular distortion at C(9) which is discussed above.

The crystal packing arrangements of I and II (Figures 4.2 and 4.4 respectively) illustrate the hydrogen-bonding that is present in the crystals, between molecules related by the c-glide plane. The geometry of the hydrogen-bonding in I and II is shown in Figure 4.5. The O(H)...N distances, 2.685(2) and 2.690(4)Å respectively, are short compared to the sum of Wallwork's donor and acceptor radii(6), 2.81Å, and suggest relatively strong hydrogen-bonding, being comparable to the values observed in the aniline-pentachlorophenol complex(7), 2.73Å and 2.60Å.

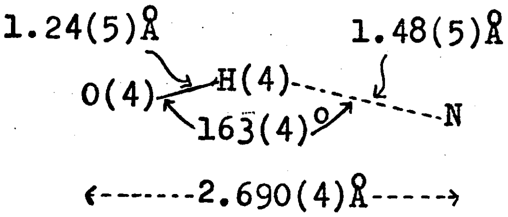
Apart from short contacts arising directly from the intermolecular hydrogen-bonding, there are no abnormally short contacts(27) indicating that the packing of the hydrogen-bonded chains of molecules is determined by van der Waal's forces.

Figure 4.5

The geometry of the hydrogen-bonding in I and II



I



II

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APPENDIX I

Structure Factor List for compound I, Part II.

Columns listed are ℓ, $|F_o|$ x 10, F_c x 10.

```
 9,-1,L

0   162   162
 9,-2,L
0   155  -149
 9,-4,L

0    53   -56

 9,-5,L

0    56   -60
 9,-6,L

3    52   -50
2    67   -68
1    36   -38
0    24   -19

 9,-7,L

1    45    44
0    23    12

 9,-8,L

5    35    39
4    63    63
3    84    84
2    70    67
1    31    34
```

```
 9,-9,L

4    75    74
3    48    46
2    35    34

 8,4,L

3    76    80
2    39    43
1    45    44

 8,3,L

5    60    66
4    72    75
3    69    71
2    34    38
0    57   -56

 8,2,L

5    69    72
4    61    64
2    72   -73
1    81   -80
0    66   -67

 8,1,L

4    37   -38
3    78   -77
2    56   -56
1    96   -97
0   100  -102
```

```
 8,0,L

4    58   -58
3    46   -48
 8,-1,L

3    29    31
2    38    39
1    89    92
0    92    92

 8,-2,L

6    61    64
5    85    84
4    97    94
3   136   139
2    35    33

 8,-3,L

7   103   108
6   116   113
5    89    88
4    87    88
3    63    65
0   103   -98

 8,-4,L

8   103   103
7   109   108
6   108   104
5    45    46
```

```
2    49   -49
1    86   -84
0   154  -155

 8,-5,L

7    29    31
6    42    41
4    41   -38
3   155  -157
2   165  -166
1   166  -163
0    81   -82

 8,-6,L

6    57   -57
5    72   -71
4   115  -113
3   162  -167
2   101   -99
1    97   -94
0    28   -29

 8,-7,L

6    60   -60
5    65   -66
4    44   -42
0    28    28

 8,-8,L

5    56   -53
3    51    49
```

```
2    39    41
1    62    58
0    52    51

 8,-9,L

6    47    47
5    55    57
4    30    27
3    20    20
0    52   -49

8,-10,L

6    56    51
3    33   -31
2    78   -80
1    83   -82
0    84   -81

8,-11,L

3    93   -90
2    88   -91
1    91   -91

 7,5,L

5    56    55
1    54    57

 7,4,L

6    80    81
3    68    69
```

```
2    35    36
0    44   -45

 7,3,L

7    63    62
6   111   116
5    52    51
4    58    57
1    86   -87
0   100  -101

 7,2,L

7    74    73
6    77    78
3    69   -70
2   185  -182
1   172  -173
0    96   -94

 7,1,L

8    45    47
6    42   -44
5    87   -85
4   153  -152
3   194  -196
2   182  -180
1   140  -143
0    80   -79

 7,0,L

6   120  -119
```

```
5   103   -98
4   140  -140
3   114  -119
2    57   -57

 7,-1,L

7    56   -53
6    60   -64
5    70    74
3    45   -44
1    66    64
0    75    71

 7,-2,L

6    47    48
3    74    73
2    71    70
0    34    38

 7,-3,L

8    80    81
7    49    45
6    53    51
1    68   -68
0   154  -156

 7,-4,L

8    42    37
```

```
 7,-4,L         4   96   -97     7,-12,L         6,5,L           6,1,L           6,-2,L         5  196  -194
                3   35   -37                                                                    4  139  -141
7  105   100    2   62    63    5  125  -129    6   57   -56    7   72   -76    7   50   -52    3  118  -118
6  128   132    1   46   -47                    1   65    69    6   79   -76    6  135  -136    2  128  -132
3  104  -103    0   59    56     7,-11,L        0  132   133    5  308  -309    5   69    66    1   98  -100
2  211  -213                                                    4  226  -229    4   75    74    0   64    66
1  160  -162     7,-8,L         0   37   -37     6,4,L          3  116  -117    3  197   192
0  107  -108                                                    2  117  -119    2  238   239     6,-6,L
                8   41   -42     7,-12,L        5   49    51    1  167  -165    1  177   176
 7,-5,L         7   35   -35                    3   36    35    0   42   -39    0   81    78    9   50   -47
                5   31    36    4   90   -92    2   61    65                                    8   80   -82
8   50    45    2   96    95    3   60   -60    1   34   -36     6,0,L           6,-3,L         7  141  -141
6   36   -39    1  114   110    2   42   -43    0   57   -58                                    6  207  -205
5  111  -113    0  134   136    0   40    35                    9   33   -30    6   34    31    5  283  -285
4  164  -161                                     6,3,L          8   61   -64    5  139   140    4   87   -81
3  220  -225     7,-9,L          6,8,L                          7  122  -123    4   51   -50    3   73   -74
2  244  -244                                    7   52    52    6  163  -160    2   52    47    1  248    47
1  130  -127    3   36    31    2   99  -103    6   71    74    5  172  -173    0  132  -134    0   56    56
0   33   -35    2   70    71    1   83   -90    5   60    60    4   68   -66
                1   32    27    0   68   -69    4   32   -31    3  210  -209     6,-4,L         6,-7,L
 7,-6,L         0   26    25                    2   44   -43    2  174  -172
                                 6,7,L          1  170  -170    1   39    41    8   43    44    9   91   -90
7   98   -96     7,-10,L                        0  196  -195    0  170   166    7   57    57    8  111  -111
6  198  -202                    4   88   -91                                    6   49    50    7   76   -73
5  202  -197    2   91   -93    3   67   -67     6,2,L           6,-1,L         4  129  -132    6   87   -84
4  162  -158    1   94  -100    2   76   -81                                    3  155  -151    5  157  -158
3  165  -165    0   65   -66    1   78   -79    8   45    46    9   60   -64    2  162  -158    4   30   -31
2  127  -131                                    7   34    32    8   71   -69    1  132  -132    2   66    66
1   32   -34     7,-11,L         6,6,L          6   32    34    7   41   -44    0  100   -97    1  189   188
                                                5   70   -70    6   84   -85                    0  284   284
 7,-7,L         5   39   -42    5   47   -50    4  111  -111    5   90   -92     6,-5,L
                4  107  -105    4   58   -59    3  236  -235    4   61   -59
7   67   -68    3  109  -113    3   68   -69    2  196  -201    2   97    97    8   41   -37
6  109  -110    2  108  -107    2   50   -49    1   78   -81    1  216   213    7  104  -104
5  105  -103    1   56   -52    0   85    86    0   88   -89    0  321   320    6   70   -74
```

```
 6,-8,L

8   47  -48
7  166  -63
6  332  -29
5  104  102
4   74   79
3   97   97
2  263  260
1  321  327
0  168  167

 6,-9,L

5  119  122
4  155  154
3  192  192
2  100   99

6,-10,L

6   46   42
5   56   55
4   37  -39
3   31  -27
1   47  -49
0   63  -60

6,-11,L

5   72  -70
4   82  -87
1   36  -39

 6,-12,L

6   71  -64
5   64  -64
1   32   29
0   59   58

6,-13,L

5   52  -52
2   49   47
1  102   95
0  105  104

 5,9,L

3   34  -41
2   47  -47
1   54  -58
0   36  -35

 5,8,L

5   56  -60
4   71  -75
3   97  -96
2   47  -43
1   94  -96
0   76  -78

 5,7,L

6   64  -65
5  135 -134
4  128 -127

3  111 -112
2   54  -60
1   36  -37

 5,6,L

7   71  -72
6   66  -64
5   87  -86
4  194  -95
3   56  -57
2   42   39
1  111  111
0  176  177

 5,5,L

7   60  -61
6  181  -84
5  147  -47
4  299  100
3  137  136
2   78   76
1  230  233
0  220  222

 5,4,L

5   32   41
4   69   68
3  165  164
2  101  102
0   26  -25

 5,3,L

8   58   58
7   61   63
6   32   31
5   57   55
3   88  -90
2   68  -68
1  174  168

 5,2,L

7   36  -34
6   47  -48
4  145 -145
3  186  -87
1   90  -92
0  121 -121

 5,1,L

8   69  -72
7  134 -130
6  164 -159
5  150 -150
4  161 -159
3  134 -133
2  115 -121
1  139 -136
0   71   70

 5,0,L

8  118 -116
7  151 -150
6  152 -155

5  216 -212
4  198 -195
3  112 -114
2  131  128
1  183  190
0  254  251

 5,-1,L

9  180  -81
8  137 -135
7   81  -81
6   73  -70
5  131 -128
4  227  226
3  318  316
2  277  273
1  376L 370
0  377  370

 5,-2,L

9   51  -57
8   71  -68
7   27  -26
6   84  481
5  126  127
4  298  297
3  360  352
2  377  377
1  296L 293
0  152  153

 5,-3,L

8   45   46
7   72   69
6   52   54
5  154  151
4  171  174
1  193  185
0   16  -12

 5,-4,L

9  133   23
8  150  150
7   45   43
6   35   39
5  185   86
4   91  -93
3   26  -23
2  183  -88
1  145 -146
0   80L -78

 5,-5,L

7   99 -100
6  123 -121
5   38   37
4  186  -87
1  104  -98
0  132 -132

 5,-6,L

9   72L -73
8   97  -97
7  108 -105

6  119 -119
5  148 -145
4  150 -148
3   57   58
2  107  105
1   70   70
0  177  180

 5,-7,L

9   91  -90
8  119 -122
7   67  -64
5   91  -92
4  137  138
3  123  130
2  248  249
1  336  339
0  263  270

 5,-8,L

8   62  -63
6  101  100
5  155  160
4  333  338
3  251  250
2  227  230
1  160  157
0  113  114

 5,-9,L

8  139  142
7  292  294
```

```
 5,-9,L

6   86   91
5  146  146
4  302  305
3  151  151
2   73   74
1   76   76

5,-10,L

8   57   59
7   72   71
6   73   68
5   62   62
3   32   29
2   34   30
1   62  -63
0  144 -146

 5,-11,L

5   59   59
4   64  -64
3   64  -63
2   66  -63
1   75  -72
0  120 -120

 5,-12,L

7   35  -33
4   43  -42
0   40   37
```

```
 5,-13,L

3   59   64
2   79   76
1   76   74
0   70   72

5,-14,L

4   97   94
3   99   95
2   74   74
1   48   44

  4,10,L

3   46   44
1   39   35
0   31   39

  4,9,L

0   84  -88

  4,8,L

6   45  -46
5   66  -65
4   51  -46
3   29  -28
2   68  -71
1   37  -36
0   38  -38
```

```
  4,7,L

7   77  -76
6   54  -53
5  103 -104
4  125 -129
3  113 -114
2   39   40
1   86   89
0  102  103

  4,6,L

7   88  -88
6   72  -72
5   69  -69
4   35   39
3   67   68
2  172  171
1  163  164
0  266  266

  4,5,L

8   72  -73
7   59  -60
5   89   91
4  226  230
3  242  239
2  277  275
1  162  162
0  201  199

  4,4,L
```

```
7   76   77
6   73   73
5   80   79
4  134  133
3  273  273
2  246  242
1  124  125
0  108  108

  4,3,L

8   43   39
7   75   75
6   77   78
5  158  155
4   76   76
1  107  107
0  242 -240

  4,2,L

6   37   42
5   58   60
4   33   28
2  301 -295
1  106 -109
0   98  -91

  4,1,L

7  125 -119
6  127 -122
5  109 -108
4  115 -112
3   43  -41
```

```
2   23   24
1   47   45
0   19   18

  4,0,L

9   96  -93
8   89  -82
7  143 -142
6  119 -118
5  105 -102
4   43  -45
3   50   54
2  257  248
1  282  282
0  290  285

  4,-1,L

10   58  -57
9   85  -83
8   92  -92
6   72   73
5   90   90
4  227  224
3  433  426
2  538  529
1  115  132
0  200  212

  4,-2,L

10   43  -46
7   58   58
6  194  196
```

```
5  360  360
4  440  439
3  406  409
2  386  393
1  196  204
0  228  206

  4,-3,L

8   53   52
7  194  198
6  192  191
5  204  208
4  246  253
3  108  104
2   70   72
1   62   52
0  166 -169

  4,-4,L

9   78   76
8   88   91
7  123 -125
6   86   86
5   43   43
4  129  125
3   36  -39
2  410 -404
1  361 -363
0  384 -378

  4,-5,L

5   35   33
```

```
4   93  -90
3  181 -183
2  116 -112
1   98 -104
0  286 -279

  4,-6,L

9   62  -67
7   53  -52
6  100  -97
5  113 -114
4   76  -74
3   51   52
2  113  111
1  202  203
0  126  130

  4,-7,L

9   59  -57
8   77  -76
7   76  -77
6   57   58
5  112  111
3  133  137
2  190  189
1  114  115
0  149  148

  4,-8,L

7   48   48
6  124  127
5  234  237
```

```
   4,-8,L

 4  240  240
 3  240  240
 2  124  127
 1   19    4
 0   27   32

   4,-9,L


 8   73   72
 7  157  158
 6  144  145
 5  140  142
 4  245  247
 3  195  198
 1  114 -115
 0  130 -130

 4,-10,L

 8   68   69
 7  130  130
 6  124  124
 3  108 -106
 2   95  -95
 1  143 -144
 0  237 -238

 4,-11,L

 7   31   33
 4   37  -40
 3  195 -194
 2  194 -192
```

```
 1  162 -159
 0  150 -149

 4,-12,L

 7   34  -31
 6   30  -29
 4   45  -42
 3   88  -91
 2   81  -77

 4,-13,L

 4   31  -36
 3   51   49
 2   59   59

 4,-14,L

 3   54   52

  3,11,L

 3  103  105
 2   84   84
 1   91   92
 0   85   87

  3,10,L

 5   63   61
 4   73   74
 3   70   72
 2   55   54
 1   34   39
```

```
  3,9,L

 5   49   51
 4   62   59
 3   46   45
 2   37  -39
 1  104 -107
 0  114 -112

  3,8,L

 4   54  -55
 3   63  -60
 2   45  -45
 0   39  -30

  3,7,L

 6   49  -50
 5   44  -46
 4  100 -101
 2   48   51
 1   52   52
 0   55   56

  3,6,L

 8   60  -58
 7   76  -75
 5   56   57
 4  113  112
 3  100   96
 2   96   91
 1  168  168
 0  143  142
```

```
  3,5,L

 8   30  -27
 6   96   93
 5  102   99
 4  291  289
 3  353  351
 2  338  336
 1  177  176
 0   95  -97

  3,4,L

 8   31   32
 7  129  130
 6  205  203
 5  157  153
 4  278  275
 3  248  246
 2  278  278
 0  104 -104

  3,3,L

 9   53   51
 8   86   83
 7  148  146
 6  181  177
 5  201  198
 4  103  102
 3  218 -208
 2  150 -148
 1  186 -184
 0  254 -249
```

```
  3,2,L

 9   81   77
 8   58   60
 7   68   71
 5   61   61
 4   33   32
 3   34  -23
 2  422 -414
 1  551 -552
 0  273 -268

  3,1,L

 8   23   25
 7   42  -36
 6  100  -98
 5   28   19
 4  188 -184
 3   82  -82
 2  115 -111
 1   42  -41
 0  118 -113

  3,0,L

 9   66  -66
 7   42  -43
 6   79  -78
 5  135 -136
 4  203 -194
 3   77   74
 2  126  125
 1  415  413
 0  135 -120
```

```
  3,-1,L

 9   59  -60
 8   38  -38
 7   31  -32
 6  132  127
 5  187  187
 4  280  276
 3  299  293
 2   61   58
 1  107  110
 0  165  164

  3,-2,L

 8   71   72
 7  130  128
 6  339  339
 5  365  368
 4  404  409
 3  214  214
 2  385  380
 1  125  124
 0  221 -220

  3,-3,L

 9   76   79
 8  164  168
 7  228  229
 6  172  171
 5  104  109
 4  299  289
 3   42   43
 2  206 -205
```

```
 1  569 -562
 0  250 -250

  3,-4,L

10   60   63
 9  111  114
 8   72   71
 7  132  133
 6   92   90
 5   36  -38
 4  194 -202
 3  351 -360
 2  466 -471
 1  722 -748
 0  424 -430

  3,-5,L

 9   60   62
 8   38   40
 7   31   29
 6   85  -87
 5   57  -60
 4  242 -244
 3  311 -313
 2  279 -285
 1  315 -325
 0  343 -351
```

```
 3,-6,L          7 141  142     4 103 -104     3  72   70      2,6,L         7 130  126     1  29  -24
                 6 160  158     3  98  -94     1 112 -114                    6 131  129     0 372 -365
 6 100 -103      5  63   63     2  83  -86     0 114 -113     7  76  -78     5  97   98
 5 130 -131      4  39   40     1  45  -43                    6  40  -43     2 479 -475      2,0,L
 4 143 -147      3  30   30                     2,9,L         5  52   51     1 602 -588
 3 112 -115      2  17  -15     3,-13,L                       4  63   62     0 493 -495     9  69  -69
 2 143 -140      1 143 -145                    6  65   64     3  62   64                    8  66  -64
 1 206  201      0 183 -184     6  63  -63     5  56   55     2  67   65      2,2,L         7 121 -118
 0 180  179                     5  46  -46     4  44   40     1  82   78                    6 167 -163
                 3,-10,L        2  54   55     3  52  -52                   9  72   69      5 142 -142
 3,-7,L                         1  75   73     2 154 -154      2,5,L        8  73  -74      4 145 -139
                 8  64   59     0  63   60     1 142 -140                   7 130  125      3 164 -152
 8  48  -44      7  66   68                    0 213 -213     7  51   50    6  31  -30      2  60  -57
 7  92  -96      6  57   56     3,-14,L                       6 163  162    5 144 -143      1 384  378
 4  48  -49      5  39  -40                     2,8,L         5 185  179    3 493 -475      0 363  373
 3  34   30      4 130 -130     2  42   36                    4 122  121    2 855 -867
 2 110  112      3 138 -137     1  57   54     7  48   47     3 318  310    1 781 -796       2,-1,L
 1 186  185      2 161 -159                    5  40  -40     2 251  247
 0  27   30      1 247 -248      2,12,L        4  39  -37     1 147 -132     2,3,L         8  47  -49
                 0 177 -179                    3 107 -107                                  7  84  -80
 3,-8,L                         3  74   71     2 200 -200      2,4,L        4  50   47     6 130  125
                 3,-11,L        2  87   85     1  58  -57                                  5 218  212
 8  50   47                     1  28   22     0 156 -158     8  85   85     2,2,L         4 109 -101
 7  24   24      6  64  -64     0  59   58                    7 190  186                   3 163  163
 6  99   92      5  62  -60                     2,7,L         6 189  187    0 420 -411     2 122 -114
 5 152  151      4 134 -134      2,11,L                       5 180  174                   1 125 -120
 4 218  220      3 260 -260                    7  59  -57     4  90   87     2,1,L         0 168  164
 3 121  119      2 283 -278     4  79   76     6  40  -38     3  51   56
 2  40  -40      1 183 -177     3  77   80     5  58  -60     2 169  165    9  48   50      2,-2,L
 1  94  -91      0  36  -35     2 127  128     4 116 -116     1  27   19    8  46   48
 0 105 -106                     0  20   23     3  93  -93     0 144 -149    6 146 -146     9  53   55
                 3,-12,L                       2  92  -90                   5 299 -293     8 132  128
 3,-9,L                          2,10,L        1  22   23      2,3,L        4 375 -368     7 108  107
                 6  91  -88                    0  45   43                   3 335 -323     6 157  153
 8 115  117      5 119 -119     4  89   87                    9  96   95    2 104  100
```

```
  2,-2,L
 5  299  293
 4  145  150
 3  173  170
 2   47  -43
 1   66  -65
 0  378 -395
  2,-3,L
10   66   64
 9   71   71
 8  127  126
 7  177  180
 6  117  118
 5   83  -80
 3  113  105
 2  293 -296
 1  367 -362
 0  310 -315
  2,-4,L
10   72   73
 9   52   54
 8   41   44
 7   45   45
 5  163 -163
 4  260 -270
 3  614 -649
 2  543 -559
 1  643 -671
 0  577 -592
```

```
  2,-5,L
 9   35   36
 7   31  -25
 6  145 -145
 5  309 -322
 4  354 -365
 3  617 -636
 2  360 -376
 1  255 -265
 0   50   43
  2,-6,L
 8   63  -61
 7  119 -120
 6  255 -262
 5  227 -233
 4   86  -92
 3  115 -115
 2   82   82
 1  226  225
 0  356  369
  2,-7,L
 9   45  -42
 8  116 -121
 7  115 -119
 6   37  -35
 5   39   35
 4   61  -58
 3  104  105
 2  109  115
 1   77  -83
```

```
 0  283  290
  2,-8,L
 8   40   44
 7   38   38
 5   78   77
 4   41   41
 3   69  -72
 2   21   17
 1  123  124
  2,-9,L
 8   53   53
 7   70   71
 6   87   88
 3  106  106
 1   64  -63
 0  175 -173
  2,-10,L
 5   26  -23
 4  106 -107
 3  193 -193
 2  154 -154
 1   99 -103
 0  116 -120
  2,-11,L
 7   54  -49
 6   91  -92
 5  152 -152
```

```
 4  124 -124
 3  210 -213
 2  200 -203
 1  104 -100
 0   63   64
  2,-12,L
 6  115 -115
 5  144 -142
 4  102  -97
 3   51  -51
 2   45   44
 1  140  139
 0   98   99
  2,-13,L
 5   26  -30
 3   63   64
 2  103  102
 1  111  108
 0  141  138
  2,-14,L
 2   63   59
 1  104  101
 0   85   83
  1,13,L
 2   56  -53
```

```
  1,12,L
 1   71   72
  1,11,L
 5   43   43
 4   45   45
 3   75   73
 2   43   45
 1   25   25
 0   40  -42
  1,10,L
 6   79   76
 5   79   79
 1  194 -197
 0  178 -178
  1,9,L
 6   50   47
 4   68  -70
 3  171 -174
 2  245 -244
 1  364 -370
 0  139 -137
  1,8,L
 7   34   35
 6   56  -56
 5  112 -112
 4  208 -206
```

```
 3  227 -228
 2  148 -151
 1  217 -218
 0   22  -20
  1,7,L
 8   57  -55
 6  161 -164
 5  175 -172
 4   57  -55
 3   79  -76
 2  177 -176
 0   85   86
  1,6,L
 8   44  -43
 7   56  -61
 6   56  -53
 4   26  -28
 3  126 -126
 2   88  -85
 1  282  289
 0   70  -66
  1,5,L
 8   56   62
 7   45   43
 6   70   67
 5   39  -37
 4   68   66
 3  196  200
 2  104  105
```

```
 1  331  323
 0   97  -94
  1,4,L
 9   50   52
 8   95   96
 7   37  -36
 6  181  182
 5  224  219
 4   41   41
 2  143  138
 1   51  -49
 0  390 -388
  1,3,L
 9   49   46
 8   68   65
 7   59   56
 6  113  109
 5   40  -43
 4  164 -160
 3  345 -340
 2  691 -703
 0  117  107
  1,2,L
 9   86   86
 8   51   46
 6  178 -174
 5  340 -332
 4  507 -493
 3  377 -373
```

```
  1,2,L

 2  418 -409

  1,1,L

 8   99  -97
 6  310 -302
 5  370 -356
 4  368 -363
 3  298 -287
 2  103  103
 1  305  306
 0  265  254

  1,0,L

 9   98  -96
 8  166 -165
 7   92  -89
 6  231 -230
 5  118 -116
 4   66  -67
 3  227 -219
 2   18   22
 0  608  621

  1,-1,L

10   38  -40
 8   64  -61
 7   91  -96
 6   69  -71
 5  149  152
 4  138  140

 3  198 -183
 2  178 -173
 0  407  405

  1,-2,L

 9   51   53
 8  108  113
 7   26  -25
 6   76   80
 5   94   96
 4  130  136
 3  383 -399
 2  606  643
 0  711 -801

  1,-3,L

 9   38   34
 8   86   92
 7   58   61
 6  159  159
 4   83   88
 3   86   77
 2  447 -466
 1  275 -278
 0   38  -32

  1,-4,L

 9   37   37
 7   52  -51
 6   59   60
 5  203 -208
 4  700 -726

 3  454 -463
 2  221 -225
 1  344 -360
 0  114  112

  1,-5,L

 8   50  -49
 7  120 -120
 6  348 -360
 5  330 -342
 4  164 -163
 3  218 -225
 2  312 -319
 1   26   26
 0  266  263

  1,-6,L

 9   76  -73
 8  132 -139
 7  105 -110
 6  170 -171
 5  120 -119
 4   23  -25
 3   66   68
 2  167  180
 1  228  234
 0  481  500

  1,-7,L

 9   77  -77
 8   70  -69
 7   41  -42

 6   95  -98
 4  111  116
 3   84   87
 2  382  397
 1  457  472
 0  357  368

  1,-8,L

 5  182   79
 4  162  167
 3  153  159
 2  243  246
 1  181  186
 0   64   69

  1,-9,L

 8   25   24
 7   47   45
 6  104  107
 5   74   78
 4   48   49
 3   82   84
 2   58   56
 1   37  -24
 0  153 -153

  1,-10,L

 6   38   43
 4   94  -93
 3   64  -62
 2  126 -127
 1   86  -83

 0   37   36

  1,-11,L

 7   53  -53
 6   98  -99
 5  113 -116
 4   90  -91
 3   63  -60
 2   71  -69
 1   68   67
 0   67   67

  1,-12,L

 6   75  -74
 5   91  -90
 3   86   86
 2   77   75
 0   70   69

  1,-13,L

 5   27   31
 4   63   58
 2  121  117
 1  192  188
 0  149  146

  1,-14,L

 3   94   90
 2  123  125
 1   89   86
 0   74   73

  0,13,L

 2   42  -38
 0   78   76

  0,12,L

 3   32   30
 2   43   38
 1   58   53
 0   96   96

  0,11,L

 4   69   68
 2   71   70
 1   83   81
 0   86  -86

  0,10,L

 6   57   56
 3   72  -73
 2  150 -147
 1  109 -108
 0  102 -107

  0,9,L

 5   56  -55
 4  168 -168
 3  258 -255
 2  186 -185
 1   69  -68
 0  196 -197

  0,8,L

 7   72  -68
 6   86  -87
 5  189 -189
 4  199 -200
 2  142 -143
 1  291 -298

  0,7,L

 7   99  -98
 6  118 -122
 5  100  -99
 4  169 -169
 3  154 -156
 1   80   84
 0  438  445

  0,6,L

 8   86  -88
 6  107 -111
 5  157 -157
 4   82  -80
 3  121  126
 2  236  240
 1  234  239
 0  593  615
```

```
  0,5,L         5  402 -408    8   89  -93    3  166 -166     0,-8,L        0,-13,L       1   75   77
                4  427 -430    7   50  -49    2   90  -98
5  101  103     3  115 -115    6  169 -167    1   72   62    7   82   80    4   51  -47     -1,9,L
4  221  226     2  146 -147    5  166  167                  5  191  191    3   90   89
3  152  157     1  317 -329    4  248  252     0,-5,L       4  277  279    2  110  107    6   41  -43
2  227  233     0  320 -337    3  517  521                  3  220  224    1  114  112    5   62  -62
1  306  314                    1  351  347    8   46  -50    2  128  133                  4   49  -47
0   94   99      0,1,L                        7  202 -208    1  141  142     0,-14,L      3  107 -107
                                0,-2,L        6  107 -110                                 2   73  -71
 0,4,L          9   51  -51                   5  196 -199     0,-9,L      1   27   28    1  176 -179
                8   91  -91    8   39   37    4  170  -70
7  181   81     7  184 -194    7  166  166    3  121 -118    7   92   92    -1,13,L        -1,8,L
6  113  113     6  100 -101    5  247  250    2  141 -140    6   88   88
5  183  185     5  216 -228    4  455  453    1   70  -66    5  159  161    2   46   49    6  101 -101
4  163  163     4  314 -318    3  380  384                  4   50   51    1   79   77    5  134 -134
3   35  -30     3  150 -151    1   51   48     0,-6,L       2   28   24                  4   86  -89
1  339  344     2  367  375                                 1  113 -115    -1,12,L       3  145 -151
0  303 -309     1   46   44     0,-3,L        9   57  -63                                 2   74  -74
                0  324  337                   8   86  -85     0,-10,L     4   39   37
 0,3,L                         9   31   32    7   78  -80                  3  104  103     -1,7,L
                 0,0,L         8   75   76    6   20  -18    7   27   24    2   93   91
9  149  150                    7  135  134    5  170 -168    5   32   33    1  135  136    7   93  -94
8   76   79     9  107 -109    6  155  153    3  299  300    3   90  -89                  6   82  -85
5   75  -75     8  164 -164    5  146  146    2  227  233    2   42  -44    -1,11,L       5   89  -89
4   88  -86     7  101  -99    4  100 -101    1  225  232                                 4  130 -130
3  289 -292     6  111 -113    3  211 -209                   0,-11,L      5   48   49    3   45   46
2  374 -392     5  109 -109    2  237  235     0,-7,L                     4   37   36    2  288  301
1  101   92     4   68  -69    1  574  595                  5   62  -63    3   95   92    1  368  381
0  485 -517     3  249  248                   8   55  -60    4   32  -31    2   76   74
                2  159 -159     0,-4,L        5  122  124    1   86  -86    1   50   50     -1,6,L
 0,2,L          1  608  632                   4  163  167
                               9   41   39    3  329  331     0,-12,L       -1,10,L       8   92  -90
9   30  -37      0,-1,L        7  120 -123    2  467  479                                 7   74  -78
7  151 -154                    5  133 -131    1  388  392    5   52  -53    4   40   36
6  103 -104     9   57  -53    4  171 -168                  1   64   62    3   52  -52
```

```
 -1,6,L

6   48  -51
4   94   98
3  317  327
2  315  318
1  492  508

 -1,5,L

6  176  178
5  161  166
4  199  203
3  431  438
2  191  204
1   38   46

 -1,4,L

8   53   56
7   98  100
6  123  126
5  203  209
4  221  228
3   98  105
2   74   73
1  216  217

 -1,3,L

8   62   59
7   65   67
5   46  -41
4   77   76
3   48   47
```

```
2   16  -10
1  226 -235

 -1,2,L

7   68  -69
6  129 -133
5  115 -113
4  159 -164
3  417 -415
2   19   15
1   70  -75

 -1,1,L

9   42  -39
8   91  -89
7   95  -96
6   71  -67
5  127 -122
4  184 -174
3  193 -188
2  297  294
1  656  690

 -1,0,L

9   41  -45
8  101  -97
7  135 -131
5   72   66
4  336  322
3  561  534
2  525  508
1  835  860
```

```
-1,-1,L

9   28  -34
8   39  -43
6  144  141
5  175  168
4  350  344
3  789  769
2  460  448
1  163 -156

-1,-2,L

8  188  187
7  170  166
6  162  160
5  180  171
4  265  265
3  294  299
2   92   95
1   97  189

-1,-3,L

8   72   69
7  165  165
6  165  159
5  198  200
4   47   43
2  108 -113
1  195 -202

-1,-4,L

8   33   24
```

```
6   86  -86
5   95   95
4   60  -59
3  275 -274
2  146 -155
1  199 -201

-1,-5,L

7   78  -80
6  179 -179
5   96  -98
4   46  -48
3  125 -121
2  151 -153
1   60  -59

-1,-6,L

8   53  -57
7   38  -40
6   50   46
5   56  -57
4   35  -35
3  147  148
2  374  378
1  274  273

-1,-7,L

6  130  129
5  108  109
4  245  248
3  267  271
2  232  233
```

```
1  180  186

-1,-8,L

7   57   56
6  146  148
5  118  120
4  204  203
3  128  126
1   37  -39

-1,-9,L

7   93   95
6   79   78
5   47   50
4   32   31
2  111 -112
1  205 -206

-1,-10,L

5   53   57
4   37  -34
3  117 -118
2  140 -139
1  151 -152

-1,-11,L

4   82  -79
3   69  -67
2   74  -70
1   70  -71
```

```
-1,-12,L

4   43  -43
2   45   41

-1,-13,L

2   45   39
1   45   42

-2,14,L

1   62   58

-2,13,L

3   74   76
2   95   98
1   83   83

-2,12,L

4   62   65
3   91   93
2  159  158
1  123  120

-2,11,L

5   68   71
4   96   93
3  127  126
2  106  108
1   96   95
```

```
-2,10,L

6   37   40
5   96   96
4   77   80
3   36   38

 -2,9,L

5   36  -36
4   39  -38
2  138 -140
1  122 -121

 -2,8,L

7   42  -46
6   52  -52
5   87  -87
4   74  -72
3   64  -63

 -2,7,L

7   62  -61
4   26   23
3   43   42
2  293  292
1  366  369

 -2,6,L

5   92   94
```

```
 -2,6,L

4  252  255
3  268  275
2  342  348
1  157  169

 -2,5,L

7   58   57
6  105  107
5  213  216
4  238  243
3  230  239
2  183  197
1   48   45

 -2,4,L

8   70   73
7  166  165
6  144  146
5  181  184
4  122  127
3  247  245
2   59   52
1  184 -186

 -2,3,L

8   66   63
7   78   75
6   66   64
5   67   67
3   48   39
```

```
2  444 -451
1  280 -289

 -2,2,L

7   43  -46
6   35  -31
5  113 -109
4  282 -274
3  272 -264
2  196 -195
1   81  -84

 -2,1,L

7   87  -84
6   79  -81
5   87  -83
3  196 -187
2   81  -81
1  133  137

 -2,0,L

8   33  -33
7   39  -37
5  113  108
4  297  280
3  204  203
2  472  443
1  155  150

 -2,-1,L

7   61   61
```

```
6  108  110
5  182  179
4  296  286
3  395  378
2  598  587
1   93  -89

 -2,-2,L

8   59   60
7  170  164
6  184  177
5  183  177
4  123  121
2  167 -158
1  158 -156

 -2,-3,L

8  166  164
7  125  123
6  168  166
5   66   64
4  123 -114
3   78  -82
2  432 -419
1  435 -434

 -2,-4,L

8   42   41
7   26  -25
6   73  -69
5   28  -29
4   48  -45
```

```
3  174 -175
2  508 -506
1  350 -349

 -2,-5,L

7   47  -47
6  107 -105
5  162 -157
4  166 -161
3  131 -128
2  139 -138

 -2,-6,L

5   39  -31
4   65  -65
2  173  173
1   21   25

 -2,-7,L

6   56   58
5  160  159
4  124  126
3   19   21
2  133  132
1  123  122

 -2,-8,L

7   58   62
6   75   79
5   72   73
4  100  100
```

```
3   67   71
1  146 -147

 -2,-9,L

6   59   61
4   41  -36
3   76  -77
2  154 -158
1  212 -212

 -2,-10,L

5   64  -62
4   77  -72
3  136 -132
2  171 -170
1  117 -114

 -2,-11,L

4   61  -63
3   65  -63
2  105 -107
1   56  -56

 -2,-12,L

3   40  -43
1   58   56

 -3,13,L

2   85   82
1  100   98
```

```
 -3,12,L

4   55  -55
3  122  119
2  121  117
1   77   73

 -3,11,L

4   90   90
3   88   86
1   31  -36

 -3,10,L

5   72   71
4   53   49
2   61  -60
1  159 -160

 -3,9,L

5   36  -34
3   72  -73
2  159 -163
1  232 -239

 -3,8,L

6   43  -42
5   48  -45
4  126 -130
3  169 -178
2   58  -56
```

```
 -3,7,L

3   28   28
2   82   85
1  159  162

 -3,6,L

7   32  -35
6   52   51
5  113  119
4  184  192
3  202  206
2  114  118
1  144  148

 -3,5,L

7   69   71
6  138  142
5   91   93
4  132  134
3  160  164
2  106  100
1  160 -156

 -3,4,L

8   88   89
7  116  117
6  129  131
5   78   76
4   36   38
```

```
 -3,4,L

3   72  -72
2  199 -201
1  404 -404

 -3,3,L

8   45   42
7   70   73
4   75  -77
3  223 -216
2  363 -362
1  444 -456

 -3,2,L

6  199 -100
5   87  -84
4  273 -269
3  331 -325
2  320 -315
1  314 -312

 -3,1,L

8   23  -23
7   44  -47
6  155 -152
5  145 -134
4  148 -142
3  142 -142
2  264 -251
1  163  156

 -3,0,L

8   34  -31
7   61  -54
5   46   45
4   82  -81
3  259  248
2  226  218
1   48   51

-3,-1,L

8   22   24
7   53   50
6  132  134
5  101  103
4  181  179
3  113  112
2  139  139
1  110  109

-3,-2,L

8   67   68
7   74   75
6  125  127
5   34   32
4   27  -19
3  178 -172
2   64  -67
1  214 -213

-3,-3,L

8   32   39

7   48   51
6   30   28
4   63  -64
3  244 -242
1  572 -570

-3,-4,L

6   98  -92
5   79  -74
4  166 -163
3  240 -235
2  269 -267
1  272 -270

-3,-5,L

6  138 -138
5  184 -184
4  194 -194
3   70  -72
2  101  -98
1  174  174

-3,-6,L

7   60  -57
6   45  -40
5   39  -36
4   94  -91
2   61   64
1  200  199

-3,-7,L

5   85   89
4  122  120
3   46  -45
1  125  124

-3,-8,L

6   53   56
4   32   29
3   35   35
2   18   16
1  180  -79

-3,-9,L

5   32  -33
4   45  -47
3   82  -82
2   39  -38
1  110 -112

-3,-10,L

4   83  -80
3  113 -113
2   99  -96
1  112 -113

-3,-11,L

3   53  -52
2   42  -42

-4,13,L

2   53  -55
1   51 -148

-4,12,L

2   65   64

-4,11,L

4   49  -44
1   91  -87

-4,10,L

2  156 -159
1  245 -253

-4,9,L

5   73  -70
4  122 -121
3  114 -117
2  230 -238
1  157 -158

-4,8,L

6   52  -56
5  111 -117
4  163 -168
3  135 -134
2  155 -150

-4,7,L

6   61  -66
4   21   23
3   66  -64
1   95   95

 -4,6,L

5   63   68
4  119  119
3   79  -79
2  131  134
1   32   25

 -4,5,L

7   52  -54
6  149  150
5   54   53
2  178  180
1   45  -40

 -4,4,L

7   63   62
6   73   74
4   41  -42
3   87  -87
2  247 -246
1  349 -349

 -4,3,L

6   34   35
5   38  -39
4  161 -157

3  281 -273
2  420 -422
1  321 -313

 -4,2,L

7  145  -43
6  115 -113
5  249 -247
4  229 -224
3  151 -147
2  244 -237

 -4,1,L

7  106 -104
6  164 -164
5  116 -116
4   79  -79
3   86  -83
2   30  -33
1  158  158

 -4,0,L

3  102  101
2  153  159
1  123  124

-4,-1,L

5  121  122
4   75  -70
3   65  -63
```

```
-4,-1,L

2  266  263
1  263  252

-4,-2,L

7   38   34
6   49   51
5   24   25
2  194  -92
1  117 -114

-4,-3,L

5   49  -54
4   95  -97
3  185 -181
2  238 -239
1  334 -332

-4,-4,L

6   65  -64
5  163 -161
4  111 -110
3  146 -148
2  153 -147
1   25  -20

-4,-5,L

6   87  -90
5  140 -140
4  105 -102
```

```
2  142  140
1  166  164

-4,-6,L

6   36  -41
4   27   27
3   38   35
2   54  -53
1  161  159

-4,-7,L

5   83   84
4   50   46
3   67   63
2  103  102
1  141  144

-4,-8,L

4   60   55
3  120  122
2   43   45

-4,-9,L

3   53  -54
1   33  -32

-4,-10,L

2   60  -61
```

```
-5,13,L

1   68   67

-5,12,L

1   67   68

-5,11,L

3   36  -37
1   91  -91

-5,10,L

4   41  -41
3  116 -116
2   87  -85
1  172 -172

-5,9,L

4  130 -131
3  131 -133
2   51  -49
1  109 -105

-5,8,L

5  101 -103
4  109 -111
3   78  -80
2   65  -67
1   38   39
```

```
-5,7,L

5   45  -44
3   61  -61
2   80  -77
1  103   99

-5,6,L

4   72   71
3  142  144
2  120  119
1  329  332

-5,5,L

6   31   33
5   46   43
4   53   50
3  111  110
2  147  149
1   39   39

-5,4,L

6   33   30
5   63   63
4   21  -19
3  248 -250
2  154 -157
1  137 -136

-5,3,L

5   79  -81
```

```
4  161 -164
3  159 -162
2   23  -16
1  268 -269

-5,2,L

6  124 -125
5  126 -131
4   65  -65
3   43  -45
2   22   20
1   22   19

-5,1,L

6   50  -51
5  105 -104
4   74  -75
3   62   61
2   51   51
1  236  232

-5,0,L

4   79   77
3  161  160
2  126  125
1  374  370

-5,-1,L

6   46   43
5  103  102
4  150  151
```

```
3  181 -176
2  144  139
1  264  260

-5,-2,L

6   43  -38
5   79   74
4   53   50
1   65  -63

-5,-3,L

4   93  -97
3  112 -114
2   71  -70
1  184 -181

-5,-4,L

5   67  -67
4   76  -79
3   54  -52
2   84   81

-5,-5,L

5   50  -55
3   69   67
2   59   58
1   62   62

-5,-6,L

4   53   48
```

```
3   39   31
2  102   99
1  230  230

-5,-7,L

4  114  111
3  140  140
2  172 -173
1   64  -65

-5,-8,L

3   48   46
2   23   29

-6,12,L

1   58   55

-6,11,L

2   33  -33

-6,10,L

3   49  -48
2   49  -53

-6,9,L

4   58  -60
3   54  -57
2   27  -23
```

```
  -6,8,L

3   46   -52
2   50    49
1   41    40

  -6,7,L

4   23    21
3   69    69
2  139   136
1  155   159

  -6,6,L

5   35    35
4  101    99
3  196   196
2  235   236
1  115   117

  -6,5,L

5   58    55
4  102    99
3   83    88
1  137   133

  -6,4,L

5   27    26
3   51   -57
2  116  -115
1   30    25

  -6,3,L

3   42   -37
2  103  -101
1   87   -89

  -6,2,L

5   40   -38
4   61   -61
2  113   115
1   46    47

  -6,1,L

4   23   -20
3   44    42
2  208   211
1  153   156

  -6,0,L

5   50    51
4   95    93
3  151   151
2  207   208
1   85    84

  -6,-1,L

5   92    93
4  161   161
3  138   138
2   37    38
1   62    58

  -6,-2,L

5   30    30
4   43    40
3   38    40
2   66   -68

  -6,-3,L

4   28   -25
3   58   -60
2   94   -97

  -6,-4,L

4   48   -47
3   47   -42
1   50   -48

  -6,-5,L

2   80    82
1   62    65

  -6,-6,L

3   66    69
2  108   111

  -6,-7,L

2   32    30

  -7,10,L

2   37   -37
1   68   -69

  -7,8,L

2   51    50
1   95    91

  -7,7,L

3   82    84
2  105   104
1  117   114

  -7,6,L

4   53    54
3  130   130
2  129   128
1   63    63

  -7,5,L

4   73    70
3   54    57
2   36    37

  -7,4,L

3   29   -31
2   88   -87
1  134  -133

  -7,3,L

3   55   -52
2  102   -98
1  141  -141

  -7,2,L

4   26   -25
3   48   -41
1   99    98

  -7,1,L

3   45    46
2   99   103
1  137   139

  -7,0,L

4   67    71
3   81    84
2   58    53

  -7,-1,L

4   47    49
3   66    64
2   46    48
1   69   -66

  -7,-2,L

2   44   -44
1  135  -137

  -7,-3,L

3   88   -89
2  105  -104
1   90   -92

  -7,-4,L

2   68   -68

  -7,-5,L

1   58    60

  -8,9,L

1   34   -32

  -8,7,L

2   77    80
1   43    42

  -8,6,L

2   43    44

  -8,5,L

2   30   -31
1   41   -38

  -8,4,L

2  102  -103
1  141  -138

  -8,3,L

3   66   -61
2  106  -110
1   96   -97

  -8,1,L

1   37    39

  -8,0,L

2   34    37

  -8,-1,L

1   62   -66

  -8,-2,L

1   65   -65
```

APPENDIX II

Structure Factor List for compound II, Part II.

Columns listed are ℓ, $|F_o| \times 10$, $F_c \times 10$.

```
 -12,0,L         -10,0,L           1  208  188     6  376 -384     3  105  -78     3   92   87      -8,4,L
                                   3  220 -198                     5  167 -147     5  294 -295
  0  176 -182     -6  146 -135     4  137  155      -9,2,L                         6  164 -176     -6  151  161
  2  110 -122     -4  283 -295     5  161 -132                      -9,5,L         7  299 -308     -4  199 -185
                   0  239  236     7  101  102     -6  102  129                    9  146  155     -3  121 -122
 -12,1,L           2  144  138                     -5  211 -211    -4  120 -127                    -1  145 -152
                   4  148 -155    -10,4,L          -3  215 -228     0  107   93     -8,2,L          0  164  168
  1  152 -168                                      -1  197  199     4  140 -122                     2  288  279
                 -10,1,L          -2  125  119      1  523  522                    -8  169  160     3  181  174
 -11,0,L                           0  107  121      2  113   92     -9,6,L         -4  295 -295     6  242 -241
                  -5  172 -195     1  147 -136      4  106  100                    -3  133 -110     7  127 -129
  1  107  -81     -3  149 -133     4  201 -187      5  323 -315    -1  181  154    -2  139 -131
                  -1  181  199     5  131  127      7  113 -125     3  112 -117    -1  169 -176      -8,5,L
 -11,1,L           0  181 -160                      9  171  156                     0  315  297
                   1  172  189    -10,5,L                           -8,0,L          1  176  165     -3  269 -269
  2  130 -122      3  162 -144                      -9,3,L                          2  421  411     -2  102  -77
  6  143  112      5  181 -171    -1  168  173                     -8  236  245     3  236  218     -1  122 -110
                                   0  103  -72     -6   99  -64    -6  163 -171     6  316 -331     1  169  176
 -11,2,L         -10,2,L           3  180 -172     -4  257 -270    -4  404 -414     7  143 -141     2  143  128
                                                   -3  200 -214    -2   98   63    10  162  153     3  117  117
 -1  112   73     -5  116  120     -9,0,L          -1  108 -122     0  256  264                     7  111  -97
  0  107 -140     -4  185 -163                      0  219  236     2  326  305     -8,3,L
  3  179 -187     -2  125   85    -5  183 -196      2   98  101     4  227 -230                      -8,6,L
                  -1  139 -112    -3  372 -379      3  114   92     6  404 -422    -5  130 -112
 -11,3,L           0  263  249    -1  170  173      4  134 -145    10  275  265    -3  346 -339    -4  110  -85
                   1  124  -85     1  468  476      5  109   97                    -2  197 -183    -2  221 -228
 -2  161  185      4  214 -207     5  343 -347      6  222 -208     -8,1,L          1  434  438     2  248  252
  0  104   70      5  166  116     9  245  240      8   94   97                     2  161  159     6  128  -95
  2  186 -174      8  114  116                                     -8  132   80     4  148  169
  4  120  -66                      -9,1,L           -9,4,L         -5  252 -252     5  225 -230      -8,7,L
                 -10,3,L                                           -3  297 -298     6  149 -135
 -11,4,L                          -4  336 -334     -5  124 -101    -1  240  241     7  177 -163     1  140  170
                  -5  122 -121     0  369  369     -2  150 -139     0  120  -96     9  116  184
  1  103  -47     -1  203  183     2  332  330     -1  128  107     1  411  412
  2  110  -72      0  128 -131     4  334 -325      1   97  104     2  264  265
```

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  -7,0,L

-3  351 -362
-1  118  129
 1  211  195
 5  325 -356
 7  255 -267
 9  137  134

  -7,1,L

-5  110 -119
-4  196 -196
-2  208 -188
-1  202  189
 0  253  262
 1  151  152
 2  497  496
 4  135 -147
 6  220 -212
 7  119  -69
10  108  112

  -7,2,L

-9  122  125
-7  130  122
-4  274 -282
-3  389 -412
-1  149 -159
 0  106   96
 1  435  432
 2  105  101
 3   94  102
 5  104 -108

 7  225 -224
11  114  125

  -7,3,L

-8  171  181
-6  166  189
-4  165 -199
-3  174 -191
-2  242 -248
-1  135  133
 1  204  185
 2  386  364
 4  159  147
 6  247 -251
 7  107 -119
 8  154 -152

  -7,4,L

-7  177  181
-5  100   71
-4  139 -147
-3  257 -269
-1  186 -201
 0  178  194
 1  152  154
 3  384  380
 7  332 -336

  -7,5,L

-6  188  184
-5  167 -179
-4   96 -115

-2  279 -294
 0  117 -120
 2  380  368
 4  255  254
 5   98  -86
 6  220 -208
 8  192 -221

  -7,6,L

-5   96  109
-3  291 -303
-1  275 -292
 1  107  109
 2   98   89
 3  334  331
 7  255 -264

  -7,7,L

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 2  349  339
 4  172  179

  -6,0,L

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-4  184  189
 0  296 -288
 2  220  220
 4  200  217
 6  115 -134
 8  240 -239

  -6,1,L

-9  188 -179
-7  105   98
-6  118 -128
-5  333  329
-4  190 -188
-3  106  -99
-1  267 -272
 1  268 -263
 2  465  442
 3  404  401
 5  241  256
 6  119 -151
 7  235 -230
 8  103   79

  -6,2,L

-10 159 -174
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-7  106  -88
-6  242  256
-5  136 -135
-4  268  260
-2  439 -443
-1  148  163
 0  608 -608
 1  175  197
 2  310  317
 3  116 -119
 4  273  272
 5  280 -267
 8  178 -174
 9  174  165

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-6  152 -161
-5  361  363
-3  172 -160
-2  133  165
-1  420 -425
 0  347  331
 1  205  208
 3  345  334
 4  246 -269
 5  130  139
 6  163 -182
 7  249 -255
 8   93  117
 9  162 -163
10  116  132

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-4  165 -159
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 2  424  404
 4  297  292
 5  195 -193
 6  163 -161
 8  207 -202

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-2  434 -443
-1  174  163
 0  614 -608
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 2  307  317
 3  130 -119
 4  261  272
 5  271 -267
 8  192 -174
 9  175  165

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-4   81  -89
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 3  347  334
 4  278 -269
 5  155  139
 6  175 -182
 7  241 -255
 9  144 -163
10  116  132

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 1  296  287
 2  405  404
 3  188  -95
 4  299  292
 5  198 -193
 6  166 -161
 8  205 -202
 9  132   99

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 3  453  444
 4  132 -127
 5  111  121
 6  114 -109
 7  281 -273
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   -6,6,L

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 1  294 -107
 2  334  334
 4  211  229
 8  283 -267

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-3  215 -224
-1  262 -259
 3  291  301
 5  152  134
 7  204 -195

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 0  122 -120
 2  169  177
 4  172  180

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 5  809  836
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11  255 -227

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-2  331 -336
-1  160  175
 0 1010-1027
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 2  175 -185
 3  141 -129
 4  382  398
 6  412  443
 7  157  124
 8  252 -253
10  316 -287

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-3  269  268
-2  267  279
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 0  133 -128
 1  528 -515
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 4  295 -296
 5  527  538
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 9  228 -236
11   95  -60

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 2   68   55
 3  307 -310
 4  455 -480
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 6  212  210
 8  253 -257
 9  107  118
10  209 -202
11  111   99

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-6  106 -108
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-1  347 -349
 0  257 -253
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 4  146 -153
 5  413 -417
 7  250 -254
 9  192 -199

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-3  124 -108
-2  172 -192
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 4  325  319
 5  132 -135
 8  258 -271

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 2  137  131
 3  280  277
 5  147 -111
 7  130 -135

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 0  232 -240
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 2  138 -139

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-1  131 -136
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 5  114  143

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12  113  -94

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-4   70  -53
-3  477  478
-2  159  151
-1  398 -393
 0  640 -598
 1 1498-1553
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 4   87  -96
 5  781  816
 7  145  139
 8  184  174
 9  332 -338
11  287 -287

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-7  165 -146
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-4 1018 1005
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-2  257  266
-1  287  273
 0 1012 -994
 1  307 -308
 2  288 -284
 3  140 -141
 4  331 -339
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 8  147 -148
 9  105  116
10  358 -340
11  111  -87

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-4  232  227
-3  350  353
-2  264  258
-1  337 -328
 1  616 -598
 2  268 -272
 4  128 -130
 5  490  514
 6  146  148
 7  155  157
 8  184 -109
 9  215 -193
11  132 -146
12  102  -63

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-7  148 -155
-4  310  317
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 6  267  276
 7  131  106
10  211 -192

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-7  122 -110
-5  138  121
-4   84  293
-3  164  133
-2  140  150
 1  467 -470
 5  252  256
 8  112  186

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-6   92 -110
-4  330  327
-2  102  109
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 2  101  -89
 6  212  209

 8  109  -74

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-7  100  -60
-3  153  162
 1  232 -221
 2  122  121

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-3  123 -133
 0  137 -131
 4   94  106
 6  169  138

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   -3,0,L

-9  273 -267
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-1  442 -428
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 9  152 -150
11  322 -318

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 3  356 -347
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 7  104  104
10  272 -282
12  117 -108

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-10  112 -108
-9  127 -130
-8  106 -113
-7  233 -227
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-4  283  282
-3  576  571
-2  161  162
-1  256  243
 0  370 -357
 1  502 -494
 2  113 -125
 3  282 -273

 5  177  173
 6  315  326
 7  308  324
 8  104   98
 9  156 -162
10  133 -115
11  244 -241

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-8  261 -265
-7  120  -83
-6  215 -216
-5  282  270
-4  395  401
-3  166   56
-2  389  377
-1  193 -185
 0  449 -448
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 2  548 -555
 3  170 -159
 5  323  345
 6  545  560
 7  106  129
 8  157  161
 9  101  -89
10  186 -186
11   96  -85
12   91  -71

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-11  147  141

-9  237 -226
-8  161 -142
-7  247 -254
-5  285  306
-4  224  221
-3  523  513
-2  128  126
-1  316  314
 0  216 -228
 1  755 -759
 2  412 -405
 3  410 -403
 5  347  364
 6  222  219
 7  257  262
11  196 -195

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-6  286 -269
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 1  257 -274
 2  567 -580
 4  137 -137
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 6  357  369
 7  182  161
 8  157  160

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-1  303  300
 0  136 -151
 1  395 -388
 3  286 -286
 7  255  267

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-6  247 -249
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-3  141 -147
-2  345  341
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 2  278 -272
 4  144 -152
 6  269  264
 8  124  108

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-2  135 -101
 1  323 -328
 2  126  131
 3  203 -195
 4   98  -53
 5  148  123
 7  157  154

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-2  169  174

 2  201 -218

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-8  122 -131
-6  172 -146
-2  523 -495
 0  725  724
 4  649 -648
 6  186  178
10  114   89
12  113 -114

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-11  169  154
-10  171 -175
-9  106  -73
-8   98  109
-6  185  189
-5  188 -202
-3  294  285
-2  263  240
-1  747  772
 0  197 -189
 1   71  -67
 2  246  257
 3  167  156
 4   80   81
 6  128 -126
 7  326  322
 9  102  196
11  155 -144
```

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-10  129  105
 -9  125 -154
 -8  144 -146
 -7  136  154
 -6  503 -484
 -5  150  144
 -4  193  167
 -3  222 -216
 -2  115  158
  0  306 -301
  1  635 -616
  2  105 -126
  3  111  105
  4  271 -274
  5  302  315
  6  291  289
  7  281  158
  8  104  111
 10  114 -119
 11   94  -98
 12  108 -100

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-12  102  -73
-11  215  204
-10   93 -125
 -8   95   71
 -7  352 -341
 -6  178  192
 -5  227 -217
 -4  302  300
 -3  604  606
 -2  265 -233
 -1  580  558
  0  398 -367
  1  310 -296
  2  219 -209
  3  458 -469
  4   88  115
  5   92  -93
  6  395  418
  7  336  338
  9  137  145
 10  183 -185
 11  154 -139

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-11  139 -131
-10  134  125
 -8  256 -266
 -7  114  138
 -6  463 -469
 -5  283  260
 -4  198  210
 -2  714  702
 -1  367 -363
  0  239  229
  2  854 -864
  4  431 -441
  5  228  236
  6  332  336
  7   83   82
  8  363  357
  9  150 -144
 12  200 -189

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 -7  340 -323
 -6  192  177
 -5  162 -148
 -3  634  626
 -2   95  -88
 -1  661  672
  0  126 -134
  1  567 -576
  3  568 -589
  4  113  107
  7  426  443
  9  189  162
 11  202 -168

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 -9  117  -89
 -8  216 -203
 -6  451 -449
 -5  135  126
 -4  222  218
 -2  488  484
  2  590 -608
  3   88   50
  4  342 -350
  6  332  340
  8  206  202

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 -5  243 -255
 -4  109   93
 -3  426  431
 -1  480  474
  1  217 -218
  2   96   50
  3  314 -334
  6   97   73
  7  355  349
  9  113  105

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  2  408 -426
  4  257 -272
  6  217  197

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  1  141 -120
  3  242 -251

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 -7  252 -247
 -5  850 -869
 -3  636  651
  1   78  -72
  3  143 -130
  5  681 -704
  9  266  260
 11   89   70

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 -6  833 -851
 -5   70   67
 -4  424 -398
 -3  147 -139
 -2  450  443
 -1  251  242
  1  178 -182
  2  379 -383
  3  580  577
  4  619 -635
  5  118  123
  6  116 -129
  7  133 -150
  8  151  166
 10  294  281
 11  110 -107

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 -6  221  220
 -5 1112-1140
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 -2  758 -763
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  0  660 -629
  1  368  371
  2  583  587
  3  224 -246
  4  204  203
  5  589 -622
  7  330  338
  8  174 -168
  9  301  309

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 -8  112  113
 -7  162  144
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 -5  548  559
 -4  188 -172
 -3  213 -198
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 -1 1087-1044
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  2  382 -381
  3  435  432
  4  706 -745
  5  187  185
  7  105 -119
  8  281  294
  9  127 -133
 12  119 -129

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 -5  306 -293
 -4  309  307
 -2  266 -236
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  2  212  208
  3  641 -670
  4  316  321
  5  153 -162
  7  326  345
  8  116 -100
  9  264  271

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 -8  116 -104
 -6  216 -205
 -2  319  315
 -1  198 -177
  0  663  656
  1  258 -263
  2  516 -527
  3  129  148
  4  544 -564
  5   89   85
  6  106  120
  7   99 -116
```

```
  -1,5,L        0  136  151       -1,9,L        -7  158  145       0,3,L         -2   63   66       0,7,L
                1  144 -137                     -5 1321-1344                     -1  171 -181
 8  266  264    2  222 -234    -2  183  180     -4  602 -570    -9  326  308      0  865  874    -9  131   96
                3   98  -99    -1  149  166     -3  928 -916    -8  189  185                     -5  253 -249
  -1,6,L        4  279 -283     0  187  181     -2  376 -355    -6  201 -190        0,5,L        -4  196  188
                6  128  151     2  125 -129     -1 1004 1070    -5  725 -721
-5  315 -315    8  229  234     4  197 -187     13  105  -81    -3  230 -232     -9  107  115       0,8,L
-3  216  211                                                    -2  111   86     -6  138  138
-2  108  107      -1,8,L          0,0,L            0,2,L        -1  591  572     -5  280 -270    -5  102   71
-1  359  343                                                                     -4  200 -202    -4  121 -135
 2   89   79   -7  149 -145   -10  479  476    -10  258  270       0,4,L         -2  115 -129     0  333  319
 3  306 -288   -6  106 -108    -8  252  236     -9  141  129                     -1  116  121
 4  179  190   -5  122 -107    -6  469 -476     -8  370  371   -11   98  -70      8   96 -105       0,9,L
 5  257 -269   -4  108  110    -4 1250-1310     -7  275  267   -10  250  253
 7  381  400   -3  169  168    -2  240  222     -6  287 -267    -9  150  156        0,6,L        -5  122 -108
 9  130  179   -1  280  282                     -5  166 -167    -8  169  147                     -1  176  154
                3  224 -239       0,1,L         -4  719 -693    -7   97   99     -8   97   64     3  113 -110
  -1,7,L        4  171 -177                     -3  238 -223    -6  291 -284     -3   91  -53
                5  111 -125   -11  140  139     -2  323  311    -5  142 -125      0  151  189
-6  219 -198    6  109  109    -9  411  399     -1  526  529    -4  401 -400
-2  200  186    7  104  120    -8  203  200      0 1055 1092    -3  113 -121
```

APPENDIX III

Structure Factor List for compound III, Part II.

Columns listed are ℓ, $|F_o| \times 10$, $F_c \times 10$.

```
  -10,0,L          -9,1,L            2  224  239     10  134 -123     11  121  -94      6   73   72     -1  121 -123
                                     4  138  120     11   71   68                       7   58  -46      0   65  -63
 -4   75  -45     -8   95  -72      8  167 -168     16   89   74      -7,1,L           9  149 -144      2  110 -119
  0  104  101     -6   82 -114     10  251 -239                                       10   88   91      3  139  140
  2   84   70     -4   93  -96     12   88  -75      -8,3,L         -10   78   66     11  171 -156      4   63  -67
                   0  159  149     14   72   69                      -7   75   79     13   66  -81      5  226  243
  -10,1,L          2  151  164     16  114  108     -5  113 -111     -6   73  -71     17   95   96      7  101  102
                   4   76   78                      -3  102 -101     -5   69   66                      11  108 -126
 -1   84   74      8  180 -163      -8,1,L           0   63  -41     -4  122 -119      -7,3,L          13   93  -84
  1   87   76     10   81  -94                       1  109   92     -2   91  -97
                                    -7  120 -102      2  119 -118     -1  104  -91    -12   78   74      -7,5,L
  -10,2,L          -9,2,L           -5  159 -148      3  166  167      0   69   63    -10  104  104
                                    -3   83  -70      7   78  -74      2  211  220     -9   67   47     -8   78   75
 -1   68   31     -5   72  -74     -1  101   96      9  106 -101      4  124  126     -7   81   91     -5   71   53
  7   73  -52     -1   66   64      1  174  187                       8  121 -117     -6   74  -68     -4  145 -140
                   1   99  113      3  133  147      -8,4,L          10  150 -149     -5  108  110     -2  128 -138
  -10,3,L          3   74   72      5   73   57                      11   70   70     -4  163 -168     -1   81  -72
                   7   74  -83      6   60  -58     -4  102 -109     12   63  -63     -2  170 -178      0   76  -54
  5   90  -45      9   87  -75      7   90  -95      2   85   79     16   70   80      0   72  -76      1   71  -72
  8   75  -52     13   72   47      9  213 -192      4   94   95     18  105   81      1  124 -122      2   79   73
                                   10   76   83     10   65  -35                       2  125  126      4  165  165
  -10,4,L          -9,3,L          11  117 -118                       -7,2,L           3  110 -116      6  124  110
                                   15   93   87      -8,5,L                            4  238  260     10   75  -72
  3   70   39      0   68   51                                      -11   71   87      6  120  134     12   91  -91
  6   80  -55                       -8,2,L           3   65   55     -9   68   49      7   87   87
                   -9,4,L                            6   69   31     -8   74   89      9   80   76      -7,6,L
  -9,0,L                           -6  100  -93     12   79  -55     -6  152  148     10  118 -133
                   7   70  -50     -5   66   74                      -5   93 -110     12  168 -157     -3   67  -74
 -7  112 -119                      -4  101 -107      -7,0,L          -3  191 -198                      -1   89  -66
 -5  120 -122      -8,0,L           0   91   89                      -2   72  -68      -7,4,L           3   99   78
 -1  108  100                       2  156  167     -9   69   62     -1   85  -70                       5   81   58
  1  203  201     -8   71  -74      3   89  -84     -3  111  -91      1  160  175    -11  107   97
  3  133  147     -6  163 -149      4  106  -97      1  116  108      2  135 -149     -9  119  117
  7  159 -153     -4  126 -129      5   71  -89      3   69   79      3  267  267     -5  162 -151
  9  178 -170      0  196  204      8  127 -135      9  150 -141      5  114  132     -3  208 -206
```

```
  -6,0,L          10   79    64   -11   81    80     3  120  -120     6   82    83    -5   88    78     4  136  -122
                  11  149  -157    -9  115   113     4  131   143    12   88   -76    -4  230   223     5  278   290
-12  112  -113    13   69   -58    -8   69    84     6  244   252                     -2  382  -397     6  191   178
-10  111   107    14  103  -106    -7   70    50     7   98   101      -6,7,L         -1   80   -82     7  330   312
 -8  280   287    19   75    55    -6  148   137     8   95    98                      0  630  -652     8  234   251
 -6  185   183                     -5   74   -59    10  113  -107    -1   69   -77     1  189  -192     9  155   167
 -4   75   -97      -6,2,L         -4   84    83    12  206  -194                      2  297  -305    10   92    82
 -2  189  -185                     -3  219  -234    14   79  -106      -5,0,L          3  277  -269    13  156  -172
  0   88  -112   -10  130   115    -2  101  -106    17   75   -46                      4   54   -53    14  130  -123
  2   98   -83    -9   77    88    -1  219  -235                    -15  155  -147     5   58   -59    15  180  -185
  6  196   191    -8  104   108     0  165  -163      -6,5,L        -13  218  -233     6  347   350    16  133  -134
 10  187  -180    -7  198   189     1   89   -74                    -11  145  -135     7  227   214
 12  100   -90    -6   65    74     2  220  -235    -9   98    92    -9  299   310     8  572   556      -5,3,L
                  -5  122   121     3  276   283    -7   87    74    -7  581   555     9  187   181
  -6,1,L          -4   90   -97     4   95   -87    -5   82   -71    -5  356   357    10  122   109   -10  103    69
                  -3  121  -127     5  356   350    -4   93    82    -3  145  -129    12  203  -200    -8   96   105
-15   90   -98    -2  286  -290     6  145   160    -3  187  -190    -1  544  -530    14  161  -169    -6  162   173
-14   70   -35    -1  185  -189     7   75    78    -1  121  -127     1  617  -599    15   71   -88    -5  117   121
-13   93   -96     0  318  -316     8  184   181     2   79   -82     3  329  -308    16  110  -110    -4   78   -66
 -9  183   182     1  186  -196    11  144  -146     3   73    82     5  253   246                    -2  235  -237
 -8  102   113     3  181  -206    13  177  -184     4   72   -78     7  679   669      -5,2,L        -1  123  -125
 -7  172   175     4  381   395    17   74    52     5  188   193     9  401   398                     0  209  -217
 -6  142   150     5   83    82                      7  148   140    11  101   -91   -15  108  -122     1   94  -117
 -5   71    57     6  274   264      -6,4,L        11  107  -104    13  210  -214   -13  132  -130     2  184  -188
 -3  112  -114     7  234   249                     13  111  -124    15  125  -117   -12   66    42     4  184   203
 -2  238  -232     9  140   148   -10   80    77                     17   70   -66   -10   73    67     5   88    68
 -1  333  -327    10   81   -72    -8  109   115      -6,6,L                          -9  177   172     6  351   361
  0  227  -229    11  100    90    -7   93    70                       -5,1,L         -7  315   300     7  131   134
  1  118  -117    12  124  -118    -5   67    72    -5   68    66                     -5  169   172     8  134   145
  2   73   -81    14  136  -136    -4  170  -180    -4   80   -63   -16   83  -104    -3   73   -70     9  107   111
  3  158    67    15  117  -121    -3   96    79    -3   87    90   -14  192  -196    -2  158  -173    12  111  -120
  5  157   165    18   87    88    -2  154  -172    -2  141  -135   -12  136  -143    -1  421  -431    13   81   -66
  6  223   214                     -1   60   -34     0  123  -102   -10   85    91     0  172  -185    14  169  -180
  7  198   222      -6,3,L          0   78   -47     1   77   -75    -8  391   390     1  495  -518    15  121  -126
  8  193   201                      1  143  -139     4  149   150    -6  389   388     3   63   -60
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   -5,3,L         12   73  -90       -4,0,L           0  389  393      8  374  367       -4,4,L           -4,6,L
                  14  101  -76                        2  451  455     10  302  302
 16   73  -56                       -16   96  -85     3  495 -500     12   72   61    -14   81  -55    -11  102 -107
 18   72   46       -5,6,L          -14  164 -149     4  117 -121     14  206 -211    -12  133 -131     -9  122 -121
                                    -12  231 -247     5  105  121     16  218 -221    -10  109 -112     -6   75   73
   -5,4,L        -10  110  -99       -8  485  485     6  168 -168                      -7  126 -115     -5  149  152
                  -6   82   74       -6  492  518     7  596  603       -4,3,L         -6  169  166     -4   81   74
 -7   70   47     -4  124  130       -4  168  165     8  118 -104                      -4  144  139     -3  144  144
 -4  106  118     -2  141  141       -2  328 -334     9  725  700    -15   71  -63     -3  146  152     -1  106  126
 -3  124 -130     -1  143 -138        0  798 -794    10  119 -116    -14   98   71     -2  103 -103      0   88  -59
  0   91  -91      1  126 -134        2  574 -536    11  155  160    -13  183 -185      1  112 -104      2  108  -99
  2  110 -128      2  103 -105        4  395 -398    13  214 -232    -11  112 -117      2  191 -193      3  155 -162
  4   99  -77      4   79  -95        6  228  202    15  292 -285    -10   89   99      6  114  108      5  137 -164
  5  168  172      5  131  133        8  804  793    17  173 -185     -8  137 -137      8  106  120      6   76   72
  7  151  156      6  133 -119       10  538  514                     -7  264  264     12   78  -88      7   74  -85
  8  121  102      7   84   73       12  136 -127       -4,2,L         -6  205 -192     14   88  -91      8   79   53
 10  131  127     10   95   94       14  260 -269                      -5  451  443                      11  138  132
 11  143 -128     13   99  -70       16  246 -254   -15  104   87     -4  102 -100       -4,5,L         14   74  -47
 13  170 -159                        18  133 -130   -14  184 -189     -2   70   92
 15   68  -44       -5,7,L                          -13  104   89     -1  267 -250    -11   97  -85       -4,7,L
 16   75  -51                          -4,1,L       -12  187 -179      1  261 -281    -10  129 -136
                  -5   81   70                      -11   96  108      2   71  -48     -6   70   63    -10   89  -81
   -5,5,L         -3  137  120      -15  146 -141   -10   61  -63      3  206 -222     -4  113  119     -5   83   53
                  -2   85  -70      -14  101  114    -8  206  208      4  207  192     -2  184  181     -4  126  121
-11  106  -89     -1   73   70      -13  181 -177    -7  259 -251      6  187  193      0   77   97     -3   91   72
 -7   82   90      0  128 -131      -11  153 -158    -6  455  449      7  200  211      2   94  -98     -2  166  146
 -5   72   88      4   69   62      -10   78  -74    -5  274 -272     10   81  -83      3   75  -96      1  163 -163
 -4  105  -87      5   94  -96       -9  179  177    -4  500  467     11  113  108      4  249 -268      2  103 -113
 -3   89   80      6   80   75       -8   80  -89    -2   53   79     12   68   75      6  136 -159      3   84  -66
 -2   71  -81                         -7  464  451     0  767 -805     15  142 -146      7  125  121      4   91  -96
  3  165 -159       -5,8,L           -5  508  487     1  475  463     16   66  -83     10  111  119      6  104 -104
  4   70   64                         -4  152 -139     2  563 -584     17   80  -54     12   85   79      9   90  103
  5  127 -121     -4   90   57       -3  213  202     3  189  196                     13   70  -65     10   79   95
  6  113  130     -1   75  -59       -2  164 -153     5  319 -317                                      12   90   88
 11   67   93      7   73   60       -1  530 -539     6  264  266
```

```
  -4,8,L

 -1   80   71
  0   96  -73
  5   86  -88

  -3,0,L

-13  129 -125
-11  127 -128
 -9  219  195
 -7  322  299
 -5  140  107
 -3  278  303
 -1  690 -673
  1  653 -660
  5  150  139
  7  360  343
  9  707  702
 11  183  192
 13  178 -177
 15  221 -215
 17  279 -281

  -3,1,L

-15  123  129
-13  133  146
-12  153 -141
-10  160 -163
 -9  196 -193
 -8  181  183
 -7  198 -184
 -6  358  360
 -5  156 -151
```

```
 -4  167  165
 -3  248 -246
 -2  139  126
 -1   88  -87
  0  243 -248
  1  742  812
  3  674  663
  4  201 -215
  5   94  -80
  6  277  285
  8  469  435
  9  212 -213
 10  427  445
 11  238 -237
 12  102  -83
 13   97  -94
 14  182 -186
 15   89   87
 16  241 -233
 17   95   97
 18  124 -152

  -3,2,L

-16   98  105
-14  128  142
-13  171 -162
-12   90   95
-11  238 -229
 -9  189 -213
 -8  144 -163
 -7  145  153
 -6  496 -482
 -5  442  437
 -4  112  -99
```

```
 -3  596  599
 -1  119  119
  0  206  214
  1  593 -599
  2  752  800
  3  688 -736
  4  320  314
  5  365 -344
  6  278 -269
  7  215  205
  8  146 -164
  9  424  419
 10  258 -257
 11  293  286
 12  190 -189
 13   68   58
 14   78   77
 15  144 -155
 17  154 -153

  -3,3,L

-16   83   76
-15  147  130
-14  121 -126
-12  282 -280
-10  273 -280
 -8  100 -122
 -7  258 -266
 -6  430  429
 -5  254 -231
 -4  649  683
 -3   67   41
 -2  428  381
 -1  273  255
```

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  0  176 -186
  1   85   93
  2  485 -516
  3  127  110
  4  673 -687
  7  126 -105
  8  284  301
  9  248 -260
 10  257  237
 11  138 -140
 12  199  187
 13  122  137
 15   83   90
 16  140 -138

  -3,4,L

-13  161 -167
-11  275 -283
 -9  157 -159
 -8  163 -172
 -6  161 -165
 -5  537  559
 -3  406  435
 -2  142  138
 -1  148  159
  0  299  290
  1  276 -298
  3  588 -582
  4  149 -152
  5  208 -214
  6  122 -135
  7  103  107
  8   97  -86
  9  216  205
```

```
 11  195  191
 12  100  100
 14   99   90
 15   87  -74

  -3,5,L

-13   91   87
-12  158 -158
-10  161 -172
 -9   98 -106
 -6  165  152
 -5  101 -100
 -4  316  328
 -3   63   57
 -2  118  136
 -1  205  218
  0   65  -61
  1  206  225
  2  210 -218
  3  161  -40
  4  319 -322
  5  210 -208
  6  165  -69
  7  205 -208
  8  125  140
 10  176  177
 11  139  141
 12  198  199

  -3,6,L

-11  122 -102
-10   67  -70
 -9  115 -105
```

```
 -8  106 -110
 -5  150  154
 -4   67   39
 -3  161  143
 -2   89   92
  0  158  167
  1   89  -93
  4  205 -206
  5  127 -132
  6  164 -160
  8   70  -61
  9   84   80
 10   71   76
 11  116  109
 12  127  125

  -3,7,L

 -3  129  125
 -2   76   90
 -1  167  161
  2  111  -98
  3  133 -128
  5  101  -83
  7  102  -99
 10   72   77
 11  107  105
 13   85   80

  -3,8,L

 -8   69  -44
 -2   76   95
  6   69  -67
```

```
  -3,9,L

  5   77  -58

  -2,0,L

-18   82   90
-16  182  175
-14  115  113
-12  141 -121
-10  263 -249
 -8   87   90
 -6  252 -238
 -4  130 -135
 -2  112  109
  0  395  385
  4  207 -227
  6  237 -227
  8  265  254
 10  553  563
 16  101 -106
 18  140 -155

  -2,1,L

-17  125  124
-15  165  160
-14  161 -153
-13  377  -79
-11  278 -274
-10  201 -190
 -9  379 -372
 -8  140 -138
 -6   57  -41
```

```
  -2,1,L           -6  154  140      -6  428 -411      -4  666  655       0  172  187      12  128  128      -7  687 -642
                   -5  262 -253      -5  225  232      -3   53   45       1  106  -96      13   79   44      -5  235 -206
  -5  268  266     -4  688  690      -3  756  771      -2  461  480       2  184  178                        -3  713  741
  -4  116  129     -3  419  411      -2  769  836      -1  299  308       3  541 -552        -2,7,L           1  567  546
  -3  122  118     -2  518  495      -1  385  407       0  205  226       4   66  -58                         5  213 -205
  -2  484 -502     -1  602  627       0  350  345       1  223  227       5  456 -471     -10   80  154       7  980 -938
  -1  582  587      0   92   62       1   69   74       2  545 -558       6  179 -175      -9   98 -106       9  197 -205
   0  685 -726      1  381  397       2  278  276       3   66   55       7   71  -74      -7   73  -55      11  266  243
   1  353 -365      2   63   94       3  350 -357       4  834 -852       8  210 -205      -6   89  -86      13  284  296
   3  561 -600      3  158  162       4   97  104       5  103 -108       9  192  196      -5   64   73      15  169  187
   4  157  117      4  592 -601       5  766 -765       6  246 -252      11  259  267      -4   83  -89
   5  128 -127      5  261 -264       6  340 -331       7  201 -195      12   83   71      -3   90   91        -1,1,L
   6  466 -432      6  637 -664       7  400 -379       8  193  193      13  188  185       0   97  121
   7   84   81      7  468 -448       8  315 -314       9  293 -280      17   99  -96       8   79  -76     -18   91   92
   8  115 -112      9   54  -51       9  247  242      10  273  273                        10   66  -36     -16  274  281
   9  238  236     10  287  287      10  284 -267      12  334  348        -2,6,L                           -14  354  347
  10   90   61     11   77  -69      11  437  431      13  184  189                          -2,8,L         -11  174 -166
  11  273  275     12  307  308      13  277  286      14  144  147     -13   81   86                       -10  470 -475
  12  130 -128     15  101  103      14  255  254      15  114  130     -12   73  -73      -7   83  -57      -9   79  -94
  15   78  -75     16   72 -100      16  102  102      18  138 -128     -11  112  115      -2   82   62      -8  886 -879
  16  115  109     17   91  104      17  132 -149                       -10  148 -155      -1   89   99      -7  101   76
  17   75 -104     18  100 -100      19   93  -94        -2,5,L         -8   69  -84       2   71  -49      -6  516 -491
  19   77  -84                                                          -5   61  -67       7   68  -57      -5  155 -155
                     -2,3,L            -2,4,L        -14   75   78      -4  189  178                        -4  254  257
    -2,2,L                                           -13  101 -123      -3  182 -178        -2,9,L          -1   89   89
                  -17  105  108     -16   86   93     -12  165  165      -2  208  224                         0  698  745
 -18   86   87    -16  135  128     -15   78   76     -11  245 -236       1  243  253       0  168   38       2   96   72
 -16  133  133    -15   80   80     -13   90   79      -9  112 -121       2   89  -84                         4  258 -222
 -15  120  130    -14   98  108     -12  284 -281      -8   91  -84       3  152  148        -1,0,L           5  351 -315
 -13  158  172    -13  105 -104     -10  240 -248      -6  165 -176       4  227 -235                         6  638 -587
 -11  155 -144    -11  249 -244      -9   76  -82      -5  268  278       5   64  -44     -17  232  247       7  626 -599
 -10  373 -374    -10   99  -81      -8  237 -237      -4  121 -133       6  191 -189     -15  346  354       8  558 -533
  -9  301 -282     -9  365 -344      -7  246 -254      -3  492  485       7   99  -79     -13  263  270      10   78   59
  -8  492 -480     -8  275 -279      -6  206  207      -2   84  -75       9   69  -88     -11  318 -320      11  200  184
  -7  375 -390     -7  157 -156      -5  139 -152      -1  258  258      10  129  132      -9  704 -751
```

```
    -1,1,L         13  284   278     15  235   241     17  112  -111     -6  103   -81    -10   86    72    -10  308  -302
                   14  158   162     17   68    61                        -5  101    76     -9   77   -57     -9  605  -568
 12  272   267     16  134   142     18  112  -116        -1,5,L         -4  229  -214     -7   75   -49     -8  443   445
 14  190   193     19   80   -89                                          -3  213   195     -6  101  -100     -7  992  -993
 15  119   138                          -1,4,L        -13  102   104     -2  260  -272     -4  107  -120     -6  272   264
 16   96    93        -1,3,L                          -12  115  -107     -1  118   118     -1  135   141     -5  765  -763
 20   77   -79                       -16   71    33    -11  152   154      0   79   -57      0  112    93     -4   95  -135
                  -16   91    92    -15   88   109    -10  114  -133      2  189   207      2   90    93     -3  438   391
    -1,2,L        -15   67    90    -14   71    73     -8   65   -78      4  194   190      4   73    77     -2  515  -468
                  -14   85    80    -11  164  -165     -7  139  -125      5  175  -174      8   73   -71
-17  106   114    -10  157  -152     -9   67   -76     -6   94   -64      6  135   117     10   95   -85        0,2,L
-15  169   177     -9  113  -109     -8  121  -119     -5   57   -81      7  142  -136
-14  100    89     -8  183  -178     -7  173  -181     -4  220   232     10   88   -84        -1,9,L        -17   66   -62
-13  204   219     -7  294  -284     -6  221  -199     -3  244  -240     11  146   140                      -16  109   104
-10  204  -205     -6  260  -252     -5  177   175     -2  339   340     13   76    82     -5   87   -73    -15  142  -134
 -9  648  -634     -5  510  -500     -4  228  -232     -1  137  -126                       -2   74    39    -14  208   221
 -8  190  -186     -4  201   202     -3  406   422      0  259   263        -1,7,L          3   91    90    -13   62   -56
 -7  641  -631     -3  213   200     -2  237   213      1  232   245                                        -12  356   352
 -6  241  -228     -2  554   521     -1  339   340      2  108  -110    -11  140   131        0,0,L         -11  119  -125
 -4   50   -71     -1  634   631      0  420   410      3  182   201    -10   77   -72                      -10   81   -80
 -3  472   497      0  208   204      1  121   124      4  412  -423     -8  141  -147    -16  295   303     -8  641  -608
 -2  594   576      1  341   340      2  246   245      5  133   148     -7   72   -71    -14  467   452     -7  262   259
 -1  455   475      2   73   -92      3  430  -428      6  300  -308     -5  152  -137    -12  228   233     -6  534  -493
  0  780   859      3  254   242      4   90    59      9  164  -156     -4   84    88    -10  491  -474     -5  487   487
  1  661   662      4  300  -313      5  719  -749     10  160   142     -3  172  -185     20   94  -119     -3  146   148
  2  258  -264      5  283  -282      6  131  -126     11   82   -72     -2   80    89                       -2  428   408
  3  368   373      6  603  -596      7  110  -122     12  217   218      1  129   121        0,1,L          -1  273   258
  4  213  -206      7  457  -450      8  250  -264     14  146   152      3  121   119
  5  586  -576      8  208  -201      9  103    97                        4   65   -74    -20   94    49        0,3,L
  6  464  -415      9  193  -215     10  203  -220        -1,6,L          6   74   -72    -19   95   -63
  7  425  -421     10  234   256     11  169   165                        9   93   -82    -17  140   145    -19  100   -71
  8  292  -271     11  141  -145     13  298   310    -12  134   133     11   71   -88    -15  363   367    -16   71   -69
  9  149  -167     12  329   344     14  126   141    -10  127   140                      -14   84   -77    -15   94    94
 11  271   283     13  169   178     15  138   141     -9  179  -163        -1,8,L        -13  317   315    -14  111  -114
 12  107   118     14  213   199     16   95    88     -8   65    51                      -12   89  -103
```

APPENDIX IV

Structure Factor List for compound IV, Part II.

Columns listed are l, $|F_o| \times 10$, $F_c \times 10$.

```
    0,3,L           -1  320   327     -2  223   226     -2  250  -249     -3  210  -193     -4  181  -175        0,9,L
                                       0  116   127     -1  203   201     -2  114   100     -3   81    71
 -13  203   208        0,4,L                                              -1  150  -132     -2  211  -212     -4  105   -94
 -11  130   135                          0,5,L             0,6,L           0   99    82     -1   84    77     -1   80    83
 -10  101   102    -18   85   -71
  -9   87   -95    -14  191   187    -15   77    66    -13   99    71        0,7,L             0,8,L
  -8  198   187    -11  115   132    -13   98    91    -12  107    92
  -7  446  -453     -9  130   117    -12   94   102    -11   86    96    -12   94    99     -9   92    87
  -6  103   114     -6  201  -207    -10  134   141     -9  103    98    -10  131   140     -5  111  -126
  -5  282  -253     -5  325  -324     -7   75   -90     -8  129  -121     -9   85   -89     -3  143  -133
  -4  318  -299     -4  110  -107     -6  142  -139     -6  137  -158     -7   99  -116      0  159   170
  -3  231   220     -3  312  -288     -5  182  -183     -5  163  -153     -6   68   -80     11   97   -89
```

APPENDIX IV

Structure Factor List for compound IV,

Part II.

Columns listed are ℓ, $|F_o|$ x 10, F_c x 10.

```
 18,2,L

3  85  -89
1 122  123

 18,0,L

0 257  255

 17,8,L

3 138  124

 17,6,L

4 114 -100

 17,5,L

2  61  -15

 17,4,L

4  84  -86
2 130 -133

 17,2,L

3 179 -167
2 113 -119

 17,0,L

4 106   96
2 273 -256
```

```
16,12,L

0 135 -141

16,11,L

1 144 -133

 16,9,L

0 119  117

 16,8,L

1  94  106

 16,7,L

2 158 -141
1  78  -83
0 174  164

 16,6,L

1  97   99
0 124  128

 16,5,L

3 153  158
1 215 -207

 16,4,L

3 156  162
```

```
2 183 -191
1 136 -145
0 107  109

 16,3,L

2 182  176
0 253 -253

 16,2,L

3 180  169
1 129 -118
0 204 -198

 16,1,L

3 123 -123
2 125  107
1 238  235
0 134 -130

 16,0,L

2 150  162

15,11,L

3 188 -172

 15,9,L

4 127  130
2 145 -152
1  72   78
```

```
 15,8,L

3  67  -58

 15,7,L

5 117 -103
4 211 -188
3 126  106
2 132 -134

 15,6,L

3 117 -105
1 101 -103

 15,5,L

5 233 -232
3 259  258
1 157 -149

 15,3,L

6 223  221
4 235 -239
2 280  265

 15,2,L

3 110 -116
2  66   84
1 134  133
```

```
 15,1,L

6 108  119
5 192  192
4 118 -114
3 270 -262
1 181  172

14,13,L

0 181 -179
2 171 -195

14,12,L

2  76   79

14,11,L

1 319 -308

14,10,L

3 120 -118

 14,9,L

2 238  240
1 111 -106
0 237 -230

 14,8,L

2  75  -42
```

```
 14,7,L

3 116 -115
2 189  186
1 119  128
0 386 -382

 14,5,L

3 247 -264
1 453  452

 14,4,L

1  79  -85
0 319  317

 14,3,L

4 187  203
2 347 -356
0 484  486

 14,2,L

1  91  -90
0 132 -128

 14,1,L

4 125  133
3 222  217
2  92  -93
1 401 -397
0 140  136
```

```
 14,0,L

2 128 -141
0 227 -226

13,14,L

3  95   88
2  72  -68

13,13,L

4 136  134

13,12,L

5  88  -78
2 155  146

13,11,L

3 199  196

13,10,L

5  91   90
4 119 -120
3 125 -144
2 144  140
```

```
 13,9,L

4  172 -178
2  137  136
1   84 -103

 13,8,L

5  132  142
3   99 -105

 13,7,L

6  112  113
5  179 -154
4  178 -164
3  160 -169
2  214  212

 13,6,L

6  142 -134
4  100   93
3  113  -97
2  221 -226
1  160  156

 13,5,L

7  125 -125
5  225  230
3  167 -158
1  246  248

 13,4,L

6  136 -123
5  167 -186
4  154  159
3  199  204
2  186 -176
1  131 -133

 13,3,L

6  260 -252
5   82   94
4  254  252
3   58   67

 13,2,L

7  100  104
5  281 -269
3   93   85
2  216  213

 13,1,L

7  101  102
6  123 -130
5  176 -176
4  150 -149
3  165  176
2  119 -121
1  326 -332

 13,0,L

6  119  129
2  280  286

12,16,L

0  188 -188

12,14,L

1  183 -180
0  203 -205

12,12,L

2  204 -203
1  163  159
0  331  336

12,11,L

0  120 -130

12,10,L

3  127  128
2  159 -156
1  248 -243
0  323  302

 12,9,L

2  136 -139
1  155 -147

 12,8,L

7  104 -119
3  153 -147
1  297 -288

 12,7,L

1  130 -129
0  225  240

 12,6,L

6  113 -112
3  124  109
2  315 -314
1  210 -210
0  460 -463

 12,5,L

4   57  -60
3   71  -55
2  211  208
1  101  -91
0   88   99

 12,4,L

7  115  111
4  124 -131
3  262 -265
2  288  283
1  344  350
0  225 -222

 12,3,L

4  126 -124
1  131 -123
0  209 -209

 12,2,L

7  169 -179
5   90  -98
3  392 -390
2  266 -266
1  188  183
0  327  323

 12,1,L

3  156  162
1  238 -232
0  357 -343

 12,0,L

6  138  144
4   69  -71
2  335 -343
0  544  543

11,16,L

2  186 -176

11,14,L

5  186  185

3  161 -147

11,13,L

4   88   97
2  118 -114

11,12,L

6  163 -157
5  200  194
4  144  138
2  188 -174

11,11,L

3  149  145
2  153  157
1  143 -148

11,10,L

6  100  -97
4  239  240
2  249 -246
1  141 -136

 11,9,L

6  117  104
2   83   90
1   98   93

 11,8,L

6  104   95
5  273 -269
3  379 -374
2  101 -104
1  235 -229

 11,7,L

4  150 -166
2   85   81

 11,6,L

6  212  211
5   98  -98
4  394 -393
3  140  135
2  254 -262

 11,5,L

8   61   24
5  204  210
4  142 -150
3  212 -218
2  238 -248

 11,4,L

8  106  -96
7  169 -185
6  105 -109
5  238  253
4  292 -292
3  173 -167
```

```
 11,4,L

2  145  140
1  130  137

 11,3,L

6  200 -197
5   61   35
4  138  136
1  132 -130

 11,2,L

7  168 -153
6   91  -84
5  331  345
4  205  190
3  342 -341
2  198 -204
1  129  136

 11,1,L

5  191 -183
4   68   61
3  112  129
2   78   76
1   89   83

 11,0,L

6  121 -112
4  524  528
2  575 -561

10,18,L

0  130  128

10,17,L

1  177 -167
0   85   67

10,16,L

4   67  -28
0  229  240

10,15,L

1  212 -208
0  112 -102

10,14,L

5   67  -44
3   97  107
1  157 -155

10,13,L

2  240  250
0  183 -189

10,12,L

3  189  183
2  127  118

10,11,L

3  178 -192
1  411  417

10,10,L

2  157  154
1  144  151
0  316 -318

 10,9,L

2  374 -377
1  220  204
0  291  277

 10,8,L

7  118  138
5  121 -114
3  133 -139
2  142 -157
1  375  375
0  113  111

 10,7,L

6  151  138
5  130  132
4   94   93
2  297 -308
1  192 -196
0  345  356

 10,6,L

8  103 -104
6  149  145
5  143 -141
4  102  109
2  306 -312
0  122  135

 10,5,L

7  150 -139
3  461  468
2  164  165
1  477 -497

 10,4,L

7  145 -141
6   92  100
3   90   93
0  308  319

 10,3,L

6  123 -121
4  367 -366
2  676  698
1   96  -91
0  530 -541

 10,2,L

6   61  -64
5  187  188

3  127  129
2  151  145
1  332 -337
0  207 -214

 10,1,L

7  129  126
6  178 -174
5  164 -162
4  147 -160
3  217 -221
2  253  254
1  486  495
0   79  -95

 10,0,L

6  194 -199
4   96  115
2  359  363
0  688 -673

 9,17,L

3  215  207
1   91  -90

 9,15,L

4  132 -127
3  218  218
2  156  151

 9,13,L

6  269  262
4  306 -298

 9,11,L

7  200 -197
5  302  311
3  394 -387
2  110   82
1  148  150

 9,10,L

3  125 -115

 9,9,L

6  251 -248
5  256  255
4  516  524
3  311 -310
2  323 -331
1  134  134

 9,8,L

3   91  -86

 9,7,L

7  157  156
6  283 -291
5  209 -213

4  366  370
3  340  349
2  350 -352
1  207 -209

 9,6,L

7  128  135
4  185  193
3   82   82
2   78   74
1  106  126

 9,5,L

7  272  288
6  143  156
5  514 -518
4  176 -187
3  442  440
2  178 -179
1  372 -370

 9,4,L

6  156  150
4  144  150
2  158  142

 9,3,L

8  150 -150
6  529  539
4  661 -670
```

```
 9,3,L

3  146  154
2  536  555
1  272 -264

 9,2,L

7  102  -98
5  138 -134
4   69  -72
2   78  -56
1  110 -100

 9,1,L

7  193 -204
6  288  304
5  313  324
4  404 -405
3  665 -663
2  257  248
1  844  836

 9,0,L

6  175 -174
4  354 -349

 8,19,L

0  185 -176

 8,18,L
```

```
1  106   86

 8,17,L

1  251  244
0  112 -119

 8,16,L

0  139  138

 8,15,L

3  138 -140
2  172 -176
1  241  236
0  197  199

 8,14,L

3  161  154
0  144  141

 8,13,L

4  187  198
2  324 -321
0  255  253

 8,12,L

4  202 -204
3  186  189
2   98   97
1  217 -222
```

```
 8,11,L

7  145 -131
3  234  224
1  558 -560
0  145  148

 8,10,L

3  308 -298
2  202  202
0  421 -427

 8,9,L

8  134  139
6  197 -199
4  138 -147
3  191  190
2  551  560
1  382 -396
0  494 -501

 8,8,L

7  106  101
6  124  136
4  125  128
3  133 -130
1  339  328
0  168  173

 8,7,L

8  156  150
```

```
6   99 -101
4  110  -96
3  280 -279
2  472  479
1  481  492
0  961 -963

 8,6,L

5  242  243
4  198  203
2  424 -422
1  460  462

 8,5,L

9  180 -174
7  230  226
4  158  156
3  310 -313
2  221 -230
1 1000 1005
0  138 -140

 8,4,L

6  157 -167
4  164 -149
3  263  263
2  646 -652
1  193 -192
0  564  574
```

```
 8,3,L

9   64  -48
8  254 -251
6  238  242
4  334  329
2  805 -812
1  280  288
0  832  876

 8,2,L

4  175 -177
2  501  510
1  532 -535
0  435 -446

 8,1,L

9  156  145
8  143 -142
7  143 -152
6  158  156
4  184  187
2  535 -525
1 1399-1436
0  712  707

 8,0,L

8   65   46
6   64   89
4  237  231
2  812  821
0  306 -317
```

```
 7,18,L

3  114 -118

 7,16,L

4  214  213
2  136 -156
1   80  -91

 7,15,L

5   86   92
4  157  168
3  174 -175
1  135  153

 7,14,L

5  322 -320
2  160 -163

 7,13,L

6  155 -157
5  115 -118
4  256  254
2  220 -217

 7,12,L

7   89  100
6  176  172
5  309 -303
4  247 -264
```

```
3  225  234
2   87   78

 7,11,L

7   71   79
6  155 -160
5  187 -186
3  305  302
1  228 -228

 7,10,L

7   73  -59
6  233  242
5  284  290
4  326 -329
2  462  470
1  262  262

 7,9,L

7  105  109
6  166  151
5  169 -167
4  366 -365
3  179  179
2  105  112

 7,8,L

7  245 -229
5  415  423
4  167  156
```

```
 7,8,L

3  514 -512
2  125 -127
1  280  271
 7,7,L

7  144 -143
6  247  256
5  283 -280
4  407 -398
3  238 -241
2  601  594
1  112  106

 7,6,L

8  112  115
7  166 -157
6  387 -383
4  515 -523
3  594 -592
2  386 -387

 7,5,L

7  175 -170
5  406  409
4  208 -205
3  638 -636
2  107 -119
1  166  167

 7,4,L

8  125  143
7  338 -338
6  309 -319
5  323 -335
4  282  293
3  294  305
2  714 -704
1  395 -392

 7,3,L

6  356 -365
5  126  128
4  602  604
1  189 -180

 7,2,L

8   64  -62
7  419  429
6  198  189
5  294 -294
4  363 -356
3  882  906
2  278  264
1  185 -193

 7,1,L

7  198  207
6  303 -296
5  372 -379
4  437  436

3  743  737
2  206 -207
1  236 -233

 7,0,L

8  172 -176
6  319  322
4  522 -533
2 1467 1480

 6,18,L

1  186 -190
0  199 -200

 6,16,L

2  248  246
0  443 -449

 6,15,L

1  171 -174

 6,14,L

7  161  158
3  302 -302
1  337  347
0  429 -428

 6,13,L

1   99   95

0  212 -215

 6,12,L

7  184  178
6  144  132
3  240 -242
2  301 -306
1  250  259
0  717  703

 6,11,L

3  112  108
2  188  199
0  148  155

 6,10,L

8  171 -168
5   65   62
4   97  110
3  175  176
2  509 -511
1  446 -447
0  788  784

 6,9,L

5   97  113
3  105  -98
2  134  128
1  267  254
0  519  515

 6,8,L

9  205  190
7  263 -258
6   72  -91
5   62  -46
4  170 -162
3  367  381
2  188 -186
1  973 -971
0  106   88

 6,7,L

5  106 -125
2  397 -394
1  436 -428
0  341  345

 6,6,L

8  226  232
7  141 -139
6  232 -230
5  105  120
4   88  -89
2  893  881
1  543 -563
0 1142-1138

 6,5,L

7  124 -103
5   59  -62
2  225 -232

1  280 -281
0  632 -617

 6,4,L

9  189 -194
8  242  246
7  221  225
5  170  168
4   81  -70
3  355 -365
2  887  880
1 1149 1184
0  367 -377

 6,3,L

8  176  175
5  145 -151
4   88   72
3  290  287
0  273 -273

 6,2,L

9  219 -223
7  396  388
6  190  194
5  238  248
3  756 -761
2  396 -387
1 1132 1177
0  298  306

 6,1,L

6  129  129
5  227  222
4  268 -271
3  261 -254
2  477  473
1  549  535
0  136 -128

 6,0,L

8  270 -273
6  150  151
4  385 -395
2 1279-1301
0 1756 1824

 5,18,L

4  140 -133
1   75  -80

 5,17,L

3  122 -110

 5,16,L

4  283 -286
2  274  278

 5,15,L

6   92  -88
3  127 -123
```

```
 5,14,L

5  331  332
3  336 -338
2  320  330
1  158  161
 5,13,L

7  102  107
6  118 -129
4  174  174
2  145 -144
1   74  -55
 5,12,L

7  100 -118
5  208  218
4  404  402
3  144 -145
2  375 -379

 5,11,L

7  113  110
5  103 -104
3  285  288
2  190  178
1  188 -189
 5,10,L

8  145  145
6  305 -300

5  220 -216
4  342  347
3  311  323
2  527 -519
1  144 -150
 5,9,L

6  166  168
5  144 -139
4  200 -210
1  146  146

 5,8,L

7  246  249
5  517 -521
3  761  761
1  292 -292

 5,7,L

7  212 -195
4  236 -235
2  323  332
1  188  181

 5,6,L

8  139 -131
6  410  403
5  130 -119
4  786 -784
3  351  367
2  598  592

 5,5,L

5  296  295
3  197 -204
2  210 -210
1  456  448

 5,4,L

7  234 -239
6  424  430
5  564  568
4  463 -472
3  736 -746
2  309  309
1  154  173

 5,3,L

6  219 -222
4  419  404
3  170  160
2  169  165

 5,2,L

7  363 -374
5  938  945
4  372  383
3  728 -745
2  609 -602
1  626 -608

 5,1,L

7   94  108
5  140 -152
4  201  213
3   89  101
2  158  -43
1  798 -794

 5,0,L

8  131  139
6  502 -525
4  855  867
2  911 -947

 4,19,L

2  129 -126
0  214  228

 4,18,L

1  129  119

 4,17,L

1  230 -228
0  159  165

 4,16,L

2  246 -242
0  357  347

 4,15,L

4   80  -91
2  173  171
1  357 -364
0  300 -302
 4,14,L

4   80  -98
3  148  160
1  337 -345
0  128 -126

 4,13,L

2  359  363
1  235  243
0  527 -527

 4,12,L

7   91 -110
3   64   71
0  342 -337

 4,11,L

7  117  114
5   70  -71
4  171 -174
1  680  680
0  277  270

 4,10,L

8  103   91
4   63   53
2  341  352
1   71   81
0  628 -617

 4,9,L

8  168 -159
7  135  130
6  123  124
5  173 -168
3  233 -224
2  444 -439
0  624  630

 4,8,L

9   87 -106
7  174  170
6   91  -90
3  205 -205
2  131  125
1  928  895
0  725  683

 4,7,L

9  148  139
8  159 -170
6  243  239
5  159 -164
4   91   83

3   77   64
2  533 -536
1  807 -784
0  762  763

 4,6,L

8  230 -234
7  133  137
4  206  205
3  209  214
2  359 -359
0  866  859

 4,5,L

9  198  185
7  316 -315
5  209  204
4   94   82
3  580  593
1  742 -761
0  213 -218

 4,4,L

9  131  125
8  192 -182
7  236 -237
6   97  103
4  136 -125
1  200 -214
0  487  503
```

```
 4,3,L

8  322  324
7  102  -94
6  499 -499
4  214 -209
3  228  225
2  608  633
1  503  499

 4,2,L

8   99  -89
7  361 -377
5  188 -180
4  393  379
3  361  356
2  214 -209
1  589 -571
0  993 -969

 4,1,L

9  154 -154
8  182  194
7  177  181
6  290 -299
5   87  -99
4  477 -484
3  439 -449
2  419  431
1 1257 1290
0 1035 1061

 4,0,L

8  253  271
4  171 -192
2  472  492
0 1844-1982

 3,19,L

4  151  148
3   62   43
2  125 -122

 3,17,L

5  173 -181
3  222  227
2  163 -166
1  151 -159

 3,16,L

4   76   57

 3,15,L

6  221  205
5  152 -141
4  226 -209
3  360  357
2  268 -269
1  344 -349

 3,14,L

5   65  -75
2  132  138

 3,13,L

7   62  -81
6  335  327
5  194  192
4  455 -440
3  175 -167
2  168  162
1   86   91

 3,12,L

2  168 -178

 3,11,L

7  204 -198
5  354  338
3  535 -531
2  164 -158
1  448  440

 3,10,L

8   68  -86
1  221 -218

 3,9,L

6  324 -317
5  301  294
4  671  665

3  440 -429
2  677 -678

 3,8,L

7   77   75
5  103  106
4  203  197
3  221 -218
1  171 -165

 3,7,L

9   94 -106
8   96   87
7  212  210
6  350 -348
5  466 -450
4  826  796
3  635  613
2  345 -340
1  470 -454

 3,6,L

5  236 -232
3   93   89
1   90  -59

 3,5,L

7  206  205
6  242 -234
5  811 -815
4   98 -100

3  984  976
1  457  431

 3,4,L

7  144 -152
4  322 -320
3  151 -148
2   90  -70
1  830  808

 3,3,L

7  136  127
6  517 -521
5  179 -170
4 1244-1239
2  346  364
1  305  290

 3,2,L

7  146 -158
5  121  124
4  149  156
3  402  386
2  253 -254
1  315 -315

 3,1,L

7  179 -176
6  487  489
5  653  669
4  881 -913

3 1444-1443
2  913 -909
1  167  159

 3,0,L

2  893  911

 2,19,L

2  131 -123

 2,18,L

3   75  -81
1   61  102

 2,17,L

6   86  -83
2  163  169
1  408  404
0  120 -108

 2,16,L

2  228 -241
1   84   98
0  273  282

 2,15,L

7   65  -71
4  115  112
3  109 -113

2  175 -166
1  366 -364
0  574  588

 2,14,L

7   86  -88
3  101  103
1  318 -318
0  368  368

 2,13,L

8  198 -196
6  222  218
5  132 -125
4  237  240
3  127  133
2  266 -279
1  220 -232
0   98   95

 2,12,L

8   87   55
4   65   51
3  196  200
2  347  348
1  188 -171
0  212 -225

 2,11,L

7  193 -185
6  139 -152
```

```
 2,11,L

3  134  124
2  339 -340
1  633 -619
0  460 -440

 2,10,L

4   87  -80
2  319  321
1  280  271
0 1021 -998

 2,9,L

8  254 -255
6  185 -192
5  114  111
4  220 -228
3  420  423
2  455  448
1  705 -695
0 1233-1252

 2,8,L

7   75   82
4  361 -357
3  279 -264
1  799  774
0  112 -135

 2,7,L
```

```
9  119 -135
8  222  214
7  237  248
6  195 -194
4  105  106
3  363 -364
2  756  751
1  983  977
0  806 -779

 2,6,L

9  164  -75
8  152 -151
7   83  778
5   96 -115
4  274  277
3  264 -248
2  514 -509
1  339  322
0  556 -573

 2,5,L

9  260 -257
8  162 -168
7  310  299
6  105  -95
5  210 -202
4  516  503
3  416 -419
2   76  -84
1  362  364
0 1430 1420
```

```
 2,4,L

9  114  117
8  141 -125
6  155  101
5  115 -112
4  409 -395
3  399 -388
2  312 -323
1 1215-1202
0 1772 1834

 2,3,L

10  130 -138
 8  459 -453
 4  212  216
 3  195 -202
 2  689 -693
 1  764  758
 0  993 -989

 2,2,L

9  174  185
7  160 -156
6  181 -169
5  232 -207
4  342  329
3 1174 1121
2  309  309
1  864 -861
0 1145-1155
```

```
 2,1,L

9  211  215
8  242 -238
7  211 -224
6  114  108
5  446 -426
4  185  168
3   91  -65
2 1384-1415
1 1462-1513
0 1094 1118

 2,0,L

8  179  174
6  155 -159
4  667 -680
0 1059-1106

 1,19,L

2   85   95

 1,18,L

5  146  139
3  215 -216

 1,17,L

5  112   99
3  175 -182
1  192  180
```

```
 1,16,L

6  143 -160
4  358  365
2  268 -254
1  369  389

 1,15,L

7   94  -89
6  131 -120
5  123 -134
4  127  115
3   72  -65
2  116 -117

 1,14,L

7  193  199
5  352 -356
3  416  422
2  227 -217
1  101  107

 1,13,L

6  190 -195
5  174 -159
4  244  243
2   86   72
1   62   72

 1,12,L

7  207  206
```

```
6  224  224
5  365 -369
4  366 -373
3  159 -153
2  176  168
1  131 -148

 1,11,L

7  110  103
5  288 -291
4  114 -117
3  255  243
2  113  111
1  156 -145

 1,10,L

8  171 -150
6  334  323
5  196  183
4  610 -600
3  525 -514
2  681  659
1  599 -573

 1,9,L

6  264  267
5  169 -163
4  481 -467
3  420  419
1  126 -129

 1,8,L
```

```
7  297 -305
5  805 -788
3  983 -972
1  510  517

 1,7,L

6   77   79
5  492  489
4  457 -427
3  359 -350
2  602  577
1  125 -106

 1,6,L

8  238  226
7  141 -130
6  575 -557
5  288  280
4 1028 1035
3   94   84
2  675 -667
1 1447 1411

 1,5,L

7  121 -104
6  236 -238
5  277  282
4  284  284
3  564 -536
2  289 -298
1  527 -496
```

```
 1,4,L

8  243  237
7  265  267
6  410 -405
5  731 -700
4  571  564
3  582  547
2  777 -764

 1,3,L

8  176  163
7  120  -99
6  342 -341
4  496  479
3  527 -510
2  289  276
1  399  383

 1,2,L

7  342  338
6  132  127
5 1351-1328
4  430 -436
3  587  585
2  393  384
1 1082-1058

 1,1,L

6  104 -101
5  188 -185
4  716  716
3 1215 1172
2 1108-1091

 1,0,L

8  378 -394

6  512  540
4 1216-1256
2 2382 2704

 0,20,L

2  146 -173
1  117 -115

 0,18,L

3  150  160
2   72   92
1  330 -327
0  168 -182

 0,16,L

2  548  559
1  115  108
0  331 -340

 0,14,L

7  196  194
6   84  -70
3  508 -513
1  460  463
0  213 -215

 0,12,L

8  225 -216
7  177  183
3  429 -429
2  530 -531
1  395  380
0  219  236

 0,10,L

8  213 -228
7  201 -199

6  183  183
5  129  135
4  196  198
3  265  261
2  732 -716
0 1345 1318

 0,8,L

9  248  233
8  114  105
7  312 -317
6  153  162
3  892  873
2  440  438
1 1888-1918
0  561  584

 0,6,L

9  129  131

8  380  383
6   85  -71
4  497 -472
3  294 -286
2 1228 1204
1 1067-1017
0 2802-2918

 0,4,L

10  194 -185
 9  294 -287
 8  261  262
 7  351  362
 6   68  -72
 5  102  108
 4  636 -615
 3  361 -353
 2  528 -520
 1  413  399
 0 2497-2634

 0,2,L

9  353 -360
8  149 -148
7  397  408
4  295  273
3  812 -804
2  183 -188
1 2095 2242
0  654  590

 0,0,L

10  212  216
 8  317 -313
 4  272  260
 2 1033 -975
```

APPENDIX V

Structure Factor List for compound V,

Part II.

Columns listed are ℓ, $|F_o|$ x 10, F_c x 10.

```
 15,1,L

 0  103  114
 15,0,L

 4  139  139

 14,3,L

-1   90   82
 14,2,L

-3  136  121
-1   83  -69

 14,1,L

 4   97   92
-2  146 -129
-4   89  -95

 14,0,L

-6   87  106

 13,3,L

-5   90   94
 3  152  140

 13,2,L

 5  109  106
```

```
 4   73   82
 2   86   87
 1  117 -110
-1  112 -117
-7   98   82

 13,1,L

 5  153 -134
 0  215 -206
-3  136  132
-5   78  101

 13,0,L

 6  200 -203
 4  198 -203
-2  152  162
-4   72   80

 12,5,L

 4   92  106
-5   74  -71

 12,4,L

 3  114  116
-1  110 -118
-3  142 -138

 12,3,L

 7  117  109
 1  169 -173
```

```
 -1  163 -162
 -7  110   91

  12,2,L

  8   95   82
  5  150 -150
  3  137 -148
  2  106  -97
  0  113 -102
 -1   96  103
 -2  118 -102
 -3  132  149

  12,1,L

  4  197 -197
  2  123 -126
  1   90  106
 -2  115  108
 -4  115  108
 -6  121  110

  12,0,L

  6  191 -165
 -2  199  198
 -4   84   99
 -8  214 -210
-10   96 -105

  11,6,L

 -4   84  -80
```

```
  11,5,L

  2   97  -86
  0  113 -112
 -6   86   65

  11,4,L

  7  177  174
  5  141  145
  4  104 -112
  3  113 -108
  1  229 -236
 -1  180 -184
 -2  103  106
 -4   95   70
 -5  115   96
-10   83  -30

  11,3,L

  5  190 -190
  3  251 -244
 -1  169  175
 -3  224  230
 -5  122  121

  11,2,L

  9  119 -123
  5   91  -79
  1  265  270
  0   75   72
 -1  250  247
 -5   85  -84
```

```
-6  117  115

 11,1,L

 8  100 -123
 6   90  -75
 5  222  219
 3  270  271
-1  218 -220
-2  192  197
-8  165 -156

 11,0,L

 6  252  247
 4  232  225
 0  179  182
-4  337 -336
-6  132 -118

 10,7,L

 4  109   90
 3   77  -59
-6   74  -66

 10,6,L

 6   76   56
 0  141 -149
-2  130 -121

 10,5,L

 7  104  103
```

```
 4  108 -121
 2  104 -112
 1  115 -114
-1  134 -153
-2  165  154
-4  124  128

 10,4,L

 6   92  -91
 5  208 -214
 3  201 -204
 0   78   87
-3  159  152
-5  179  170

 10,3,L

 9  120 -101
 7  175 -172
 5  238 -241
 1  281  285
-1  194  196
-3  147  140
-7  195 -188
-9  130 -124

 10,2,L

 8   90 -111
 5  214  216
 3  261  269
 1  139  147
-1  165 -176
-3  249 -256
```

```
 -8   86  -61

  10,1,L

 12  125 -146
  8  106  116
  7  207  213
  6  210  213
  4  166  161
  3  138 -137
  1   73  -74
 -1  212 -221
 -2  183 -190
 -4  191 -172
 -9   88 -103

  10,0,L

 10  131  121
  8  136  143
  2  176 -172
  0  279 -282
 -2  346 -339
 -6  230  234
 -8  211  198
-10  115  145

  9,7,L

  2   71  -62
  0  139 -133
```

```
  9,6,L

  6  102  -111
 -2  137   139
 -4  148   145

  9,5,L

  8  112   -90
  6  157  -170
  4  110   -95
  2  134   131
  0  118   119
 -2  131   132
 -3   69    64
 -6  123  -131
 -8  138  -132

  9,4,L

  9  117  -128
  7  144  -150
  5  138  -129
  4  180   187
  2  110   118
  1  182   187
 -1  209   209
 -3  113   127
 -6   88  -111
 -7  157  -160
-10   69    60

  9,3,L

 13   86   -94

  7  138   -130
  6  120  -127
  5  225   227
  3  230   236
  2   99   184
  0   77    85
 -1  142  -132
 -3  180  -173
 -5  216  -222
 -7   85   -65

  9,2,L

  9  158   152
  8  111   116
  7  200   211
  6  180   170
  4  225   229
  3  120  -128
  1   89   -97
  0  120  -106
 -1  309  -293
 -2  166  -159
 -3   86   -79
 -4  175  -173
 -5   93    98
 -9  144   139

  9,1,L

 10  116   131
  8  197   184
  6  210   196
  5  208  -204
  2  244  -251

  0  562  -555
 -2  247  -256
 -3  184   178
 -6  182   183
 -8  238  -230
-10  117   110

  9,0,L

 12  160   153
 10  153   159
  8  107   124
  4  585  -595
  2  538  -539
  0  246   259
 -2  398   391
 -4  318   316
 -6  158   153
 -8   88  -121
-10  123  -130

  8,8,L

  0  101   -85

  8,7,L

  4  121  -114

  8,6,L

  8  142  -135
  6  162  -149
  3   72    88
  0  243   242

 -2  206   211
 -6  173  -161

  8,5,L

 10   84   -76
  9  121  -128
  6  121   115
  4  184   183
  2  127   121
 -1  108   127
 -2   93   -86
 -3   91    95
 -4  237  -245
 -6   91   -78

  8,4,L

 13  125  -128
  7  171   163
  5  226   218
  3  116   115
 -3  183  -173
 -5  179  -172
 -7  112  -107
 -8  143   147
-13   88    62

  8,3,L

  9  192   183
  7  190   192
  5   91   109
  4  134   140
  3  123  -121

  1  283  -282
 -1  237  -246
 -3  134  -129
 -7  307   317
 -8  166  -163
 -9  160   174

  8,2,L

 13  123   127
 11  201   198
  7  208  -208
  6  193   195
  5  278  -283
  4  281   274
  3  210  -217
  2  363  -367
  0  283  -286
 -1  236   235
 -3  276   278
 -5  104   121
 -6  144   141
 -8  133   139
-10   84    89
-11  134  -138

  8,1,L

 11  116  -108
 10  164   159
  9  138  -127
  8  101   102
  7  122  -123
  6  204  -202
  4  461  -464

  2  408  -415
  1  126   130
 -1  278   280
 -2  459   465
 -3  187   184
 -4  272   281
 -9  223  -207

  8,0,L

  8  408  -397
  6  594  -607
  2  386   377
  0  570   570
 -2  556   550
 -4  142   144
 -6  233  -227
 -8  264  -263
-10  145  -128

  7,8,L

  2   83   -68
 -1   66    88

  7,7,L

  6  141  -140
  2  165   170
  0  154   134

  7,6,L

  6  204   207
  4  201   211

  2   91   -97
 -1   71    86
 -2  316  -323
 -4  191  -190

  7,5,L

 11   82   -81
  8  159   158
  7  221   225
  5  103   113
  4   70    68
  2  110  -103
  0  302  -313
 -2  131  -140
 -3  111  -110
 -4   93    98
 -5  117  -116
 -6  191   178
 -7   95   -99
 -8  179   178

  7,4,L

  9  109   111
  7  160   150
  5  163   170
  4  125  -129
  2  153  -159
  1  285  -280
 -1  248  -256
 -2  127   111
 -3  151  -143
 -4  185   169
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   7,4,L

 -6  102  103
 -7  285  281
 -9  232  240

   7,3,L

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  8   74  -70
  7  105 -109
  5  386 -390
  4  126  140
  3  472 -471
  2   82  104
 -1  129  115
 -3  197  197
 -4   87  -85
 -5  286  294
 -7  111  110
 -9   82  -87
-11  134 -135
-13  109  -85

   7,2,L

 15  119  118
 11  109 -134
  9  232 -229
  7  301 -295
  6  142 -141
  5   79  -94
  4  375 -375
  3  203  195
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  2  176 -179
  1  188  199
  0  136  126
 -1  417  425
 -2  130 -123
 -3  400  382
 -4  195  206
 -6  119  119
 -7  275 -281
 -8  106 -104
 -9  236 -244
-11  100 -109

   7,1,L

 12   83   98
  9   72  -65
  8  404 -399
  6  434 -422
  3  120  124
  2  283  277
  1  141  135
  0  632  639
 -1  125 -126
 -2  387  397
 -3  132 -138
 -4  222 -215
 -5  305 -296
 -6  186 -203
 -8  169 -179
-11   93  107

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 12   84  -97
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 10  326 -331
  6  279  282
  4  371  374
  2  381  363
  0  155 -165
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 -6  106 -111
-10  208  207

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 -2   79   73

   6,7,L

  6   89   99
  4  151  149
  2   84   90
  0   96 -100
 -1  130 -133
 -2  125 -125
 -4  102 -102
 -7   64   86

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  8  202  207
  2  198 -198
  0  337 -326
 -1  131 -119
 -2  146 -145
 -4  130  111
 -6   99  105
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 -7  135 -146
 -8  100  100
-10   99   78

   6,5,L

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  9   86   95
  7  185  195
  6  111 -112
  4  356 -369
  3  107  104
  2  214 -225
 -1  367 -374
 -2  108  103
 -3  127 -138
 -4  131  139
 -5   76   79
 -6  104  114
 -7  162  160
 -9  110  127

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  7  142 -140
  6  181 -173
  5  300 -301
  3  223 -230
  2  215  210
  0  268  266
 -2   91   88
 -3  141  154
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 -7  114  107
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 -9   90   84
-13   98 -110

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  7  237 -239
  5  238 -245
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  2  245  244
  1  623  639
  0  142 -130
 -1  262  274
 -2  254 -248
 -3  238  241
 -5   52  -70
 -7  300 -308
 -9  275 -285
-15   95   76

   6,2,L

 13  124 -118
  8  106  -96
  7  172  176
  6   86  -94
  5  299  314
  2  240  251
  1  230  221
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 -2  292  288
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 -3  510 -506
 -4   85  102
 -5  475 -482
 -6  472 -470
 -8  327 -320
 -9  196  188
-11  106   97

   6,1,L

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  9   94   92
  7  361  361
  6  364  378
  5  134  131
  4  306  308
  3   99  -94
  2  272  275
  1  161  162
 -1  166 -164
 -2  748 -717
 -3  312 -309
 -4  427 -434
 -7  108  110
-10  206  195
-11   87  109

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  4  315  297
  2  359 -361
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 -4   94  106
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 -8  237  243
-10  152  145

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 -3   98 -101

   5,8,L

  6   74   57
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 -4   77  -66

   5,7,L

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  5   84  -55
  4   77   75
  2  119 -134
  1  119 -132
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 -8  111  109

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 12   99  109
 10  143  145
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   5,6,L

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  5   119   114
  4   248  -251
 -4   155   138
 -6   120   126

   5,5,L

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  8   166  -150
  6   178  -190
  5   199  -209
  3   134  -147
  2   222   218
  1   164  -163
  0   203   201
 -2   167   158
 -3   327   313
 -4   102   118
 -6   106   -98
 -8   224  -213
 -9    61    59
-10    77   -91

   5,4,L

 12    75   -66
  9   140  -133
  8   160  -163
  7   277  -274
  5   123  -125
  4   318   319
  2    80    95

  1   393   388
 -1   535   535
 -2   105   -84
 -3   110   113
 -5   150  -150
 -7   213  -210
 -9   244  -232
-13    83    77

   5,3,L

 13   173  -159
 12    95   -72
 11   255  -251
 10    80   -67
  9   127  -139
  8   140   129
  6   169   168
  5   425   415
  4    65   -61
  3   564   567
  0   323   307
 -1   277  -276
 -3   164  -167
 -4   150  -143
 -5   393  -390
 -8   143  -138
 -9   162   152

   5,2,L

 13   140  -159
 12   253  -260
  9   282   289
  8   149   147

  7   462   456
  5   499   494
  4   375   385
  3    83   -88
  2   282   288
  1   788  -770
  0   242  -245
 -1   742  -747
 -2    88   -87
 -3   154  -143
 -4   261  -257
 -5   354   364
 -6   190  -195
 -7   375   376
 -8   136   130
 -9   117   128
-10   130   127

   5,1,L

 14   163  -154
 11    81    81
 10   235   231
  8   389   404
  7   196  -206
  6   351   356
  4   203  -191
  3   263  -251
  2   252  -255
  1   474  -482
  0   502  -495
 -1   572   571
 -2   867  -857
 -3   497   484
 -6   445   432

 -7   355   349
 -8   321   335
 -9    67   -79
-10   228   223
-11   222  -227
-16   105   -96

   5,0,L

 14   266   250
 12   132   119
  8   265  -255
  6   613  -608
  2   226  -228
  0    80    71
 -2   446   456
 -4   589   575
 -6   352   352
-10    93   -88
-12   158  -146

   4,9,L

 -1   102   -88

   4,8,L

  5    95   -98
  3   124  -136
 -2    69   -87
 -3   110   123

   4,7,L

  6   155  -142

  4   169  -168
  2   114  -109
  0   130   126
 -1   153   151
 -2    74    69
 -6   171   169
 -9   109  -102

   4,6,L

 10    89   -97
  8   224  -222
  1    66   -49
  0   227   222
 -2   308   313
 -3   138   138
 -6   127  -119
-10   110  -114

   4,5,L

 12   137  -131
 10   163  -160
  8   105    98
  7   214  -214
  6   166   176
  5   152  -159
  4    93    99
  1   246   233
  0    71   -76
 -1   401   399
 -2   123  -117
 -4   223  -217
 -5   311  -300
 -7   188  -177

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 13   104  -107
 11   126  -121
  8   117   118
  6   264   263
  5   344   325
  4   101  -106
  3   395   406
  2   422  -422
  1   149  -141
  0    70   -72
 -1   300  -299
 -2   178  -182
 -3   214  -203
 -4   129   124
 -5   189  -190
 -6   135   126
 -9   159   165

   4,3,L

  9   179   183
  7   442   447
  6    69   -61
  5   456   455
  4   145   133
  3   137  -151
  1   913  -936
  0   238  -241
 -1   756  -788
 -3   323  -325
 -4   244   242
 -5    92    91
 -6   159   148

 -7   500   504
 -8   149  -145
 -9   233   240
-10    62   -78

   4,2,L

 11   130   129
 10   157   184
  9   200   205
  8   252   253
  6   306   298
  5   371  -379
  4   202   206
  3   663  -657
  2   617  -600
  1   683  -677
  0   668  -680
 -1   336   332
 -2   588  -588
 -3   792   809
 -4   349  -351
 -5   436   433
 -6   214   214
 -7   139   133
 -8   332   328
 -9   182  -185
-10   198   204
-11   154  -160

   4,1,L

 14   187   201
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     4,1,L          4  146   148      6  152   151        3,4,L           -5  369   371        3,1,L           -2  423  -425
                    2  659   662      5  110  -117                        -6  329  -333                        -4  436   414
  13  151   135     0  586   605      4  134   133     12  152   136     -7   92    77     15  127  -113     -6  621  -622
  12  282   278    -2  282  -273      2  198   205     11   76   102     -9  182  -183     14  144   157     -8  732  -716
  10  116   115    -6  149  -138      1  184   187      9  180   186    -10  178   183     12  103   124    -10  357   363
   9  165  -167    -8  305  -293      0  181   184      7  341   333    -11  138  -150     10  179  -175    -12  386   395
   8  140  -159   -10  375  -392     -1   83    80      5  231   231    -13   99  -112      9  180  -179
   7  138  -137   -12  125  -128     -2  239  -247      4  347  -344                        8  432  -430        2,9,L
   6  583  -593   -14  239   239     -4  272  -271      3  207  -200        3,2,L            7  413   403
   5  394  -394   -16  144   147     -6   99  -100      1  488  -483                        6  674  -672     -7   76   -91
   4  397  -409                      -7   85   -95      0  245   247     13   91   105      5  575   568
   3  106   -91       3,9,L         -12   68    94     -1  784  -782     12  114   115      4  182  -163        2,8,L
   1  757   744                                        -2  195   189     11  133   119      2  528   552
   0  471  -468     5  124  -118        3,5,L          -3  169  -177     10  213   217      1  460   454      5  153   140
  -1  136   121                                        -4  403   398      9  254  -260      0  574   563      3  163   161
  -2  223   245       3,8,L          14   75   -71     -5  396   405      8  108    94     -1  188  -183      2   88   106
  -3  312  -301                      10  159   153     -7  276   274      7  637  -637     -2  863   832     -1  145  -156
  -4  613   632     6   81   -79      9   94   -94     -8  172  -165      6  171  -172     -3  557  -564     -2   94    86
  -5  279  -288     1  136   145      8  216   205     -9  166   151      5  345  -341     -4  227   221
  -6  314   326    -4  101    97      7  142   139    -10  117  -101      4  396  -395     -6  384  -382        2,7,L
  -7  303  -292                       6  108   114    -12   98   -83      3  342   342     -7  142   144
  -8  208   206       3,7,L           5  233   239                        1  671   676     -8  505  -523     12   75   -58
  -9  147  -142                       4   65    78        3,3,L            0  668   656    -10  283  -290      7   92    84
 -10  156  -160    10   62   -85      3  275   278                       -1  603   600    -14  142   152      6  102    99
 -11  100    98     9  113  -110      2  237  -229     13  181   171     -2  449  -424                        5   62   -49
 -12  264  -256     8  129  -123      1   89    96     11  156   160     -3  228   235        3,0,L            4  117   128
 -13   74    75     5  118   127      0  481  -475      8  124   134     -4  194   202                        2  206   217
                    0  230   221     -1  154  -152      6  116   113     -5  330  -346     14  164  -167     -2  165  -164
     4,0,L         -2   72    86     -2  259  -259      5  297  -304     -6  454   471     12  357  -344     -4  123  -122
                   -8  190  -192     -3  203  -199      4  297  -290     -7  517  -520     10  160  -163     -6   88   -71
  16  139   153   -10   96   -90     -5  182  -180      3  559  -547     -8  147  -159      8  318   322
  14  192   200                      -6  212   229      1   65   -82     -9  164  -186      6  590   576        2,6,L
  10  316  -311       3,6,L          -7   84    92      0  187   189    -12   89   -88      4  449   433
   8  580  -572                      -8  214   207     -1  402   413                        2  737   760      8  107    95
   6  360  -366    12  131  -118    -10  123   111     -3  541   531                        0  285   298
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  2,6,L

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  3  152   149
  2  167   -78
  1  479   -70
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 -2  447  -453
 -6  178   175
 -8  241   242
-10  177   189

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  9  172   174
  7  119   121
  6  103  -108
  4  290  -287
  2  335  -344
  1  216  -211
  0  237   232
 -1  331  -329
 -2  285   284
 -3  147  -143
 -4  264   260
 -6  329   336
 -7  255   268
 -8   98  -101
 -9  188   184
-10  153  -156

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 13   96   105
 11  217   218
 10  140  -127
  7  217  -227
  6  329  -329
  5  344  -334
  4  215  -203
 -3  531  -517
 -2  350   351
  0  263   269
 -1  569   563
 -2  160   173
 -3  615   606
 -4  257    74
 -5  227   226
 -6  166  -170
-13  138  -119

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 15  124   123
 10   60    62
  9  295  -292
  7  698  -677
  6  186  -184
  5  627  -617
  4  132  -117
  3  311   314
  2  293   292
  1  704   709
  0  456   450
 -1  931   890
 -2  229   230
 -3  509   497
 -4  150  -153
 -5  469  -477
 -6  109  -101
 -7  409  -405
 -9  228  -228

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-13  210  -215
-11  219  -230
 10   84   -89
  9  168  -162
  8  363  -354
  7  314   307
  6  434  -422
  5  671   673
  4   50   -48
  1  357   355
  0  293   298
 -1  338   339
 -3  648  -643
 -4  303   302
 -5  408  -409
 -6   67   -77
 -7  224  -231
 -8  141  -145
-11  275   261
-13   95    86

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 13  135  -143
 12  159  -150
  9  391   384
  7  286   284
  6  264   269
  5  177  -165
  4  479   492
  3   65   -63
  2  313  -308
  1 1724 -1821
  0  383   394
 -1 1022 -1004
 -2  512   497
 -3 1564  1528
 -4  661  -673
 -5  443   432
 -6  381  -385
 -7  121   135
 -9  207   207
-10  145   141
-12  172   175

  2,0,L

 12  198  -204
 10  168   162
  8  498   483
  6  211   214
  4  367   369
  2 1141 -1138
  0 1003  -980
 -2  225  -186
 -4  444  -437
 -6  815   828
 -8  986   987
-10  156   140
-16  124  -122

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  5   87    87
  3   99    81
 -3  106  -108
 -5   84   -95

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  9   89    92
  7   88   -89
  4  158  -163
  1  147  -159
 -1  124  -125

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  4  114  -102
  2  161  -171
  0  342  -353
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 -2  133  -126
 -6  113  -117
 -8  189  -188

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  6  128  -129
  4  289  -293
  2  233  -232
 -1   92   -87
 -2  177   182
 -4  278   279
 -6  123   122
-10  115  -107

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 11  103   111
  8  296  -298
  7  197  -198
  6  293  -295
  5   78   -75
  2   96   102
  1  157  -168
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 -5   81   -83
 -6  251  -255
 -7  170   171
 -8  177  -169
-14  122  -108

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 15  129   146
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  7  388  -385
  5  373  -365
  4  297   298
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 -1  296   313
 -2  126  -122
 -3  280   281
 -4  295  -284
 -6  100   -95
 -7  293  -295
 -9  333  -325
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-15   96    94

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  7  134   150
  6  133  -140
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 -2  640   618
 -3  274  -285
 -4  441  -431
 -5  774  -784
 -6  254  -249
 -7  346  -337
 -8  154   148
-11  216   208
-13  161   177

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 13  126  -119
  9  304   308
  8  151   151
  7  452   454
  6  278   274
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  1,2,L

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 4  200   195
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 0  314  -307
-1 1052 -1042
-2  793  -792
-3  618  -605
-4  213  -211
-5  221   229
-6  170  -188
-7  556   576
-9  352   370
-14  99   102

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13  229   245
11  242   250
10  100   111
 8  527   523
 7  107  -110
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 3  113  -132
 2 1012 -1037
 1  206  -217
 0 1089 -1118
-1  153   166
-2  733  -744
-3  185   184
-4  418   417
-5  525  -505
-6  903   896
-7  281   283
-8  403   409
-9  120   120
-11 304  -293

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14  172   165
12  250   241
10  299   303
 8  124  -138
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  2 1202 -1231
 -2 1119  1126
 -4 1046  1038
 -6   67    65
 -8  428  -419
-10  247  -252
-12  250  -232

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 1   71    39

  0,9,L

 7   88    87
 3   72   -56
 1  117  -109

  0,8,L

 6  113   123
 3  120  -115
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  0,7,L

 8   96    82
 4  160  -152
 2  222  -232

  0,6,L

10   67   -80
 8  231  -225
 6  202  -201
 3   87   100
 2  252   268
 1   72    68
 0  293   298

  0,5,L

12   84   -81
10  191  -194
 9  210  -206
 7   91   -89
 6  243   244
 5  185   177
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 3  154   148
 2  465   454
 1   72    71

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11  173  -176
 8   94    87
 7  332   329
 6  306   305
 5  372   367
 4  120   129
 3  252   262
 2  236  -234
 1  160   174

  0,3,L

15  155  -168
13  150  -143
11  107   113
10   71    86
```

```
 9  267   268
 7  476   483
 6  184  -174
 5  258   251
 4  481   478
 3  245  -245
 2  590   585
 1  345  -349

  0,2,L

16   94   -89
13  227   229
11  166   161
 9  101   -76
 8  112   113
 7   99   -94
 6  655   638
 5  480  -478
 3  172   171
 2  570  -568
 1  842   838
 0   93    87
```

```
  0,1,L

12  210   218
10  183   182
 9  337  -336
 7  303  -316
 6  247  -260
 4  885  -883
 3  622   614
 2  770  -782
 1  497   489

  0,0,L

12  170   173
10  151  -153
 8  867  -864
 6  524  -520
 4 1608 -1635
 2  773   784
```

APPENDIX VI

Structure Factor List for Compound I,
Part III.

Columns listed are ℓ, $|F_o| \times 10$, $|F_c| \times 10$, α.

```
   0•14•L

 5    32    24   166
 3    25    28   112

   0•13•L

 6    28    27   154
 5    30    29   179
 4    15    15   322
 3    16    19    54
 2    30    26   176
 1    74    76   187
 0    79    78     0

   0•12•L

 6    27    29   194
 5    22    26   239
 4    52    54   341
 3    26    28   343
 2    50    51   196
 1    38    40   115
 0    53    52     0

   0•11•L

 6    31    32   160
 5    29    29   357
 4    39    36   110
 2    66    67   178
 1    41    41   353
 0    94    92   180

   0•10•L

 8    29    30   288
 7    22    26   169
 6    23    24   144
 5    59    60   349
 4    50    51     5
 3    53    50   165
 2    94    97   131
 1    45    44   348
 0    43    45     0

   0,9•L

 7    45    45   159
 5    32    26     1
 4    37    41   317
 3    51    48   171
 2    78    80   186
 1    25    27   335
 0    49    50     0

   0•8•L

 9    27    29   349
 8    20    18   138
 7    53    55   167
 6    51    52   335
 5    67    67   359
 4    32    29   187
 3    99    99   172
 2    34    32   265
 1    91    92   348

   0•7•L

 9    17    22   355
 8    49    47   183
 7    48    49   176
 6    48    46    34
 5    71    74   349
 4    51    48   232
 3   131   131   177
 2    20    20    44
 1   133   136     3
 0    23    21     0

   0•6•L

 8    81    81   196
 6    80    80    24
 5    24    24   176
 4   118   121   196
 2   197   191    29
 1    80    74   172
 0    66    73   180

   0•5•L

10    33    35   357
 8    59    59   164
 7    32    28    41
 6    73    75     0
 5    70    69   256
 4   156   155   186
 3    82    88    29
 2   142   139   334
 1   129   128   171
 0    50    42     0

   0,4,L

10    35    33   358
 9   269   267   187
 8    58    58   160
 7   161   159    23
 6    62    64   346
 5    33    31   202
 4    23    20   324
 3   269   267    12
 2   126   119   174
 1   168   163   222
 0    62    61     0

   0,3•L

10    16    18   329
 9    50    48   163
 8    38    40   257
 7    40    41   331
 6    48    51    19
 5   100   100   181
 4    22    16    85
 3   248   251   338
 2   245   239   138
 1   150   146    80
 0   170   168     0

   0•2•L

 9    24    24   186
 8    48    47   347
 7   118   118   346
 6    46    46    35
 5   153   157   174
 4   110   108   328
 3    73    69   107
 2   267   274   183

   0,1,L

10   125   126   158
 7    94    93   170
 6    65   163   200
 5   120   119   185
 4   185   183   341
 3   108   113    53
 2   255   272   174
 1   230   236   233

   0•0•L

 8    38    36     5
 6   229   233   170
 4   129   130     3

   -1,14,L

 5    48    46   336
 2    21    24    34
-1    36    34   163

   -1,13•L

 4    24    20   151
 2    26    29   337
 1    58    58     5
 0    51    49   186
-5    33    35   205
```

```
      -1,12,L           -2   54   55   24     -4   67   66  317      1   31   26  238      5   87   85    1
                        -3   52   53  195     -5   56   56  354      0   85   84   53      4  143  137   45
  4   46   44  168      -4   56   56  131     -6   38   38  165     -1   78   79  184      3  348  334  199
  3   30   33  115      -5   49   50  353     -7   55   55  191     -2  208  210  179      2  260  267  169
  2   40   43  165                                                  -3   58   57  212      1  169  175  355
  1   57   56  285            -1,9,L                -1,7,L          -4  101  102   19      0  199  196  313
  0   58   56  207                                                  -6   79   78  197     -1  100  100  171
 -2   43   45   15       9   50   48  175      9   27   24  155     -8   71   71  359     -2  112  114  110
 -4   31   32  222       7   46   47    5      8   31   36  353                           -3  146  143   22
 -6   23   17  352       6   23   22  343      7   25   22  323           -1,5,L          -4  138  143  349
                         5   59   56  210      6   37   39  260                           -5   28   30  269
      -1,11,L            4   53   56  178      4   64   62  351      9   32   35  297     -6   77   77  162
                         3  139  141  359      3   14   19   35      8   41   41  346     -7   43   44  357
  8   38   39  170       2   55   54  254      2   81   77  142      6   34   37  167     -9   40   39  183
  6   38   38  355       1  107  105  179      1   56   54  250      4   60   60  352
  4   66   67  203       0   55   55  236     -1  157  154   23      3  154  149  117           -1,3,L
  3   40   37  214      -1   45   49  359     -2  101  101  169      2   99   98  101
  2  116  118   11      -2   58   57   18     -3  107  111  190      1   78   72  195      9   52   52   18
  1   24   23  169      -3   82   80  184     -4   79   80  343      0  161  159  327      8   36   36  100
  0   63   63  190      -4   33   29  318     -5   49   50   23     -1   81   77  285      7   98  100  170
 -2   29   28   47      -5   45   47  348     -6   45   44  178     -2  237  229  174      6   40   42  172
 -4   45   41  203                            -7   60   60  197     -3   46   45  343      5  189  185  349
 -5   41   40    9            -1,8,L        -8   38   32  351     -4  177  176  340      4   79   77  168
                                                                    -5   23   21  199      3  273  279  156
      -1,10,L            7   36   39    0           -1,6,L          -6   85   83  168      2  334  334  313
                         6   49   48  157                           -7   41   41   21      1  332  333  299
  7   33   38  344       5   66   68  194     10   38   40  169     -8   56   53   16      0  176  174   11
  6   47   47  359       4   42   45  130      9   29   29  152                           -1  229  226  151
  5   35   37  179       3   80   82  343      8   54   55    5           -1,4,L          -2   73   70  132
  4   67   69  180       2   33   31   96      7   22   27  109                           -3  209  204  338
  3   36   38   84       1   59   58  174      6   27   32  230     10   29   28  182     -4   55   53   62
  2  104  105  315       0  137  140  329      5   28   25  336      9   92   90  337     -5  129  126  131
  1   67   68  185      -1  135  135   15      4   71   69    9      8   54   54  320     -7   34   31  337
  0   61   61  166      -2   64   63  154      3  101  106   11      7   72   74  195     -9   40   39  199
 -1   81   80    5      -3  108  109  174      2   78   77  245      6   38   42  224
```

```
    -1,2,L

10   41   38   21
 9   31  129    0
 8  104  105  189
 7  106  107  179
 6   74   75  351
 5  100  102    8
 4  327  319  188
 3   59   68  173
 2  509  518   19
 1  572  605  355
 0   75   73  110
-1  131  145  165
-2   70   73   39
-3   24   19  266
-4   36   35  298
-5  182  188  194
-6   56   53  196
-7   82   80    7
-8   22   14  186
-9   20   22  161

    -1,1,L

 8   54   53  186
 7   53   52  198
 6  196  197  348
 5  167  162  333
 4  299  300  161
 3  151  139  337
 2  146  147  333
 1  297  291  100
 0  189  191  178
-1  205  209  206
```

```
-2  114  119   15
-3   87   87   76
-4   42   43  201
-5   67   66  243
-6   39   34  305
-7   42   44  337
-8   30   28  177

    -1,0,L

10   29   27  345
 8   53   54  155
 6  192  198  356
 4  119   25  200
-2  168  139  157
-4  130  129  234
-6  204  203   25
-8   47   46  172

    -2,14,L

 5   37   40  154
 3   29   28  355
 2   15   17  260
-1   42   41  353

    -2,13,L

 6   35   33  211
 1   29   24  176

    -2,12,L

 6   54   54  166
 4   38   35    0
```

```
 3   25   21  239
 2   42   43  197
 0   54   53  353
-2   27   24  160

    -2,11,L

 6   44   42  168
 5   29   30    2
 4   63   61   15
 3   38   37   97
 2   77   78  203
 0   32   31    0
-2   30   29  205
-4   46   47   19

    -2,10,L

 8   31   30  342
 7   55   51  166
 6   45   48  202
 5   17   20   64
 3   42   42  267
 2   31   29  145
 1  110  110  355
 0   44   44   38
-1   41   42  160
-2   34   30  208
-4   52   52  320

    -2,9,L

 9   32   32    4
 8  125   28  329
 7   33   35  199
```

```
 5   79   79    1
 4   52   52  352
 3  142  144  190
 2   26   27  276
 1   88   89   15
 0   27   29   99
-1   87   89  188
-2   18   19  187
-3  102  102   15
-4   24   27  198
-5   43   42  183

    -2,8,L

10   32   32  119
 9   34   35  352
 7   43   45  198
 5   89   88   19
 4  132  135  323
 3  107  109  159
 2   49   48    6
 1   67   65  351
 0  121  125  173
-1  115  115  191
-2   24   19  148
-3   77   77  332
-4   23   25  168
-6   39   37    7

    -2,7,L

10   33   33  336
 9   43   43  352
 7   38   34  191
 6   42   41   23
```

```
 5   76   76   36
 4  196  198  158
 3   80   79  157
 2  126  128  326
 1   73   69  321
 0   72   74  175
-1   82   82  166
-2  178  176  359
-3   56   57  283
-4   71   69  173

    -2,6,L

10   46   46    0
 8   55   55  178
 7   27   28  268
 6   40   40    0
 5   93   96  314
 4  191  189  163
 3  141  140  174
 2  161  162  335
 1   22   25  100
 0  128  128  165
-1   37   36  130
-2  173  176  350
-3   90   89   23
-4   31   32  189
-6   35   35   47
-8   35   35  192

    -2,5,L

 9   42   46  145
 8   48   46  173
```

```
  -2,5,L

 6   52   53  212
 5  113  113  166
 4  154   57  185
 3  236  233  307
 2  188  189  328
 1  154  149   24
 0  228  225  163
-1   50   50    9
-2  134  135  348
-3   98  101  146
-4   84   86  153
-6   53   56    2
-7   23   21  217

  -2,4,L

 9   82   84  178
 8   45   47  257
 7   40   36  341
 6   17   23  324
 5   69   64  145
 4   74   71  158
 3  229  230   25
 2  210  207   16
 1   98  100  226
 0  181  183  170
-1  114  117  359
-2  132  127    9
-3  122  127  213
-4  162  164  200
-5   48   48   47
-6   45   48  341

  -2,3,L

 9   39   40  178
 7  100   99  350
 6  150  153  309
 5   77   73  192
 4   54   48    8
 3   91  100   47
 2  161  150    5
 1  264  275  181
 0  300  289  158
-1  193  191   16
-2   39   39  331
-3  140  140  185
-4   49   51  272
-5  124  130  348
-7   62   63  175

  -2,2,L

10   34   34  164
 9   30   32  216
 8   66   68    4
 7   95   96   10
 6   20   22   64
 5   88   84  184
 4  138  139   62
 3   58   61   27
 2  343  339  258
 1  197  206  190
 0  121  113  111
-1   25   29  330
-2  122  114  245
-3   75   81  185
-4   86   89   48

-5  122  122    5
-6   47   46  166
-7   34   37  159

  -2,1,L

10   51   50  161
 9   36   36  155
 8   91   90  344
 7  103  105  343
 6  191  190  171
 5  191  186  156
 4  125  127   11
 3  119  114  308
 2   94  100  209
 1  236  224  162
 0  193  193   32
-1  178  176  333
-2   88   87  189
-4   70   71  351
-5   22   19   68
-6   73   71  169
-7   28   27  204
-8   47   43    0

  -2,0,L

10   54   55  191
 8   87   84  358
 6  199  201  191
 4   70   79    5
 2   23   29  263
 0   72   72   86
-2  142  123   28
-4   74   72  345

-6   74   75  181
-8   34   31  329

  -3,14,L

 3   38   37  177

  -3,13,L

-1   23   26  178

  -3,12,L

 2   51   52  359
 1   34   34   24
 0   38   39  159
-2   33   29  346

  -3,11,L

 7   31   30   17
 6   38   38  338
 2   28   28   19
 0   53   52  149
-2   41   40  342

  -3,10,L

 8   40   40  172
 7   52   53  352
 6   48   51   24
 3   29   30  353
 1   75   76  170
 0   33   34  222
-5   34   32    9

  -3,9,L

 8   20   15   97
 7   48   46  341
 6   49   48  139
 5   95   96  149
 4   29   31  234
 3   57   56  343
 1   41   38  150
-1   71   70  346

  -3,8,L

 9   54   52  166
 8   43   40  319
 7   42   42  358
 6   24   25  188
 5   73   75  190
 4   34   35  176
 3   92   97  339
 2   69   74  157
 1   37   36  181
-1   69   68   28
-2   89   88  349
-3   51   49  163

  -3,7,L

10   31   29  178
 9   45   47  160
 8   29   26  352
 7   30   30   48
 6   79   79  164
```

```
    -3,7,L          -3   97  103  183    3  115  112  155    4   86   85  203    4   15   15   13
                    -2  181  173  170    2  160  148  164    3  194  191  185    0   53   55  338
  5   86   85  231   1   45   47  102    1  181  177  253    2  150  144  226
  4  164  168  345   0  121  121   25    0  168  162  304    1  192  183  355      -4,10,L
  3  104  104  354  -1  163  168  199   -1  167  166  186    0  152  147  177
  2   61   62  160  -2   39   37  219   -2   54   49  320   -1  123  117  175    8   22   26   11
  1   50   46  187  -3  107  108  338   -3  150  151  210   -2  112  110  344    7   30   33  176
  0   81   83  218  -4   37   40  116   -4   47   49   69   -3  108  115  200    6   55   56  208
 -1   52   48  245  -6   39   39  203   -5  178  178  193   -4  114  115  170    5   24   23  326
 -2  132  134  191                                          -5   65   65  166    4   44   44  348
 -3   32   34  142      -3,4,L               -3,2,L         -6   61   63  349    3   30   31  176
                                                                                2   48   46  171
    -3,6,L           9   57   60  359   10   34   35  339      -3,0,L           1   38   39  219
                     8  153  152    4    9   37   35  132                        0   61   60  119
 10   47   49  179   6  174  181  135    7  116  121  169   10  147  147  150   -2   33   36  162
  8   45   44  342   5   69   71  324    6   47   47  234    8   68   68  185
  7   21   26  333   4  110  111  302    5  186  183  336    6  133  134   35      -4,9,L
  6   28   30  164   3  146  143  188    3   86   83  255    4  212  198  272
  5  128  131  125   2   51   49  187    2   63   57  127    2  161  164  334    9   19   19   15
  4  197  195  355   1   66   62  330    1  168  164  322    0  163  154  183    7   32   28  185
  2  141  138  169   0   86   83  337    0  114  106   89   -2  116  118  347    6   20   22  356
  0  101  100  207  -1  133  137  155   -1   73   75  174   -4  126  125  154    5   49   47   33
 -1   74   76  327  -2   36   30  227   -2  154  156  303   -6   57   57  329    4   39   38  332
 -2  136  138  186  -3   86   85    6   -3   74   70  307                        2   36   40  105
 -3   40   39  212  -4   56   57  176   -4   33   33  216      -4,13,L          1   47   45  352
 -4   47   45  357  -5   40   40  191   -5   57   59  170                       -1   66   68  164
                                                             2   32   29  168   -2   21   23  169
    -3,5,L              -3,3,L               -3,1,L          1   31   34  162
                                                                                   -4,8,L
  9   28   26    2   9   56   57  354   10   42   38  345      -4,12,L
  8   77   78  356   8   25   24  278    9   19   18  357                        9   51   49  341
  7   30   32  261   7  136  134  189    8   73   70  199    7   28   27   31    8   35   36  154
  6  118  118  195   6   55   55   95    7   37   39  202                        7   42   36  167
  5  123  127   25   5  118  117  354    6  109  108   31      -4,11,L          6   42   45  110
  4  142  143  350   4   60   57  289    5   75   76  130
```

```
   -4,8,L

 5   62   62   13
 4   36   36  160
 3   66   68  174
 2   58   62    4
 1   38   37   15
 0   26   27  243
-1   58   58  205

   -4,7,L

10   35   32    6
 9   45   44  322
 8   43   37  165
 6   51   50    0
 5   31   28    6
 4   69   68  199
 3   58   56  163
 2   26   25   41
 1   25   23   73
 0   51   50  209
-1   45   47  248
-2   47   50   18
-3   41   42   13

   -4,6,L

10   66   63  348
 8   53   51  145
 6   37   36  319
 5   21   17  296
 4  106  110  187
 3   53   58  312
 2   30   33   20

-1   50   50  157
-2   69   69   22

   -4,5,L

10   46   46  327
 9   34   32  172
 8   68   66  180
 7   23   21  348
 6  110  109   11
 5   49   50  211
 4  113  110  175
 3   29   27  349
 2  108  105   34
 0  114  113  235
-1   67   68   43
-2   52   54   18
-4   45   43  192

   -4,4,L

 9   48   48  188
 8   61   59  170
 6  110  110  348
 5   96   97  161
 4   52   51  218
 3   89   89  354
 2  104   99   38
 1   53   53  127
 0  113  112  179
-1  104  106  331
-3   47   45  166

   -4,3,L

 9   53   53  205
 7  140  142   28
 6   42   43  255
 5  166  167  176
 3  133  134  354
 2   41   43   75
 1  162  161  201
 0   61   64    9
-1  104  110  353
-3   68   68  163

   -4,2,L

10   27   30  197
 9   49   51  159
 8   47   48  104
 7  133  140  338
 6   24   21  181
 5   55   55  211
 4  104   98  329
 3   90   94   10
 2   75   78  127
 1  191  193  168
 0  149  150  309
-1   58   56  356
-2  100  104  132
-3   37   39  197
-5   47   46  358

   -4,1,L

10   36   35  218
 9   32   35  221
 8   82   82   48
 6   79   77  190

 5   30   30   93
 4  104  104  340
 3   60   59   25
 2  114  116  163
 1   33   24   76
 0   96   96  335
-2   91   96  169
-3   74   77  206
-4   68   68  358
-5   29   32  341

   -4,0,L

10   30   30  218
 8  119  124  325
 6   64   62  168
 4   51   48   98
 2  224  222  154
 0  126  125  335
-2   48   47  221
-4   74   76    5

   -5,11,L

 4   36   37  168

   -5,10,L

 7   26   24  351
 6   36   33   15
 5   21   25  177
 4   33   33  139
 2   27   27  350
 0   50   48  212

   -5,9,L

 5   41   44  209
 4   37   36  160
 3   26   32   18
-1   37   39    2
-2   20   17   12

   -5,8,L

 9   31   30  178
 7   42   40   10
 6   20   18  215
 5   54   57  195
 3   58   56  359
 1   58   57  180
 0   19   24   36
-1   49   50  359

   -5,7,L

 8   27   30   36
 7   32   29  346
 6   38   39  232
 5   51   50  166
 4   46   47   44
 3   61   61  344
 2   28   26  212
 1   53   51  162
-1   44   42  339

   -5,6,L

10   52   54  183
```

```
     -5,6,L
 8    47    48     9
 6    64    65   189
 4    93    95    19
 2    49    48   179
 0    53    52   333
-2    39    40   161

     -5,5,L

10    31    30   155
 9    30    28     1
 8    40    38     6
 6    67    69   193
 5    24    23   348
 4    59    61   353
 3    33    37   140
 2    51    51   204
 0    69    68    17
-2    56    59   159

     -5,4,L

 9    43    47     2
 8    32    31    25
 7    18    20   177
 6    59    58   244
 5   101   102   355
 4    45    47    66
 3    53    51   184
 2    59    55   217
 0    45    41    27
-1    56    58   176

     -5,3,L

 8    22    22    52
 7    57    61   190
 5    78    80   347
 4    76    74    93
 3    38    40   188
 2    35    35   275
 1    86    84    46
 0    40    39   247
-1    84    87   192

     -5,2,L

10    38    39   344
 9    57    60   331
 7    91    92   171
 6    30    36   330
 5    33    34    21
 4    70    71   152
 3   128   126   168
 1   131   130   347
 0    49    46   203
-1    22    20   201
-2    45    43    17
-3    54    50    11

     -5,1,L

10    38    34    42
 9    59    59    50
 8    51    53   191
 7    65    64   155
 6    88    87   325
 5    35    36   339

 4    58    63   160
 3    66    65   228
 2    58    53    13
 1    50    50   297
 0    58    59   178
-2    56    55    20

     -5,0,L

10    25    25   342
 8   133   136   153
 6    81    84   332
 4    99    99   149
 2   248   251   336
 0    77    78   150
-4    70    69   188

     -6,9,L

 5    56    56   352

     -6,8,L

 5    29    32   346
 3    28    30   161
 2    34    32   293
 1    43    40     1

     -6,7,L

 8    23    25   233
 7    27    30   188
 1    46    44   354

     -6,6,L

 8    37    37   214
 6    53    55    12
 5    34    31   335
 4    48    50   194
 2    46    43     9
 0    51    54   169

     -6,5,L

10    21    21     2
 8    31    30   186
 6    43    41    17
 4    41    41   145
 3    15    15    70
 2    51    47   324
 0    45    45   160

     -6,4,L

 9    33    34   181
 8    33    33   210
 7    33    31    12
 5    90    88   190
 4    53    50   153
 3    47    49    21
 2    33    31   302
 1    35    33   201
-1    44    48    12

     -6,3,L

 9    36    35   153
 7    45    43   345

 5    46    45   171
 4    33    34   271
 3    44    42   327
 2    21    19   311
 1    37    37   174
 0    30    29    96
-1    40    40   357

     -6,2,L

10    46    44   158
 9    42    43   180
 7    53    51    11
 6    50    48   175
 5    31    28   177
 4    68    69     4
 3    83    82   354
 1    52    51   181
 0    36    35    53

     -6,1,L

 9    27    28   223
 8    50    49   332
 7    52    52   335
 6    54    55   153
 4    48    46    38
 3    69    69    64
 2    61    60   206
 1    56    56   173
 0    47    52    12

     -6,0,L

 8    71    73   359
```

APPENDIX VII

Structure Factor List for compound [illegible]

Part III.

Columns listed are ℓ, $|F_o| \times 10$, $|F_c| \times 10$, α.

-6,0.L			
6	38	37	180
4	63	61	8
2	129	127	191
0	46	47	17
-2	43	44	195
-7,7,L			
7	29	25	25
6	41	43	145
-7,5,L			
8	27	28	359
-7,4,L			
7	18	23	188
5	58	57	8
3	28	33	189
-7.3.L			
9	37	37	353
7	36	37	192
5	35	38	21
3	59	57	167
1	36	38	346
-7,2,L			
9	36	35	18
7	35	35	188
6	41	42	30
4	60	61	206
3	39	43	192
-7,1,L			
8	45	43	175
7	33	37	150
6	42	43	8
4	48	45	199
2	50	47	359
1	31	29	345
-7.0.L			
8	54	56	200
6	43	40	19
0	19	16	172

APPENDIX VII

Structure Factor List for compound II, Part III.

Columns listed are ℓ, $|F_o| \times 10$, $|F_c| \times 10$, α.

```
     0,0,L

-10  104  103  205
 -6  321  332  325
 -4  296  284  190
 -2  858  906  113

     0,1,L

-11   79   79  357
 -9   62   64  217
 -7   96   94   92
 -5  164  164   30
 -3  182  170   85

     0,2,L

-10   46   46  102
 -9   20    0    0
 -8   75   74   70
 -6  130  131  282
 -4  250  241  151
 -2  331  320  114
 -0  402  396  180

     0,3,L

 -9  186  189  211
 -7  166  168  110
 -5   74   74  181
 -3   92   94  287
 -1   33   35  148

     0,4,L

 -8  106  107  268
 -6   90   90  164
 -4  202  200   84
 -2  205  205  302
 -0  148  148  330

     0,5,L

 -7   56   55  284
 -5   64   63  150
 -3  178  178   86
 -1  135  137  341

     0,6,L

 -4   65   65  125
 -2   84   81  188
  0   42   41    0

     0,7,L

 -5   46   46  185
 -3   38   38   48
 -1   60   57  281

     0,8,L

 -0   69   68    0

     1,1,L

 -9   71   72   93
 -8  104  103  251
 -7  134  133   35
 -6  156  158   98
 -4  251  248   29
 -3  175  165  275
 -2  340  352  295
 -1  327  336   11
 -0   70   69  180

     1,2,L

-11   49   55  145
-10   63   54  187
 -9   87   86   59
 -8   42   43   89
 -7  144  139  319
 -6   33   37  294
 -5  243  249  198
 -4  221  206  149
 -3  404  400   86
 -2   69   69  352
 -1  188  189  314
 -0   44   38  180

     1,3,L

-10   61   60  165
 -7   59   62   65
 -6  146  152  352
 -5  123  122  351
 -4  231  231  218
 -3  199  192  227
 -2  226  222   76
 -1  120  117   88
 -0  177  176    0

     1,4,L

 -7   34   37   52
 -6   40   39  187
 -3   49   49  171
 -2   72   72  175
 -1  108  107   86
 -0   88   86  180

     1,5,L

 -8   34   35   73
 -6   51   49  332
 -5   25   30   19
 -4  170  166  186
 -3  200  198  277
 -2  124  121  108
 -0  103  100    0

     1,6,L

 -7   40   43  129
 -5   93   92  354
 -4   50   54   79
 -3  129  125  239
 -2   64   64  302
 -1  119  119  150

     1,7,L

 -2   36   38  296
 -1   16    9   23

     2,0,L

-10   31   33  204
 -9   47   45  187
 -8  193  193   56
 -7  404  409   72
 -6  346  360  292
 -5  199  215  341
 -4  290  287  222
 -3  208  208  308
 -2  448  460  120
 -1  502  527   99
  0  314  366    0

     2,1,L

-11   35   35  348
-10   28   27  103
 -9   67   64  240
 -8   70   68  238
 -7  194  198   97
 -6  194  196  141
 -5  154  160  188
 -4  231  220  103
 -3  217  216  317
 -2  215  209  253
 -1  115  115  109
 -0  304  316  180

     2,2,L

 -9   33   38  183
 -7  102  102   53
 -6   47   49  177
 -5  107  103  275
 -4  106  105  164
 -3  160  149  255
 -2  153  145  119
```

```
      2,2,L

 -1  261  256  181
  0  205  207    0

      2,3,L

 -9   66   64  237
 -8   49   46  264
 -7   68   67  162
 -6   93   92  181
 -5   74   75   23
 -4  106  101   51
 -3  123  117  274
 -2  168  163  298
 -1  200  195  174
  0  322  309  180

      2,4,L

 -9   43   43   21
 -8   74   70  266
 -7   70   72   16
 -6   81   78  157
 -5   68   68  200
 -4  137  132   13
 -3   86   83  348
 -2  176  173  297
 -1   68   64  342
  0  267  262  180

      2,5,L

 -8   29   27  108
 -7   49   47  284

 -5   75   73  146
 -4   75   74  165
 -3  100   99   62
 -2   49   48  138
 -1  152  153  334
  0   28   29    0

      2,6,L

 -3   75   80  276
 -1   44   40  205

      2,7,L

 -5   38   38  193
 -4   12   19  266
 -1   66   66  324
  0   73   70    0

      3,1,L

-11   26   25  167
-10   61   61  333
 -9   68   69   70
 -8   41   43  200
 -7   81   81  315
 -6  198  194  163
 -5   87   86  187
 -4  467  445    4
 -3  257  249  128
 -2  652  678  249
 -1  411  435    8

      3,2,L

-11   56   54  158
-10   65   64  174
 -9   73   70   27
 -8   83   85   77
 -7  103  102  307
 -6  119  121  319
 -5  175  173  198
 -4  232  231  226
 -3  191  182  356
 -2  283  284  124
 -1  158  157  239
  0  200  204    0

      3,3,L

 -8   55   54  110
 -7   67   67   97
 -6   62   61   16
 -5  146  148   22
 -4   91   91  270
 -3  271  263  261
 -1  238  227  115
  0  219  212  180

      3,4,L

 -7   28   29  269
 -6   33   34  178
 -5   58   58  322
 -4   96   98  132
 -3   95   95  212
 -1   47   48  154
  0   61   59  180

      3,5,L

 -8   30   36   89
 -7   27   29  155
 -6   41   38  321
 -5   87   86  341
 -4  126  129  300
 -3  177  173  235
 -2   86   81  118
 -1   80   81  144

      3,6,L

 -7   47   49   89
 -6   43   42  154
 -5   45   44    4
 -4   93   90   18
 -3   97   97  264
 -2   84   82  287
 -1   65   66  118
  0   63   65  180

      3,7,L

 -4   52   49   19
 -2   37   38  282
  0   19   16  180

      4,0,L

-11   89   88  354
-10   37   39  164
 -9   96   97  242
 -8   34   35   85
 -7  107  108  158

 -6  141  142  190
 -5  208  213   22
 -4  134  136  184
 -3  112  109  137
 -2  324  324  126
  0  218  228  180

      4,1,L

-10   76   74   30
 -9   53   55  251
 -8   47   46  220
 -7   50   48  214
 -6  136  133  165
 -5   29   29  167
 -4  114  117   32
 -3  256  241  298
 -2  155  151  260
 -1  431  444  184

      4,2,L

 -9   29   34  254
 -8   25   22  280
 -7   68   65  182
 -5   75   79  217
 -4   69   70  256
 -2  150  142    4
 -1  148  144  283
  0  496  508  180

      4,3,L

-10   50   49  336
 -9   43   45  274
```

```
        4,3,L

  -8   110   111   263
  -7    38    41   175
  -6    91    92   129
  -5    54    53    44
  -4   129   126    25
  -3   141   145   310
  -2   190   194   304
  -1    91    92   258
   0    40    37     0

        4,4,L

  -9    63    65    34
  -8    56    54   242
  -7   120   122   283
  -6    90    91   111
  -5   136   133   180
  -4    88    87   343
  -3   307   310    85
  -2   110   114   335
  -1   157   157   321
   0   213   214   180

        4,5,L

  -8    56    57    84
  -6    46    45   317
  -5    37    38   156
  -4    93    93   227
  -2   132   130   127
  -1   116   115   325
   0    63    64     0

        4,6,L

  -4    78    77   326
  -3    31    29    61
  -2    20    23   357
  -1    39    40   242

        4,7,L

  -4    38    39   225
  -3    35    36    66
  -1    26    26   359

        5,1,L

 -10    53    50   239
  -9    75    75     9
  -8    77    78   146
  -7   234   232   258
  -6   103    95   138
  -5   247   241   176
  -4   253   244    43
  -3   458   447    63
  -2   399   384   247
  -1   372   368   267

        5,2,L

 -10    51    51   205
  -9    29    23   255
  -8   113   108    80
  -7    29    29   326
  -6   220   224   340
  -5   112   108   267
  -4   318   318   236

  -3   182   179   153
  -2   396   395    92
  -1   156   148   177
   0   431   440   180

        5,3,L

  -9    53    52   239
  -8    44    43   147
  -7    85    87   162
  -5    97   104     9
  -4   103   100   344
  -3    65    64   179
  -2    67    64   208
  -1   141   129   138
   0    80    74   180

        5,4,L

  -6    27    28    14
  -4    63    62   288
  -3   138   142   269
  -2    51    48   140
  -1    43    39   170
   0    65    65     0

        5,5,L

  -7    41    40   140
  -5    68    68    12
  -4    64    64    66
  -2    63    63   317
  -1    99    97   162
   0   108   109     0

        5,6,L

  -6    55    59   170
  -4    80    80    35
  -3    48    47   151
  -2    95    93   299
  -1    39    43   126
   0   120   122   180

        5,7,L

  -5    35    38   183
  -3    89    90    80
  -1    52    52   325
   0     0     9     0

        6,0,L

 -11    46    49   336
 -10    50    50   128
  -9   102   100   241
  -7   179   178   135
  -6    59    59   119
  -5   272   274     6
  -4   356   344   144
  -3   411   402   278
  -2   235   222   116
  -1   121   116   256
   0   559   592     0

        6,1,L

 -10    50    52   357
  -9    44    44   208
  -8   132   134   257

  -7    58    55   245
  -6   179   185   120
  -5   101   102   224
  -4   193   188    35
  -3   107   109   101
  -2   175   181   312
  -1   356   348   260
   0   191   188     0

        6,2,L

  -8    54    55   286
  -7   150   156   250
  -6    60    57   328
  -5    62    65   108
  -4    87    87   190
  -3    72    71   108
  -2   326   312    53
  -1   146   143   259
   0   371   379     0

        6,3,L

 -10    66    68     0
  -9    18    22    17
  -8    55    54   277
  -5    67    70   149
  -4   172   172     3
  -3   164   160    59
  -2   167   164   308
  -1   132   125   357
   0   173   177   180
```

```
      6,4,L              7,1,L           -3   122   131   268      0    46    45     0     -4   102   101   180
                                         -2   114   112   320                               -3    96   100   258
 -7   101   101   282    -11    57    56   149     -1   150   161   168          8,0,L           -2    96    93    75
 -6    42    44    30    -10    29    33   181      0    18    22   180                               -1   249   244    10
 -5   141   143   154     -9    57    59    12                             -10    99    98    20     -0   430   427     0
 -4   162   163   167     -8    44    44    66          7,4,L               -9    86    85   207
 -3   245   250    72     -7    77    76   339                              -8   183   180   323          8,3,L
 -2    76    74    70     -6   156   159   356     -6    23    22   309     -7   108   106    78
 -1   316   317   331     -5   196   193   208     -5    63    66   304     -6   144   144   226     -9   146   149    49
  0    76    72     0     -4   136   134   256     -4    55    58   351     -5   113   114   320     -8    47    47   250
                          -3   252   249    27     -3   136   141   164     -4   131   130    23     -7   150   149   311
      6,5,L               -2   191   181   146     -2    45    43    17     -3   467   442   255     -6   112   115   147
                          -1   366   379   291     -1    62    59    87     -2   191   193   152     -5    97   100   144
 -8    48    49    81     -0   581   623     0                              -1   317   322   142     -4   121   123    72
 -7    46    44   210                                  7,5,L               -0    99    97     0     -3   282   288    77
 -6    68    71   326          7,2,L                                                               -2    98   100   304
 -4    73    75   221                              -8    38    37   296          8,1,L               -1   127   131   339
 -3    28    27   188    -10    60    60   183     -7    91    93    87                               0   124   133   180
 -2   102   106   110     -9    52    51   174     -5   147   148    11    -10    35    35     7
 -1    39    43   289     -8    89    88    66     -3    79    79   288     -9    37    37    46          8,4,L
 -0   145   147     0     -7   119   125    74     -2    53    52   250     -8    68    65   291
                          -6   169   168   349     -1   106   103   126     -7   140   140   349     -9    43    43    46
      6,6,L               -5    82    82   351                              -5   171   177   186     -8    73    73    74
                          -4   197   200   220          7,6,L               -4   107   102    39     -7    65    69   290
 -4     0    13   140     -3    93    91   276                              -3   218   213    43     -6    95    99   300
 -3   162   162    90     -2   226   229    91     -6    61    63   134     -2   347   338   313     -5   185   185   167
 -1    50   147   347     -1   301   296   137     -4    73    70    58     -1   299   300   325     -4   177   182   207
                           0   330   347     0     -2    92    90   276     -0   394   415   180     -2   204   206   123
      6,7,L                                       -0    59    57   180                              -1   154   156   346
                               7,3,L                                           8,2,L                0   196   189     0
 -4    44    42   219                                  7,7,L
 -2    54    53   126     -9    47    48   222                              -8    72    73   331          8,5,L
 -0   143   144     0     -7    81    85    99     -4    57    57   155     -7   110   107    54
                          -5   114   118   359     -3    55    57    66     -6    99    99   308     -6    43    47   329
                          -4   150   158   128     -2    32    29   145     -5    84    86    14     -5    42    42    32
```

```
   8,5,L

 -3   56   52  274
 -2   44   45  130
  0  108  115    0

   8,6,L

 -3  146  145  285

   8,7,L

 -3   35   35  274
 -2   23   22  125

   9,1,L

-10   24   29  216
 -8  282   83   65
 -7   96  101   34
 -6  127  125  339
 -5   97   97  231
 -4  197  196  264
 -3  122  125  122
 -2   96   96   63
 -1  137  133   83
  0  169  163  180

   9,2,L

-10   41   43  151
 -9   62   62  222
 -7  145  143   98
 -6   49   43  296
 -5  162  167  358
 -4  117  117  206
 -3  216  211  246
 -2  101  102  113
 -1  375  377  134
  0  110  109  180

   9,3,L

-10   43   51   19
 -8   78   76  263
 -7   74   77   84
 -6   93   92  123
 -5   53   59  333
 -4  119  119  330
 -3  235  238  256
 -2  138  135  286
 -1  160  162  125
  0  359  350  180

   9,4,L

 -9   23   30   86
 -7   23   25   34
 -5   48   50   40
 -4   78   73  103
 -2   77   78  285
 -1   64   64  126

   9,5,L

 -6   73   72  156
 -5   50   48  340
 -4   36   34   39
 -3   84   82  236
 -2   65   66  313
 -1  112  116  143
  0  177  182  180

   9,6,L

 -6   24   32  165
 -5   58   59  203
 -4   38   41   31
 -3   54   56   97
 -2   28   31  257
 -1   95   98  339
  0   57   61  180

   9,7,L

 -4   45   46  231
 -2   46   47  117

  10,0,L

-10   78   77  340
 -9   70   70  199
 -8  105  106  273
 -7   76   74  106
 -6  247  253  168
 -5   94   90  290
 -3  149  146  136
 -2  294  301  294
 -1  174  175  168
  0  134  134  180

  10,1,L

 -9   61   61   27
 -8   55   54  259
 -7  137  139  283
 -6   50   47  171
 -5  161  161  165
 -4   74   77  325
 -3  243  239   74
 -2   95   92   33
 -1  103  100  279

  10,2,L

-10   36   34  354
 -8   45   46   81
 -7   37   35   41
 -6   90   92  227
 -5   33   37  139
 -4   68   71  349
 -3   63   60   96
 -2   25   18  127
 -1  255  257  104
  0  253  254  180

  10,3,L

 -9   57   53   22
 -7   58   58  272
 -6   53   52  157
 -5  134  132  158
 -4  107  109  161
 -3  159  157   31
 -2   81   80  206
 -1  228  227  323
  0  156  164  180

  10,4,L

 -8   75   74   97
 -7   53   51  243
 -6   77   79  324
 -5   39   41  246
 -4  110  108  237
 -3   45   43  200
 -2  159  160  109
 -1   56   59  270
  0  166  165    0

  10,5,L

 -7   45   42  131
 -6   32   33  274
 -5   63   61   20
 -3   63   62  257
 -1   48   45  127

  10,6,L

 -6   16   16  152
 -4   48   49  337
 -2   39   36  176
 -1   26   28  167

  10,7,L

 -1   36   31  152

  11,1,L

-10   68   70  195
 -9   19   19   99
 -8   80   84  113
```

```
      11,1,L

-7    46    45   202
-6    58    55    66
-5    82    79    56
-4    55    58   286
-3    65    68   101
-2    37    39   176
-1   114   110   133
 0   125   124   180

      11,2,L

-9   184   183   221
-7    84    84   120
-6   146   147   119
-5   161   162   357
-4    54    56   172
-3   282   289   261
-1   362   374   160
 0   131   125   180

      11,3,L

-8    79    78   222
-7    75    73   246
-6   117   121   138
-5    36    37   354
-4   175   178    22
-3   138   144   153
-2   222   230   318
-1   136   136   354
 0   335   337   180
```

```
      11,4,L
-4    51    54   304
-3   171   170   233
-2    65    69   180
-1   147   149    82

      11,5,L

-6    92    91   115
-4    86    89    16
-2    87    89   287
-1   143   141   305
 0   176   175   180

      11,6,L

-5    53    54   185
-3   163   165    83
-2    13    12   108
-1    70    67   310

      11,7,L

-2    51    48   175

      12,0,L

-9   159   160     7
-8   102    98   263
-7    52    53   263
-6   123   126   166
-5   144   147   175
-4   188   187   261
-3   276   274   230
```

```
-2   282   287   293
-1   163   160   254
 0   216   225   180

      12,1,L

-9    48    46    38
-7    57    55   324
-6    80    86     8
-5    76    74   171
-4   126   124   202
-3   208   207    57
-2    43    44    57
-1   253   250   323
 0   139   136     0

      12,2,L

-8    46    48   186
-7    52    54   225
-6    86    88   130
-5    31    32    46
-4   119   118   133
-3   170   171    71
-2    80    78   104
-1   137   139   255
 0   103    98     0

      12,3,L

-9    17    21   331
-7   122   119   261
-5   141   140   195
-4   106   106   248
-3   152   151   268
```

```
-2   159   160   113
-1   177   179   300
 0    72    72     0

      12,4,L

-8    40    40    59
-7    31    32   155
-6   117   115   341
-4    78    79   230
-2    89    86    81
-1    41    45   247
 0   186   196   [illegible]

      12,5,L

-5    66    66    29
-4    24    24    22
-3    46    46   268
-1    62    62   148

      12,6,L

-3    54    54    61
-1    35    35   239

      12,7,L

 0    42    42   180

      13,1,L

-10   52    49   184
-8    56    56   112
-7    43    43   161
```

```
-6   176   173   349
-5    73    77    15
-4    90    87   208
-3   131   128   284
-2   168   173   164
-1    70    67   236
 0   161   165     0

      13,2,L

-9    65    65   218
-8    69    73   263
-7   176   175    97
-6    79    80   103
-5   123   119   321
-4   116   117   358
-3   198   199   247
-2   121   118   300
-1   144   144   152
 0   111   110   180

      13,3,L

-9    60    57    61
-8   155   152   270
-7    67    63   285
-6    41    44   100
-5    70    68   108
-4    99   102    65
-3    72    67    39
-2   164   164   276
-1   155   157   324
```

```
    13,4,L

-3   48   46  155
-2   34   30   12
 0   27   24    0

    13,5,L

-7   23   32  295
-5   47   44  182
-4   65   64   59
-3   77   76   98
-2   57   59  289
-1  107  105  342

    13,6,L

-4   39   41  233
-2   49   52  127
-1   42   42  329
 0   75   74    0

    13,7,L

 0   91   87    0

    14,0,L

-10  46   42   27
-9   54   54    2
-8  100   99  280
-7  108  107  304
-6   37   32  166
-5  157  158  195
-4   32   35  237

-3  170  174   69
-2   99   99   81
-1  235  239  308
 0  187  185    0

    14,1,L

-9   41   40   29
-8   55   59   75
-7   58   56  315
-6   83   81  330
-5  109  106  172
-4  123  120  231
-3  110  110   58
-2  162  161  100
-1   63   63   29
 0   48   46    0

    14,2,L

-6   69   70  334
-5   46   47  190
-4  183  184  189
-3  113  112  301
-2   66   66  128
-1  122  123  322
 0   33   28    0

    14,3,L

-8   36   36   40
-7   29   29  269
-6  101   99  341
-5   38   38  212
-4   56   56  212

-3   78   80   79
-2  100   99   56
-1  161  166  307
 0  209  211    0

    14,4,L

-7   62   63  108
-6   85   82  317
-5   93   89   33
-4   97   99  206
-3   76   75  255
-2   92   91   76
-1   96   99  117
 0   94   98    0

    14,5,L

-7   25   28  110
-6   35   32  141
-5   38   40   17
-4   64   59   34
-2   52   53  263
-1   29   26   93
 0   24   23  180

    15,1,L

-9   76   74  228
-8   35   38   48
-7   87   88   83
-6   59   58  318
-5   73   76  308
-4   54   55  287
-3  184  188  260

-2   53   59  161
-1  156  161  145
 0   77   75    0

    15,2,L

-8   78   74  266
-7   38   40   58
-6   77   79  146
-5   37   37  355
-4  162  165   42
-3   38   40  184
-2  240  246  315
-1   84   86  127
 0  222  229  180

    15,3,L

-7   37   37  344
-6   40   36  253
-5   87   86  196
-4   30   30  329
-3   49   50  130
-2   39   42  211
-1  130  134   18
 0   45   52  180

    15,4,L

-7   32   31   46
-6   21   18   77
-2   51   50  244
-1   34   34   34

    15,5,L

-5   53   52  163
-3   33   32   45
-2   27   27  183

    15,6,L

-4   37   40  217
-2   64   60   98
 0   74   68    0

    16,0,L

-8   55   58   14
-7   91   88  342
-6   41   42  301
-5  116  115  193
-4   39   37  197
-3  174  178   83
-2   94   94   27
-1  182  183  353
 0   29   34    0

    16,1,L

-8   52   49   97
-5   39   40   39
-4  138  135  191
-3   59   56   94
-2  149  148   98
-1   36   43  288
 0   97   96    0
```

```
     16,2,L

-5    38    38   232
-4    63    59   298
-3   121   122   207
-2   137   142    72
-1    51    49    82

     16,3,L

-8    41    44    30
-7    20    23    97
-6    92    89   314
-5    60    57   102
-4    71    71   231
-3   145    43   356
-2    54    53    83
-1    51    54    76
 0    81    83     0

     16,4,L

-7    58    58   112
-5   118   114    25
-4    23    21   217
-3   125   125   249
-1   139   139   123

     16,5,L

-6    50    52   168
-4    66    64    57
-2    61    61   272
 0    75    76   180

     16,6,L

 0    58    54   180

     17,1,L

-9    46    44   210
-7    90    87    98
-6    58    57   129
-5    89    85   336
-4   129   132     9
-3    54    56   230
-2   128   131   317
-1   195   198   146
 0   145   146   180

     17,2,L

-8    76    71   257
-6   102    99   137
-5    48    49   117
-4    82    82    40
-3    41    41    42
-2   152   152   282
-1    29    26    90
 0   181   185   180

     17,3,L

-8    40    42   139
-7    50    49   293
-6    25    30   123
-3    92    89    89
-2    37    35    33
-1    33    34   266

 0    49    48   180

     17,4,L

-6    31    33   222
-1    35    34    87
 0    60    61   180

     17,5,L

-5    55    53   236
-4    41    40   268
-2    41    42   124
-1    25    30   306

     17,6,L

-3    19    18   255
 0    73    71     0

     18,0,L

-9    66    65    49
-8    49    47    90
-7    67    65   288
-5    98    95   155
-4    20    21   196
-3   169   168    70
-2   117   119   114
-1    37    35   351
 0    67    70     0

     18,1,L

-8    36    34    83

-6    59    61   338
-4   128   126   208
-3   112   111   279
-2    83    81   133
-1    60    61   155

     18,2,L

-5    68    70    23
-4    51    51    67
-3    32    35    88
-2    61    65   325
-1    61    58   271
 0    48    50     0

     18,3,L

-8    23    27   122
-7    37    32   140
-5    66    64    38
-4    72    72   217
-2   106   108   107
-1    64    63   136
 0    57    56     0

     18,4,L

-6    55    55   145
-5    73    72     0
-4    67    67    37
-3    62    60   235
-2    57    56   256
-1    34    34   152
 0    65    65   180

     18,5,L

-4    34    34    39
-2    46    43   249
-1     0    36   301
 0    44    45   180

     18,6,L

-1    45    43   261

     19,1,L

-8    58    57   239
-6    77    77   115
-5    70    70    37
-4    68    68    49
-3    34    35   357
-2   142   143   284
-1    76    77   175
 0   151   155   180

     19,2,L

-8    45    43   214
-7    58    56   294
-6    54    53   132
-5    74    78   204
-3    69    70    99
-2    37    40   280
-1    92    96   334
 0   119   120   180
```

```
   19,3,L
-4   50   49  217
-3   44   44   80
-2   38   39  195
-1   99  100  320
 0   38   38    0
   19,4,L
-3   17   17  253
-2   40   40  158
-1   32   37  217
 0   47   48    0

   19,5,L
 0   50   48    0
   19,6,L
-1   62   57  132
   20,0,L
-8   47   44   96
-6   62   62  327
-4  178  173  191
-3   83   81   43
-2  169  170  135
-1  108  103  287
 0  161  161    0
   20,1,L
-5   51   50  328
-3   97   97  238
-2   85   85   82
-1   49   53  176
 0   54   55    0
   20,2,L
-5   43   39  141
-3   41   41  342
-2   51   53  194
 0   67   70    0

   20,3,L
-6   24   23   26
-5   55   53  359
-4   41   38  191
-3   53   55  273
-1   32   35  173
 0   23   26    0
   20,4,L
-4   75   76   66
-2   88   87  278
 0   47   45  180
   20,5,L
-4   14   20   29
-3   28   29   72
-1   55   53  305
   21,1,L
-6   46   47  128
-3   37   35  265
-2   75   74  246
-1   38   40    6
 0   77   81  180
   21,2,L
-7   66   68  300
-5   64   65  199
-3   69   70   76
-2   30   31  340
-1  111  114  312
   21,3,L
-6   56   56  312
-5   25   28  156
-4   55   56  206
-2   63   63   98
-1   45   47   25
 0   49   50    0
   21,4,L
-5   42   37  266
   21,5,L
-1   41   34   66
 0   68   69    0
   22,0,L
-6   71   74  317
-5   77   77  228
-4  131  130  220
-3   81   85  271
-2  142  140  105
-1   43   40  161
 0  113  111    0
   22,1,L
-5   66   64   13
-3   54   54  268
-2   81   81  323
-1   48   46  166
   22,2,L
-4   18   20  197
-2   72   74   73
   22,3,L
-4   30   29   45
-3   46   46  249
-2   28   26  325
-1   32   29  110
   22,4,L
-4   35   37   33
 0   52   46  180
   23,1,L
-6   42   41  164
-4   75   72   20
-2   51   55  330
 0   77   73  180
   23,2,L
-6   41   39  339
-5   49   48  178
-3   49   49   86
-1   69   65  348
 0   29   29    0
   23,3,L
-5   38   39    3
-3   45   43  233
-2   53   55  115
-1   31   33  141
 0   68   64    0
   23,4,L
-1   32   32  137
   23,5,L
-1   59   57  123
   24,0,L
-6   26   27  319
-5   69   68  342
-3   46   49  232
-2  113  110   51
```

```
    24,0,L          0   22   27  180       25,1,L              26,0,L           -2   49   49  129
                                                                                 0   45   46    0
-1   71   72  173        24,3,L        -4   48   45   27   -5   64   68   37
 0   62   58    0                      -3   67   66   63   -1   77   76  144        28,0,L
                   -5   32   35   56   -2   61   60  286
    24,1,L         -1   28   26  155    0   26   27  180       26,1,L           -3   36   39  254
                                                                                -1   61   59   99
-5   32   31   61        24,4,L             25,2,L         -5   31   27   30
-1   76   75  109                                           0   62   58  180        28,1,L
                   -1   46   43  308   -4   50   53  216
    24,2,L          0   46   46  180   -2   66   66  102       27,2,L           -2   34   38  261
```

APPENDIX VIII

Structure Factor List for compound III,
Part III.

Columns listed are ℓ, $|F_o|$ x 10, F_c x 10.

```
  9,0,L            9,-5,L           8,-2,L           8,-6,L           8,-11,L          7,-3,L          -5  142  -142
 -1   76    79      0   74   -72      0  122   119      0  142  -135      0   22   -20      0  102    98     7,-7,L
 -3   90    88     -1  201  -196     -1  127   130     -1   83   -82     -1   56    56     -1  161   160
                   -2   79    80     -2   29   -29     -2   34    29     -2   45   -45     -2   75   -74      0   28   -24
  9,-1,L           -3  111   110     -3  180  -182     -3   49   -46     -3   33   -31     -3   19   -19     -1  125   119
                                     -4   35   -31                                         -4   48    41     -2   35   -35
  0   69    71     9,-6,L            -5   75    77     8,-7,L           8,-12,L           -5   68   -69     -3   47   -41
 -2   62   -62                                                                            -6   35   -34     -4   57   -54
 -3   68   -71      0   25   -28     8,-3,L             0   48   -49     -1   44   -43                      -5   60   -59
 -4   18   -18     -1   31    31                       -1  136   136                       7,-4,L
                   -2   66    67      0   57   -54     -3   27    25     7,0,L                              7,-8,L
  9,-2,L           -3   53   -53     -1   30   -31     -4   26    22                        0   23   -17
                                     -2  133   133                      -1   81   -77     -1   54   -58      0   29    34
  0  106   102     9,-7,L            -3   52   -54     8,-8,L           -3   63   -61     -2  187  -185     -1   19    19
 -2   33    31                       -4   28   -28                      -5   63    65     -4  207   207     -2   42    40
 -3   55    52      0  146  -143     -5   78    77      0  126  -125                      -5   41    39     -3   78    73
 -4   91   -93     -1   24   -20                       -1  136   135     7,-1,L           -6   70   -69     -4   87   -86
                   -2  175   171     8,-4,L            -2   24   -27                                        -5   88   -84
  9,-3,L           -3   42   -42                       -3  113  -112      0  102  -104     7,-5,L
                                      0  152   151     -4   57    56     -1  153   149                      7,-9,L
  0   89    88     8,0,L             -1   88   -85                      -2  181   180      0   20   -20
 -1  129  -128                       -2  124  -128     8,-9,L           -3  116  -121     -1   47    42      0  214   215
 -2  126  -125      0   63   -61     -4   53    50                      -4   42   -43     -2   13    15     -1   45    41
 -3   31    27     -2  223   225     -5   28    29     -1   68    63     -5   11    -6     -3   60    59     -2  169  -166
 -4   56    53     -4  144  -142                       -3   43   -44     -6   64   -62     -4   27    25     -3   28   -26
                                     8,-5,L                                               -5  121  -122     -4   30   -33
  9,-4,L           8,-1,L                              8,-10,L          7,-2,L                              -5   33    35
                                      0  149  -149                                         7,-6,L
 -1   53   -55      0   19   -18     -1   71    70      0   12    13      0   39   -31                      7,-10,L
 -2  110   112     -1  137  -135     -2   69    59     -1   79    79     -2  113  -115      0   91   -89
 -4   61   -60     -2   74    72     -3   26   -21     -2  115  -107     -3  124  -122     -1   33   -28      0   52    52
                   -3   89    88     -4  106   104     -3   15    15     -4   60    61     -2   73   -70     -4   10     3
                   -4   63   -65                                         -5   79    74     -3  192   192     -5   35    32
                   -5   14    14                                         -6   52    48     -4  114   109
```

```
 7,-11,L
                                                  
-1  184 -181
-2  183  -80
-3   77  -76
-4  121 -123
 7,-12,L

 0   62   59
-1   26  -29
-3   99 -101
-4  221  -22
 7,-13,L

 0   78  -76
-1   62  -57
-2   82   79
-3  140   41

 7,-14,L

 0   52   53
-2   76  -74
 6,0,L

 0  262 -257
-4  237  232
-6  140 -137

 6,-1,L

 0   78  -68
```

```
-1  182  182
-2   64   47
-3   21  -24
-4   96  -99
-5  112 -108
-6   99   99
 6,-2,L

 0   78  -71
-1   52   41
-2  144 -143
-3   90   86
-4  134  131
-5  160 -158
-6   28  -23

 6,-3,L

 0  169  177
-1  213  204
-2  169 -168
-3  259 -253
-4   24  -24
-5   86   82
-6   95   97

 6,-4,L

 0   42   41
-1  113 -116
-2   38   35
-3  264  265
-4   58  -62
-5  127 -131
```

```
-6   56   57

 6,-5,L

 0  220  213
-1  187 -188
-2  296 -287
-3   64   64
-4  162  160
-5   59   60

 6,-6,L

 0  145 -146
-1   83  -84
-2  257  256
-3  123  118
-4  126 -128
-5   46  -43

 6,-7,L

 0   56   55
-1  281 -274
-3  228  219
-4   91  -88
-5   67  -63
-6   90   90

 6,-8,L

 0  103   95
-1   94   95
-2  116  114
-4  195 -190
```

```
-5   16  -13
-6   30   32

 6,-9,L

-1  141 -133
-2  160  157
-3   28  -17
-4  159 -157
-5  123  123

 6,-10,L

 0  231  228
-1   55  -54
-2   34  -35
-3   68  -65
-4   91  -86
-5   72   73

 6,-11,L

 0   46  -47
-1   24  -14
-2   19   18
-4   67   65
-5   68   64

 6,-12,L

 0   66  -64
-1  155 -154
-3   36  -32
-5   94   93
```

```
 6,-13,L

 0   96  -98
-1   49  -51
-2   93   89
-3   90   86

 6,-14,L
 0   78  -77
-1   63   60
-3   75  -74
-4   36   34

 6,-15,L

 0   63  -64
-1  127  120
-2  137  137
-3   64  -64

 6,-16,L
 0   56   56
-1   29   30
-2   95  -92

 5,0,L

-1  155 -168
-3  451  463
-5  253 -248
-7   41   42
```

```
 5,-1,L

 0   78  -72
-2  203 -194
-3   33   30
-4  205  209
-5   60  -59
-6   39  -39
-7   76   76

 5,-2,L

 0   81  -71
-1  318  313
-2  125  421
-3   53  -61
-4  345 -342
-5  110 -108
-6  112  111
-7   22   27

 5,-3,L

 0  283  285
-1  213 -192
-2  292 -297
-3  210  214
-4   47  -43
-5   11  -13
-6  128  123
-7   36  -36

 5,-4,L

 0  405  394
```

```
-1  251  254
-2   40  -39
-3  257 -265
-4  126 -119
-5  136  138
-6   17   20
-7   23  -25

 5,-5,L

 0   44  -45
-1  447 -455
-2  103  104
-3   98   94
-4   40  -39
-5  152  153

 5,-6,L

 0  142  128
-1  172 -167
-2  100  -95
-3   88   90
-4   31   29
-5   29   32

 5,-7,L

 0  411 -421
-1  145 -146
-2  263  266
-3   73   66
-6  123 -124
```

```
 5,-8,L

-1  170 -175
-2  173  167
-3   55  -53
-4  139 -138
-5   58   58
-6   43   41

 5,-9,L

 0  119 -122
-1  243 -242
-2  255  249
-3   77  -81
-4  127 -127
-5   49  -48
-6   11   -6

 5,-10,L

 0  159 -159
-1  115  117
-2   77   76
-3  243 -240
-4   57   58
-5  158  153
-6   52  -53

 5,-11,L

 0   24  -10
-1  168  169
-2   60   58
-3  208 -206
```

```
-4   25   29
-5   68   72

 5,-12,L

 0   81  -77
-2  135 -128
-4  175  172

 5,-13,L

 0   36  -31
-1   75   75
-2   49  -51
-3   79  -79
-4   62   63
-5   17   15

 5,-14,L

 0  164 -161
-1   74  -76
-2  106  104
-3   78   77

 5,-15,L

 0   76   78
-1   63   57
-2   79  -80
-3   20  -18

 5,-16,L

 0   17  -21
```

```
-1  130  130
-2   42   43

 5,-17,L

 0  121  116
-1   70  -68
-2   80  -75
-3   36   34

 5,-18,L

 0  107  101

 4,0,L

 0  608  608
-2  144 -145
-4   42  -35
-6   33  -34

 4,-1,L

 0  382 -395
-1  430 -444
-2  302  302
-3  304  305
-4   26  -21
-5   33   32
-6   34  -40
-7   90  -89

 4,-2,L

 0  347  344
```

```
-1  263 -241
-2  170 -167
-3  109   97
-4  148 -143
-6   96   90
-7   55   54

 4,-3,L

 0   60  -33
-1  192  193
-2  109  120
-3   54  -54
-4   74  -76
-5   29  -38
-6   57  -57

 4,-4,L

 0  159  171
-1  107 -100
-2   24   26
-3  150 -153
-4  108 -101
-5  172  174
-6   73   72
-7   84  -85

 4,-5,L

 0  152  141
-2   41   39
-3  109  107
-5   33  -32
-6   71  -65
```

```
 4,-6,L

 0  267 -265
-1   56  -55
-2  117 -116
-3  224 -208
-4  294  301
-5  142  137
-6  129 -124

 4,-7,L

 0  288 -275
-1  102   93
-2  219  210
-3   54  -52
-5   86  -85
-6   29  -25

 4,-8,L

 0  275 -281
-1   87   89
-2   70  -63
-3  108  114
-4  118  109
-5  135 -138
-6   36  -34

 4,-9,L

 0  178 -177
-1  306  297
-2   55   43
-3  279 -280
```

```
-4   30   37
-5   32   23
-6   47  -47

 4,-10,L

 0   73  -75
-1  184  182
-2  128  132
-3  104 -112
-4   34  -42
-6   44   43

 4,-11,L

 0  196  190
-1  216  210
-2  322 -315
-3   88  -86
-4  182  180
-5   19  -19
-6   17   12

 4,-12,L

 0   38  -44
-1  180  179
-2   45  -44
-3   46  -50
-4  107  107
-5   35   35

 4,-13,L

 0   91   89
```

```
-1  256 -250
-2  178 -173
-3  141  145
-4   26   27
-5   36  -35

 4,-14,L

 0  101  104
-1   86   84
-2   69  -73
-3  100   97
-5  123 -119

 4,-15,L

 0   97  -95
-1   30  -26
-2   89   84
-4   66  -63

 4,-16,L

 0  115  114
-2   22   15
-3   55   54
-4   89  -85

 4,-17,L

 0   53   54
-1   53   52
-2   70  -68
```

```
 4,-18,L

 0   39  -38
-1   57  -54
-3   47  -42

 4,-19,L

-1  112 -111

  3,0,L

-1  601 -638
-3  168  160
-5  238  239
-7  144 -146

 3,-1,L

 0  474  464
-1  345 -357
-3  166  155
-4   24   19
-5  134 -127
-6  138 -129
-7  123  122

 3,-2,L

-1  122 -121
-2  105  105
-3  158 -143
-4  210  207
-5   85   79
-6  104 -103
```

```
 3,-3,L

 0  375 -379
-1   56   53
-2  371  367
-3   84   77
-4  280 -276
-5  185 -186
-6  104  104
-7  101   99

 3,-4,L

 0   86   78
-1  116 -105
-2  328 -315
-3   23   15
-4  177  170
-6   47  -42
-7   45   44

 3,-5,L

 0   68  -63
-1  402  416
-2  236  218
-3  391 -391
-4   48  -46
-5   91   84
-6   13   10
-7   18   20

 3,-6,L

 0   39  -42
```

```
-1  122 -109
-3  164  148
-4  158  146
-5   82  -84
-6   24  -23
-7   29  -28

 3,-7,L

 0   17   13
-1   91   99
-2  362 -358
-3   60   61
-4  229  230
-5   64  -61
-6   25  -25
-7   67   68

 3,-8,L

 0  117 -125
-1   36   38
-2   57   58
-3   80   74
-4   42  -37
-5  131 -124

 3,-9,L

 0  184  191
-1  175 -176
-2  109 -103
-3  200  195
-4  126 -127
-5  106  -98
```

```
-6  145  148

 3,-10,L

 0  264  260
-1  260  251
-2   45  -53
-3   52   54
-4   93  -89
-5   91  -86
-6   30   28

 3,-11,L

 0   20   23
-1   82  -76
-2   54  -49
-3   26  -22
-5  124  119
-6   76   72

 3,-12,L

 0  365  374
-1   54  -49
-2  201 -212
-3  110  114
-4   48  -44
-5   44  -41
-6  112  111

 3,-13,L

 0   47   44
-1   68  -68
```

```
-2  156 -150
-3  152  155
-4   98   94

 3,-14,L

 0   21  -15
-1  173 -175
-2   78   71
-3   27   27
-4   80  -78
-5   39   38

 3,-15,L

-1   79  -79
-2   94   89
-3  123  120
-4   28  -29
-5  101 -103

 3,-16,L

-1  143  138
-2   23    5
-3  117 -114

 3,-17,L

 0   33  -32
-1   43   42
-2  135  130
-3   44  -43
-4   64  -62
```

```
 3,-18,L

 0   78   79
-1   59  -56
-2   96  -93
-3   56  -53

 3,-19,L

 0   32  -29
-1   33   27
-2   23  -22

 3,-20,L

 0   85  -82
-1   67  -64

  2,0,L

 0  342 -367
-2   14    7
-4  500  498
-6  295 -283

  2,-1,L

-1  284  290
-2  477  475
-3  223 -222
-4   72   68
-5   30   25
-6   66  -62
-7   31   30
```

```
 2,-2,L

-1  130 -123
-2   59   65
-3  377  381
-4  190  185
-5  273 -263
-6   78  -76
-7  114  112

 2,-3,L

 0   25   35
-1  422  429
-2  113 -119
-3  410 -399
-5   35  -35
-6   48   58
-7  141  136

 2,-4,L

 0   71   70
-1  240  248
-2  304  297
-4  273 -277
-5  145 -147
-6   88   88
-7   25   28

 2,-5,L

 0  408  426
```

```
 2,-5,L

-1   112 -116
-2   361 -370
-3    26   26
-4    42   43
-5   125  136
-6   134  128
-7    78  -86

 2,-6,L

 0   294  302
-1   154 -146
-2    10   -8
-3    34   21
-4    13  -19
-5    29   24

 2,-7,L

 0    20   16
-1   400 -394
-2   172 -164
-3   179  177
-4   130  121
-5    62   66
-7   138 -136

 2,-8,L

 0    26  -19
-1   242 -251
-2    76   67
-3   353  355

-4   197 -196
-5   146 -142
-6    96   92
-7    14  -19

 2,-9,L

 0   123 -115
-1   291 -276
-2   150  142
-3   287  277
-4   132 -135
-5    58  -59
-6    46  -42

 2,-10,L

 0    25   25
-1    21  -21
-2   264  239
-3   169 -168
-4   282 -264
-5   102  105
-6   122  117

 2,-11,L

 0   102  105
-1   118  126
-2   224  220
-3    23   23
-4   173 -173
-5    35  -36
-6   160 -160

 2,-12,L

 0   120  126
-1    43   56
-2   196 -191
-3   185 -173
-4    98  108
-5   206  202

 2,-13,L

 0    41  -41
-1    94  -95
-2   128  132
-3    62  -63
-4    46  -39
-5    77   77

 2,-14,L

 0    43   55
-1   296 -293
-2   139 -134
-3    65   68
-4   120  111
-5    28   26

 2,-15,L

 0   147 -149
-1   111  102
-2   155  157
-3    52  -54
-5    24  -22

 2,-16,L

 0   189 -185
-1    85  -95
-2   157  159
-3    32   27

 2,-17,L

 0    96   91
-1   130  125
-2    44  -43
-3    33  -30
-4    23  -24

 2,-18,L

-1   119  115
-2    18  -14
-3    43  -41

 2,-19,L

 0    75   74
-1    64  -62
-2    67  -62
-3    31  -33

 2,-20,L

 0    40   36
-1    14  -13
-2    94  -92

 1,0,L

-1   431  449
-3   109 -108
-5    30   33
-7    51  -55

 1,-1,L

-3   430  423
-4   343  328
-6    21  -22
-7    44  -45

 1,-2,L

 0   244  243
-2    40   18
-3    93  -80
-4    80   74
-5   218 -215
-6    56  -55
-7   124  125

 1,-3,L

-2    55  -44
-3   451  440
-4    50   51
-5    80  -83
-6    27   21
-7    89  -87

 1,-4,L

-1   176  191
-2   255 -249
-3   259  249
-4   393 -397
-5   177 -172
-6   218  213
-7    69   69

 1,-5,L

 0   366  387
-1   133 -108
-2    25   -6
-3    49  -54
-4    50  -42
-5    55   54
-6    18  -13
-7    22  -28

 1,-6,L

 0   156  178
-1    37   33
-2   245  236
-3   175 -170
-4   196 -189
-5   212  215
-6   140  134
-7   135 -132

 1,-7,L

 0   143 -127
-1   187 -176
-2    66  -62

-3   223  227
-4    62   60
-5    38  -30
-6    14  -14
-7    13  -13

 1,-8,L

 0   366 -360
-1   211 -216
-2    85  -75
-3   159 -152
-4   184  195
-5   197  193
-6   118 -117

 1,-9,L

 0   276 -301
-1    30   25
-2   487  505
-3    52  -55
-4   285 -288
-5    31  -30
-6    15   10

 1,-10,L

 0   310 -300
-1    56  -69
-2   157  152
-3    33   23
-4    74   67
-6   103 -103
```

```
 1,-11,L

-1  492  487
-2  297  293
-3  468 -483
-4   71  -65
-5  152  153
-6   61  -62

 1,-12,L

-0  162 -168
-2   84   89
-3  105 -106
-4   45   44
-5   51   48
-6   18   15

 1,-13,L

-0  269  272
-1  205  197
-2  277 -276
-3  177 -170
-4  127  133
-5   60   63

 1,-14,L

 0  213 -216
-1   61  -61
-2   57   60
-4   79   74
-5   50   46

 1,-15,L

-1  196 -198
-2   89  -90
-3  135  134
-4   67  -72
-5   32  -29

 1,-16,L

-0   58  -60
-1  153  154
-2   24   26
-3   81   81
-4   18   13

 1,-17,L

-0   68  -69
-1   51   53
-3   29   29
-4   19  -16

 1,-13,L

 0  101   91
-1   33   34
-3   40   37

 1,-19,L

-0   89   88
-1   15   -9
-2  112 -110

 1,-20,L

-0   54   50
-2   23  -22
-4  158 -160
-6  178  177

 0,-1,L

-1  254 -260
-2   28   26
-3  318  322
-4  220  220
-5   29   31
-6  124 -126
-7  117 -115

 0,-2,L

 0  302  336
-2  340 -325
-3  393  371
-4   28  -24
-5   83   89
-6   89   86
-7   90  -92

 0,-3,L

-2  277 -254
-3  508  498
-4   21  -19

-5  255 -250
-6   13  -18
-7   78   83

 0,-4,L

-1   38  -41
-2  356  357
-3   54  -55
-4  111 -110
-5   17   13

 0,-5,L

-1   68   68
-2  539  572
-3   63   44
-4  418 -415
-6  102  100

 0,-6,L

 0   90  -81
-1  175  159
-3  171 -158
-4  133  137
-5  123  122
-6   47  -49

 0,-7,L

-1  425  437
-2  105  105
-3  589 -593
-4   78   80

-5  190  182
-6   68  -63

 0,-8,L

 0  272 -253
-1   60  -67
-2   42  -33
-3   90   92
-4  118  119
-6   43  -39

 0,-9,L

-2  319 -312
-3   49  -37
-4  207  210
-6  114 -113

 0,-10,L

 0  369 -364
-1  112  104
-2  305  305
-3  127 -133
-5   19  -16
-6  103  -96

 0,-11,L

-1   79   83
-2   65  -72
-4   37   40
-5   67  -69
-6   59   53

 0,-12,L

-0   44   42
-1  522  530
-2   64  -65
-3   67  -71
-4   61   58
-5   91  -88

 0,-13,L

-1   41  -45
-2  204 -204
-3   38  -32
-4  107  109
-5   37   82

 0,-14,L

 0  307  286
-1   57   64
-2  194 -194
-3   60   56
-5   80  -80

 0,-15,L

-1   54  -52
-2  162 -159
-3  100   98
-4  122  118
-5   47  -48

 0,-16,L

-0   17  -17
-1   24  -14
-2   45   45
-3   33  -34
-4   29  -28

 0,-17,L

-1   48  -41
-2   27   22
-3  123  117
-4   42  -39

 0,-18,L

 0   63   65
-1   44   45
-2   31  -34
-3   20  -20

 0,-19,L

-2  121  115
-3   46  -41

 0,-20,L

-0   29   33
-1  134 -132
-2   30  -32
```

```
-1,0,L

-3   57   50
-5  197  187
-7  133 -128

-1,-1,L

-1  181 -170
-2  180  171
-3   58  -48
-4  200 -191
-5  118  119
-6   23   23
-7   25  -24

-1,-2,L

-2  250  243
-3   80   56
-4  219  219
-5   55   53
-6  143 -136
-7   13   -8

-1,-3,L

-1  188  182
-2  305  304
-3  212 -199
-4   33  -35
-5   22  -27
-6   60  -58
-7   64   67

-1,-4,L

-1  441 -463
-2  266  254
-3  172  162
-4   71  -68
-6   26  -20

-1,-5,L

-1   14   15
-2  103  104
-3  185 -186
-4  122 -124
-5   18  -26

-1,-6,L

-1  413  414
-2  311  296
-3  317 -303
-4   16   24
-5   86   85
-6   49  -54

-1,-7,L

-1  125 -116
-2   47  -53
-3   71   64
-4   65   66
-5   58   55
-6   67   68

-1,-8,L

-1  135  134
-2  454 -460
-3   18   19
-4  193  191
-5   88  -89
-6   49  -49

-1,-9,L

-1  152 -146
-2   56  -52
-3   84   81
-4   84   78

-1,-10,L

-1   48  -30
-2   50  -48
-3  263  254
-4  173 -176
-5  207 -200
-6   79   80

-1,-11,L

-1   94   90
-2   76  -76
-3  125  130
-4   99   96
-5   84  -83
-6   17  -17

-1,-12,L

-1  182  187
-2   24   24
-3  125 -129
-4  134 -131

-1,-13,L

-1   17   -9
-2  178 -179
-3  191  196
-4   22  -24
-5   60  -63

-1,-14,L

-2  207 -205
-3   38  -35
-4   65   68
-5   81   80

-1,-15,L

-1  233 -239
-2  104  101
-3   49   47
-4   32  -35

-1,-16,L

-1  180 -175
-2   58  -63
-3  113  112
-4   28   28

-1,-17,L

-1   93   87
-2  118  120
-4   30  -28

-1,-18,L

-1   99 -100
-2  151  142

-1,-19,L

-1   26   23
-2   15  -19

-1,-20,L

-1   73   71

-2,0,L

-2  290  292
-4   41  -41
-6   50  -51

-2,-1,L

-2   43  -53
-3  505 -513
-4  155  155
-5  143  134
-6   61  -58

-2,-2,L

-1   54   51
-2  281  281
-3   72  -71
-4  219  226
-5   83   80
-6  160 -159

-2,-3,L

-1  199 -196
-2  254 -270
-3   18   16
-4  142  137
-5   29  -23

-2,-4,L

-1  153  167
-2   93  -91
-3   30   25
-4   71   66
-5  212 -216
-6   82  -77

-2,-5,L

-1   92   92
-2  211  227
-3   75   73
-4  106 -110
-6   54   52

-2,-6,L

-1  119 -104
-2   46  -55
-3  102  103
-4  178 -180
-5  104  -98
-6  144  143

-2,-7,L

-1  265  249
-2  123 -108
-3   93  -89
-4  145  142
-5   49   54

-2,-8,L

-1   38   25
-2   47  -47
-3   30  -23
-4   93  -96
-5   51   53
-6  140  136

-2,-9,L

-1  257 -261
-2  135 -126
-3  348  356
-4   31   26
-5   81  -82
-6   16  -12
```

```
-2,-10,L

-2  138  -29
-3  248  -49
-5   68   68
 -2,-11,L

-1   40  -47
-2  368  365
-3   54   46
-4  204 -205
-5   70  -69

 -2,-12,L

-1   42  -33
-2   31  -35
-3   50   39
-4   22  -21
-5   30   28

 -2,-13,L

-1  149  149
-2  121  112
-3  145 -147
-4  100  -95
-5   67   66

 -2,-14,L

-1  266 -270
-3   44  -39

-2,-15,L

-1   50  -44
-2   37  -37

 -2,-16,L

-1   87  -96
-2   55   56
-4   96   95

 -2,-17,L

-1   81  -80
-2   93  -95
-3   26   24

 -2,-18,L

-1   87  -85
-3   56  -65

 -2,-19,L

-1   91   88
-2   23   29

 -2,-20,L

-1   22   21

  -3,0,L

-3  242 -229
-5   80  -77

-3,-1,L

-1  292 -281
-2  386 -370
-3   64   63
-4  112  108
-5  114  112
-6   28   29

 -3,-2,L

-1  189 -184
-2  440 -443
-3   14  -10
-4   82   77
-5   90  -86
-6   80   75

 -3,-3,L

-1  208 -204
-2  187 -190
-3  269  271
-4  322  318
-5   91  -88
-6  119 -117

 -3,-4,L

-1  162 -177
-2  140 -133
-3  264  256
-4  126 -128
-5  100  -99
-6  123  121

-3,-5,L

-1  112  -91
-2   39   35
-3  321  322
-4   83  -87
-5  218 -210

 -3,-6,L

-1  225  224
-2  198  199
-3  173 -170
-4  147 -148
-5   50   47
-6   55   55

 -3,-7,L

-1  229  219
-2  214  213
-3   55  -49
-4  213 -209
-6  111  107

 -3,-8,L

-1  120 -114
-2  207 -220
-3   51  -52
-4  133  132
-5  127  129

-3,-9,L

-1   58  -48
-3  232 -232
-4   40  -45
-5  133  130

 -3,-10,L

-1  362 -355
-2  117  118
-3  148  153
-4   59   61
-5   53   50

 -3,-11,L

-1   16   18
-2  101  100
-3   86  -92
-4   29  -23
-5   17  -19

 -3,-12,L

-1   26   21
-2  240  244
-3   41  -37
-4   27   27

 -3,-13,L

-1  167  172
-2   50   44
-3  137 -142

-4   72  -68

 -3,-14,L

-1  117  111
-2   25  -18
-3   23  -19
-4   22   17

 -3,-15,L

-1   13   13
-2  105 -104
-3  142 -136
-4   96  -95

 -3,-16,L

-1   14  -15
-2   25  -17

 -3,-17,L

-2  122 -118
-3   84  -83

 -3,-18,L

-1   70   73
-2   61  -61

 -3,-19,L

-1   65  -62

  -4,0,L

-2  247 -246
-4  235 -241
-6  180  180

 -4,-1,L

-1   48  -49
-2   33  130
-3  313  317
-4   99 -100
-5  184 -185
-6   60   62

 -4,-2,L

-1   27  -26
-2  245 -244
-3   94  -84
-4   70   68
-5  123  121

 -4,-3,L

-1  305 -292
-2   54   48
-3  180  172
-4  124 -123
-5   12   15

 -4,-4,L

-1  341 -344
```

```
  -4,-4,L

-2  182 -184
-3  223  220
-4   99   97
-5   69  -66

  -4,-5,L

-1   17   11
-2  242  233
-3   89  -89
-4  131 -128
-5   44   44

  -4,-6,L

-1  300 -298
-2  360  370
-3  198  189
-4  168 -161

  -4,-7,L

-1  185 -180
-2   52  -52
-3  260 -256
-4   13  -10
-5   59   58

  -4,-8,L

-1  207  211
-2  266  270
-3  168 -172

-5   98   95

  -4,-9,L

-1  138 -137
-2  209 -212
-3   26  -26
-4   36   38
-5   77   75

  -4,-10,L

-1   82   84
-2   50  -53
-3   46  -46
-4  115  112

  -4,-11,L

-1   75  -79
-3   61  -59
-4   93   92

  -4,-12,L

-1  194  196
-2   33   31
-3   58   60
-4   27  -28

  -4,-13,L

-1  129  129
-2  108 -104
-3   19   19

-4  130  131

  -4,-14,L

-1  175  177
-2   26  -24
-3  105 -103

  -4,-15,L

-1   29  -24
-2  127 -127
-3   80  -77

  -4,-16,L

-1   39   38
-2  136 -133
-3   33  -36

  -4,-17,L

-1   79  -77
-2   39   33

  -4,-18,L

-1  100  -98

  -5,0,L

-1  203 -196
-3  170  169
-5   71  -70

  -5,-1,L

-1  164  160
-2  249  245
-3  199 -201
-4  195 -192
-5  104  102

  -5,-2,L

-1  268 -257
-2  229  224
-3   46   38
-4  117 -115
-5   77   76

  -5,-3,L

-1   64   61
-2  112 -107
-3  201 -200
-4   70   70
-5   85   79

  -5,-4,L

-1  117 -120
-2  233  228
-3   26  -28
-4   20   22
-5   89   89

  -5,-5,L

-1  407 -417

-2   38  -35
-3   87  -86
-4   43  -43

  -5,-6,L

-1  187  183
-2  145  145
-3   80  -79
-5   45  -44

  -5,-7,L

-2  229  232
-3   57  -51
-4   24  -26

  -5,-8,L

-1  203  201
-2   86  -81
-3   40  -39
-4   36  -36

  -5,-9,L

-1  152  156
-2  130 -124
-3   36  -34
-4  151  147

  -5,-10,L

-1   78   78
-2  100  -95

-3   88  -87
-4   11  -16

  -5,-11,L

-1   84  -75
-2  102 -101
-3  197  194
-4   77   75

  -5,-12,L

-1   79   83
-2  115 -117
-3   39  -44

  -5,-13,L

-2   83   79
-3   79   75

  -5,-14,L

-1   33  -28
-2   97 -101
-3   85   85

  -5,-16,L

-1  157 -158
-2   23   22

  -5,-17,L

-1   42  -40

  -6,0,L

-2  233  234
-4   63  -56

  -6,-1,L

-1   24  -30
-2   31   38
-3  127 -123
-4   51  -52

  -6,-2,L

-1  166  161
-2  109  109
-3  103  -98
-4   51   51

  -6,-3,L

-2   33  -24
-3  111 -111
-4   68   67

  -6,-4,L

-1   17  -13
-2   92  -94
-4   55   51
```

```
-6,-5,L

-2   24  -23
-3   52   53
-4  110  108

-6,-6,L

-1   49   48
-2   19   14
-3   23  -24
-4   49  -48

-6,-7,L

-1   96  100
-2   58   58
-3   87   86
-4   14  -16

-6,-8,L

-1  214  213
-2  131 -128
-3  136 -134
-4   21   19

-6,-9,L

-1   82   83
-2   36   37
-3   22   19

-6,-10,L

-1  160 -159
-2  198 -195
-3   53   53

-6,-12,L

-1  181 -179
-2   84   84
-3   84   82

-6,-13,L

-1   30  -28
-2   26   24

-6,-14,L

-2   82   75

-6,-15,L

-1   53  -54

-7,0,L

-1   67   59
-3   65   64

-7,-1,L

-1  104  100
-2   56  -57

-7,-2,L

-1  112  112
-2   23  -21
-3   57  -57

-7,-3,L

-1   90   90
-3   74   74

-7,-4,L

-1   81   85

-2  184 -182
-3   66  -63

-7,-5,L

-1   64  -60
-3  143  139

-7,-6,L

-1  103 -100
-2  105 -102
-3   73   70

-7,-7,L

-1  111  111
-2  127  126
-3   16  -17

-7,-8,L

-1   91  -88
-2   52   55
-3   66   65

-7,-9,L

-1   61   58
-2   40  -43

-7,-10,L

-1   58  -59
-2   40   39

-7,-11,L

-1   91  -90

-7,-12,L

-1   69  -69

-8,0,L

-2   97 -101

-8,-1,L

-1   27  -25
-2  108  105

-8,-2,L

-1   32   31

-2   99  -97
-8,-3,L

-1   85   84
-2   74   68

-8,-4,L

-1  171 -167
-2   62  -61

-8,-5,L

-1   48  -48
-2   80  -81

-8,-6,L

-1  168 -168
-2  136  134

-8,-7,L

-1  129 -130

-8,-8,L

-1   72   73

-8,-9,L

-1   17   18

-8,-10,L

-1   83   83

-9,0,L

-1  205 -202

-9,-1,L

-1   40  -40

-9,-2,L

-1   50  -50

-9,-3,L

-1  103 -103

-9,-4,L

-1   73   72
```

APPENDIX IX

Structure Factor List for compound I,

Part IV.

Columns listed are ℓ, $|F_o|$ x 10, F_c x 10.

```
   0,8,L

 8  117 -109
 6  162 -158
 0  131 -131

   0,7,L

11   79  100
 7  173 -181
 5  164 -162
 3  155  153
 1  141  147

   0,6,L

14  111 -100
 8  126  130
 6   77  -83
 4  119  135
 2  192 -193
 0  985-1009

   0,5,L

17  109  -97
13  123  121
11   47  -48
 7  289 -291
 5  150 -141
 1  381 -379

   0,4,L

16   87  -87
```

```
12   84  -79
10  268 -279
 8  158  -53
 6  238  241
 0  301  287

   0,3,L

19  204 -185
15  109 -106
13  365  366
11  568  569
 9  268  270
 7  267  251
 5  199 -179
 3  219 -212
 1  102  100

   0,2,L

18  131  124
16  140 -127
14  239  226
12  570  559
10  533  526
 8  107 -102
 6 1031-1010
 4  182 -185
 0  801 -823

   0,1,L

17  251 -254
13  273  267
11  347 -328
```

```
 9   87   71
 7  295  288
 5  627  619
 3  185  173
 1  694 -729

   0,0,L

20   85   78
18  428 -433
16  223 -218
14  105  125
12  294 -299
10  203 -192
 8  485 -459
 6  515  506
 4 2212-2368
 2 1084 1147

  -1,8,L

 9  175 -166
 1  163  167
-3  105  -96

  -1,7,L

 4  109 -107
 2  261 -262
 0  200 -199
-2  121  128
-4  116  112
-12  60  -52
```

```
   -1,6,L

13  199  196
 7  151 -161
 1  660 -674
-1  139 -133
-5  110 -117
-7  153  168
-9  174  187
-13  91  -78

   -1,5,L

14  130 -131
12  178 -185
10  171  183
 8  288  313
 4  206  203
 0  263 -269
-2  176 -177
-8   93  -94
-10  67  -78
-12 153 -152
-14 139 -128
-16  78   73

   -1,4,L

11  131  135
 9   71   65
 5  451  439
 3   93  -77
 1  190  207
-3  238  198
-5  456  442
```

```
 -7  211 -200
 -9   47   36
-11  318 -311
-13  185 -183
-15  142  141

   -1,3,L

 -6  137 -116
 14  113  116
 12  191  197
  6  185 -181
  4  492 -483
  2  468  471
  0  440  433
 -2  183 -186
 -4  870 -825
 -8  532  518
-10  401 -391
-12  177 -175
-14  178  178
-18   73   61

   -1,2,L

 15  100  -97
 13  251 -251
 11  509  517
  9  529  517
  7  652 -651
  5  134  129
  3  445  437
  1  241  236
 -1  349 -348
 -3  617  605
```

```
 -5  962  957
 -7  327 -313
-11  233 -239
-13  274 -284
-15  121  130
-17   89  -77

   -1,1,L

 18  240 -240
 14  155  160
 12  233  234
  8  992 -997
  6  417 -412
  4  316 -327
  2  891  930
  0 1416 1495
 -2   94  110
 -4  330  343
 -6  645 -648
 -8   76   67
-10  549  549
-12  464  470
-14  183 -169
-16  266 -266
-20  101  103

   -2,8,L

  6  176 -165
  4  102 -117
  0   71   62
 -2  124 -123
 -6  204  198
```

```
   -2,7,L

  7  122 -121
  5  173  171
  3  256  253
  1   96 -106
 -1  222 -225
 -5  168  165
 -9  114  -98

   -2,6,L

  8  163  174
  6  302  313
 -4  114  108
 -6  306 -316
 -8  177 -208
-12   84  -83

   -2,5,L

 13   94  105
  1  314 -328
 -1  257 -253
 -5  327 -331
 -7  171  171
-11  250 -253
-13  238  232
-15  219  216

   -2,4,L

 14  115  124
 12  108  109
  8  174 -176
```

```
   -2,4,L           -2,2,L           -9  507  503     -8  129 -137     -5  209 -201     -9  191 -193     -1  158 -180
                                    -11  274 -295    -10   45  -54     -7   69   55    -11  572  576    -11  101  108
   6  261 -260     20  165 -155     -13  344  357       -3,6,L         -9   53  -47    -13  406  421       -4,6,L
   4  266 -246     14  269 -274     -15  379  391                     -11   74   76    -15   60  -48
   2  212 -218     12  288  290     -19  115 -113     11  130 -138    -13   98  107    -17  140 -133     10  130 -145
   0   76   84     10  325 -305                        7  135  143    -15  142  145    -19  151 -136      8  109 -113
  -2  135  129      8  279 -249        -2,0,L          5   93  -86    -17  106  -90                       6   87   89
  -4   92   87      6  565  547                        3  175  171                        -3,1,L          2  431  447
  -6  243  245      4  294  283      18  201 -198      1  149 -145       -3,3,L                           0  426  439
  -8   79  -85      2 1134 1165      16  120   85     -1  225 -234                     16  226 -239     -2  126  126
 -10   89  -88      0  185 -180      14  282  290     -3   96   94     14   84  -89     10   44  -35     -4   80   72
 -12   75  -70     -4  333 -313      12   80   77     -5  142 -143     12  228  237      8  311 -302     -6   66  -82
 -14   71  -75     -6  671 -668       8  722 -712     -7   78   68      8   76   70      6  207 -226    -12   71  -72
                   -8  312  299       6 1694-1742     -9   94  105      6  169  160      4 1926 1998
   -2,3,L         -10  278  281       4  297  305                       4  237 -229      2 1168-1199       -4,5,L
                  -12  156 -160       0  434 -530        -3,5,L         0  164 -160      0 1128-1178
  19  231 -223    -14  330 -326      -2  725 -785                      -4  442  418     -2  342  355     11  216 -231
  15  188 -188    -18  148  144      -4 1621-1704     16  155  149     -6  286  269     -4  953-1003      9  146   50
  13  584 -584                       -6 1623 1640      6  112  -98     -8  193  193     -6  564  571      7  386  396
  11  434  435       -2,1,L          -8 1006  993      4  155 -166    -12  344 -356     -8  446  454      5  120 -119
   7  181  180                      -10  253 -263      2  207  214                    -10  153  156      3  270  267
   5 1003  951     19  156  152     -12  272  277      2  176  214       -3,2,L       -12  312 -321      1  218  218
   3  252 -265     17  257  283     -16  263  293     -4   81  -72                    -14  256 -278     -1   83 -101
   1  270  271     15  195  209     -20  174  148    -12  145  136     19   77  -72    -16  212  226     -3   48   53
  -1  102   99     13  218  214                      -14  173  184     15  160 -168    -18  132  147     -7  188 -183
  -3 1638 1627     11  103 -104        -3,8,L                          13  145 -151    -20  128  125     -9  101 -101
  -5  791  749      9  196 -190                         -3,4,L         11   67   74                     -13  105  117
  -7  703 -684      7  531  531       5   85   90                       7  414  412       -4,8,L        -15  125 -106
  -9  374  383      5  573 -605                       13  220 -215      5  263  263
 -13  402 -409      3 2167-2321        -3,7,L         11  103 -106      3  332  333      6  201 -196       -4,4,L
 -17  126 -121      1  459 -466                        7  107  114      1  578 -610
 -19  228 -217     -1 1452 1546       2  249  247      3   98  101     -1  820 -848       -4,7,L         16   68   59
                   -3  152 -155       0  235  245      1   53   55     -3  604  608                      14  187  189
                   -5 1234-1270      -4   97   86     -1  275  273     -5  269  251     11  114 -110     12  155  160
                   -7  663  644      -6  136 -139     -3   84   78     -7  215 -220      1  253 -261
```

```
  -4,4,L           -2   371  -363     8    77   -13      -5,5,L           4   330   324     6   195  -191     7   295   311
                   -4   184   196     6  1023 -1016                         2   140  -134     4   671  -664     5   154   151
   8   269   281   -8   203   195     4    92   -74    12   126  -135     0   119  -114     0  1069 -1086     3   217  -220
   6   120   100  -12   688  -699     2  2000 -2121    10   255  -275    -2   407  -388    -2   351  -353     1   392   388
   4    63    49  -14   103   111     0  1561 -1711     2   170   186    -4   358   348    -4   201   200    -3   168   161
   2   329  -320  -16   104   112    -2  1017 -1068     0   215   224    -6   176   169    -6   441  -435    -5   102   106
   0   784  -766  -18   108  -114    -4   345  -332    -2   194   197    -8    79   -81    -8   325   328    -7   101  -101
  -4   215   191                     -6  1178  1159    -4    70   168                     -10    81   -69   -11   110  -116
 -10   146   136    -4,1,L           -8   538   518    -6   179   170     -5,2,L          -14   130  -154   -15   109   -91
 -12   164   177                    -12    70    83   -10   211  -202                     -18   131   123
                   17   301  -314   -16   134  -129   -14   155   127    21   117   107                      -6,4,L
  -4,3,L           15   232  -232   -18   179   180                      15   107   104     -6,8,L
                   13   167   162                       -5,4,L           13   506  -517                      14   452  -467
  15    69    80   11   255  -257     -5,8,L                             11   181  -198     8   185   186    12   224  -237
  13   521  -528    9    89   -64                      15   183   182     9   182   186     6   173   168    10   211   215
  11   354  -350    7   500   497     3   162  -173    11   253  -261     7   952  -906                       8   158   161
   9   238   246    5   271  -277     1   127  -126     9    95    92     5   192  -191     -6,7,L           6   118   114
   7   781  -747    3  1005  1034    -7   113   103     7   269  -268     3   375   373                       4   147   138
   3   216   199    1  1786  1869                       5    70   -65     1   675   679    -3    91    75     2   377   375
   1   375  -376   -1   464   462     -5,7,L            3   176  -188    -1   123   122                       0   100   107
  -1   399   411   -3   111  -112                      -1   146  -133    -3   394  -372     -6,6,L          -2   126   128
  -3   878  -837   -7   146   137     2   140  -145    -3   402  -370    -5   174   174                      -4   232   218
  -5   100    90   -9   395  -377   -10   117   115    -5   222   220    -7   437  -450    16    86   -88    -6   138  -133
  -9   272   266  -11   437  -432                      -7   142  -134    -9   329   327     8   244  -256   -10    64    78
 -11  1039  1052  -15   285   268     -5,6,L           -9   154   147   -11   506   508     6    86    92   -12   152  -149
                  -17   179  -173                     -11   387   389   -13   142  -143     4   212  -221
  -4,2,L          -19    85   -76     9   129   122   -13    68    67   -15   193  -197     2   534  -535     -6,3,L
                                      7   242   256                                         0   131   135
  14   289  -290    -4,0,L            5   208   208     -5,3,L            -5,1,L          -4   120   113    19   288   275
  12   209  -198                      3   353   366                                        -6   252   279    15   167   159
  10   165   141   20   234   240     1   179   182    18   136  -130    16    97    90   -12    97    89     9   127   116
   8   218  -238   16   350  -352    -1   291  -292    14   148  -153    14    92    92                       7   568  -525
   6   555   554   14   293   292    -7   243  -263    10   177   171    12    96   -75     -6,5,L           5   565  -561
   4   561   567   12    62   -53                       8   298  -286    10   294   280                       1   412  -393
   0   897   918   10   380   370                       6   348   344     8   246   234     9   171  -179    -1   336  -308
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 -5  505 -494
-11  119  126
-13  160  158
-17  195  176

  -6,2,L

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  6  538 -522
  4  627 -611
  2  389 -374
  0  178 -192
 -2  204 -189
 -6  568  535
-12  204  205
-16  165  171
-18   97  -91

  -6,1,L

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 17  120 -148
 13   93   89
 11  354  349
  9  470 -466
  7  392  381
  5  423  431

  3 1835-1880
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 -7   54   36
 -9  224  226
-11   75  -75
-15  111 -113
-17  153 -157

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  8 1441 1449
  6  498  556
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  2 2439 2631
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 -6 1551-1531
 -8  250 -230
-10  282 -293
-14  320 -340
-16  146 -150
-18  134  148

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 -3   80   78

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  -7,6,L

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  3  343 -339
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 -4   92   96
-10  113 -108
-14  159  149

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  7  202  197
  5  402 -381

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 -3  151  148
 -5  289 -282
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-11  133 -136
-15  115 -104

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  6  331 -326
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-12  207  209
-16  104   91

  -7,2,L

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  7  461  470
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  3  401 -388
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 -1  261  270
 -3  197 -191
 -5  312 -304

 -9  580 -594
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-15   45  -49
-17  134  131

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 16  126  140
 14  226  224
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  8  181 -173
  4 1681 1734
  2 1141 1129
  0  345 -353
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 -8  187 -189
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 -3   88   89
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  7  117 -118
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  8  132 -133
  6  252 -252
  4  111  106
  2  269  262
  0  232 -227
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 -4  357  358
 -6  219 -210
 -8  375 -362
-12  165  168
-14   79   81

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  6   476  474
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  2  1124-1146
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 -4   529 -518
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 -8    49  -15
-10   136 -147
-14   117  115

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  9   184  171
  7   759 -769
  5   586 -581
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 -8   160 -160
-10   235  244
-12   107 -108
-14   199  202
-16   100  -93

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  4   172  170
  0    95 -100
 -8    95  -82

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-10   135  123
-12    77  -60

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  9   224  223
  7   210 -224
  5   177 -181
  3   231  233
  1   387  386
 -5   105 -110
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 -9    57   44
-11    90   91

   -9,3,L

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  0   526  497
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-10   302 -312
-12   133  136

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  9   236  227
  7  1001-1013
  5   767 -731
  3   224  217
  1   906  877
 -1   546  526
 -3   278 -293
 -5   142  142
 -7    64   72
 -9    74   77
-11    95  -96
-17   114 -119

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-14   170  173
-16   123 -123

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  8   132 -123

   -10,7,L

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  7   135 -116
  3   155 -166
 -9    63  159

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  8   269  264
  6   129  138
  4   139  124
  0    86   94
 -4   267 -278
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-10    93  -88

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  5   223  212
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 -3   270 -285
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 -2   211  205
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-10   250  244
-12   139  127

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  9   682 -684
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  5   115  106
  3   415 -413
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-10   227 -226
-14   131 -129

   -10,1,L

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 11   283  292
  9   530  512
  5   326  300
  3  1018  995
  1   384  371
 -1   272 -261
 -3   538 -529
 -5   520 -490
-11   125  131
-15   147 -147
-17    67   52

   -10,0,L

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 14   431 -445
 12   159 -158
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                 -11   56  -55     -4  352 -351    -10  185  185                                       18  219 -215
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  8  373 -364     -11,5,L                          -14  123 -129     16  184 -194     16  160 -163     14  346  340
  6  145 -147                      -11,2,L                           14  358  362     14  362 -361     12  500  490
  4 1491-1508     10  235  232                      -12,8,L          12  205  199     10  104  -99     10  616  599
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 -11,8,L          -11,4,L           3 1339 1284     -1   91  -79     -6  376 -387     -6  274  275     -6  497  488
                                    1  169 -172     -3  115 -115    -14  159 -156     -8  287  283     -8  107  118
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                  -6   302   296                     10    71   -73    -2   142  -130    -4   477  -503     5   123  -126
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 10   149   152                      9   133   134    -6   111   120    -8   251  -251                      -1   140   141
  6   401  -396    -13,2,L           5   137   132    -8   453   459   -10    99    99     -15,7,L          -5   144  -143
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  2   465   450   17   125   137                                        -14,1,L           5   138   131
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-12   140   134   13   176  -173                                       17    92    88
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  0   87  -85     10  502 -504     -2  240 -259     -14  131  120      8  116 -111                      13  346 -346
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 -2  137 -137     -1  184  180    -11  179 -187       -17,4,L         -1  210 -222                       8  141  142
                  -3  203 -205                                        -3  327 -312       -18,4,L         6  197 -195
                  -5  304  301       -16,0,L         17   58  -52     -5  301  301                       4  125  122
```

```
-18,2,L

 2   71   -78
 0  148  -165
-2  229   237
-4  263   275
-6  213   223

-18,1,L

21  190   182
19  132   134
17  172  -174
13  128   131
11  270  -280
 9  126   118
 7  511   492
 5  634   636
 3  311  -309
 1   90  -103
-1  161  -165
-3  269  -263
-5  102  -113
-7  152  -156

-18,0,L

20  150  -141
18  168   152
16  242   241
12  447  -463
10  357  -356
 8  695   698
 6   80   -76
 4  645  -653

  2  346  -335
  0  137  -142
 -2  205  -214
 -4  175   179
 -8  144  -143
-12  280   289

-19,7,L

 8  167  -156
 4  172   166
 2  109   109
 0   50    23

-19,6,L

11  108  -103
 5   90   -95
 3  195  -188
-3   89   -91

-19,5,L

16  119   115
12   87   104
 6  234   226
-2  191  -183
-4  129  -115
-6   94   -94

-19,4,L

17  132  -122
15  344  -346
-7  283   302

 5  147   154
 1  136  -146
-1   61   -65
-7  160  -165

-19,3,L

16   51   -63
14  154  -151
12  157  -153
10  147   156
-8  125  -141
-6  101  -111
-2  125   116
 0  193   198
-8  122  -120

-19,2,L

19  226   217
17   55   -58
15  307  -290
13  249  -265
 9  229   223
 7   94    78
 1  171  -167
-1  280   277
-3  254   257
-7  219   207

-19,1,L

20   94    89
16  208  -211
 8  291   287

  6  234  -228
  4  343  -348
  2  479  -480
  0  259  -258
 -2  308   306
 -4  255   262
 -6  125   124
 -8  160  -161
-12   58    59

-20,7,L

 7   77   -74
 3   65    34

-20,6,L

10  187  -175
 6  159   160
 4  278   270
 0   81   -68

-20,5,L

15  227  -234
13   96   -92
 7   63    49
 5  165   160
 1  127   120
-1  177   191
-3  144  -133
-7  110    97

-20,4,L

 16  259   263
-12  124  -115
  0  103   119
 -4   48    53
 -8  102  -104

-20,3,L

17   88   -89
15  171  -169
13  123  -126
 9  234   233
 7  149   150
 5  210  -220
 3  211  -205
 1  305  -304
-1  121  -125
-3  156  -142
-5  101    97
-7  239   234

-20,2,L

20  202   196
16  558  -560
14  109   -96
12  165   173
10   68   -63
 6   99    88
 4   98  -110
 2  391  -395
 0  198   211
-2  337   341

-20,1,L

17  177  -171
13  216  -214
11  435  -436
 9   96   -87
 5  323   320
-3  133  -134
-1  648   656
-7  216   220

-20,0,L

20  107   -93
14   81   -92
12  139   120
10  718   730
 8  323   330
 6  661  -686
 4  857  -860
 2  103   -95
 0   96    92
-2  258  -262
-4  167   182
-6   46   -67
-8  177  -176

-21,6,L

 5   97    86
 1  100    92
-3  103  -102

-21,5,L

14  106  -102
12  127  -122
 8   98  -100
 6   97   -89
 4  279   276
-6  128   116

-21,4,L

 7  183  -161

-21,3,L

14   71    75
10  159   163
 8  128   133
 6  130  -151
 4  156  -167
-2   51   -60
-6   93    85

-21,2,L

17  269  -266
15  208  -213
13  110   101
 7  153  -149
 5  188   182
 3  100   111
 1  166  -176
-1  139  -135
-3   73   -65
-5  116   109
```

```
 -21,1,L           9  200 -201     -22,0,L          -23,3,L          -2  130 -140     14   77  -70     -8  117  115
                   5  128  134                                       -4  274 -274     10   86  -93
 18  145 -136      1  112 -125     16  143 -131     16  131 -124     -8   98   99      8  130 -131     -25,5,L
 16  344 -351     -1   72  -69     14  162 -157     14   77  -83    -10  182  165      6  116  112
 12  349  357     -3  102  103     12  168  172      4  116  129                       4  152  162      6  157 -152
  6   65   77     -5  183 -186     10  161  163      2   98  114     -24,6,L           2  211  216      2   89  -79
  4  508 -518     -7   59  -56      8  128 -132     -2  104 -104                       0  161  149      0  146 -141
  0  359  369     -9  124  120      6  404 -392     -4   82  -89      8   92   71     -2  162 -166
 -4  177 -182                       4  121 -132     -6  104  100      4  184 -168                      -25,4,L
 -6  251 -255     -22,2,L           2  655  668                                      -24,1,L
                                    0  276  269     -23,2,L          -24,5,L                            9  175  183
 -22,6,L          18  128 -108     -2  181 -190                                      17  224  232      1  114  109
                  14  169  178     -6  103 -105     19  162  161      7  141 -152     15  162  166
  8   71   59     12  268  278     -8  104 -107     17  174  170      5  123 -127     13  185  190     -25,3,L
  2  162 -157     10  149 -152                      15   65  -53      1   58  -50     11  113  113
                   8   68  -87     -23,6,L          13  100   91                       9  168  167      6  119  122
 -22,5,L           4  117 -124                       9  226 -217     -24,4,L           7   72  -79      4   90  102
                   0  132 -134      5  166  151      7  113 -104                       5  452 -465      0  157 -151
 15  139  146     -4  348 -365      3  102  102      5   61  -67      6  116 -121      3  148 -161     -6   69  -68
  7  180 -181     -6  224 -229                       1  339 -330      2  222 -212      1  161 -154
 -5   58   49     -8  204  195     -23,5,L          -1   95   99      0   98  -86     -1  184 -192     -25,2,L
                 -10   99   96                      -3  278  271     -2  142  122     -3   54  -64
 -22,4,L                           14  107  -93     -5  284 -285                      -9  139 -136     13  120  136
                  -22,1,L          12   92  -98     -7  120 -127     -24,3,L                            7  117  119
 12  123 -119                       6  119 -120                                      -24,0,L            1  134  149
 10   94   92     17   82   71                      -23,1,L          17   78   76                      -7  245 -228
  4  201  203     15   96   95     -23,4,L                            7   50   55     12  188  194
 -4  105  101     13  208 -219                      16  162  162     -1  228  221     10   83   72     -25,1,L
 -6  178  173     11  254 -254     15  112   98     14  130  130     -5  143 -151      8  394 -400
                   9  263  277      9  109 -107     12   75   89     -7  172 -178      6  363  367      8  128 -135
 -22,3,L           7  164 -166      7   84  -84     10  134 -140                       4  772  791      6  142  148
                   5  515 -524     -3  134  113      8  122 -115     -24,2,L           2  125 -127      2  111  108
 15  140 -150      3  239  244                       6  125  138                       0  257 -269      0  151  146
 13   98  -95      1  270  279                       4  296  298     18  108  114     -2  155 -155     -2   51  -42
 11   57   80     -9   65  -54                       2   82   95     16   69   82     -6   57  -60     -8  135  137
```

```
-26,5,L

 9  167  162
 7  128  132

-26,4,L

10   85  -99
 6   50   59
 0  115 -119

-26,3,L

11  149  150
 7  116 -126
 5  140 -144
 1  173  173

-26,2,L

10  105  112
 2  110  115
-4  151  152

-26,1,L

17   93 -113
15   71  -73
 9  108  116
 7  152  156
 3  212  215
 1  224  214
-1  151 -148
-3  117  109
-5   53   43
-7  141 -129

-26,0,L

10   96  -94
 8  122 -137
 6  183 -173
 4  132 -123
-2  146  154

-27,4,L

 7  161  152
 3   48  -63

 1   78  -79

-27,2,L

15   93  -94
11  141  143
 9   89   78
 1   78   74
-1   74   72

-27,1,L

18  184 -190
16   88   91
14  118  109
10   68   73
 6  228 -243
-4   80   86

-28,4,L

12  147  144
 2   59   51

-28,3,L

 9   80   65
 7   95   98
 3  131 -122
 1   81  -80

-28,2,L

16  560  139
14  165  165
12  135 -128
 6  158 -173
 4  168 -163
 2   97 -108
-4   96  109

-28,1,L

17   53  -38
15   99 -103
13  108  -93
 7  199  207
 5  151  155
 3  127 -124

-1   91   75
-3   94  -90

-28,0,L

 8  246 -243
 4  310  315
-2   75   81

-29,3,L

 8   80   62
 4   69  -65

-29,2,L

15   84  -74
 3   82  -80
 1   70   66

-29,1,L

14  120  113
12   90  -88
10  142 -136

 4   71  -69
-2   77  -82

-30,3,L

 5  113 -110
 1  209  191

-30,2,L

12  149 -155
 8  172  176

-30,1,L

13   49  -61
 9  195 -213
 7  382 -385
 3   30   27

-30,0,L

 8  162  169
 6   27  -24
 4  146 -157

 0  120 -127

-31,2,L

13  130  120
 9  158 -164
 7  232 -225

-31,1,L

12  105  -94
 8  220  237
 2   55  -42

-32,2,L

 4  166  157

-32,0,L

12   52  -44
 6  103  105
```

APPENDIX X

Structure Factor List for compound II,

Part IV

Columns listed are ℓ , $|F_o|$ x 10, F_c x 10.

```
-31,-2,L

7  227  213

-30,-1,L

7  312  309

-30,0,L

4  123 -129

-29,-3,L

8    0   61

-28,-4,L

6  113  116

-28,-2,L

6  141 -175

-28,-1,L

3  160  147

-28,0,L

-4  261  254
8  162 -153
```

```
-27,-4,L

7  148 -136

-27,-2,L

5    0    9
9   31  -79

-27,-1,L

6  204 -209

-26,-3,L

5  159  154

-26,-2,L

10  109   96

-26,-1,L

-7  135  110
1  221 -216
3  190 -219
7  153 -167

-26,0,L

-6    0    8
4  115  -73
8  127 -142
```

```
-25,-5,L

6  168 -153
8   55  -23

-25,-4,L

5  127  150
13   69  -29

-25,-3,L

10   67  -79

-25,-2,L

-1    0  -11

-25,-1,L

12   19  -27

-24,-6,L

8    0   43

-24,-5,L

3   84  -67

-24,-4,L

2  229 -215
10   67 -114
```

```
-24,-3,L

-5  119  122
11    0  -25

-24,-2,L

2  245  243
4  205  196
6   83   88
8  196 -177
14  138 -122

-24,-1,L

5  430  446
11  140 -154
13  148 -158
15  174 -164
17  198 -207

-24,0,L

0  407 -416
4  637  639
6  208  217
8  321 -327
12  216  206

-23,-4,L

7  124  139
9   86   63
```

```
-23,-3,L

2  126  127
4  134  162
14  100 -100

-23,-2,L

-5  195  191
-3  231 -216
-1   68  -71
1  259  271
7  131  159
9  175  172
17  197 -158
19   78 -106

-23,-1,L

-10  143  129
-8  117  113
-4  194 -192
2  155  167
4  177  182
10  128 -142
14  113  138
16  184  162

-22,-6,L

-2    0   50

-22,-5,L

7  192  185
```

```
15  169 -159

-22,-4,L

4  175  166
16   93 -122

-22,-3,L

1  103  122
9   79  108
13   57   74

-22,-2,L

-4  287 -283
8   79  -67
12  288  284

-22,-1,L

3  178 -178
5  492  491
7  124  125
9  258 -274
11  222  225
13  143  135
15   90  -86

-22,0,L

-2  232 -213
0  423  415
2  580  581
6  370 -376
```

```
8  179 -193
10  167  158
12  118 -127
16  133 -137

-21,-5,L

4  230  236
12  138 -132
14  110 -121

-21,-3,L

-6   79   62
4  173 -194
8  149  150
10  110  125

-21,-2,L

-1   92  106
1  229  220
7  102   94
15  293  288
17  224  205

-21,-1,L

-6  167 -159
-4  253 -246
0  312  320
2  135 -137
4  356 -360
12  338  337
16  319 -316
```

```
-20,-6,L

 4  244  223
 6  103  115
 8  119 -103

-20,-5,L
-1  103 -109
 5  140 -145
15  122  169

-20,-4,L

 0  177  165
 6  111  112
-16 199  188

-20,-3,L

-1  162  136
 1  184  198
 3  208  211
 9  159 -171
11  131 -154
15  205  209
19   42  -74

-20,-2,L

-2  332  342
 2  351 -352
 4  173 -170
12  152  156
16  437 -431
```

```
-20,-1,L

-1  591 -588
 5  303 -308
 9  153  148
11  424  431
13  238  231
17  125  130

 -20,0,L

-10  155  -83
 -4  164  172
  4  801 -812
  6  642 -656
  8  376  375
 10  616  623
 14  114 -122

 -19,-7,L

 2   99  125

 -19,-6,L

-3  176  164
 5  137  138

-19,-5,L

 6  192  200

 -19,-4,L

-1  175  186
```

```
-5  252 -256
-7  190 -196
15  295  300
17  107  110

-19,-3,L

 2  109  106
 4   48   29
 8  139  153
10  142  158
12  223 -230
14  119 -140

-19,-2,L

-3  168 -186
-1  231 -225
 9  253 -259
13  288  292
15  262  237
19  204 -197

-19,-1,L

-4  356  362
-2  234  219
 0  261 -254
 2  340 -334
 4  424 -429
 6  146 -137
 8  260  256
16  194 -200
```

```
 -18,-7,L

-5  279  275

 -18,-6,L

 0   59   63

 -18,-5,L

-3  186  177
-5  161 -159
 7  132 -128
11  108 -109
15   72   70

 -18,-4,L

-6  121 -120
-2  270 -262
 0  174 -181
 4  104  -79
 6  139  150
12  152  148
16  273  263

 -18,-3,L

-3  188 -192
-1  146 -132
 7  239 -234
 9  301 -309
11  316  307
13  231  214
```

```
 -18,-2,L

-6  266  293
-4  327  325
-2  134  134
 4  100   85
 6  209 -203
12  219 -207
16  170 -174

 -18,-1,L

-3  348  344
 3  236  233
 5  569 -666
 7  471 -460
 9  142 -139
11  191 -206
17  171  168
21  149 -129

 -18,0,L

-8  211 -193
 2  135  147
 4  520 -515
 8  618  612
10  239 -254
12  418 -418
16  228  235

 -17,-6,L

 5  186  166
```

```
 -17,-5,L

 4  192 -164

 -17,-4,L

 7  167 -160
11  212  214

 -17,-3,L

 8  150 -126
10  262 -270
14  173  202
16  234  213

 -17,-2,L

-9  201  189
-5  183 -180
-3  231  228
 9  264 -237
11  140 -149
15  287 -280
17  105 -116

 -17,-1,L

-4  107 -109
 0  133  145
 2  176  155
 4  203  190
 8  123  129
12  113 -115
```

```
 -16,-7,L

-1  151 -145

 -16,-6,L

 2  160 -158
10  139  109
12  137  107

 -16,-5,L

 1  197 -181
 3  200  208
 5  227  222

 -16,-4,L

-8  211  208
 8  279 -267
10  447 -446
14  143 -160

 -16,-3,L

-9  316  316
-5  212 -217
 1  304 -306
 3  134 -124
 5  116  129
 7  208  206
11  231  234
13  109 -117
15  440 -440
```

```
 -16,-3,L

 19  100   69

 -16,-2,L

 -8  232 -225
 -6  252 -254
 -4  224 -231
  0  126  122
  4  244  243
 10  332  344
 16  330  332

 -16,-1,L

-11  204  209
 -1  136  125
  1  159  140
  3  519  533
  5  212 -206
  9  253  263
 11  315 -312
 13  250 -259
 15   42  -71

 -16,0,L

 -2  333  330
  0  227 -240
  2  309  303
  4  740  768
  6  224 -235
  8  242 -242
 10  309 -319

 12  201 -215

 -15,-7,L

 -2   97 -128
  6  132  121
  8   66   49

 -15,-6,L

  1  152 -181
  3  173 -178
  5  169  170

 -15,-5,L

 -4  240  248
 -2   59   -8
  2  111  123
  6  187 -173
  8  161 -171
 10  250 -242

 -15,-4,L

 -1  110 -123
  3  242  239
  7  139  160
 11  219 -237
 13  233 -253
 15  194 -174

 -15,-3,L

 -6  140 -145
 -4  165 -164
 -2  157 -153
  0  198 -204
  4  231  238
  6  163  165
 10  156  137
 14  107 -123

 -15,-2,L

 -7  444  432
 -3  216 -208
  9  133  113
 11  137  123
 15  209 -199
 17  136 -124

 -15,-1,L

 -6  184 -171
 -2  302  289
  4  454  447
 12  218 -202
 16  238  241

 -14,-7,L

  9  128 -139

 -14,-6,L

  8  121 -120

 -14,-5,L

 -3  457 -477
 -1  164 -168
  5  227  230
  7  159  150
  9  147  134

 -14,-4,L

 -8  418  418
 -4  226 -228
  2   76   83
 10  132 -149
 16  190 -196

 -14,-3,L

 -7  254  241
 -3  344  339
 -1  447  440
  5  117 -109
  9  384 -371
 11  192 -193
 13  220  214
 15  191 -192
 17   83  -87

 -14,-2,L

 -8  319 -304
 -4  497  494
 -2  404 -395
  0  460 -451
  2  426  403

  4  220  226
  6  247 -244
  8  305 -302
 12  113 -108
 16  332  353

 -14,-1,L

 -9  246 -247
 -7  172 -165
 -5  159 -152
 -3  279 -272
  1  290 -310
  3  584  576
  5  772  763
  9  352  348
 11  179  177
 15  164  161

 -14,0,L

-10  364 -360
 -6  182  183
 -4  325 -333
  2  440 -449
  4  707  694
  6  523  514
  8  321  324
 10  176  193
 18  144  129

 -13,-7,L

  4  152 -149

 -13,-6,L

 -7  122 -115
 -3    0   18
  1   95   61
  3   79  -97
  9  129 -165
 11   93  118

 -13,-5,L

 -2  226 -215
  2  602  593
  4  242  251
  6  330 -318
 10  118  105

 -13,-4,L

 -7  238  240
 -1  327 -330
  1  214  219
  3  155 -144
  5  196 -220
 11  192  205
 13  234  240

 -13,-3,L

-10   94 -114
 -8  178  181
 -6  322  316
  0  143  148
  2  108  117
  4  109 -116

  6   99  106
  8  286 -275
 10  349 -361
 12  155 -149
 16  139 -162

 -13,-2,L

 -9  191 -199
 -5  329 -334
 -3  124 -124
 -1  706  702
  1  500  478
  5  230 -226
  7  183 -206
  9  346 -326
 13  179 -170
 17  156 -158

 -13,-1,L

-12  188 -191
 -4  228 -224
 -2  277 -283
  0  283 -281
  2  744 -761
  6  501  506
 10  149  128

 -12,-7,L

 -7   79  -22
 -3   36   87
```

```
 -12,-6,L

  2  424  413
  6  226 -227
 10  154 -129

 -12,-5,L

 -1  256  260
  1  276  281
  5  332 -324

 -12,-4,L

 -6  297 -310
 -4  432 -440
 -2  341  336
  0  282  288
  2  230 -233
  4  335  326
  6  375  392
 12  274  259
 14  324  320
 16  187 -194
 18  175 -174

 -12,-3,L

-11  177  173
 -9  532 -538
 -7  641 -646
 -5  125 -131
 -3  398  400
 -1  271  254
  3  447  447
```

```
  5  282 -260
  7  440 -424
  9  425  429
 11  392  396
 13  403  397
 15   19   77
 17  165 -180

 -12,-2,L

 -8  368  374
 -6  257  250
 -4  201  200
 -2  177 -161
  0  248 -235
  2  395  392
  4   96  -99
  6  396 -399
  8  450 -454
 10  133 -132
 14  366 -363
 18   96   86

 -12,-1,L

 -7  107   74
 -3  508 -519
 -1  174  154
  1  249  233
  3 1243-1247
  5  357 -353
  9  100   99
 11  404  403
```

```
 -12,0,L

-12  399 -424
-10  209 -195
 -8  160  166
 -6  448  429
 -4  567 -554
 -2  696 -690
  0  189  222
  2 1093-1095
  4  508 -502
  6  105  108
  8  148 -137
 10  524  516
 12  582  566
 14  223  225
 16  167 -181
 18  174 -161

 -11,-8,L

  7  154  116

 -11,-6,L

 -5  223  227
 -3  240  253
 -1  147 -123
  1  223  217
  3  216  211
  5  238 -239
  7  211 -225

 -11,-5,L
```

```
 -4  232 -261
  0  219  233
  2  373  376
  4  173  179
  6  252 -250
  8  105   80
 10  268  264

 -11,-4,L

 -9  298 -297
 -7  334 -344
 -1  364  374
  3  515 -524
  5  317 -312
  7  463  446
  9  452  449
 13  133  121
 17  208 -195

 -11,-3,L

 -8  241  256
 -4  293 -287
 -2  211  200
  0  120  129
  4  285 -289
  6  330 -331
  8  274  261
 10  370  357
 12  263  256
 20    0  -35

 -11,-2,L
```

```
 -9  257 -245
 -7  173 -164
 -5  144  145
 -3  139  135
 -1  509  495
  3 1161-1114
  5  822 -799
  7  275 -281
  9    0  274
 15  234  255

 -11,-1,L

 -8  114  123
 -4  164  170
 -2  184  155
  2  552 -553
  6  262  264
  8  503 -503
 12  257  264
 14  192 -196
 16  241 -252

 -10,-7,L

 -1   68   15
  3  146  156
  7  123  109
  9  125  112

 -10,-6,L

 -6  171 -191
 -4  192 -203
 -2  125  112
```

```
  4  200  189
  8  212  218

 -10,-5,L

-13   33   53
 -3  252  269
 -1  158  180
  3  500 -485
  5  135 -119
  7  443  450
  9  173 -159
 11  201 -212
 13  113   94

 -10,-4,L

-12  161  172
-10  209  221
 -8  244 -234
 -6  138 -129
 -4  227  203
 -2  174  177
  2  327 -326
  6  468 -475
  8  546 -550
 10  131  150
 12  286  277
 14  145  171

 -10,-3,L

-11  122  118
 -9  594 -600
 -7  336 -329
```

```
 -5  452  443
 -3  278 -261
 -1  535 -526
  1  164 -168
  3  366  355
  5  109  -65
  7  386 -364
  9  688  676
 13  477 -482
 17  144  130
 19  197  171

 -10,-2,L

-10  163 -159
 -4  206 -209
 -2  122 -122
  0  320  302
  2  867  839
  4  607 -580
  8 1138 1124
 10  256  249
 14   86 -104
 16  237 -231

 -10,-1,L

-15  143  146
-11  132 -159
 -7  125  132
 -5  500  493
 -3  642  636
 -1  122  108
  1  233 -225
  3 1137-1139
```

```
 -10,-1,L           -9,-5,L            -9,-2,L             12    81   107     7   474  -463    -2   676  -682     8   150   131
                                                            16   131  -151    11   225  -215     0   710   727
   5   319  -321    -10   119   106    -11   189   181                        13   881  -878     2  2495  2669    -7,-4,L
   9   606  -604     -8   111   116     -9   105   107    -8,-5,L            15   101   115     4   737  -748
  11   161  -166      2   417  -420     -7   216  -212                        17   412   397    10   724  -746   -11   176   196
  21   160   176      4   477  -482     -5    93   100     -5   209  -212                        12   252  -234    -9   272   269
                      6   202  -187     -1   658  -629     -3   167   161    -8,-2,L            14   119  -120    -7    47   -41
 -10,0,L              8   190   200      1   707  -673     -1   171  -170                        16   430   457    -5    95   -98
                     10   193   209      3   354  -359      3   750   741   -14    84    95    18   296   310    -1   412  -409
 -10   237   241                         5   820   786      5   464   456   -10   308  -318                        3   227   226
  -8   165  -169    -9,-4,L              7   759   744      9   215  -210    -4   622  -624    -7,-8,L             5   339   318
  -6   141   159                        11   467  -440     13   112    99    -2   546   549                        9   236  -244
  -4   624   632     -7   162   188     13   364  -359                         0   414   405    -3    75   -72
   0   875   905     -5   196   187                        -8,-4,L             2   995 -1006     7   176  -170    -7,-3,L
   2   288  -286      1   325  -316    -9,-1,L                                 6   655   646
   4  1308 -1333      3   297  -298                         -8   249  -242     8   378   353    -7,-7,L           -10   333   336
   6   112  -121      5   258  -256    -16    64   -86     -4   304   307    10   348  -334                       -4   105    97
   8   438  -441      9   215  -217     -4   324   322     -2   140  -141    12   119  -133     2   111  -107    -2    61   -87
  10   148  -164     11   303  -311      4   575  -579      0   154  -127    14   390   400                        0   269  -256
  12   250  -244     13   141  -137      6   309   310      6   179  -169                       -7,-6,L             2   310  -300
  14   280  -271     15   136   131      8   212   201      8   271  -257    -8,-1,L                                6   343  -348
                                        10   257  -246     10   206   201                       -5   185  -206    12   359  -352
 -9,-7,L            -9,-3,L             20    92    81     14   382  -389   -11   213  -224    -1   106  -120    16   246   236
                                                                             -5   309  -294     1   121  -135
   4   122   159    -12   148   145    -8,-8,L            -8,-3,L            -1    22   -46     3   297   302
  10   160   175    -10   251  -261                                           1   318   327     9   218   233    -7,-2,L
                     -8   435  -429      0     0    -4    -11   396   380     3   347   346
 -9,-6,L             -4   164  -152                        -9   622   608     5   522  -531                       -9   373   378
                      0   507   484    -8,-6,L             -7   213   224     7   703   687    -7,-5,L            -3   371   374
  -1   285  -286      2   230   235                        -5   509   511    15   223  -235                       -1   177  -190
   3   401  -396      8   161   138     -4   125  -122     -3   333  -337                      -14   136   136     1   144  -154
   9   160  -157     12   169  -155      2   507  -503     -1   997  -938    -8,0,L             -8    79   -57     3   585   573
                     16     0   -35      4   138  -158      1   266  -263                       -2   158   149     5   641   608
                                         8   134   111      3   123  -140    -6   127   140     2   492  -487     7   184  -187
                                        10   177   184      5   147   122    -4   754   764     4   297  -294     9   224  -223
                                                                                                 6   334   338    13   242  -238
```

```
 -7,-1,L

-10  199 -176
 -6  235 -230
 -2  128  100
  0  342 -329
  2 1233 1247
  4 1360 1370
  6  252  254
  8  386 -390
 10  285 -278
 14  124  133
 16  165  178

 -6,-8,L

  6  130  121

 -6,-7,L

 -1   60  -11

 -6,-6,L

 -6  200  213
  2  457 -445
  8  195 -216

 -6,-5,L

 -5  146 -164
 -3  148 -136
  1  322 -319
  7  232 -238
  9  165  182

 13   99   79
 15 [illegible]   10

 -6,-4,L

-12  133 -120
 -6  178 -190
 -4  342  338
  2  476  475
  6   62   47
  8  245  248
 12  249 -253
 14  390 -398

 -6,-3,L

-17  158 -144
-11  192 -202
 -5  365  363
 -3  594  554
  1  541  531
  3  180 -185
  5  539  507
  7  596  584
  9  181 -179
 11  114  105
 15  141 -123
 19  283 -250

 -6,-2,L

-16  140  144
-12   89   92
 -6  496  500
 -2  403 -395

  2  537 -519
  4  465 -460
  6  687 -670
  8  656 -645
 10  163 -172
 12    0   32
 14  395  406
 16  170  167
 20  133  137

 -6,-1,L

 -9  159 -150
 -7  212 -214
 -5  193 -184
 -3  116  119
 -1  595 -629
  1  323  330
  3 1806 1841
  5  314 -328
  7  299 -307
  9  239  258
 11  249 -247
 13   57  -55
 17  146  157

 -6,0,L

-16  177 -182
-14  272 -291
 -8  281 -255
 -6 1490-1436
 -4  171 -175
  0 2205-2400
  2 2142 2296

  4 2146 2257
  6  478 -500
  8 1285 1314
 10  261  232
 12  220 -217
 16  209  228
 20  474 -455

 -5,-8,L

 -7  105  -82
 -5    0  -62
  1   74   96
  3  126  140

 -5,-7,L

  2   96  -76

 -5,-6,L

 -7  173  200
 -1  213  241
  1  281 -280
  3  414 -423
  5  174 -157
  7  220 -220
  9  115  -96

 -5,-5,L

-14  151  149
-10  213 -195
 -8   72  -82
 -6  133  131

 -4  149  131
 -2  105  107
  0  338  347
  2  194  196
  6  144  148
 10  275 -303

 -5,-4,L

-11  382 -389
 -3  301  277
 -1  237  235
  1  171  180
  3  123  157
  5  126  138
  7   74   68
 11  214  218

 -5,-3,L

 -6  222  216
 -4  294  295
 -2  405 -404
  0  120 -134
  4  304  294
  6  240  253
  8  141 -136
 14  186 -182

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-11  441 -436
 -9  217 -217
 -7  234  225
 -3  191  182

 -1  154 -158
  1  510 -508
  3  626 -637
  5  423  416
  7  670  645
  9  183 -185
 11  224  235
 13  413  413

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-14  229 -232
 -8  143  123
 -4  103  -87
 -2  175 -178
  0  996-1020
  4  293 -295
  6  451 -447
  8  463  433
 10  125  143
 16    0   13

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  2  105   86
  6  173 -156

 -4,-7,L

 -1  125  141
  1  178  180

 -4,-6,L

  0  576  572

  2  354  349
  6  118  128
  8  183 -206
 10  163 -183

 -4,-5,L

  1  282 -284
  3  157 -144
  7  392 -391

 -4,-4,L

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 -4  101  100
 -2   52   79
  0  626 -613
  2  348 -349
  6  155  142
  8  237  234
 12   67   82
 14   85   96

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 -9  471 -471
 -3  557  537
  1  197  209
  7  687  678
  9  180 -182
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 13  573  573
 15  138 -128
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  -4,-2,L

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 -6  154  178
 -2  234 -223
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  2  123  118
  4  384  394
  6  712  724
  8  154 -158
 14  263 -258

  -4,-1,L

-17  183  173
-15  153 -134
-11  503  508
 -9  295  277
 -1  239 -236
  1 2044-2147
  3  906 -895
  5  166  180
  7  476 -497
  9  260  243
 11  111  115
 15  269  256
 17  290  281

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-14  147 -169
-10  353 -360
 -8  608  601
 -6 1211 1182

 -4  539 -563
 -2  567 -588
  0 2008-2228
  2 1508-1575
  4  264 -279
  6  891 -924
  8  298  292
 10  213  206
 14  181  189
 16  203 -195

  -3,-8,L

  3  140  133

  -3,-7,L

  0  239  253
  2  233  239

  -3,-6,L

 -9   42  -84
 -1  268  273
  1  269  277

  -3,-5,L

 -4  137 -130
 -2  178 -176
  2  193  190

  -3,-4,L

 -7    0   44

 -5  102   63
 -1  291 -283
  1  217 -205
  5   82 -101
 13  219  220

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-12  354 -359
-10  159 -152
 -8  237  225
 -6  259  254
 -4  520  496
 -2  127  123
  0  203 -203
  4  106 -121
  6  261  252
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-13  262 -272
-11  602 -612
 -7  477  487
 -5  604 -591
 -3  433 -411
 -1  754  751
  1  387  400
  3  121 -119
  5  571 -571
 13  253  250

  -3,-1,L

-16  132  141
-14  196 -182
-12  227 -216
 -8  676  660
 -6  178  156
 -4  645 -663
 -2  244  224
  0 1184-1236
  2 1177-1211
  4 1575 1580
  6  152  125
  8  536 -528
 14  138 -133
 16  117 -116

  -2,-8,L

 -6  186  181
  6  203 -202

  -2,-7,L

 -5  231 -223
 -3   64  -74
 -1  225  236
  1  221  211
  5  162 -159

  -2,-6,L

 -8  111 -143
 -6  350 -369
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  0  245 -250
  2  137  142

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  6  280  271
  8  183  190

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 -7  117 -113
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 -3   84   91
 -1  243  236
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 11  105  116

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  6  269 -273
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 -5  750 -715
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  2 1075 1097
  4  430  422
  6  306  302
  8  252 -237
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 -7  578 -565
 -5 1176 1209
 -3  249  264
 -1 1697-1780

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  3 2070 2144
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-14  181  203
-12  151  147
 -8  863  853
 -6 1577 1574
 -4 1442-1464
 -2 1144-1241
  2  116 -319
  4  609  616
  6 1686-1714
  8  821 -793
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  8   75   98

  -1,-6,L

 -1  238  228
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 -1,-6,L

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  13   99  -98

 -1,-5,L

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   8  291  309
  10  152  133
  12  164 -146

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  -3  315 -295
   5  371 -344

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  -8  365  370
  -4  882 -875
  -2  392 -405
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   4  493 -481
   6  341 -327
  12  212  221

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 -13  126  136
 -11  334  341
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  -7  118  105
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   3  625 -620

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  11  480 -472
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  14   89  -88

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   7  345  340

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  -1  328  320

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   5  113  101
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   7  376 -370
  11  286  282
  13  150 -153
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