SOME ORGANIC CRYSTALS:
AN X - RAY STUDY.

THESIS
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by
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Preface.

This thesis describes the results of the research carried out in the years 1956 - 59 in the Chemistry Department of the University of Glasgow. For the first two of these years I am indebted to J.Anderson & Co.Ltd. of Paisley for a grant and to the University of Glasgow for an Assistant Lectureship for the third year.

I wish to express my sincerest thanks to Dr.S.C. Abrahams for his supervision during the first nine months of this work and for arranging the computations on the IBM 704 and ORACLE computers. I am also indebted to Professor J.M.Robertson for his advice and encouragement during the course of this work.

I wish to acknowledge Dr.H.H.Szmant of Duquesne University, Dr.N.J.Cartwright of Birmingham University and Dr.N.J.McCorkindale of Glasgow University for the provision of crystals, and to thank the latter for help in the estimation of intensities for the fumagillin work and for much helpful discussion of the problem. I must also thank Dr.S.C.Abrahams and Mr.J.B.Findlay for the photographs of the diagrams.

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Finally, and by no means least, I must express my most sincere thanks to my wife for her help and constant encouragement during the last three years.

SUMMARY.

This thesis deals with the study of some organic crystal structures using the method of x-ray diffraction; it is divided into three parts.

Part I consists of a description of some theoretical aspects of x-ray crystal analysis. The techniques described have been limited to those which have actually been used by the author. X-ray investigations are undertaken with one of two aims in view, either to obtain more accurate molecular dimensions for molecules of known crystal structure or else to determine the structure of a molecule whose crystal, or even chemical, structure is not known. Both types of approach are described in this thesis.

Part II describes the determination of more accurate parameters for three sulphone molecules. 4-4'-dichlorodiphenyl sulphone has been fully refined using the method of least squares. Accurate bond lengths and angles have been found and an analysis of the anisotropic thermal vibrations is given. The positions of the hydrogen atoms have been determined and found to be in

good agreement with the positions found in a neutron diffraction study of this compound by other workers. The other two molecules studied are 4-4'-dibromodiphenyl sulphone and 4-4'-diiododiphenyl sulphone; these three sulphones are isomorphous. The analyses of these two molecules are not so complete as the previous one although they have also been approached by the three - dimensional least squares method. The molecular geometry is given although the values are not as accurate as in the case of 4-4'-dichlorodiphenyl sulphone.

In Part III the attempts to elucidate the crystal structures of two molecules are described. The investigations were undertaken because of the lack of conclusive chemical evidence about their molecular structures. The study of prodigiosin, a bacterial pigment, was unsuccessful and the reasons for this are discussed. The study of a derivative of an antibiotic, fumagillin, has, however, been more satisfactory. So far only one projection has been studied but the molecule has been located in this and a possible chemical structure for the compound is suggested. A complete analysis to determine the stereochemistry will require three - dimensional data.

There are two appendices to this thesis, the first is composed of all the structure factor data for the compounds studied. The second appendix gives details of the programs written for the DEUCE electronic digital computer which have been used in the crystal analyses described.

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Part I.

X-Ray Crystal Analysis.

1. X-RAY DIFFRACTION.

1.1 Introduction.

Although x-rays were discovered in 1895 by Roentgen, x-ray crystallography really originated with von Laue's discovery in 1912 that crystals can diffract an x-ray beam. Since then considerable advances in the subject have been made and today it is becoming a very powerful method of analysis, particularly in the investigation of compounds of completely unknown chemical structure. Another important use of the method is in determining accurately the details of the atomic arrangement of atoms in molecules and crystals.

The greatest problem in the application of the method arises in the making of the initial observations. The measurement of the amplitudes of the diffracted x-ray beams can now be carried out with considerable accuracy particularly if electronic counting apparatus is used; no method,however, has yet been devised for the determination of the relative phases of these waves. These phases must be known before the structure can be solved. Several methods have been suggested for overcoming this problem, in particular by Patterson(1935), Harker and Kasper(1948), Karle and Hauptmann(1950) and Sayre(1952). None of these is generally applicable and each case must be considered on its own merits. Details of some of the methods used in this thesis are given below.

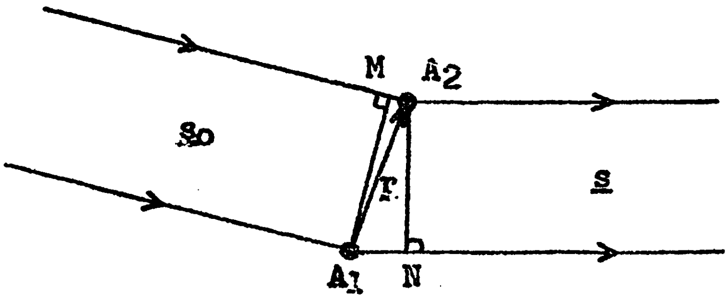
Firstly, if we know the positions of the atoms in the crystal we must be able to calculate structure factors from these for comparison with the observed values.

1.2 Structure factor expression.

If a primitive lattice is defined by the lattice constants a, b and c, then the two lattice points A_1 and A_2 (Fig.1) are related by

$$\underline{r} = u.\underline{a} + v.\underline{b} + w.\underline{c} \quad \ldots\ldots\ldots\ldots\ldots \quad (i)$$

where u, v and w are integers.



Fig,1.

If a parallel x-ray beam of wavelength λ falls on the lattice in a direction defined by a vector $\underline{s}_0$, of length $1/\lambda$, then after diffraction travels in the direction of a second vector $\underline{s}$, also of length $1/\lambda$, the path difference of the two scattered waves as in Fig. 1 is given by

$$\begin{aligned} \text{path difference} &= A_1.N - A_2.M \\ &= \lambda(\underline{r}.\underline{s} - \underline{r}.\underline{s}_0) \\ &= \lambda.\underline{r}(\underline{s} - \underline{s}_0) \\ &= \lambda.\underline{r}.\underline{S} \quad \ldots\ldots\ldots\ldots \text{(ii)} \end{aligned}$$

where $\underline{S} = \underline{s} - \underline{s}_0$.

For the scattered waves to be in phase this difference must be a whole number of waves, ie. $\underline{r}.\underline{S}$ must be integral. By (i), $(u.\underline{a} + v.\underline{b} + w.\underline{c}).\underline{S}$ must be integral, and this will only be true if each term is integral since u, v, and w are integers; hence

$$\begin{aligned} \underline{a}.\underline{S} &= h \\ \underline{b}.\underline{S} &= k \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(iii)} \\ \underline{c}.\underline{S} &= \ell \end{aligned}$$

where h, k and ℓ are integers.

These are Laue's equations and the integers h, k and ℓ are the Miller Indices of the diffracting plane.

If, now, we consider an atom in the unit cell with fractional coordinates (x_n, y_n, z_n), its position will be defined by the vector

$$\underline{r}_n = x_n.\underline{a} + y_n.\underline{b} + z_n.\underline{c} \quad \ldots\ldots \text{(iv)}$$

and the phase change of the wave scattered by this atom with respect to a wave scattered by an atom at the origin of the cell will be

$$\frac{2\pi}{\lambda}.\lambda.\underline{r}_n.\underline{S} = 2\pi.\underline{r}_n.\underline{S} \quad \ldots\ldots\ldots\ldots\ldots \quad (v)$$

Thus the expression for the wave scattered by this atom is

$$f_n.\exp(2\pi i\underline{r}.\underline{S})$$

where f_n is the atomic scattering factor of the nth atom. The complete wave scattered by all of the N atoms in the unit cell is given by

$$F = \sum_{n=1}^{N} f_n.\exp(2\pi i\underline{r}_n.\underline{S}) \quad \ldots\ldots\ldots\ldots\ldots \quad (vi)$$

where F is called the structure factor.

By substituting (iv) in (vi), we get

$$F = \sum_n f_n.\exp\left\{2\pi i(x_n.\underline{a}.\underline{S} + y_n.\underline{b}.\underline{S} + z_n.\underline{c}.\underline{S})\right\}$$

and by (iii)

$$F = \sum_n f_n.\exp\left\{2\pi i(hx_n + ky_n + lz_n)\right\} \quad \ldots. \quad (vii)$$

In general the quantity measured, the intensity, is proportional to $|F^2|$; the phase, however, is not measurable.

Now if $F = A + iB$, then

$$F^2 = F.F^* = A^2 + B^2$$

F^* being the complex conjugate of F, then

$$A = \sum_n f_n . \cos 2\pi (hx_n + ky_n + lz_n)$$

$$\qquad \qquad \qquad \qquad \ldots\ldots\ldots \text{(viii)}$$

$$B = \sum_n f_n . \sin 2\pi (hx_n + ky_n + lz_n)$$

These are the quantities used in practice and they can be simplified for the various space-groups, eg. $P\bar{1}$ where the equivalent positions are (x_n, y_n, z_n) and $(-x_n, -y_n, -z_n)$. Substitution in (viii) gives

$$A = 2 \sum_{n=1}^{N/2} f_n . \cos 2\pi (hx_n + ky_n + lz_n)$$

$$B = 0$$

and, therefore, we need only calculate A for half of the number of atoms in the unit cell.

1.3 Atomic scattering factors.

These are numbers representing the amplitudes of the x-ray beam scattered by an atom, and for any particular atom are proportional to Z, the atomic number, and a function of θ, the Bragg angle. They are available in tabular form and have been determined from theoretical considerations by James and Brindley(1931), McWeeny(1951), Stam and Tomiie(1958) and others, and also by empirical methods, for example by Abrahams(1955).

These atomic scattering factors are determined for atoms at rest, and since in crystals atoms are undergoing thermal vibrations, the atomic scattering factors must be modified to allow for this. If $\bar{u}$ is the mean displacement of the atom from its mean position, then by analogy with equation (v) the phase change will be

$$2\pi.2\bar{u}.\underline{S} \quad = \quad 4\pi\bar{u}.\underline{S} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (v')$$

and hence for this atom

$$\begin{aligned} f_n &= f_o.\exp(4\pi i\bar{u}.\underline{S}) \\ &= f_o\left\{\cos(4\pi\bar{u}.\underline{S}) + i.\sin(4\pi\bar{u}.\underline{S})\right\}. \end{aligned}$$

If the atomic vibration is spherically symmetric, then

$$f_n \quad = \quad f_o.\cos(4\pi\bar{u}.\underline{S}) \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (ix)$$

Now

$$\cos x \quad = \quad 1 \; - \; x^2/2 \; + \; x^4/24 \; - \; \ldots\ldots$$

and

$$\exp(-\tfrac{1}{2}x^2) \; = \; 1 \; - \; x^2/2 \; + \; x^4/8 \; - \; \ldots$$

whence

$$\cos x \quad \doteqdot \quad \exp(-\tfrac{1}{2}x^2) \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (x)$$

By applying (x) to equation (ix) we get

$$\begin{aligned} f_n &= f_o.\exp-\tfrac{1}{2}(4\pi u.\underline{S})^2 \\ &= f_o.\exp(-8\pi^2\bar{u}^2\underline{S}^2). \end{aligned}$$

This is generally written as

$$f_n \quad = \quad f_o.\exp(-B.s^2) \qquad \ldots\ldots\ldots\ldots\ldots\ldots \quad (xi)$$

where $B = 8\pi^2.\bar{u}^2$ and is generally known as the Debye temperature factor (Debye,1914).

If now we have a set of observed structure factors derived from x-ray intensity data, then we may give these the signs of the corresponding structure factors calculated from the positions of the atoms in the unit cell. These signed, observed structure factors may then be used as coefficients in a Fourier series to determine the electron density at any point in the unit cell.

1.4 Fourier representation of a crystal.

If $\rho(xyz)$ is the electron density at the point (xyz) then $\rho(xyz)dxdydz$ gives the number of electrons in the volume element dx.dy.dz. When the unit cell has volume V, we get

$$F(hk\ell) = V\int_0^1\int_0^1\int_0^1 \rho(xyz)\exp\{2\pi i(hx + ky + \ell z)\}\,dx.dy.dz \quad ..(xii)$$

Now the electron density may be represented by a three-dimensional Fourier series (Bragg, 1915), viz.

$$\rho(xyz) = \sum_{-\infty}^{\infty}\sum\sum A(pqr).\exp\{2\pi i(px + qy + rz)\} \quad ....(xiii)$$

If we now insert this in (xii) we get

$$F(hk\ell) = V\int_0^1\int_0^1\int_0^1\left\{\sum_{-\infty}^{\infty}\sum\sum A(pqr).\exp 2\pi i(px + qy + rz)\right\}.$$
$$\exp\{2\pi i(hx + ky + \ell z)\}\,dx.dy.dz$$

and on integrating all terms are zero except that for which

$$p = -h; \quad q = -k; \quad r = -\ell \qquad \text{giving}$$

$$F(hk\ell) = V\int_0^1\int_0^1\int_0^1 A(\overline{hk\ell})dx.dy.dz$$
$$= V.A(\overline{hk\ell})$$

ie. $A(hk\ell) = 1/V.F(hk\ell)$

and so

$$\rho(xyz) = 1/V.\sum_{-\infty}^{\infty}\sum\sum F(hk\ell).\exp\{-2\pi i(hx + ky + \ell z)\} \quad ....(xiv)$$

If $h = k = \ell = 0$, then we find that $F(000) = Z$, where Z is the total number of electrons in the unit cell. Since f_n will fall off with $\sin\theta/\lambda$ the terms in the series will decrease and in consequence the series will converge if sufficient $F(hk\ell)$ data is available.

The disadvantage of this Fourier expression is that the signs of the coefficients, the phases, must be known, and these can only be calculated when the positions of the atoms in the crystal are, at least approximately, known. A method for overcoming this is to use $F^2(hk\ell)$ as coefficients in the Fourier expression instead of $F(hk\ell)$.

1.5 Patterson's Fourier series.

Patterson (1935) showed that the Fourier series

$$P(u,v,w) = 1/V.\sum_{-\infty}^{\infty}\sum\sum F^2(hk\ell).\exp\{-2\pi i(hu + kv + \ell w)\} \quad ...(xv)$$

would give a peak with coordinates (u,v,w) when two atoms of the structure are related to each other by a vector (u,v,w), the value of P(u,v,w) being proportional to the product of the electron densities of the two atoms concerned. This function has the advantage that it is real for all values of (u,v,w) since if we collect the coefficients in h,k,l and $\bar{h},\bar{k},\bar{l}$ and put

$$F^2(hkl) = F^2(\overline{hkl})$$

then (xv) becomes

$$P(u,v,w) = 1/2V.\sum_{-\infty}^{\infty}\sum\sum F^2(hkl)\left[\exp\{-2\pi i(hu + kv + lw)\} + \exp\{2\pi i(hu + kv + lw)\}\right]$$

$$= 1/V.\sum_{-\infty}^{\infty}\sum\sum F^2(hkl).\cos 2\pi(hu + kv + lw) \quad .....(xvi)$$

This function has the disadvantage that it gives rise to a large number of peaks, $n(n - 1)/2$ if there are <u>n</u> atoms in the unit cell. Its chief value lies in the location of 'heavy atoms', ie. ones whose atomic number is larger than the others.

This arises since the value of P(u,v,w) is proportional to the atomic number of the two atoms considered and in consequence these peaks will be better resolved.

This series, then, gives us a method for using our observations, the F^2's in a direct attempt to determine the atomic arrangement in the crystal. Having once determined the approximate atomic positions we then require some methods for improving these values. Successive cycles of Fourier series and structure factor calculations will accomplish this but improved methods have been suggested.

1.6 Difference Fourier series.

In the least squares refinement process the function minimised is

$$\phi = \sum_n w(F_o - F_c)^2$$

If $w = 1/f_j$ is used the function to be minimised becomes

$$\phi' = \sum_n 1/f_j(F_o - F_c)^2$$

and the condition that ϕ' should be a minimum with respect to the coordinates of the jth atom is

$$\frac{\partial \phi'}{\partial x_j} = \frac{\partial \phi'}{\partial y_j} = \frac{\partial \phi'}{\partial z_j} = 0$$

For a centrosymmetric structure

$$F_c = 2.\sum_{j=1}^{N/2} f_j.\cos\theta_j \qquad \ldots\ldots\ldots\ldots\ldots \text{(xvii)}$$

where $\theta_j = 2\pi(hx_j + ky_j + lz_j)$.

Now

$$\frac{\partial F_c}{\partial x_j} = -4\pi h f_j.\sin\theta_j$$

and

$$\frac{\partial \phi'}{\partial F_c} = -2.\sum_n 1/f_j(F_o - F_c)$$

and hence

$$\frac{\partial \phi'}{\partial x_j} = \frac{\partial \phi'}{\partial F_c} \cdot \frac{\partial F_c}{\partial x_j} = 8\pi.\sum_n h(F_o - F_c)\sin\theta_j \ \ldots \ \text{(xviii)}$$

If we let $D_j = (\rho_o - \rho_c)_j$ = the difference electron density at the centre of the jth atom then

$$D_j = 1/V.\sum_n (F_o - F_c)\cos\theta_j$$

whence

$$\left(\frac{\partial D}{\partial x}\right)_j = -\frac{2\pi}{V}\sum_n h(F_o - F_c)\sin\theta_j \quad \ldots\ldots\ldots \text{(xix)}$$

Combining (xviii) and (xix) we get

$$\left(\frac{\partial D}{\partial x_j}\right) = \frac{1}{4V}\left(-\frac{\partial\Phi'}{\partial x}\right)_j$$

and since $(\partial\Phi'/\partial x) = 0$ minimises Φ', then so does $\left(\frac{\partial D}{\partial x}\right)_j = 0$ and similarly $\left(\frac{\partial D}{\partial y}\right)_j = \left(\frac{\partial D}{\partial z_j}\right) = 0.$

If the positions of the atoms used for the structure factor calculations are found to coincide with points of zero electron density gradient on the difference map, then Φ' has been minimised with respect to these coordinates. If, however, the gradient at an atomic position is non-zero, then the atom must be moved to a more positive region by an amount proportional to the gradient. The expression used to calculate the magnitude of this shift is

$$\Delta r_j = -\left(\frac{\partial D}{\partial r}\right)_j \Big/ \left(\frac{\partial^2\rho}{\partial r^2}\right)_j \quad \ldots\ldots\ldots \text{(xx)}$$

where $\underline{r}$ is the vector along the line of maximum gradient through the atom.

If we assume that the electron density near the centre of an atom can be represented (Costain, 1941) by

$$\rho(r) = \rho(0).\exp(-pr^2)$$

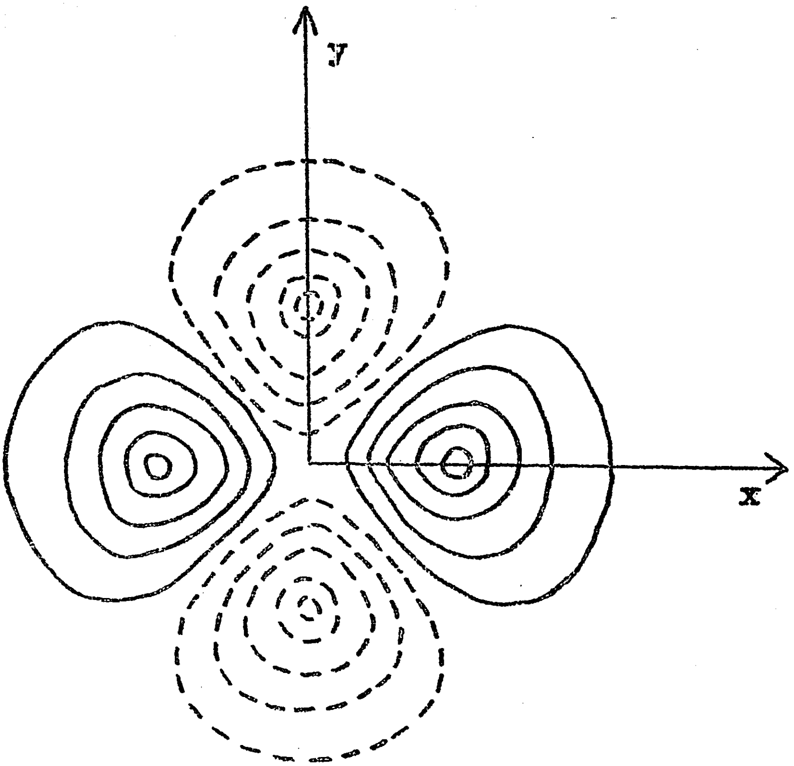


Fig.2. Anisotropic thermal vibration.

The negative electron density contours are dashed. These features indicate that the temperature factor should be increased along the x - direction and decreased along the y - direction.

where p is a constant dependent on the temperature factor of the atom, then

$$\left(\frac{\partial^2\rho(r)}{\partial r^2}\right)_{r = 0} = -2p\rho(0)$$

and hence equation (xx) becomes

$$\Delta r_j = \left(\frac{\partial D}{\partial r}\right)_j \div 2p\rho(0) \quad \ldots\ldots\ldots \quad (xxi)$$

The constants p and $\rho(0)$ are evaluated by plotting $\log\rho$ against r^2, the values of ρ and r being measured from well resolved atoms, of the same type, on the corresponding Fourier map.

Temperature parameters can also be improved from the information on these maps. If, for instance, the value of B_j for an atom is too high then $\exp(-B_j s^2)$ will be too low and correspondingly $F_o - F_c$ will be too high. In this way $\rho_o - \rho_c$ will bepositive at the corresponding atomic position; conversely, if B_j is too low the value of $\rho_o - \rho_c$ will be negative. Evidence of anisotropic thermal vibration can found by features such as are shown in Fig.2. These allow suitable thermal parameters of the form

$$B = \alpha + \beta.\sin^2(\phi - \gamma) \quad \ldots\ldots\ldots \quad (xxii)$$

to be chosen (Hughes, 1941; Cochran, 1951) for the two-dimensional case, where α, β and γ are constants and $(2\sin\theta, \phi)$ are the polar coordinates of the reciprocal lattice point considered.

1.7 Method of least squares.

When the function

$$\Phi = \Sigma\, w(hk\ell) \left\{ |F_o| - |F_c| \right\}^2$$

is near to its minimum, then a small change Δx_j in the x - coordinate of the jth atom will change F_c by an amount

$$\Delta F_c = \frac{\partial F_c}{\partial x_j} . \Delta x_j$$

Simultaneous changes to all the atomic coordinates will result in a change of F_c of

$$\Delta F_c = \sum_j \left(\frac{\partial F}{\partial x_j} \Delta x_j + \frac{\partial F}{\partial y_j} \Delta y_j + \frac{\partial F}{\partial z_j} \Delta z_j \right) \quad \ldots \text{(xxiii)}$$

The correct values of Δx_j etc. will therefore be those which most nearly equate ΔF_c to $F_o - F_c$ for all possible equations. For the least squares proceedure to work this number should be considerably greater than the number of unknown parameters to be determined - generally 3 positional and 6 thermal parameters per atom plus the scale factor. If we consider only the positional parameters for N atoms, then the observational equations will be of the type shown in equation (xxiii). To form the normal equations, each of the q observational equations, where q is the number of independent observations, must be multiplied by the weighted coefficient of each of the unknowns in turn. The resulting q equations in each case are then summed to give the 3N normal equations which can be solved for ΔX_j, Δy_j and Δz_j. The jth of these normal equations will be obtained by multiplying the q equations (xxiii) by $w.\partial F_c/\partial x_j$ and adding to produce

$$\sum_q w\left\{\left(\frac{\partial F_c}{\partial x_j}\right)^2 \Delta x_j + \frac{\partial F_c}{\partial x_j}.\frac{\partial F_c}{\partial y_j}\Delta y_j + \frac{\partial F_c}{\partial x_j}.\frac{\partial F_c}{\partial z_j}\Delta z_j + \sum_k \frac{\partial F_c}{\partial x_j}\left(\frac{\partial F_c}{\partial x_k}\Delta x_k + \frac{\partial F_c}{\partial y_k}\Delta y_k + \frac{\partial F_c}{\partial z_k}\Delta z_k\right)\right\} = \sum_q w(F_o - F_c)\frac{\partial F_c}{\partial x_j} \quad ..\text{(xxiv)}$$

where k denotes all the atoms except the jth.

Solution of these q equations is frequently a very large problem and some simplification can be made. If the atoms are well resolved it can be shown that quantities such as

$$\sum_q w \frac{\partial F_c}{\partial x_j}.\frac{\partial F_c}{\partial x_k}$$

are likely to be small compared with

$$\sum_q w\left(\frac{\partial F_c}{\partial x_j}\right)^2$$

and can therefore be neglected. If the axes are orthogonal, or nearly so, terms of the form

$$\sum_q w \frac{\partial F_c}{\partial x_j}.\frac{\partial F_c}{\partial y_j}$$

can also be neglected. This reduces equation (xxiv) to

$$\Delta x_j . \sum_q w\left(\frac{\partial F_c}{\partial x_j}\right)^2 = \sum_q w(F_o - F_c)\frac{\partial F_c}{\partial x_j} \quad \ldots\ldots\ldots \text{(xxv)}$$

If the temperature parameters are also being refined the problem is a much larger one and best carried out on an electronic digital computer.

In many cases it is obvious that the atoms in a crystal are not subject to isotropic thermal vibrations and analytical methods have now been developed to allow for anisotropic vibration.

1.8 Anisotropic thermal vibrations.

In section 1.3 it was shown that if the atoms were vibrating with spherical symmetry, then the scattering factors should be corrected by the expression

$$T = \exp(-Bs^2)$$

where $B = 8\pi^2.\bar{u}^2$. In general, however, this is not true and the vibration of the atoms is anisotropic; this can be represented by

$$\bar{u}^2 = \sum_{i=1}^{3} \sum_{j=1}^{3} U^r_{ij}.\ell_i.\ell_j \quad \ldots\ldots \text{(xxvi)}$$

where U^r_{ij} is a symmetric tensor and ℓ_1, ℓ_2 and ℓ_3 are the components of the unit vector $\underline{\ell}$ along which the vibration is taking place. Hence

$$T = \exp -8\pi^2(\sum_{i=1}^{3} \sum_{j=1}^{3} U^r_{ij}.\ell_i.\ell_j)s^2$$

which can conveniently be written in the form

$$T \;=\; \exp -(h^2b_{11} + k^2b_{22} + l^2b_{33} + hkb_{12} + klb_{23} + lhb_{31}) \qquad \text{.......} \; (xxvii)$$

where

$$\begin{aligned} b_{11} &= 2\pi^2(a^*)^2U^r_{11} \\ b_{22} &= 2\pi^2(b^*)^2U^r_{22} \\ b_{33} &= 2\pi^2(c^*)^2U^r_{33} \\ b_{12} &= 4\pi^2.a^*.b^*.U^r_{12} \\ b_{23} &= 4\pi^2.b^*.c^*.U^r_{23} \\ b_{31} &= 4\pi^2.c^*.a^*.U^r_{31} \end{aligned} \qquad \text{........} \; (xxviii)$$

If the molecule under consideration can be assumed to be a rigid body then Cruickshank (1956a) showed that the U^r tensors for these atoms can be represented by two tensors T_{ij} and ω_{ij}. The tensor T_{ij} gives the mean square amplitude of the translational vibrations along the molecular axes and the ω_{ij} tensor gives the mean square angular oscillation about the molecular axes.

These two tensors may be calculated by the least squares method; the normal equations are

$$\sum_{q=1}^{12}\left\{\sum_n \left(\frac{\partial U_n^{calc}}{\partial A_p}\right)\left(\frac{\partial U_n^{calc}}{\partial A_q}\right)\right\} A_q \;=\; \sum_n U_n^{obs}\left(\frac{\partial U_n^{calc}}{\partial A_p}\right)$$

where $U_n^{obs} = U^r_{ij}$ obtained from the b_{ij}; $U_n^{calc} = U^r_{ij}$ calculated from T_{ij} and ω_{ij}; A_q are the unknown components of T_{ij} and ω_{ij} and n is the number of independent U_{ij}. These are twelfth order equations and can be solved for the twelve values A_q.

1.9 Methods of computation.

Various methods have been used to perform some of the lengthy calculations involved in x-ray crystal analysis. Several of these have been programmed by the author for the DEUCE computer; details of some of these programs are contained in Appendix 2.

Structure factors have been calculated by two methods. Firstly, hand calculations were carried out with the help of tables which give values of sin $2\pi\theta$ and cos $2\pi\theta$ for values of θ where $0 \leqslant \theta \leqslant 1$. The tables compiled by Buerger (1941) which contain values of sin $2\pi hx$ and cos $2\pi hx$ for values of h from 1 to 30 and of x from 0 to 1 at intervals of 0.001 have also been used. Secondly calculations have been carried out on DEUCE using the structure factor program written by Dr.J.S.Rollett.

Fourier summations have also been carried out in several ways. Hand calculations were performed using Beevers-Lipson strips (Beevers and Lipson, 1934, 1936a and 1936b; Beevers, 1952) and also using RUFUS, a fast mechanical computer designed by Prof.J.M.Robertson to perform Fourier summations. The design of this machine has been described in two papers (Robertson, 1954 and 1955). The machine gives values of F.cos $2\pi hx$ for x

between 0 and 1 at intervals of 1/30 and for values of h from 0 to 15. The values of F are set on the counter which corresponds to the required value of h by means of an electric motor. This operation simultaneously sets up on 32 other counters the values of F.cos $2\pi hx$ by means of an appropriate train of gears. Values of sin $2\pi hx$ can be obtained at the same time and summations of the form

$$\sum_m F_m.\cos 2\pi h_m x \; - \; \sum_n F_n.\sin 2\pi h_n x$$

are performed in one operation.

Automatic computations have also been carried out on DEUCE, again using a program written by Dr.J.S.Rollett.

Part II.

4-4'-dihalogeno-diphenyl sulphones.

1.1 Introduction.

The chemistry of sulphur has long been of interest to chemists. This is because of its ability to form a varying number of bonds from two in compounds such as H_2S to as many as six in SF_6. The reason for this wide variation is the expansion of the outer shell of electrons in sulphur atoms beyond the normal octet of electrons to a decet or even a duodecet. This is accomplished by accomodating the extra electrons in the 3d orbitals which are normally unoccupied. The bonding arrangement in sulphur atoms has recently been reviewed by Abrahams (1956).

Particular interest in the past has been shown in the sulphur - oxygen bond and there has been much argument about its bond order, especially in sulphone molecules. It is now generally agreed that this bond has a high percentage of double bond character; the accepted double bond length being 1.43A while the single bond length is 1.60A. The sulphur - oxygen bond length has been measured in sulphuryl chloride by electron diffraction (Palmer,1938) and found to be 1.43 ± 0.02A; this is the same value found in dimethyl sulphone and quoted by Allen and Sutton (1950). In β - isoprene sulphone the sulphur - oxygen bond has been measured by x-ray analysis and found to be 1.436 ± 0.017A (Jeffrey,1951). These measurements are all, however, considerably shorter than the bond length found by Toussaint (1945) in 4-4'-dibromodiphenyl sulphone of 1.54 ± 0.05A which suggests that the sulphur - oxygen bond in this molecule may only have about 60% of double bond character.

The carbon - sulphur bond has been shown in several molecules to have as much as about 40% of double bond character but in 4-4'-dibromodiphenyl sulphone this bond is almost certainly a pure single bond, the bond length given by Toussaint being 1.84 ± 0.04A. The accepted carbon - sulphur single bond length is 1.82A and the double bond length is 1.61A(Abrahams,1956).

The angular distribution of the bonds in sulphone molecules is also interesting, the four bonds are approximately tetrahedrally distributed but the O - S -O angle is always significantly larger than the tetrahedral value of 109.5°. In these molecules the X-S-O angle appears remarkably constant at about 107°; the X-S-X angle on the other hand varies considerably. Three measurements have been reported for the F-S-F angle in F_2SO_2, the first by Stevenson and Russell (1939) was 100 ± 8°. The second, obtained by Fristrom (1952) using the microwave method was 92.8 ± 0.5°, and the third determination by the same method was 96°7' ± 10' (Lide, Mann and Fristrom, 1957). Electron diffraction on Cl_2SO_2 shows the Cl-S-Cl angle to be 111.2 ± 2° (Palmer, 1938). This change in bond angle can be attributed to two sources, firstly increased steric repulsion caused by the greater size of the chlorine atom, and secondly, a change in the hybridisation of the sulphur atom with a less electronegative substituent. To study this second effect in more detail, substituents with varying electronegativities but the same effective size are required. Such a series of compounds are the 4-4'-dihalogenodiphenyl sulphones in which the halogen atoms are directly conjugated through the benzene ring to the sulphur atom. Any change in the electronegativity of the halogen can thus alter the hybridisation of the sulphur electrons and cause any change in the X-S-X angle without the accompanying steric effect of the larger groups.

It has also been predicted by Koch and Moffitt (1951) that the benzene rings in diphenylsulphone should be normal to the C-S-C' plane because of the overlap of the sulphur 3d and carbon 2p orbitals. This has been found to be the case in diphenyl sulphoxide (Abrahams, 1957) where the angle between the ring planes and the C-S-C' plane is 81.9°. It has also been shown that the diphenyl sulphone and diphenyl sulphoxide molecules are so similar that they form a continuous series of solid solutions having the crystal structure of diphenyl sulphone in proportions up to 90% of diphenyl sulphoxide (Abrahams and Silverton, 1956). It seems likely then, that this will also be true in the substituted diphenyl sulphone molecules.

Koch and Moffitt (1951) also state that the more electronegative the groups attached to the sulphone the stronger will be the sulphur - oxygen bond. This appears to be true in the case of sulphuryl fluoride and sulphuryl chloride where the sulphur - oxygen bond lengths are 1.37 ± 0.01A and 1.43A respectively. This effect should also be present in the dihalogenodiphenyl sulphone molecules although probably to a lesser extent. To observe these effects, however, will require analyses of more accuracy than have so far been carried out on sulphone molecules.

1.2 Historical.

Compounds of the general formula $(p\text{-}R\text{-}C_6H_4)_2SO_2$ have been studied by several workers. Table 1 gives values of some physical constants of these molecules together with their unit cell dimensions. The data for the compound with R = H, viz. diphenyl sulphone, are taken from a paper by

Table 1.

$(p - R - C_6H_4)_2SO_2$: some physical constants.

	R = H	R = F	R = Cl
M.Wt.	218.27	254.25	287.16
M.Pt.	124°C	98°C	147.5°C
a	12.21 ± 0.03A	10.10 ± 0.02A	12.3kX
b	7.82 ± 0.02	13.05 ± 0.02	5.01
c	11.31 ± 0.03	8.22 ± 0.02	20.5
β	98°25' ± 10'	99.53 ± 0.2°	90°31'
Unit cell volume	1071A^3	1069A^3	1263A^3
Density	1.355	1.56	1.52
No. of mols/cell	4	4	4
Space group	$P2_1/c$	$P2_1/a$	$I2/a$

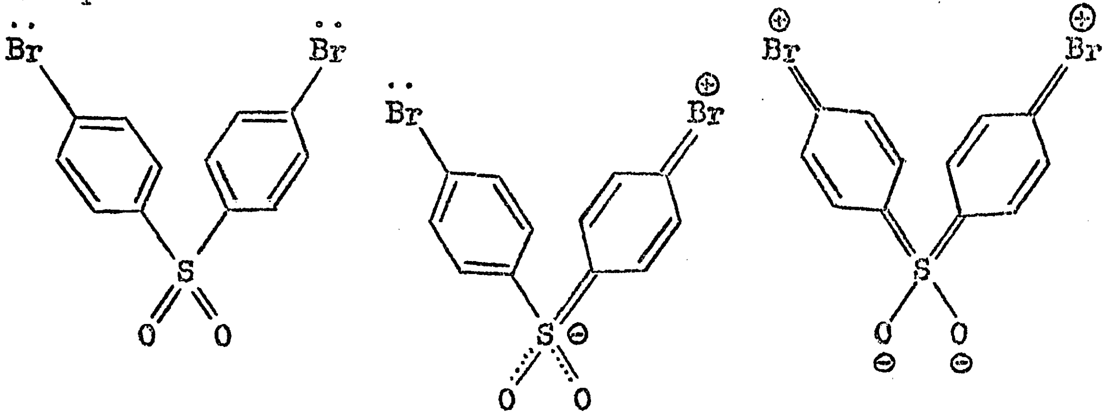
	R = Br	R = I	
M.Wt.	376.08	470.09	
M.Pt.	172°C	213.5°C	
a	12.32 ± 0.03A	19.67A	21.37A
b	5.04 ± 0.02	4.92	4.92
c	20.75 ± 0.03	14.37	14.37
β	92°40'	104°	116.7°
Unit cell volume	1286A^3	1349A^3	
Density	1.88	2.25 ± 0.01	
No. of mols/cell	4	4	
Space group	$I2/a$	$I2/a$	$C2/c$.

Abrahams and Silverton (1956) which shows the formation of a series of solid solutions of diphenyl sulphoxide and diphenyl sulphone. The data for the compound $(p\text{-}F\text{-}C_6H_4)_2SO_2$ has been measured by Sime(1956). As can be seen in Table 1 the compounds with R = Cl, Br and I form an isomorphous series. The first two of these compounds have been studied by Toussaint (1948 and 1944 resp.), and the third by Keil and Plieth (1951).

So far no detailed study of the diphenyl sulphone and 4-4'-difluorodiphenyl sulphone molecules have been reported. The structure of 4-4'-dibromodiphenyl sulphone has been reported in three papers by Toussaint (1944, 1945 and 1946). This work was, however, carried out in relation to optical studies of the crystals and not to determine detailed molecular geometry. He does, however, give the coordinates of the two heaviest atoms, bromine and sulphur, as determined from projections down the b- and a- axes. These coordinates are given in Table 2. The following bond lengths and angles are also given, assuming the benzene ring to be a regular hexagon of sides 1.41A;

Br - C = 1.89 ± 0.04A   Br-S-Br = $100 \pm 0.5^\circ$
S - C = 1.79 ± 0.04A   O-S-O = $131 \pm 3^\circ$
S - O = 1.54 ± 0.05A.

The Br-S-Br' plane is reported to be at an angle of 90 ± 1° to the benzene ring plane and at an angle of 24° to the c- axis. The length of the sulphur - oxygen bond agrees with the prediction of Koch (1949) that this bond should be longer than the normal S - O bond length of 1.43A. He suggests that the following resonance forms are possible



(a) (b) (c)

Contributions from (b) and (c) indicate that C - S should be shorter than the normal single bond, and that S - O should be longer than the normal double bond as in (a).

4-4'-dichlorodiphenyl sulphone has also been studied by Toussaint (1948). This analysis, again carried out in conjunction with an optical study, was only done for the $h0l$ projection. The signs of the structure factors used to calculate the Fourier synthesis for this projection were obtained by comparison with the structure factors of the isomorphous bromo - compound. Several Fourier series were calculated for this projection but no atomic coordinates are given; the following angles are reported - the Cl - S - Cl' plane is at about 90° from the benzene ring plane and makes an angle of 24° with the c- axis. The Cl - S - Cl' angle is 100 ± 1°.

Two papers have been published on 4-4'-diiododiphenyl sulphone by Keil and Plieth (1951 and 1955). The second of these papers is the more complete and contains all of the information given in the first. Their analysis was carried out without any reference to any of Toussaint's earlier work. The unit cell they chose is the alternative orientation of the $I_{2/a}$ cell chosen by Toussaint and this orientation is also recorded in Table 1.

The structure was determined from the $h0\ell$ zone for which a list of observed and calculated structure factors is given. The y- coordinates were obtained by assuming bond lengths and calculating hk0 structure factors based on different iodine positions. They also assumed in this calculation that the benzene ring plane was at 90° to the I - S - I' plane. A complete set of the x, y and z coordinates for all the atoms are given and these values, transformed to the $I_{2/a}$ orientation for comparison purposes, are given in Table 2.

Bergmann and Tschudnowsky (1932) give the Cl - S - Cl' angle of 4-4'-dichlorodiphenylsulphoxide as 109°.

Two papers on 4-4'-dichlorodiphenyl sulphone are now being published. The first by Sime and Abrahams (1959) is a full three dimensional study of this molecule and forms the subject matter of part of this thesis. The second paper, by Bacon and Curry (1959) is a two dimensional neutron diffraction study of this molecule and is commented on in section 2.9.

2. 4-4'-Dichlorodiphenyl sulphone.

2.1 Unit cell data.

Precession and Weissenberg camera photographs were taken with the crystal set about the b- axis using molybdenum K_α radiation (λ= 0.7107A). The axial lengths were determined from the precession photographs and corrected for film shrinkage; the β - angle of the monoclinic cell was measured on the Weissenberg photograph. These gave the following results

$a = 20.204 \pm 0.010A$

$b = 5.009 \pm 0.010$

$c = 12.259 \pm 0.010$

$\beta = 90.57 \pm 0.25^\circ$

The values given by Toussaint (1948) were

$a = 12.3$ kX

$b = 5.01$

$c = 20.5$

$\beta = 90^\circ 31'$

ie. the a- and c- axes have been interchanged.

The volume of the unit cell

$$V = a.b.c.\sin\beta$$

is $1240.6A^3$; the density determined by flotation in an aqueous solution of zinc chloride is 1.533 gm/c.c. which gives four molecules per unit cell and using the formula

$$D = \frac{1.66020 \, . \, \Sigma A}{V}$$

(Bragg,1947) the calculated density D is 1.537 gm/c.c.. The total number of electrons per unit cell, F(000) is 584.

Examination of the precession and Weissenberg photographs showed the absent spectra to be in

hkl when h + k + l is odd

h0l when h or l is odd

0k0 when k is odd

which indicates that the space group is either C^{6}_{2h} - $I_{2/a}$ or C^{4}_{s} - I_{a} (Toussaint states $I_{2/a}$). The centred space group $I_{2/a}$ was assumed initially and later confirmed.

2.2 Intensity data.

(a). For the initial work on the h0l zone the x-ray data were obtained using a Weissenberg camera and rotation about the b - axis. A pack of five films was used in the camera and the intensities estimated visually; this multiple film technique has been described by Robertson (1943). The radiation used for this was copper K_{α} (λ= 1.5418A). These intensities were corrected for Lorentz and polarisation factors by the usual formula

$$F^2 = I.\sin 2\theta/(1 + \cos^2 2\theta)$$

giving a set of |F| values on an arbitrary scale.

(b). For the three dimensional analysis all of the data were recorded using molybdenum K_α radiation and Ilford 'Industrial G' film. Since the linear absorption coefficient for this radiation is small, 0.718 mm^{-1}, sufficiently small crystals were chosen to make the errors due to absorption negligible. The crystals used were 0.5 x 0.3 x 0.3 mm and 1.0 x 0.5 x 0.5 mm. the latter only being used for measuring the weakest intensities. Equi - inclination Weissenberg photographs were taken with rotation about the b- axis of the layers $h0\ell$ to $h7\ell$ using the multiple film technique and a modified Weissenberg camera based on a design of Abrahams (1954). Since, however, x-ray film does not absorb Mo K_α radiation to the same extent as it does Cu K_α radiation it was necessary to interleave the films with sheets of nickel foil 0.0008" thick. In order to determine the resulting intensity reduction for normal beam photographs a small portion of data was photographed four times on a four film pack with a 3 : 1 ratio in the exposure times of sucessive exposures - a stabilised x-ray output was used for this. An approximate reduction factor was then determined and the process repeated using this ratio as the ratio of the exposure times; in this way a reduction ratio of 2.65 : 1 was derived.

For the upper layers recorded on the Weissenberg camera this factor was modified by the obliquity factor (Rossman, 1956), viz.

$$R = \frac{I_o}{I} = \frac{1}{1 - C} \exp(\mu t . \sec\nu).$$

Since the values of the constants given by Rossman were for Cu K_α radiation new values of the constants were determined. The value of μt was determined from the known linear absorption coefficient for nickel and the thickness of the foil; this gave $\mu t = 0.842$. By substituting this value of μt and a value of 2.65 for R when $\nu = 0$, it was found that $1/(1 - C) = 1.142$. A graph of R against ν was then plotted and the reduction factor determined for the individual layers. These intensities were also estimated visually and corrected by the Lorentz and polarisation factors and Tunell's rotation factor (1939), D_e, for the upper layer lines where

$$D_e = (\cos^2\nu - \cos^2\theta)^{\frac{1}{2}}/\sin\theta$$

where ν = equi - inclination angle = $\sin^{-1}(n\lambda/2d)$, and n is the layer being photographed, d the length of the rotation axis and λ the wavelength of the x-rays.

In order to place these eight layers on the same scale, five other zones, hk0 to hk4, were photographed on a precession camera, a series of six or more photographs being taken of each layer with a 3 : 1 time ratio between the exposure of each. These intensities were also estimated visually and corrected for the Lorentz and polarisation factors by using the Waser and the Grenville - Wells and Abrahams (1952) charts. The ratio of the strongest to the weakest intensity (taken as unity) was 8,800 in hk0; 37,200 in hk1; 8,800 in hk2; 3,645 in hk3 and 3,000 in hk4. In the other layers the ratio was 37,950 in h0ℓ; 22,300 in h1ℓ; 3,905 in h2ℓ; 646 in h3ℓ; 374 in h4ℓ; 315 in h5ℓ; 92 in h6ℓ and 4 in h7ℓ. The 351 common reflections were then used to place the resulting structure factors on the same scale; in all 1,706 structure factors were determined and are listed in Appendix 1(a).

Standard deviation.

Since 351 of the reflections have been estimated twice, it was possible to obtain some indication of the accuracy of the structure factors. The method used for this was the one suggested by Abrahams (1955) based on the formula of Whittaker and Robinson (1944), viz.

$$\sigma(F_i) = \left\{ \sum_{i} (\bar{F} - F_i)^2 \div (n - 1) \right\}^{\frac{1}{2}}$$

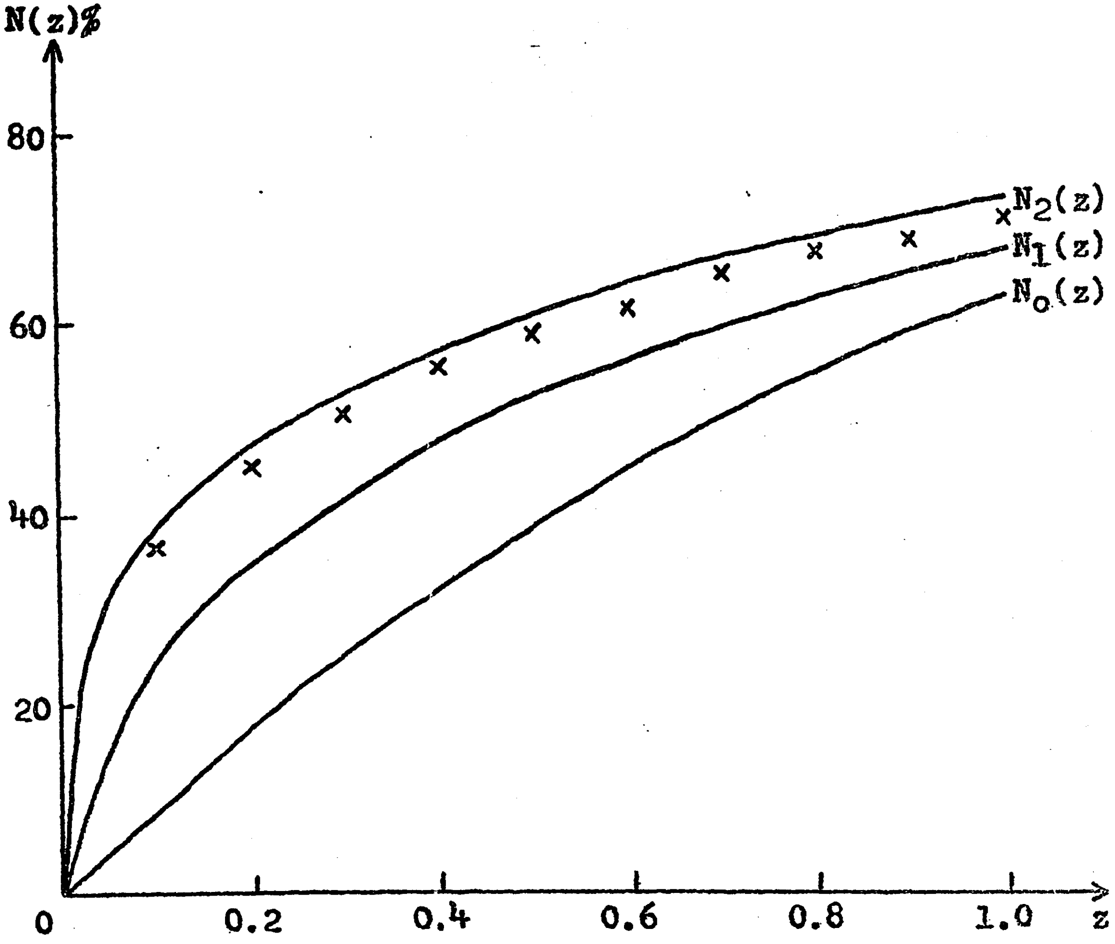


Fig. 3. N(z) test for 4-4'-dichlorodiphenyl sulphone: the crosses indicate the experimental data.

where $\bar{F} = \sum_i F_i/n$.

This clearly holds for n large, but although in this case n = 2 the results may be somewhat ambiguous, $\sigma(F)$ was evaluated for each of the 351 F(hkℓ)'s. When this had been done it was found that the standard deviation of each was very nearly a constant percentage of the magnitude of the structure factor with

$$\sigma(F_i) \approx 0.092|F_i|.$$

Test for centro - symmetry.

The 1,706 structure factors were divided into five ranges of $\sin^2\theta$ and the test of Howells, Phillips and Rogers (1950) was applied. This gave the following figures

z	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
N(z)%	36.1	44.8	50.2	55.4	58.8	61.7	65.2	67.2	68.4	70.9

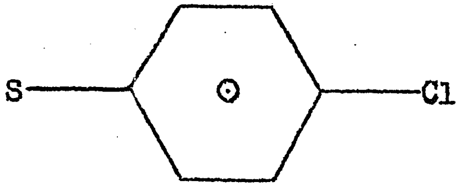
which are shown graphically in Fig.3. Also shown in the figure are three curves

(i) non - centred $N_0(z) = 1 - \exp(-z)$

(ii) centred $N_1(z) = \mathrm{erf}(\frac{1}{2}z)^{\frac{1}{2}}$

(iii) the 'hyper - centred' curve of Rogers and Wilson (1953) $N_2(z) = 2/\pi \int_0^{\pi/2} \mathrm{erf}(\frac{1}{2}z^{\frac{1}{2}}.\sec\psi).d\psi.$

The experimental curve is seen to lie between curves (ii) and (iii) which confirms that the space group is in fact the centred one C_{2h}^{6} - $I2/a$. The justification for the curve lying so near the hypercentred curve (iii) can be based on the structure of the molecule as indicated in the diagram



The benzene ring has a centre of symmetry and the sulphur and chlorine atoms have almost the same atomic number (S = 16, Cl = 17); in this way each sulphone molecule can be seen to have two approximate centres of symmetry which cannot coincide with any of the crystallographic centres of symmetry.

2.3 Analysis of the structure.

In the space group $I2/a$ the general position is eight fold and since there are four molecules in the unit cell the sulphur atoms must lie on special positions; this demands that the molecular symmetry is C_2 or $\bar{1}$. The known bonding arrangements in sulphone groups (Abrahams, 1956) eliminate the latter possibility and require the sulphur atom to have coordinates

$$(\tfrac{1}{4},y,0),\ (\tfrac{3}{4},\tfrac{1}{2}+y,\tfrac{1}{2}),\ (\tfrac{3}{4},\bar{y},0)\text{ and }(\tfrac{1}{4},\tfrac{1}{2}-y,\tfrac{1}{2}).$$

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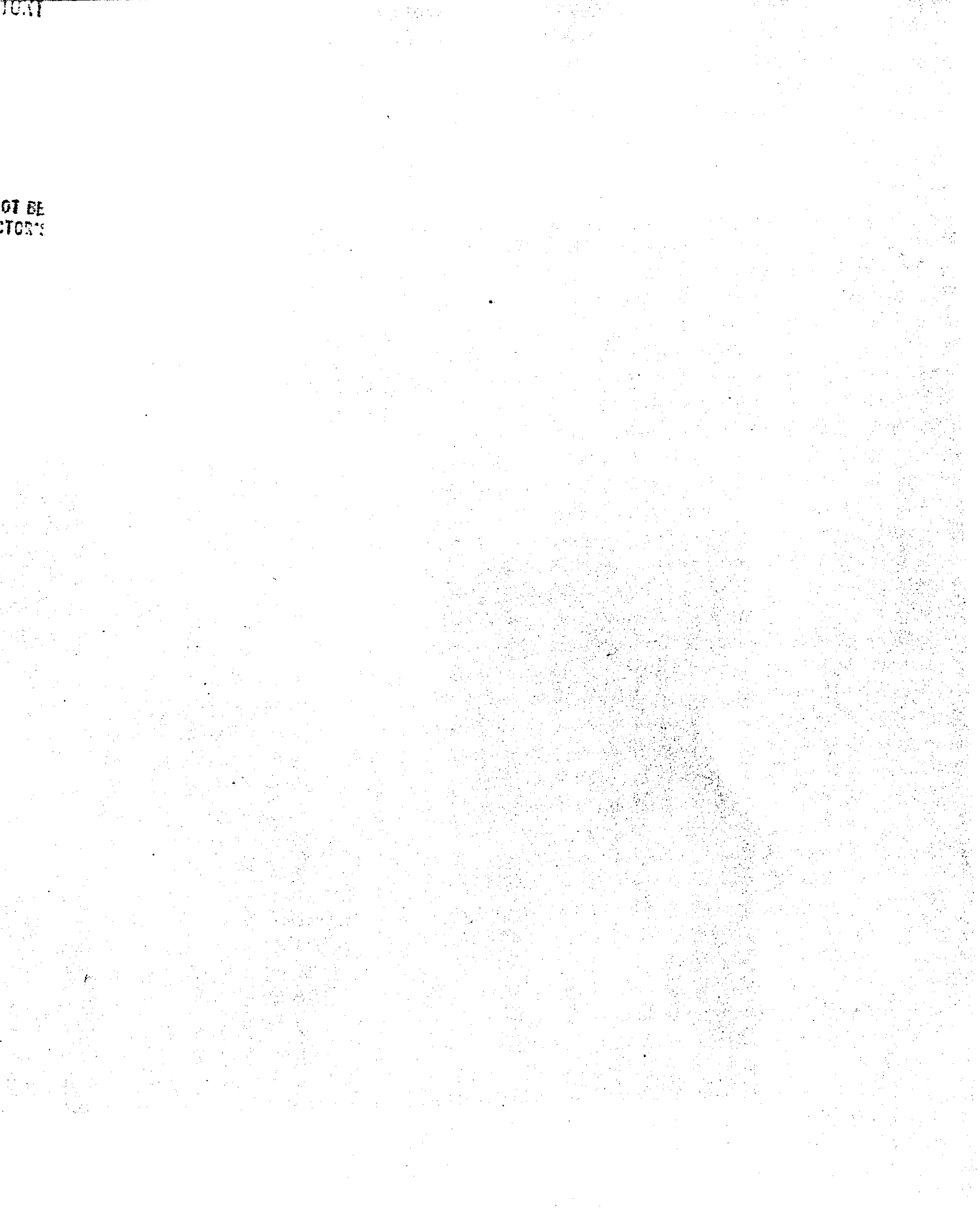

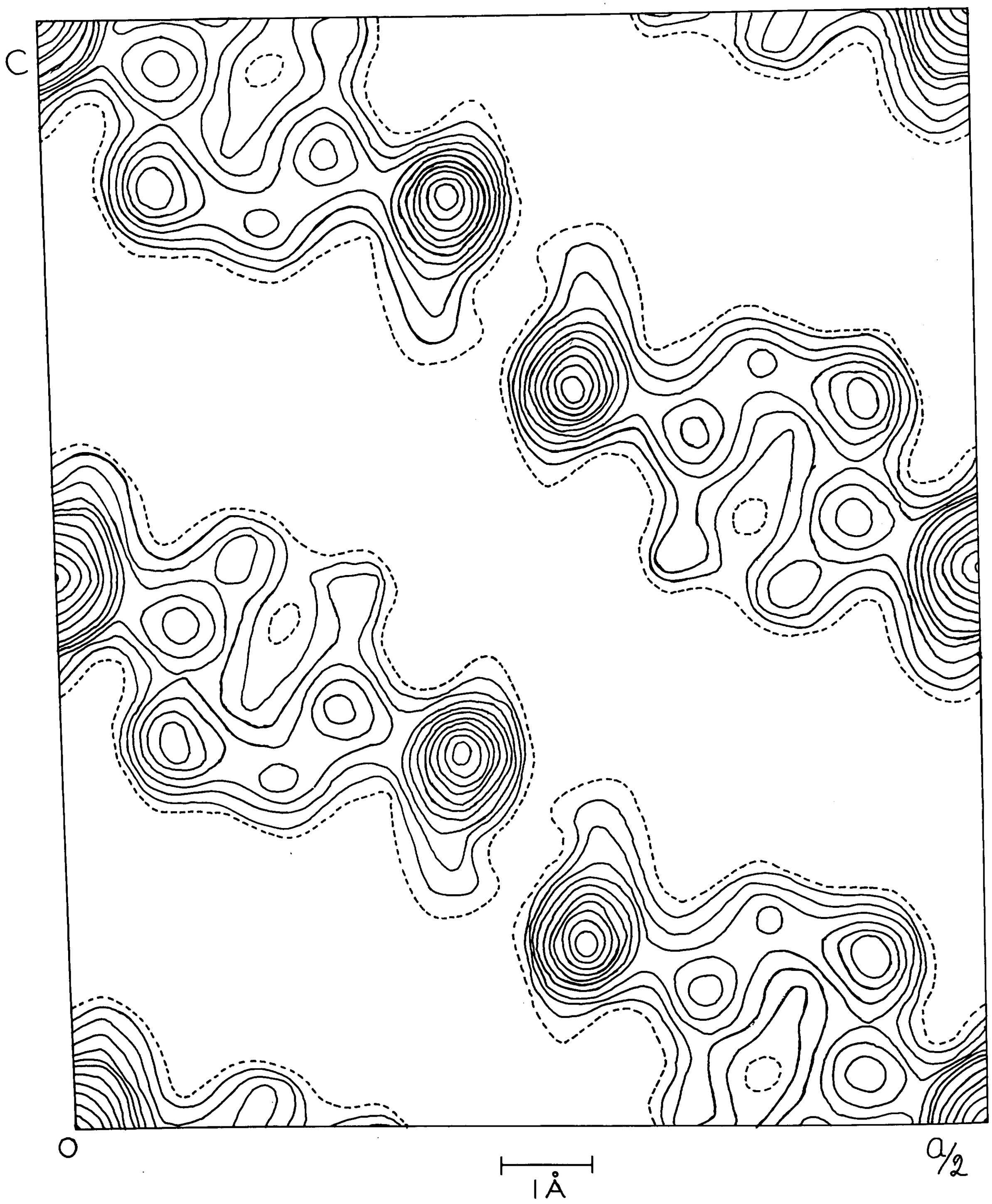

Fig. 4. 4-4'-dichlorodiphenyl sulphone. h0l Patterson map.

The 160 $(h0l)$ reflections measured using Cu K_α radiation were used to compute the Patterson projection along the b- axis (Fig.4); in this projection the x- and z- coordinates of the chlorine and carbon atoms are immediately apparent. The coordinates of the oxygen atom were obtained by assuming the S - O bond length to be 1.43A and the O - S - O' bond angle to be 120°. A graph of $\ln\langle F^2\rangle/\langle f^2\rangle$ against $(\sin\theta/\lambda)^2$ indicated an overall value of the isotropic temperature factor B, in the expression $\exp(-B.\sin^2\theta/\lambda^2)$, of $3.76A^2$ (Wilson,1942). By using these parameters, together with the atomic form factors of Mc.Weeny (1951) for carbon and oxygen and of James and Brindley (1931) for sulphur and chlorine, to calculate structure factors, an agreement factor

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

of 0.43 was obtained.

Refinement of this projection was effected by making use of the difference Fourier syntheis method which clearly indicated large anisotropic thermal vibrations of the chlorine and sulphur atoms. The expression used to allow for this was $\exp\left\{-s^2\left[L + M.\cos^2(\omega - \beta)\right]\right\}$ where $L = \frac{1}{4}B(\text{min.})$, $M = \frac{1}{4}(B(\text{max.}) - B(\text{min.}))$, $s = \sin\theta/\lambda$, $\omega = \tan^{-1}(l/h)$ and β = angle between the direction of

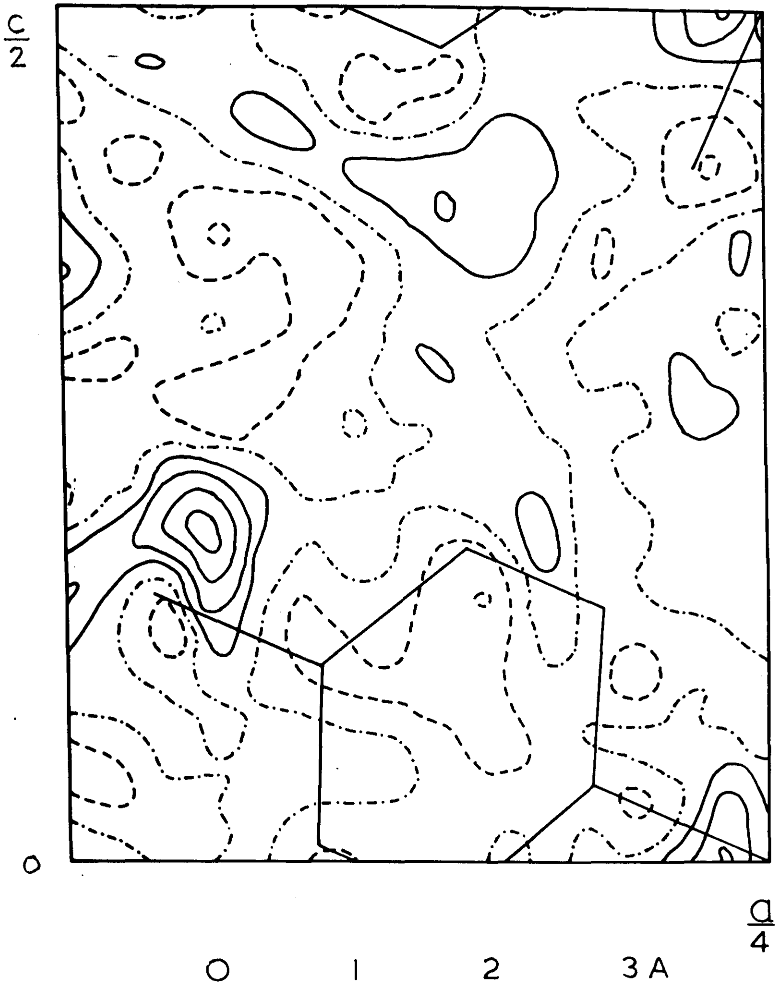

Fig. 5. h0l difference map. Contours at 0.5 e/A^2 intervals; the dashed contours represent negative - the dot-dash zero.

maximum vibration and the a- axis (Cochran,1951). After four difference syntheses,the structure factors obtained with Mo K_{α} radiation being introduced after the first,

B(max.) for chlorine = 6.40 for sulphur = 6.00
B(min.) for chlorine = 3.80 for sulphur = 3.00

and $\beta = 65^{\circ}50'$; the original isotropic B being used unchanged for the carbon and oxygen atoms. The value of R at this stage was 0.185, the last of these difference maps is shown in Fig.5. This map shows that some shifts in atomic coordinates were still required particularly for the chlorine atom. Temperature factor changes for oxygen and sulphur are also indicated. The changes to the temperature factors were not made but the atomic coordinates were adjusted and the final values from this map are given in Table 3.

To obtain values for the y - coordinates of the atoms, the values of y for all the atoms relative to y(sulphur) taken as zero were calculated by assuming the following bond lengths

S - O = 1.43A C - C (aromatic) = 1.40A
S - C = 1.85 C - Cl = 1.75.

A Patterson projection along the c- axis was then computed using a sharpening function such that

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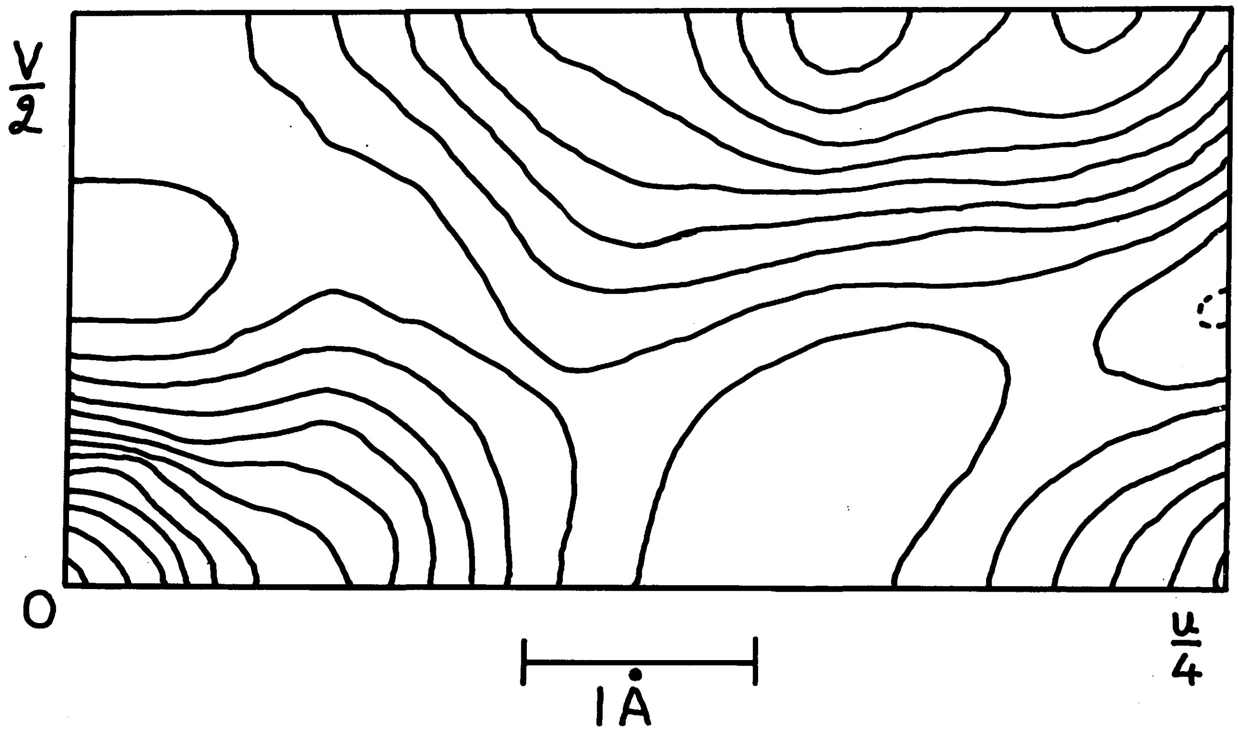

Fig. 6. 4-4'-dichlorodiphenyl sulphone. hk0 Patterson map.

Zero contour shown dotted.

$$|F(\mathrm{mod})|^2 = M(s).|F(hk0)|^2$$

where $$M(s) = (1/\hat{f})^2 \exp(-\pi^2 s^2/p)$$

where $\hat{f}$ is the scattering factor per electron, $s = 2\sin\theta/\lambda$ and p is a constant, here equal to 7.25 (Lipson and Cochran, 1953). The resulting map, Fig.6, showed so little resolution that it was not possible to recognise the Cl - Cl or any other vector with any certainty. Because of this the true y- coordinates were found by calculating structure factors for the 020, 040, 060 and 310 planes with values of y(sulphur) ranging from 0 to 0.25 at intervals of 0.05 and then drawing a graph of $F_{calc.}$ against y(sulphur) for the four planes. Only values of y(sulphur) from 0 to $\frac{1}{4}$ were considered as values of y(sulphur) from $\frac{1}{4}$ to $\frac{1}{2}$ are related to these by the glide plane at $y = \frac{1}{4}$, and values from $\frac{1}{2}$ to 1 correspond to a shift of the origin from $y = 0$ to $y = \frac{1}{2}$, these being equivalent to each other apart from a possible change of sign. From the graphs the value of y(sulphur) giving the best agreement between the F_{obs} and F_{calc} values was chosen and hence the y- coordinates for all of the atoms determined; this value of y(sulphur) was 0.135. Using these coordinates the complete set of (hk0) structure factors was calculated and the R - factor found to be 0.43.

One Fourier projection along the c- axis showed that the high amount of overlap would considerably hinder the refinement. Using the x- coordinates from the (h0ℓ) projection the best y- coordinates were obtained and a second set of structure factors calculated; these gave R = 0.344. As a result of the overlap in this projection no further two dimensional analysis was carried out; the second set of y- coordinates are listed in Table 3 along with the final two dimensional x- and z- coordinates.

Table 3.

Final two-dimensional positional coordinates.

Atom	x	y	z
Cl	0.0319	0.946	0.1592
S	0.25	0.135	0
O	0.2250	0.000	-0.0949
C_1	0.1870	0.368	0.0458
C_2	0.1362	0.505	-0.0245
C_3	0.0884	0.697	0.0106
C_4	0.0903	0.726	0.1162
C_5	0.1433	0.583	0.1845
C_6	0.1917	0.399	0.1497.

2.4 Three - dimensional refinement.

The method used to refine the structure fully was that of least squares. This was carried out in two stages, initially using an IBM 704 computer and finally the ORACLE.

2.4(a) IBM 704 refinement.

For the work on the IBM 704 computer the NY XR2 program was used. This program uses the diagonal approximation method referred to at the end of 1.7 of Part I, the temperature factors, as well as the coordinates, are refined but only isotropically. The refinement was carried out using 1,071 observed and 475 unobserved structure factors giving 1,546 conditional equations, the unobserved terms being used at one-half their maximum value. The weighting system used was that suggested by Abrahams (1955), viz. $w(hk\ell) \propto 10{,}000/|F_m^2(hk\ell)|$ with $w(\max) = 25$ for $|F_m(hk\ell)| \leqslant 20$; unobserved terms having a weight of unity. The atomic form factors used were those of Berghuis et al (1955) for carbon and oxygen and of Viervoll and Ögrim (1949) for sulphur and chlorine. The initial parameters used were those from the final two - dimensional work as listed in Table 3; the temperature parameters used were the original ones for oxygen and carbon. For chlorine and sulphur the anisotropic values were replaced by the isotropic values $B = 5.00A^2$ for chlorine and $4.30A^2$ for sulphur. The first set of structure factors had an R' factor of 0.446 and a value of $\Sigma w\Delta^2$ of 1,373,060. The R' factor differs from the normal agreement factor, R, in the treatment of the unobserved terms; in R' the unobserved terms are taken as one - half their maximum value and in consequence

$$R' = R + 0.03.$$

After three least squares iterations in which only the x_i, y_i and z_i and scale factor varied the value of R' had fallen to 0.341 and of $\Sigma w\Delta^2$ to 700,940. In the following two cycles the individual values of B_i were also allowed to vary and in the next two cycles the contributions from the hydrogen atoms were included although these atomic parameters were not allowed to vary. The positions of the hydrogen atoms for this were determined by assuming that the atoms lie on the extended lines $C_2 - C_5$ and $C_3 - C_6$ with C - H = 1.08A. At this stage the value of R' was 0.269 and of $\Sigma w\Delta^2$, 465,666; the complete details of the course of this refinement are given in Table 4. The rather constant values of R' and $\Sigma w\Delta^2$ in the final cycles suggest that refinement of the

Table 4.

Course of refinement using NY XR2 program.

	R'	$\Sigma w\Delta^2$
Parameters obtained from 2D - refinement	0.446	1,373,060
1st cycle: $x_i y_i z_i$ variable B_i constant	0.397	988,090
2nd cycle: do.	0.360	804,880
3rd cycle: do.	0.341	700,940
4th cycle: $x_i y_i z_i$ and B_i variable	0.306	545,070
5th cycle: do.	0.293	462,310
6th cycle: do. (hydrogen atoms included in structure factors but not varied)	0.273	522,667
7th cycle: do.	0.269	465,666

structure is probably as complete as this program will permit. Comparison of the coordinate shifts ($\Delta\xi$) with the corresponding standard deviations ($\sigma\xi$), Table 5, reveals that some of the parameters, particularly the thermal ones, still have significant shifts. It was therefore decided that for any further useful refinement to be obtained the anisotropy of the thermal vibrations would have to be considered. The final parameters from

Table 5.

Comparison of coordinate shifts and corresponding standard deviations from 7th NY XR2 least squares cycle (x 10^3)

	Δx	σx	Δy	σy	Δz	σz	ΔB	σB
Cl	0.05	0.20	0.10	0.92	0.19	0.32	0.319	0.08
S	0	0	-0.05	0.85	0	0	-0.023	0.07
O	-0.17	0.39	0.23	1.77	-0.58	0.66	0.192	0.15
C_1	0.16	0.48	0.80	2.00	0.71	0.79	0.104	0.16
C_2	0.28	0.48	1.27	2.00	0.25	0.79	0.106	0.16
C_3	0.04	0.48	-0.63	2.00	0.92	0.79	0.173	0.16
C_4	0.37	0.48	0.66	2.00	1.71	0.79	0.298	0.16
C_5	0.27	0.48	-0.68	2.00	0.91	0.79	0.295	0.16
C_6	0.03	0.48	1.27	2.00	0.83	0.79	0.105	0.16.

the NY XR2 program are given in Table 6 and Fourier projections along the b- and c- axes drawn out at this stage are shown in Figs. 7 and 8 resp..

2.4(b) ORACLE refinement.

The final least squares refinement of this compound was carried out using the comprehensive least squares program written by Dr.H.A.Levy and Dr.W.R.Busing for the ORACLE computer. In this program the anisotropic temperature factors are treated in the form

Table 6.

Coordinates from NY XR2 refinement.

Atom.	x	y	z	B.
Cl	.0328	.9380	.1621	6.96
S	.25	.1549	0	3.94
O	.2247	.0127	-.0940	4.95
C_1	.1871	.3726	.0449	3.69
C_2	.1357	.4337	-.0261	4.73
C_3	.0867	.6058	.0087	5.39
C_4	.0932	.7154	.1168	5.50
C_5	.1439	.6433	.1873	5.09
C_6	.1901	.4738	.1490	4.38
H_2'	.1320	.3472	-.1049	4.60
H_3'	.0476	.6615	-.0454	4.60
H_5'	.1466	.7085	.2629	4.60
H_6'	.2289	.4209	.1993	4.60

' these parameters were not refined.

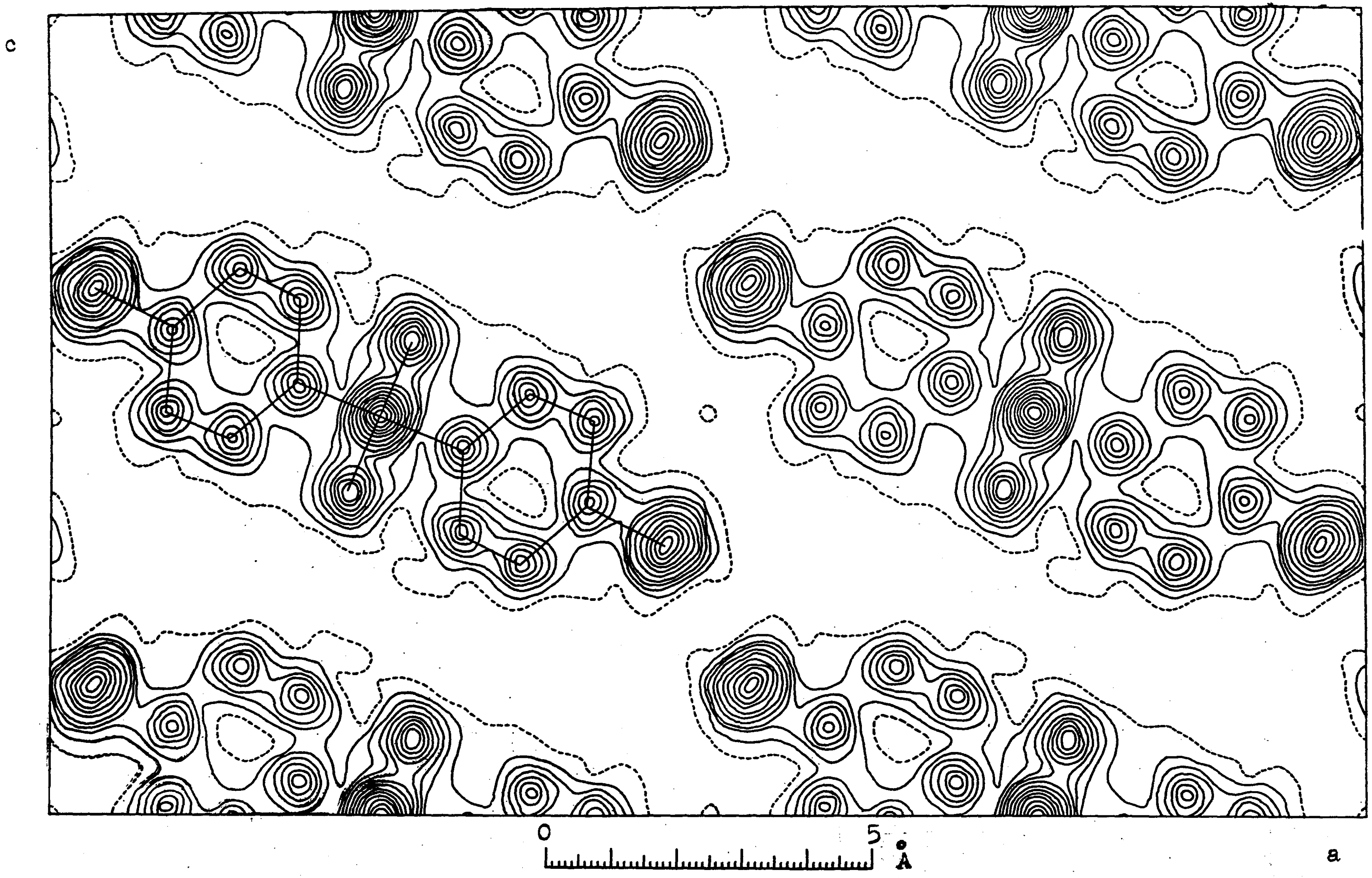

Fig.7. 4-4'-dichlorodiphenyl sulphone. h01 Fourier map.
Contour intervals as in Fig. 8.

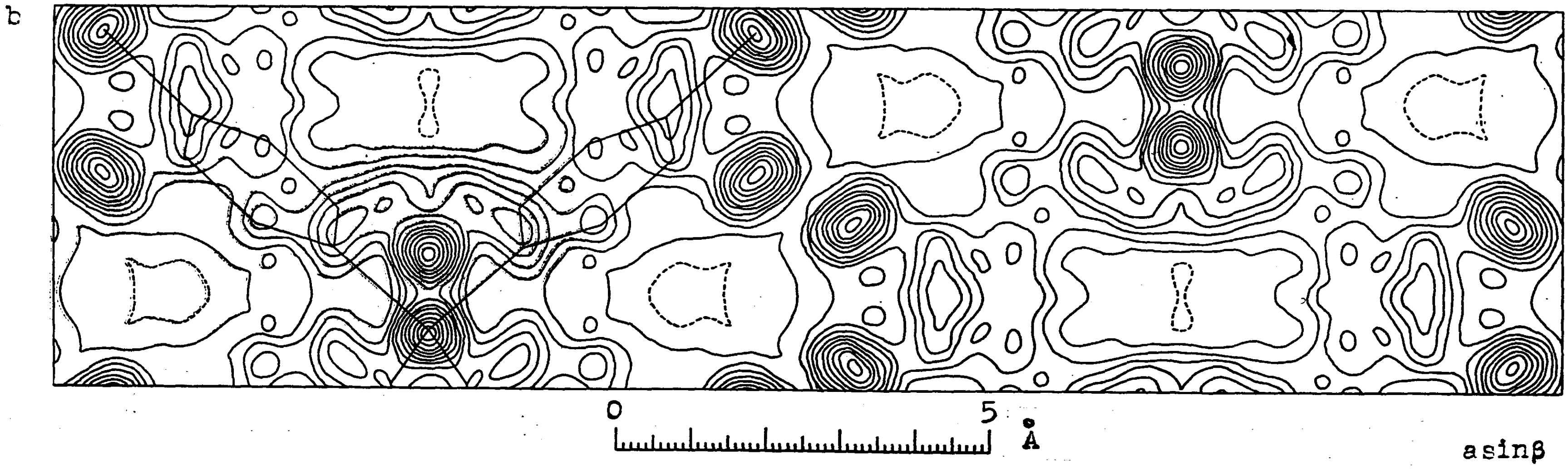

Fig. 8. 4-4'-dichlorodiphenyl sulphone. hk0 Fourier map.

Contour interval 1 e/A^2 to 4 e/A^2 and then at 2 e/A^2 intervals.

Zero contour dashed.

$\exp -(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}\ell^2 + 2\beta_{12}hk + 2\beta_{23}k\ell + 2\beta_{31}\ell h)$ and in the least squares process the complete set of normal equations, including off - diagonal terms, is solved.

For the general positions in the space group $I_{2/a}$ all the symmetry related atoms have the same values of the coefficients β_{ij} except for a sign change in β_{12} and β_{23} for atoms related by the glide plane or two - fold axis. Consequently, for the sulphur atom which lies on a special position, $\beta_{12} = \beta_{23} = 0$ (Levy,1956). The atomic form factors used for this refinement were the same as before for oxygen and carbon, but for sulphur those of Tomiie and Stam (1958) were used. For chlorine a modified Berghuis et al (1955) curve was used with f_{Cl^-} replacing f_{Cl} at values of $\sin\theta/\lambda \geqslant 0.2$. The weighting system was the same as for the NY XR2 refinement except that the unobserved terms (again taken as one - half their maximum value) were now assigned a weight of 25. The contribution of the hydrogen atoms was included in the structure factors, the coordinates being Bacon's (1957) x- and z- coordinates together with the y- coordinates obtained by solving for these with the equation of the benzene ring plane determined from the coordinates from the 7th NY XR2 cycle (Table 6). The values of these coordinates are given in Table 7 together with Bacon's isotropic values of B.

Table 7.

Initial hydrogen atom coordinates (Bacon,1957).

Atom.	x	y	z	B.
H_2	.1375	.3452	.8944	6.1
H_3	.0447	.6703	.9558	6.9
H_5	.1489	.7183	.2708	6.9
H_6	.2319	.4152	.2044	6.1

The ORACLE is able to solve a determinant of order not exceeding 48. For this refinement we have 25 positional, 52 thermal and 1 scaling parameters which requires the solution of a 78th order determinant. This was accomplished by solving two, overlapping, parts; all of the parameters for any atom being kept as a group and in general the nearest neighbours being included in each cycle. The total number of terms used was increased to 1,706 of which 1,158 were observed structure factors. A further requirement placed on each term rejected it from inclusion as an observational equation if $3.F_{calc} < F_{meas}$; these terms are indicated by a dagger in Appendix 1(a).

The structure factors based on the coordinates from the 7th NY XR2 cycle contained 141 such terms and those based on the final ORACLE coordinates contained 126; of these 76 refer to unobserved terms and need not have been rejected.

In all, six least squares iterations were carried out, the final value of R' being 0.1414 and of $\Sigma w\Delta^2$, 107,481. After the second cycle the hydrogen atom coordinates were replaced by new values based on C - H = 1.08A and such that they were on the extended lines C_2 - C_5 and C_3 - C_6. These values are given in Table 8.

Table 8.

Atom.	x	y	z
H_2	.1321	.3557	.8943
H_3	.0473	.6646	.9568
H_5	.1463	.7257	.2685
H_6	.2310	.4210	.2042

After the fourth cycle no significant changes in R' or $\Sigma w\Delta^2$ occurred, the final two cycles being carried out to ensure complete convergence; more significantly, in the final cycles no value of $\Delta\xi_i$ was greater than the corresponding $\sigma\xi_i$. The variations of R' and $\Sigma w\Delta^2$ during the ORACLE refinement are shown in Table 9.

Table 10.

Final atomic coordinates for 4-4'-dichlorodiphenyl sulphone.

Atom.	x	y	z
Cl	0.0327	0.9381	0.1621
S	0.25	0.1546	0
O	0.2244	0.0126	-0.0927
C_1	0.1868	0.3696	0.0456
C_2	0.1352	0.4367	-0.0240
C_3	0.0877	0.6117	0.0112
C_4	0.0926	0.7173	0.1164
C_5	0.1431	0.6448	0.1867
C_6	0.1910	0.4743	0.1503

Atom.	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl	0.00454	0.07857	0.01700	0.00883	0.00281	0.01043
S	0.00312	0.03686	0.00755	0	-0.00025	0
O	0.00403	0.04319	0.00926	-0.00275	-0.00045	-0.00551
C_1	0.00281	0.03571	0.00762	-0.00069	-0.00047	0.00373
C_2	0.00272	0.05968	0.00808	-0.00053	-0.00048	0.00333
C_3	0.00296	0.07263	0.01019	0.00207	-0.00011	0.00680
C_4	0.00297	0.05671	0.01165	0.00190	0.00143	0.00785
C_5	0.00347	0.06119	0.00922	0.00313	-0.00011	0.00051
C_6	0.00331	0.04502	0.00773	0.00192	-0.00006	0.00073

Table 9.

Course of refinement using ORACLE program.

	R'	$\Sigma w\Delta^2$
Final NY XR2 coordinates	0.2562	406,987
1st cycle: all parameters variable	0.1759	183,484
2nd: do.	0.1467	116,892
3rd: do.	0.1419	109,379
4th: do.	0.1415	107,434
5th: do.	0.1415	107,548
6th: do.	0.1414	107,481.

The final values of the atomic positional and thermal parameters are listed in Table 10. These correspond to a value of R = 0.108 if, for the unobserved terms F_{meas} is taken as its maximum value, ie. twice the asterisked value in Appendix 1(a), and $|F_{meas}| - |F_{calc}| = 0$ if this value of $|F_{meas}|$ is greater than $|F_{calc}|$. The actual calculated values of the structure factors are listed in Appendix 1(a).

A plot of $\Delta = |F_{meas}| - |F_{calc}|$ against $|F_{meas}|$ was made. These point were fairly widely distributed but for values of F_{meas} between about 10.0 and 80.0, it was found that $\Delta \approx 0.104|F_{meas}|$ which is comparable with $\sigma(F) \approx 0.092|F|$ as found earlier although no significance is attached to this because of the fairly wide spread of the Δ values.

The standard deviations of the atomic coordinates in Table 10 are given in Table 11.

Table 11.

Standard deviations in the final positional coordinates (all x10^3)

Atom.	x	y	z
Cl	0.10	0.43	0.18
S	0	0.35	0
O	0.20	0.76	0.32
C_1	0.24	0.91	0.38
C_2	0.26	1.23	0.43
C_3	0.29	1.42	0.51
C_4	0.28	1.23	0.53
C_5	0.29	1.31	0.49
C_6	0.27	1.08	0.42.

These have been obtained from the variance - covariance matrix derived from the least squares process; the standard deviation in a function f is given by

$$\left[\sum_i \sum_j \left(\frac{\partial f}{\partial p_i}\right)\left(\frac{\partial f}{\partial q_j}\right) C_{ij} \quad + \quad \sum_i \left(\frac{\partial f}{\partial q_i}\right)^2 \sigma_i^2\right]^{\frac{1}{2}}$$

where p_i, p_j are the least squares parameters, C_{ij} is the corresponding variance - covariance matrix element, q_i are the cell parameters and σ_i their standard deviations.

2.4(c) Comparison of the two refinements.

During the course of the IBM 704 refinement the value of R' fell from 0.446 to 0.269 and of $\Sigma w\Delta^2$ from 1,373,060 to 465,666; ie. $\Sigma w\Delta^2$ has been reduced by a factor of 1/2.95. At this stage the refinement was almost complete as can be seen by examining Tables 4 and 5: only for 9 of the 34 parameters being refined does $\Delta\xi$ exceed $\sigma\xi$ (these values have been underlined in Table 5).

In the ORACLE program where the full 78th order matrix was solved, the value of R' fell to 0.1414 and $\Sigma w\Delta^2$ to 107,481; ie. a further reduction in $\Sigma w\Delta^2$ by a factor of 1/4.33. It is clear then, that considerable improvement has been achieved by using the complete determinant and by allowing for anisotropy in the thermal parameters instead of using the diagonal approximation with isotropic thermal parameters.

A comparison of the results of the two methods is given in three tables. In Table 12 the values of

$$\frac{\xi(\text{ORACLE}) \; - \; \xi(\text{NY XR2})}{\sigma\,\xi(\text{ORACLE})}$$

are given. If the value given is less than unity then no significant improvement in this coordinate has been achieved; if, however, the value is greater than unity then the change in this coordinate is greater than its standard deviation and it can be considered significant.

Table 12.

Ratio of ξ(ORACLE) - ξ(NY XR2) to $\sigma\xi$(ORACLE).

Atom.	x	y	z
Cl	1.0	0.3	0
S	0	0.8	0
O	1.5	0.3	2.6
C_1	1.1	2.5	1.5
C_2	1.8	2.4	4.5
C_3	3.7	4.8	5.4
C_4	2.2	1.5	0.9
C_5	2.9	1.2	1.3
C_6	3.3	0.4	2.6.

Only eight of the twenty - seven values given in the table are less than unity.

In Table 13 the values of the isotropic values B_i

Table 14.

Comparison of bond lengths obtained from the NY XR2 and ORACLE programs.

Bond.	NY XR2.	ORACLE.
Cl - C_4	1.731A	1.736A
$C_1 - C_2$	1.389	1.382
$C_2 - C_3$	1.380	1.373
$C_3 - C_4$	1.436	1.395
$C_4 - C_5$	1.400	1.378
$C_5 - C_6$	1.345	1.367
$C_6 - C_1$	1.371	1.386
C - C(mean)	1.387	1.380
C_1 - S	1.762	1.765
S - O	1.446	1.432.

from the NY XR2 program are compared with the B_{ij} values from the ORACLE program. The relationship between the B_{ij}'s in the table and the β_{ij}'s obtained by ORACLE are

$B_{11} = 4\beta_{11}/(a^*)^2$; $B_{22} = 4\beta_{22}/(b^*)^2$; $B_{33} = 4\beta_{33}/(c^*)^2$;
$B_{12} = 4\beta_{12}/a^*.b^*$; $B_{23} = 4\beta_{23}/b^*.c^*$; $B_{31} = 4\beta_{31}/c^*.a^*$.

Table 13.

Comparison of NY XR2 B_i and ORACLE B_{ij}.

Atom.	B_i	B_{11}	B_{22}	B_{33}	B_{ii}	B_{12}	B_{23}	B_{31}
Cl	6.96	7.41	7.89	10.19	8.50	3.57	2.56	2.78
S	3.94	5.09	3.70	4.53	4.44	0	0	-0.24
O	4.95	6.58	4.33	5.55	5.49	-1.11	-1.35	-0.44
C_1	3.69	4.58	3.58	4.56	4.24	-0.28	0.91	-0.46
C_2	4.73	4.44	5.99	4.84	5.09	-0.21	0.81	-0.47
C_3	5.39	4.83	7.29	6.11	6.08	0.84	1.67	-0.10
C_4	5.50	4.84	5.69	6.98	5.84	0.77	1.92	1.42
C_5	5.09	5.66	6.14	5.52	5.77	1.26	0.12	-0.10
C_6	4.38	5.41	4.52	4.63	4.85	0.77	0.18	-0.06.

Note. $B_{ii} = (B_{11} + B_{22} + B_{33})/3$.

These values illustrate the very marked anisotropic vibration of the atoms.

In Table 14 the bond lengths obtained from the two refinement programs are compared.

Table 15.

Molecular Dimensions.

$C_1 - C_2 = 1.382 \pm 0.007\text{A}$

$C_2 - C_3 = 1.373 \pm 0.009$

$C_3 - C_4 = 1.395 \pm 0.009$

$C_4 - C_5 = 1.378 \pm 0.009$

$C_5 - C_6 = 1.367 \pm 0.008$

$C_6 - C_1 = 1.386 \pm 0.007$

$C_2 - C_6' = 3.854 \pm 0.011$

$Cl - C_4 = 1.736 \pm 0.007$

$S - C_1 = 1.765 \pm 0.006$

$S - O = 1.432 \pm 0.005$

$C_6 - C_1 - C_2 = 121.1 \pm 0.52^\circ$

$C_1 - C_2 - C_3 = 119.2 \pm 0.53$

$C_2 - C_3 - C_4 = 119.2 \pm 0.55$

$C_3 - C_4 - C_5 = 121.8 \pm 0.54$

$C_4 - C_5 - C_6 = 118.9 \pm 0.56$

$C_5 - C_6 - C_1 = 120.1 \pm 0.52$

$C_3 - C_4 - Cl = 119.7 \pm 0.49$

$C_5 - C_4 - Cl = 118.7 \pm 0.52$

$S - C_1 - C_2 = 119.8 \pm 0.47$

$S - C_1 - C_6 = 119.1 \pm 0.40$

$C_1 - S - O = 107.3 \pm 0.29$

$C_1' - S - O = 108.0 \pm 0.28$

$C_1 - S - C_1' = 104.8 \pm 0.40$

$Cl - S - Cl = 101.8 \pm 0.25$

$O - S - O = 120.4 \pm 0.42.$

2.5 Molecular Geometry.

The coordinates given in Table 10 were used to calculate the bond lengths and angles given in Table 15. The mean of the aromatic carbon - carbon bond lengths is 1.380 ± 0.003A and the sum of the internal angles of the benzene ring is 719.9 ± 0.4°. The shortest contact between the two benzene rings is C_2 - C_6' which is 3.854 ± 0.011A. The intermolecular distances less than 4A are given in Table 16; these were obtained by an exhaustive program written by Dr. Busing for the ORACLE.

Table 16.

Intermolecular distances less than 4A.

$C_6 \ldots O = 3.211 \pm 0.009$A
$C_5 \ldots O = 3.243 \pm 0.010$
$C_6 \ldots O = 3.272 \pm 0.011$
$C_5 \ldots O = 3.455 \pm 0.010$
$C_2 \ldots O = 3.508 \pm 0.012$
$C_3 \ldots O = 3.654 \pm 0.010$
$C_1 \ldots O = 3.721 \pm 0.013$A
$C_1 \ldots O = 3.729 \pm 0.013$
$C_4 \ldots O = 3.996 \pm 0.011$
$C_4 \ldots Cl = 3.981 \pm 0.010$
$C_2 \ldots Cl = 3.976 \pm 0.010$
$Cl \ldots Cl = 3.564 \pm 0.009$.

Three of the carbon - oxygen contacts, 3.211, 3.243 and 3.272A are shorter than the sum of the accepted van der Waal's radii, viz. 3.3A, the remainder are all longer than this value. The Cl ... Cl distance of 3.564 ± 0.009A

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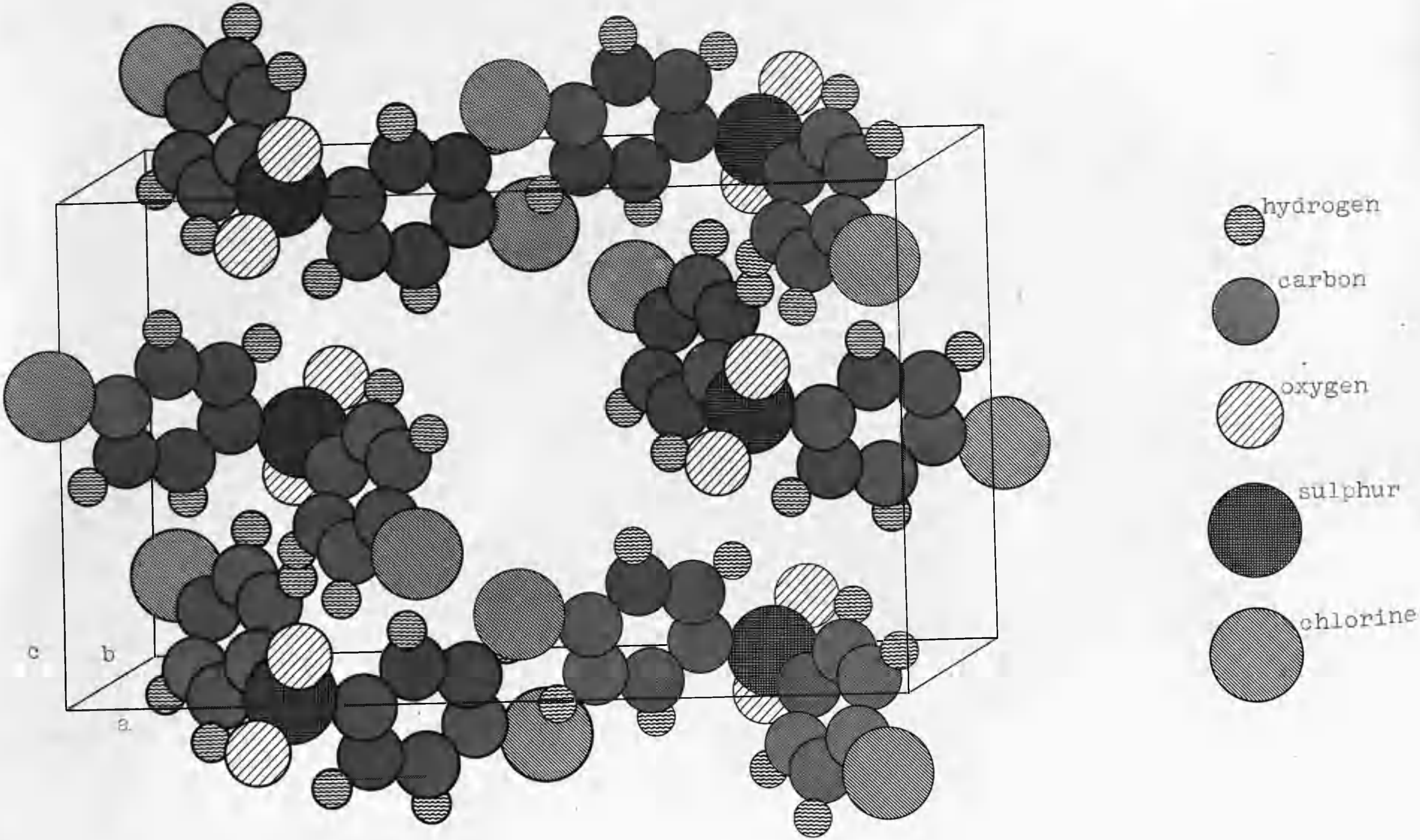

[illegible] Clinometric view of 4-4'-dichlorodiphenyl sulphone.

agrees with the van der Waal's $Cl \ldots Cl$ distance of 3.60A.

A general view of the whole structure is given in Figure 9; it consists of columns of molecules stacked along the two - fold axes, the alternate columns 'pointing' in opposite directions.

After transforming the coordinates to orthogonal axes defined by

$$x' = x + z.\cos\beta$$
$$y' = y$$
$$z' = z.\sin\beta$$

the least squares plane of the benzene ring, the sulphur and the chlorine atoms was determined. In forming the equation of this plane the sulphur and chlorine atoms were given three times the weight of the carbon atoms since the standard deviations of their coordinates is about one - third of that of the carbon atoms. The equation of this plane, determined on the DEUCE computer (see Appendix 2) is

$$x' + 1.4422y' - 0.6327z' - 6.1304 = 0 \quad \ldots\ldots \text{(a)}$$

The least squares derived equation of the plane of the carbon atoms alone is

$$x' + 1.4208y' - 0.6327z' - 6.0373 = 0 \quad \ldots\ldots \text{(b)}$$

The distances of the atoms from these planes are given in Table 17. None of the carbon atoms lies significantly

Table 17.

Out-of-plane distances.

Atom.	Distance from plane 'a'	Distance from plane 'b'
S	0.0200 ± 0.0018A	0.0616 ± 0.0018 A
Cℓ	0.0160 ± 0.0020	0.0123 ± 0.0020
C_1	-0.0244 ± 0.0047	0.0043 ± 0.0047
C_2	-0.0295 ± 0.0055	-0.0079 ± 0.0055
C_3	-0.0150 ± 0.0065	-0.0002 ± 0.0065
C_4	0.0028 ± 0.0062	0.0117 ± 0.0062
C_5	-0.0279 ± 0.0062	-0.0150 ± 0.0062
C_6	-0.0157 ± 0.0055	0.0070 ± 0.0055.

out of plane 'b' but three of them, C_1, C_2 and C_5 lie out of plane 'a'. The sulphur atom is very significantly out of plane 'b' and both the sulphur and chlorine atoms are further from plane 'a' than might have been expected.

The following angles have also been calculated -

Plane a / Plane a' = 79.5 ± 0.3°
Plane b / Plane b' = 78.7 ± 0.3
Plane a / Cℓ.S.Cℓ' = 84.6 ± 0.3
Plane b / Cℓ.S.Cℓ' = 84.4 ± 0.3

2.6 Three dimensional Fourier section.

The electron density in plane 'b' has been evaluated using only the 1,158 observed non-equivalent structure factors on an IBM 704 computer. The program used was one specially written (Treuting and Abrahams, 1959) to compute a three dimensional Fourier series on a general plane in a crystal of monoclinic or higher symmetry. The method used is to select a grid of points x,y in fractions of the unit cell edge and to solve these against the equation of plane 'b'. The resulting values of z are then rounded off to the nearest 1/3600 th; this means that the error in z is less than c/7200 or 0.0017A which is less than the distance of all of the atoms except C_3 from the plane. The synthesis was then performed at each of the resulting points for values of x from 0 to 1200/3600 at intervals of 30/3600 and y from 0 to 3960/3600 at intervals of 90/3600. The resulting array of electron

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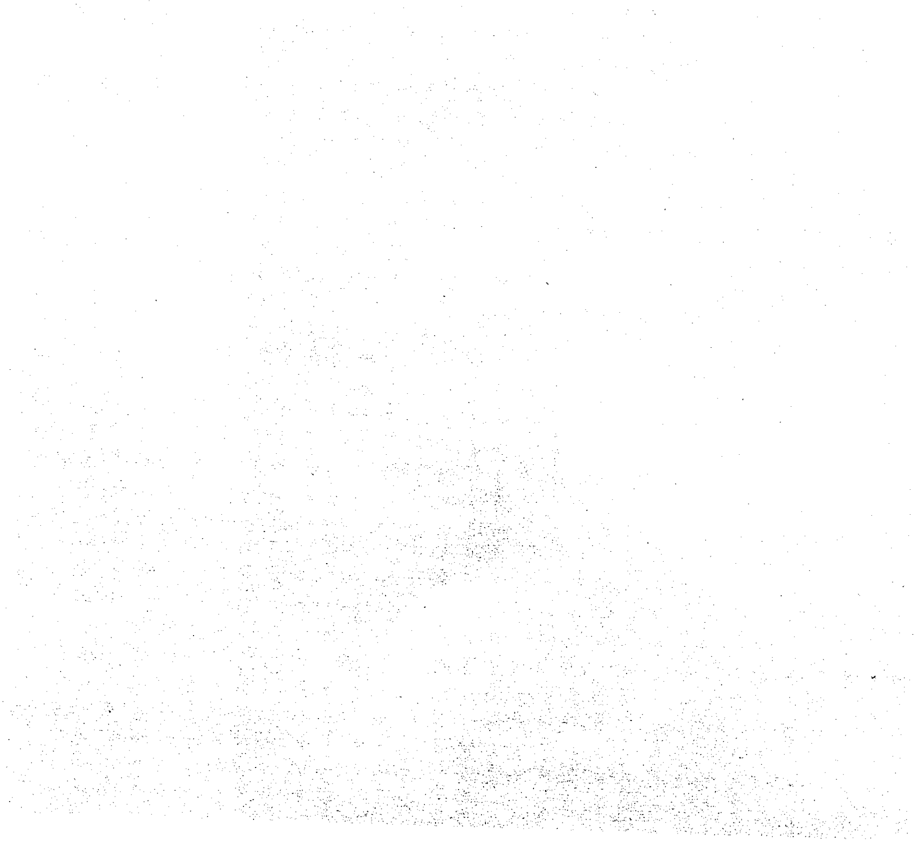

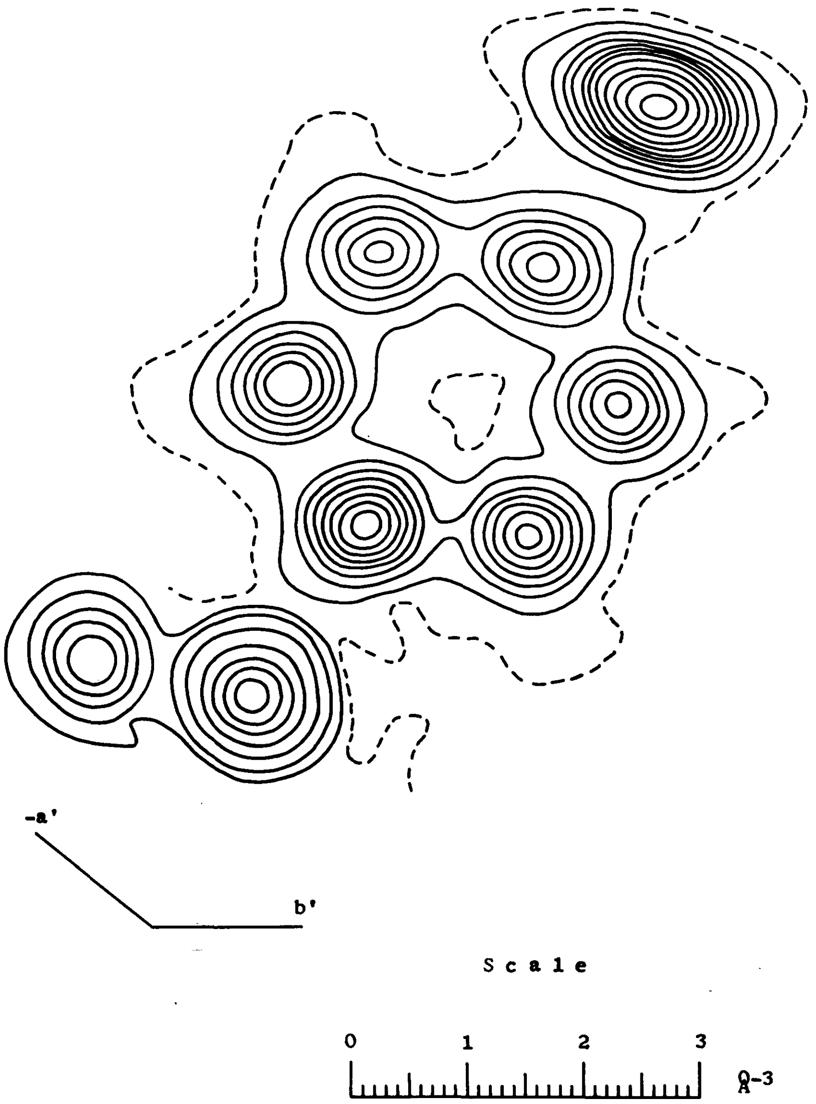

Fig. 10.

Electron density of 4, 4' - dichlorodiphenylsulfone in the plane

$$x + 1.4239y - 0.6320z - 6.0393 = 0$$

(Fmeas Fourier coefficients). The broken line represents $0.5e\text{Å}^{-3}$ and the first solid line $1e\text{Å}^{-3}$. Contours thereafter are at $1e\text{Å}^{-3}$ intervals for the oxygen and carbon atoms; for sulfur the contours above $2e\text{Å}^{-3}$ are at $5e\text{Å}^{-3}$ and for chlorine above $6e\text{Å}^{-3}$ at $2e\text{Å}^{-3}$ intervals.

densities was drawn out with the projected axes a' and b', where a' = 11.22 and b' = 10.31A with γ' = 39°50'; this is shown in Fig.10.

This map shows several interesting features, firstly the positional parameters show good agreement with the earlier least squares values, and secondly, the marked ellipticity of the chlorine atom offers confirmation of the anisotropic thermal vibration found in the least squares refinement. The third feature is the line shape of the 0.5e/A^3 contour in the region of the atoms C_2, C_3, C_5, and C_6 which suggests the presence of hydrogen atoms. This third feature prompted the calculation of a difference synthesis in the same plane using structure factors evaluated using the final atomic parameters for all of the atoms except the hydrogens which were omitted. These F(calc)'s were then subtracted from the F(meas) values of Appendix 1(a) and the difference electron density in plane 'b' computed; this is shown in Fig.11.

This map shows the expected maxima which are distinctly above the average background (0.45 - 0.65 e/A^3) and in the correct location to be hydrogen atoms. The remaining atoms, except sulphur, are also seen to be in

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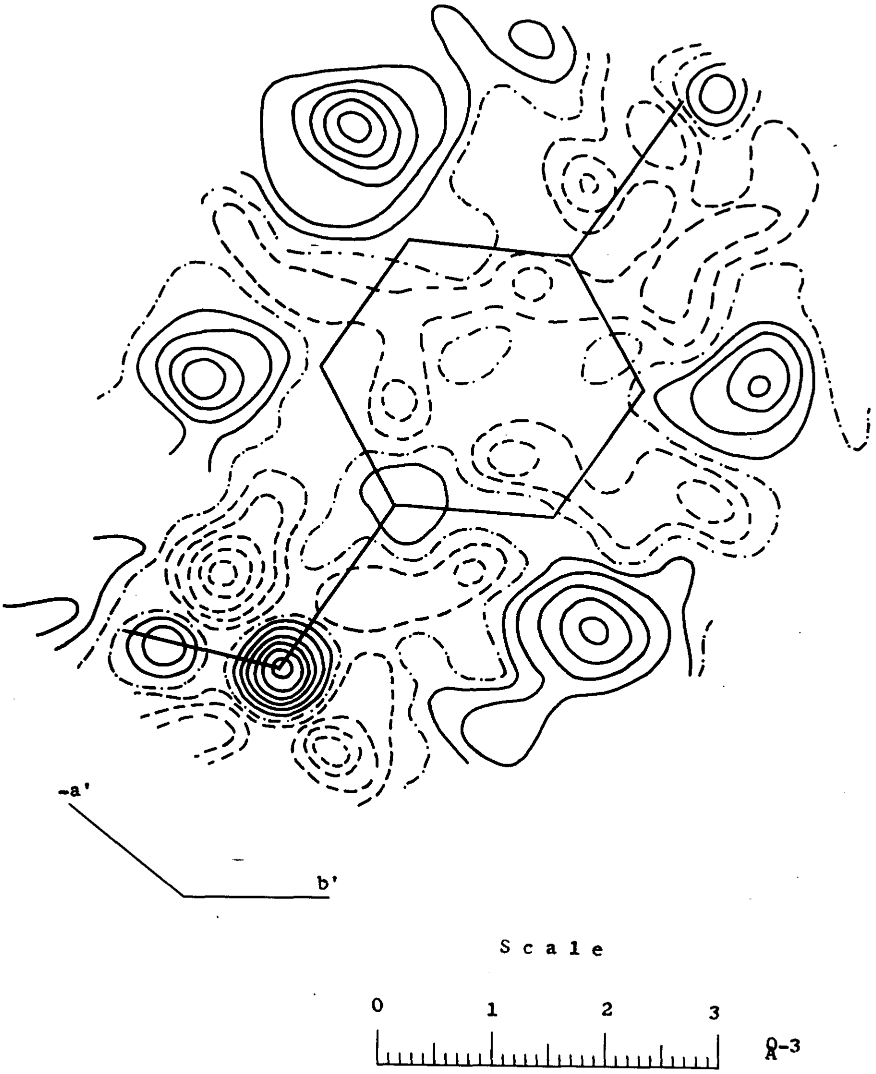


Fig. 11.

Difference electron density of 4, 4' - dichlorodiphenylsulfone in the plane

$$x + 1.4239y - 0.6320z - 6.0393 = 0$$

(Fmeas - Fcalc Fourier coefficients). Contours are at 0.1eÅ^{-3} intervals. The dot-dash line represents 0eÅ^{-3}, the solid lines are positive and the broken lines negative densities.

regions of very small slope and small absolute height which gives further confirmation of the least squares derived parameters.

2.7 Position of hydrogen atoms.

The positional coordinates of the hydrogen atoms were then independently determined by computing the electron density along lines parallel to the crystal axes and through the expected centres of the hydrogen atoms. This was then repeated taking new lines corresponding to any apparent changes in the positions of the centres of gravity of the atoms; the coordinates obtained in this way are listed in Table 18.

Table 18.

Fourier derived hydrogen atom coordinates.

Atom.	x	y	z
H_2	0.144	0.400	-0.104
H_3	0.048	0.663	-0.037
H_5	0.134	0.721	0.273
H_6	0.222	0.386	0.198.

Using these coordinates structure factors were calculated based on the hydrogen atoms alone with Bacon and Curry's (1959) temperature factors and McWeeny's (1951) atomic scattering factor. These structure factors were then subtracted from the F(meas) - F(calc) values used in evaluating Fig.11 and the resulting residuals taken as coefficients to calculate F(error) syntheses around the hydrogen and sulphur atoms. These syntheses were performed to confirm that the electron density peaks in the region of the hydrogen atoms were caused by scattering from the hydrogen atoms and not by errors in the observed structure factors. The residual electron density around the sulphur atom was calculated in this case to investigate the relatively large electron density around the sulphur atom in Fig.11. Table 19 gives the

Table 19.

Maximum electron densities.

Atom.	Density (a).	Density (b).
H_2	0.45e/A^3	0.09e/A^3
H_3	0.62	0.25
H_5	0.41	0.04
H_6	0.54	0.13
S	0.64	0.64.

Table 20.

Carbon - hydrogen bond lengths.

$C_2 - H_2$	1.02A
$C_3 - H_3$	1.02
$C_5 - H_5$	1.14
$C_6 - H_6$	0.96.

Table 21.

Out-of-plane distances.

Atom	Plane 'a'	Plane 'b'
H_2	0.261A	0.289A
H_3	-0.043	-0.033
H_5	-0.196	-0.187
H_6	-0.223	-0.197.

maximum electron density values at all of these atoms in both syntheses for comparison. Density (a) is that based on F(meas) - F(S,Cℓ,O,C) and density (b) is based on F(meas) - F(S,Cℓ,O,C,H).

All of the 'hydrogen' atom peaks can be seen to have been significantly reduced although that for H_3 is still about double the background density. The 'sulphur' peak is clearly unaffected by the hydrogen atoms, the maximum change in electron density in the neighbourhood of this atom being less than $0.05e/A^3$.

The coordinates of the hydrogen atoms were used to evaluate carbon - hydrogen bond lengths and these are given in Table 20; the mean of these values is 1.04A. The distance of the hydrogen atoms from planes 'a' and 'b' has also been evaluated and these are given in Table 21.

2.8 Analysis of thermal vibrations.

The anisotropic motion of an atom in a crystal can be completely described by its ellipsoid of vibration. The ellipsoid is uniquely determined by the thermal parameters b_{ij} in the expression (xxvii) of Part I; where in this case $b_{ii} = \beta_{ii}$, $b_{ij} = 2\beta_{ij}$. Rollett and Davies (1955) describe a method for obtaining the principal axes of the ellipsoid in terms of orthogonal reciprocal axes. Waser (1955) and Busing and Levy (1958) describe a similar method but using direct lattice vectors, the latter method being more suitable for automatic computation. Calculation of the principal axes has been carried out independently by both methods, the first method being used in a hand calculation and the second on ORACLE. The results of these calculations are identical, apart from errors in rounding off; the ORACLE results are given in Table 22 since the standard deviations were also determined in this calculation. The first part of the table gives values of $\mu(r)$, the root mean square displacement of the atom along the rth principal axis; the second part gives $\phi(r,i)$ in degrees, the angles made by the rth principal axis with the direct lattice vectors.

It is, however, easier to visualise the thermal motions of the atoms if these are given with respect to some fixed molecular axes. A natural choice of axes is that given by

Table 22.

The principal axes; R.M.S. displacements and orientations.

Atom.	$\mu(1)$ A	$\mu(2)$ A	$\mu(3)$ A
Cℓ	0.427 ± 0.003	0.227 ± 0.002	0.297 ± 0.002
S	0.257 ± 0.002	0.217 ± 0.002	0.236 ± 0.002
O	0.197 ± 0.004	0.299 ± 0.004	0.284 ± 0.004
C_1	0.264 ± 0.005	0.196 ± 0.005	0.231 ± 0.005
C_2	0.287 ± 0.006	0.226 ± 0.006	0.245 ± 0.006
C_3	0.329 ± 0.007	0.231 ± 0.006	0.263 ± 0.006
C_4	0.336 ± 0.007	0.228 ± 0.006	0.237 ± 0.006
C_5	0.302 ± 0.007	0.241 ± 0.006	0.266 ± 0.006
C_6	0.272 ± 0.006	0.225 ± 0.006	0.244 ± 0.006

Atom	r	$\phi(r,a)^\circ$	$\phi(r,b)^\circ$	$\phi(r,c)^\circ$
Cℓ	1	58.5 ± 0.52	57.2 ± 0.59	49.2 ± 0.75
	2	138.6 ± 0.78	48.8 ± 0.85	86.5 ± 0.92
	3	66.1 ± 1.05	58.6 ± 1.00	139.0 ± 0.76
S	1	157.2 ± 3.83	90.0	66.7 ± 3.83
	2	90.0	180.0	90.0
	3	112.8 ± 3.82	90.0	156.7 ± 3.83

Atom	r	$\phi(r,a)^\circ$	$\phi(r,b)^\circ$	$\phi(r,c)^\circ$
O	1	71.3 ± 1.79	36.5 ± 1.91	60.2 ± 2.07
	2	23.9 ± 8.27	113.7 ± 6.56	87.1 ± 11.4
	3	75.6 ± 12.5	64.0 ± 6.23	150.0 ± 2.47
C_1	1	123.0 ± 6.82	64.7 ± 3.86	43.4 ± 5.15
	2	89.3 ± 5.89	148.9 ± 4.47	58.9 ± 4.35
	3	147.0 ± 6.83	106.8 ± 6.56	116.9 ± 6.79
C_2	1	102.4 ± 5.40	31.8 ± 6.05	61.0 ± 5.24
	2	43.7 ± 13.2	101.2 ± 7.93	49.0 ± 10.9
	3	48.9 ± 13.4	60.6 ± 6.95	125.4 ± 11.6
C_3	1	80.9 ± 3.70	34.7 ± 3.52	56.9 ± 4.04
	2	41.4 ± 8.57	117.4 ± 4.26	62.2 ± 7.19
	3	50.0 ± 8.70	70.3 ± 5.75	134.1 ± 6.74
C_4	1	69.6 ± 2.62	57.5 ± 2.81	40.1 ± 2.63
	2	136.2 ± 24.5	111.6 ± 23.2	53.6 ± 9.18
	3	126.7 ± 25.7	40.6 ± 16.4	104.6 ± 17.4
C_5	1	129.6 ± 4.64	140.4 ± 4.66	89.4 ± 7.82
	2	41.1 ± 5.14	128.5 ± 4.68	78.4 ± 10.9
	3	80.9 ± 10.1	97.8 ± 8.80	168.4 ± 10.8
C_6	1	149.9 ± 5.76	120.1 ± 5.77	89.5 ± 8.58
	2	61.6 ± 5.87	145.2 ± 7.85	71.9 ± 13.6
	3	80.9 ± 10.2	105.8 ± 12.3	161.9 ± 13.6.

$$\vec{x} \propto \overrightarrow{S - Cl}$$

$$\vec{y} \propto \overrightarrow{C_5 - C_3} + \overrightarrow{C_6 - C_2}$$

$$\vec{z} \propto \vec{x}, \vec{y}$$

The amplitudes of the thermal vibration of the atoms along these axes, u(m) were obtained from the values of $\mu(r)$ and $\phi(r,i)$ given in Table 22 using the known angles between the principal axes and the molecular axes. These values of u(m) are given in Table 23.

Table 23.

R.M.S. displacements along the molecular axes.

Atom.	u(1) A	u(2) A	u(3) A
Cl	0.239 ± 0.002	0.395 ± 0.002	0.330 ± 0.002
S	0.242 ± 0.001	0.236 ± 0.002	0.233 ± 0.001
O	0.281 ± 0.004	0.255 ± 0.004	0.254 ± 0.004
C_1	0.253 ± 0.005	0.232 ± 0.005	0.209 ± 0.005
C_2	0.273 ± 0.006	0.237 ± 0.006	0.252 ± 0.006
C_3	0.274 ± 0.007	0.275 ± 0.007	0.283 ± 0.007
C_4	0.249 ± 0.006	0.316 ± 0.007	0.244 ± 0.006
C_5	0.247 ± 0.006	0.264 ± 0.006	0.297 ± 0.007
C_6	0.236 ± 0.006	0.246 ± 0.005	0.261 ± 0.006.

It is interesting to note that the vibrations u(1) are essentially constant ranging from 0.236A to 0.274A for atoms in the plane of the benzene ring whilst the values of u(2) vary from 0.236A at sulphur to 0.395A at chlorine. In view of this it was considered that the atoms C_{1-6} and chlorine could be considered as a rigid body and the method of Cruickshank (1956a) applied. Since the seven atoms considered lie in the plane $z = 0$, the twelfth order determinant can be reduced to three fourth order ones. The molecular axes defined above were used and the origin taken to be at the sulphur atom, the resulting equations being solved for the components of the symmetric tensors T_{ij} and ω_{ij}. These equations are

$$\begin{bmatrix} 1 & 0 & 0 & y^2 \\ & 1 & 0 & x^2 \\ & & 1 & -xy \\ & & & x^4 + y^4 + x^2y^2 \end{bmatrix} \begin{bmatrix} T_{11} \\ T_{22} \\ T_{12} \\ \omega_{33} \end{bmatrix} = \begin{bmatrix} U_{11} \\ U_{22} \\ U_{12} \\ y^2U_{11} + x^2U_{22} - xyU_{12} \end{bmatrix}$$

$$\begin{bmatrix} 1 & y^2 & x^2 & -2xy \\ & y^4 & x^2y^2 & -2xy^3 \\ & & x^4 & -2x^3y \\ & & & 4x^2y^2 \end{bmatrix} \begin{bmatrix} T_{33} \\ \omega_{11} \\ \omega_{22} \\ \omega_{12} \end{bmatrix} = \begin{bmatrix} U_{33} \\ y^2U_{33} \\ x^2U_{33} \\ -2xyU_{33} \end{bmatrix}$$

Table 24.

The values, in A^2, have been multiplied by 100.

Atom.	U_{11}^{obs}	U_{11}^{calc}	U_{22}^{obs}	U_{22}^{calc}	U_{33}^{obs}	U_{33}^{calc}
Cl	5.646	6.162	15.653	15.101	10.879	10.446
C_1	6.389	6.163	5.418	4.895	4.368	3.775
C_2	7.421	6.606	5.646	5.699	6.319	6.444
C_3	7.525	6.602	7.603	8.146	7.989	7.877
C_4	6.149	6.163	10.056	9.773	5.944	6.962
C_5	6.113	6.558	7.038	8.169	8.827	8.713
C_6	5.567	6.556	6.094	5.723	6.795	6.909

Atom.	U_{12}^{obs}	U_{12}^{calc}	U_{23}^{obs}	U_{23}^{calc}	U_{31}^{obs}	U_{31}^{calc}
Cl	-2.372	-1.213	3.944	3.850	-0.540	-0.165
C_1	-0.815	-1.239	0.368	0.111	0.766	-0.189
C_2	-1.063	-2.085	0.327	0.490	-0.723	-0.591
C_3	-2.157	-2.568	1.430	1.520	-1.114	-0.770
C_4	-1.642	-1.240	1.766	1.903	-0.851	-0.186
C_5	-0.540	0.061	0.762	1.142	0.097	0.191
C_6	-0.096	-0.400	0.732	0.310	0.688	0.035.

$$\begin{bmatrix} 1 & 0 & -x^2 & xy \\ & 1 & xy & -y^2 \\ & & x^4 + x^2y^2 & -xy^3 - x^3y \\ & & & y^4 + x^2y^2 \end{bmatrix} \begin{bmatrix} T_{23} \\ T_{13} \\ \omega_{23} \\ \omega_{13} \end{bmatrix} = \begin{bmatrix} U_{23} \\ U_{13} \\ -x^2U_{23} + xyU_{13} \\ xyU_{23} - y^2U_{13} \end{bmatrix}$$

where the 4 x 4 matrices are symmetric and, together with the right-hand side vector elements, are summed over all the atoms. The U^r_{ij} are obtained from the b_{ij} by the relations (xxviii) of Part I and these are then transformed to the U_{ij} with respect to molecular axes by the rule for transforming second order tensor components. The transformed U_{ij}'s are given under U^{obs}_{ij} in Table 24; the values of $U_{ii}^{\frac{1}{2}}$ correspond to the values of u(m) in Table 23. Solution of the above equations gives

$$T_{ij} = \begin{pmatrix} 6.162 \pm 0.248 & -1.221 \pm 0.248 & -0.172 \pm 0.257 \\ & 4.011 \pm 0.398 & -0.221 \pm 0.398 \\ & & 3.197 \pm 0.633 \end{pmatrix} \times 10^{-2} \text{A}^2$$

$$\omega_{ij} = \begin{pmatrix} 53.371 \pm 12.624 & 1.718 \pm 1.390 & 1.901 \pm 2.696 \\ & 6.132 \pm 0.806 & -3.447 \pm 0.695 \\ & & 9.381 \pm 0.694 \end{pmatrix} \text{deg.}^2$$

The values of U_{ij}^{calc} given in Table 24 are obtained from the equations

$$\begin{aligned}
U_{11} &= T_{11} + y^2\omega_{33} \\
U_{22} &= T_{22} + x^2\omega_{33} \\
U_{33} &= T_{33} + y^2\omega_{11} + x^2\omega_{22} - 2xy\omega_{12} \\
U_{12} &= T_{12} - xy\omega_{33} \\
U_{23} &= T_{23} - x^2\omega_{23} + xy\omega_{13} \\
U_{13} &= T_{13} - y^2\omega_{13} + xy\omega_{23}
\end{aligned}$$

The root mean square value of the $\Delta U_{ij} = U_{ij}^{obs} - U_{ij}^{calc}$ is $0.607 \times 10^{-2}A^2$. These tensors correspond to librations of the ring of 0.248, 0.200 and 0.179A along these axes and oscillations of 7.31, 2.48 and 3.06° about them.

When the DEUCE computer became available it was condidered to be of interest to repeat this analysis using all 17 atoms in the molecule (except hydrogens). This required choosing a new set of molecular axes since the previous set referred only to the plane of one ring of the molecule. In the new system

$$\begin{aligned}
\vec{x} &\propto \overrightarrow{Cl - Cl'} \\
\vec{y} &\propto b\text{- axis} \\
\vec{z} &\propto \vec{x}.\vec{y}
\end{aligned}$$

The new origin was chosen to be the centre of mass of the

Table 25.

The values, in A^2, have been multiplied by 100.

Atom.	U_{11}^{obs}	U_{11}^{calc}	U_{22}^{obs}	U_{22}^{calc}	U_{33}^{obs}	U_{33}^{calc}
Cl	7.280	6.987	9.987	10.458	14.910	14.738
C_1	6.292	6.185	4.539	5.282	5.344	5.152
C_2	6.208	6.625	7.586	7.722	5.593	5.673
C_3	6.534	6.598	9.232	9.669	7.351	7.587
C_4	5.232	6.209	7.208	7.778	9.707	9.012
C_5	7.284	6.608	7.778	5.808	6.917	7.399
C_6	6.765	6.556	5.722	5.211	5.969	5.408
O	8.586	8.262	5.490	5.558	6.821	7.500
S	6.601	6.905	4.685	4.796	5.612	5.898

Atom.	U_{12}^{obs}	U_{12}^{calc}	U_{23}^{obs}	U_{23}^{calc}	U_{31}^{obs}	U_{31}^{calc}
Cl	2.767	2.349	4.803	2.455	0.914	0.553
C_1	-0.809	-0.289	0.908	-0.305	-0.398	-0.298
C_2	-0.682	-0.401	0.829	-0.561	-0.607	-1.305
C_3	0.081	0.388	2.356	0.510	-0.727	-1.814
C_4	-0.136	0.764	2.617	0.801	0.114	-0.277
C_5	1.397	0.219	0.803	0.082	-0.054	0.897
C_6	0.802	-0.048	0.610	0.036	0.291	0.372
O	-0.567	-0.826	-2.135	-1.615	0.092	1.286
S	0	0	0	0	0.041	0.464

molecule and has coordinates (0.25, 0.5378, 0). The complete calculation was then carried out using the second program described in Appendix 2; this gave

$$T_{ij} = \begin{pmatrix} 6.013 \pm 0.216 & 0 & -0.470 \pm 0.219 \\ & 4.796 \pm 0.295 & 0 \\ & & 4.076 \pm 0.329 \end{pmatrix} \times 10^{-2}A^2$$

$$\omega_{ij} = \begin{pmatrix} 16.244 \pm 2.570 & 0 & -8.317 \pm 1.133 \\ & 12.167 \pm 0.932 & 0 \\ & & 7.952 \pm 0.839 \end{pmatrix} \text{deg.}^2$$

The corresponding values of U_{ij}^{obs} and U_{ij}^{calc} for these axes are given in Table 25, values for the symmetry related atoms are the same except for a sign change in U_{12} and U_{23}. The root mean square value of the ΔU_{ij} is $0.891 \times 10^{-2}A^2$. These tensors correspond to librations of the centre of mass of 0.245, 0.219 and 0.202A and to oscillations of 4.03, 3.49 and 2.82° respectively about the axes x, y and z. These two analyses show by the relatively good agreement of the U_{ij}^{obs} and U_{ij}^{calc} values that the molecule can reasonably be considered to be vibrating as a rigid body.

The method of Cruickshank (1956b) has been used to determine any errors in bond length due to the angular oscillations of the molecule. If we assume that the sulphur atom only undergoes translational vibrations then we find that the resultant displacement of the atoms towards the sulphur atom is 0.003A for C_1, 0.009A for C_4 and 0.012A for chlorine. The resulting apparent reduction in the bond lengths is thus less than their standard deviations and has consequently been ignored.

2.9 Neutron diffraction study.

Concurrently with the present study a two dimensional neutron diffraction study of 4-4'-dichlorodiphenyl sulphone has been carried out by Bacon and Curry (1959). Data for the h0l zone were used and structure factors calculated using the chlorine coordinates obtained from the x-ray Patterson map (Fig.4 of this thesis), together with coordinates for the remaining atoms estimated from Keil and Plieth's (1955) paper on the diiodo compound. This gave an R- factor of 0.51. Refinement was carried out using Fourier and difference Fourier syntheses and finally four cycles of 'least squares'. This reduced the R- factor to 0.08.

Table 26.

Final x-ray and neutron diffraction parameters.

	x		z		X		N	
	X	N	X	N	B_{11}	B_{33}	B_{min}	B_{max}
Cl	.0327	.0343	.1621	.1636	7.4	10.2	5.2	10.6
S	.25	.25	0	0	5.1	4.5	2.7	6.2
O	.2244	.2234	.9073	.9064	6.1		5.2	
C_1	.1868	.1883	.0456	.0456	4.6		4.1	
C_2	.1352	.1345	.9760	.9738	4.6		4.4	
C_3	.0877	.0867	.0112	.0114	5.5		5.6	
C_4	.0926	.0923	.1164	.1164	4.8	7.0	4.3	6.8
C_5	.1431	.1420	.1867	.1874	5.6		5.0	
C_6	.1910	.1919	.1503	.1509	5.0		4.3	
H_2	.144	.1356	-.104	-.1021	-		3.7	10.0
H_3	.048	.0462	-.037	-.0424	-		6.4	10.6
H_5	.134	.1465	.273	.2685	-		6.3	9.9
H_6	.222	.2308	.198	.2020	-		5.2	7.5

X denotes x-ray results

N denoted neutron diffraction results.

The x- and z- coordinates for all of the atoms including hydrogen atoms are given in Table 26 together with the final x-ray x- and z- coordinates for comparison. Also compared in this table are the final temperature parameters from the two analyses; in the neutron data anisotropic values have only been considered for S, C2, C_4 and the hydrogen atoms and consequently the x-ray values, B_{11} and B_{33}, have been averaged for easy comparison. With the exception of the hydrogen atoms, the parameters of all the atoms agree (within the limits of their standard deviations) except for the value of B_{11} for the sulphur atom. The reason for the discrepancy in this parameter may well have arisen in the x-ray data by using an atomic form factor which has small deviations from the true value. The good agreement of the other parameters is of great importance in illustrating that the two types of diffraction do in fact produce the same results.

The only bond lengths given by Bacon and Curry are those of carbon - hydrogen, these are

$C_2 - H_2 = 1.02A$
$C_3 - H_3 = 1.08$
$C_5 - H_5 = 1.06$
$C_6 - H_6 = 1.04$

These values were obtained by taking the x-ray equation for the plane of the benzene ring and assuming that the hydrogen atoms lie in it. This gave y- coordinates for the atoms which were then used in the bond length calculation. The mean value of these is 1.05A which compares with 1.04A found in the x-ray study.

2.10 Discussion.

As was expected, the bond arrangement in this molecule is not that of a regular tetrahedron. The O-S-O' angle of 120.4 ± 0.42° is very significantly greater than the tetrahedral value of 109.5°: the C-S-C' and C-S-O angles are less than the tetrahedral value, although to a lesser extent, and again this difference is significant. The sulphur - oxygen bond length is, as expected, very close to the double bond length of 1.43A; the carbon - sulphur bond length of 1.765 ± 0.006A on the other hand, is very significantly shorter than the accepted single bond length of 1.82A, a fact which agrees with measurements on this bond in comparable molecules, eg. 1.76A in diphenylsulphoxide (Abrahams, 1957).

The slight but significant deviation of several of the atoms from the least squares derived planes is very interesting. A similar effect has been found in another aromatic molecule, paradichlorobenzene, by Housty and Clastre (1957) who find that the carbon atoms are 0.04A from the mean plane. The only close contacts of the chlorine atoms in this sulphone molecule are distances of Cl ... Cl, 3.56A and Cl ... C_4, 3.98A which are no shorter than the van der Waal's distances of about 3.6A. Three of the C ... O contacts are shorter than the usual van der Waal's distance of 3.3A viz. 3.21, 3.24 and 3.27A but there are no angular relations involving these distances to suggest that they are any other type of bond. Many cases of C ... O contacts between 3.14 and 3.25A can now be found in the literature, eg. 3.14A in furoic acid (Goodwin and Thomson, 1954) and 3.24A in nicotinamide (Wright and King, 1954), which suggests that the van der Waal's C ... O distance should probably be shortened to to about 3.2A.

The thermal vibration of this molecule has also proved rather interesting. The r.m.s. atomic displacements along the length of the molecule are reasonably constant at about 0.25A whilst normal to the plane of the ring they increase from 0.23 at the centre to 0.33A at the periphery. Normal to both of these directions the displacements increase even more rapidly from 0.24 to 0.40A. Two sets of molecular axes have been chosen and to which the thermal parameters have been referred. In both cases an attempt has been made to represent these as translations of the molecule as a rigid body coupled with oscillations of this rigid body about the axes. Both sets of axes seem reasonably good for this purpose but the first set, viz. the axes of the aromatic ring, appear to be slightly better in that the off-diagonal terms in the T and ω tensors are smaller and the e.s.d. of the U_{ij} is smaller, $0.0067A^2$ compared with $0.0087A^2$ for the case of the complete molecule.

Simultaneously with this study a neutron diffraction study has been carried out by Bacon and Curry (1959) and the results of this study and the x-ray one have already been compared (Table 26). That the parameters agree so well is valuable in showing that the methods do in fact give identical results within the experimental errors of each. The largest discrepancy which occurs is in the sulphur thermal parameters and whereas the suggestion made earlier may account for this, it must be remembered that x-ray diffraction locates the electron cloud associated with the atom while the neutron diffraction method locates the nucleus of the atom. It may well be then, that while the nucleus of the sulphur atom exhibits an anisotropic vibration, that of the electron cloud may be essentially isotropic.

3. 4-4'-dibromodiphenyl sulphone.

3.1 Unit cell data.

Precession camera and Weissenberg camera photographs were taken with the crystal set about the b- axis using molybdenum Kα radiation ($\lambda = 0.7107A$). The axial lengths were determined from precession photographs and corrected for film shrinkage, the β- angle of the monoclinic cell was determined from a Weissenberg photograph. These gave the following

$a = 20.752 \pm 0.010A$

$b = 5.031 \pm 0.010$

$c = 12.359 \pm 0.010$

$\beta = 92.62 \pm 0.25^\circ$

and the values given by Toussaint (1945) were

$a = 12.32 \pm 0.03A$

$b = 5.04 \pm 0.02$

$c = 20.75 \pm 0.03$

$\beta = 92^\circ 40'$

ie. with the a- and c- axes interchanged.

The volume of the unit cell obtained from the formula $V = a.b.c.\sin\beta$, was $1289.0A^3$. Since the density given by Toussaint (1945) is 1.88gm/c.c. there are four molecules in the unit cell and the calculated density is 1.938gm/c.c.. The total number of electrons in the unit cell F(000) is therefore 728.

Examination of the precession and Weissenberg camera photographs showed the absent spectra to be in

$hk\ell$ when $h + k + \ell$ is odd

$h0\ell$ when h or ℓ is odd

$0k0$ when k is odd.

The space group is therefore either $C_s^4 - I_a$ or $C_{2h}^6 - I_{2/a}$: the latter has been adopted because this compound is isomorphous with the chloro- compound.

3.2 Intensity data.

Data for the $h0\ell$ zone were obtained using the modified Weissenberg camera (Abrahams, 1954) with 0.0008" thick nickel foils interleaved between five films. The data for the hk0, hk1, hk2, hk3 and hk4 layers were collected on a precession camera using a stabilised x-ray source, a series of six films, with a time ratio of three to one between the exposure of each, being taken for each zone. All of the intensities were estimated visually, the ratio of the strongest to the weakest intensity (taken as unity) for each zone was 33,598 in h0ℓ, 2,970 in hk0, 7,380 in hk1, 2,100 in hk2, 1,680 in hk3 and 591 in hk4.

Since for these crystals the linear absorption coefficient for molybdenum Kα x-rays is 7.17 mm^{-1}, it was decided that absorption corrections should be applied. The size of the crystal used for the collection of the data was 0.44 x 0.27 x 0.25 mm.. Corrections were only applied to the h0ℓ zone since no method was available for correcting precession camera data. The method used to correct the h0ℓ data was to approximate the cross section of the crystal to a cylinder and use the data tabulated by Bond (1959). The value of the radius of the crystal used was 0.155 mm. and hence μR was 1.11; the corrections were applied using a program written for the DEUCE computer (Appendix 2). The initial refinement was, however, carried out before this program had been written and so the h0ℓ data at that stage were not corrected for absorption. Both sets of h0ℓ data (ie. with and without absorption corrections) were corrected with the usual Lorentz and polarisation factors. The precession camera

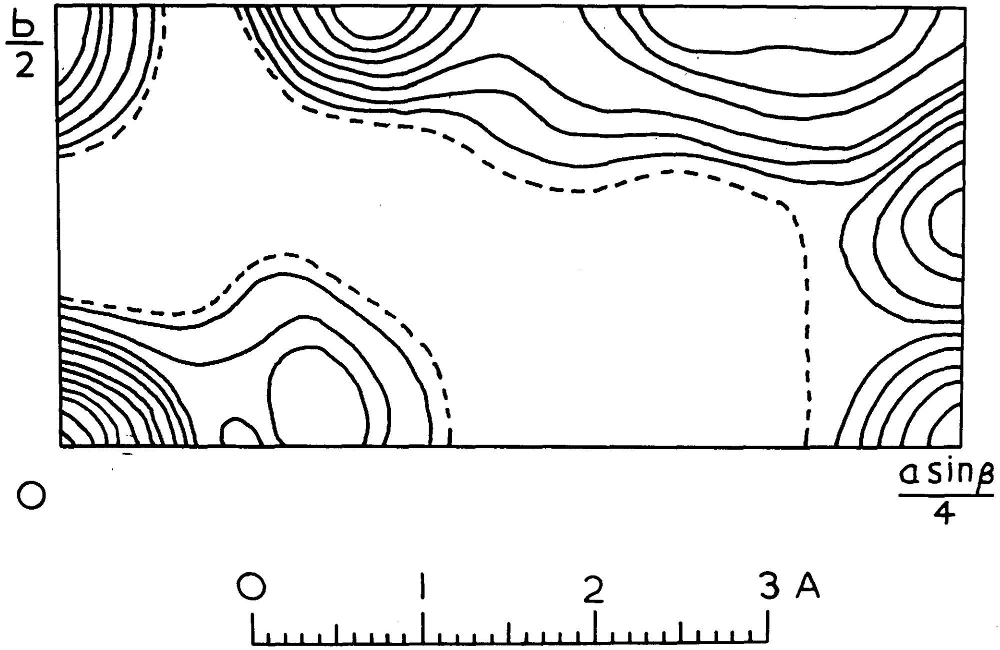


Fig. 12. 4-4'-dibromodiphenyl sulphone.

hk0 Patterson map; contours arbitrary,

dashed contour is zero.

data were corrected for these factors using the charts of Waser (1951) and Grenville-Wells and Abrahams (1952).

The values of these structure factors are listed in Appendix 1(b) under F(meas). No unobserved terms are given, since, although they were included in early calculations they were later removed. In all there are 459 of these observed values.

3.3 Structure Analysis.

Work on this structure was started with the hk0 zone at the stage when the y- coordinates for the chloro-compound were being sought. It had been hoped that the increase in atomic number of the bromine atom (over chlorine) would allow the Br - Br vector peaks to be resolved on the hk0 Patterson map. This, however, did not prove to be the case as can be seen in Fig. 12. The hk0 data for this work was approximately scaled using the method of Wilson (1942); no sharpening function was applied.

Values of $|F_o|$ were then obtained from the scaled F^2 values and signs obtained for these by comparison with the hk0 zone of the isomorphous chloro- compound which had by this time, been fully refined. These signed structure factors were then used to compute an hk0 Fourier synthesis from which coordinates for the bromine, sulphur and oxygen atoms were obtained. These coordinates together with coordinates for the carbon atoms in the chloro- compound were then used, together with an isotropic temperature factor of $B = 4.00A^2$ for all of the atoms, to calculate a set of hk0 structure factors. The atomic scattering factors used were those of McWeeny (1951) for carbon and oxygen and of James and Brindley (1931) for sulphur and bromine. This gave an R- factor of 0.65. Two further Fourier syntheses and a difference Fourier synthesis reduced this to R = 0.28; only changes in the coordinates were made.

3.4 Least squares refinement.

The program used for this least squares process was that written by Dr.J.S.Rollett for the DEUCE computer. This program refines nine parameters per atom, three positional and six thermal, together with the overall scale factor; no provision has been made to prevent refinement of any of these, ie. refinement of isotropic temperature factors is not possible. The program uses the diagonal approximation method as discussed in Part I. Three weighting systems are possible, firstly if

$|F_o| \leqslant |F^*|$ then $w^{\frac{1}{2}} = 1$, and if
$|F_o| > |F^*|$ then $w^{\frac{1}{2}} = |F^*|/|F_o|$

where $|F^*|$ is a suitable, preselected, value of $|F_o|$; secondly, if

$|F_o| \leqslant |F^*|$ then $w^{\frac{1}{2}} = |F_o|/|F^*|$, and if
$|F_o| > |F^*|$ then $w^{\frac{1}{2}} = |F^*|/|F_o|$;

and thirdly, the weight for each reflection is allocated manually and punched on the input card for that reflection. The second method has been used throughout. Provision has also been made for applying full, half or quarter of the calculated shifts to the new input parameters. In this work 'quarter shifts' were used in the early stages and 'half shifts' when the structure seemed to be refining reasonably.

The atomic scattering factors used in these structure factor calculations were those of Berghuis et al. (1955) for carbon and oxygen, and of James and Brindley (1931) for sulphur and bromine. The values of these at the intervals required by the program, were determined using a short program for DEUCE which performs the calculation using the method suggested by Forsyth and Wells (1959). They approximate the atomic scattering factor to an expression

$$f(s) = A.\exp(-as^2) + B.\exp(-bs^2) + C$$

and list values of A,a,B,b and C for the atoms up to uranium.

The first structure factors were calculated for the h0ℓ, hk0, hk2 and hk4 zones. These had been placed on a common, approximately absolute, scale using the reflections in the h0ℓ zone common to the other three zones; the hk0 data were used to give the approximately correct value of the scale factor. The initial coordinates used were the final two dimensional ones together with the z- coordinates for the chloro- compound, and an isotropic temperature of B = 4.00 for all of the atoms. The value of R resulting from this was 0.502 but the program which solves for the new parameters failed to converge to a limit with the bromine parameters. The value of F^* used in this calculation and in the subsequent ones was 50.0, the second of the weighting systems being employed.

The 'solve routine' was then repeated using only the hk0 data for which R = 0.309 (including unobserved terms at half their maximum value). The new coordinates produced were then used for a second least squares cycle which gave R = 0.313 and again failed to produce new bromine parameters.

At this stage the $h0\ell$ structure factors were calculated using the new x- coordinates and the z- coordinates from the chloro- compound; this gave R = 0.289 which fell with two further least squares to 0.266. A further cycle, however, gave R = 0.44 accompanied by the previous failure to produce new bromine parameters. Several further least squares cycles were then carried out with various trial sets of coordinates and temperature factors; the same pattern of events was, however, found repeatedly, viz. decrease in R and $\Sigma w\Delta^2$ for one or two cycles followed by rapid increases in the values of these, and failure to produce fresh bromine parameters.

By this time the program for applying the absorption corrections had been written (see Appendix 2) and consequently the $h0\ell$ data were corrected as described above. At the same time the unobserved terms were removed from the structure factor calculations in case the bad agreement of some of these was contributing to the failures to solve for new bromine parameters. An $h0\ell$ Fourier was then drawn out using the structure factors for which $R = 0.266$. From the coordinates measured from this map an R-factor of 0.248 was obtained and the value of $\Sigma w\Delta^2$ was 355. Six further least squares cycles on this zone reduced R to 0.176 and $\Sigma w\Delta^2$ to 98.

Two further cycles including hk0, hk2 and hk4 data again resulted in an increase in the R-factor and consequently the complete set of structure factors were calculated and used as coefficients for a series of line Fourier syntheses parallel to the y- axis through the expected atomic centres. From these a new set of y- coordinates were obtained which, together with the previous x- and z- coordinates gave $R = 0.236$ and $\Sigma w\Delta^2 = 1,085$ for the complete data; one cycle of refinement using these parameters resulted in $R = 0.287$ and $\Sigma w\Delta^2 = 1,442$.

It was then decided to carry refinement of the two projections to a more complete state before trying three dimensional refinement again. Four cycles were then carried out on the h0ℓ zone with the following results

Table 27.

Final parameters for 4-4'-dibromodiphenyl sulphone.

Atom.	x	y	z
Br	0.0371	0.9536	0.1655
S	0.25	0.1606	0
O	0.2248	0.0264	-0.0876
C_1	0.1909	0.3694	0.0398
C_2	0.1396	0.4423	-0.0202
C_3	0.0945	0.6433	0.0187
C_4	0.1020	0.6922	0.1204
C_5	0.1532	0.6666	0.1853
C_6	0.1970	0.4815	0.1447

Atom.	b_{11}	b_{22}	b_{33}	b_{12}	b_{23}	b_{31}
Br	0.0049	0.0825	0.0186	0.0082	0.0046	0.0054
S	0.0041	0.0580	0.0110	0	0	0.0003
O	0.0062	0.0971	0.0215	-0.0038	0.0232	0.0002
C_1	0.0022	0.0627	0.0109	-0.0035	-0.0088	-0.0006
C_2	0.0049	0.0702	0.0192	-0.0052	0.0441	-0.0010
C_3	0.0034	0.1334	0.0240	-0.0139	0.0051	-0.0087
C_4	0.0044	0.0556	0.0107	-0.0128	-0.0361	0.0027
C_5	0.0047	0.1187	0.0080	0.0089	-0.0405	-0.0091
C_6	0.0055	0.0534	0.0159	-0.0063	0.0387	0.0054.

	R	$\Sigma w\Delta^2$
(a)	0.169	92
(b)	.161	80
(c)	.158	80
(d)	.153	74
(e)	.151	77

This was followed by one cycle of refinement on the hk0 zone which reduced the R- factor for this zone from 0.173 to 0.133.

The parameters from these refinement cycles were then used to calculate the structure factors for the complete data giving R = 0.220; failure to solve for the new bromine parameters again resulted. The new coordinates for all of the atoms except bromine were then used together with the previous ones for bromine and another set of structure factors was calculated, for these R = 0.208 but the shifts for the bromine atom were again not produced. At this stage the refinement was terminated, the final set of structure factors being listed in App.1(b) under F(calc). The parameters used for the calculation of these are given in Table 27.

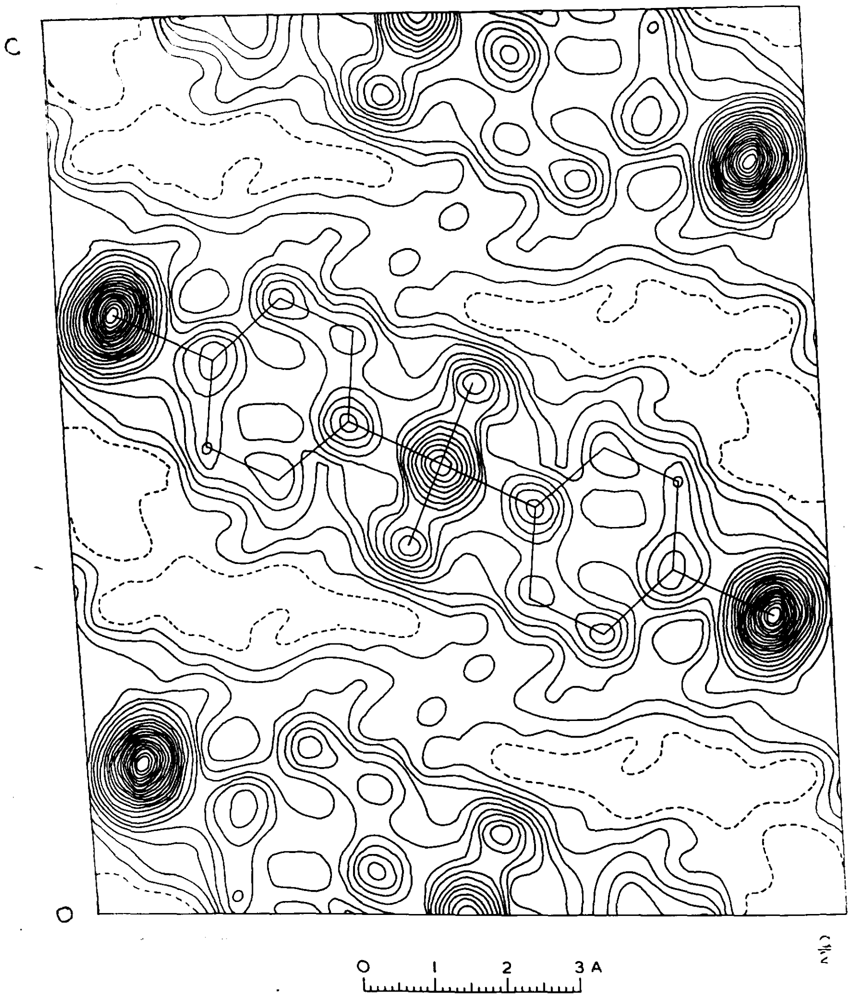


Fig. 13. 4-4'-dibromodiphenyl sulphone. h0l Fourier map. Contours at 1 e/A^2 intervals up to 8, thereafter at 2 e/A^2 on bromine and sulphur. Zero contour dashed. This corresponds to R = 0.151.

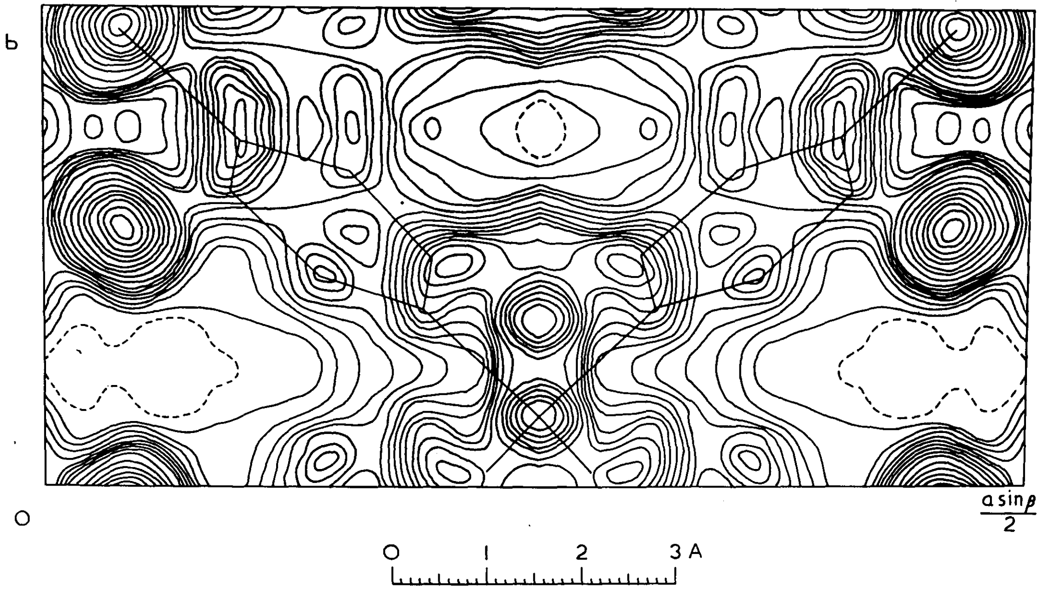


Fig. 14. 4-4'-dibromodiphenyl sulphone. hk0 Fourier map. Contours at 1 e/A^2 intervals up to 10, thereafter at 2 e/A^2 on sulphur and 5 e/A^2 on bromine. Zero contour dashed.

This corresponds to R = 0.133.

3.5 Molecular Geometry.

The coordinates given in Table 27 have been used to evaluate the bond lengths within the molecule and these are given in Table 28.

Table 28.

Bond Lengths.

	$C_1 - C_2$	1.32A
	$C_2 - C_3$	1.47
	$C_3 - C_4$	1.28
	$C_4 - C_5$	1.31
	$C_5 - C_6$	1.41
	$C_6 - C_1$	1.38
Mean	C - C	1.36
	C_4 - Br	1.98
	C_1 - S	1.71
	S - O	1.36.

The sulphur - oxygen bond length is rather shorter than expected (1.43A) and the carbon - bromine bond is slightly longer (1.90A) but these are probably not significant.

Only two angles have been worked out,

Br - S - Br' = 102.3°

O - S - O' = 120.5°

The equation of the mean plane of the aromatic ring and sulphur and bromine atoms has been calculated with respect to the orthogonal axes defined in Appendix 2. The sulphur atom was given three times and the bromine atom five times the weight of a carbon atom in the least squares process, and the equation determined on DEUCE as

$$x' + 1.4635y' - 0.6503z' - 6.3741 = 0$$

The distances of all of the atoms from this plane are given in Table 29.

Table 29.

Out-of-plane distances.

Atom.	Distance.
Br	-0.0024 A
S	-0.0021
C_1	-0.0188
C_2	-0.0248
C_3	0.0859
C_4	-0.1033
C_5	0.0642
C_6	0.0083.

In order to examine the temperature parameters for

Table 30.

R.M.S. atomic vibrations along molecular axes.

Atom.	$\bar{u}_1$	$\bar{u}_2$	$\bar{u}_3$
Br	0.276A	0.402A	0.333A
S	0.288	0.293	0.283
C_1	0.278	0.280	0.234
C_2	0.390	0.373	0.233
C_3	0.439	0.334	0.368
C_4	0.285	0.296	0.279
C_5	0.319	0.131	0.456
C_6	0.353	0.392	0.166
O	0.400	0.401	0.323

the atoms, the r.m.s. vibration of each atom has been computed along a set of molecular axes defined as for the chloro- compound, viz.

$$\vec{x} \propto \overrightarrow{S - Br}$$
$$\vec{y} \propto \overrightarrow{C_5 - C_3} + \overrightarrow{C_6 - C_2}$$
$$\vec{z} \propto \vec{x}.\vec{y}$$

The components of the b_{ij} along these axes were determined on DEUCE using the first section of the second program described in Appendix 2. The values of the r.m.s. vibrations along these axes are given in Table 30. It can be seen that the type of vibration found in the chloro- compound is not apparent at this stage, but this is probably due to incomplete refinement. Some atoms, particularly C_5 and C_6 show vibrations $\bar{u}_2$ and $\bar{u}_3$ which are very different from those for neighbouring atoms and these anomalies have probably arisen by refining the anisotropic temperature parameters at too early a stage in the least squares process.

3.6 Discussion.

The refinement of this structure has been most disappointing; it had been expected that this would follow a similar course to that of the chloro- compound. Various reasons for the trouble in refining the bromine parameters have been suggested and alternative proceedures tried, but all were unsuccessful. The reason for the failures has, at last, been found; to understand it the method of storing numbers in DEUCE must first be understood.

DEUCE stores numbers in 'chinese binary', ie. the binary pattern of the number is written so that the most significant digits come at the right-hand end of the number as opposed to the left-hand end in the decimal system. Each number has thirty-two binary digits which allows numbers to be stored which are less than 2^{31} in magnitude. The convention used in DEUCE for a negative number is that the thirty-second digit, denoted P32, should be present. If now we start to accumulate a positive number in DEUCE, the binary pattern will build up, from the left-hand end, until the number exceeds 2^{31}

at which stage a P32 will be added to the number and the positive number will be treated as 'negative'. What this really means is that we have exceeded the capacity of the number store.

Now, in the least squares process numbers such as $\Sigma w(\partial F/\partial f_j)^2$, which must be positive, are accumulated. Since these terms include f_j, the atomic scattering factor, they will be correspondingly larger if the atom is a 'heavy' one, for example a bromine atom. The cause of the failures to solve for new bromine parameters has been causedthen, by these numbers being so large that they have become negative. Further, if such a number is much larger than 2^{31} it is quite likely that it has become so large that the P32 is absent and that the number is positive again but considerably too small: this will cause the production of too great 'shifts' for the parameter and result in the rapid increases in R- factor which were sometimes experienced.

Standard deviations for the atoms and bond lengths are not given here in any detail as the refinement is not complete. These have, however, been estimated from the formula

$$\sigma^2(\xi) = \frac{\Sigma w\Delta^2}{(n - u).\Sigma w(\partial F/\partial\xi)^2}$$

where ξ is the parameter being considered, n is the number of independent reflections included in the refinement and u is the total number of parameters being refined. The standard deviations in the positional coordinates are 0.006A for bromine and sulphur, 0.05A for the carbon atoms and 0.04A for the oxygen. Some of the coordinate shifts from the last refinement cycle are greater than these values, particularly for the y- coordinates, and refinement is thus not complete. The largest deviations are probably to be found in the y-coordinates because a considerable amount of refinement has been done on the overlapped hk0 zone giving incorrect shifts for some of the badly overlapped carbon atoms. The deviations of the bond lengths found, from the expected values are thus not significant. The mean distance of the carbon atoms from the least squares derived plane is 0.05A and so none of these atoms are lying significantly out of it.

No real conclusions can be drawn about the thermal vibration of the molecule until the refinement process is complete because errors in positional parameters frequently cause even larger errors in the thermal parameters in the early stages of refinement.

The Br - S - Br' angle is larger (102.3°) than the value found by Toussaint (1945), viz. 100 ± 0.5°; a greater difference is, however, found in the O - S - O' angle, where Toussaint found 131 ± 3° the new value is 120.5° which is in better agreement with the angle in the chloro- sulphone. The angle made with the aromatic ring plane and the Br - S - Br' plane is also less than that given by Toussaint, 84.5° as opposed to 90 ± 1°, this again being in better agreement with the chloro- sulphone. The bromine - carbon bond length of 1.98A is longer than Toussaint's value of 1.89 ± 0.04A although as indicated above this bond will probably decrease in length on further refinement. The sulphur - carbon bond length found is 1.71A which is shorter than Toussaint's value of 1.79 ± 0.04A but to increase its length in the present study is consistent with shortening the carbon - bromine bond. The sulphur - oxygen bond length of 1.36A is significantly shorter than Toussaint's value of 1.54 ± 0.05A but is probably not significantly different from the expected value of 1.43A.

4. 4-4'-diiododiphenyl sulphone.

4.1 Unit cell data.

Precession camera photographs were taken with the crystal set about the b^*- and a^*- axes using molybdenum $K\alpha$ radiation ($\lambda = 0.7107$A). the dimensions of the monoclinic cell were determined from these photographs and corrected for film shrinkage; they were

$a = 19.715 \pm 0.010$A

$b = 4.946 \pm 0.010$

$c = 14.448 \pm 0.010$

$\beta = 103.25 \pm 0.25^\circ$

These dimensions correspond to the first values given by Keil and Plieth (1955) viz.

$a = 19.67$A

$b = 4.92$

$c = 14.37$

$\beta = 104^\circ$

The volume of the unit cell is thus 1,371.4A^3; Keil and Plieth give the density of the crystals as 2.25 ± 0.01 gm/c.c. at 20°C and hence there are four molecules in the unit cell. The calculated density is 2.276 gm/c.c. and F(000) = 952.

From precession photographs of hk0, hk1, h0ℓ and 0kℓ the absent spectra were found to be in

hkℓ when h + k + ℓ is odd

h0ℓ when h or ℓ is odd

0k0 when k is odd.

These absences correspond to the space groups $C_s^4 - I_a$ and $C_{2h}^6 - I_{2/a}$.

4.2 Intensity data.

Apart from the data for the hk0 zone which were collected on a precession camera, the complete three dimensional data were collected on the modified Weissenberg camera of Abrahams (1954). Molybdenum Kα x-rays were used throughout with the multiple film pack technique and Ilford 'Industrial G' film. The size of the crystal used for collecting these data was 0.36 x 0.22 x 0.20 mm.. All of the intensities were estimated visually, allowance being made for the obliquity factor of Rossman (1956) modified as in 2.2. The ratio of the strongest to the weakest intensity (taken as unity) for each zone was 11,244 for hk0; 20,950 for h0ℓ; 30,585 for h1ℓ; 4,330 for h2ℓ; 8,740 for h3ℓ; 628 for h4ℓ; 430 for h5ℓ and 55 for h6ℓ.

Since the linear absorption coefficient for these crystals is 5.10 mm.$^{-1}$ it was decided to apply absorption corrections to the intensity data. This was done by the same method as with the bromo- compound. The radius of the cylinder was taken as 0.13 mm. and hence R = 0.66. For upper layers taken on an equi-inclination Weissenberg camera the table given by Bond (1959) of θ vs. A^* (where A^* is the absorption correction) is entered with $\Upsilon/2$ instead of θ, where

$$\cos(\Upsilon/2) = \cos\theta/\cos\nu,$$

and where ν is the equi-inclination angle. In place of μR the value used is $\mu R.\sec\nu$ and the resultant value of A^* is multiplied by $\cos\nu$. This calculation and the subsequent one to correct for the Lorentz and polarisation factors and Tunnell's rotation factor was carried out on the DEUCE computer using the programs described in Appendix 2. The resulting, scaled, structure factors are listed under F(meas) in Appendix 1(c). In all there are 1,609 of these which were used in the following analysis, no unobserved terms have so far been included.

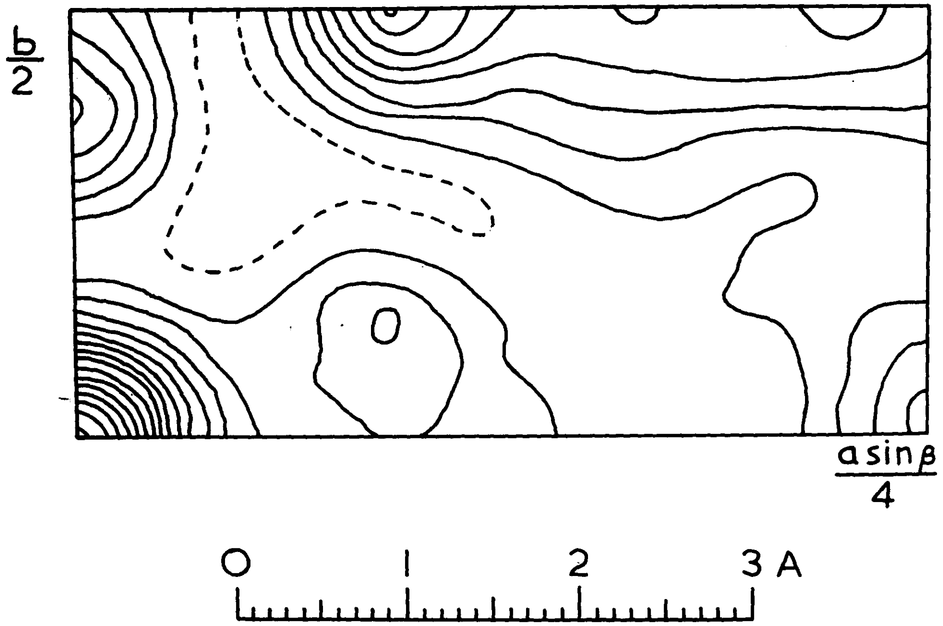


Fig. 15. 4-4'-diiododiphenyl sulphone.

hk0 Patterson map, zero contour dashed.

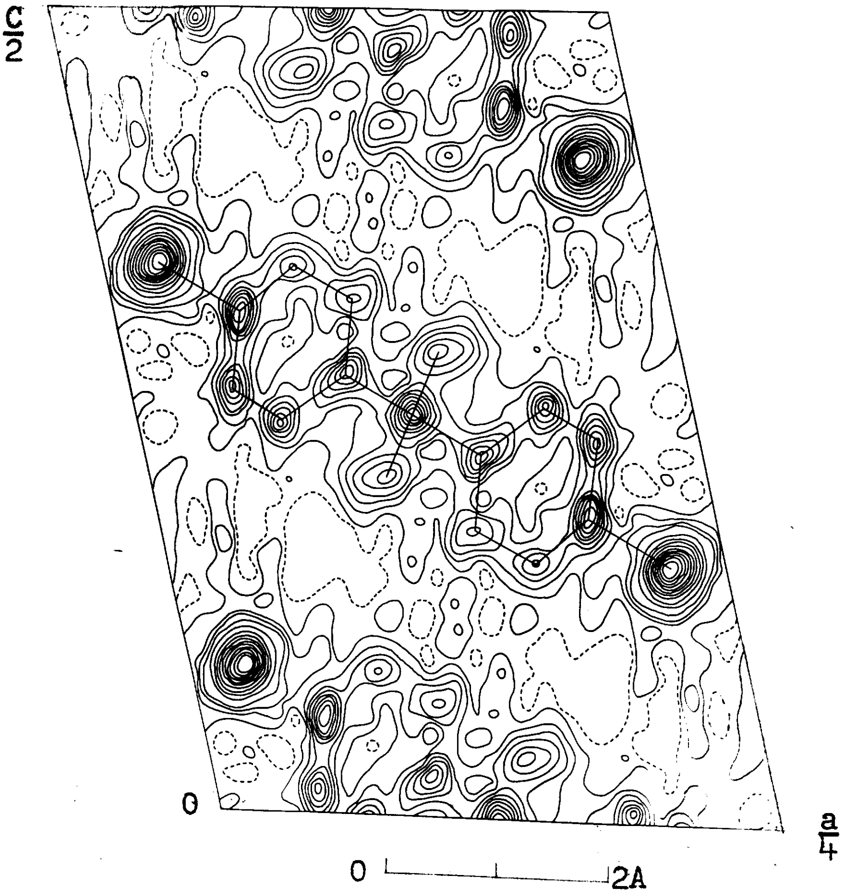


Fig. 16. 4-4'-diiododiphenyl sulphone. h0l Fourier map. Contours at 1 e/A^2 intervals except on sulphur and iodine. After 4 e/A^2 the interval is 2 e/A^2 on sulphur and 5 e/A^2 on iodine.

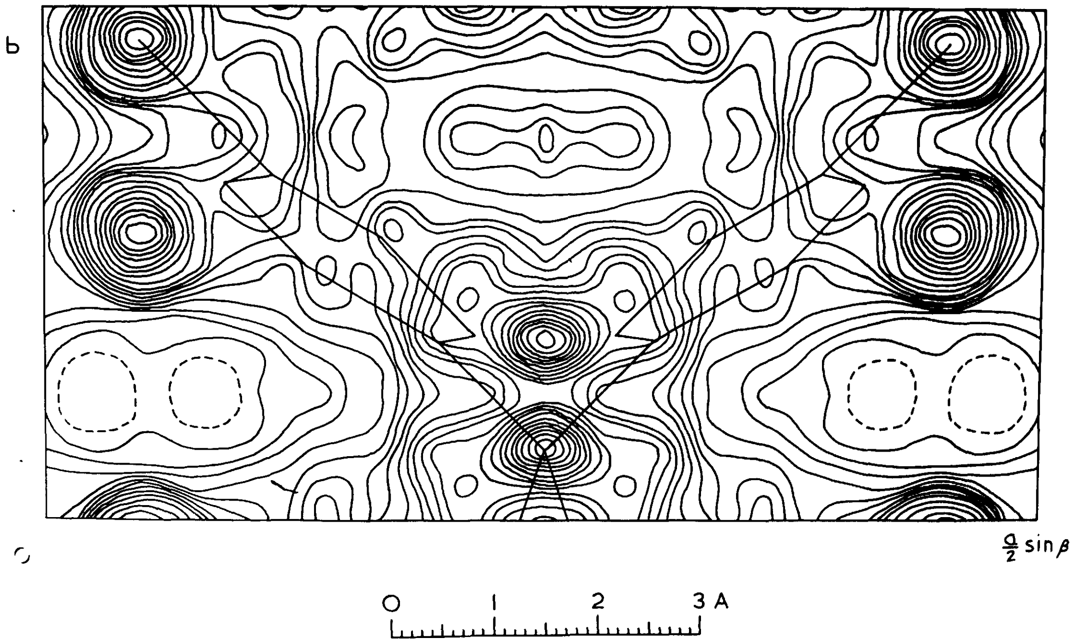


Fig. 17. 4-4'-diiododiphenyl sulphone. hk0 Fourier map. Contour interval 1 e/A^2 except on iodine. The iodine contours are 1,2,... 8,10,15,20... Zero contour dashed.

4.4 Least squares refinement.

At this stage it was decided to try refining by the method of least squares using the program of J.S.Rollett as used in 3.4. The weighting system used was the same as for the bromo- compound with $F^* = 50.0$. Initially three cycles of refinement were carried out on the hk0 zone, only half of the shifts calculated actually being used. This gave

	(1)	(2)	(3)
R	0.222	0.206	0.205
$\Sigma w\Delta^2$	289	98	92

from which it seems that useful refinement has ended. It was also considered inadvisable to refine this projection too far because of the overlap probably leading to wrong coordinates as appears to have occurred with the bromo-compound. The coordinates used for this third cycle were consequently also used to calculate the complete three dimensional set of structure factors in order to scale the observed values more accurately; each zone was scaled to the corresponding calculated set.

New coordinates for the next calculation were obtained

Table 31.

Final parameters for 4-4'-diiododiphenyl sulphone.

Atom.	x	y	z
I	0.0473	0.9360	0.1823
S	0.25	0.1405	0
O	0.2110	-0.0232	-0.0769
C_1	0.1982	0.3511	0.0404
C_2	0.1334	0.4208	-0.0135
C_3	0.0966	0.6192	0.0342
C_4	0.1123	0.6864	0.1258
C_5	0.1666	0.6090	0.1722
C_6	0.1922	0.4266	0.1325

Atom.	b_{11}	b_{22}	b_{33}	b_{12}	b_{23}	b_{31}
I	0.0073	0.1166	0.0131	0.0018	0.0003	0.0052
S	0.0044	0.0907	0.0082	0	0	0.0050
O	0.0057	0.1017	0.0097	-0.0104	-0.0131	0.0015
C_1	0.0055	0.0507	0.0098	0.0115	0.0062	0.0057
C_2	00.0046	0.1551	0.0070	0.0145	0.0005	0.0085
C_3	0.0015	0.0829	0.0153	-0.0046	0.0068	0.0068
C_4	0.0001	0.0950	0.0100	-0.0209	0.0069	0.0016
C_5	0.0111	0.0588	0.0182	0.0125	-0.0033	0.0060
C_6	0.0145	0.0339	0.0168	0.0114	0.0301	-0.0028.

from the hk0 and h0ℓ data only. Again only half of the calculated shifts in parameters were applied except for the iodine atom which was kept fixed because of possible overshifting as occurred repeatedly with the bromine atom in the bromo- compound. Two cycles of refinement on the complete data were then performed and the value of R fell from 0.326 to 0.311 while that of $\Sigma w\Delta^2$ fell from 5,832 to 4,920. The parameters used for the second cycle are listed in Table 31 and the corresponding values of F(calc) are in Appendix 1(c).

None of the standard deviations have been calculated at this stage because of the incompleteness of the refinement process; the positions of the iodine and sulphur atoms will, however, be the most accurate.

4.5 Molecular geometry.

Although this analysis is incomplete some of the geometry has been evaluated at this stage. The bond lengths are given in Table 32, the only angles which have been evaluated are

$$I - S - I' = 106.5^\circ$$

$$O - S - O' = 111.9^\circ$$

Table 32.

Bond lengths.

$C_1 - C_2$	1.38A
$C_2 - C_3$	1.48
$C_3 - C_4$	1.33
$C_4 - C_5$	1.19
$C_5 - C_6$	1.24
$C_6 - C_1$	1.37
Mean C - C	1.39
$C_4 - I$	2.08
$S - C_1$	1.66
S - O	1.45

The equation of the ring plane has also been computed, the sulphur atom being given three times the weight of the carbon atoms and the iodine atom five times. The equation determined with respect to the orthogonal axes defined in Appendix 2 is

$$x' + 1.4205y' - 0.3967z - 5.8888 = 0$$

and the distances of the atoms from it are listed in Table 33. Some of the atoms appear to be at relatively large distances from this plane but these are probably not significant at this stage in the analysis.

Table 33.

Out-of-plane distances.

Atom.	Distance.
I	-0.0008 A
S	0.0150
C_1	0.0709
C_2	-0.1029
C_3	0.0354
C_4	0.0167
C_5	0.0808
C_6	-0.1569.

Molecular axes have been chosen for the half-molecule as in the case of the chloro- compound, viz.

$$\vec{x} \propto \overrightarrow{S - I}$$

$$\vec{y} \propto \overrightarrow{C_5 - C_3} + \overrightarrow{C_6 - C_2}$$

$$\vec{z} \propto \vec{x}.\vec{y}$$

and the thermal parameters have been transformed to these axes. These are given in Table 34 as root mean square vibrations along the molecular axes and are comparable with Tables 23 and 30 for the chloro- and bromo- compounds respectively. They were calculated using one of the programs in Appendix 2.

Table 34.

R.M.S. atomic vibrations along molecular axes.

Atom.	$\bar{u}_1$	$\bar{u}_2$	$\bar{u}_3$
I	0.339A	0.380A	0.367A
S	0.260	0.313	0.296
C_1	0.208	0.332	0.291
C_2	0.205	0.318	0.399
C_3	0.243	0.384	0.211
C_4	0.328	0.293	0.147
C_5	0.327	0.442	0.327
C_6	0.477	0.386	0.385
O	0.345	0.324	0.325.

The values of $\bar{u}_m$ for C_4 and C_6 are the only ones which appear at this stage to be significantly 'out of line' with the others but this is probably caused by positional errors for these atoms.

4.6 Discussion.

The same comments as were made about the least squares refinement of the bromo- compound (3.6) also apply to the refinement of this compound. Here the least squares totals will be even larger since the atomic number of iodine is still higher than that of bromine, and further, there are considerably more data to be refined; this will consequently increase the likelyhood of the totals becoming 'negative'.

The accuracy of the parameters at this stage is similar to that of the parameters in the bromo- compound; although the final R- factor and $\Sigma w\Delta^2$ values are higher there are more data being refined and consequently n in the expression for $\sigma^2(\xi)$ will be larger. The standard deviation of the position of the iodine and sulphur atoms is thus about 0.007A and about 0.06A for the carbon and oxygen atoms.

The high value of these standard deviations mean that no significance can be attached to the deviations of the bond lengths, particularly carbon - carbon, from the expected values. The atoms do, however, appear to be planar within the limits of the present accuracy. As with the bromo- compound no conclusions about the thermal vibrations can be drawn at this stage because possible errors in the positional parameters may be causing anomalous values of the temperature parameters.

Comparison of these results with those of Keil and Plieth (1955) is not possible since most of their bond lengths and angles were assumed to obtain the y- coordinates. The two angles they give, are however, in good agreement with the values found here, viz.

$$O - S - O' = 111 \pm 4^{\circ}$$

and $$C - S - C' = 106.3 \pm 2^{\circ}$$

which agree with the present values of

$$O - S - O' = 111.9^{\circ}$$

and $$I - S - I' = 106.5^{\circ}.$$

5. Final Discussion.

Although the accuracy of analysis aimed at has not yet been achieved for the structures of 4-4'-dibromodiphenyl sulphone and 4-4'-diiododiphenyl sulphone, it is fortunate that the highest accuracy which has so far been attained is in those details of the molecular geometry which are of most interest. In particular, since the halogen and sulphur atoms are those most accurately determined, the X - S - X' angle will be sufficiently well determined that the values are not expected to change significantly with further refinement. Examination of Table 12 shows that the positions of the chlorine and sulphur atoms did not change significantly during the ORACLE refinement. These values are

$$\mathrm{Cl - S - Cl'} = 101.8^\circ$$

$$\mathrm{Br - S - Br'} = 102.3^\circ$$

$$\mathrm{I - S - I'} = 106.5^\circ.$$

This shows that the increase in this X - S - X' angle is in fact present as suggested in Section 1.1. The relatively large increase in this angle from X = Br to X = I is somewhat surprising but is thought to be genuine. Since the molecules are lying on two - fold axes parallel to the b- axis the decrease in the length of this axis reflects the increase in this angle. The lengths of the b- axis in these crystals are

X = Cl	5.009A
X = Br	5.031
X = I	4.946,

The increase in going from the chloro- to the bromo-compound is most likely caused by the increased size of the halogen atom; the decrease on going to the iodo-compound must then result from an increase in the X - S - X' angle. To allow for the increased size of the iodine atom the molecule in the iodo- compound is inclined at a greater angle to the a- axis, resulting in a longer c-axis and a greater β- angle. The angles made by all three molecules with their a- axes and the lengths of their c-axes are

X	Angle with a- axis.	Length of c- axis.
Cl	24.3°	12.259A
Br	24.4°	12.359A
I	29.1°	14.448A.

The bond lengths have not yet been determined with sufficient accuracy to allow any reasonable comparisons to be made. More accurate values for the C_4 - X bond length when X = Br and I can, however, be found. Since, in these last two compounds the positions of the sulphur and halogen atoms are the most accurately determined, the S - X distances will be the most accurate. These are

$$S - Cl = 6.229A$$
$$S - Br = 6.360$$
$$S - I = 6.574$$

and if from these we subtract the value for S - C_4 as measured in the chloro- compound, viz. 4.493A, we obtain the following bond lengths

$$C - Cl = 1.736A$$
$$C - Br = 1.87$$
$$C - I = 2.08.$$

The value for carbon - iodine found in this way is in fact the same as that obtained by direct calculation and agrees with the (assumed) value of Keil and Plieth (1955) of 2.10A. The carbon - bromine distance is, however, considerably shorter than the directly calculated distance of 1.98A and is in much better agreement with the value of Toussaint (1945) of 1.89A.

The sulphur - oxygen bond lengths are again not sufficiently well determined for accurate comparison but their values

in X = Cl, S - 0 = 1.432A
X = Br, S - 0 = 1.36A
X = I, S - 0 = 1.45A

definitely confirm that this bond in sulphone molecules is essentially a pure double bond.

As predicted by Koch and Moffitt (1951), the plane of the aromatic rings is almost at right angles to the X - S - X' plane, the actual angles being

X = Cl	84.6°
X = Br	84.5°
X = I	85.4°.

These values are also remarkably constant. The dihedral angles made by the normals to the two aromatic rings are also fairly constant, the deviation in the iodo- compound not being considered significant; these values are

X = Cl	78.7°
X = Br	78.4°
X = I	74.3°

Table 35.

Comparison of mean B_{11}.

Atom.	Chloro-	Bromo-	Iodo-
Hal.	10.19A^2	9.33A^2	9.63A^2
S	4.53	6.54	6.50
O	5.55	11.18	7.73
C_1	4.56	5.57	6.02
C_2	4.84	9.06	8.52
C_3	6.11	11.31	6.02
C_4	6.98	6.57	4.84
C_5	5.52	8.31	5.51
C_6	4.63	8.21	5.70.

which are in good agreement with the values found in other molecules eg. 75.8° in diphenyl sulphoxide (Abrahams, 1957).

As with the positional parameters, the thermal parameters have not yet been found sufficiently accurately to allow detailed comparisons. The mean values of the principal components B_{11}, B_{22} and B_{33} have been determined for all the atoms in the three compounds and these are compared, as Debye temperature factors, in Table 35. Some interesting features are apparent in these figures; apart from C_3 and O in the bromo- compound the temperature factors for the halogen atoms are the highest in each molecule and suggests that all three molecules probably exhibit a similar type of vibration. One interesting feature of all of these molecules is that the temperature factors for all the atoms on one side of the molecule are consistently higher than on the other, viz. the values of B for C_2 are higher than those for C_6 and for C_3 are higher than for C_5. The reason for this has not been investigated at this stage because of the incompleteness of the refinement of two of the structures but the effect appears to be genuine.

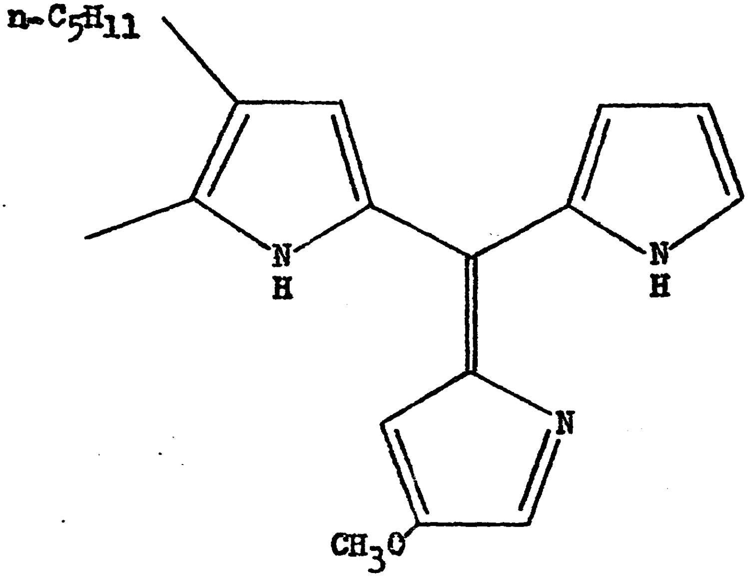
Part III.

Other Compounds Studied.

1. Prodigiosin.

1.1 Introduction.

Prodigiosin is a bacterial pigment and forms crystals in the form of very thin plates. These are very dark brownish red in colour with a greenish lustre. The chemistry of this pigment has been discussed in a series of papers by Wrede and Rothaas (1932,1933a,1933b and 1934). They state that the crystals have no definite melting point but sinter at 70 - 80°C and have a molecular weight of 323. Mass spectrometric evidence (Snedden,1957) confirms this value. The molecular formula for the compound is then $C_{20}H_{25}ON_3$ and the structure suggested is



It is believed that this formulation is reasonably near the truth but confirmation of it is very desirable. An x-ray study of these crystals was thus undertaken using material supplied by Dr.N.J.Cartwright.

Since the prodigiosin molecule has no atom with atomic number higher than 8, attempts were made to introduce one of higher value. Crystals of the 'perchlorate' had been provided by Dr.Cartwright but these were in the form of extremely fine needles and unsuitable for an x-ray study; it was also found to be impossible to grow larger crystals. The preparation of a 'zinc salt' has been described by Wrede and Rothaas(1932) but several attempts to repeat this preparation failed. As prodigiosin has two >N-H groups it was thought likely that a hydrobromide should be formed but the preparation was also unsuccessful.

Finally recrystallisation of prodigiosin from various organic solvents, particularly petroleum ether and methanol, was tried but the crystals formed were no larger than the original ones. The x-ray study was therefore carried out with the largest crystal that could be found.

1.2 Unit Cell Data.

Precession camera photographs were taken with the crystal set about the a - axis using molybdenum K_α radiation ($\lambda = 0.7107A$). The axial dimensions were determined from these photographs and corrected for film shrinkage; the monoclinic cell had the dimensions

$$a = 19.22 \pm 0.01A$$
$$b = 20.55 \pm 0.01$$
$$c = 9.66 \pm 0.01$$
$$\beta = 94.88 \pm 0.25^\circ.$$

The volume of the unit cell (a.b.c.sinβ) is therefore $3{,}800A^3$. The density of the crystals was determined by flotation in aqueous potassium iodide solution and was found to be 1.127 gm/c.c.. This gives the number of molecules per unit cell as 8 and the calculated density as 1.129 gm/c.c.. The total number of electrons per unit cell, F(000) is 1,392.

Examination of photographs of the $h0\ell$, hk0 and hkl zones showed that the absent spectra were in

$hk\ell$ when $h + k + \ell$ is odd

$h0\ell$ when h or ℓ is odd

0k0 when k is odd.

This indicates that the space group is either the

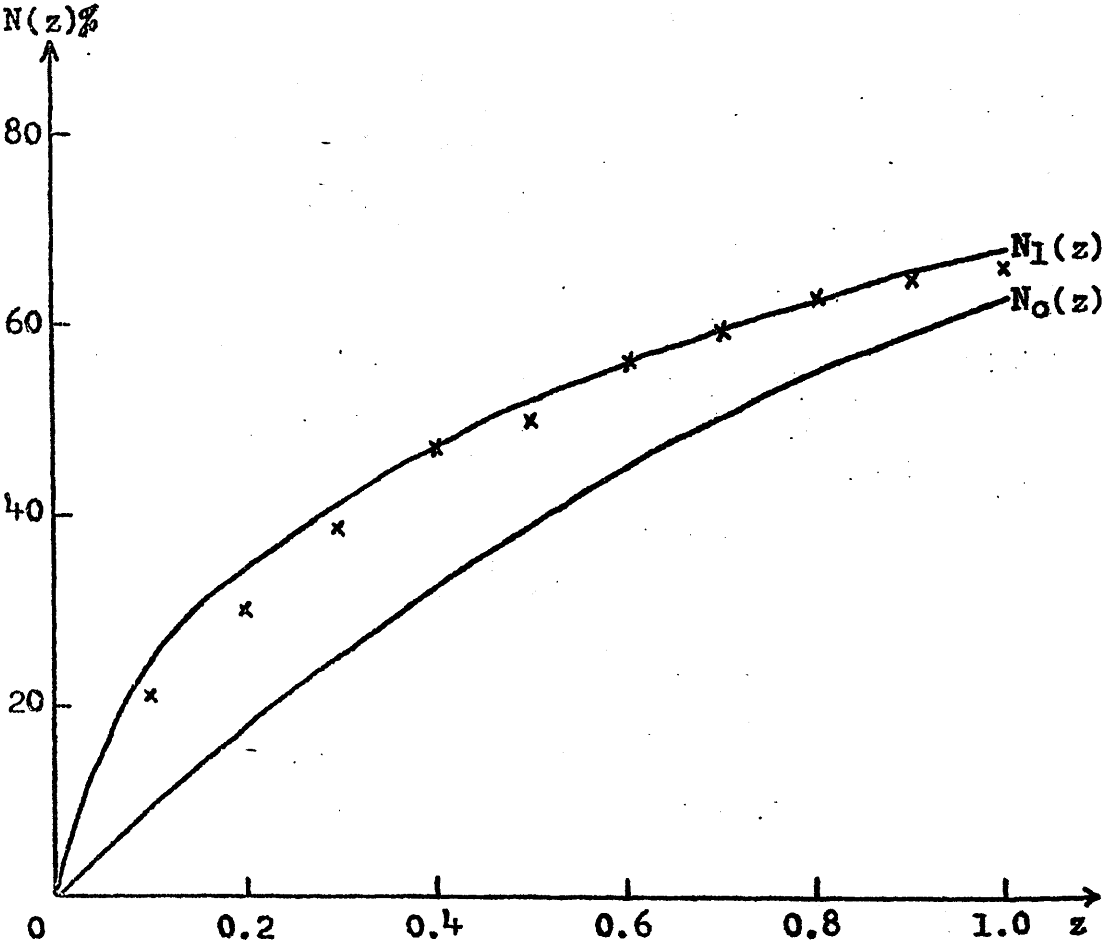


Fig. 18. N(z) test for Prodigiosin: the crosses indicate the experimental data.

centrosymmetric C_{2h}^{6} - $I_{2/a}$, or the non-centrosymmetric C_{s}^{4} - I_a.

1.3 Intensity data.

Since the c- axis is the shortest, hk0 data were collected as a series of timed exposures, using a precession camera and molybdenum K_α radiation from a stabilised x-ray generator. The intensities were estimated visually and corrected with Lorentz and polarisation factors obtained using the charts of Grenville - Wells and Abrahams(1952). The ratio of the strongest to the weakest intensity was 8,748 to 1.

As the space group $I_{2/a}$ is centrosymmetric in all of its projections and I_a has no centrosymmetric projections, a test for centrosymmetry on any zone of intensities should indicate which of the two possible space groups is correct. Consequently, the N(z) test of Howells, Phillips and Rogers(1950) was applied to the hk0 data. This gave the following result which is shown graphically in Fig.18.

z	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
N(z)%	21.0	29.5	38.3	47.7	50.0	56.1	59.5	61.5	65.2	66.2

From this information the correct space group

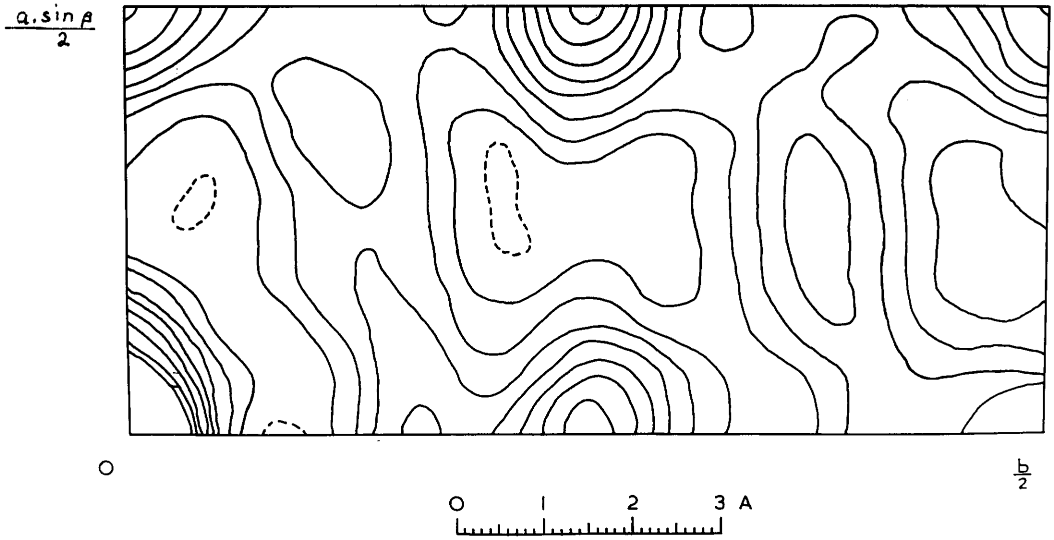


Fig. 19. Prodigiosin - hk0 Patterson map.

Contours arbitrary.

appears to be the centrosymmetric C_{2h}^{6} - $I_{2/a}$.

1.4 Patterson synthesis.

Using the structure factors for the hk0 zone the Patterson projection down the c- axis was computed. This map is shown in Fig.19. It can be seen that this has relatively few features and has proved to be uninterpretable. This was not entirely unexpected because of the comparitively long c- axis (9.66A), which means that there will be considerable overlap of the atoms in this projection. The absence of any 'heavy atom' also means that no vector peaks will be sufficiently well resolved to indicate the molecular orientation.

1.5 Conclusions.

In order to solve the structure of the prodigiosin molecule one of two proceedures will have to be adopted: both of these involve preparing more suitable crystals.

Probably the simpler would be to prepare a derivative containing a heavy atom which would then give the possibility of a two - dimensional analysis if the derivative had a short axis. The second method is to obtain larger crystals of prodigiosin which would be suitable for the collection of three - dimensional data. This method demands computing facilities which were not available when this study was carried out.

2. Fumagillin.

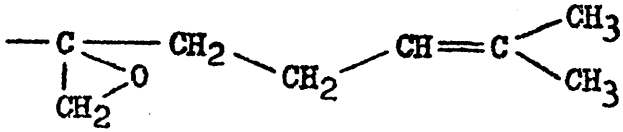
2.1 Introduction.

The discovery of fumagillin followed observations of its activity against bacteriophage (Elbe and Hanson, 1951; Asheshov, Strelitz and Hall, 1952). Fumagillin, is a metabolite of Aspergillus Fumigatus and has recently aroused some interest as an anticancer agent. This together with its other biological properties make the elucidation of its structure a matter of particular interest.

Chemical approach has proved very difficult owing to the tendancy of the molecule to undergo complex rearrangements and as yet the final structure has not been determined. It has been shown (Schenck, Hargie, Tarbell and Hoffman, 1953; Brown and Landquist, 1953) that fumagillin, $C_{26}H_{34}O_7$, is rapidly hydrolysed by cold 0.1 N sodium hydroxide solution giving an alcohol, $C_{16}H_{26}O_4$ and designated alcohol - 1, and octa-1:3:5:7-tetraene-1:8-dicarboxylic acid. Alcohol - 1 has been the subject of most of the investigation so far, and has been attributed the following features

(i) a carbocyclic ring with a secondary hydroxyl on it,

(ii) a side chain



(iii) an ether ring

(iv) a methoxyl group.

Alcohol - 1 may also be reduced to another alcohol known as tetrahydroalcohol - lab in which itiis assumed that the double bond in the side chain has been saturated and the epoxide ring has been hydrogenolysed. Treatment of the latter alcohol with p-bromobenzenesulphonyl chloride in pyridine has resulted in a crystalline compound of formula $C_{22}H_{32}O_6SBr$, molecular weight 505.5, in which the 'brosyl' group is presumably attached to the secondary hydroxyl of the carbocyclic ring. These crystals take the form of large colourless prisms which have a melting point of 103 - 104°C and were used for the x-ray study. They have the disadvantage of being sensitive to heat, decomposition occuring even on standing for 24 hours in a warm room. Fortunately they did not prove too unstable in an x-ray beam provided that the room was kept as cold as possible. The chemical study has been the subject of a series of papers, see Cross and Tarbell (1958) and earlier papers.

A previous x-ray study has been made on the parent compound, fumagillin, by Brown and Landquist (1953) to determine its molecular weight. They found that the unit cell of this compound was monoclinic with

$$\begin{aligned} a &= 15.62\text{A} \\ b &= 13.68 \\ c &= 6.05 \\ \beta &= 92.2^{\circ} \end{aligned}$$

The space group is $P2_1$ and there are two molecules in the unit cell, whence the molecular weight is 458.

2.2 Unit cell data.

Precession camera photographs were taken of a crystal of the brosyl derivative of tetrahydroalcohol-lab set about the b- axis. Molybdenum K_α radiation ($\lambda = 0.7107$A) was used, and photographs were taken of the hk0 and 0kℓ zones. The axial lengths were measured from these photographs and corrected for film shrinkage; the monoclinic cell had the dimensions

$$\begin{aligned} a &= 16.80 \pm 0.01\text{A} \\ b &= 6.12 \pm 0.01 \\ c &= 11.77 \pm 0.01 \\ \beta &= 97.25 \pm 0.2^{\circ}. \end{aligned}$$

The β- angle was measured from an h0ℓ Weissenberg photograph. The volume of the unit cell (a.b.c.sinβ) is thus 1199A^3. The density of the crystals was determined by flotation in aqueous potassium iodide solution and found to be 1.38 gm/c.c.. This gives the number of molecules per unit cell as two and a calculated density of 1.40 gm/c.c.. The total number of electrons in the unit cell is then F(000) = 526.

Examination of photographs of the hk0, 0kℓ, h0ℓ and h1ℓ zones showed that the only absent spectra were in 0k0 when k is odd. The space group is therefore either C_2^2 - $P2_1$ or C_{2h}^2 - $P2_1/m$. The second of these can be eliminated as it demands four equivalent positions; with only two molecules in the cell this infers some molecular symmetry which is not present without disorder.

2.3 Intensity data.

An h0ℓ series was taken on the modified Weissenberg camera of Abrahams (1954) design using molybdenum K_α radiation. The multiple film pack technique was used for this with Ilford Industrial - G film interleaved with 0.0008" nickell foils. The ratio of the strongest to the weakest of the visually estimated intensities was 31,579 to 1. Lorentz and polarisation correction factors were applied to this data by the program written for the DEUCE computer (Appendix 2). The 518 structure factors resulting from this are listed in Appendix 1(e) scaled to the last set of calculated structure factors.

2.4 Structure analysis.

Since the molecule contains two relatively heavy atoms, bromine and sulphur, it was hoped that the 'heavy atom' method would be very likely to yield a solution to the structure. If the sum of the squares of the atomic numbers of the heavy atoms is greater than the sum of the squares of the atomic numbers of the light atoms, and if the positions of the heavy atoms are known, the structure factors calculated for these atoms should have sufficient of the phases correct to give a Fourier synthesis which will show the positions of at least some of the other atoms (Lipson and Cochran, 1953). For this compound Σf^2(heavy atoms) = 1,421 and Σf^2(light atoms) = 1,209 and so if the bromine and sulphur atoms can be located the Fourier synthesis based on these should lead to the solution of the structure.

As there are only two bromine atoms in the unit cell it was hoped that a Patterson projection onto the centrosymmetric $h0\ell$ zone would reveal the position of

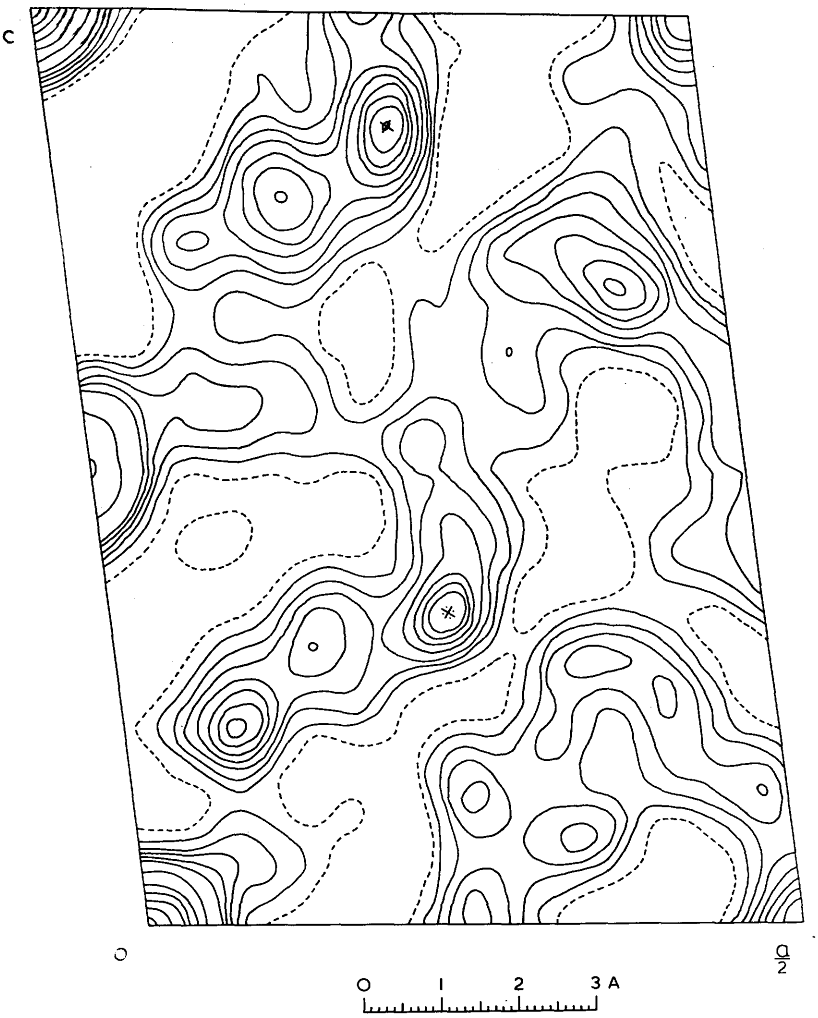


Fig. 20. h0l Patterson map of Fumagillin (derivative). Contour interval arbitrary.

the Br - Br vector. Accordingly the F^2 data for the h0ℓ zone, on an arbitrary scale, was used to compute a Patterson synthesis; this is shown in Fig.20.

The Br - Br vector is marked on this map with a cross. Since the b- axis is relatively short it was considered that the Br - S vector which is actually 6.36A long would be about 5A long in this projection. Accordingly a vector peak was sought at this distance from the origin, it was found at 5.7A and is marked in Fig. 20 with an asterisk. The coordinates of the bromine and sulphur atoms from this are

	x	z
Br	0.627	0.438
S	0.372	0.100.

The structure factors based on these positions with a temperature factor of $B = 3.6A^2$ gave an R- factor of 0.61. After rejecting about 1/5 th of the structure factors for which |F(calc)| was small, an h0ℓ Fourier synthesis was computed. This map showed the bromine and sulphur atoms in the expected places and about 20 other peaks. Using the coordinates for these peaks together with new bromine and sulphur positions a new set of

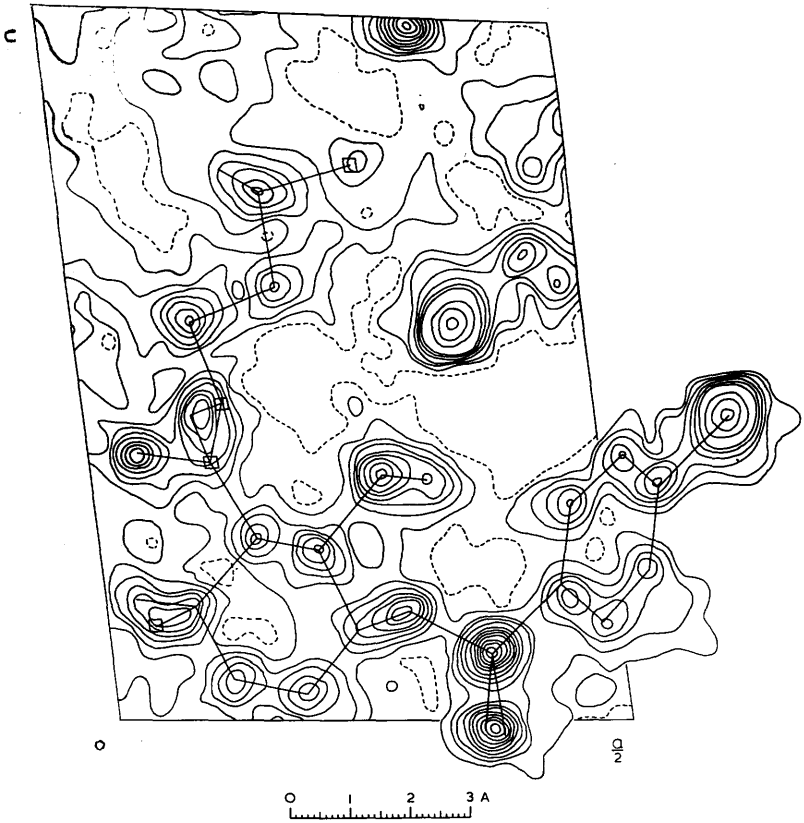


Fig. 21. h0l Fourier map. Contours at 1 e/A^2 except on sulphur and bromine. After 4 e/A^2 the interval is 2 e/A^2 on sulphur and 5 e/A^2 on bromine. Zero contour is dashed.

structure factors was calculated; these gave R = 0.51. Four further Fourier series and structure factor calculations were then performed resulting in an R- factor of 0.36 for the 26 atoms included. The last Fourier synthesis computed from these structure factors is shown in Fig.21. An outline of the postulated structure is shown on this - the atomic positions marked with a square are those not included in the final structure factor calculation. The numbering system corresponding to this structure is shown in Fig.22 and the final coordinates for all of the atoms are given in Table 36. The structure factors calculated from these are listed in Appendix 1(e).

In order to confirm the positions of these atoms and find the others not included in the last set of structure factors an error synthesis was computed at this stage using $F_o - F_c$ as coefficients for the Fourier series. This map is shown in Fig.23; it shows where the errors in the atomic positions are and none of the atoms appear to be completely wrong, except for one of the sulphone oxygen atoms. The positive peak on the sulphur atom position and the negative area where the two oxygen atoms have been placed suggests that the two oxygen atoms are not so close

Table 36.

Two dimensional coordinates.

Atom.			Atom.		
Br	.3701	.5642	C_8	.3320	.3438
S	.3700	.0971	C'_9	.1142	.3620
O_1	.2827	.1510	C'_{10}	.1348	.4448
O'_2	.0447	.1353	C_{11}	.1141	.5642
O_3	.2859	.3446	C_{12}	.2055	.6256
O_4	.1146	.4312	C_{13}	.2009	.7487
O_5	.3535	.9850	C_{14}	.1440	.7800
O_6	.3700	.9775	C'_{15}	.2893	.7770
C_1	.1818	.0352	C_{16}	.0460	.3746
C_2	.1167	.0583	C_{17}	.4515	.1811
C_3	.0731	.1436	C_{18}	.4843	.1342
C_4	.1554	.2635	C_{19}	.4631	.7744
C_5	.2137	.2478	C_{20}	.4505	.6683
C_6	.2285	.1250	C_{21}	.4816	.6229
C_7	.0217	.1633	C_{22}	.4653	.3088

' not included in last set of structure factors.

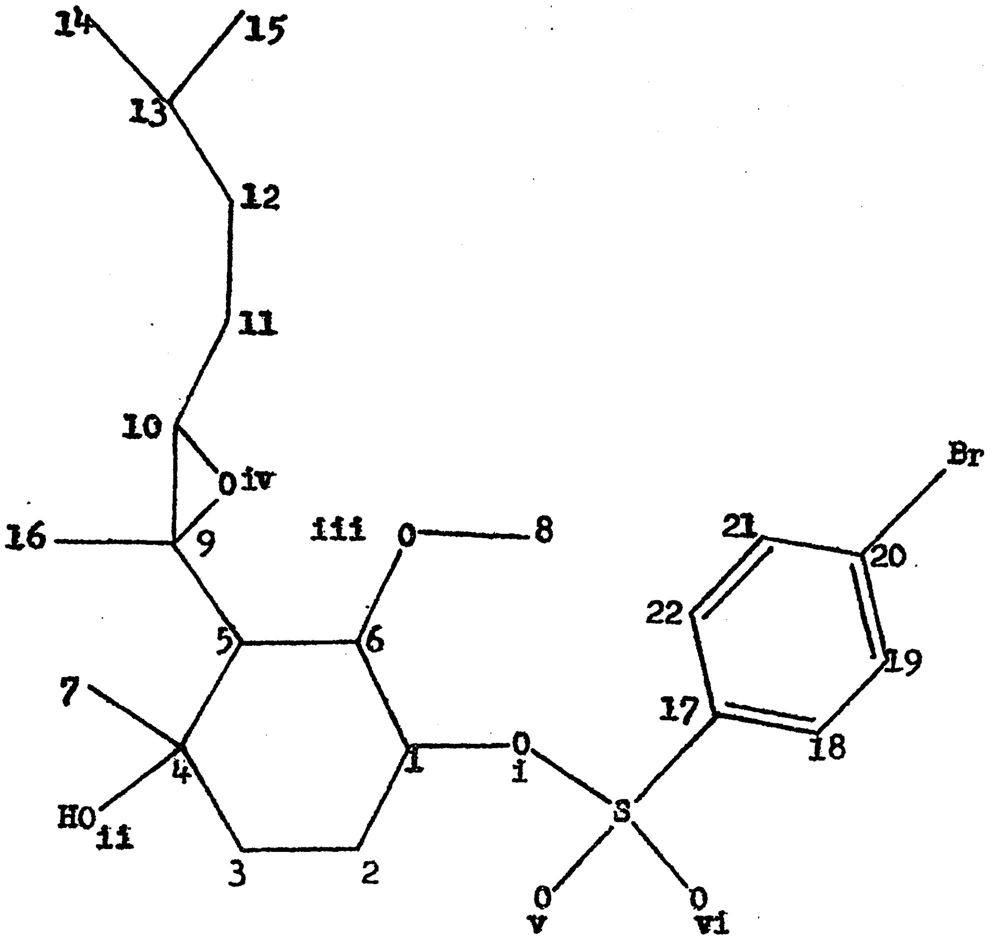


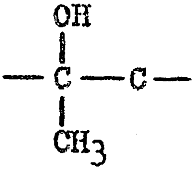
Fig. 22. Numbering system in Fumagillin (derivative)
Oxygen atoms numbered in italics.

Fig. 23. h0l difference map. Contours at 1 e/A^2 intervals. Zero contour is dot-dashed, negative dashed.

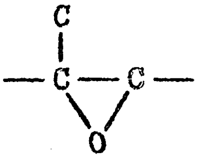
in projection, but that one of them lies directly above (or below) the sulphur atom. The map does, however, show that some of the atoms require to be moved slightly, in particular the bromine atom.

2.5 Discussion.

While the structure of this compound has not been determined completely unambiguously, it is felt that the structure shown is probably reasonably correct - the error synthesis seems to confirm this. So far it has not been possible, and probably will not be in projection, to distinguish between



and



in the side chain, the latter being the one shown because of more recent chemical evidence (McCorkindale, 1959). It is also now thought that the 'ether' ring mentioned in 2.1 is in fact the epoxide in the side chain and the epoxide which has been opened by the reduction of alcohol - 1 is in fact on the six - membered ring. This carbocyclic ring is consequently shown with a tertiary hydroxyl group.

To distinguish between these possibilities and determine the other stereochemistry of the molecule it is clear that a three dimensional study must be undertaken. This should not prove too difficult since once the data has been collected, the phases of the structure amplitudes can be immediately calculated without firstly computing a three dimensional Patterson synthesis. This is possible because the origin of the unit cell can be chosen anywhere along the two - fold screw axis; it may therefore be chosen so as to make the y- coordinate of the bromine atom equal to zero. If this atom alone were included in the structure factor calculation a false centre of symmetry would be induced in the structure resulting in the superposition on the structure of its mirror image..This difficulty may be overcome by including the coordinates of the sulphur atom and of the atoms of the benzene ring whose y- coordinates may be calculated using the known dimensions of the p-bromobenzene sulphonyl group(see Part II). The phase angles based on these coordinates should lead to a rapid solution of this structure in three dimensional space.

APPENDICES.

APPENDIX 1.

Structure Factor Data.

1(a). 4-4'-dichlorodiphenyl sulphone.

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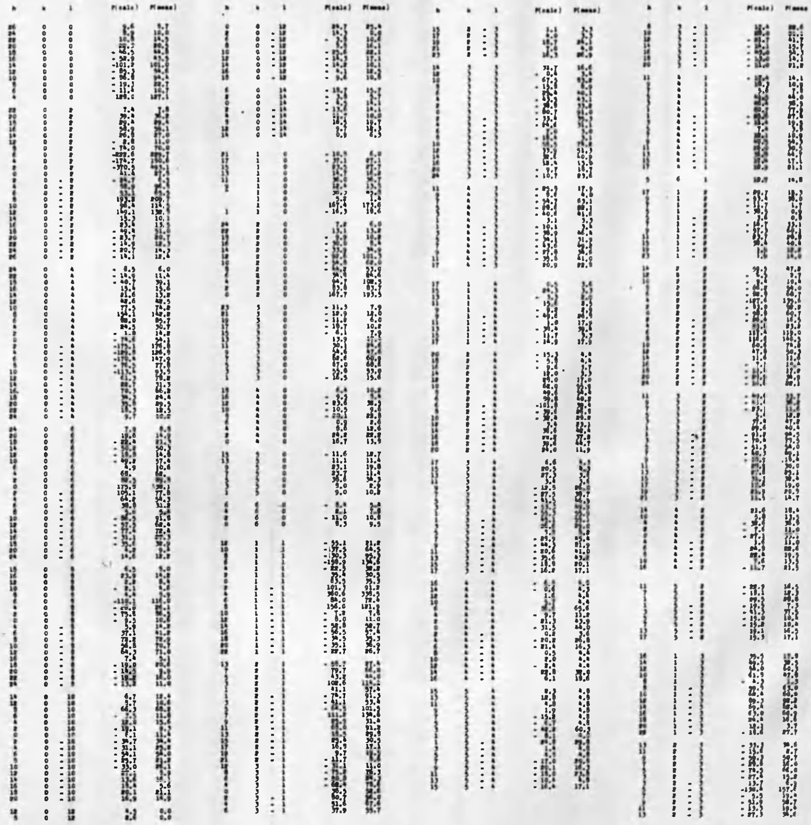
1(b). 4-4'-dibromodiphenyl sulphone.



1(c). 4-4'-diiododiphenyl sulphone.

h	k	l	F(calc)	F(meas)	h	k	l	F(calc)	F(meas)	h	k	l	F(calc)	F(meas)	h	k	l	F(calc)	F(meas)
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

(d) Prodigiosin Structure Factors.

h	k	ℓ	F_o
14	0	0	2.6
12	0	0	2.2
10	0	0	2.8
8	0	0	11.7
6	0	0	2.3
4	0	0	38.6
13	1	0	1.1
11	1	0	4.6
9	1	0	2.0
7	1	0	2.2
5	1	0	10.1
3	1	0	16.8
16	2	0	1.5
14	2	0	1.1
12	2	0	3.2
10	2	0	<0.7
8	2	0	5.4
6	2	0	3.9
4	2	0	5.2
13	3	0	1.8
11	3	0	<0.7
9	3	0	2.5
7	3	0	3.2
5	3	0	1.8
3	3	0	6.3
1	3	0	14.7
18	4	0	0.9
16	4	0	<0.9
14	4	0	<0.8
12	4	0	0.8
10	4	0	<0.7
8	4	0	9.4
6	4	0	2.3
4	4	0	27.0
2	4	0	9.7
0	4	0	8.8

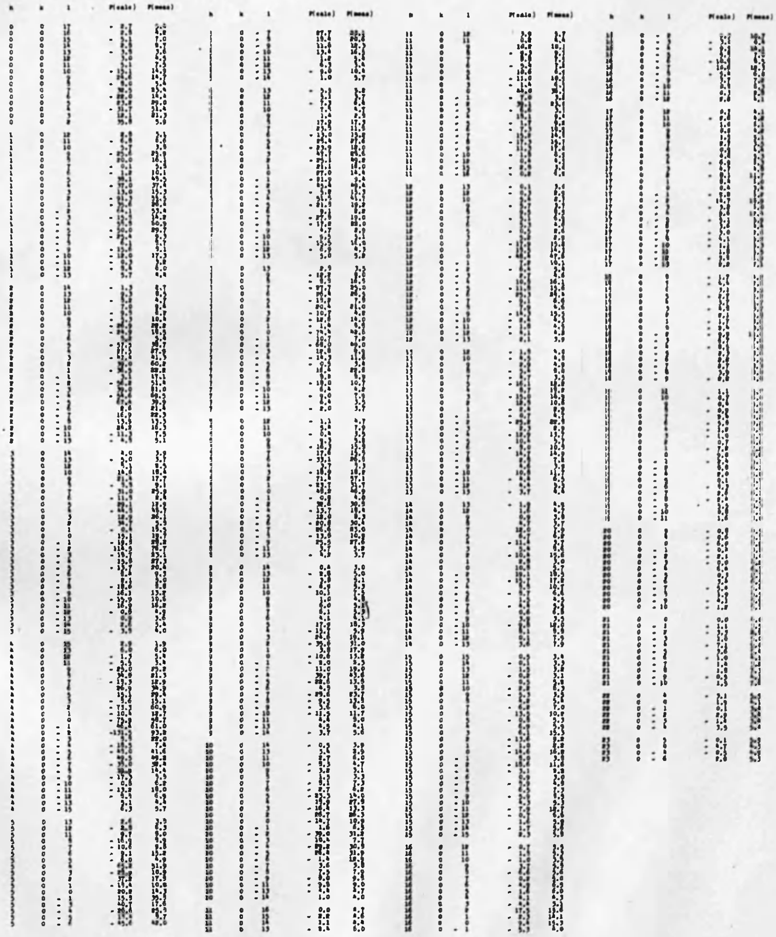
h	k	ℓ	F_o	h	k	ℓ	F_o
17	5	0	3.5	15	7	0	<0.9
15	5	0	<0.8	13	7	0	1.7
13	5	0	5.2	11	7	0	<0.8
11	5	0	<0.8	9	7	0	<0.8
9	5	0	3.2	7	7	0	4.4
7	5	0	4.3	5	7	0	6.6
5	5	0	4.1	3	7	0	12.1
3	5	0	13.3	1	7	0	12.7
1	5	0	15.0				
				18	8	0	1.6
14	6	0	3.8	16	8	0	1.8
12	6	0	1.8	14	8	0	3.1
10	6	0	1.1	12	8	0	3.4
8	6	0	2.5	10	8	0	0.8
6	6	0	5.8	8	8	0	1.1
4	6	0	3.8	6	8	0	1.8
2	6	0	10.3	4	8	0	6.7
0	6	0	4.1	2	8	0	2.3
				0	8	0	19.7
17	7	0	2.3				

h	k	ℓ	F_o
15	9	0	2.9
13	9	0	<0.9
11	9	0	4.2
9	9	0	<0.8
7	9	0	<0.8
5	9	0	5.1
3	9	0	2.8
1	9	0	2.6
14	10	0	3.5
12	10	0	<0.9
10	10	0	3.0
8	10	0	<0.8
6	10	0	2.8
4	10	0	<0.8
2	10	0	2.7
0	10	0	<0.8
11	11	0	1.3
9	11	0	<0.9
7	11	0	<0.8
5	11	0	<0.8
3	11	0	2.6
1	11	0	3.3
16	12	0	0.9
14	12	0	0.9
12	12	0	<0.9
10	12	0	1.3
8	12	0	0.9
6	12	0	2.7
4	12	0	3.6
2	12	0	2.4
0	12	0	7.9
13	13	0	0.9
11	13	0	<0.9
9	13	0	<0.9
7	13	0	<0.9
5	13	0	3.2

h	k	ℓ	F_o
3	13	0	1.7
1	13	0	5.0
6	14	0	1.6
4	14	0	<0.9
2	14	0	<0.9
0	14	0	2.3
9	15	0	0.9
7	15	0	3.0
5	15	0	<0.9
3	15	0	3.9
1	15	0	0.9

h	k	ℓ	F_o
2	16	0	0.9
0	16	0	<0.9
11	17	0	1.0
9	17	0	<0.9
7	17	0	<0.9
5	17	0	0.9
3	17	0	0.9
1	17	0	<0.9
4	18	0	0.9
2	18	0	<0.9
0	18	0	<0.9.

1(e). Fumagillin.



APPENDIX 2.

DEUCE Programs.

This appendix contains details of a number of programs which have been written for the electronic digital computer, DEUCE, situated in the Computing Laboratory of the University of Glasgow.

Brief description.

DEUCE is a serial machine with numbers and instructions consisting of 32 binary digits; the digit rate is one million per second. Punched cards form the input - output medium. The store comprises

(i) 402 words in mercury delay lines (access time, 32 - 1024 microseconds) and

(ii) 8192 words on the magnetic drum (access time, approx. 13 - 48 milliseconds).

Programming Aids.

There are a number of "automatic programming" aids. Using these it is possible to write programs in a language more sophisticated than the basic machine language and 'closer' to accepted mathematical usage. A number of programs are available which translate from a variety of these subject languages to the object language viz, the basic machine language. The following interpretive program has been used.

Alphacode.

This program handles protracted calculations involving single variables; it is best used on so-called "one-off" jobs e.g., exploratory calculations in research studies.

In this case, simplicity of programming is achieved at the expense of the speed of the subsequent operation. For repetitive or standard calculations it may be better to reverse the emphasis and spend time in producing a fast program, making efficient use of the machine facilities. The burden of this 'optimum coding' is reduced considerably by a special translation program, STAC.

STAC. (Storage Allocation and Coding Program).

This program translates instructions from a semi-symbolic form to the fundamental form required by the control circuits of DEUCE.

Program 1.

Description.

This program evaluates the least squares plane through a number of atoms; each atom can be given a different weighting factor. The distances of all the atoms from the plane are also determined.

Input.

This consists of the unit cell dimensions (monoclinic cell) and sets of fractional coordinates and weighting factors.

Output.

The orthogonal coordinates in Angstroms for each atom; the equation of the plane; the distances of all of the atoms from it and the mean and root mean square of these distances.

Time.

Approximately 2 minutes for 9 atoms.

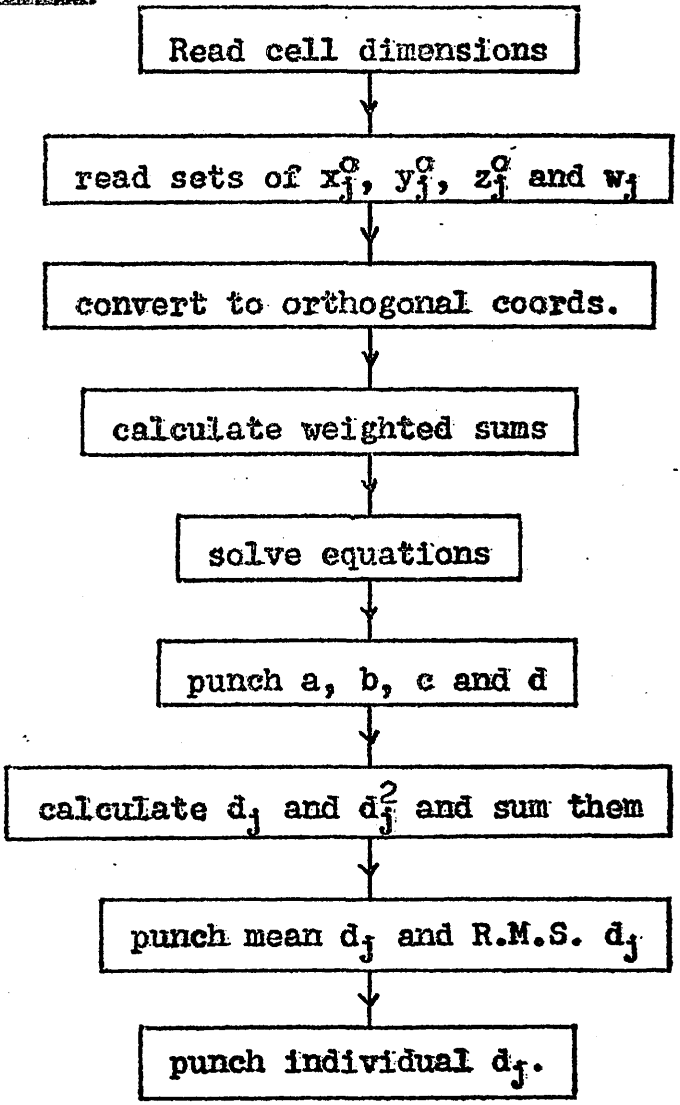
System.

Alphacode.

Method.

The coordinates are first converted to orthogonal coordinates by

Flow diagram.



$$x_j = a.x_j^o + c.z_j^o.\cos\beta$$
$$y_j = b.y_j^o$$
$$z_j = c.z_j^o.\sin\beta$$

If the plane has equation

$$a.x + b.y + c.z + d = 0$$

then the normal equations are

$$a.\Sigma w_j x_j^2 + b.\Sigma w_j x_j y_j + c.\Sigma w_j x_j z_j + d.\Sigma w_j x_j = 0$$
$$a.\Sigma w_j x_j y_j + b.\Sigma w_j y_j^2 + c.\Sigma w_j y_j z_j + d.\Sigma w_j y_j = 0$$
$$a.\Sigma w_j x_j z_j + b.\Sigma w_j y_j z_j + c.\Sigma w_j z_j^2 + d.\Sigma w_j z_j = 0$$

where the summations are over all of the j atoms. These equations are solved for b, c, and d by putting $a = 1$. The distance of the jth atom from the plane is then

$$d_j = \frac{a.x_j + b.y_j + c.z_j + d}{(a^2 + b^2 + c^2)^{\frac{1}{2}}} .$$

Program 2.

Description.

This program calculates the T and ω tensors of Cruickshank (1956a). The program is in five sections.

Input.

The monoclinic cell dimensions, fractional coordinates, temperature parameters from the expression

$$\exp -(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}\ell^2 + \beta_{12}hk + \beta_{23}k\ell + \beta_{31}\ell h),$$

and the direction cosines and origin of the molecular axes.

Output.

$U_{ij}^{obs.}$ and $U_{ij}^{calc.}$ with respect to the molecular axes, the components of T_{ij}, ω_{ij}, $\sigma(T_{ij})$ and $\sigma(\omega_{ij})$.

Time.

Approximately 10 minutes for sections 1 and 2 with nine atoms. Section 3 takes about 1½ minutes and section 4 10 minutes. The last section requires about 5 minutes. These sections cannot all be run consecutively as the output and input forms of the data are incompatible.

System.

Sections 1,2 and 5 are alphacode.

Section 3 is LE01 - solve n simultaneous linear equations where $n \leqslant 14$.

Section 4 is LV01 - invert nth order matrix with $n \leqslant 83$.

These last two sections are DEUCE library programs.

Method.

The coordinates are transformed to orthogonal axes as defined in program 1, the origin is then changed and they are converted to molecular axes by

$$\begin{pmatrix} x_m \\ y_m \\ z_m \end{pmatrix} = \begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} . \begin{pmatrix} x_j \\ y_j \\ z_j \end{pmatrix}$$

where the a_{ij} are the direction cosines of the molecular axes with respect to the orthogonal axes.

The temperature parameters are then transformed to the same orthogonal axes by

$$b_{11} = a^2\beta_{11} + c^2\beta_{33}\cos^2\beta + 2ca\beta_{31}\cos\beta$$

$$b_{22} = b^2\beta_{22}$$

$$b_{33} = c^2\beta_{33}\sin^2\beta$$

$$b_{12} = ab\beta_{12} + bc\beta_{23}\cos\beta$$

$$b_{23} = bc\beta_{23}\sin\beta$$

$$b_{13} = c^2\beta_{33}\sin\beta.\cos\beta + ca\beta_{13}\sin\beta$$

(Rollett & Davies, 1955).

The b_{ij} are then transformed to molecular axes by

$$U_{ij} = a_{ik} . a_{kj} . b_{ij}$$

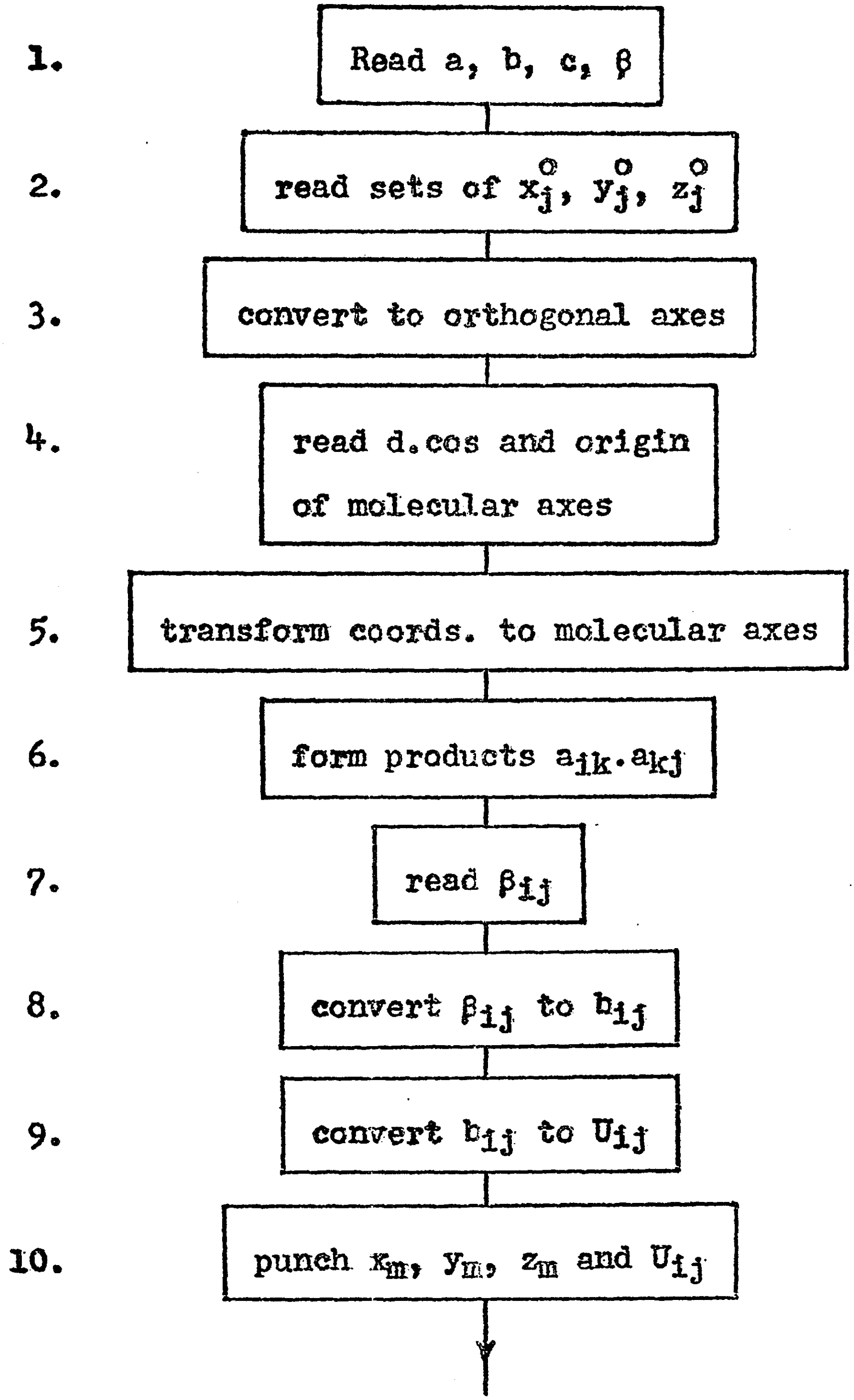
(Nye, 1957).

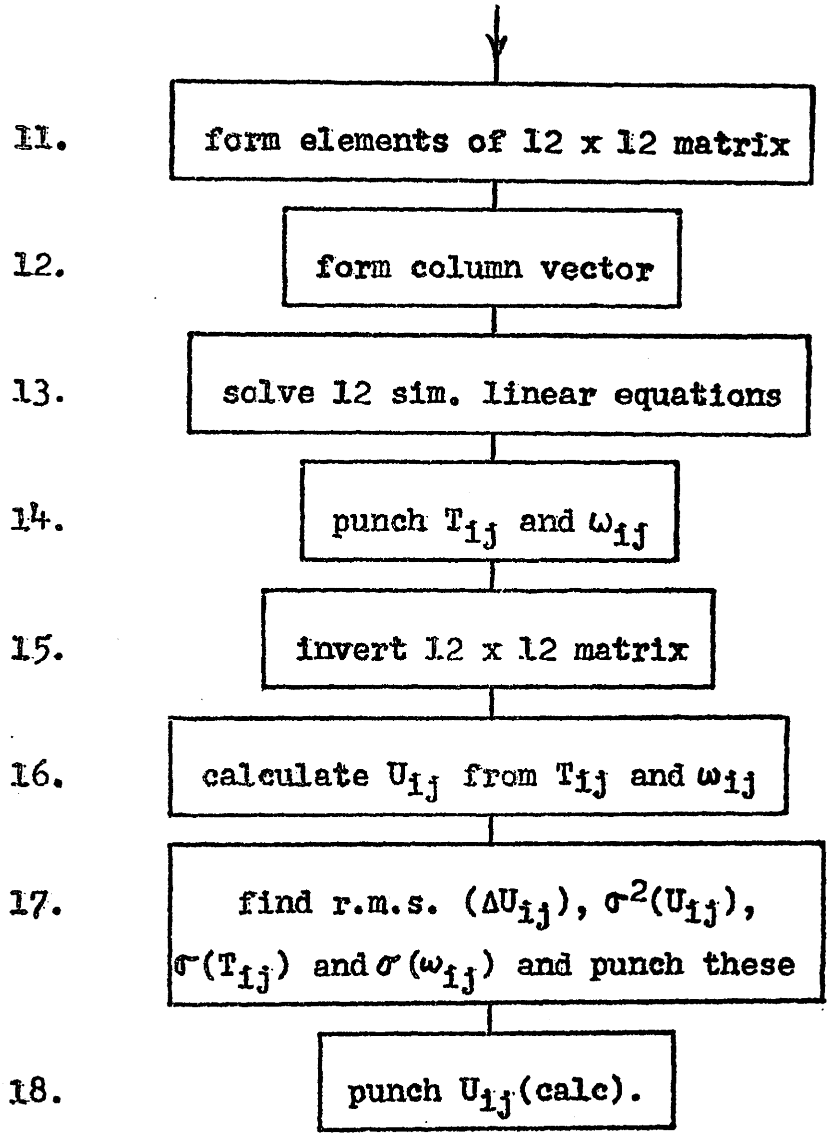
The method then follows that described by Cruickshank.

Flow Diagram.

Section 1 is blocks 1 - 10
2 11,12
3 13,14
4 15
5 16 - 18.

(continued overleaf).


1. Read a, b, c, β
2. read sets of $\overset{o}{x}_j$, $\overset{o}{y}_j$, $\overset{o}{z}_j$
3. convert to orthogonal axes
4. read d.cos and origin of molecular axes
5. transform coords. to molecular axes
6. form products $a_{ik} \cdot a_{kj}$
7. read β_{ij}
8. convert β_{ij} to b_{ij}
9. convert b_{ij} to U_{ij}
10. punch x_m, y_m, z_m and U_{ij}


11. form elements of 12 x 12 matrix
12. form column vector
13. solve 12 sim. linear equations
14. punch T_{ij} and ω_{ij}
15. invert 12 x 12 matrix
16. calculate U_{ij} from T_{ij} and ω_{ij}
17. find r.m.s. (ΔU_{ij}), $\sigma^2(U_{ij})$, $\sigma(T_{ij})$ and $\sigma(\omega_{ij})$ and punch these
18. punch U_{ij}(calc).

Program 3.

Description.

The program corrects intensity values for equi - inclination Weissenberg cameras with Lorentz and polarisation and Tunnell factors. A test is included to ensure that no value of $\sin^2\theta$ is greater than unity.

Input.

Unit cell dimensions (triclinic cell), wavelength of the x-rays and the cosine of the equi - inclination angle for each zone. The intensity data has h, k, ℓ and I punched on one card for each reflection.

Output.

R_{ij} in binary to 31 binary places as required for input data by Rollett's structure programs for DEUCE. This is followed by h, k, ℓ and $|F|$ punched on one card per reflection.

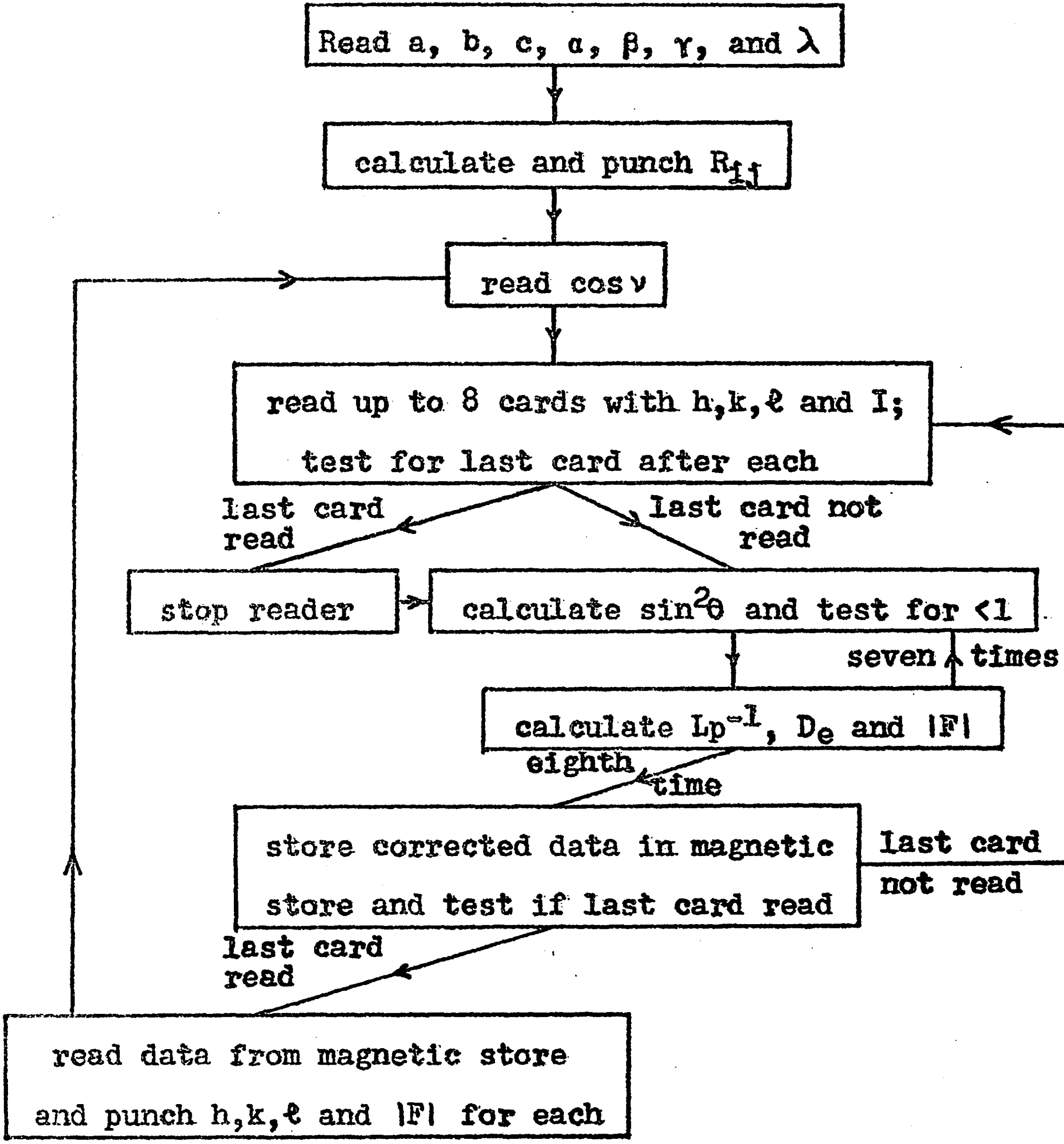
Time.

Approximately 2n + 1 minutes, where n is the number of reflections in hundreds.

System.

Stac.

Flow Diagram.



Method.

$$\sin^2\theta = h^2R_{11} + k^2R_{22} + \ell^2R_{33} + hkR_{12} + k\ell R_{23} + h\ell R_{13}$$

where

$R_{11} = \frac{1}{4}\lambda^2(a^*)^2$ $\quad R_{12} = \frac{1}{2}\lambda^2a^*b^*\cos\gamma^*$

$R_{22} = \frac{1}{4}\lambda^2(b^*)^2$ $\quad R_{23} = \frac{1}{2}\lambda^2b^*c^*\cos\alpha^*$

$R_{33} = \frac{1}{4}\lambda^2(c^*)^2$ $\quad R_{13} = \frac{1}{2}\lambda^2c^*a^*\cos\beta^*$

where $a^*, b^*, c^*, \alpha^*, \beta^*$ and γ^* are the usual reciprocal coordinates. The Lorentz and polarisation factor is

$$Lp^{-1} = \frac{\sin 2\theta}{1 + \cos^2 2\theta},$$

and Tunnell's rotation factor is

$$D_e = \frac{(\cos^2\nu - \cos^2\theta)^{\frac{1}{2}}}{\sin\theta}$$

where ν is the equi - inclination angle.

Then

$$|F| = (I \times Lp^{-1} \times D_e)^{\frac{1}{2}}.$$

Program 4.

Description.

This program has been developed from the preceding one to calculate absorption corrections for a crystal by assuming it to be of cylindrical cross - section. The data used are those given by Bond (1959).

Input.

As in the previous program plus the appropriate absorption curve for the value of $\mu R.\sec\nu$ under consideration.

Output.

One card per reflection punched h, k, ℓ and I(corrected).

Time.

Approximately $2\frac{1}{2}n + 1$ mins., where n is the number of reflections to be corrected in hundreds.

System.

Stac.

Method.

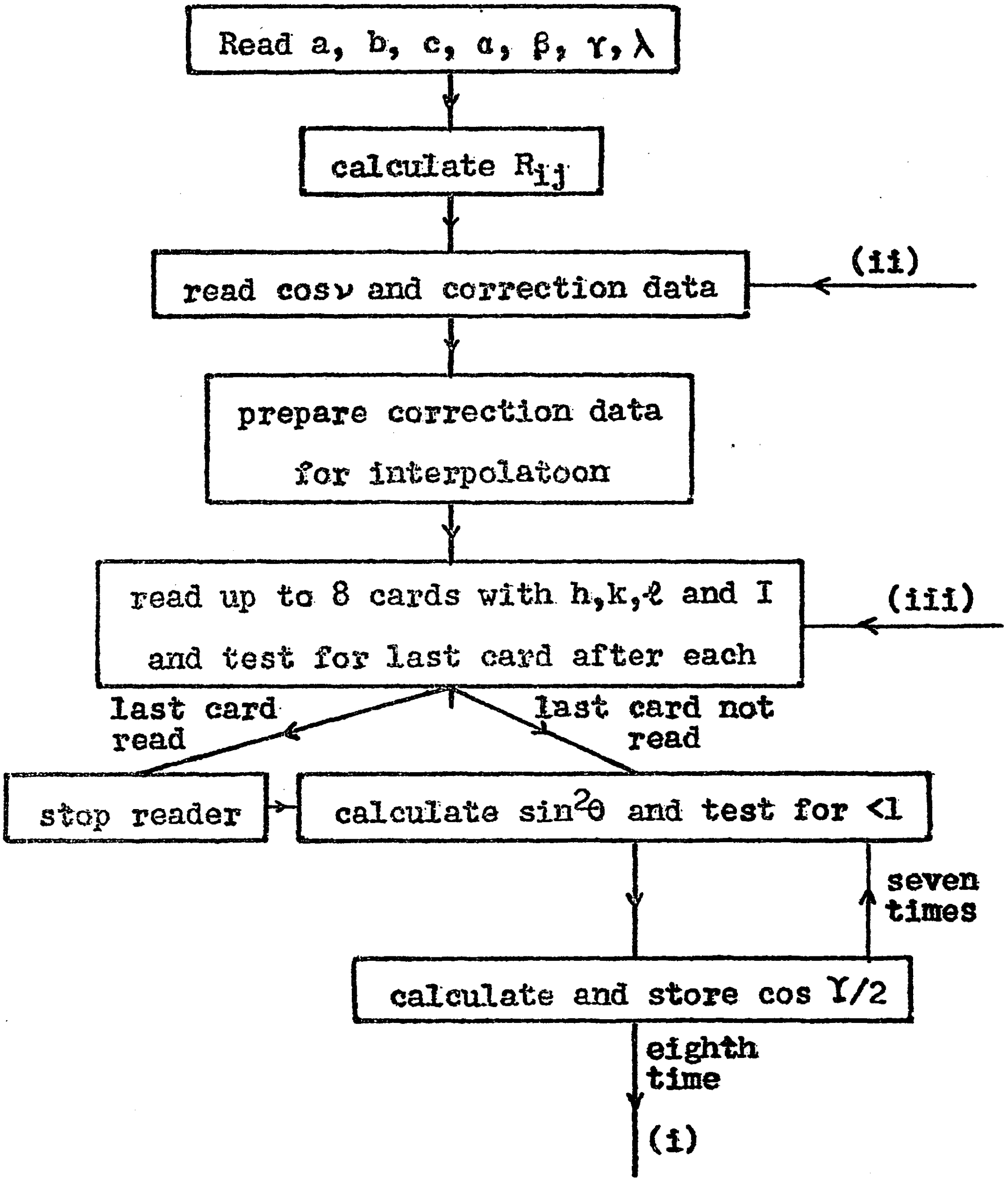
$\sin^2\theta$ is calculated as before and then

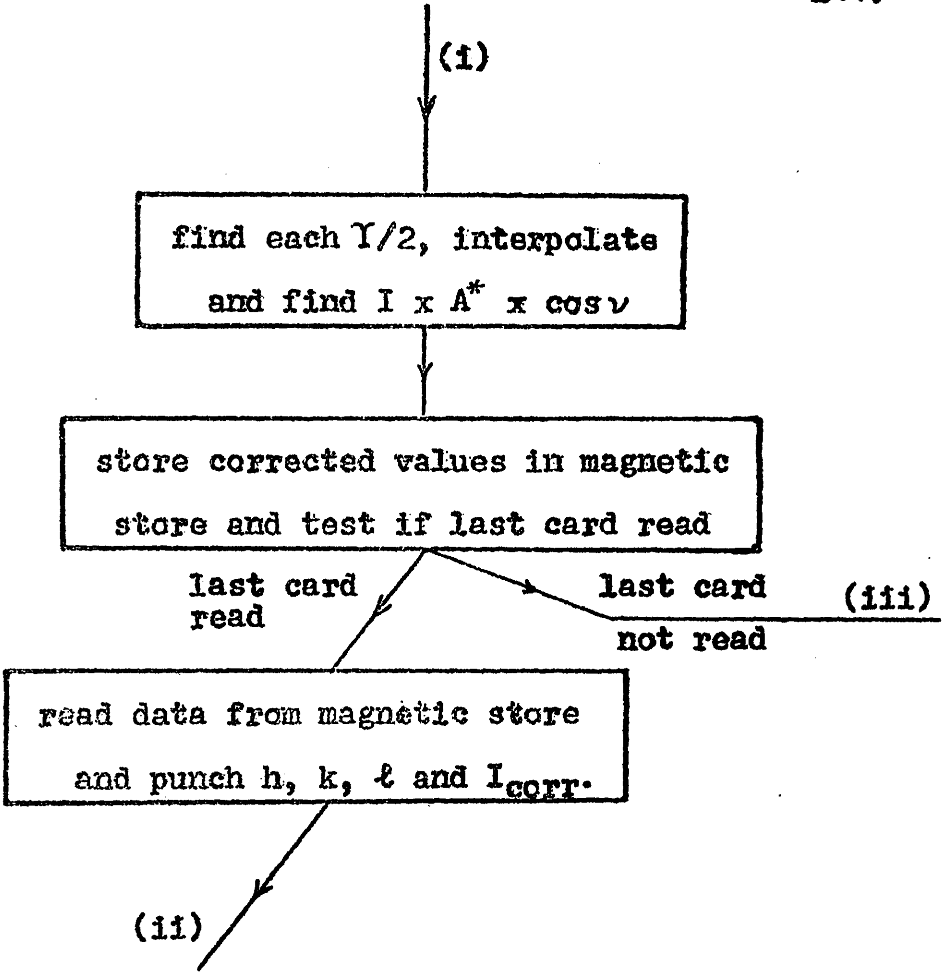
$$\Upsilon/2 = \cos^{-1}\{(1 - \sin^2\theta)^{\frac{1}{2}}/\cos\nu\}$$

This value of $\Upsilon/2$ is used to interpolate, linearly, in the table of A^* values and then

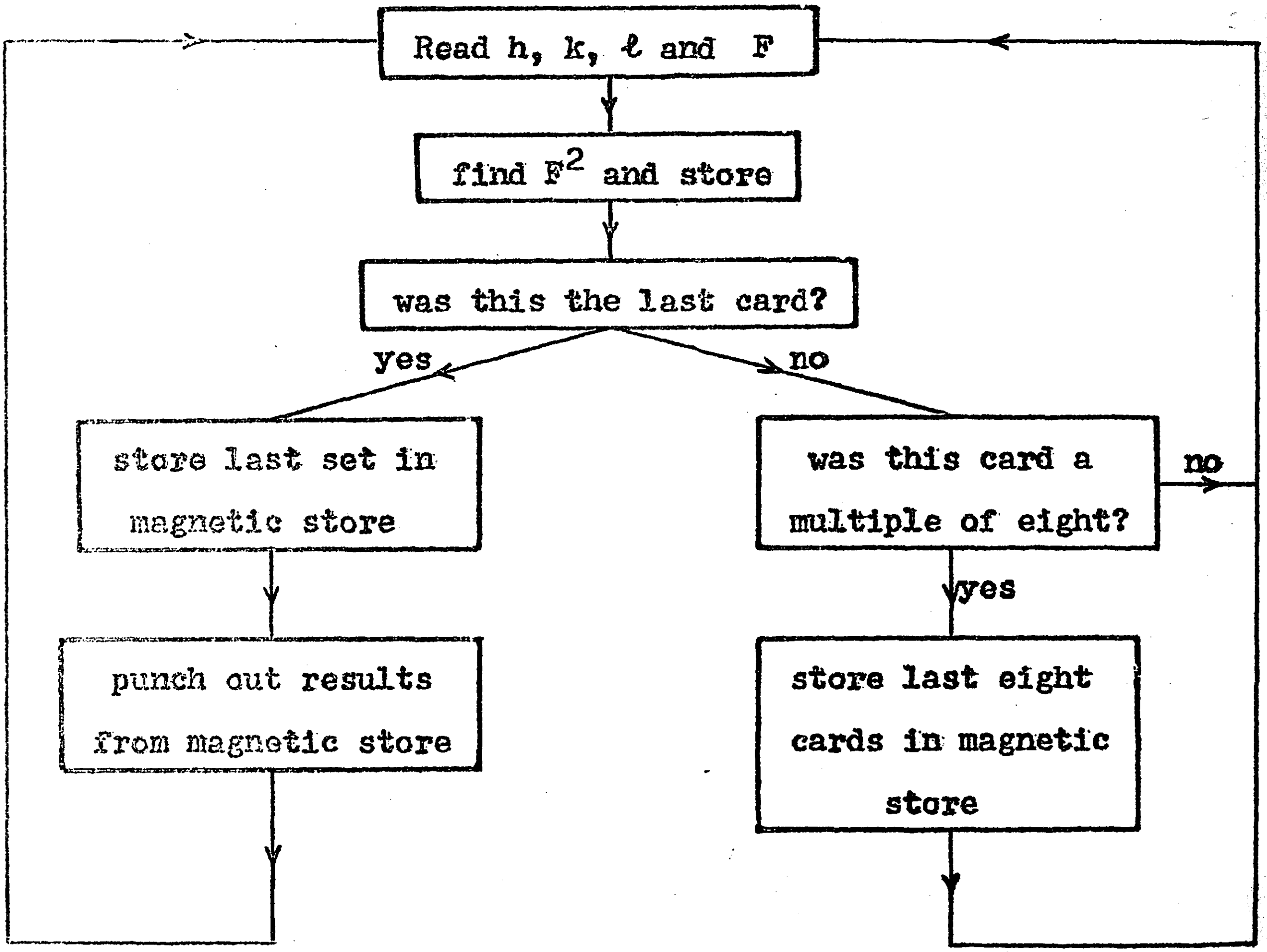
$$I(\text{corrected}) = I(\text{obs.}) \times A^* \times \cos\nu.$$

Flow Diagram.




(i)
find each $\Upsilon/2$, interpolate and find $I \times A^* \times \cos\nu$
store corrected values in magnetic store and test if last card read
last card read
last card not read
(iii)
read data from magnetic store and punch h, k, ℓ and $I_{corr.}$
(ii)

Flow Diagram.



Program 5.

Description.

This program will read data from program 2 and convert $|F|$ to F^2.

Input.

Data cards punched with h, k, ℓ, and $|F|$.

Output.

Cards punched with h, k, ℓ and F^2.

Time.

$1\frac{1}{2}n + \frac{1}{2}$ minutes if there are n hundred cards.

System.

Stac.

Method.

The reader and punch are allowed to run continuously since this is faster than reading and punching acard alternately. Up to 1,500 cards may be read in at one time.

Program 6.

Description.

This program will calculate the distance between each pair of up to 32 points. The range of distances required is selected and only values in this range are punched out.

Input.

Monoclinic cell dimensions, maximum and minimum required distances and fractional coordinates for each point.

Output.

One card per distance containing the numbers of the two points concerned and the actual distance.

Time.

About 3 minutes for 20 atoms.

System.

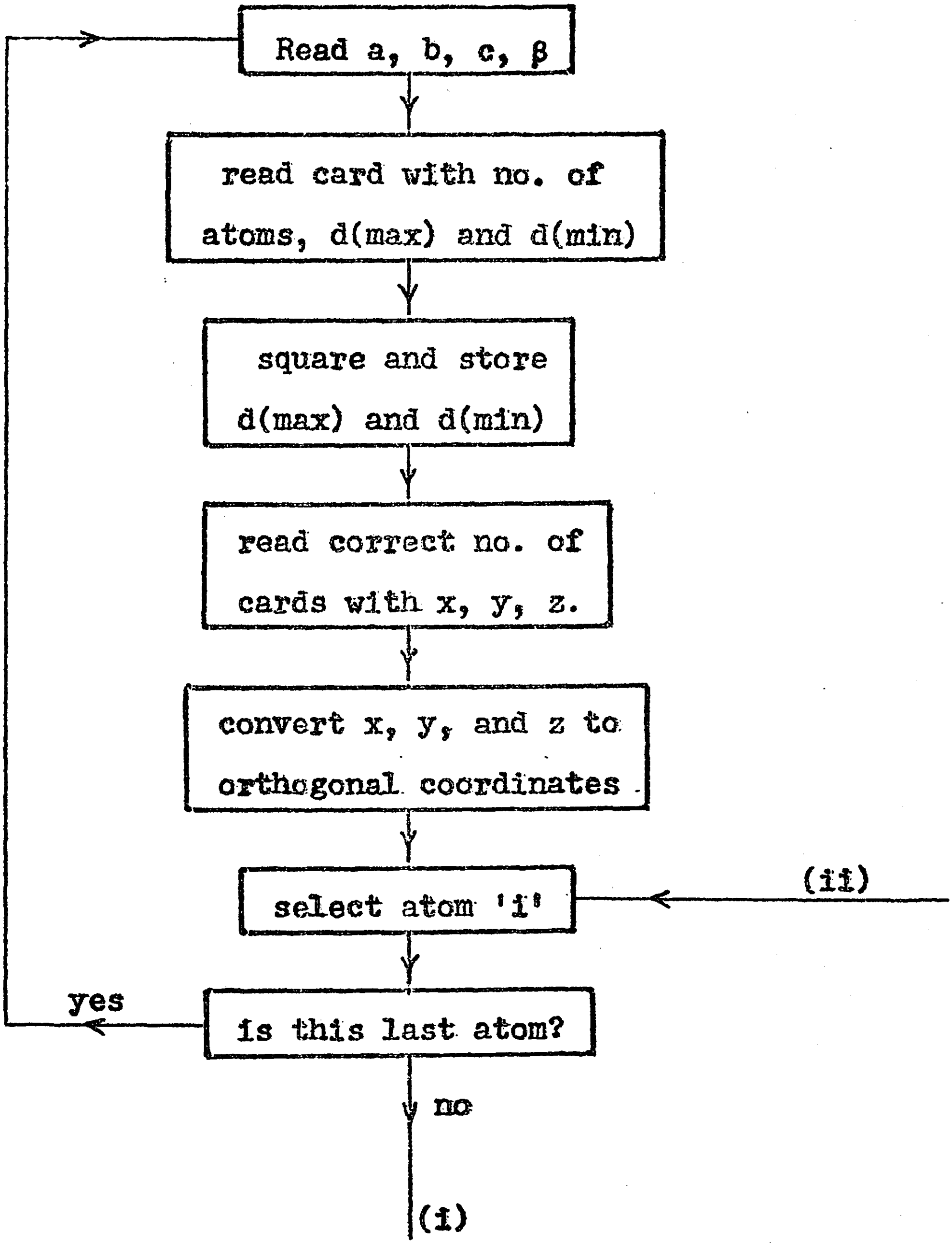
Stac.

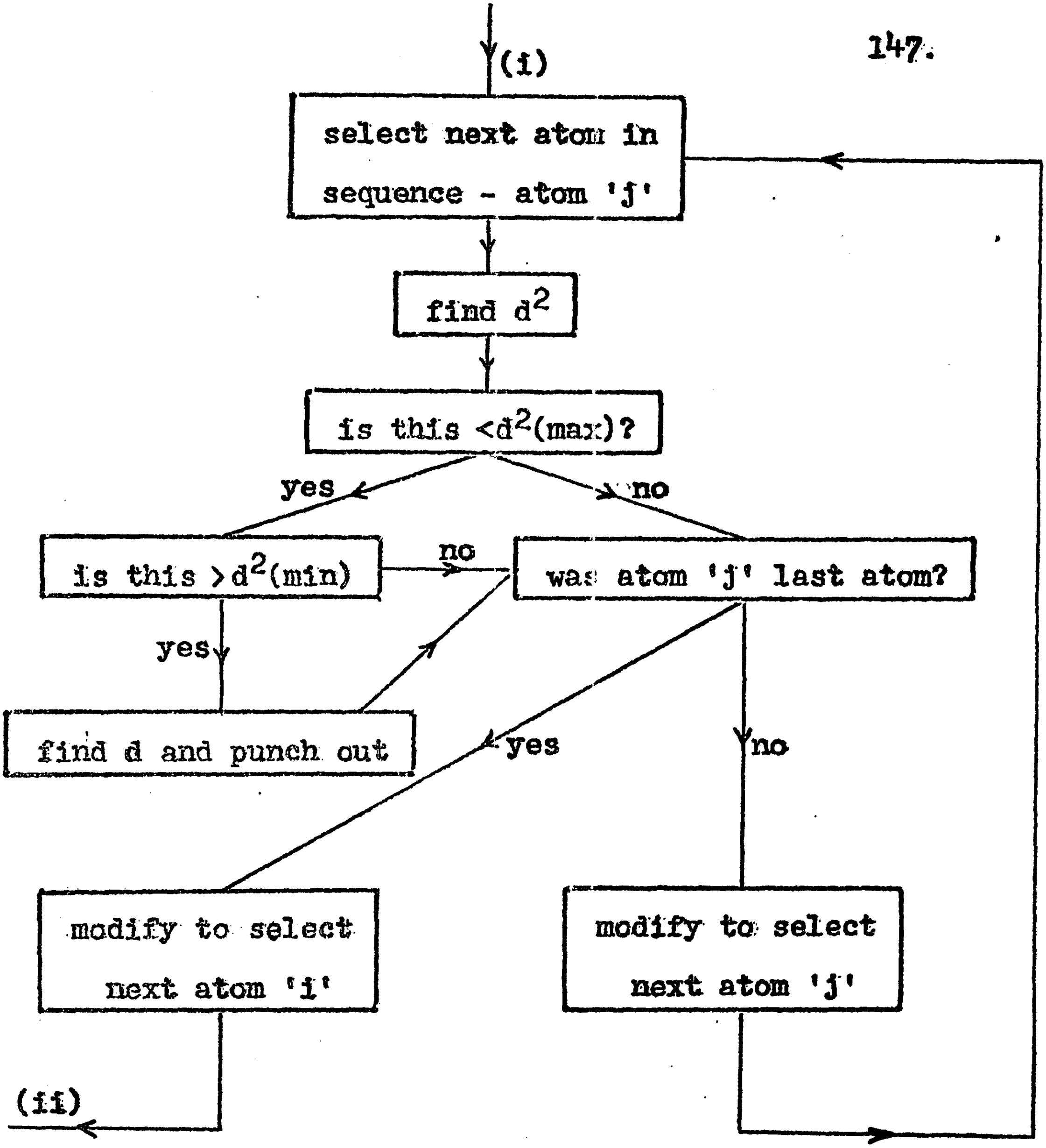
Method.

The coordinates are read in for a monoclinic cell and are first converted to an orthogonal set using the equations in program 2. The distances are then calculated from

$$d_{ij} = \left\{(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2\right\}^{\frac{1}{2}} .$$

Flow Diagram.




(i)
select next atom in sequence - atom 'j'
find d^2
is this $<d^2$(max)?
yes
no
is this $>d^2$(min)
no
was atom 'j' last atom?
yes
find d and punch out
yes
no
modify to select next atom 'i'
modify to select next atom 'j'
(ii)

Program 7.

Description.

This program will read and scale observed structure factors to the calculated ones - the agreement factor R is also determined.

Input.

Usually the output from Rollett's structure factor programs.

Output.

$\Sigma|kF_o|$, $\Sigma|F_c|$, $\Sigma|\Delta|$, k and R. Optional output is the input data with F_o values on scale and Δ's with correct signs.

Time.

Approximately $\frac{1}{2}n + 1$ minutes for n hundred data
$1\frac{1}{2}n + 1$ minutes for n hundred data if the optional output is also required.

System.

Stac.

Method.

The program first finds

$$F_o = \Delta + F_c$$

and then evaluates

$$k = \Sigma|F_c| \div \Sigma|F_o|.$$

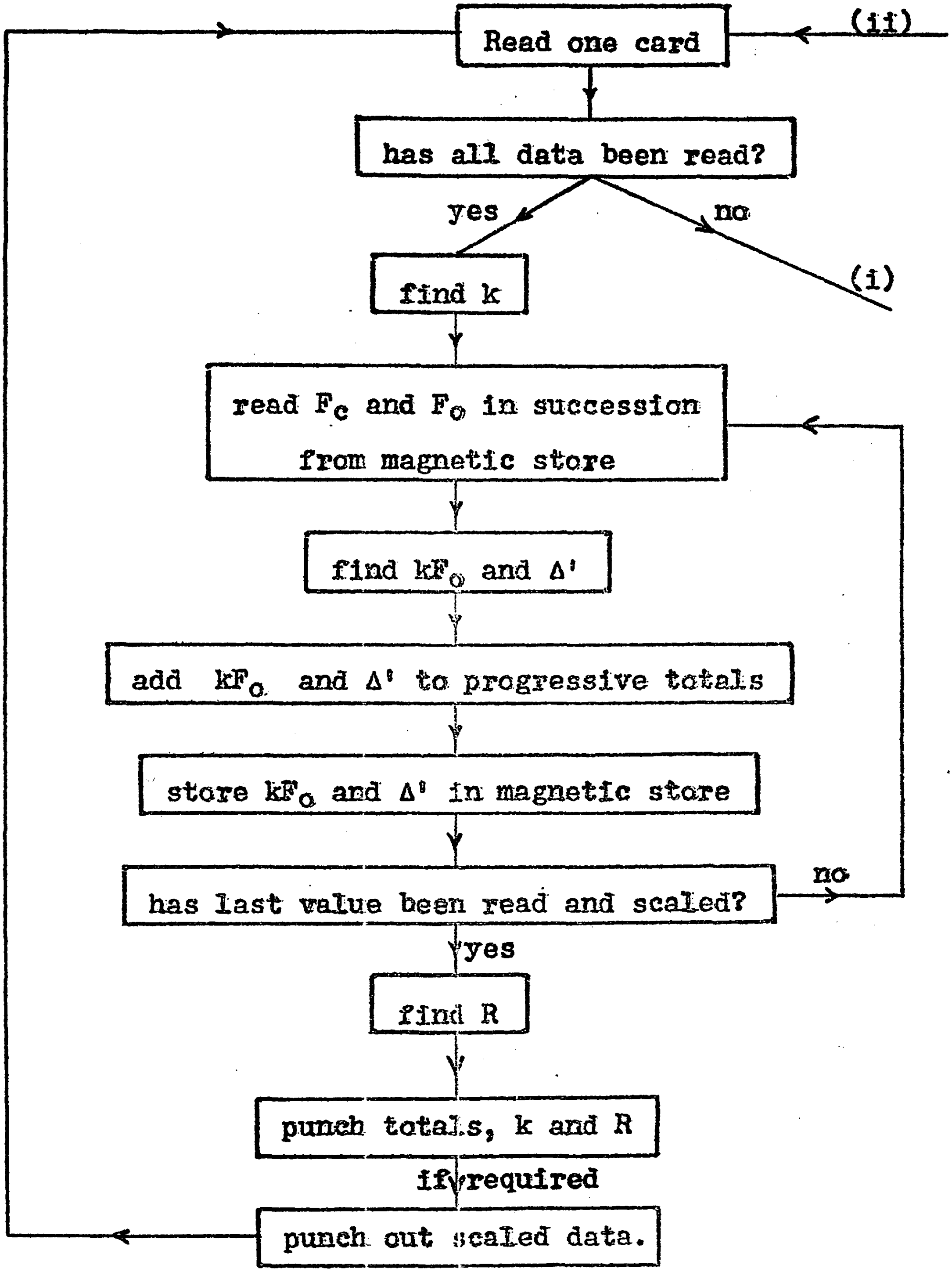
The F_o values are then scaled by this factor and

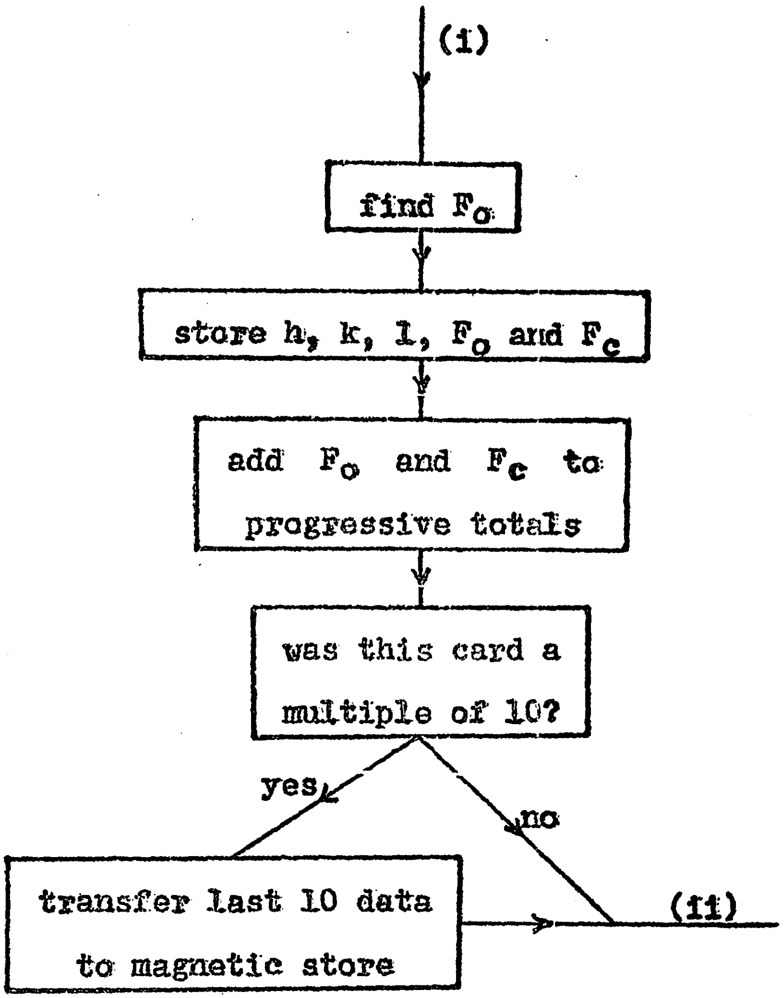
$$\Delta' = kF_o - F_c \qquad (\text{not } |kF_o| - |F_c|)$$

is found. The agreement factor R is then determined from

$$R = \frac{\Sigma|\Delta'|}{\Sigma|kF_o|}.$$

Flow Diagram.




(i)
find F_o
store h, k, l, F_o and F_c
add F_o and F_c to progressive totals
was this card a multiple of 10?
yes
no
transfer last 10 data to magnetic store
(ii)

REFERENCES.

Abrahams, S.C. (1954). Acta Cryst. 7, 423.

Abrahams, S.C. (1955). Acta Cryst. 8, 661.

Abrahams, S.C. (1956). Quart. Rev. Chem. Soc. Lond. 10, 407.

Abrahams, S.C. and Silverton, J.V. (1956). Acta Cryst. 9, 283.

Abrahams, S.C. (1957). Acta Cryst. 10, 417.

Allen, P.W. and Sutton, L.E. (1950). Acta Cryst. 3, 46.

Asheshov, I.N., Strelitz, F. and Hall, E.A. (1952). Antiobotics and Chemotherapy 2, 361.

Bacon, G.E. (1957). Private communication.

Bacon, G.E. and Curry, N.A. (1959). Acta Cryst. in press.

Berghuis, J. et al. (1955). Acta Cryst. 8, 478.

Bergmann, E. and Tschudnowsky, M. (1932). Ber. 65, 457.

Beevers, C.A. and Lipson, H. (1934). Phil. Mag. 17, 855.

Beevers, C.A. and Lipson, H. (1936a). Nature 17, 825.

Beevers, C.A. and Lipson, H. (1936b). Proc. Phys. Soc. (Lond) 48, 772.

Beevers, C.A. (1952). Acta Cryst. 5, 670.

Bond, W.L. (1959). Acta Cryst. 12, 375.

Bragg, W.H. (1915). Trans. Roy. Soc. (London) A215, 253.

Bragg, W.L. (1947). J. Sci. Instr. 24, 27.

Brown, C.J. and Landquist, J.K. (1953). Chem. and Ind. 973.

Buerger, M.J. (1941). Geol. Soc. of Amer., Special Paper No. 33.

Busing,W.R. and Levy,H.A. (1958). Acta Cryst. 11, 450.

Cochran,W. (1951). Acta Cryst. 4, 408.

Costain,W. (1941). Ph.D. Thesis - University of Birmingham.

Cross,A.D. and Tarbell,D.S. (1958). J. Amer. Chem. Soc. 80, 3682.

Cruickshank,D.W.J. (1956a). Acta Cryst. 9, 754.

Cruickshank,D.W.J. (1956b). Acta Cryst. 9, 757.

Debye,P. (1914). Ann. Physik 43, 49.

Elbe,T.E. and Hanson,F.R. (1951). Antibiotics and Chemotherapy 1, 54.

Forsyth,J.B. and Wells,M. (1959). Acta Cryst. 12, 412.

Fristrom,R.M. (1952). J. Chem. Phys. 20, 1.

Goodwin,T.H. and Thomson,C.M. (1954). Acta Cryst. 7, 166.

Grenville-Wells,H.J. and Abrahams,S.C. (1952). Rev. Sci. Instrum. 23, 328.

Housty,J. and Clastre,J. (1957). Acta Cryst. 10, 695.

Harker,D. and Kasper,J.S. (1948). Acta Cryst. 1, 70.

Howells,E.R., Phillips,D.C. and Rogers,D. (1950). Acta Cryst. 3, 210.

James,R.W. and Brindley,G.W. (1931). Z. Kristallogr. 78, 470.

Jeffrey,G.A. (1951). Acta Cryst. 4, 58.

Karle,J. and Hauptmann,H. (1950). Acta Cryst. 3, 436.

Keil,C. and Plieth,K. (1951). Naturwissenschaften 38, 546.

Keil,C. and Plieth,K. (1955). Z. Kristallogr. 106, 388.

Koch,H.P. (1949). J. Chem. Soc. 408.

Koch,H.P. and Moffitt,W.E. (1951). Trans. Farad. Soc. 47, 7.

Leonhard,N.J. and Sutton,L.E. (1948). J. Amer. Chem. Soc. 70, 1564.

Levy,H.A. (1956). Acta Cryst. 9, 679.

Lide,D.R., Mann,D.E. and Fristrom,R.M. (1957). J. Chem. Phys. 26, 734.

Lipson,H. and Cochran,W. (1953). 'The Crystalline State', Vol. 3, London: Bell.

McCorkindale,N.J. (1959). Personal communication.

McWeeny,R. (1951). Acta Cryst. 4, 513.

Nye,J.F. (1957). 'Physical Properties of Crystals' : Oxford.

Palmer,K.J. (1938). J. Amer. Chem. Soc. 60, 2360.

Patterson,A.L. (1935). Z. Kristallogr. 90, 517.

Robertson,J.M. (1943). J.Sci.Instr. 20, 176.

Robertson,J.M. (1954). Acta Cryst. 7, 817.

Robertson,J.M. (1955). Acta Cryst. 8, 286.

Rogers,D. and Wilson,A.J.C. (1953). Acta Cryst. 6, 439.

Rollett,J.S. and Davies,D.R. (1955). Acta Cryst, 8, 125.

Rossmann,M.G. (1956). Acta Cryst. 9, 819.

Sayre,D.M. (1952). Acta Cryst. <u>5</u>, 60.

Schenck,J.R., Hargie,M.P., Tarbell,D.S. and Hoffman,P.(1953). J. Amer. Chem. Soc. <u>75</u>, 2274.

Sime,J.G.(1956). B.Sc. Thesis - University of Glasgow.

Sime,J.G. and Abrahams,S.C. (1959). Acta Cryst. in press.

Snedden,W. (1957). Personal communication.

Stevenson,D.P. and Russell,H. (1939). J. Amer. Chem. Soc. <u>61</u>, 3264.

Tomiie,Y. and Stam,C.H. (1958). Acta Cryst. <u>11</u>, 126.

Toussaint,J. (1944). Bull. Soc. Roy. Sci. (Liege) <u>13</u>, 163.

Toussaint,J. (1945). Bull. Soc. Chim. Belges <u>54</u>, 319.

Toussaint,J. (1946). Bull. Soc. Roy. Sci. (Liege) <u>15</u>, 86.

Toussaint,J. (1948). Bull. Soc. Roy. Sci. (Liege) no.4, 157.

Treuting,R.G. and Abrahams,S.C. (1959). In press.

Tunell,G. (1939). Amer. Min. <u>24</u>, 448.

Viervoll,H. and Ögrim,O. (1949). Acta Cryst. <u>2</u>, 277.

Waser,J. (1951). Rev. Sci. Instrum. <u>22</u>, 567.

Waser,J. (1955). Acta Cryst. <u>8</u>, 731.

Whittaker,E.T. and Robinson,G. (1934). 'The Calculus of Observations', 4th. ed. Glasgow: Blackie.

Wilson,A.J.C. (1942). Nature, London <u>150</u>, 151.

Wrede,F. and Rotthaas,A. (1932). Z. Physiol. Chem. 210, 125.

Wrede,F. and Rotthaas,A. (1933a).Z. Physiol. Chem. 219, 267.

Wrede,F. and Rotthaas,A. (1933b).Z. Physiol. Chem. 222, 203.

Wrede,F. and Rotthaas,A. (1934). Z. Physiol. Chem. 226, 95.

Wright,W.B. and King,G.S.D. (1954). Acta Cryst. 7, 283.