X-RAY INVESTIGATIONS OF MOLECULAR OVERCROWDING.

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GEORGE FERGUSON, B. Sc.

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SUMMARY.

The crystal structures of a series of substituted benzoic acids and of a camphane derivative have been examined by X-ray diffraction methods.

o-Chlorobenzoic acid crystallises in the monoclinic system, space group C2/c, with eight molecules in the unit cell. The crystal structure, which consists of centrosymmetrical hydrogen-bonded dimers, was elucidated initially in projection by Patterson methods. The final atomic coordinates were obtained from a three-dimensional least-squares refinement involving 1034 observed structure amplitudes. The hydrogen atoms bonded to the benzene carbon atoms have been clearly revealed in difference syntheses but the hydroxyl hydrogen atom proved more difficult to locate. The strain which would be imposed on a planar ideal molecule is relieved by the carboxyl group rotating 13.7° out of the plane of the benzene ring, by the chlorine atom and exocyclic carbon atom being displaced by +0.036 Å and -0.058 Å, respectively, out of the plane of the benzene ring, and by in-plane displacements of the exocyclic carbon-carbon and carbon-chlorine bonds away from one another so that two of the exocyclic valency angles are increased from the normal value of 120° to 122.5° and 124.7° respectively.

o-Bromobenzoic acid is monoclinic, space group C2/c, with eight molecules per unit cell; it is isomorphous with o-chlorobenzoic acid. The final atomic parameters were obtained from a least-squares treatment of the three-dimensional data, a total of 1145 observed structure amplitudes being employed. The plane of the carboxyl group is inclined at an angle of 18.3° to that of the aromatic ring. The bromine and exocyclic carbon are also displaced sideways and out of the benzene plane in opposite directions.

2-Chloro-5-nitrobenzoic acid forms monoclinic crystals, space group $P2_1/c$, with four molecules in the unit cell. The crystal structure has been solved by two-dimensional Patterson methods. The final atomic coordinates were obtained from a least-squares analysis of the 1027 observed structure amplitudes. Difference syntheses served to reveal the positions of the hydrogen atoms. The molecules occur as centrosymmetrical dimers with hydrogen bonds (2.61 Å) between adjacent carboxyl groups. The carboxyl group is rotated 23°, and the nitro group 7°, out of the plane of the benzene ring. This is discussed in terms of an intramolecular buttressing effect.

4-Chloro-3-nitrobenzoic acid and 4-bromo-3-nitrobenzoic acid are isomorphous, monoclinic, of space group $P2_1/c$, with four molecules per unit cell. The structures have not yet been refined extensively, refinement (by Fourier methods using both F_o and F_c syntheses) having been confined to the $h0\ell$ and $h3\ell$ data. In 4-chloro-3-nitrobenzoic acid the nitro group is rotated 46° and the carboxyl group 7° out of the plane of the benzene ring. The corresponding angles in 4-bromo-3-nitrobenzoic acid are 49° and 9°.

Crystals of (+)-10-bromo-2-chloro-2-nitrosocamphane are orthorhombic, of space group $P2_12_12_1$, with eight molecules in the unit cell. The asymmetric crystal unit consists therefore of two crystallographically independent molecules necessitating the location of 28 atoms other than hydrogens. The positions of the bromine atoms were obtained by Patterson methods, successive three-dimensional Fourier syntheses served to locate the remaining atoms. The two crystallographically independent molecules appear to be conformationally identical, differing only in orientation in the unit cell. The presence of the bulky chlorine atom cis to the CMe_2 bridge causes some distortion of the camphane molecular framework.

An Appendix which contains details of some programs devised by the author for the DEUCE computer, is included.

PREFACE.

This thesis describes the investigations carried out in the years 1958 - 1961 in the Chemistry Department of the University of Glasgow, of the crystal structures of some substituted benzoic acids and of a camphane derivative.

I wish to express my sincere thanks to my supervisors, Dr. G.A.Sim and Professor J.Monteath Robertson, for their encouragement and advice during the course of this work.

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PART I.

Some methods of crystal structure analysis.

1.1. Introduction.

With the discovery by von Laue in 1912 of the diffraction of X-rays by crystals, modern crystallography had its birth and a powerful new technique became available for investigating the structure of matter on an atomic scale. Since that time, considerable advances have been made. The subject has been put on a sound theoretical basis and the structures of many simple molecules have been examined in detail to provide evidence about the nature and length of chemical bonds. In addition, the structures of many quite complex molecules, where the chief interest lies in the order in which the various atoms are bonded together, have been determined. Both types of structure determination are described in this thesis. The availability of fast computing facilities in recent years has meant that many structures which could not have been tackled previously, because of the sheer magnitude of the labour involved, can now be investigated. For smaller molecules it has meant more intensive refinement to the limits of the available data.

The major difficulty facing modern crystallographers is that no method has yet been devised for measuring the phases of the diffracted spectra. Although the amplitudes of the diffracted beams can be measured accurately by using electronic counting techniques, the phases of the diffracted rays must be obtained by other methods. Many investigators have devoted their energies to this "phase problem". Methods for overcoming it have been devised by Patterson (1934, 1935), Harker and Kasper (1948), Karle and Hauptmann (1950) and Sayre (1952). Since no completely general method for solving a crystal structure is available, the methods used will depend on the particular problems which the structure poses.

1.2. Structure factor expression.

If the positions of the atoms in the asymmetric crystal unit are known, it is possible to calculate structure factors for comparison with those obtained from the experimental data. The structure factor expression may be derived from considerations of a primitive lattice defined by the lattice vectors $\underline{a}$, $\underline{b}$ and $\underline{c}$. It is assumed that each lattice point is the site of an electron, for example, A_1 and A_2 in Fig.1 below. The two lattice points A_1 and A_2 are related by the vector

$$\underline{r} = u\underline{a} + v\underline{b} + w\underline{c} \quad \ldots\ldots\ldots (1)$$

where u, v and w are integers.

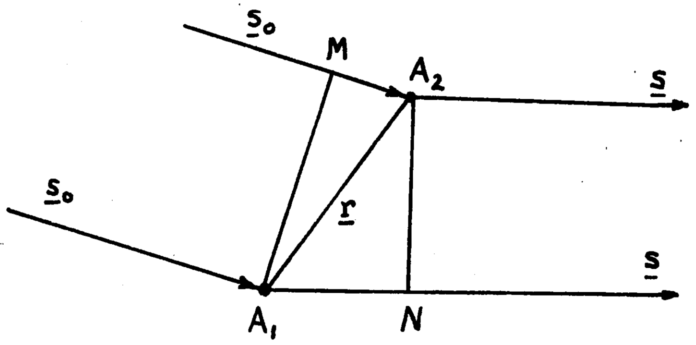


Fig.1.

If a parallel beam of X-rays of wavelength λ falls on the lattice in a direction specified by a vector $\underline{s}_0$ of magnitude $1/\lambda$, and after diffraction travels in the direction defined by the vector $\underline{s}$ of magnitude $1/\lambda$, the path difference between the two scattered waves is

$$A_1N - A_2M = \lambda.(\underline{r}.\underline{s} - \underline{r}.\underline{s}_0)$$

$$= \lambda.\underline{r}.\underline{S} \quad . \; . \; . \; . \; . \; . \; . \; . \; (ii)$$

$$\text{Where } \underline{S} = \underline{s} - \underline{s}_0$$

To ensure that the waves scattered by A_1 and A_2 are in phase, this path difference must be a whole number of wavelengths, i.e. $\underline{r}.\underline{S}$ must be integral.

Hence by (i) $(u\underline{a} + v\underline{b} + w\underline{c}).\underline{S}$ must be integral and since u, v and w are integral, each term must be integral, i.e.

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

where h, k and ℓ are integers.

These are known as Laue's equations; the integers h, k and ℓ are the Miller indices of the diffracting plane.

If the unit cell of a crystal contains N atoms, the nth of which has coordinates (x_n, y_n, z_n), the position of the nth atom can be defined by the vector $\underline{r}_n$ where

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

The path difference of the wave scattered by this atom and an atom at the origin of the unit cell is, by (ii), $\lambda\,\underline{r}_n\underline{S}$ and the phase change is

$$\frac{2\pi}{\lambda}\lambda\,\underline{r}_n\underline{S} = 2\pi\,\underline{r}_n\underline{S}$$

Thus the expression for the wave scattered by the nth atom contains the term

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

where f_n is the atomic scattering factor of the nth atom. The complete wave scattered by the N atoms in the unit cell will thus contain the term

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

By substituting (iv) in (v)

$$F = \sum_{n=1}^{N} f_n \exp 2\pi i(x_n\underline{a}.\underline{S} + y_n\underline{b}.\underline{S} + z_n\underline{c}.\underline{S})$$

Hence by (iii)

$$F = \sum_{n=1}^{N} f_n \exp 2\pi i(hx_n + ky_n + \ell z_n)$$

The quantity F is called the structure factor and its modulus, the structure amplitude, is defined as the ratio of the amplitude of the radiation scattered in the order h,k,ℓ by the contents of one unit cell, to that scattered by a single electron under the same conditions, i.e. $|F|$ is a pure number, a number of electrons.

As was mentioned in 1.1, the phase of the scattered wave is not an observable quantity; what is observed, the intensity of the scattered wave, is proportional to $|F|^2$.

Then if $F = A + iB$

$F.F^* = F^2 = A^2 + B^2$ where F^* is the complex conjugate of F and

$$A = \sum_n f_n \cos 2\pi(hx_n + ky_n + \ell z_n)$$

$$\ldots\ldots \text{(vi)}$$

$$B = \sum_n f_n \sin 2\pi(hx_n + ky_n + \ell z_n)$$

These are the equations used in practice. Important simplifications can be made if there are symmetry related atoms in the unit cell. With a centre of symmetry for example, for each atom at (x y z), there is a corresponding atom at ($\bar{x}$ $\bar{y}$ $\bar{z}$). This causes (vi) to reduce to

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

$$B = 0$$

the summation now being made over half the unit cell.

1.3. The atomic scattering factor.

In 1.2 it was implied that the scattering unit in the crystal is the electron; this in turn implies that to calculate structure factors the positions of all the electrons in the unit cell must be known. The difficulties inherent in this procedure are avoided on recognising that each atomic species has a specific number of electrons associated with it. The general distribution of electrons with respect to the centre of an atom, though difficult to calculate, may be found. This has been done for many of the elements by McWeeny (1951), Berghuis et al (1955), Tomiie and Stam (1958) and others.

The scattering power of an atom, f_o, is expressed in terms of the scattering power of a single free electron. The maximum value of f_o is equal to Z, the atomic number of the atom and falls off more or less readily as a function of θ, the Bragg angle. The atomic scattering factors available in the literature are calculated for atoms undergoing no thermal motion. Since this is never the case in practice, the atomic scattering factor must be modified to allow for the thermal vibration of the atom. If $\bar{U}$ is the mean displacement of the atom from its mean position, then it may be shown that for simple isotropic motion the scattering factor f_o should be modified by a factor

$$\exp - 8\pi^2 \bar{U}^2 \sin^2\theta / \lambda^2$$

$$\text{i.e.} \quad f_n = f_o \exp - B \sin^2\theta / \lambda^2$$

where $B = 8\pi^2\bar{U}^2$ and is known as the Debye temperature factor (Debye, 1914). A method of finding an approximate overall value for B has been described by Wilson (1942).

If, however, the thermal vibration of the atom is anisotropic, the scattering factor f_o must be modified by a factor such as

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

(Cruickshank, 1956)

where the b_{ii} and b_{ij} terms characterise the time-averaged elipsoidal volume through which the electron density is distributed.

1.4. Fourier series.

A periodic function can usually be represented by an appropriate sum of sines and cosines known as a Fourier series. In 1915 W.H.Bragg first suggested that since a crystal is periodic its electron density could be represented by such a series.

If $\rho(xyz)$ is the density of scattering matter at any point with fractional coordinates (xyz) in the unit cell, then

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

The number of electrons in the volume element dxdydz is given by $\rho(xyz)$.dxdydz. When the unit cell has a volume V it may be shown that

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

The values of the coefficients A(pqr) in (vii) are obtained by substituting for $\rho(xyz)$ in (viii) and obtaining

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

On integrating, all terms in (ix) vanish except those for which p = h, q = k and r = z.

Consequently

$$F(hk\ell) = V\int_0^1\int_0^1\int_0^1 A(pqr).dx\,dy\,dz = V\,A(pqr)$$

and $$A(pqr) = \frac{F(hk\ell)}{V}$$

Equation (vii) is thus converted to

$$\rho(xyz) = \frac{1}{V}\sum\sum_{-\infty}^{\infty}\sum F(hk\ell)\,\exp - 2\pi i(hx + ky + \ell z) \qquad \ldots\ldots (x)$$

The zero term F(000) = Z, the total number of electrons in the unit cell. Since f_n falls off with $\sin\theta$, the terms in this series will decrease and consequently the series will converge if sufficient data are available.

Equation (x) is not suitable for the quantitative evaluation of electron densities; it may be conveniently expressed in the form

$$\rho(xyz) = \frac{1}{V}\sum\sum_{-\infty}^{\infty}\sum|F(hk\ell)|\cos\left[2\pi(hx + ky + \ell z) - \alpha_{hk\ell}\right] \qquad \ldots\ldots (xi)$$

where $\alpha hk\ell$ is the phase angle associated with the amplitude $F(hk\ell)$

If the crystal structure contains a centre of symmetry, α is then limited to values of 0° or π° and equation (xi) reduces to

$$\rho(xyz) = \frac{1}{V}\sum\sum_{-\infty}^{\infty}\sum \pm F(hk\ell)\cos 2\pi(hx + ky + \ell z) \qquad \ldots\ldots (xii)$$

If only the projection of the electron density of a centrosymmetric structure on a plane is being considered, equation (xii) simplifies further to

$$\rho(xy) = \frac{1}{A}\sum\sum_{-\infty}^{\infty} \pm F(hk) \cos 2\pi(hx + ky)$$

The major drawback associated with the Fourier series, as expressed in equation (xi), is that initially the phase angles associated with the structure amplitudes are not known. The methods utilised in this thesis to overcome this "phase problem" are described below.

1.5. Trial and error methods.

From information culled from a knowledge of the space group, known bond lengths, van der Waal's radii, previous work on structures of the same type, etc., it may often be possible to postulate a set of coordinates for the atoms in a molecule. Structure factors are then calculated to see if these atomic parameters lead to values of $|F|$ which agree with those observed experimentally. If a very poor agreement is obtained the proposed structure may not be worth attempting to refine and some other trial model tested. This process may be continued until good agreement between the observed and calculated structure factors is obtained or until a solution is found by other methods.

1.6. The Patterson series.

A.L.Patterson (1934, 1935) devised the synthesis which bears his name as a method of obtaining information about crystal structures using only the phaseless $|F|^2$'s. The Patterson function of an electron-density distribution

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

is defined as

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

$$\quad \ldots\ldots \quad \text{(xiii)}$$

and can be expressed as the Fourier series

$$P(uvw) = \frac{1}{V} \sum \sum_{-\infty}^{\infty} \sum |F(hk\ell)|^2 \exp -2\pi i(hu + kv + \ell w)$$

which can be computed without ambiguity since the $|F(hk\ell)|^2$'s are directly related to the observed intensities.

The function P(uvw) in equation (xiii) can only have a large value when both $\rho(xyz)$ and $\rho(x+u, y+v, z+w)$ are large. This will happen, for example, when one atom occurs at (xyz) and another at (x+u, y+v, z+w) separated by a vector distance (uvw). A peak in the function P(uvw) at $(u_1v_1w_1)$ corresponds to an interatomic distance in the crystal defined by a vector with components u_1, v_1, w_1 and the height of the peak is proportional to the product of the scattering factors of the two atoms concerned.

If the structure contains a large number of atoms in the asymmetric crystal unit, the vector map may be difficult to interpret because, when N atoms are considered, $N (N - 1)/2$ distinct vector peaks are possible.

The Patterson method has had many successful applications and is especially useful for small molecules containing relatively few atoms of atomic number much greater than the remainder. In such cases it may be possible to identify all the peaks in the Patterson function and hence solve the structure.

The method loses a little of its power for organic structures containing many carbon, oxygen and nitrogen atoms because of the multiplicity of interatomic vectors of approximately equal weight which cannot be interpreted. However, the vectors arising from "heavier" atoms can usually be located, allowing coordinates for these atoms to be derived. Use may then be made of the heavy-atom method in obtaining coordinates for the remaining atoms in the structure.

1.7. The heavy-atom method.

One of the most important phase determining methods is that which involves the use of an atom or atoms with atomic number high compared to other atoms in the structure.

A "heavy atom" will, in general, tend to dominate the phases of the diffracted spectra although complications may occur if the atom is situated at a special position in the unit cell. The heavy-atom coordinates can usually be found fairly readily by Patterson methods, as described in the previous section. Structure-factor calculations based on the heavy-atom contributions alone provide a set of phase angles which can be applied to the observed structure amplitudes in the summation of a Fourier series. In the resulting electron-density distribution some or all of the lighter atoms may be distinguished. These atoms are included in the next structure-factor calculation which provides an improved set of phase angles, successive rounds of Fourier summation and structure-factor calculation serving to reveal the positions of all the atoms in the structure.

It is not necessary for the heavy atom to scatter more than all the other atoms combined, as was the case with platinum phthalocyanine (Robertson and Woodward,1940). Lipson and Cochran (1953) have suggested that the heavy-atom method will be most successful when the sums of the squares of the atomic numbers of the heavy atoms and of the light atoms are equal.

Situations may arise which make application of the heavy-atom method difficult. For example with the space group $P2_1$ a heavy atom at (xyz) also occurs at $(\bar{x}, \frac{1}{2}+y, \bar{z})$. If only the heavy atom coordinates are known they are in effect related by a centre of symmetry. In the ensuing electron-density distribution based on the heavy-atom phases, each light atom will be accompanied by its mirror image. A decision then has to be made as to which peaks are spurious; this may be very difficult, especially for large structures.

Weighting functions for improving the resolution in approximate electron-density distributions have been proposed in recent years by Luzzati (1953), Woolfson (1956) and Sim (1959, 1960, 1961). The advantages of using a weighting scheme are that the best representation of the structure is obtained from the approximate phase angles available and that all the structure amplitude data are included from the beginning in the structure analysis. The use of a weighting scheme also obviates the need for an examination of the list of structure factors to decide in some semi-empirical manner which planes ought to be omitted from the Fourier calculation. Dr. Sim's weighting procedure is being programmed by the author for DEUCE.

When the coordinates of the atoms in the asymmetric crystal unit have been determined they can be refined by successive cycles of Fourier summation and structure-factor calculation. Theoretical justification for this has been given by Cochran (1948). Other methods of parameter refinement have been developed, those used in this thesis being described below.

1.8. Difference Fourier syntheses.

The difference synthesis, a Fourier synthesis with coefficients ($F_o - F_c$), was first suggested as a method of refinement by Booth (1948a) and developed by Cochran (1951).

The difference synthesis has several advantages over the F_o synthesis. When the proposed and actual structures are nearly the same, their series-termination errors are substantially identical, so that difference syntheses are not subject to termination-of-series errors. The coordinates obtained from an F_o synthesis might be subject to termination-of-series errors and more accurate coordinates would be obtained by minimising

$$\phi = \sum_{\ell} w(F_o - F_c)^2$$

If instead, the function

$$\phi_n = \sum_{\ell} \frac{1}{f_n} (F_o - F_c)^2$$

is used, the coordinates which minimise ϕ_n satisfy the conditions that

$$\frac{\partial \phi_n}{\partial x_n} = \frac{\partial \phi_n}{\partial y_n} = \frac{\partial \phi_n}{\partial z_n} = 0$$

that is $\sum_{\ell} \frac{1}{f_n} \cdot (F_o - F_c) \cdot \frac{\partial F_c}{\partial x_n} = 0$

For a centrosymmetric structure

$$F_c = 2 \sum_{n=1}^{N/2} f_n \cos \textcircled{H}_n$$

$$\text{where } \textcircled{H} = 2\pi(hx + ky + \ell z)$$

and $\frac{\partial F_c}{\partial x_n} = \frac{-4\pi h}{a} f_n \sin \textcircled{H}_n$

The condition that $\frac{\partial \phi_n}{\partial x_n} = 0$ becomes

$$\frac{-4\pi}{a} \sum_{\ell} h(F_o - F_c) \sin \textcircled{H}_n = 0 \quad \ldots\ldots \text{(xiv)}$$

However, the function

$$D = \rho_o - \rho_c = \frac{1}{V} \sum_{\ell} (F_o - F_c) \cos \textcircled{H}$$

has a slope in the x- direction at the point x_n, y_n, z_n given by

$$\left(\frac{\partial D}{\partial x}\right)_n = -\frac{2\pi}{aV} \sum_{\ell} h(F_o - F_c) \sin \textcircled{H}_n$$

Comparison with equation (xiv) shows that the condition for ϕ_n to be a minimum with respect to the coordinates of the n^{th} atom is that

$$\left(\frac{\partial D}{\partial x}\right)_n = \left(\frac{\partial D}{\partial y}\right)_n = \left(\frac{\partial D}{\partial z}\right)_n = 0$$

i.e. when D has zero slope at the atomic centre, ϕ_n has been minimised. When the slope of D is not zero at a point taken to be an atomic coordinate the $(\rho_o - \rho_c)$ map has the characteristic feature shown in Fig.2. Corrections to the atomic coordinates are made by moving the atom up the direction of the steepest slope. The expression used to calculate the magnitude of the required shift is

$$\Delta r_n = \left(\frac{\partial D}{\partial r}\right)_n \Big/ \left(\frac{\partial^2 \rho}{\partial r^2}\right)_n \quad \ldots\ldots(xv)$$

where $\underline{r}$ is the vector along the line of maximum gradient. If we assume that the electron density at a distance $\underline{r}$ from the centre of an atom can be represented by

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

where $\rho(0)$ is the maximum density and p is a constant depending upon the temperature factor of the atom, then

$$\frac{\partial^2 \rho}{\partial r^2} = 2p\rho(0)$$

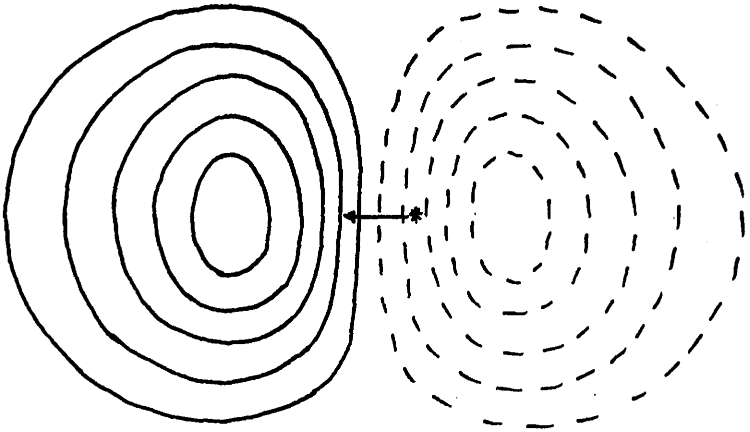


Fig.2. Difference synthesis feature resulting from a small error in atom location, the atom to be moved up the direction of steepest slope.

and hence equation (xv) becomes

$$\Delta r_n = \left(\frac{\partial D}{\partial r}\right)_n \Big/ 2p\rho(0)$$

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

Refinement of the thermal parameters, both isotropic and anisotropic, is possible from the information given by a difference synthesis. When the position of an atom has been corrected, if the temperature parameter B (assuming isotropic motion) has been underestimated, $\rho_o < \rho_c$ at the atomic centre and the atom involved appears in a hollow in the $(\rho_o - \rho_c)$ distribution. Conversely, if the atom lies on a small hill in the difference map, the value of B for that atom must be reduced.

If the thermal motion is anisotropic, the observed electron-density distribution is drawn out in the direction of maximum vibration and narrowed in a direction at right angles to it; this results in the difference map having the characteristic feature shown in Fig.3. Suitable thermal parameters of the form

$$B = \alpha + \beta \sin^2(\phi - \psi)$$

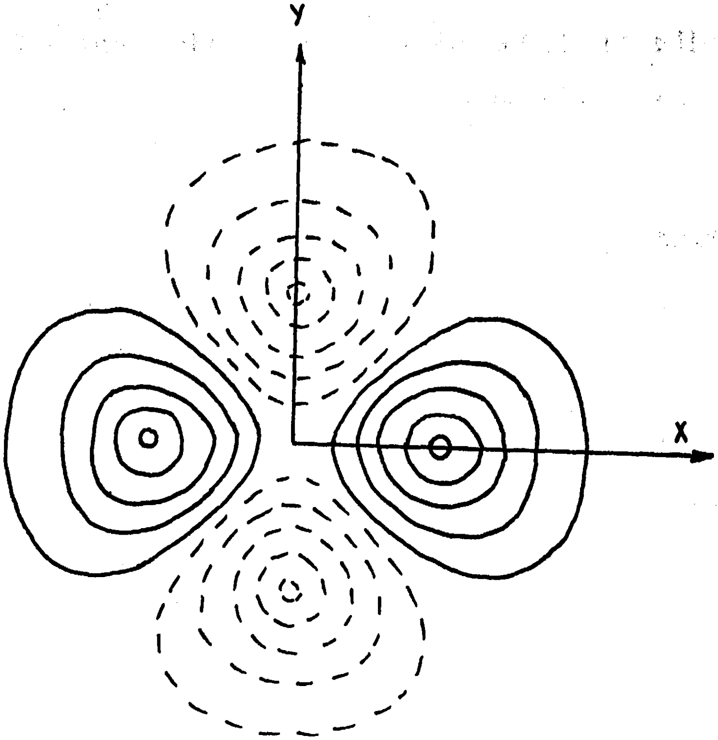


Fig.3. Difference synthesis features showing the effect of assuming an isotropic thermal motion for an atom which is in fact vibrating anisotropically. These features indicate that the temperature factor should be increased along the X-direction and decreased along the Y-direction.

can be chosen (Hughes, 1941; Cochran, 1951) for the two-dimensional case, where α and β are constants, ψ is the angle between the direction of maximum vibration and one of the axes, and $(2\sin\theta, \phi)$ are the polar coordinates of the reciprocal lattice point considered.

Difference maps may also be used to locate hydrogen atoms. These are not usually observable on F_o maps although a half-electron contour line may provide evidence for them. If the hydrogen atom contributions are not allowed for in the structure-factor calculations, they may be observable in a difference synthesis if the experimental errors in F_o are not too large.

A disadvantage of the F_o and $(F_o - F_c)$ syntheses is that although the investigator may be aware that some of the Fourier coefficients are more liable to error than others, there is no obvious way of decreasing the effect of the less reliable terms on the final result. Alternative methods have been developed, prominent among them the method of least squares.

1.9. <u>Least-squares refinement</u>.

The best atomic parameters are those which minimise the quantity

$$\phi = \sum w(hkl)\,(F_o - F_c)$$

$$\phi = \sum_{l} w(hkl)\,(F_o - F_c)$$

where q is the number of independent observations and w(hkl) is the weight allocated to a particular plane; the weight should be inversely proportional to the square of the probable error in the corresponding F_o.

When ϕ is near to its minimum, a small change Δx_n in the x- coordinate of the nth atom changes F_c by an amount

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

Simultaneous changes to all coordinates result in a change in F_c of

$$\Delta F_c = \sum_{n=1}^{N} \left(\frac{\partial F_c}{\partial x_n} . \Delta x_n + \frac{\partial F_c}{\partial y_n} . \Delta y_n + \frac{\partial F_c}{\partial z_n} . \Delta z_n \right) \quad . \; . \; . \; . \; . \; (xvi)$$

The correct values of the Δx_n etc., are therefore those which most nearly equate ΔF_c to $(F_o - F_c)$ for the q possible equations which can be set up. For the least-squares refinement to provide reasonably accurate results, the number of observational equations must be considerably greater than the number of unknowns, which are generally three positional and six thermal parameters per atom and an overall scale factor.

When only the positional parameters for N atoms are being refined, ΔF_c has the form of equation (xvi).

In order to obtain values for Δx_n etc., the q observational equations must be reduced to 3N normal equations. This is done by multiplying each of the q equations, $\Delta F_c = F_o - F_c$, by the weighted coefficient of each of the unknowns in turn. This results in 3N sets of q equations; each set is then summed to produce one normal equation. The nth of these normal equations is obtained by multiplying the q equations of the type

$$\sum_{n=1}^{N}\left(\frac{\partial F_c}{\partial x_n}\cdot\Delta x_n + \frac{\partial F_c}{\partial y_n}\cdot\Delta y_n + \frac{\partial F_c}{\partial z_n}\cdot\Delta z_n\right) = F_o - F_c$$

by $w\,\frac{\partial F_c}{\partial x_n}$ and adding to produce an equation

$$\sum_{q} w\left\{\left(\frac{\partial F_c}{\partial x_n}\right)^2\cdot\Delta x_n + \frac{\partial F_c}{\partial x_n}\cdot\frac{\partial F_c}{\partial y_n}\cdot\Delta y_n + \frac{\partial F_c}{\partial x_n}\cdot\frac{\partial F_c}{\partial z_n}\cdot\Delta z_n\right.$$

$$\left. + \sum_{m}\frac{\partial F_c}{\partial x_n}\left(\frac{\partial F_c}{\partial x_m}\cdot\Delta x_m + \frac{\partial F_c}{\partial y_m}\cdot\Delta y_m + \frac{\partial F_c}{\partial z_m}\cdot\Delta z_m\right)\right\}$$

$$= \sum_{q} w(F_o - F_c)\,\frac{\partial F_c}{\partial x_n} \qquad \ldots\ldots \text{(xvii)}$$

where $\sum_m$ denotes the sum over all atoms except the nth.

The 3N normal equations have then to be solved for the 3N unknowns. If no simplifications were made this would be a formidable task. However, if the atoms are well resolved, it can be shown that quantities such as

$$\sum_{q} w \frac{\partial F_c}{\partial x_n} \cdot \frac{\partial F_c}{\partial x_m}$$

are likely to be small compared with

$$\sum_{q} w \left(\frac{\partial F_c}{\partial x_n}\right)^2$$

and may be neglected.

If the axes are orthogonal, or nearly so, quantities of the form

$$\sum_{q} w \frac{\partial F_c}{\partial x_n} \cdot \frac{\partial F_c}{\partial y_n}$$

can also be neglected and equation (xvii) reduces to

$$\Delta x_n \sum_{q} w \left(\frac{\partial F_c}{\partial x_n}\right)^2 = \sum_{q} w(F_o - F_c) \frac{\partial F_c}{\partial x_n}$$

which can be evaluated more quickly than equation (xvii).

For a full three-dimensional refinement $(9N + 1)$ normal equations have to be solved for $(9N + 1)$ parameters. Even with simplifications as above this could not be done in a reasonable time without the use of high speed computing equipment.

The use of least-squares procedures for refinement purposes was first suggested by Hughes (1941) and used by him in the refinement of the structure of melamine.

1.10. Significance tests based on the χ^2 distribution.

The significance tests used on the results of the mean molecular plane calculations discussed in later chapters of this thesis depend on a statistic χ^2. The χ^2 distribution leads to tests of correspondence between experimental and theoretical data: this has led to it being described as a test of "goodness of fit".

The mathematical derivation of this statistic is difficult; fortunately its distribution has been worked out and tables are available showing the frequency with which different values of χ^2 are exceeded and also the value of χ^2 corresponding to particular frequencies (Fisher and Yates, 1957). The quantity χ^2 may generally be regarded as the sum of the squares of n variables which vary normally and independently about zero. For the purpose of this thesis it is computed from the expression

$$\chi^2 = \sum \Delta^2/\sigma^2 \qquad \ldots\ldots\ldots \text{(xviii)}$$

where Δ is the deviation in Å of an atom from the calculated plane and σ is the mean standard deviation (in Å) in positional parameter of the atoms.

The χ^2 test is used here as an objective method of estimating the merit of a particular plane. With the value of χ^2 found from equation (xviii) and knowing the number of degrees of freedom involved (n - 3), the probability that no atoms deviate significantly from the calculated plane is found from tables. If the probability that the plane is a good fit is less than one in one hundred, it is usually safe to assume that one or more of the atoms included in the mean plane calculation does deviate significantly from the calculated plane.

1.11. Methods of computation.

The many calculations required in the structure analyses described in this thesis were performed for the most part on the English Electric DEUCE computer, which came into general use in Glasgow in January, 1959. A feature of the Glasgow University Computing Laboratory is that a general computing service is not operated; instead, prospective DEUCE users are given initial training in the programming and efficient use of the machine.

Structure factors were calculated by hand initially, using tables compiled by Buerger (1941) which give values of cos $2\pi hx$ and sin $2\pi hx$ for values of h from

1 to 30 and of x from 0 to 1 by 0.001. When DEUCE became available, an "Alphacode" program was written for the plane group P2 and used to check the hand structure-factor calculations in the o-chlorobenzoic acid analysis. Details of this and other programs devised by the author are contained in the appendix. The Alphacode structure factor program was soon rendered obsolete by the arrival of Dr. J.S.Rollett's program (Rollett, 1961).

Fourier summations were carried out using Beevers-Lipson strips (Beevers and Lipson, 1934, 1936a, 1936b; Beevers, 1952) and also using RUFUS, a mechanical computer designed by Professor J. Monteath Robertson to perform Fourier summations (Robertson, 1954, 1955, 1961). The majority of the Fourier summations were computed on DEUCE using Dr. J.S.Rollett's or Dr. J.G.Sime's programs.

PART II.

Overcrowded Halogenobenzoic Acids.

1. Introduction.

The study of steric interactions between adjacent non-bonded atoms, both from the experimental and theoretical viewpoints, has been of some interest in recent years. Theoretical calculations by Coulson and Senent (1955) on the molecular deformation of the overcrowded aromatic hydrocarbon 3:4-5:6-dibenzphenanthrene agree well with the X-ray diffraction results of McIntosh, Robertson and Vand (1954).

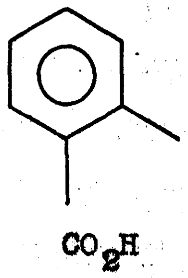
In the case of hexahalogenobenzenes, no such satisfactory agreement has been reported. From considerations of known bond lengths and van der Waal's radii, these molecules, with the exception of C_6F_6, are expected to be overcrowded. This does not necessarily mean that they will be non-planar, although it is tempting to suppose that at some stage in the series when the imposed strain becomes too great, it will be relieved by the molecules buckling in such a way that the halogen atoms are displaced alternately above and below the mean molecular plane. Electron-diffraction investigations of several gaseous chloro- and bromo-benzenes by Bastiansen and Hassel (1947) led them to conclude that deformation does occur, and is mainly of the out-of-plane bending variety with a magnitude of from 12° to 18°. Infra-red and ultra-violet studies on hexachlorobenzene by Kopelman and Schnepp (1959a, 1959b) led to self-contradictory results and theoretical models do not yet appear to be sufficiently precise (Coulson and Stocker, 1959; Gafner and Herbstein, 1960). X-ray studies by Tulinsky and White (1958) on hexachlorobenzene favour a planar molecule. However, as their analysis was confined to projections, it is likely that small deviations from planarity would be undetected.

In their analysis of 1:2-4:5-tetrachlorobenzene using X-ray diffraction and nuclear quadrupole resonance techniques, Dean, Pollak, Craven and Jeffrey (1958) found that the angle between carbon-chlorine vectors was 63 ± 1° but have not determined whether this represented in-plane or out-of-plane bending of the carbon-chlorine bonds. The isomorphous 1:2-4:5-tetrabromobenzene has been examined by Gafner and Herbstein (1960) and refined by three-dimensional least-squares methods. They concluded that the molecule was planar to within the accuracy of their measurements and that the deviations found by Dean <u>et al</u> (1958) in 1:2-4:5-tetrachlorobenzene were best explained by in-plane splaying-out of the carbon-chlorine bonds, increasing the relevant bond angles by $1\frac{1}{2}^{\circ}$, as they had found in

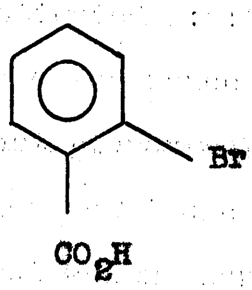
1:2-4:5-tetrabromobenzene. Recently Dean, Richardson and Sakurai have investigated 1:2:3:4-tetrachlorobenzene using nuclear quadrupole resonance techniques. Their results favour an almost planar molecule in the crystal, although small deviations of the carbon-chlorine bonds of about 1° from the molecular plane could not be discounted.

One of the major difficulties associated with the X-ray investigations of the polyhalogenobenzenes is that although the heavy atom positions may be determined with some precision, the same cannot be said for the lighter atoms. This is brought out clearly by Gafner and Herbstein's work on 1:2-4:5-tetrabromobenzene where the standard deviations in positional parameters of the bromine atoms are 0.003 Å compared with 0.026 Å for the carbon atoms. Thus a really detailed description of the molecular geometry is made difficult. This difficulty can be minimised by studying polysubstituted benzene derivatives containing only one halogen atom, thus offering a greater likelihood of locating the lighter atoms more accurately. For this reason, the structures of the overcrowded benzoic acids shown below as compounds I . . . V have been investigated.

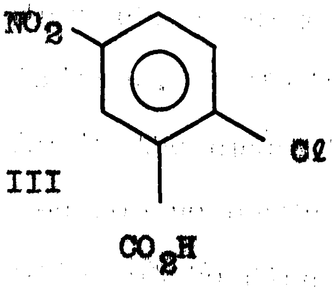
I



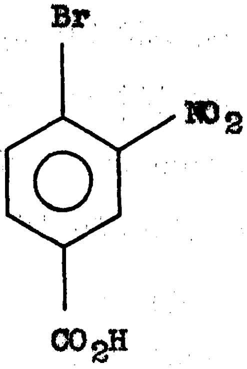
II



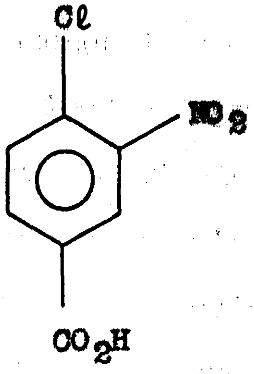
III



IV



V



The structures of o-chlorobenzoic acid (I), o-bromobenzoic acid (II) and 2-chloro-5-nitrobenzoic acid (III), have been refined by three-dimensional least-squares procedures. The analysis of o-bromobenzoic acid was not carried out quite so thoroughly as those of o-chlorobenzoic acid and 2-chloro-5-nitrobenzoic acid since the bromine atom in the molecule limits the accuracy obtainable. Although the structures of the remaining two acids, 4-bromo-3-nitrobenzoic acid (IV) and 4-chloro-3-nitrobenzoic acid (V), have not yet been refined extensively, none the less interesting information about the deviations from planarity in these molecules has been obtained.

The unit cell data for the acids have been published (Ferguson and Sim, 1959) and preliminary publication of results has been made (Ferguson and Sim, 1961a). A full account of the analysis of o-chlorobenzoic is being published (Ferguson and Sim, 1961b).

2. o-Chlorobenzoic acid.

2.1. Unit cell data.

Rotation, oscillation and Weissenberg photographic methods were used with copper $K\alpha$ radiation ($\lambda = 1.542$ Å). Single crystals of o-chlorobenzoic acid in the form of narrow laths elongated in the direction of the **b** crystal axis were obtained by crystallisation from acetone. Single crystal oscillation and rotation photographs were taken about the three crystallographic axes; Weissenberg photographs were taken of the $h0\ell$, $h1\ell$, $h2\ell$, $h3\ell$, and $0k\ell$ reciprocal lattice nets. The cell dimensions were obtained from rotation, and equatorial layer line moving-film photographs. From these, the monoclinic cell parameters were found to be

$$a = 14.73 \pm 0.03 \text{ Å}$$
$$b = 3.90 \pm 0.02 \text{ Å}$$
$$c = 25.50 \pm 0.05 \text{ Å}$$
$$\beta = 112^\circ 40' \pm 20'$$

The morphology of o-chlorobenzoic acid has been studied by Steinmetz (1914), whose axial ratios 3.782 : 1 : 6.625 differ slightly from those obtained in the present investigation (3.777 : 1 : 6.539).

The volume of the unit cell, obtained from the formula $V = abc.\sin\beta$, is 1351 Å^3. The density as determined by Steinmetz (1914), is 1.544 $g.cm^{-3}$, hence the number of molecules in the unit cell, given by

$$n = d\,V / 1.6602\,M$$

where d = density in $g.cm.^{-3}$
V = volume in Å^3
M = gram-molecular weight

is eight. This in turn leads to a calculated density of 1.539 $g.cm.^{-3}$

Inspection of the Weissenberg photographs showed that the systematic absences are

$hk\ell$ when $h + k$ is odd,
$h0\ell$ when h is odd and ℓ is odd,
$0k0$ when k is odd.

These conditions, however, do not uniquely determine the space group since they apply to space groups $C2/c$ (C^6_{2h}) and Cc (C^4_s).

2.2. Intensity data.

For the initial study, the $h0\ell$ set of spectra was collected using a Weissenberg camera. A pack of five films was used in this camera. This multiple-film technique has been described by Robertson (1943). The intensities were corrected for Lorentz and polarisation factors by the usual formula

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

and a set of $|F_o|$ values on an arbitrary scale derived.

For the three-dimensional analysis, the intensity data were obtained from multiple-film equi-inclination Weissenberg photographs of the $h1\ell$, $h2\ell$ and $h3\ell$ layers. The total number of independent reflexions observed was 1034. These intensities were estimated visually and corrected for Lorentz, polarisation, and rotation factors (D_e) appropriate to upper layers (Tunell, 1939) where

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

where μ is the equi-inclination angle $= \sin^{-1} \frac{n\lambda}{2d}$

and n is the number of the layer being corrected.

d is the length of the rotation axis.

λ is the wavelength of the radiation used.

Small crystals of uniform cross-section (with crystal sides between 0.10 and 0.15 mm. in length) perpendicular to the rotation axis were employed, and no corrections for absorption were made. The absorption coefficient for X-rays of wavelength 1.542 Å is 44.8 cm^{-1}

The sets of $|F_o|$ data were put on the same absolute scale during refinement by ensuring that $\sum k|F_o| = \sum |F_c|$ for each layer.

2.3. Structure determination.

At the outset it seemed probable that o-chlorobenzoic acid would occur as centrosymmetrical dimers in the crystal lattice with hydrogen bonding between adjacent carboxyl groups. The space group C2/c is based on a C face-centred lattice and the number of equivalent positions is eight. If the structure is composed of four centrosymmetrical dimers in the unit cell, these dimers must be situated on a set of space group centres of symmetry. The space group was assumed therefore to be C2/c and not Cc. This assumption was later justified by the good measure of agreement obtained between the observed and calculated structure factors.

An additional ambiguity arose at this stage in that the space group C2/c allows of an acid dimer packing around either the centre of symmetry at (0, 0, 0) or that at $(\frac{1}{4}, \frac{1}{4}, 0)$, (International Tables, Vol.I,p.101). In the analysis of the b-axis projection it is not possible to decide between these alternatives and initially the centre of symmetry at $(0, 0, 0)$ was chosen. However, during the refinement of the b-axis projection of o-chlorobenzoic acid, a study of o-bromobenzoic acid was begun, the two acids being isomorphous. Various trial structure factor calculations with the o-bromobenzoic acid three-dimensional data indicated clearly that the space group centre of symmetry at $(\frac{1}{4}, \frac{1}{4}, 0)$ was being utilised, not that at $(0, 0, 0)$.

2.4. The (010) projection.

Because of the short length of the b-axis it was evident that good resolution of the atoms would be obtained in the projection along this axis. The 156 observed $h0\ell$ data were used to compute a Patterson projection along the b-axis; this is shown in Fig.4. In determining the orientation of the molecule in the asymmetric unit use was made of the six peaks nearest the origin of the Patterson map since they represent the vectors between the carbon atoms of the benzene ring. The highest pair of these peaks also defines the direction

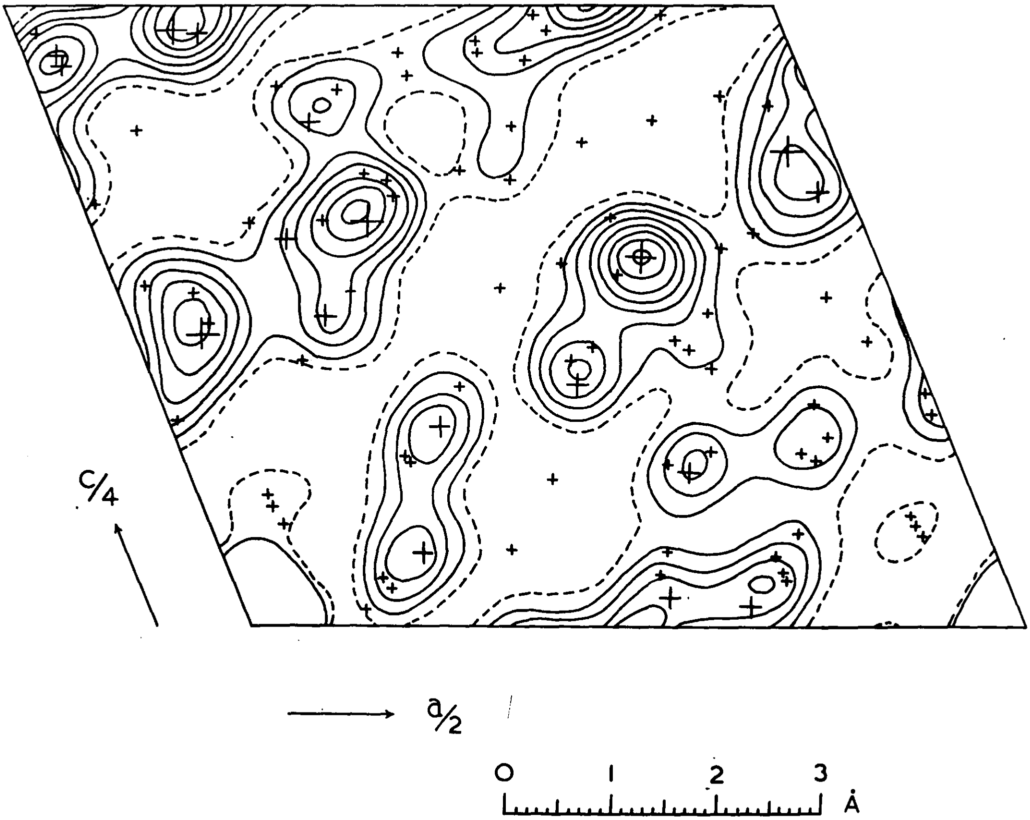


Fig.4. Patterson projection along the b axis. Contours at equal arbitrary intervals, the lowest contour being broken, origin peak contours omitted. The interatomic vectors are marked by crosses.

TABLE 1.

Coordinates of the carbon, oxygen and chlorine atoms as determined from the Patterson projection on (010), expressed as fractions of the unit cell sides assuming packing of the molecular dimer around the centre of symmetry at (0,0,0).

Atom c.f.Fig.8	$\underline{x}$	$\underline{z}$
C(1)	-0.065	0.056
C(2)	-0.113	0.098
C(3)	-0.049	0.153
C(4)	-0.094	0.191
C(5)	-0.194	0.169
C(6)	-0.259	0.113
C(7)	-0.215	0.075
O(1)	0.033	0.073
O(2)	-0.122	0.002
Cl	0.076	0.177

of the carbon-chlorine bond in the molecule. The highest peak on the map corresponds to a chlorine-chlorine vector between the chlorine atoms of a dimer. By assuming that the O - H . . . O hydrogen bonds between dimers are approximately 2.64 Å in length the structure was defined and x and z coordinates for the chlorine, carbon and oxygen atoms derived. These are listed in Table 1. The numbering system adopted for the molecule is shown in Fig.8.

The positions of the vectors to be expected from this structure are superimposed on the Patterson map in Fig.4. The height of a peak due to the interaction of a pair of atoms is proportional to the atomic number of the atoms involved. Crosses are used to show this on the Patterson map, the size of a cross being proportional to the peak height expected at that point.

Assuming an overall isotropic temperature factor $B = 4.0\ \text{Å}^2$ structure factors were calculated on DEUCE using an Alphacode program (see Appendix), the atomic form factors employed being those of Tomiie and Stam (1958) for chlorine and those of Berghuis <u>et al</u> (1955) for carbon and oxygen. The value of the usual discrepancy factor

$$R = \sum \left|(k|F_o| - |F_c|)\right| / \sum k|F_o|$$

was 0.321 for the 156 observed reflexions.

With measured structure amplitudes as coefficients and calculated signs a Fourier projection of electron density on (010) was computed. All the atoms included in the structure factor calculation were well resolved in this projection. New atomic coordinates were chosen from the Fourier map and structure factors recalculated. The value of R dropped to 0.160.

2.5. Least-squares refinement of the (010) projection.

The least-squares refinement program used in this and in all subsequent least-squares refinement described in this thesis was that devised by Dr. J.S.Rollett for the DEUCE computer (Rollett,1961). The program refines three positional and six thermal parameters per atom (in this projection two positional and three thermal parameters are refined), together with an overall scale factor. No facility is provided for refinement of, for example, the positional parameters alone keeping constant the isotropic temperature factors.

Three alternative weighting schemes are available for use with the program. The first of these is

$$\sqrt{w_1} = 1 \text{ if } |F_o| < F^*, \quad \sqrt{w_1} = \frac{F^*}{|F_o|} \text{ otherwise;}$$

the second is

$$\sqrt{w_2} = \frac{|F_o|}{F^*} \text{ if } |F_o| < F^*, \quad \sqrt{w_2} = \frac{F^*}{|F_o|} \text{ otherwise;}$$

where F^* is some preselected constant. The third scheme allows the square root of the weight for each reflexion to be punched on the decimal cards containing the reflexion data. The second weighting scheme was used throughout.

The program is divided into two parts. The first computes structure factors and accumulates the normal equation totals. Any number of the atoms included in the structure factor calculation may be omitted from the refinement process. A second program is used to solve the least-squares-produced normal equations for the new parameters. This makes use of the Gauss-Seidel iterative procedure, limitation of storage space in DEUCE making the full matrix treatment impossible. The program then punches out the new parameters in a form suitable for the next round of refinement. Flexibility is introduced by having simple facilities for punching out new parameters based on half or a quarter of the calculated shifts. The "Solve" program can also be made to punch out the normal equation totals from which the standard deviations of the parameters being refined can be obtained, in addition to the current value of $\sum w\,(k|F_o| - |F_c|)^2$, the quantity being minimised.

Before the least-squares refinement was commenced, coordinates for the hydrogen atoms were calculated by placing them radially at a distance of 1 Å from the appropriate benzene ring carbon atoms. The hydrogen atom of the carboxyl group was placed 1 Å away from O(2) on the line to O(1) of the carboxyl group related to it by the centre of symmetry. The atomic form factors chosen for hydrogen in the least-squares structure-factor calculations were those of McWeeny (1951). The temperature factor B was again assumed to be 4.0 Å^2.

After several cycles of refinement in which the positional and thermal parameters of the atoms other than hydrogen were adjusted, the value of R was reduced to 0.108. The x and z coordinates obtaining at this stage are listed in Table 2. A difference Fourier synthesis was then computed with all the atoms including hydrogens subtracted. The absence of any significant peaks on this map (Fig.5) is indicative of the fact that refinement in this projection was complete. When the

TABLE 2.

Coordinates of the carbon, oxygen and chlorine atoms obtained from the least-squares refinement of the *b*-axis projection. For each atom two possible values of x are given. These differ by ¼, depending on the symmetry centre chosen as the centre of the molecular dimer.

Atom	x	$x + \frac{1}{4}$	z
C(1)	-0.0566	0.1934	0.0532
C(2)	-0.1023	0.1477	0.0969
C(3)	-0.0528	0.1972	0.1493
C(4)	-0.0990	0.1510	0.1854
C(5)	-0.2006	0.0494	0.1674
C(6)	-0.2466	0.0034	0.1162
C(7)	-0.2003	0.0497	0.0793
O(1)	0.0247	0.2747	0.0612
O(2)	-0.1073	0.1427	0.0124
Cl	0.0751	0.3251	0.1777

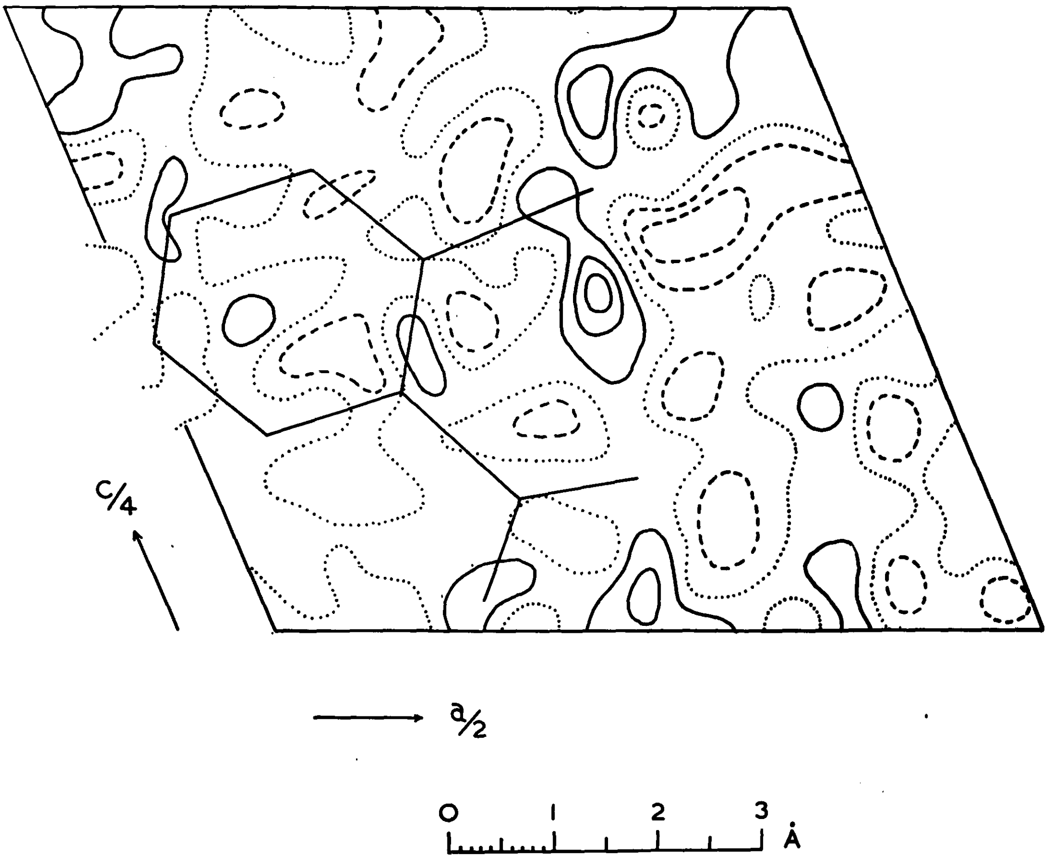


Fig.5. Final ($F_o - F_c$) synthesis. All atoms including hydrogen subtracted. Contour interval 0.2 eÅ^{-2}, negative contours broken, zero contour dotted.

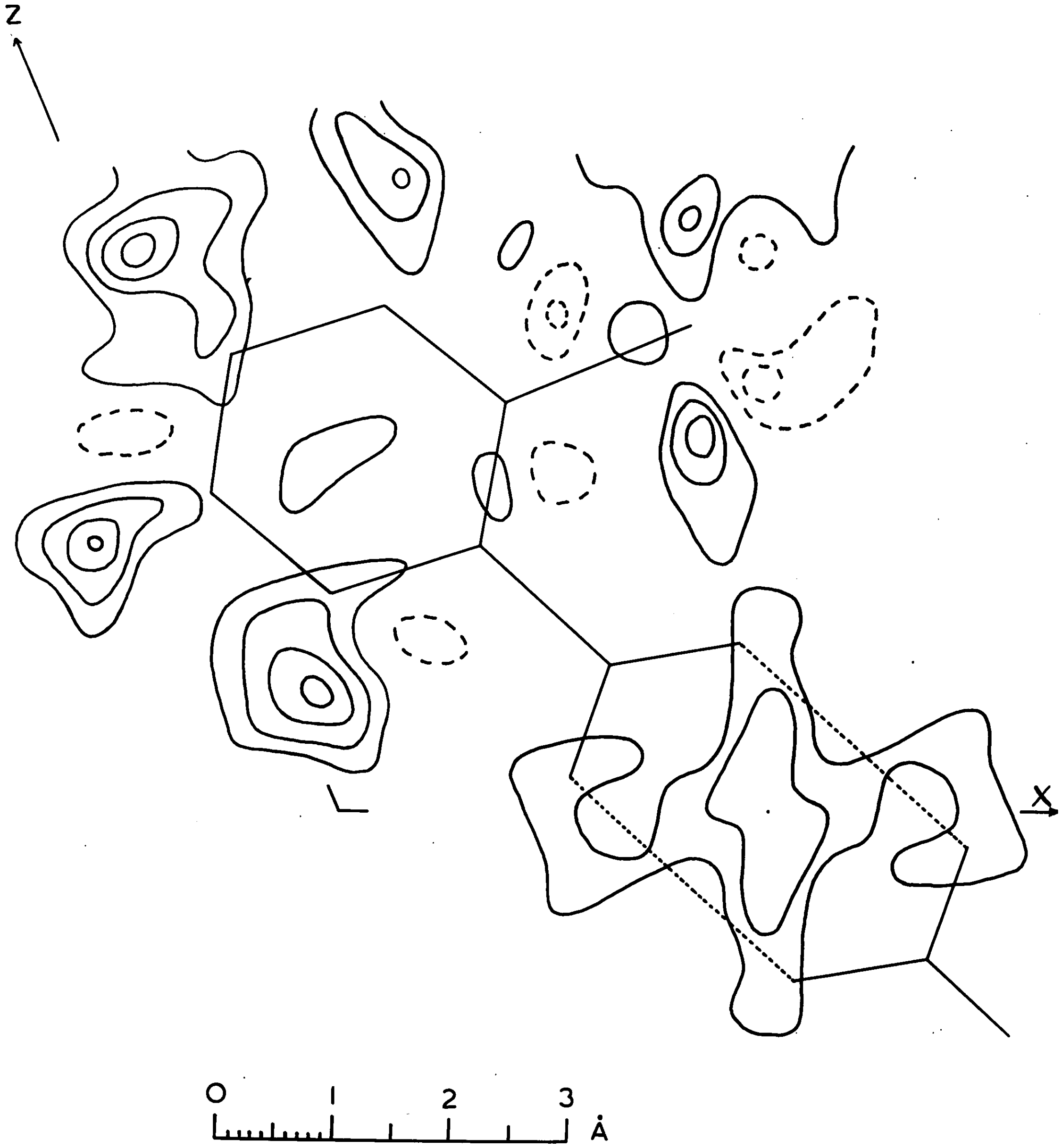


Fig.6. Difference-synthesis projection on (010) to show the electron distribution due to the hydrogen atoms. Contours at intervals of 0.2 eÅ^{-2}, negative contours broken, zero contour omitted.

hydrogen atoms were omitted from the structure-factor calculation the value of R rose to 0.124. With the $F_o - F_c'$ values obtained from this calculation, a further h0ℓ difference Fourier was computed (Fig.6). The peaks on this map, with the exception of those around the chlorine atom, are clearly attributable to the hydrogen atoms. The carboxyl hydrogen atom which takes part in the hydrogen bond between two molecules has a more diffuse peak than any of the hydrogen atoms attached to the carbon atoms of the benzene ring. This has been found to be the case in salicylic acid (Cochran, 1953) and benzoic acid (Sim, 1955) and is probably connected with the partial ionisation of the hydrogen atom of the carboxyl group.

2.6. Three-dimensional refinement.

As mentioned earlier (2.3.) structure analysis of o-bromobenzoic acid was begun during the course of the h0ℓ refinement of o-chlorobenzoic acid. Because of their isomorphous character it was possible to use y-coordinates for the atoms of o-bromobenzoic acid as a starting point for the detailed three-dimensional analysis of o-chlorobenzoic acid. Accordingly with x and z coordinates from the two-dimensional analysis, y-coordinates from the o-bromobenzoic acid refinement, and an isotropic temperature parameter B = 4.0 Å^2 for all atoms including hydrogen, structure factors were calculated for the h2ℓ and h3ℓ reflexions (the h1ℓ intensities were being estimated at this time), R values of 0.300 and 0.360 being obtained. The y- coordinates of the atoms apart from hydrogens were improved by computing difference Fourier line syntheses passing close to the atomic centres and in a direction parallel to the b crystal axis. In the next structure-factor calculation, by which time the h1ℓ data were available, the values of the residual R for the various sets of data were 0.174 for the h1ℓ , 0.200 for the h2ℓ and 0.263 for the h3ℓ reflexions.

The good measure of agreement between the observed and calculated structure amplitudes appeared to justify proceeding to a least-squares refinement of positional and anisotropic temperature-factor parameters for all the atoms other than hydrogen. In the least-squares calculations 223 unobserved terms were included each with a value of $|F_o|$ equal to one half of the minimum $|F_o|$ locally observable. The values of R and $\sum w\Delta^2$

TABLE 3.

Values of R and $\sum w\Delta^2$ obtained during the three-dimensional least-squares refinement.

Cycle	R	$\sum w\Delta^2$
1	0.192	256 *
2	0.163	244
3	0.150	206
4	0.132	173
5	0.120	140
6	0.112	116
7	0.105	- ≠

* h0ℓ data omitted from cycle 1.

≠ Structure factor calculation only.

The values of R are based on observed data only.

Table 4: Calculated and measured values of the structure factors.

h	k	l	F(calc)	F(meas)
0	0	4	-100.9	77.6
0	0	6	101.5	90.7
0	0	8	-133.5	120.0
0	0	10	14.4	15.5
0	0	12	91.6	70.8
0	0	14	-47.4	44.9
0	0	16	37.5	34.1
0	0	18	31.5	30.9
0	0	20	-19.8	19.2
0	0	22	17.4	15.6
0	0	24	-11.3	10.7
0	0	26	-15.4	15.7
0	0	28	7.0	< 3.2
0	0	30	-9.2	< 2.0
2	0	-30	-4.1	< 5.0
2	0	-28	-0.4	< 4.0
2	0	-26	27.6	29.3
2	0	-24	13.8	19.2
2	0	-22	7.8	< 4.2
2	0	-20	5.6	< 4.7
2	0	-18	-37.1	31.8
2	0	-16	14.6	12.4
2	0	-14	34.0	33.8
2	0	-12	-14.1	11.2
2	0	-10	38.5	34.2
2	0	-8	77.9	79.4
2	0	-6	-58.8	63.2
2	0	-4	35.8	43.7
2	0	-2	50.0	49.5
2	0	0	-112.0	108.3
2	0	2	-74.9	72.4
2	0	4	-107.5	104.8
2	0	6	-44.3	44.5
2	0	8	74.8	71.7
2	0	10	2.2	< 3.4
2	0	12	-10.9	13.0
2	0	14	-20.4	23.3
2	0	16	-51.5	53.0
2	0	18	9.2	< 4.0
2	0	20	-10.9	< 4.9
2	0	22	-30.6	34.3
2	0	24	18.6	17.3
2	0	26	2.0	< 3.7
2	0	28	-7.2	< 2.6
4	0	-30	14.6	13.6
4	0	-28	-10.8	8.3
4	0	-26	5.2	< 4.7
4	0	-24	19.9	19.4
4	0	-22	-66.7	73.5
4	0	-20	-1.3	< 4.7
4	0	-18	67.4	73.1
4	0	-16	-32.2	28.8
4	0	-14	37.2	33.7
4	0	-12	-18.3	20.6
4	0	-10	-187.3	182.6
4	0	-8	2.8	6.3
4	0	-6	-47.5	41.8
4	0	-4	-111.8	124.4
4	0	-2	72.2	87.2
4	0	0	-10.9	11.3
4	0	2	-37.8	44.2
4	0	4	14.5	20.8
4	0	6	-29.2	34.9
4	0	8	-21.9	20.9
4	0	10	25.4	24.2
4	0	12	-41.7	44.0
4	0	14	11.6	12.7
4	0	16	25.4	21.3
4	0	18	-22.4	20.2
4	0	20	7.3	9.4
4	0	22	11.5	9.7
4	0	24	-3.2	< 3.7
4	0	26	3.5	< 2.7
6	0	-30	-14.4	13.5
6	0	-28	18.1	16.1
6	0	-26	-4.9	< 4.7
6	0	-24	-30.1	27.5
6	0	-22	15.0	11.4
6	0	-20	-22.5	20.8
6	0	-18	-17.9	18.7
6	0	-16	28.0	27.2
6	0	-14	-64.9	64.0
6	0	-12	-30.3	27.6
6	0	-10	46.5	46.4
6	0	-8	-7.8	12.3
6	0	-6	57.7	61.8
6	0	-4	-28.9	33.5
6	0	-2	-27.0	31.0
6	0	0	133.6	134.7
6	0	2	-32.0	37.4
6	0	4	-18.2	18.0
6	0	6	78.7	78.5
6	0	8	-21.4	19.9
6	0	10	27.6	25.1
6	0	12	46.8	43.4
6	0	14	-36.0	35.1
6	0	16	8.4	< 4.9
6	0	18	19.0	18.7
6	0	20	-9.8	< 4.3
6	0	22	12.9	10.1
6	0	24	2.2	< 2.5
8	0	-30	-2.5	< 3.6
8	0	-28	-14.5	18.7
8	0	-26	20.5	17.2
8	0	-24	-6.5	< 4.9
8	0	-22	-5.2	< 4.9
8	0	-20	32.9	29.4
8	0	-18	-7.7	< 4.6
8	0	-16	21.6	22.1
8	0	-14	28.8	25.3
8	0	-12	-30.8	30.8
8	0	-10	41.0	42.6
8	0	-8	44.5	47.7
8	0	-6	-22.5	24.6
8	0	-4	76.3	85.8
8	0	-2	58.0	75.8
8	0	0	-47.0	49.9
8	0	2	15.8	15.4
8	0	4	-24.9	26.2
8	0	6	-33.1	31.9
8	0	8	50.2	52.8
8	0	10	13.2	< 4.8
8	0	12	-21.8	19.5
8	0	14	3.2	< 4.0
8	0	16	-11.9	12.7
8	0	18	-3.5	< 4.1
8	0	20	4.3	< 3.3
8	0	22	-3.9	< 1.9
10	0	-30	7.0	9.3
10	0	-28	2.3	< 4.0
10	0	-26	0.3	< 4.5
10	0	-24	16.7	13.4
10	0	-22	-20.0	22.8
10	0	-20	-1.0	< 4.9
10	0	-18	42.9	35.4
10	0	-16	-10.6	9.2
10	0	-14	30.3	30.4
10	0	-12	10.2	10.6
10	0	-10	-53.0	54.1
10	0	-8	29.2	28.6
10	0	-6	-6.0	< 4.5
10	0	-4	-62.9	71.8
10	0	-2	17.0	14.9
10	0	0	-16.2	16.1
10	0	2	-22.5	23.5
10	0	4	30.7	29.7
10	0	6	-6.7	< 4.9
10	0	8	-6.9	< 4.9
10	0	10	4.7	< 4.9
10	0	12	-36.6	32.4
10	0	14	-5.5	< 4.8
10	0	16	10.9	7.1
10	0	18	-3.5	< 2.7
12	0	-30	-14.3	13.3
12	0	-28	14.5	10.1
12	0	-26	-3.5	< 4.2
12	0	-24	-10.7	15.5
12	0	-22	26.2	24.2
12	0	-20	-7.9	< 4.9
12	0	-18	-14.2	16.9
12	0	-16	20.3	19.4
12	0	-14	-72.5	67.3
12	0	-12	-53.2	58.8
12	0	-10	41.1	44.1
12	0	-8	-1.9	< 4.8
12	0	-6	19.9	13.9
12	0	-4	19.5	20.2
12	0	-2	-35.3	34.9
12	0	0	6.4	< 4.9
12	0	2	-3.8	< 4.9
12	0	4	-24.5	26.3
12	0	6	12.8	11.5
12	0	8	-2.9	< 4.6
12	0	10	0.9	< 4.1
12	0	12	17.8	14.2
12	0	14	-3.4	< 2.8
14	0	-28	-12.6	9.9
14	0	-26	6.4	< 3.5
14	0	-24	-12.9	13.0
14	0	-22	-14.8	12.1
14	0	-20	12.8	< 4.6
14	0	-18	-6.8	< 4.7
14	0	-16	0.9	< 4.8
14	0	-14	16.1	16.7
14	0	-12	2.6	< 4.9
14	0	-10	25.9	28.0
14	0	-8	11.8	11.0
14	0	-6	-29.6	31.9
14	0	-4	-3.7	< 4.9
14	0	-2	5.5	< 4.8
14	0	0	1.9	< 4.7
14	0	2	23.2	23.0
14	0	4	4.6	< 4.2
14	0	6	-4.6	< 3.9
14	0	8	15.1	14.7
14	0	10	-4.1	< 2.6
16	0	-24	24.4	21.9
16	0	-22	9.9	10.9
16	0	-20	-6.2	< 3.8
16	0	-18	17.5	20.5
16	0	-16	-9.8	10.2
16	0	-14	-3.7	8.5
16	0	-12	9.6	11.2
16	0	-10	-12.0	15.0
16	0	-8	12.0	15.8
16	0	-6	13.8	15.5
16	0	-4	-11.4	15.0
16	0	-2	11.5	10.0
16	0	0	4.6	< 3.6
16	0	2	-13.6	12.2
18	0	-18	-3.4	< 2.7
18	0	-16	13.3	10.8
18	0	-14	-11.2	19.0
18	0	-12	-4.0	< 3.1
18	0	-10	14.6	20.8
18	0	-8	-8.5	12.4
18	0	-6	-3.2	< 2.7
18	0	-4	-0.0	< 2.3
1	1	-29	5.7	8.8
1	1	-28	4.1	4.3
1	1	-27	6.7	8.4
1	1	-26	4.3	5.7
1	1	-25	-2.0	< 2.5
1	1	-24	-14.1	15.2
1	1	-23	17.5	18.6
1	1	-22	-1.3	5.5
1	1	-21	-8.5	7.9
1	1	-20	-1.4	< 2.7
1	1	-19	-11.1	10.3
1	1	-18	-8.1	10.1
1	1	-17	25.9	24.1
1	1	-16	34.1	35.3
1	1	-15	-27.9	28.7
1	1	-14	16.0	18.2
1	1	-13	-0.9	< 2.0
1	1	-12	10.8	8.0
1	1	-11	46.3	43.1
1	1	-10	64.3	64.1
1	1	-9	-59.6	59.9
1	1	-8	-21.8	19.0
1	1	-7	14.5	10.1
1	1	-6	-0.6	6.6
1	1	-5	93.0	83.6
1	1	-4	83.5	85.5
1	1	-3	-87.4	98.1
1	1	-2	-129.0	118.6
1	1	-1	-13.5	5.9
1	1	0	-80.2	57.0
1	1	1	-64.7	58.9
1	1	2	152.4	149.7
1	1	3	-206.0	197.0
1	1	4	64.4	53.7
1	1	5	43.7	42.1
1	1	6	58.6	53.3
1	1	7	21.2	19.9
1	1	8	15.4	13.1
1	1	9	-36.9	32.7
1	1	10	-70.7	65.0
1	1	11	29.6	28.2
1	1	12	-13.4	14.4
1	1	13	-42.2	40.7
1	1	14	-7.7	9.0
1	1	15	-24.8	25.4
1	1	16	-12.6	11.8
1	1	17	12.4	12.2
1	1	18	-0.5	< 2.6
1	1	19	-30.3	28.9
1	1	20	-10.3	9.4
1	1	21	1.5	< 2.7
1	1	22	10.6	10.4
1	1	23	8.7	9.1
1	1	24	5.4	5.5
1	1	25	-11.9	10.6
1	1	26	-11.5	11.8
1	1	27	8.6	9.0
3	1	-29	-2.1	< 1.9
3	1	-28	-3.5	6.1
3	1	-27	9.6	10.3
3	1	-26	0.0	4.5
3	1	-25	-20.0	22.8
3	1	-24	-4.6	4.9
3	1	-23	-21.5	21.0
3	1	-22	17.0	18.4
3	1	-21	10.3	9.0
3	1	-20	42.8	45.0
3	1	-19	-17.3	18.9
3	1	-18	-11.3	9.3
3	1	-17	10.6	11.3
3	1	-16	-23.5	25.6
3	1	-15	25.5	24.4
3	1	-14	0.8	< 2.0
3	1	-13	-63.7	60.2
3	1	-12	45.8	41.6
3	1	-11	-14.9	13.6
3	1	-10	-3.6	4.7
3	1	-9	-7.8	10.8
3	1	-8	32.3	35.3
3	1	-7	-84.9	85.6
3	1	-6	-16.3	13.9
3	1	-5	12.7	15.0
3	1	-4	27.6	28.4
3	1	-3	2.2	4.1
3	1	-2	-2.0	4.1
3	1	-1	-54.0	53.0
3	1	0	-63.1	61.8
3	1	1	22.9	22.8
3	1	2	-17.3	16.6
3	1	3	-7.0	7.8
3	1	4	-43.4	38.5
3	1	5	-18.1	19.8
3	1	6	-53.4	45.3
3	1	7	46.6	42.0
3	1	8	-5.8	5.7
3	1	9	-23.7	22.1
3	1	10	-19.0	15.9
3	1	11	-20.6	20.2
3	1	12	6.0	8.2
3	1	13	26.7	26.2
3	1	14	27.9	27.7
3	1	15	-14.4	11.2
3	1	16	-21.6	17.7
3	1	17	3.4	5.4
3	1	18	-10.1	9.3
3	1	19	22.9	20.9
3	1	20	17.3	12.1
3	1	21	-7.0	6.4
3	1	22	-7.0	8.8
3	1	23	8.4	8.2
3	1	24	-4.1	4.8
3	1	25	10.7	11.3
3	1	26	3.7	4.6
3	1	27	-9.5	9.8
5	1	-31	6.2	5.0
5	1	-30	4.8	5.4
5	1	-29	0.6	< 2.0
5	1	-28	4.7	7.1
5	1	-27	-20.3	20.0
5	1	-26	-22.2	23.5
5	1	-25	14.8	14.1
5	1	-24	10.8	10.9
5	1	-23	-5.3	6.3
5	1	-22	14.1	17.7
5	1	-21	-13.6	15.7
5	1	-20	-39.3	45.1
5	1	-19	46.4	50.2
5	1	-18	-4.2	< 2.5
5	1	-17	-25.9	25.1
5	1	-16	-7.8	5.2
5	1	-15	-43.2	42.2
5	1	-14	-20.7	25.0
5	1	-13	35.3	33.8
5	1	-12	58.1	56.4
5	1	-11	-30.3	31.1
5	1	-10	-4.8	7.5
5	1	-9	30.9	32.9
5	1	-8	-67.1	71.6
5	1	-7	77.3	76.8
5	1	-6	-18.1	18.1
5	1	-5	-24.7	25.7
5	1	-4	-20.7	19.7
5	1	-3	67.7	67.0
5	1	-2	7.1	5.7
5	1	-1	31.8	35.3
5	1	0	-4.5	6.7
5	1	1	-35.5	35.7
5	1	2	-9.2	11.7
5	1	3	49.9	47.6
5	1	4	54.8	50.3
5	1	5	1.9	4.0
5	1	6	11.0	12.8
5	1	7	-2.7	5.1
5	1	8	-17.4	16.0
5	1	9	50.6	45.7
5	1	10	15.5	17.3
5	1	11	-11.5	10.4
5	1	12	-11.0	11.6
5	1	13	-3.6	5.9
5	1	14	-3.5	4.9
5	1	15	26.7	24.2
5	1	16	9.7	9.8
5	1	17	-8.2	8.6
5	1	18	1.0	< 2.6
5	1	19	4.8	5.8
5	1	20	2.9	< 2.4
5	1	21	10.3	10.5
5	1	22	3.6	5.5
5	1	23	-9.5	10.2
5	1	24	-5.6	5.6
7	1	-30	-9.9	9.9
7	1	-29	10.1	8.9
7	1	-28	-1.6	4.1
7	1	-27	4.3	4.8
7	1	-26	4.8	5.7
7	1	-25	-11.4	10.3
7	1	-24	-5.3	< 2.7
7	1	-23	17.3	15.4
7	1	-22	6.3	6.1
7	1	-21	4.8	6.6
7	1	-20	0.5	< 2.6
7	1	-19	-5.6	4.8
7	1	-18	-17.0	17.8
7	1	-17	20.3	20.8
7	1	-16	1.4	< 2.4
7	1	-15	-7.3	7.2
7	1	-14	-1.4	< 2.2
7	1	-13	5.8	5.7
7	1	-12	5.9	6.2
7	1	-11	54.0	49.6
7	1	-10	20.4	20.0
7	1	-9	-10.6	8.3
7	1	-8	-12.0	8.5
7	1	-7	17.5	17.7
7	1	-6	44.1	39.3
7	1	-5	46.3	44.0
7	1	-4	56.5	47.7
7	1	-3	-49.7	46.8
7	1	-2	-50.7	51.9
7	1	-1	10.8	13.3
7	1	0	-6.2	< 2.0
7	1	1	-0.6	< 2.0
7	1	2	37.6	36.9
7	1	3	-60.8	58.6
7	1	4	-13.5	15.9
7	1	5	45.3	42.2
7	1	6	34.6	32.4
7	1	7	16.5	17.4
7	1	8	14.9	11.5
7	1	9	-30.2	29.9
7	1	10	-30.2	32.7
7	1	11	16.7	15.0
7	1	12	17.9	16.5
7	1	13	-18.1	15.0
7	1	14	10.6	10.7
7	1	15	-17.7	19.2
7	1	16	11.0	10.8
7	1	17	14.1	14.6
7	1	18	2.6	< 2.3
7	1	19	-10.0	10.8
7	1	20	5.0	7.2
7	1	21	-5.2	6.6
9	1	-31	4.1	4.2
9	1	-30	12.6	12.1
9	1	-29	-12.0	10.8
9	1	-28	-1.6	< 2.1
9	1	-27	9.1	9.4
9	1	-26	-3.8	7.0
9	1	-25	-0.3	< 2.5
9	1	-24	3.4	< 2.6
9	1	-23	-14.8	13.8
9	1	-22	0.4	< 2.7
9	1	-21	20.8	20.2
9	1	-20	19.2	18.4
9	1	-19	-2.7	4.9
9	1	-18	6.7	9.2
9	1	-17	-8.6	7.6
9	1	-16	-0.2	4.7
9	1	-15	16.7	16.3
9	1	-14	23.4	22.1
9	1	-13	34.4	34.4
9	1	-12	-4.6	4.4
9	1	-11	-9.0	9.2
9	1	-10	-5.8	6.4
9	1	-9	14.7	14.2
9	1	-8	7.3	7.3
9	1	-7	-41.5	36.2
9	1	-6	-23.6	24.0
9	1	-5	-8.8	11.2
9	1	-4	-1.3	4.2
9	1	-3	2.0	< 2.2
9	1	-2	17.4	21.0
9	1	-1	-36.2	43.2
9	1	0	2.6	< 2.3
9	1	1	7.8	8.8
9	1	2	14.5	13.9
9	1	3	13.9	15.9
9	1	4	5.0	5.1
9	1	5	-14.1	17.1
9	1	6	-25.5	24.9
9	1	7	3.0	< 2.6
9	1	8	-23.0	20.6
9	1	9	-17.1	18.5
9	1	10	-8.6	8.2
9	1	11	-22.4	21.4
9	1	12	7.2	7.9
9	1	13	6.3	7.7
9	1	14	9.1	9.9
9	1	15	3.5	4.3
9	1	16	-4.9	5.8
9	1	17	2.6	< 1.9
9	1	18	-2.6	4.6
9	1	19	6.1	6.7
11	1	-30	6.1	5.6
11	1	-29	2.4	< 1.7
11	1	-28	3.1	4.9
11	1	-27	-14.3	12.8
11	1	-26	-9.2	5.7
11	1	-25	9.6	8.6
11	1	-24	14.9	13.7
11	1	-23	-2.3	< 2.6
11	1	-22	8.3	8.4
11	1	-21	-14.9	13.6
11	1	-20	-23.2	21.5
11	1	-19	22.9	20.5
11	1	-18	-1.4	< 2.7
11	1	-17	-28.3	24.7
11	1	-16	-22.6	20.5
11	1	-15	-40.6	37.4
11	1	-14	-17.0	16.1
11	1	-13	23.4	29.0
11	1	-12	48.9	40.6
11	1	-11	-17.0	16.8
11	1	-10	-1.4	< 2.6
11	1	-9	7.3	7.2
11	1	-8	-25.1	25.3
11	1	-7	39.3	38.7
11	1	-6	16.0	16.6
11	1	-5	-31.2	32.2
11	1	-4	-20.4	19.3
11	1	-3	1.4	< 2.6
11	1	-2	-14.1	15.6
11	1	-1	16.2	18.4
11	1	0	3.0	< 2.6
11	1	1	-26.5	27.5
11	1	2	22.6	22.6
11	1	3	13.1	14.1
11	1	4	2.4	6.3
11	1	5	6.1	8.0
11	1	6	8.1	8.7
11	1	7	-13.2	13.4
11	1	8	-3.6	4.8
11	1	9	16.8	18.3
11	1	10	13.8	15.7
11	1	11	3.4	5.2
11	1	12	1.2	< 2.2
11	1	13	0.2	< 2.0
11	1	14	-8.0	9.1
11	1	15	11.8	12.9
11	1	16	0.9	3.2
13	1	-28	-5.1	6.4
13	1	-27	3.5	< 1.8
13	1	-26	1.1	< 2.0
13	1	-25	-12.4	9.7
13	1	-24	-9.0	8.3
13	1	-23	8.4	5.8
13	1	-22	-0.1	< 2.4
13	1	-21	5.0	5.0
13	1	-20	5.5	6.0
13	1	-19	-14.7	12.8
13	1	-18	-9.4	8.5
13	1	-17	12.0	11.3
13	1	-16	8.2	7.8
13	1	-15	8.2	9.6
13	1	-14	18.0	20.2
13	1	-13	4.1	5.9
13	1	-12	-10.5	12.0
13	1	-11	33.4	30.0
13	1	-10	22.3	24.4
13	1	-9	-1.2	< 2.7
13	1	-8	-19.2	19.8
13	1	-7	-18.6	20.2
13	1	-6	0.4	< 2.7
13	1	-5	5.1	9.4
13	1	-4	20.2	23.1
13	1	-3	-8.2	10.0
13	1	-2	9.9	10.0
13	1	-1	10.5	13.6
13	1	0	6.4	9.2
13	1	1	19.3	22.9
13	1	2	3.8	5.4
13	1	3	-5.4	8.2
13	1	4	-4.6	6.3
13	1	5	9.7	11.9
13	1	6	4.6	8.2
13	1	7	4.2	5.5
13	1	8	-2.3	< 2.1
13	1	9	-10.4	12.7
13	1	10	-8.5	10.5
13	1	11	3.8	5.0
13	1	12	5.8	7.4
15	1	-27	9.4	10.7
15	1	-26	4.1	6.8
15	1	-25	9.9	10.3
15	1	-24	5.9	6.9
15	1	-23	5.9	5.6
15	1	-22	-10.6	11.7
15	1	-21	15.2	16.2
15	1	-20	2.2	3.6
15	1	-19	0.7	< 2.3
15	1	-18	-0.9	< 2.3
15	1	-17	-10.7	10.0
15	1	-16	-8.0	9.4
15	1	-15	12.0	13.5
15	1	-14	12.6	14.8
15	1	-13	-7.5	8.9
15	1	-12	1.4	4.1
15	1	-11	-5.1	4.2
15	1	-10	1.1	4.1
15	1	-9	10.1	12.2
15	1	-8	16.7	16.0
15	1	-7	-12.2	14.3
15	1	-6	0.2	4.1
15	1	-5	2.4	< 2.4
15	1	-4	2.0	< 2.4
15	1	-3	13.7	15.4
15	1	-2	1.8	5.5
15	1	-1	-8.5	9.7
15	1	0	-15.5	16.1
15	1	1	0.9	< 2.1
15	1	2	-0.3	< 2.0
15	1	3	-0.1	3.2
15	1	4	8.8	9.9
15	1	5	-11.9	12.1
15	1	6	-3.1	5.2
17	1	-22	6.5	6.8
17	1	-21	-14.1	14.8
17	1	-20	4.9	7.0
17	1	-19	2.0	< 1.6
17	1	-18	5.6	5.6
17	1	-17	-1.7	< 1.8
17	1	-16	-0.6	< 1.9

Table 4: (Continued)

h	k	l	F(calc)	F(meas)
17	1	-15	-9.0	11.4
17	1	-14	-3.1	<1.9
17	1	-13	11.3	11.2
17	1	-12	6.7	8.0
17	1	-11	-1.9	<2.0
17	1	-10	-7.5	10.2
17	1	-9	-5.3	7.6
17	1	-8	-9.8	12.4
17	1	-7	6.0	6.9
17	1	-6	5.2	6.7
17	1	-5	-11.5	13.6
17	1	-4	-2.2	3.1
17	1	-3	-3.4	4.0
17	1	-2	0.3	<1.5
17	1	-1	6.2	8.6
0	2	2	12.3	16.8
0	2	3	68.9	63.1
0	2	4	-24.4	25.5
0	2	5	74.4	72.3
0	2	6	-25.5	25.4
0	2	7	-90.2	86.8
0	2	8	12.4	12.8
0	2	9	-5.7	8.1
0	2	10	-13.0	12.4
0	2	11	-0.7	3.1
0	2	12	-16.9	14.5
0	2	13	-45.1	42.4
0	2	14	7.8	7.2
0	2	15	11.3	11.9
0	2	16	-10.3	8.9
0	2	17	-12.3	11.4
0	2	18	-2.8	<2.7
0	2	19	-13.6	10.8
0	2	20	13.2	12.9
0	2	21	13.7	14.0
0	2	22	-8.8	7.8
0	2	23	-9.7	10.3
0	2	24	-5.7	6.2
2	2	-26	-5.9	6.0
2	2	-25	-3.3	4.2
2	2	-24	8.4	8.9
2	2	-23	12.5	12.3
2	2	-22	-3.7	6.0
2	2	-21	15.3	16.0
2	2	-20	-14.3	14.7
2	2	-19	-8.7	6.2
2	2	-18	6.0	5.4
2	2	-17	2.4	4.9
2	2	-16	-6.4	9.2
2	2	-15	-12.0	10.5
2	2	-14	-7.3	6.2
2	2	-13	-32.6	35.5
2	2	-12	17.2	17.4
2	2	-11	7.3	6.0
2	2	-10	-1.3	<1.9
2	2	-9	-13.3	13.1
2	2	-8	9.0	13.4
2	2	-7	-36.3	35.3
2	2	-6	10.8	10.8
2	2	-5	8.4	9.8
2	2	-4	-31.2	32.0
2	2	-3	-23.6	25.4
2	2	-2	-4.8	4.4
2	2	-1	-24.7	24.2
2	2	0	5.5	3.6
2	2	1	30.3	29.2
2	2	2	-44.6	39.4
2	2	3	-30.0	27.9
2	2	4	19.2	17.8
2	2	5	-52.7	48.9
2	2	6	33.9	31.8
2	2	7	-24.0	23.1
2	2	8	-8.8	6.5
2	2	9	-23.3	20.0
2	2	10	21.5	20.7
2	2	11	21.9	22.0
2	2	12	-1.6	<2.5
2	2	13	7.9	11.2
2	2	14	-26.8	24.2
2	2	15	-13.8	11.7
2	2	16	14.8	11.8
2	2	17	18.5	15.3
2	2	18	10.8	9.4
2	2	19	-3.0	5.7
2	2	20	-8.0	8.4
2	2	21	-5.7	7.2
2	2	22	6.3	7.1
2	2	23	11.3	10.4
2	2	24	1.2	<1.9
2	2	25	-9.1	8.9
4	2	-29	-12.5	11.6
4	2	-28	1.2	<1.8
4	2	-27	4.7	6.5
4	2	-26	4.6	5.0
4	2	-25	13.9	16.2
4	2	-24	-2.3	<2.5
4	2	-23	-20.6	19.7
4	2	-22	4.0	<2.7
4	2	-21	1.3	<2.7
4	2	-20	5.1	6.6
4	2	-19	-19.2	19.2
4	2	-18	11.2	11.3
4	2	-17	-50.6	49.1
4	2	-16	15.8	14.2
4	2	-15	37.9	34.2
4	2	-14	-11.2	11.3
4	2	-13	16.3	14.6
4	2	-12	-11.8	14.0
4	2	-11	-28.7	28.9
4	2	-10	4.0	3.7
4	2	-9	34.2	33.6
4	2	-8	-7.7	7.6
4	2	-7	-22.8	21.2
4	2	-6	23.8	25.6
4	2	-5	-24.9	23.4
4	2	-4	22.4	21.9
4	2	-3	29.9	29.1
4	2	-2	-9.8	10.1
4	2	-1	-24.2	26.9
4	2	0	25.2	25.6
4	2	1	16.1	18.5
4	2	2	18.9	20.0
4	2	3	40.5	34.3
4	2	4	-19.5	16.8
4	2	5	-15.5	14.9
4	2	6	1.4	<2.1
4	2	7	25.9	24.4
4	2	8	2.7	4.7
4	2	9	18.6	15.9
4	2	10	-13.2	12.3
4	2	11	-11.1	10.2
4	2	12	10.5	8.7
4	2	13	24.2	21.2
4	2	14	12.3	11.3
4	2	15	7.0	6.2
4	2	16	5.4	5.0
4	2	17	-7.6	9.0
4	2	18	6.6	5.9
4	2	19	12.3	11.9
4	2	20	-5.7	4.7
4	2	21	-3.5	4.4
4	2	22	-5.3	6.3
4	2	23	-7.1	6.6
6	2	-29	6.5	5.6
6	2	-28	-0.9	<1.8
6	2	-27	-6.5	5.6
6	2	-26	7.6	7.6
6	2	-25	-3.7	6.0
6	2	-24	-1.4	<2.5
6	2	-23	16.7	16.4
6	2	-22	-11.9	10.7
6	2	-21	-16.5	16.0
6	2	-20	10.2	9.0
6	2	-19	-0.1	5.5
6	2	-18	-6.4	7.9
6	2	-17	33.6	31.6
6	2	-16	-15.5	14.5
6	2	-15	-1.4	<2.5
6	2	-14	20.0	19.7
6	2	-13	16.4	16.2
6	2	-12	-1.0	<2.3
6	2	-11	3.4	5.6
6	2	-10	5.4	8.4
6	2	-9	-18.0	16.1
6	2	-8	48.3	47.1
6	2	-7	40.7	39.8
6	2	-6	-26.5	26.4
6	2	-5	-1.1	4.6
6	2	-4	-46.7	44.2
6	2	-3	-0.9	4.6
6	2	-2	10.0	12.5
6	2	-1	39.3	41.0
6	2	0	-16.5	14.6
6	2	1	-15.7	16.7
6	2	2	1.3	6.2
6	2	3	28.8	26.9
6	2	4	21.8	21.8
6	2	5	28.4	25.8
6	2	6	-7.3	8.3
6	2	7	-43.4	40.4
6	2	8	4.7	<2.6
6	2	9	12.0	9.8
6	2	10	7.9	10.0
6	2	11	12.6	11.5
6	2	12	-13.2	11.6
6	2	13	-20.9	19.2
6	2	14	-2.6	5.5
6	2	15	11.6	11.1
6	2	16	-4.4	5.1
6	2	17	-4.0	5.7
6	2	18	-7.5	8.9
6	2	19	-12.5	13.0
6	2	20	4.5	4.6
6	2	21	8.2	8.8
8	2	-28	-6.3	7.7
8	2	-27	14.1	11.3
8	2	-26	-7.8	7.1
8	2	-25	-4.2	<2.4
8	2	-24	6.4	7.1
8	2	-23	5.5	8.3
8	2	-22	3.3	5.6
8	2	-21	12.4	10.0
8	2	-20	-5.0	5.1
8	2	-19	-11.7	8.8
8	2	-18	9.2	8.8
8	2	-17	11.7	11.2
8	2	-16	-3.1	<2.7
8	2	-15	8.4	7.7
8	2	-14	-17.6	15.9
8	2	-13	-14.9	12.7
8	2	-12	-0.4	<2.5
8	2	-11	16.0	12.9
8	2	-10	-6.5	6.7
8	2	-9	-6.8	7.7
8	2	-8	-15.6	16.9
8	2	-7	-22.0	19.5
8	2	-6	0.0	<2.3
8	2	-5	21.0	20.4
8	2	-4	0.1	<2.4
8	2	-3	-10.6	10.1
8	2	-2	9.1	7.7
8	2	-1	-12.1	14.0
8	2	0	16.3	17.3
8	2	1	29.8	29.8
8	2	2	-14.4	11.7
8	2	3	-25.1	26.3
8	2	4	-11.0	13.3
8	2	5	-38.8	37.3
8	2	6	-7.2	7.7
8	2	7	-0.1	<2.7
8	2	8	-11.7	10.1
8	2	9	-11.3	10.8
8	2	10	7.0	5.5
8	2	11	5.8	9.3
8	2	12	1.9	<2.6
8	2	13	13.2	14.0
8	2	14	-6.6	6.9
8	2	15	-10.6	13.6
8	2	16	8.9	8.9
8	2	17	-2.5	<1.9
8	2	18	2.9	3.7
10	2	-28	4.5	5.2
10	2	-27	-4.8	<1.8
10	2	-26	11.4	10.9
10	2	-25	7.4	8.7
10	2	-24	-7.8	8.6
10	2	-23	-10.5	11.1
10	2	-22	-1.4	4.7
10	2	-21	-2.4	4.8
10	2	-20	-2.2	4.9
10	2	-19	-8.6	10.6
10	2	-18	-14.0	14.3
10	2	-17	-25.6	23.8
10	2	-16	10.5	10.1
10	2	-15	22.8	23.7
10	2	-14	9.6	10.8
10	2	-13	3.7	5.0
10	2	-12	-4.0	6.5
10	2	-11	-25.6	21.5
10	2	-10	14.2	11.9
10	2	-9	15.1	12.7
10	2	-8	1.7	<2.6
10	2	-7	-18.6	19.0
10	2	-6	-8.5	9.8
10	2	-5	-19.2	19.0
10	2	-4	1.4	<2.6
10	2	-3	18.3	18.5
10	2	-2	-10.7	9.9
10	2	-1	-20.1	21.7
10	2	0	-1.7	<2.7
10	2	1	-9.6	8.2
10	2	2	11.4	13.1
10	2	3	10.3	10.9
10	2	4	-3.4	5.1
10	2	5	-11.0	10.1
10	2	6	6.6	6.1
10	2	7	14.1	14.8
10	2	8	11.6	12.5
10	2	9	14.8	13.7
10	2	10	-6.4	6.9
10	2	11	-5.7	7.0
10	2	12	-0.7	<2.2
10	2	13	1.6	<2.0
10	2	14	4.0	6.3
10	2	15	-6.2	6.9
12	2	-27	-8.2	7.2
12	2	-26	2.0	<1.7
12	2	-25	-4.6	6.2
12	2	-24	2.6	3.8
12	2	-23	10.2	7.4
12	2	-22	-3.8	<2.3
12	2	-21	-18.3	14.1
12	2	-20	5.7	<2.5
12	2	-19	0.6	<2.5
12	2	-18	6.8	8.3
12	2	-17	29.6	25.9
12	2	-16	-1.1	<2.7
12	2	-15	-9.8	9.1
12	2	-14	2.5	<2.7
12	2	-13	-0.8	<2.7
12	2	-12	-8.3	8.8
12	2	-11	-2.8	5.1
12	2	-10	-3.2	<2.8
12	2	-9	-32.6	29.0
12	2	-8	16.6	16.1
12	2	-7	18.0	20.9
12	2	-6	-5.1	5.1
12	2	-5	23.1	25.2
12	2	-4	-4.7	7.5
12	2	-3	-2.5	<2.7
12	2	-2	15.0	16.5
12	2	-1	17.0	20.7
12	2	0	-2.9	<2.7
12	2	1	-0.3	<2.6
12	2	2	-0.2	<2.6
12	2	3	-3.3	<2.5
12	2	4	6.3	8.9
12	2	5	10.4	10.9
12	2	6	-9.5	9.1
12	2	7	-8.8	11.6
12	2	8	-1.2	<2.1
12	2	9	0.6	<1.9
12	2	10	6.2	8.8
12	2	11	5.7	7.1
14	2	-21	7.3	5.0
14	2	-20	-5.8	5.8
14	2	-19	-5.3	4.5
14	2	-18	3.8	5.0
14	2	-17	5.3	6.4
14	2	-16	3.5	6.5
14	2	-15	3.9	5.3
14	2	-14	-7.2	6.8
14	2	-13	-9.4	6.2
14	2	-12	6.1	6.8
14	2	-11	7.9	8.9
14	2	-10	4.8	5.7
14	2	-9	9.5	8.1
14	2	-8	-11.0	12.8
14	2	-7	8.2	6.5
14	2	-6	-0.8	<2.5
14	2	-5	11.2	10.8
14	2	-4	-1.1	<2.5
14	2	-3	-12.5	12.2
14	2	-2	-4.5	7.5
14	2	-1	-11.1	11.7
14	2	0	8.8	10.7
14	2	1	5.2	8.4
14	2	2	-0.1	<2.1
14	2	3	-5.1	6.9
14	2	4	-7.2	10.1
16	2	-19	10.5	7.6
16	2	-18	-8.0	7.2
16	2	-17	-5.8	4.8
16	2	-16	3.6	3.1
16	2	-15	3.0	3.5
16	2	-14	1.5	<1.4
16	2	-13	2.9	<1.5
16	2	-12	-6.6	8.0
16	2	-11	-13.3	12.1
16	2	-10	3.5	2.5
16	2	-9	3.1	3.0
16	2	-8	1.6	2.7
16	2	-7	-2.5	2.7
16	2	-6	-2.8	3.5
16	2	-5	-9.5	7.3
16	2	-4	3.8	3.7
16	2	-3	5.9	6.3
16	2	-2	-0.7	<1.3
16	2	-1	-3.4	4.6
1	3	-24	6.1	5.8
1	3	-23	0.6	<1.6
1	3	-22	-7.6	6.0
1	3	-21	3.1	5.2
1	3	-20	-3.2	4.8
1	3	-19	-3.0	4.1
1	3	-18	5.6	6.4
1	3	-17	0.6	<2.2
1	3	-16	-15.5	14.5
1	3	-15	2.0	<2.2
1	3	-14	2.1	<2.2
1	3	-13	2.3	<2.2
1	3	-12	6.4	7.2
1	3	-11	9.1	9.2
1	3	-10	-27.2	24.9
1	3	-9	-8.9	8.7
1	3	-8	-0.5	3.8
1	3	-7	-1.9	3.8
1	3	-6	-6.2	6.0
1	3	-5	17.3	19.2
1	3	-4	-23.8	20.3
1	3	-3	-5.1	3.8
1	3	3	-25.2	23.1
1	3	4	20.5	16.5
1	3	5	2.9	4.6
1	3	6	-30.2	26.4
1	3	7	24.8	22.8
1	3	8	-10.0	8.2
1	3	9	-1.9	3.5
1	3	10	22.3	19.7
1	3	11	-13.4	12.9
1	3	12	-15.2	12.5
1	3	13	-1.3	3.9
1	3	14	10.9	11.4
1	3	15	5.7	5.6
1	3	16	12.2	10.4
1	3	17	-3.4	3.8
1	3	18	-14.6	12.3
1	3	19	0.1	<2.0
1	3	20	8.9	7.3
1	3	21	3.8	4.1
1	3	22	4.1	4.1
1	3	23	-4.0	3.1
3	3	-24	-1.4	<1.5
3	3	-23	-2.6	4.5
3	3	-22	4.3	4.1
3	3	-21	-0.8	<2.0
3	3	-20	-14.0	15.2
3	3	-19	3.3	4.4
3	3	-18	-2.1	4.5
3	3	-17	11.4	15.1
3	3	-16	4.2	<2.2
3	3	-15	0.6	<2.2
3	3	-14	-9.2	8.7
3	3	-13	-12.3	15.5
3	3	-12	15.1	11.9
3	3	-11	-4.0	4.4
3	3	-10	6.7	7.6
3	3	-9	-2.2	3.3
3	3	-8	-9.0	7.7
3	3	-7	-4.7	6.3
3	3	-6	20.4	20.3
3	3	-5	-0.5	2.9
3	3	-4	3.4	3.6
3	3	-3	-1.6	<1.4
3	3	-2	-4.5	3.9
3	3	-1	3.9	4.8
3	3	0	21.3	16.9
3	3	1	0.3	2.1
3	3	2	-8.6	9.1
3	3	3	-2.4	3.4
3	3	4	-7.5	7.4
3	3	5	12.9	12.5
3	3	6	20.5	16.9
3	3	7	-1.7	<2.0
3	3	8	1.6	3.7
3	3	9	-11.9	10.9
3	3	10	11.6	10.0
3	3	11	9.0	7.6
3	3	12	20.8	16.2
3	3	13	7.3	6.1
3	3	14	-6.1	6.1
3	3	15	-0.8	<2.2
3	3	16	-1.9	3.7
3	3	17	5.4	6.5
3	3	18	1.4	<1.9
3	3	19	-2.5	<1.7
3	3	20	-6.3	6.2
3	3	21	-4.5	5.2
5	3	-26	7.0	4.7
5	3	-25	-0.3	<1.4
5	3	-24	-7.4	7.1
5	3	-23	1.7	<1.8
5	3	-22	-1.4	4.2
5	3	-21	-5.5	5.3
5	3	-20	15.1	13.4
5	3	-19	7.9	9.5
5	3	-18	-6.0	4.8
5	3	-17	-3.6	4.9
5	3	-16	18.9	17.1
5	3	-15	-23.6	19.8
5	3	-14	22.5	21.1
5	3	-13	3.4	5.2
5	3	-12	-19.2	15.4
5	3	-11	15.4	13.1
5	3	-10	10.8	9.6
5	3	-9	1.5	<2.0
5	3	-8	-5.0	8.4
5	3	-7	-8.7	4.7
5	3	-6	-25.7	25.5
5	3	-5	-0.4	<1.8
5	3	-4	31.1	26.6
5	3	-3	-3.4	<1.8
5	3	-2	5.0	7.0
5	3	-1	0.7	<1.8
5	3	0	-8.1	6.2
5	3	1	10.6	10.3
5	3	2	27.9	25.1
5	3	3	1.6	<2.0
5	3	4	-11.3	10.2
5	3	5	-7.1	9.1
5	3	6	-6.7	6.0
5	3	7	9.9	9.8
5	3	8	11.3	9.9
5	3	9	5.1	6.1
5	3	10	-17.4	14.7
5	3	11	-7.4	8.4
5	3	12	-2.6	4.7
5	3	13	1.4	<2.1
5	3	14	2.0	<2.1
5	3	15	-3.1	<2.0
5	3	16	-11.3	10.6
5	3	17	-4.1	5.8
5	3	18	5.4	6.0
5	3	19	3.4	4.6
7	3	-24	9.1	7.7
7	3	-23	-0.8	<1.7
7	3	-22	-3.8	<1.9
7	3	-21	5.6	6.1
7	3	-20	-4.4	3.7
7	3	-19	2.1	3.8
7	3	-18	8.2	6.7
7	3	-17	-4.5	5.6
7	3	-16	-13.7	12.6
7	3	-15	3.7	<2.2
7	3	-14	-7.0	7.4
7	3	-13	8.9	8.8
7	3	-12	6.0	5.7
7	3	-11	-2.3	3.5
7	3	-10	-19.7	17.5
7	3	-9	-5.6	5.4
7	3	-8	6.0	5.3
7	3	-7	2.9	4.6
7	3	-6	17.7	16.9
7	3	-5	-2.8	3.7
7	3	-4	-11.3	9.5
7	3	-3	4.1	4.4
7	3	-2	5.7	5.9
7	3	-1	13.4	13.3
7	3	0	-13.3	10.6
7	3	1	-11.9	14.9
7	3	2	-29.2	28.1
7	3	3	-17.6	17.0
7	3	4	3.8	<2.2
7	3	5	7.6	9.4
7	3	6	-9.4	7.4
7	3	7	2.6	3.9
7	3	8	-3.6	3.9
7	3	9	-3.7	3.8
7	3	10	15.8	13.9
7	3	11	1.2	<2.0
7	3	12	-6.7	6.8
7	3	13	-4.0	6.3
7	3	14	-0.6	<1.7
7	3	15	-0.4	<1.5
7	3	16	4.1	3.9
9	3	-24	-10.1	8.4
9	3	-23	-1.0	<1.6
9	3	-22	4.1	<1.7
9	3	-21	-3.9	3.8
9	3	-20	-10.1	9.0
9	3	-19	2.2	3.6
9	3	-18	1.6	3.7
9	3	-17	4.5	6.6
9	3	-16	11.7	9.5
9	3	-15	-1.3	3.5
9	3	-14	10.4	7.9
9	3	-13	-2.7	3.9
9	3	-12	2.1	<2.2
9	3	-11	3.3	3.9
9	3	-10	-0.1	<2.2
9	3	-9	-1.0	<2.2
9	3	-8	-16.4	14.0
9	3	-7	-3.8	4.8
9	3	-6	5.8	4.8
9	3	-5	1.2	<2.2
9	3	-4	-2.2	3.9
9	3	-3	-4.6	4.9
9	3	-2	-11.6	9.8
9	3	-1	4.7	4.0
9	3	0	10.7	9.4
9	3	1	-1.8	<2.2
9	3	2	0.6	<2.2
9	3	3	3.6	<2.2
9	3	4	0.2	<2.2
9	3	5	10.5	10.4
9	3	6	15.4	14.2
9	3	7	-0.8	<2.0
9	3	8	-1.6	<2.0
9	3	9	-6.6	7.5
9	3	10	-3.8	4.1
11	3	-23	-5.4	5.2
11	3	-22	-1.2	3.8
11	3	-21	2.5	4.7
11	3	-20	13.2	11.9
11	3	-19	9.0	10.4
11	3	-18	-4.3	<1.9
11	3	-17	-7.0	8.5
11	3	-16	-1.5	4.8
11	3	-15	-9.6	9.3
11	3	-14	6.8	5.7
11	3	-13	1.4	<2.1
11	3	-12	-14.1	11.7
11	3	-11	-2.6	<2.2
11	3	-10	6.6	5.2
11	3	-9	4.1	8.2
11	3	-8	11.6	11.9
11	3	-7	6.2	6.7
11	3	-6	-5.1	4.7
11	3	-5	-5.7	7.0
11	3	-4	17.2	16.6
11	3	-3	0.9	2.9
11	3	-2	3.4	3.7
11	3	-1	3.8	2.9
11	3	0	-12.1	10.4
11	3	1	0.5	<2.0
11	3	2	10.6	9.9
11	3	3	1.3	<1.9
11	3	4	-2.2	3.6
11	3	5	-3.5	6.0
11	3	6	-4.0	4.2
11	3	7	0.1	2.7
11	3	8	8.5	10.4
11	3	9	2.7	4.9
13	3	-19	-2.6	<1.4
13	3	-18	7.4	5.6
13	3	-17	-4.7	5.4
13	3	-16	-5.7	5.1
13	3	-15	3.2	3.7
13	3	-14	-2.5	<1.8
13	3	-13	5.2	6.1
13	3	-12	9.5	8.9
13	3	-11	3.2	3.6
13	3	-10	-5.3	4.4
13	3	-9	2.9	3.6
13	3	-8	3.5	4.9
13	3	-7	-6.1	5.7
13	3	-6	-9.3	8.4
13	3	-5	-9.0	11.2
13	3	-4	-10.5	11.7
13	3	-3	5.5	5.3
13	3	-2	-1.8	<1.7
13	3	-1	6.5	6.9
13	3	0	0.3	<1.5
13	3	1	-3.9	3.9
13	3	2	-7.3	8.8
13	3	3	-6.6	<1.7

for the six cycles of refinement completed are listed in Table 3. By the sixth cycle the parameter shifts had become negligible, the average shift in positional parameter being less than 0.002 Å. Prior to cycle 5 new coordinates were calculated for the benzene hydrogen atoms by placing them radially 1.0 Å away from the relevant carbon atoms; for the carboxyl hydrogen, coordinates were obtained by placing it 1.0 Å away from O(2) on the line to O(1) of the opposite carboxyl group. The final values of R are 0.090 for the $h0\ell$, 0.098 for the $h1\ell$, 0.109 for the $h2\ell$ and 0.167 for the $h3\ell$ reflexions. The overall final value of R for the 1034 observed terms is 0.105. The measured structure amplitudes together with those calculated from the final cycle of the calculations are listed in Table 4.

2.7. Coordinates, Molecular geometry and Estimations of accuracy.

The final coordinates of the carbon, oxygen and chlorine atoms and the coordinates assigned by calculation to the hydrogen atoms are in Table 5. Table 6 contains the corresponding anisotropic temperature parameters. The bond lengths and valency

TABLE 5.

Final atomic coordinates.

Coordinates *x*, *y* and *z* are referred to the monoclinic crystal axes and are expressed as fractions of the axial lengths, with origin at the centre of symmetry on glide plane *c*. Coordinates *X'*, *Y* and *Z'* are referred to orthogonal axes *a*, *b*, and *c'*, *c'* being taken perpendicular to the *a* and *b* crystal axes, and are expressed in Å units.

Atom (c.f. Fig.8)	*x*	*y*	*z*	*X'*	*Y*	*Z'*
C(1)	0.1961	0.3430	0.0550	2.347	1.338	1.295
C(2)	0.1480	0.4213	0.0969	1.228	1.643	2.280
C(3)	0.1997	0.5710	0.1503	1.465	2.227	3.537
C(4)	0.1498	0.6447	0.1852	0.386	2.514	4.358
C(5)	0.0501	0.5751	0.1676	-0.910	2.243	3.943
C(6)	0.0009	0.4282	0.1159	-1.126	1.670	2.726
C(7)	0.0501	0.3488	0.0798	-0.047	1.360	1.878
O(1)	0.2760	0.4551	0.0610	3.465	1.775	1.435
O(2)	0.1427	0.1498	0.0132	1.973	0.584	0.310
Cl	0.3247	0.6642	0.1775	3.038	2.591	4.176

- Cont'd -

TABLE 5.

(Cont'd)

Atom (c.f. Fig.8)	x	y	z	X'	Y	Z'
H(02)	0.1735	0.1100	-0.0149	2.703	0.429	-0.351
H(C4)	0.1857	0.7515	0.2233	0.542	2.931	5.254
H(C5)	0.0147	0.6306	0.1931	-1.682	2.459	4.544
H(C6)	-0.0709	0.3767	0.1034	-2.067	1.469	2.433
H(C7)	0.0141	0.2420	0.0417	-0.203	0.944	0.982

[illegible]

The temperature factor is expressed in the form

[illegible]

TABLE 6.

Anisotropic temperature-factor parameters ($b_{ij} \times 10^5$).

Atom	b_{11}	b_{22}	b_{33}	b_{23}	b_{13}	b_{12}
C(1)	608	12749	265	-738	381	-283
C(2)	734	10160	233	- 60	442	529
C(3)	983	9792	256	24	498	1457
C(4)	1026	12289	325	-447	518	1064
C(5)	1106	12716	312	-138	626	1384
C(6)	799	18327	330	95	574	826
C(7)	740	13293	317	-375	429	570
O(1)	836	19388	398	-1820	590	-1236
O(2)	1033	16397	316	-1678	561	-1131
Cl	866	15218	265	-879	458	-1104
Hydrogen Atoms, B=4.0 Å^2	780	9485	260	-	347	-

The temperature factor is expressed in the form:

$$e^{-(b_{11}h^2 + b_{22}k^2 + b_{33}\ell^2 + b_{23}k\ell + b_{13}h\ell + b_{12}hk)}$$

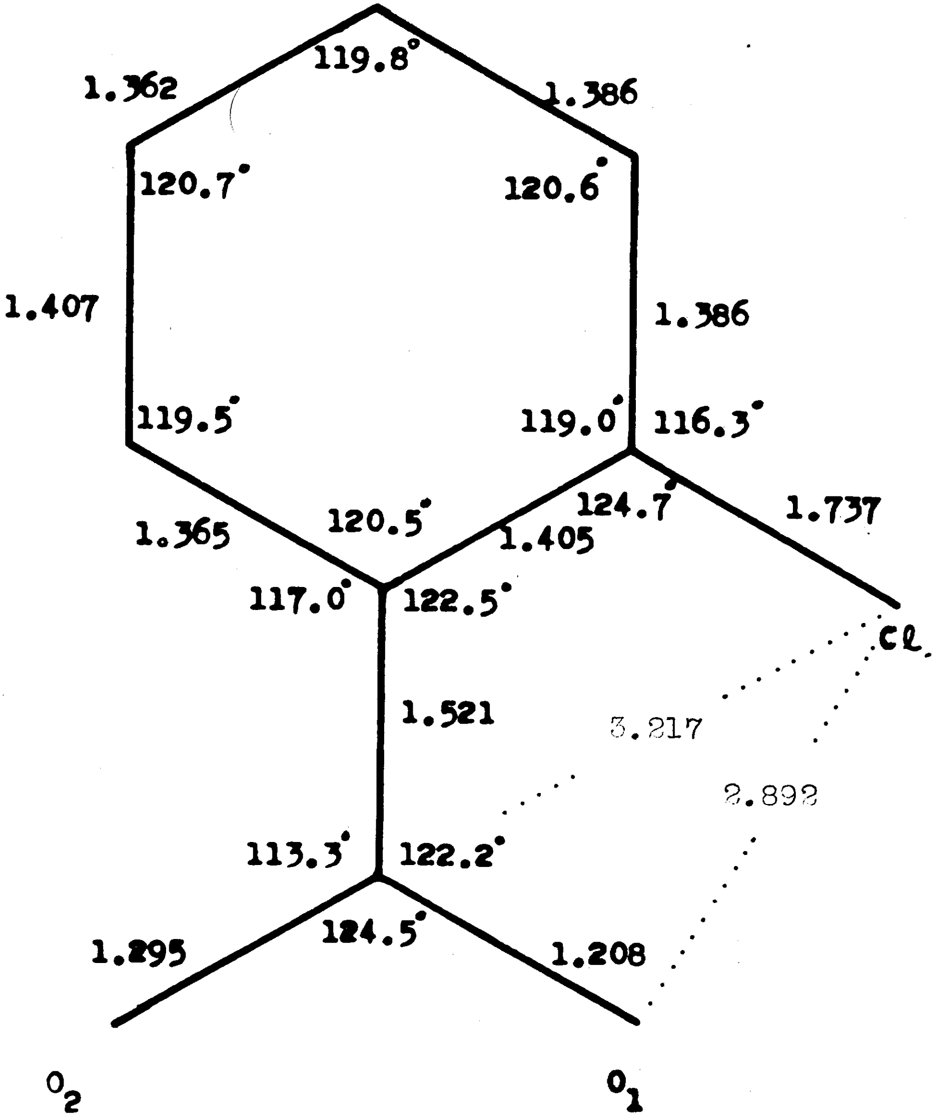


Fig.7. Interatomic distances and valency angles in o-chlorobenzoic acid.

angles, calculated from the coordinates given in Table 5, are shown in Fig.7, the shorter intermolecular contacts being listed in Table 7. Some of these contacts are shown in Fig.8, which illustrates the arrangement of the molecules in the b-axis projection. The shortest intermolecular distance, 2.632 Å, is between oxygen atoms of a dimer, and is normal for this type of bonding. All other intermolecular approach distances (Table 7 and Fig.8) are greater than 3.0 Å and correspond to normal van der Waal's interactions.

The standard deviations of the positional parameters, calculated from the equation

$$\sigma(x) = a\sqrt{\left\{\sum w\Delta^2\Big/(n-s)\left[\sum w(\partial\Delta/\partial\,{}^{x}/_{a})^2\right]\right\}}\ \mathring{A}$$

where n = total number of reflexions used in the refinement and s = number of degrees of freedom,

using the normal equation totals obtained from the sixth least-squares cycle, are given in Table 8. From these results, the standard deviation in length of a carbon-carbon bond is 0.009 Å , that of a carbon-oxygen bond is 0.008 Å and that of a carbon-chlorine bond is 0.007 Å. The estimated standard deviation in bond angle, computed from the equation given by Cruickshank and Robertson (1953), is found to be 0.6°.

TABLE 7.

The shorter intermolecular contacts.

$O(1)\ldots O(2)_{I}$	2.632 Å	$C(4)\ldots C(7)_{II}$	3.726 Å
$O(1)\ldots O(2)_{II}$	3.291	$C(5)\ldots C(7)_{II}$	3.757
$O(1)\ldots O(1)_{I}$	3.315	$C(4)\ldots C(2)_{II}$	3.769
$C(1)\ldots O(2)_{II}$	3.318	$C(3)\ldots C(7)_{II}$	3.773
$C(1)\ldots O(1)_{I}$	3.349	$C(4)\ldots C(6)_{II}$	3.780
$C(1)\ldots O(2)_{I}$	3.443	$C\ell\ldots C(5)_{V}$	3.781
$C(7)\ldots O(2)_{III}$	3.504	$C(1)\ldots C(1)_{I}$	3.791
$C(7)\ldots O(2)_{IV}$	3.510	$C(6)\ldots C(7)_{II}$	3.844
$C(2)\ldots O(2)_{II}$	3.536	$C(2)\ldots C(7)_{II}$	3.856
$C(5)\ldots C(6)_{II}$	3.550	$C(3)\ldots C(1)_{II}$	3.856
$C(3)\ldots C(2)_{II}$	3.555	$C(4)\ldots C(3)_{II}$	3.859
$C(6)\ldots O(2)_{IV}$	3.556	$C\ell\ldots C(4)_{VIII}$	3.859
$O(2)\ldots O(2)_{I}$	3.563	$C(4)\ldots C(5)_{II}$	3.875
$O(1)\ldots C(6)_{V}$	3.573	$C(6)\ldots O(2)_{III}$	3.875
$O(1)\ldots C(1)_{II}$	3.642	$C(2)\ldots C(1)_{II}$	3.892
$C\ell\ldots C(6)_{V}$	3.662	$C(7)\ldots C(7)_{IV}$	3.937
$C(6)\ldots O(1)_{VII}$	3.686	$C(4)\ldots C(4)_{VIII}$	3.990
$O(1)\ldots O(1)_{VI}$	3.704		

-Cont'd-

TABLE 7.

(Cont'd)

The subscripts refer to the following positions:

I	$\frac{1}{2}-x$	$\frac{1}{2}-y$	$-z$
II	x	$1+y$	z
III	$-x$	$-y$	$-z$
IV	$-x$	$1-y$	$-z$
V	$\frac{1}{2}+x$	$\frac{1}{2}+y$	z
VI	$\frac{1}{2}-x$	$1\frac{1}{2}-y$	$-z$
VII	$x-\frac{1}{2}$	$\frac{1}{2}+y$	z
VIII	$\frac{1}{2}-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$

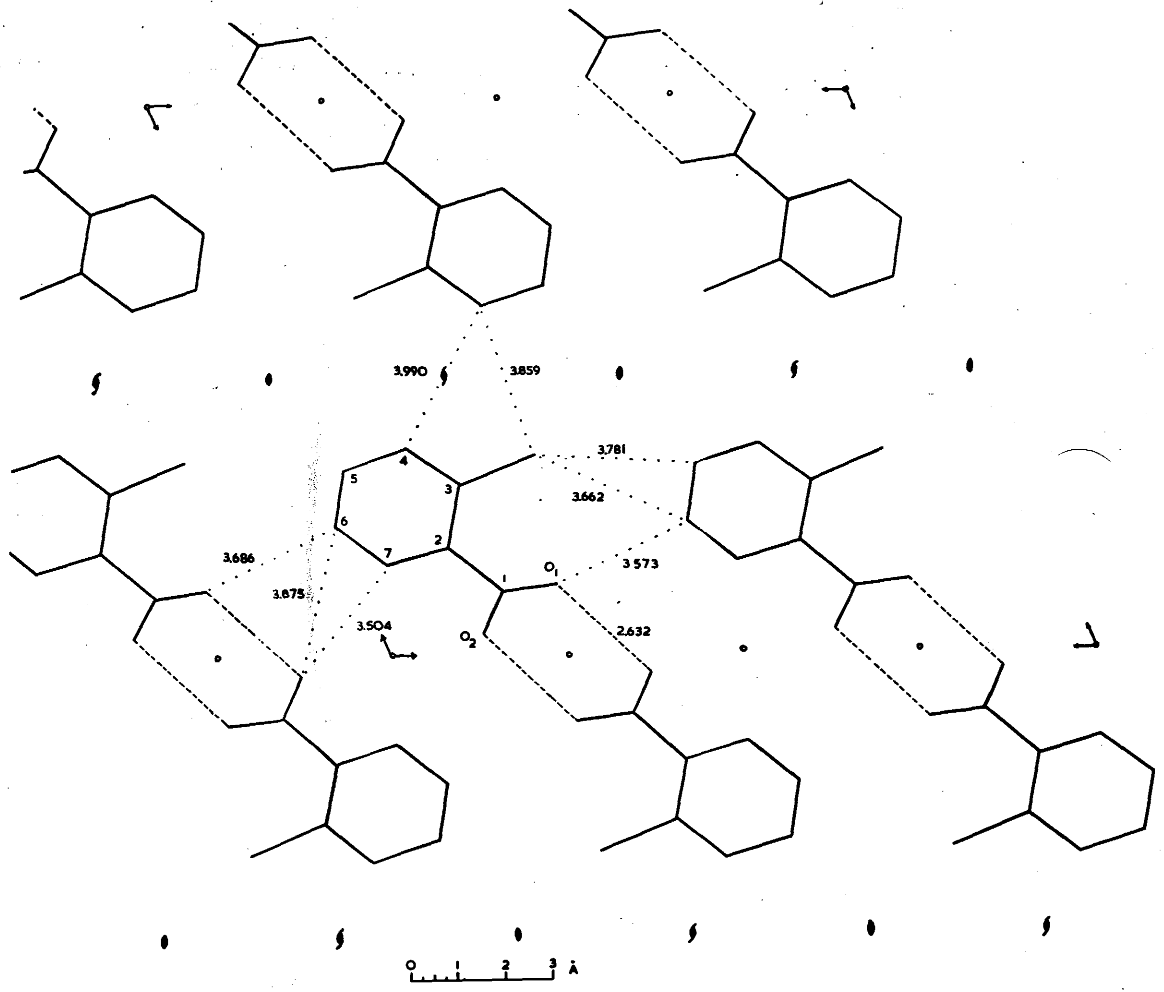


Fig. 8. Structure viewed along the b axis with the true unit cell halved in the c direction. Some of the shorter intermolecular contacts are shown.

TABLE 8.

Estimated standard deviations in atomic coordinates (Å).

Atom	(*x*)	(*y*)	(*z*)
C(1)	0.0049	0.0076	0.0053
C(2)	0.0050	0.0064	0.0051
C(3)	0.0058	0.0065	0.0055
C(4)	0.0062	0.0079	0.0061
C(5)	0.0062	0.0073	0.0061
C(6)	0.0057	0.0082	0.0061
C(7)	0.0054	0.0080	0.0057
O(1)	0.0039	0.0055	0.0043
O(2)	0.0039	0.0052	0.0039
Cl	0.0015	0.0022	0.0015

2.8. Mean molecular plane calculations.

The best plane through the chlorine, oxygen and carbon atoms, derived by the method of Schomaker et al (1959), has equation

$$0.09504\ X' - 0.90257\ Y + 0.41992\ Z' + 0.41813 = 0$$

where X', Y, Z' are coordinates expressed in Ångstrom units and referred to orthogonal axes a, b and c'. The deviations of the atoms from this plane (Table 9) show that the molecule is markedly non-planar and that the main cause of non-planarity is the oxygen atoms.

The equation of the best plane through the seven carbon atoms and the chlorine atom is

$$0.06636\ X' - 0.91457\ Y + 0.39895\ Z' + 0.52237 = 0$$

The deviations of these atoms from this plane (Table 9) are still large, (the root mean square deviation = 0.0176 Å) and since

$$\chi^2 = \sum \Delta^2 / \sigma_x^2 = 50$$

they must be highly significant (see Part I, 1.10). The deviations suggest that the exocyclic carbon atom and the chlorine atom are displaced from the plane of the benzene ring.

The carbon atoms of the benzene ring are best fitted by the plane with equation

TABLE 9.

Deviations from the mean planes.

(a) Plane through C(1)....C(7), O(1), O(2), Cℓ.

(b) Plane through C(1)....C(7), Cℓ.

(c) Plane through the benzene ring atoms C(2)....C(7).

(d) Plane through C(1), C(2), O(1), O(2).

Atom (c.f.Fig.8)	(a)	(b)	(c)	(d)
C(1)	-0.022 Å	-0.029 Å	-0.058 Å	0.003 Å
C(2)	0.009	0.011	-0.004	-0.001
C(3)	0.033	-0.006	-0.001	-
C(4)	0.016	-0.013	0.005	-
C(5)	-0.037	-0.016	-0.005	-
C(6)	-0.052	0.008	0.000	-
C(7)	-0.026	0.024	0.004	-
O(1)	-0.252	-0.299	-0.323	-0.001
O(2)	0.209	0.243	0.197	-0.001
Cℓ	0.123	0.021	0.036	-

$$0.06604\ X' - 0.90890\ Y + 0.41176\ Z' + 0.47017 = 0.$$

The deviations of the benzene carbon atoms from this plane (Table 9) are small, (the root mean square deviation = 0.0035 Å) and since $\chi^2 = 1.5$ for these atoms, the deviations are insignificant and the benzene ring may be assumed strictly planar.

The atoms of the carboxyl group C(1), O(1) and O(2) and carbon atom C(2) of the benzene ring can be fitted to the plane with equation

$$0.24764\ X' - 0.81107\ Y + 0.52994\ Z' - 0.18001 = 0.$$

The angle which this plane makes with that of the benzene ring is 13.7°.

The equation of the plane through the oxygen atoms O(1), O(2), O(1)' and O(2)' of an acid dimer and the centre of symmetry at ($\frac{1}{4}$, $\frac{1}{4}$, 0) was required in one of the mean plane Fourier calculations described below; it was found to be

$$0.27819\ X' - 0.82045\ Y + 0.49946 Z' - 0.22448 = 0.$$

2.9. Three-dimensional Fourier sections.

The electron-density distribution in the plane of the benzene ring carbon atoms (Fig.9) was evaluated using the procedure devised by Treuting and Abrahams (1961)

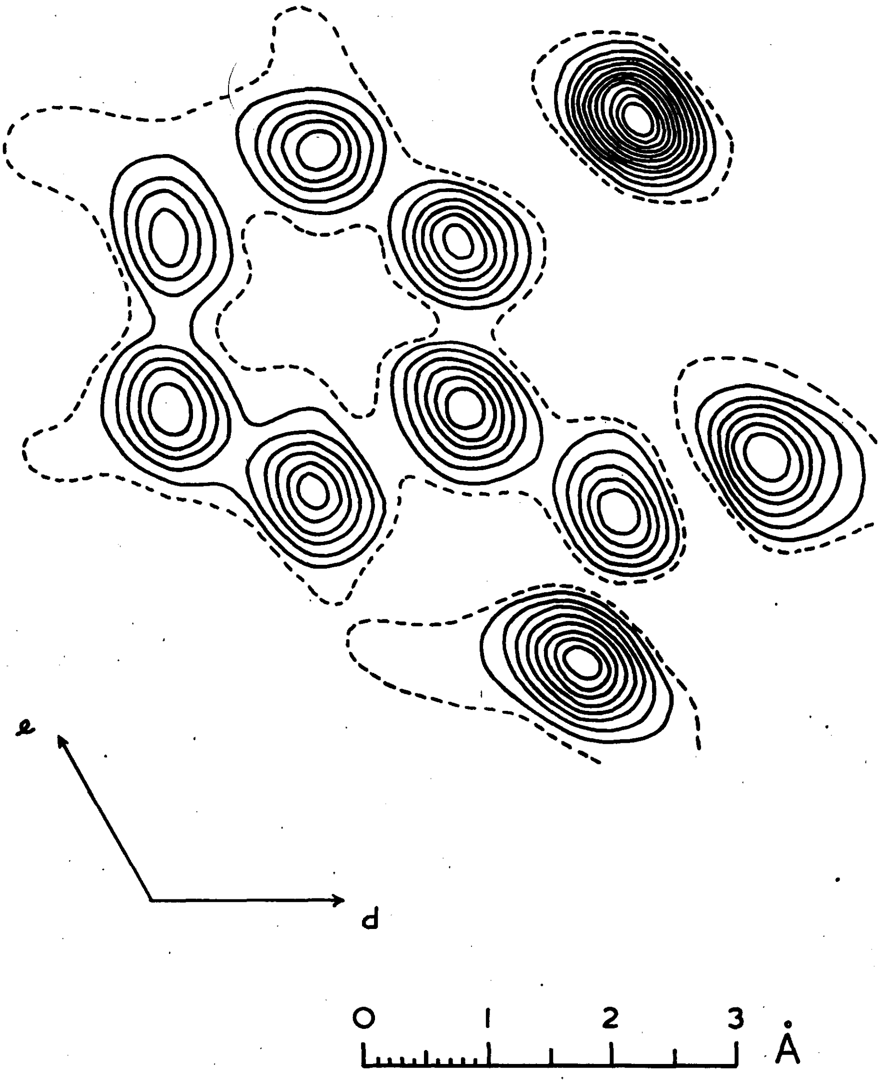


Fig.9. A section through the plane of the carbon atoms of the benzene ring. Contours are drawn at intervals of 1 eÅ^{-3}, except around the chlorine atom where the interval is 2 eÅ^{-3}. The half-electron line is broken.

and programmed for DEUCE by Dr. J.G.Sime. The method used is to calculate values for Z' which correspond to a specified grid of X' and Y points which lie on the general plane:

$$AX' + BY + CZ' + D = 0$$

and then to compute values of the triple Fourier series at these points which are integral multiples of 1/3600th of the cell edges. The Z' values are rounded off to the nearest 1/3600th: the maximum deviation from this plane is thus c/7200 = 0.0035 Å.

The two-dimensional array of electron densities obtained is defined by the projection of the a and b crystal axes onto the plane (in this instance that of the benzene ring carbon atoms), which results in the new axes d and e, where d = 15.99 Å and e = 10.73 Å, the angle between d and e being 119°23'.

In Fig.9 the chlorine atom and O(2) are above the benzene plane while C(1) and O(1) lie below it, the displacements being given in Table 9. The half-electron contour in Fig.9 provides distinct evidence of the hydrogen atoms attached to carbon atoms of the benzene ring. These hydrogen atoms are shown in more detail in Fig.10. This map was obtained in an analogous

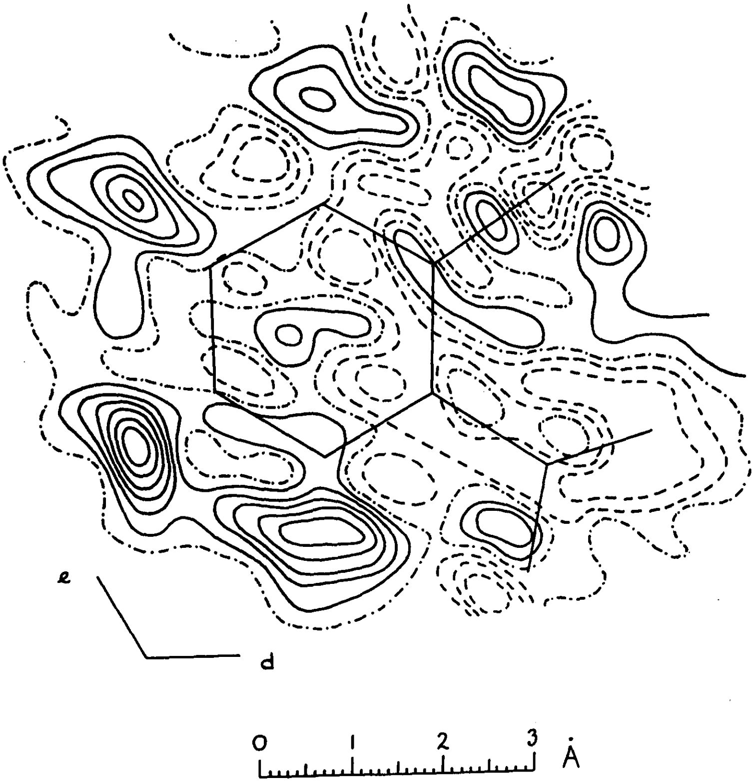


Fig.10. Difference synthesis in the plane of the benzene ring to show the hydrogen atoms. Contour interval 0.1 eÅ^{-3} with negative levels broken, zero contours dot-dashed.

manner to that shown in Fig.9 but in this case the Fourier coefficients were (F_o - F_c') in place of F_o, where F_c' is the value of the structure factor calculated for oxygen, carbon and chlorine atoms alone. The hydrogen atoms appear as well resolved peaks of from 0.32 eÅ^{-3} to 0.66 eÅ^{-3} in height.

The carbon-hydrogen bond lengths measured directly on this map are shown below, the average value being 1.01 Å.

C(4) - H = 1.11 Å   C(6) - H = 1.00 Å
C(5) - H = 1.09 Å   C(7) - H = 0.85 Å

The successful location of the hydrogen atoms in the benzene ring plane prompted an attempt at finding the hydroxyl hydrogen atoms in the plane through the four oxygen atoms O(1), O(2), O(1)' and O(2)' of an acid dimer and the centre of symmetry at ($\frac{1}{4}$, $\frac{1}{4}$, 0). The resultant Fourier map is shown in Fig.11, where the axes <u>f</u> and <u>g</u> have length 21.97 Å and 9.86 Å respectively, the angle between them being 136°11'. The expected locations of the hydrogen atoms on the dotted lines joining O(1) with O(2)' and O(2) with O(1)' are indicated by crosses at distances of 1.0 Å from O(2) and O(2)'. The rather diffuse peaks of 0.27 eÅ^{-3} are in reasonable agreement with this assignment.

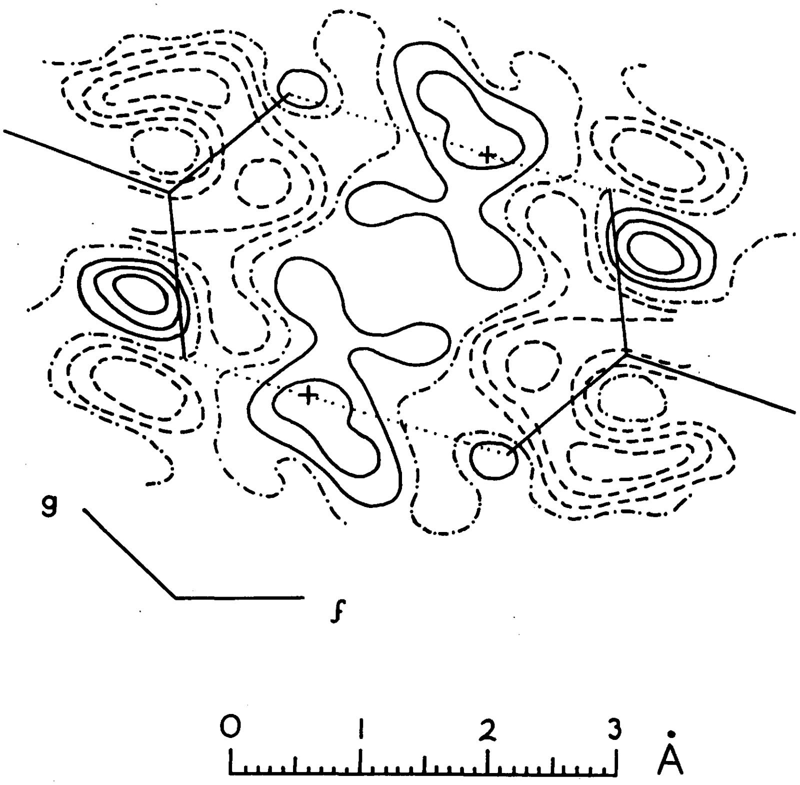


Fig.11. Difference synthesis in the oxygen plane to show the hydrogen atom of the carboxyl group. Contour interval 0.1 eÅ^{-3}, negative levels broken, zero contours dot-dashed.

2.10. Discussion.

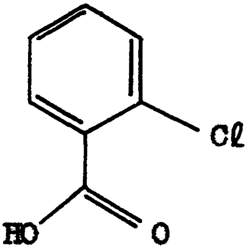
The Cl ...O(1) (2.892 Å) and Cl ...C(1) (3.217 Å) intramolecular separations are distinctly shorter than the sums of the van der Waal's radii, 3.20 Å and 3.80 Å respectively, and it is reasonable to expect the molecule to be under some strain.

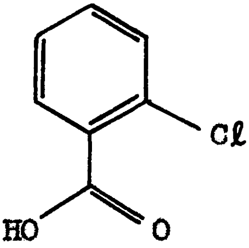
The strain which would be imposed on a strictly planar molecule is relieved by rotation of the carboxyl group about the exocyclic carbon-carbon bond so that the plane of the carboxyl group makes an angle of 13.7° with that of the benzene ring. Further there are significant in-plane displacements of the carbon-chlorine and exocyclic carbon-carbon bonds away from one another so that two of the exocyclic valency angles are increased from their normal values of 120° to 124.7° and 122.5°, while the adjacent angles are decreased to 116.3° and 117.0° (Fig.7). These deviations are significant, the standard deviation in bond angle being 0.6°.

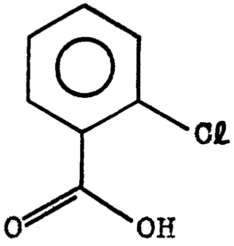
The deviations of the carbon atoms of the benzene ring from a plane (Table 9), vary from zero to 0.005 Å. These deviations are insignificant and the ring may be assumed to be strictly planar. The displacements of the atoms C(1) and Cl from the benzene plane are

−0.058 Å and +0.036 Å respectively; these deviations, although small, are significant (see 2.8.). These displacements correspond to the exocyclic carbon-carbon bond and the carbon-chlorine bond bending in opposite directions out of the plane of the benzene ring through angles of -2.2° and $+1.2^{\circ}$ respectively; this must also contribute to relieving the imposed strain.

Consideration of the bond lengths found in the benzene ring provides some evidence of bond length alternation around the ring. The difference in the mean length of the bonds C(2) - C(3), C(4) - C(5), and C(6) - C(7) (1.399 Å) and the mean length of the bonds C(3) - C(4), C(5) - C(6), and C(7) - C(2) (1.371 Å) is 0.028 Å. Compared with the standard deviation in carbon-carbon bond length of 0.009 Å this length alternation may just be significant. It can be attributed to repulsion between the carboxyl carbon atom and the chlorine atom, which will tend to favour Kekulé structure I rather than II


I


II


III

and consequently their unequal contribution to the molecular structure.

The conformation adopted by the carboxyl group is as shown in I, with the carbonyl oxygen atom adjacent to the chlorine atom and the hydroxyl group remote. In a completely planar model the O...Cℓ separation would be approximately 2.5 Å; this should be compared with the sum of the van der Waal's radii of the atoms (3.2 Å) and the distance found in the crystal (2.89 Å). By adopting the conformation shown in I above, the separation O...Cℓ can be increased for a smaller inclination of the carboxyl plane to the benzene plane than would be the case if the opposite conformation (III) were adopted. The reasons for this may be found in the shortness of the C = O bond (1.208 Å) as compared to the C-OH bond (1.295 Å), these values being normal for unionised carboxyl groups (see Part II, 6).

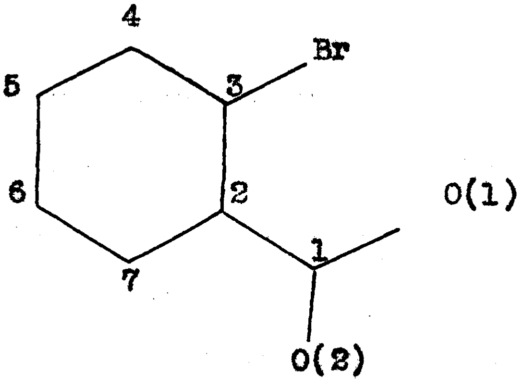
The exocyclic carbon-carbon bond to the carboxyl group is 1.521 Å in length. Dewar and Schmeising (1959) have estimated the standard single-bond distance between carbon atoms in the sp^2 hybridised state as 1.479 Å, which compares well with the values of 1.483 Å in butadiene (Tables of Interatomic Distances, 1958), 1.48 Å in benzoic acid, 1.477 Å in p-benzoquinone (Trotter, 1960) and 1.458 Å in salicylic acid. There are, however, examples of markedly longer bonds between carbon atoms in the sp^2 state of hybridisation. In oxalic acid dihydrate (Ahmed and Cruickshank, 1953) for example, the length of the central carbon-carbon bond is 1.53 Å. The mean length of the _peri_-bonds in quaterrylene (Shrivastava and Speakman, 1960) is also 1.53 Å, while in benzene hexacarboxylic acid (Darlow, 1961) the mean length of the exocyclic carbon-carbon bonds is 1.521 Å. That the mean length of the _peri_-bonds in quaterrylene is longer than was expected has been attributed to repulsion between overcrowded hydrogen atoms and to the _cis_-interactions of carbon-carbon bonds. The length of the exocyclic carbon-carbon bond in o-chlorobenzoic acid is probably similarly related to the intramolecular overcrowding.

The carbon-chlorine bond length of 1.737 Å is appreciably shorter than the average carbon-chlorine distance in halogenated aliphatic compounds (1.767 Å: Tables of Interatomic Distances, 1958). The contraction of 0.03 Å is expected for the decrease in radius of a carbon atom on changing from sp^3 to sp^2 hybridisation. The value found for the carbon-chlorine bond length agrees well with that found in 4:4'-dichlorodiphenylsulfone (1.736 Å: Sime and Abrahams, 1960).

3. o-Bromobenzoic acid.

When the refinement of the h0ℓ structure factor data for o-chlorobenzoic acid was proceeding smoothly, crystals of o-bromobenzoic acid were obtained with a view to studying the effect of replacing the chlorine atom in an o-halogenobenzoic acid by the bulkier bromine atom. o-Bromobenzoic acid appeared to be particularly suitable because optical studies by Steinmetz (1914) indicated that o-chloro- and o-bromo-benzoic acids are isomorphous.

The convention adopted for the numbering of the atoms in the various calculations was



3.1. Preparation of crystals.

The impure powdered material available commercially was purified by boiling an aqueous solution with animal charcoal and recrystallising from chloroformether mixtures. The crystals are soft lath-like growths; good small crystals were difficult to find, mainly because of bending and splitting.

3.2. Unit cell data.

Rotation, oscillation and Weissenberg photographs taken with copper $K\alpha$ radiation showed that the crystals are monoclinic, with cell parameters

$$a = 14.82 \pm 0.04 \text{ Å}$$
$$b = 4.10 \pm 0.02 \text{ Å}$$
$$c = 25.90 \pm 0.05 \text{ Å}$$
$$\beta = 118^{\circ}15' \pm 20'$$

The density, as found by Steinmetz (1914), is 1.929 $g.cm.^{-3}$ If there are eight molecules in the unit cell the calculated density is 1.926 $g.cm.^{-3}$ The volume of the unit cell is 1386 $Å^3$ and the total number of electrons therein = F(000) = 784.

The systematic absences, determined from the $h0\ell$, $h1\ell$, $h2\ell$, $h3\ell$ and $0k\ell$ Weissenberg photographs, proved to be

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

$h0\ell$ when h or ℓ is odd

$0k0$ when k is odd.

These conditions allow the space group to be either C2/c (C_{2h}^6) or Cc (C_s^4). For reasons discussed in 2.3, C2/c was chosen, the results of the three-dimensional refinement again confirming this choice.

3.3. Intensity data.

The data used in the analysis were obtained from a survey of the $h0\ell$, $h1\ell$, $h2\ell$ and $h3\ell$ reciprocal lattice nets. In all, the intensities of 1145 reflexions were estimated visually and a further 100 were too weak to be observed. A small crystal of dimensions 0.10 x 0.17 x 0.45 mm. was chosen for the analysis. The linear absorption coefficient for copper Kα radiation is 77.6 cm.$^{-1}$; no absorption corrections were applied. The intensities were corrected for Lorentz, polarisation and Tunell factors (Tunell 1939) and put on the same absolute scale at a later stage by comparing $\sum |F_o|$ with $\sum |F_c|$ for each set of data.

3.4. The b-axis projection

The Patterson projection shown in Fig.12 was computed with the $h0\ell$ $|F_o|^2$ data. The large peak on the map

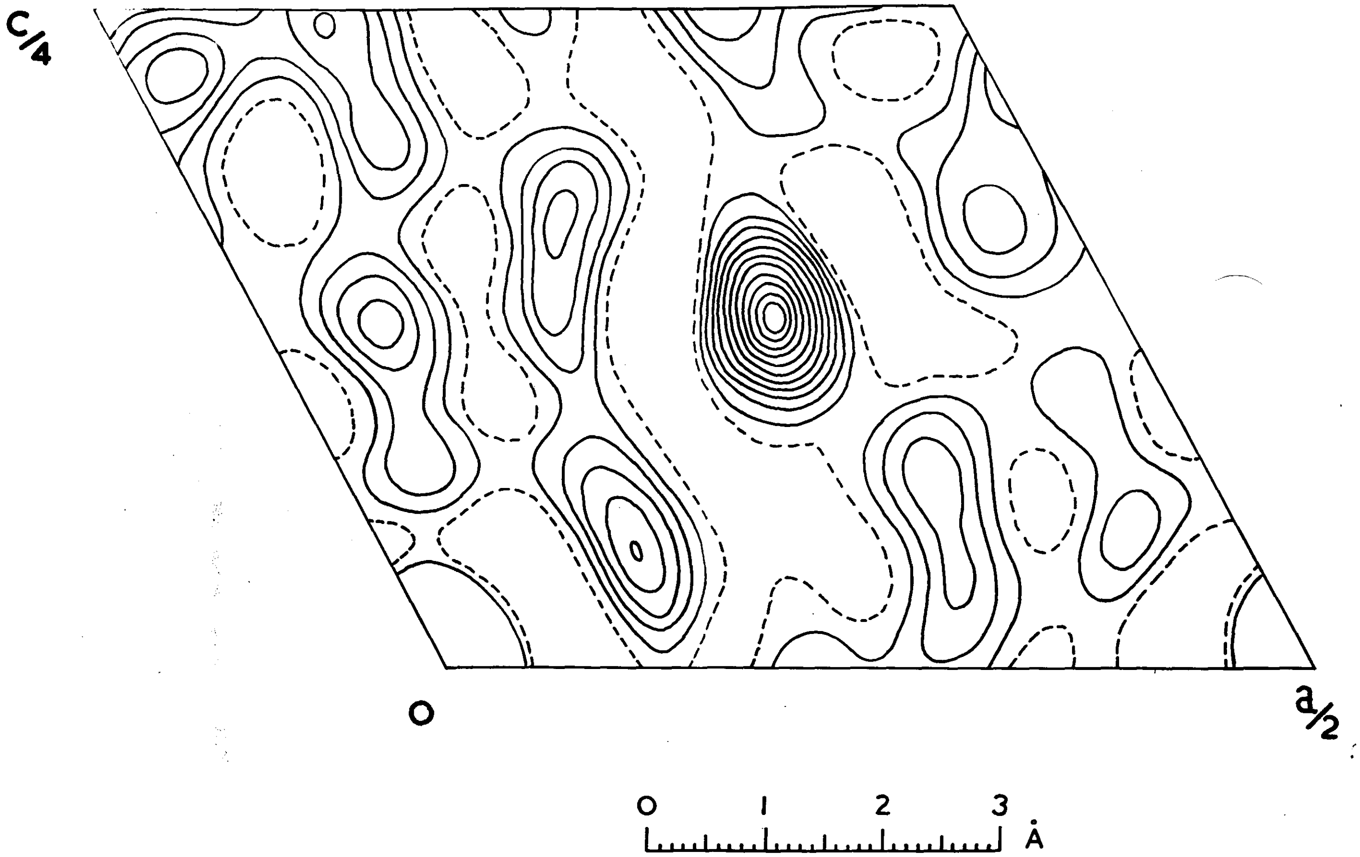


Fig. 12. Patterson projection along the b axis. Contours at equal arbitrary intervals, the lowest contour broken, origin peak omitted.

corresponds to the bromine-bromine vector across an acid dimer. This vector peak would arise if the bromine atom had coordinates x = 0.100, z = 0.183, assuming (wrongly as it was later shown) that the molecules are centred on the centre of symmetry at (0,0,0) and not that at ($\frac{1}{4}$,$\frac{1}{4}$,0). The choice is immaterial from the point of view of the h0ℓ projection since this does not affect the magnitude of the F(h0ℓ); it is critical, however, when working with upper layer data.

Knowing the positions of the bromine atom, approximate x and z coordinates for the carbon and oxygen atoms were obtained by comparison with the o-chlorobenzoic (010) projection. Structure factors were then calculated; the scattering curves of Berghuis <u>et al</u> (1955) for carbon and oxygen were used along with the Thomas-Fermi values for bromine (Internationale Tabellen, Vol.II, 1935), an isotropic temperature factor B = 4.0 $\overset{o}{A}^2$ being applied to all the atoms. The value of the residual R for the observed reflexions was 0.21. The refinement proceeded by computing an F_o synthesis from which a new set of coordinates was obtained. In the next structure-factor calculation R was 0.17. The refinement was continued by three rounds of least-squares calculations in which the two positional and

TABLE 10.

Coordinates obtained from the least-squares refinement of the projection on (010), expressed as fractions of the axial lengths. For each atom, two possible values of x are given. These differ by $\frac{1}{4}$, depending on the symmetry centre chosen as the centre of the molecular dimer.

Atom	x	$x + \frac{1}{4}$	z
C(1)	-0.0500	0.2000	0.0567
C(2)	-0.0917	0.1583	0.0967
C(3)	-0.0382	0.2118	0.1476
C(4)	-0.0903	0.1597	0.1830
C(5)	-0.1856	0.0644	0.1621
C(6)	-0.2394	0.0106	0.1106
C(7)	-0.1922	0.0578	0.0762
O(1)	0.0302	0.2802	0.0591
O(2)	-0.0990	0.1510	0.0144
Br	0.1020	0.3520	0.1827

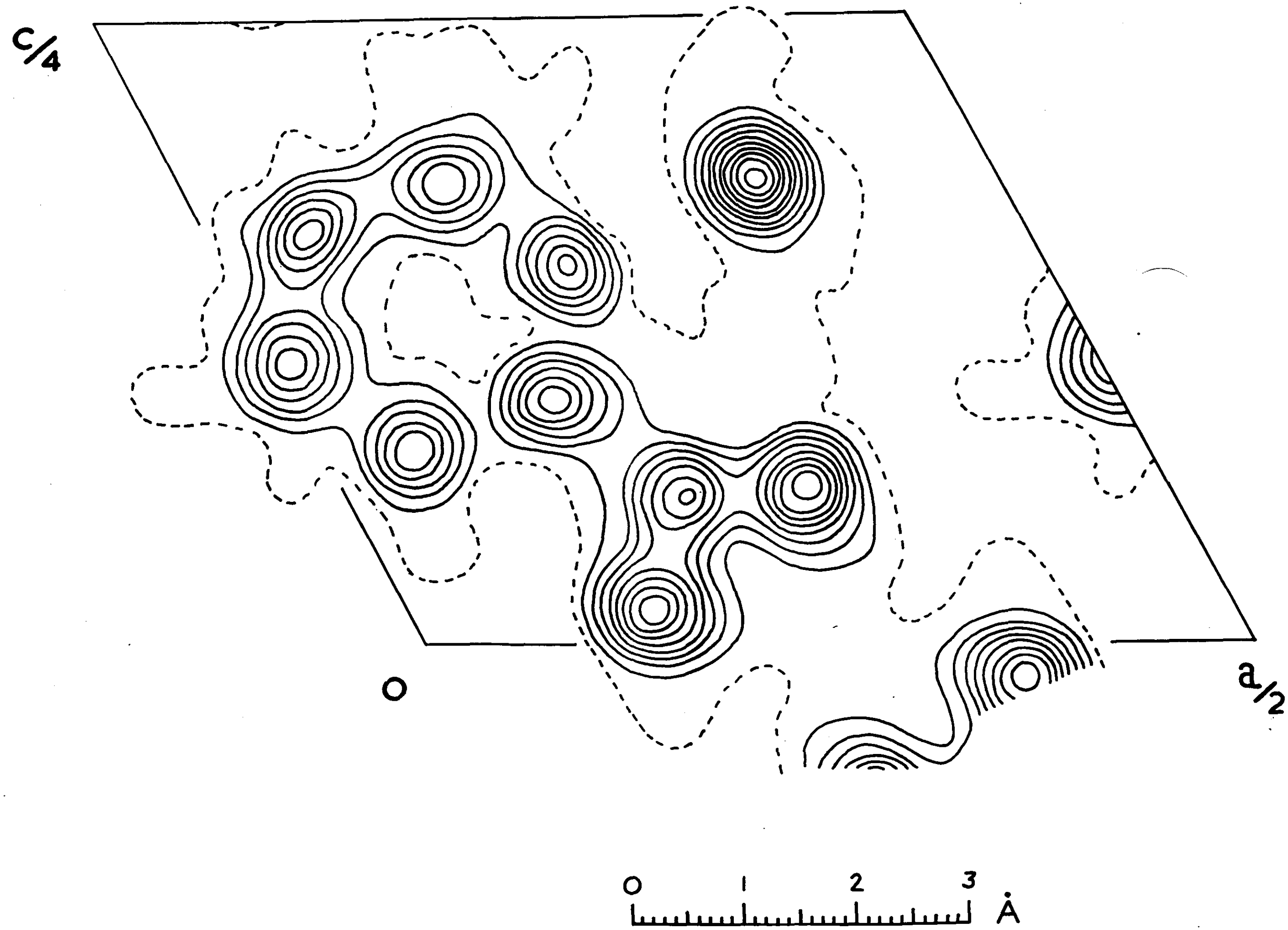


Fig. 13. Electron-density projection on (010). Contours at intervals of 1 $e\text{Å}^{-2}$ except around the bromine atom where the interval is 5 $e\text{Å}^{-2}$. The one-electron line is broken.

three thermal parameters per atom were refined together with an overall scale factor, and R was thus reduced to 0.149 for the observed reflexions. The coordinates obtained from the two-dimensional least-squares refinement are listed in Table 10. The final Fourier projection on 010 is shown in Fig.13.

3.5. Calculation of y-coordinates.

The x and z coordinates obtained from the b-axis projection were converted to orthogonal coordinates X' and Z', and expressed in Ångstom units. The orthogonal system chosen was a, b and c', where c' is perpendicular to the a and b crystal axes.

These coordinates were then referred to a new set of axes with directions parallel to a, b and c', the origin being at the centre of the benzene ring. Since the centre of the benzene ring has coordinates

$$X' = 1/6 \sum_{n=2}^{7} X'_{C(n)}, \quad Y' = \xi \, , \quad Z' = 1/6 \sum_{n=2}^{7} Z'_{C(n)} \qquad \ldots\ldots\ (xix)$$

where ξ is to be determined later, the new coordinates, X" and Z", were easily found.

It was assumed at this point, for the sake of simplicity, that the seven carbon atoms and the bromine atom would be coplanar. On the basis of known bond lengths, it was then calculated that the distance from the centre of the benzene ring to any carbon atom in the ring would be 1.39 Å, to the exocyclic carbon atom would be 2.89 Å and to the bromine atom would be 3.25 Å. Y" coordinates could now be calculated from the equation

$$(Y'')^2 = G^2 - (X'')^2 - (Z'')^2$$

where $G = 1.39$, 2.89 or 3.25 Å depending on the atom involved.

Because the origin of this coordinate system has been taken as the centre of the aromatic ring, the coordinates should satisfy an equation of the type

$$AX'' + BZ'' = Y'' \quad \ldots\ldots\ldots (xx)$$

Values for A and B were obtained by a least-squares reduction of the eight equations in A and B obtained by substituting the known values of X", Y" and Z" in (xx). A was found to be 0.04289, B was 0.54763. New Y" coordinates were then calculated from the equation

$$Y'' = 0.04289\,X'' + 0.54763\,Z''$$

The next step was to find the value of ξ. This was derived from the knowledge that in benzoic acid and salicylic acid for example, the distance of the exocyclic carbon atom from the origin is of the order of 2 Å.

Thus an approximate Y' coordinate for C(1) was calculated and hence, assuming that the acid dimer was centred on the space group centre of symmetry at (0,0,0), a value for ξ in (xix) of 1.3 Å was obtained. If, however, the symmetry centre at ($\frac{1}{4}$,$\frac{1}{4}$,0) were being utilised the ring centre would be at Y' = 2.3 Å, in which case all the x-coordinates must also be increased by 0.250. Fractional x, y and z coordinates for the bromine and carbon atoms were derived for the two cases

At this stage it was noticed that for the case of the dimer centred on (0,0,0) the bromine y-coordinate was almost 0.5. Since the structure factor expression involves terms such as

$$\cos 2\pi(hx + \ell z) \cos 2\pi ky \quad \text{for } \ell \text{ even}$$

$$\text{and} \quad \sin 2\pi(hx + \ell z) \sin 2\pi ky \quad \text{for } \ell \text{ odd}$$

the bromine atom would contribute little to the $hl\ell$ structure factors when ℓ was odd and fully when ℓ was even. The reverse of this would be true if, on the other hand the centre of the acid dimer was at ($\frac{1}{4}$,$\frac{1}{4}$,0) resulting in a bromine y-coordinate of 0.75. The fact that

$$\sum_{\ell=2n+1} |F_o(hl\ell)| \approx 2\sum_{\ell=2n} |F_o(hl\ell)|$$

was evidence in favour of the latter possibility.

Using the $hl\ell$ data, structure factors were calculated on the basis of bromine and carbon contributions for the two possibilities. In the first case (dimer centre at 0,0,0) the value of R was 0.76. In the second case R was 0.46, confirming that ($\frac{1}{4}$,$\frac{1}{4}$,0) was the correct choice for the dimer centre. When the y-coordinates for the ($\frac{1}{4}$,$\frac{1}{4}$,0) possibility were increased by 0.03, R in the structure-factor calculation was 0.45. On decreasing the y values by 0.03, R fell to 0.36. A further decrease of 0.03 in the y-values resulted in R having the value 0.28.

The oxygen atom y-coordinates were obtained, and those for the bromine and carbon atoms improved by computing Fourier line syntheses parallel to the <u>b</u> axis and passing close to the atom centres. On recalculating the $hl\ell$ structure factors with these new y-coordinates, R was found to be 0.17.

3.6. Three-dimensional least-squares refinement.

For the first three-dimensional least-squares calculation, the x and z coordinates from the $h0\ell$ refinement and the y-coordinates from the $hl\ell$ Fourier line syntheses were used. An isotropic temperature

TABLE 11.

Values of R and $\sum w\Delta^2$ from the three-dimensional least-squares refinement.

Cycle	R	$\sum w\Delta^2$
1	0.181	1568 *
2	0.163	1424
3	0.157	1104
4	0.146	896
5	0.141	848
6	0.136	800
7	0.132	784

* $h3\ell$ data not included.

Unobserved planes were omitted when calculating R.

Table 12: Measured and calculated values of the structure factors.

o-BROMOBENZOIC ACID.

h	k	ℓ	$10\lvert F_o\rvert$	$10\,F_c$
0	0	2	337	-537
		4	978	-1095
		6	1438	1704
		8	2048	-2549
		10	745	684
		12	994	834
		14	1156	-1019
		16	1090	1030
		18	< 84	-49
		20	231	-235
		22	538	430
		24	604	-585
		26	< 71	-47
		28	121	147
2	0	-30	107	78
		-28	207	-171
		-26	595	488
		-24	173	93
		-22	319	-278
		-20	650	523
		-18	796	-678
		-16	< 73	86
		-14	1003	1086
		-12	827	-921
		-10	1251	1552
		-8	776	963
		-6	1251	-1609
		-2	344	-365
		0	1617	-1488
		2	342	340
		4	2249	-2430
		6	361	306
		8	1048	1005
		10	928	-874
		12	895	810
		14	734	-576
		16	867	-754
		18	645	579
		20	645	-516
		22	165	-188
		24	292	318
		26	163	-150
4	0	-30	278	254
		-28	< 74	-25
		-26	167	-149
		-24	291	271
		-22	1109	-827
		-20	224	253
		-18	1036	1068
		-16	949	-985
		-14	816	831
		-12	325	-423
		-10	2017	-2561
		-8	1313	1274
		-6	1445	-1341
		-4	1441	-1294
		-2	2221	1936
		0	1456	-1524
		2	497	419
		4	563	489
		6	1957	-1900
		8	1050	891
		10	126	-72
		12	950	-702
		14	1135	870
		16	340	-290
		18	< 87	-86
		20	377	361
		22	212	-254
		24	162	155
6	0	-30	228	-215
		-28	480	443
		-26	346	-359
		-24	422	-435
		-22	575	595
		-20	667	-737
		-18	109	154
		-16	379	431
		-14	1258	-1553
		-12	608	806
		-10	275	202
		-8	476	-461
		-6	1757	1452
		-4	1639	-1469
		-2	731	511
		0	1969	1713
		2	1889	-1664
		4	1014	900
		6	577	481
		8	810	-761
		10	1310	1213
		12	106	-114
		14	408	-410
		16	435	447
		18	247	-278
		20	61	78
		22	148	175
8	0	-32	213	214
		-30	151	-181
		-28	157	-183
		-26	351	383
		-24	317	-378
		-22	213	257
		-20	429	587
		-18	446	-579
		-16	638	750
		-14	143	-116
		-12	636	-726
		-10	1752	1514
		-8	519	-475
		-6	< 64	-5
		-4	2006	1555
		-2	987	-821
		0	199	247
		2	234	220
		4	1152	-1058
		6	666	628
		8	211	155
		10	197	-186
		12	229	276
		14	383	-436
		16	< 72	-8
		18	117	167
		20	103	-213
10	0	-32	153	-142
		-30	296	338
		-28	121	-156
		-26	< 83	48
		-24	185	187
		-22	482	-632
		-20	441	591
		-18	206	223
		-16	391	-467
		-14	781	958
		-12	620	-782
		-10	435	-366
		-8	1118	970
		-6	1557	-1233
		-4	< 77	34
		-2	381	322
		0	1047	-976
		2	627	678
		4	< 87	-30
		6	357	-393
		8	415	490
		10	450	-470
		12	166	-175
		14	198	249
		16	127	-191
12	0	-32	187	-209
		-30	< 61	-67
		-28	215	263
		-26	356	-446
		-24	239	249
		-22	275	361
		-20	422	-554
		-18	392	478
		-16	358	-474
		-14	979	-1074
		-12	771	621
		-10	240	-159
		-8	170	147
		-6	664	549
		-4	756	-639
		-2	290	244
		0	< 88	36
		2	445	-457
		4	379	407
		6	179	-185
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		-23	104	-77
		-22	47	-75
		-21	88	92
		-20	231	-176
		-19	56	54
		-18	348	299
		-17	204	-196
		-16	268	-303
		-15	232	165
		-14	< 60	24
		-13	90	90
		-12	355	296
		-11	139	-136
		-10	653	-693
		-9	135	113
		-8	214	232
		-7	146	-85
		-6	< 22	10
		-5	179	84
		3	136	-122
		4	600	616
		5	269	-370
		6	526	-624
		7	408	465
		8	101	96
		9	119	77
		10	194	185
		11	421	-492
		12	276	-346
		13	152	180
		14	387	428
		15	< 32	2
		16	71	-58
		17	156	-186
		18	116	-148
		19	169	169
		20	194	236
		21	48	-80
		22	128	-145
3	3	-24	107	-106
		-23	48	21
		-22	179	195
		-21	166	-170
		-20	217	-211
		-19	201	169
		-18	96	-75
		-17	82	110
		-16	239	174
		-15	228	-224
		-14	352	-349
		-13	106	40
		-12	323	304
		-11	197	-162
		-10	130	113
		-9	184	-186
		-8	349	-300
		-7	176	179
		-6	492	577
		-5	417	-261
		-4	204	-194
		-3	63	-66
		-2	91	-56
		-1	315	245
		0	551	527
		1	162	-318
		2	362	-504
		3	127	150
		4	183	215
		5	219	243
		6	179	245
		7	249	-291
		8	250	-309
		9	95	86
		10	416	491
		11	95	88
		12	< 32	35
		13	83	-61
		14	111	-134
		15	208	204
		16	163	205
		17	< 28	-22
		18	206	-235
		19	69	-58
5	3	-26	153	175
		-25	103	-104
		-24	200	-166
		-23	80	84
		-22	61	-45
		-21	< 30	43
		-20	400	341
		-19	92	-59
		-18	263	-270
		-17	< 32	10
		-16	390	346
		-15	311	-297
		-14	353	331
		-13	< 29	41
		-12	468	-435
		-11	450	439
		-10	361	385
		-9	206	-209
		-8	331	-299
		-7	51	2
		-6	260	-293
		-5	254	302
		-4	556	684
		-3	229	-293
		-2	287	-363
5	3	-1	150	204
		0	178	161
		1	312	320
		2	304	375
		3	287	-385
		4	423	-513
		5	185	158
		6	318	395
		7	188	164
		8	101	-96
		9	143	-121
		10	288	-358
		11	108	154
		12	256	298
		13	63	-85
		14	206	-238
		15	182	-100
		16	< 25	-50
		17	111	120
		18	144	193
7	3	-26	73	-65
		-25	< 23	55
		-24	214	282
		-23	98	-61
		-22	151	-151
		-21	283	200
		-20	< 31	4
		-19	< 30	-36
		-18	155	139
		-17	204	-188
		-15	307	318
		-14	181	173
		-13	< 31	31
		-12	111	-98
		-11	189	-145
		-10	304	-339
		-9	197	289
		-8	512	507
		-7	186	-117
		-6	146	-173
		-5	46	-14
		-4	46	-36
		-3	299	290
		-2	286	288
		-1	153	-146
		0	586	-654
		1	142	-108
		2	57	60
		3	57	-106
		4	58	67
		5	117	-85
		6	276	-335
		7	162	217
		8	316	316
		9	56	-91
		10	54	-41
		11	142	-125
		12	49	-71
		13	96	108
		14	140	189
		15	72	-106
9	3	-26	199	-238
		-25	109	111
		-24	83	-37
		-23	49	-89
		-22	96	112
		-21	107	-126
		-20	249	-231
		-19	197	178
		-18	259	237
		-17	89	-58
		-16	< 39	9
		-15	184	-90
		-14	235	-242
		-13	154	153
		-12	300	311
		-11	148	-194
		-10	307	-289
		-9	71	-50
		-8	108	-103
		-7	107	88
		-6	231	249
		-5	239	-251
		-4	405	-384
		-3	< 39	17
		-2	203	188
		-1	58	14
		0	97	157
		1	214	-195
		2	199	-208
		3	216	245
		4	397	354
		5	78	42
		6	85	-70
		7	180	-168
		8	66	-112
		9	102	93
		10	149	181
		11	67	-95
		12	202	-199
11	3	-26	120	163
		-25	163	-161
		-24	131	-137
		-23	84	97
		-22	188	181
		-21	121	94
		-20	109	94
		-19	119	-79
		-18	293	-293
		-17	< 30	-43
		-16	248	265
		-15	114	-155
		-14	162	-117
		-13	58	-17
		-12	124	-140
		-11	164	117
		-10	424	383
		-9	71	-65
		-8	221	-220
		-7	63	83
		-6	220	160
		-5	70	28
		-4	252	270
		-3	145	-119
		-2	298	-302
		-1	179	190
		0	223	177
		1	57	1
		2	56	-17
		3	189	-151
		4	150	-173
		5	130	117
		6	226	214
		7	< 19	-27
		8	99	-105
13	3	-24	115	106
		-23	< 19	-14
		-22	113	-133
		-21	95	66
		-20	119	123
		-19	124	-150
		-18	< 26	-9
		-17	< 26	-3
		-16	113	-129
		-15	214	222
		-14	217	199
		-13	63	-39
		-12	142	-135
		-11	< 28	88
		-10	57	9
		-9	109	98
		-8	153	152
		-7	289	-257
		-6	206	-191
		-5	53	60
		-4	117	87
		-3	211	152
		-2	84	-54
		-1	146	-116
		0	162	-167
		1	42	60
		2	169	177
15	3	-19	73	85
		-18	149	156
		-17	75	-38
		-16	177	-155
		-15	35	7
		-14	< 20	-18
		-13	100	37
		-12	156	142
		-11	90	-114
		-10	215	-197
		-9	< 19	-2
		-8	107	47
		-7	40	43

parameter B = 4.0 Å^2 was assigned to the bromine, oxygen and carbon atoms, no allowances being made for hydrogen atoms.

In the first refinement cycle, in which only the $h0\ell$, $h1\ell$ and $h2\ell$ data were used, the value of the residual R was 0.181. In the second and subsequent cycles the $h3\ell$ data were included. In all, six rounds of calculation were completed in which the three positional and six thermal parameters were refined. After the sixth cycle the parameter shifts were small in comparison with the parameter standard deviations and refinement was terminated. The values of R and $\Sigma w\Delta^2$ for the refinement cycles are shown in Table 11. The values of the observed structure amplitudes and of the final calculated structure factors are listed in Table 12. In the least-squares calculations, 100 unobserved terms were included with a value of half the minimum $|F_o|$ locally observable. These terms were omitted when R was calculated.

3.7. Coordinates, Molecular geometry and Estimation of accurary.

The final coordinates of the carbon, oxygen and bromine atoms are given in Table 13, while Table 14

TABLE 13.

Final atomic coordinates.

Coordinates x, y, z are referred to the monoclinic crystal axes and are expressed as fractions of the axial lengths, with origin at the centre of symmetry on glide plane c. Coordinates X' , Y and Z' are referred to orthogonal axes a, b and c', c' being taken perpendicular to the a and b crystal axes, and are expressed in Å units.

Atom	x	y	z	X'	Y	Z'
C(1)	0.2029	0.3511	0.0567	2.312	1.440	1.293
C(2)	0.1583	0.4335	0.0958	1.171	1.777	2.185
C(3)	0.2117	0.5871	0.1484	1.319	2.407	3.385
C(4)	0.1636	0.6701	0.1830	0.181	2.748	4.175
C(5)	0.0611	0.5978	0.1629	-1.092	2.451	3.717
C(6)	0.0078	0.4434	0.1104	-1.238	1.818	2.518
C(7)	0.0560	0.3571	0.0753	-0.093	1.453	1.718
O(1)	0.2801	0.4633	0.0596	3.421	1.899	1.360
O(2)	0.1489	0.1268	0.0156	2.013	0.520	0.356
Br	0.3523	0.6911	0.1833	2.974	2.834	4.181

TABLE 14.

Anisotropic temperature-factor parameters ($b_{ij} \times 10^5$).

Atom	b_{11}	b_{22}	b_{33}	b_{23}	b_{13}	b_{12}
C(1)	652	10898	251	-273	415	-1475
C(2)	850	4668	213	-191	550	554
C(3)	912	5377	293	553	574	926
C(4)	1194	8734	293	-173	756	1398
C(5)	1032	8000	385	-168	871	673
C(6)	836	13500	289	699	530	1221
C(7)	730	15955	271	-419	559	705
O(1)	1028	14574	289	-1490	709	-1210
O(2)	1115	10024	315	-844	648	457
Br	827	11888	283	-937	473	-1022

The temperature factor is expressed in the form

$$2^{-(b_{11}h^2 + b_{22}k^2 + b_{33}\ell^2 + b_{23}k\ell + b_{13}h\ell + b_{12}hk)}$$

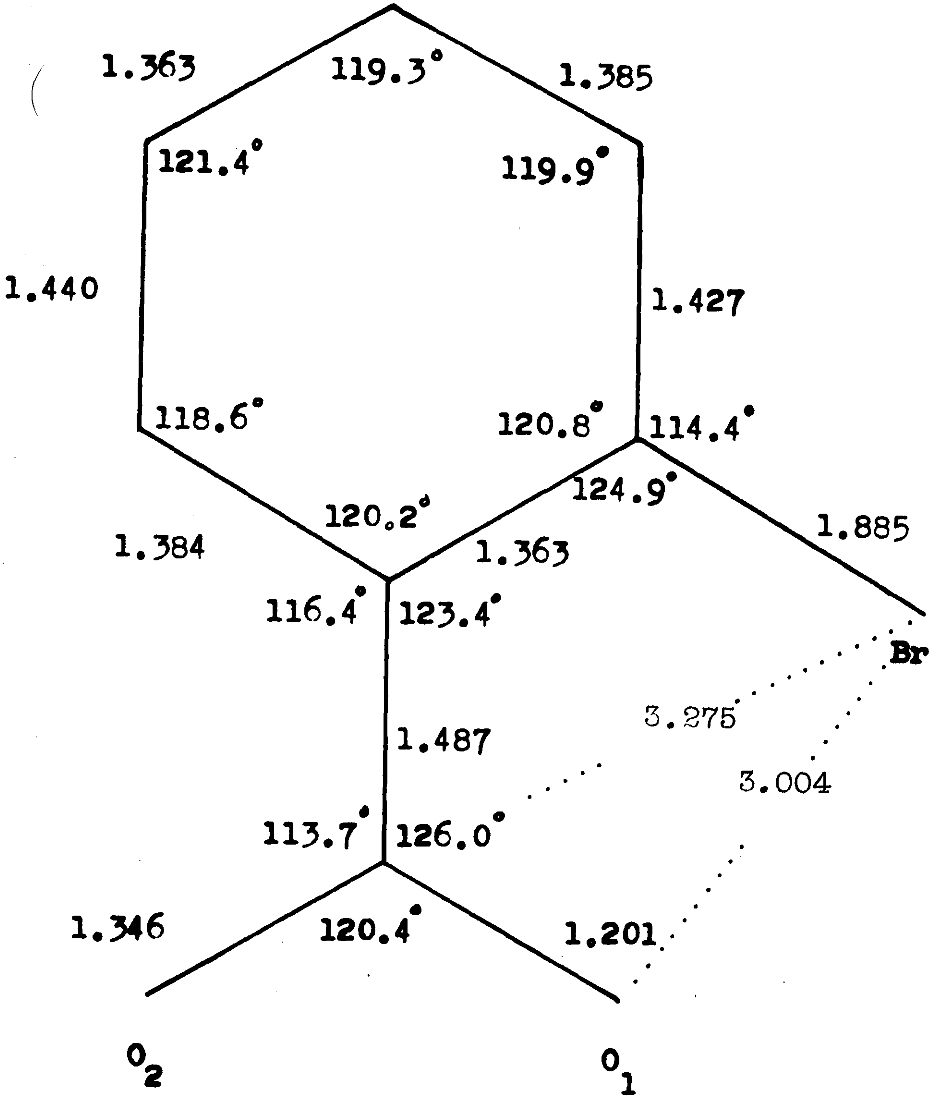


Fig.14. Interatomic distances and valency angles in o-bromobenzoic acid.

contains the corresponding anisotropic temperature parameters. The bond lengths and valency angles, illustrated in Fig.14, were calculated from the coordinates listed in Table 13. The shorter intermolecular contacts are shown in Table 15.

The average standard deviations in positional parameter calculated from the results of the seventh least-squares cycle are

carbon: $\sigma_x = \sigma_z = 0.013$ Å, $\sigma_y = 0.016$ Å.
oxygen: $\sigma_x = \sigma_z = 0.009$ Å, $\sigma_y = 0.012$ Å.
bromine: $\sigma_x = \sigma_y = \sigma_z = 0.002$ Å.

The estimated standard deviations in bond length derived from these results are 0.020 Å for a carbon-carbon bond, 0.017 Å for a carbon-oxygen bond and 0.014 Å for the carbon-bromine bond. The estimated standard deviation in bond angle calculated from Cruickshank and Robertson's (1953) formula is 1.3°.

TABLE 15.

The shorter intermolecular contacts.

$O(1)\ldots O(2)_{I}$	2.643 Å	$C(3)\ldots C(2)_{II}$	3.675 Å
$O(1)\ldots O(2)_{II}$	3.224	$C(4)\ldots C(7)_{II}$	3.748
$O(1)\ldots O(1)_{I}$	3.284	$Br\ldots C(6)_{V}$	3.751
$C(1)\ldots O(2)_{II}$	3.329	$Br\ldots C(5)_{V}$	3.766
$C(1)\ldots O(1)_{I}$	3.393	$C(6)\ldots O(2)_{III}$	3.785
$C(7)\ldots O(2)_{III}$	3.454	$C(4)\ldots C(4)_{VIII}$	3.794
$C(6)\ldots O(2)_{IV}$	3.459	$O(1)\ldots C(1)_{II}$	3.806
$C(2)\ldots O(2)_{II}$	3.484	$C(3)\ldots O(2)_{II}$	3.815
$C(1)\ldots O(2)_{I}$	3.498	$C(5)\ldots C(7)_{II}$	3.832
$C(7)\ldots O(2)_{IV}$	3.531	$C(3)\ldots C(7)_{II}$	3.839
$O(1)\ldots C(6)_{V}$	3.576	$C(4)\ldots C(2)_{II}$	3.839
$O(2)\ldots O(2)_{I}$	3.602	$C(4)\ldots C(6)_{II}$	3.848
$C(7)\ldots C(7)_{IV}$	3.635	$C(1)\ldots C(1)_{I}$	3.890
$O(1)\ldots O(1)_{VI}$	3.640	$C(3)\ldots C(1)_{II}$	3.896
$C(6)\ldots O(1)_{VII}$	3.668	$C(7)\ldots C(1)_{IV}$	3.927
$C(5)\ldots C(6)_{II}$	3.671	$Br\ldots C(5)_{VIII}$	3.932
		$C(6)\ldots C(7)_{II}$	3.998

The subscripts refer to the following positions:-

I.	$\frac{1}{2}-x,\ \frac{1}{2}-y,\ \bar{z}$	V.	$\frac{1}{2}+x,\ \frac{1}{2}+y,\ z$
II.	$x,\ 1+y,\ z$	VI.	$\frac{1}{2}-x,\ 1\frac{1}{2}-y,\ \bar{z}$
III.	$\bar{x},\ \bar{y},\ \bar{z}$	VII.	$-\frac{1}{2}+x,\ \frac{1}{2}+y,\ z$
IV.	$\bar{x},\ 1-y,\ \bar{z}$	VIII.	$\frac{1}{2}-x,\ \frac{1}{2}+y,\ \frac{1}{2}-z$

3.8. Mean molecular plane calculations.

Only two equations of mean molecular planes were calculated for o-bromobenzoic acid. They were the equation of the plane through the six carbon atoms of the benzene ring, and that of the carboxyl group and C(2), the method of Schomaker *et al* (1959) being used. The equations found are

$$0.04782\,X' - 0.88713\,Y + 0.45903\,Z' + 0.51657 = 0$$

for the benzene plane, and

$$0.26961\,X' - 0.73115\,Y + 0.62669\,Z' - 0.38458 = 0$$

for the carboxyl plane. The deviations of the atoms from these planes are shown in Table 16. The angle which the carboxyl plane makes with the benzene plane is 18.3°.

3.9. Discussion.

The Br ...O(1) (3.004 Å) and Br ... C(1) (3.275 Å) separations are appreciably shorter than the sums of the van der Waal's radii (3.35 Å and 3.95 Å respectively). The molecule is distorted from the ideal planar configuration with valency angles of 120° at the benzene carbon atoms as a result of steric strain.

The carboxyl group is twisted out of the plane of

TABLE 16.

Deviations from the mean planes.

(a) Plane through the benzene ring atoms C(2)....C(7).

(b) Plane through C(1), C(2), O(1), O(2).

Atom	(a)	(b)
C(1)	-0.057 Å	-0.003 Å
C(2)	-0.001	0.001
C(3)	-0.002	-
C(4)	0.005	-
C(5)	-0.004	-
C(6)	0.001	-
C(7)	0.002	-
O(1)	-0.380	0.001
O(2)	0.315	0.001
Br	0.064	-

the benzene ring by 18.3°; this is accompanied by small out-of-plane and larger in-plane deflections of the exocyclic valency bonds. Thus the bromine atom and the exocyclic carbon atom are displaced from the plane of the aromatic ring by +0.064 Å and -0.057 Å respectively, corresponding to the valency bonds bending out of the plane of the benzene ring by +1.9° and -2.2°. In addition, two of the exocyclic valency angles are increased from the normal value of 120° to 124.9° and 123.4°, while the adjacent angles are decreased to 114.4° and 116.4°, (Fig.14). These effects are slightly larger than, though similar to, those observed in o-chlorobenzoic acid, (see 2.10).

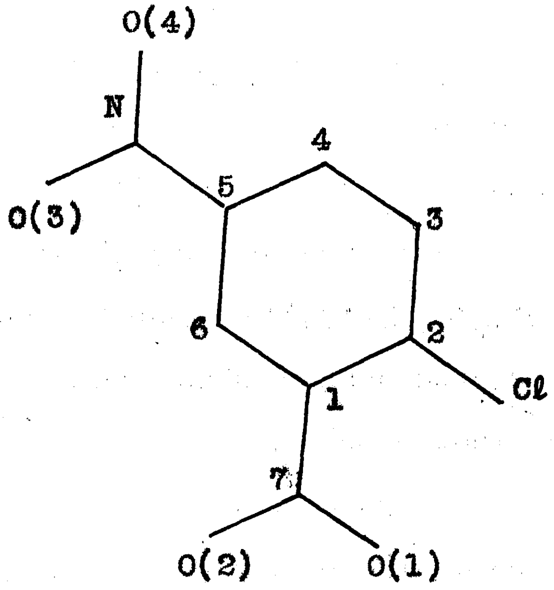
The average length of a carbon-carbon bond is 1.394 Å which is comparable with the mean value of 1.385 Å found in o-chlorobenzoic acid. The exocyclic carbon-carbon bond (1.487 Å) appears to be shorter than that in o-chlorobenzoic acid (1.521 Å); as the standard deviation in bond length is 0.020 Å, little significance can be given to this difference. The valency angles in the carboxyl group conform to the pattern generally found in carboxylic acids. The angle C(2)C(1)O(1) (126.0°) is however slightly enlarged; this may be a further steric effect caused by the proximity of the bulky bromine atom. The carbon-oxygen bond lengths of 1.201 Å and 1.346 Å (Fig.14) indicate that the carboxyl hydrogen atom is bonded to O(2) as is the case in o-chlorobenzoic acid.

The carbon-bromine distance of 1.885 Å appears to be slightly longer than the average value of 1.85 Å for aromatic carbon-bromine bonds (Tables of Interatomic Distances, 1958). As the standard deviation of this bond length is 0.014 Å, the difference may not be significant.

The closest intermolecular approach occurs between oxygen atoms of adjacent carboxyl groups related by a centre of symmetry. The OH...O distance here is 2.643 Å which is normal for this type of hydrogen bonding. All other intermolecular contacts (Table 15) are over 3 Å and correspond to normal van der Waal's interactions.

4. 2-Chloro-5-nitrobenzoic acid.

A detailed X-ray investigation of the crystal and molecular structure of 2-chloro-5-nitrobenzoic acid was undertaken because of the possibility that the molecule might exhibit a relayed steric effect. In particular, the buttressing of the hydrogen atom at position 6, by the nitro group at position 5, might cause the carboxyl group to be tilted more steeply to the benzene plane than was found in o-chlorobenzoic acid; this did in fact prove to be the case.



4.1. Crystal Data.

Lath-like crystals elongated along the direction of the **b** crystal axis (but occasionally along **a**) were obtained by crystallisation from aqueous ethanol. Small crystals suitable for recording intensity data were obtained by cutting the lath-shaped crystals. The monoclinic cell dimensions were determined from rotation and equatorial layer-line moving-film photographs taken with copper Kα radiation, the following values being obtained:-

$$a = 5.86 \pm 0.02\ \mathring{A}$$

$$b = 5.13 \pm 0.02\ \mathring{A}$$

$$c = 26.65 \pm 0.05\ \mathring{A}$$

$$\beta = 97^{\circ}54' \pm 20'.$$

The volume of the unit cell is 794 $\mathring{A}^3$. The experimentally determined density is 1.678 g.cm.$^{-3}$, consequently there are four molecules of $C_7H_4O_4NCl$ in the unit cell. The calculated density is 1.687 g.cm.$^{-3}$. The linear absorption coefficient for copper Kα radiation is $\mu = 42.0$ cm.$^{-1}$

Examination of the equatorial-layer-line Weissenberg photographs showed that the absent spectra are

$h0l$ when l is odd

$0k0$ when k is odd.

The space group is therefore uniquely determined as $P2_{1/c}$ (C^5_{2h}).

4.2. Intensity Data.

The data used in the initial two-dimensional work consisted of the $h0\ell$ and $0k\ell$ reflexions. For the three-dimensional analysis the $h1\ell$, $h2\ell$, and $h3\ell$ sets of data were collected using the equi-inclination multiple-film Weissenberg technique. The intensities were estimated visually and were corrected for Lorentz, polarisation and the Tunell factors appropriate to upper layers in the usual way. No absorption corrections were applied as care had been taken in cutting small crystals of approximately uniform cross-section. The structure amplitudes were put on the same relative scale by means of the $0k\ell$ zone. They were later put on an absolute scale by comparison with the calculated structure factors.

4.3. Structure determination:- the b-axis projection.

As in the case of o-chlorobenzoic acid use was made of the Patterson projection on (010) (Fig.15) in solving the structure. The largest peak on this map represents

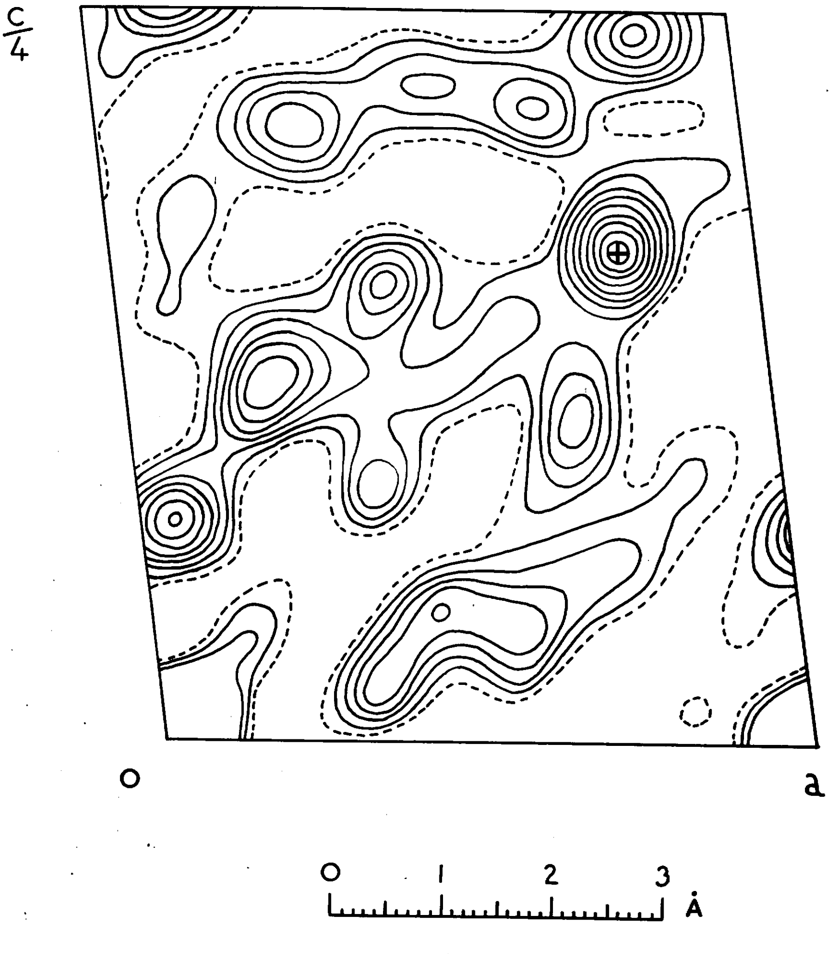


Fig.15. Patterson projection along the b-axis. Contours at equal arbitrary intervals, the lowest contour being broken and origin peak contours omitted. The chlorine-chlorine vector is marked with a cross.

the chlorine-chlorine vector between chlorine atoms of an acid dimer, and the peaks nearest the origin define the orientation of the benzene ring. This enabled approximate x and z coordinates for the chlorine, oxygen, nitrogen and carbon atoms to be deduced. Structure factors were calculated using the Tomiie and Stam (1958) scattering factor curve for chlorine and those of Berghuis _et_ _al_ (1955) for carbon, oxygen and nitrogen with an overall isotropic temperature factor $B = 4.0 \text{ Å}^2$. The value of R, the discrepancy factor, was 0.52. With the signs of the calculated structure factors allocated to the measured amplitudes, the Fourier projection on (010) was computed. All the atoms (apart from hydrogens) were clearly visible on this map although there was considerable overlap in the carboxyl group. New coordinates were chosen and in the second structure-factor calculation R was 0.26.

4.4. Refinement of the b-axis projection.

This projection was refined by least-squares methods, no allowances being made for hydrogen atoms at this early stage. In all, six rounds of calculations, in which positional and anisotropic temperature parameters were

TABLE 17.

The x and z coordinates obtained from the least-squares refinement of the b-axis projection, expressed as fractions of the axial lengths.

Atom (c.f.Fig.20)	x	z
C(1)	-0.2544	0.1023
C(2)	-0.4599	0.1163
C(3)	-0.5312	0.1626
C(4)	-0.4110	0.1912
C(5)	-0.2105	0.1739
C(6)	-0.1255	0.1312
C(7)	-0.1438	0.0561
N	-0.1063	0.2011
O(1)	-0.2099	0.0317
O(2)	-0.0238	0.0383
O(3)	0.0931	0.1935
O(4)	-0.1770	0.2392
Cl	-0.6042	0.0816

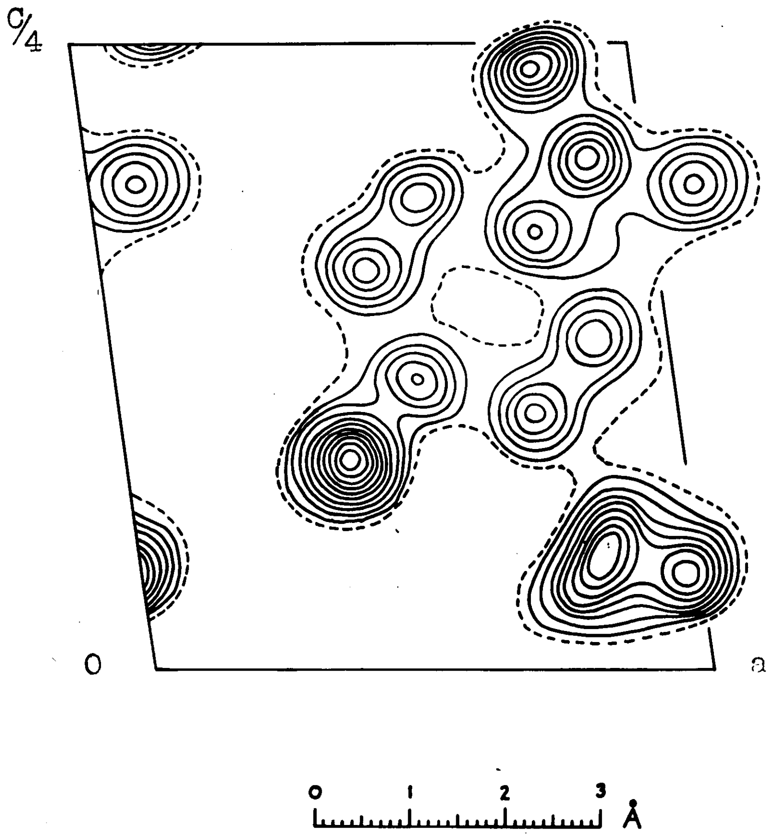


Fig.16. Electron-density projection on (010). Contours at intervals of 1 eÅ^{-2} except around the chlorine atom where, above the 3 eÅ^{-2} contour, the interval is 2 eÅ^{-2}. The one-electron line is broken.

adjusted, were completed. The value of R was reduced to 0.15. The coordinates obtained after the sixth refinement cycle are listed in Table 17. Because of the relatively small amount of data available (approximately 150), and the overlap of some of the atoms, no further refinement of the projection on its own was attempted. The final electron-density projection on (010) is shown in Fig.16.

4.5. The a-axis projection.

The length of the a axis (5.86 Å) encouraged attempts at solving the Patterson projection on (100), (Fig.17). Symmetry relationships predict that an atom with coordinates (y,z) should give rise to peaks on this Patterson projection at (2y, 2z), ($\frac{1}{2}$-2y, $\frac{1}{2}$) and ($\frac{1}{2}$, $\frac{1}{2}$-2z). Since the value of 2z for the chlorine atom was known from earlier work on the (010) projection, the y-coordinate for the chlorine atom was readily found. On the basis of the chlorine atom alone, structure factors were calculated for the $0k\ell$ data: R was 0.58. The signs of the chlorine atom contributions were then used in computing an electron-density projection along

Fig.17. Patterson projection along the a axis. Contours at equal arbitrary intervals, the lowest contour being broken and origin peak contours omitted. The chlorine-chlorine vectors are marked by crosses.

TABLE 18.

The y and z coordinates obtained from the refinement of the *a*-axis projection expressed as fractions of the axial lengths.

Atom (c.f. Fig. 21)	y	z
C(1)	0.1950	0.1019
C(2)	0.0476	0.1189
C(3)	0.1424	0.1633
C(4)	0.3554	0.1925
C(5)	0.4592	0.1696
C(6)	0.3912	0.1283
C(7)	0.1029	0.0580
N	0.6728	0.2032
O(1)	-0.1040	0.0336
O(2)	0.2537	0.0357
O(3)	0.7321	0.1934
O(4)	0.7669	0.2389
Cl	-0.1737	0.0822

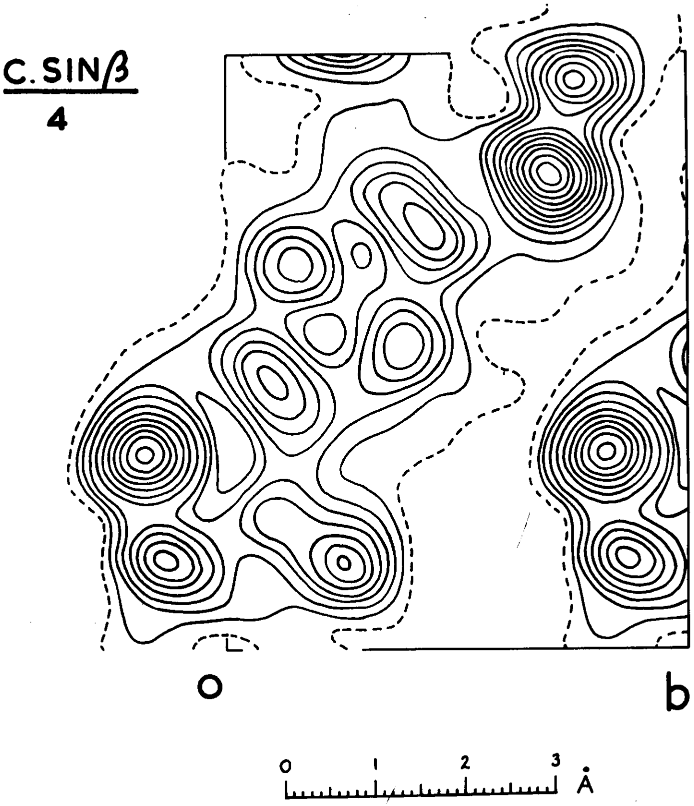


Fig.18. Electron-density projection on (100). Contours at intervals of 1 eÅ^{-2} except around the chlorine atom where, after the 4 eÅ^{-2} contour, the interval is 2 eÅ^{-2}. The one-electron line is broken.

the a axis. From this projection, y-coordinates for the lighter atoms were chosen and refinement continued by Fourier and difference syntheses, four rounds of calculations reducing R to 0.15. Table 18 shows the y and z coordinates obtained. The final electron-density projection on (100) is shown in Fig.18.

4.6. Three-dimensional refinement.

As a starting point for the three-dimensional analysis the x and z coordinates from the (010) projection and the y-coordinates from the (100) projection, with an isotropic temperature factor $B = 4.0$ Å^2, were used in calculating structure factors for the $h1\ell$, $h2\ell$ and $h3\ell$ sets of data. The values of R were 0.26, 0.27 and 0.29 respectively. Improved positional parameters were then obtained by interpolation in three-dimensional electron-density distributions (Booth, 1948b). Both F_o and F_c syntheses were computed in order that back-shift corrections for termination-of-series errors could be made (Booth, 1946, 1947). In the next structure-factor calculation the values of R were 0.19, 0.21 and 0.21 for the $h1\ell$, $h2\ell$ and $h3\ell$ data respectively.

Allowances were now made for hydrogen atoms; those of the benzene ring were placed radially at a distance of 1.0 Å from the appropriate carbon atoms, that of the carboxyl group was 1.0 Å from O(2) on the line to O(1) of the opposite carboxyl group. The scattering curve chosen for hydrogen was that of McWeeny (1951) and the hydrogen temperature factor B was kept constant at 4.0 $Å^2$ throughout the refinement.

When seven cycles of least-squares refinement had been completed the parameter shifts were negligible. In the least-squares calculations 205 unobserved reflexions were included each with a value of $|F_o|$ at half the minimum value locally observable. After the fifth cycle, new coordinates were calculated for the hydrogen atoms; these, although included in the structure-factor calculations, were not refined by the least-squares program. In Table 19 are listed the values of R and $\sum w(F_o-F_c)^2$ for the refinement cycles. The final value of R is 0.090 for the 1027 observed reflexions. The observed structure amplitudes are listed with the final values of the calculated structure factors in Table 20.

TABLE 19.

Progress of the least-squares refinement.

Cycle	*R*	$\sum w \Delta^2$
1	0.185	748
2	0.155	532
3	0.132	426
4	0.110	356
5	0.102	328
6	0.093	288
7	0.090	276

Table 20: Measured and calculated values of the structure factors.

2-CHLORO-5-NITROBENZOIC ACID

h k l 10|F_o| 10 F_c

4.7. Coordinates, Molecular dimensions and Estimation of Accuracy.

The coordinates obtained from the final least-squares refinement cycle are given in Table 21, where the coordinates assigned by calculation to the hydrogen atoms are also shown. The anisotropic temperature factors are listed in Table 22. In Fig.19 the bond lengths and angles of the molecule defined by the coordinates given in Table 21 are shown. The arrangement of the molecules in the b-axis and the a-axis projections is shown in Figs.20 and 21 respectively. On these two diagrams some of the shorter intermolecular contacts are indicated. These and the other intermolecular approach distances less than 3.7 Å are listed in Table 23, where some of the more interesting intramolecular contacts are also given. The closest intermolecular approach occurs between oxygen atoms of adjacent carboxyl groups related by a centre of symmetry, the OH...O distance being 2.613 Å. All other intermolecular contacts correspond to normal van der Waal's interactions.

The standard deviations in positional parameters, calculated from the least-squares normal-equation totals,

TABLE 21.

Final atomic coordinates.

Coordinates *x*, *y* and *z* are referred to the monoclinic crystal axes and are expressed as fractions of the axial lengths, with origin at the centre of symmetry. Coordinates *X'*, *Y* and *Z'* are referred to orthogonal axes *a*, *b* and *c'*, *c'* being taken perpendicular to the *a* and *b* crystal axes, and are expressed in Å units.

Atom	*x*	*y*	*z*	*X'*	*Y*	*Z'*
C(1)	-0.2551	0.1807	0.1006	-1.863	0.927	2.654
C(2)	-0.4479	0.0736	0.1162	-3.051	0.378	3.068
C(3)	-0.5264	0.1526	0.1598	-3.670	0.783	4.218
C(4)	-0.4142	0.3503	0.1889	-3.119	1.797	4.986
C(5)	-0.2209	0.4581	0.1734	-1.930	2.350	4.577
C(6)	-0.1431	0.3791	0.1300	-1.315	1.945	3.432
C(7)	-0.1520	0.0996	0.0550	-1.092	0.511	1.451
O(1)	-0.1858	-0.1173	0.0367	-1.223	-0.602	0.968
O(2)	-0.0226	0.2753	0.0384	-0.273	1.412	1.015
O(3)	0.0806	0.7441	0.1922	-0.232	3.817	5.075
O(4)	-0.1861	0.7523	0.2391	-1.966	3.859	6.312
N	-0.1002	0.6646	0.2034	-1.332	3.409	5.370
Cℓ	-0.6040	-0.1761	0.0822	-3.840	-0.903	2.169

- Cont'd -

TABLE 21

(Cont'd)

Atom	x	y	z	X'	Y	Z'
H(C2)	0.0559	0.2158	0.0099	0.291	1.107	0.262
H(C3)	-0.6651	0.0728	0.1705	-4.523	0.374	4.500
H(C4)	-0.4714	0.4100	0.2202	-3.569	2.103	5.811
H(C6)	-0.0029	0.4580	0.1191	-0.453	2.350	3.144

TABLE 22.

Anisotropic temperature factors ($b_{ij} \times 10^5$).

	b_{11}	b_{22}	b_{33}	b_{23}	b_{13}	b_{12}
C(1)	3747	6267	177	229	346	877
C(2)	4226	6153	202	63	136	491
C(3)	4235	7689	184	197	539	787
C(4)	4323	6392	193	124	570	-695
C(5)	3945	7596	172	100	275	661
C(6)	3879	6685	202	152	479	1316
C(7)	4479	4345	207	-174	563	149
O(1)	5562	6854	232	-472	777	194
O(2)	6093	5526	247	-126	1180	-350
O(3)	5570	7369	273	-276	837	-2034
O(4)	5680	6546	228	-354	556	1240
N	4611	5570	213	- 48	518	-558
Cℓ	4241	6091	221	-188	230	-660

The temperature factor is expressed in the form

$$2^{-(b_{11}h^2 + b_{22}k^2 + b_{33}\ell^2 + b_{23}k\ell + b_{13}h\ell + b_{12}hk)}$$

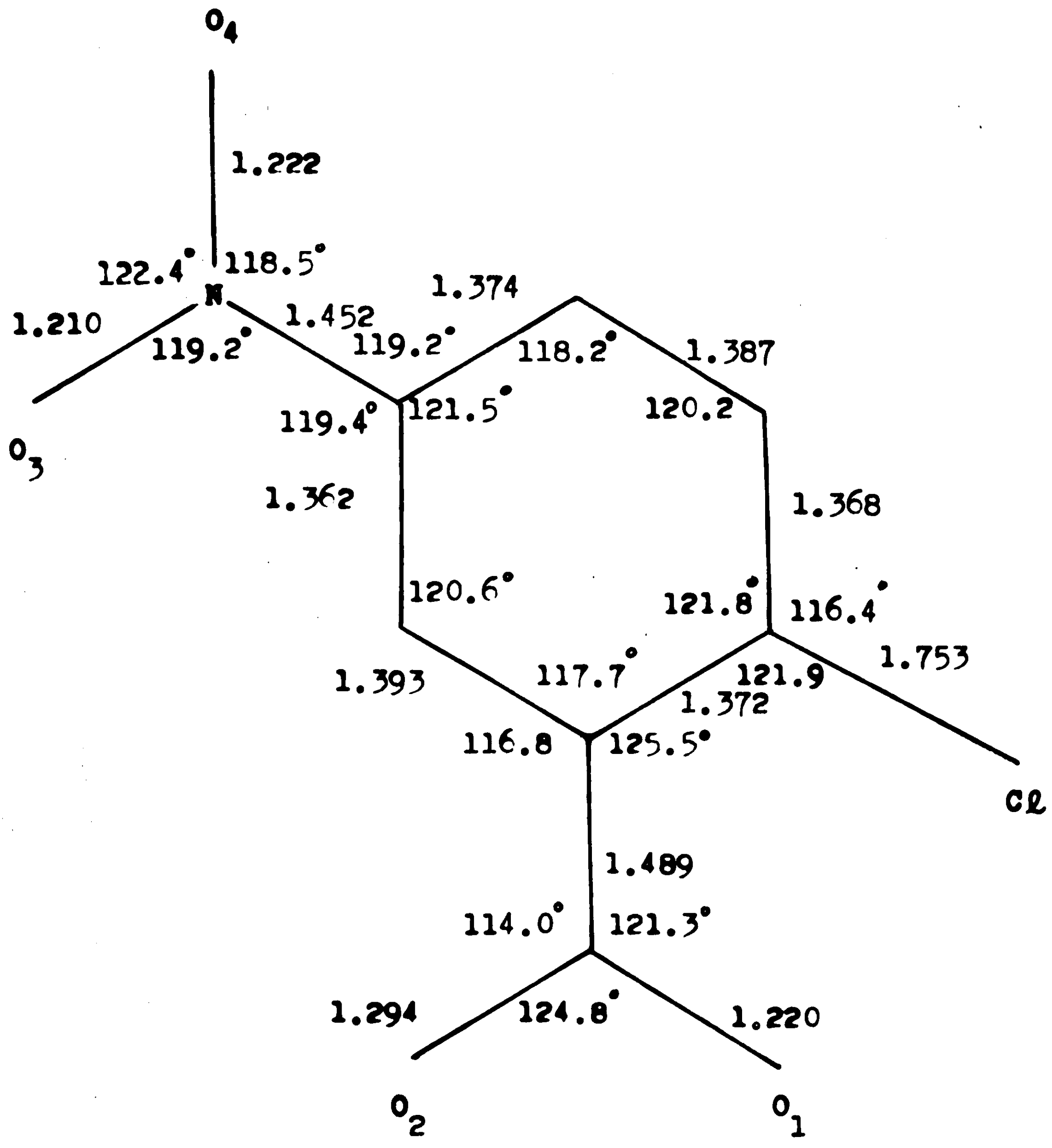


Fig.19. Interatomic distances and valency angles in 2-chloro-5-nitrobenzoic acid.

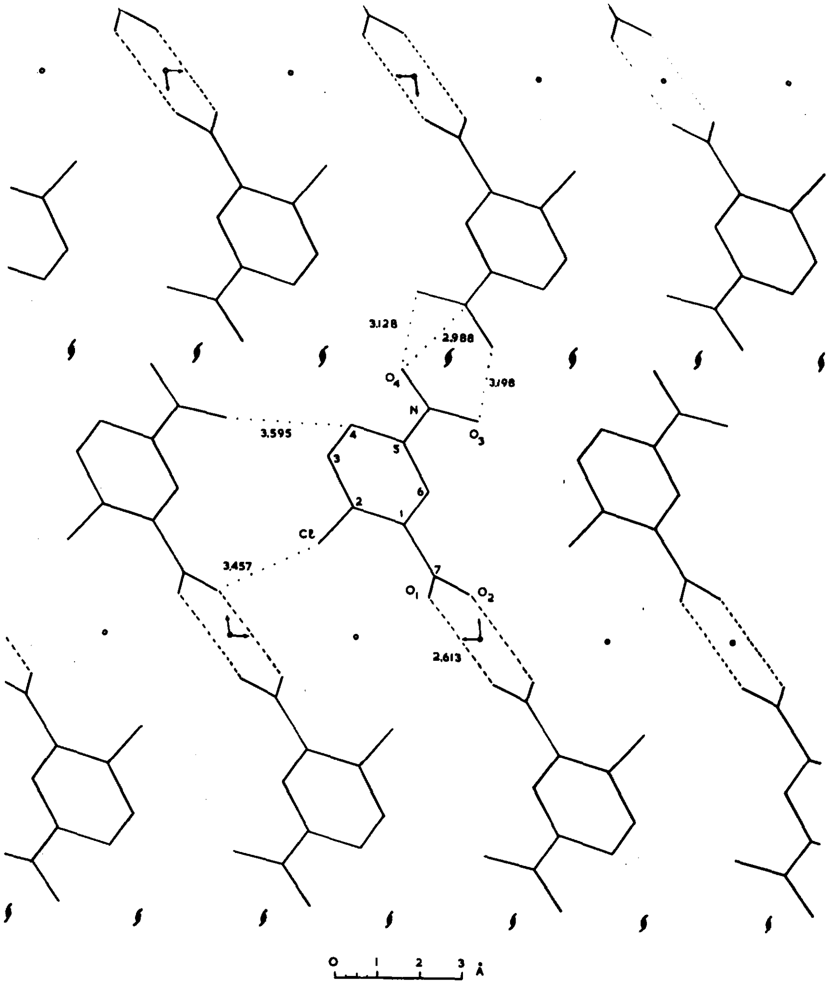


Fig.20. The crystal structure of 2-chloro-5-nitrobenzoic acid as viewed in projection along the b axis with the true unit cell halved in the c direction. Some of the shorter intermolecular contacts are shown.

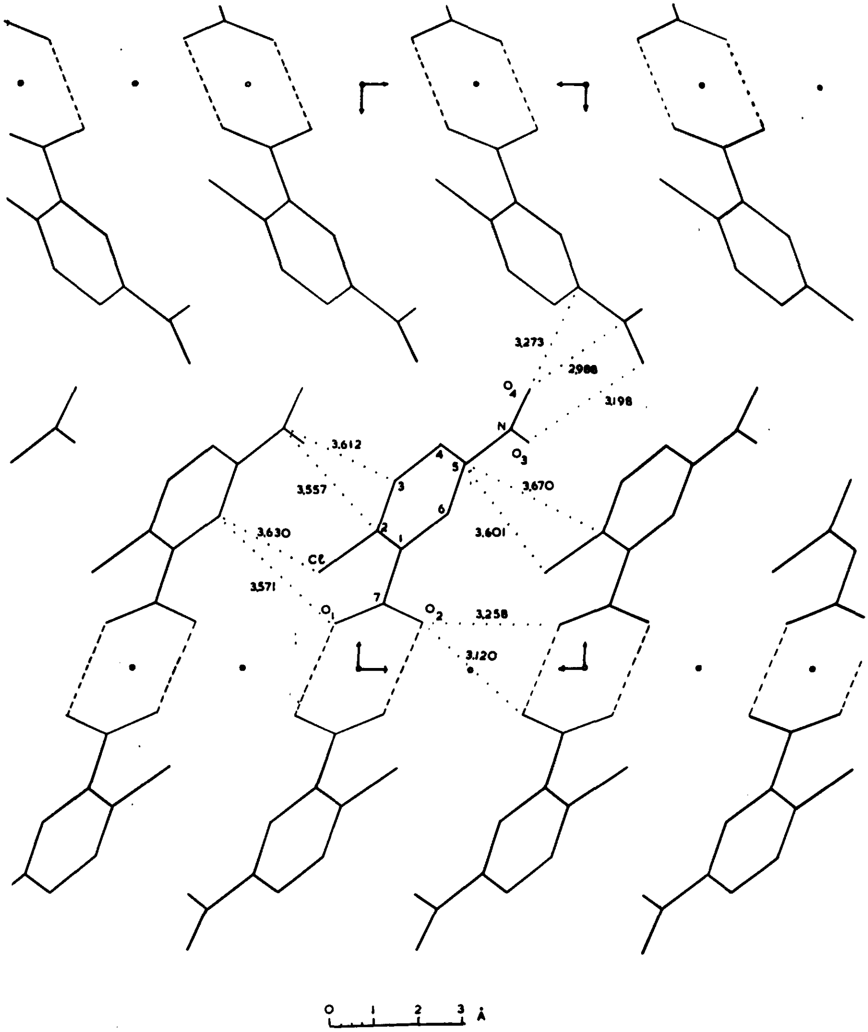


Fig.21. Structure viewed along the *a* axis with the true unit cell halved in the *c* direction. Some of the shorter intermolecular contacts are shown.

TABLE 23.

Shorter Intermolecular distances.

$O(1)\ldots O(2)_{I}$	2.613 Å
$O(4)\ldots N_{II}$	2.988
$O(2)\ldots O(2)_{III}$	3.120
$O(4)\ldots O(3)_{II}$	3.128
$O(3)\ldots O(4)_{II}$	3.198
$O(2)\ldots O(1)_{IV}$	3.258
$O(4)\ldots C(5)_{II}$	3.273
$O(3)\ldots C(3)_{V}$	3.315
$O(1)\ldots O(1)_{I}$	3.343
$C(7)\ldots O(1)_{I}$	3.349
$O(4)\ldots O(4)_{II}$	3.365
$O(4)\ldots C(3)_{IV}$	3.392
$C(7)\ldots O(2)_{I}$	3.412
$C\ell\ldots O(2)_{VI}$	3.457
$C\ell\ldots O(1)_{VI}$	3.472
$C\ell\ldots C(7)_{VI}$	3.493
$O(3)\ldots N_{II}$	3.509 Å
$O(2)\ldots O(2)_{I}$	3.521
$O(3)\ldots C(4)_{II}$	3.528
$O(4)\ldots C(4)_{IV}$	3.535
$N\ldots C(2)_{IV}$	3.557
$C(6)\ldots O(1)_{IV}$	3.571
$C(4)\ldots O(3)_{VI}$	3.595
$C(5)\ldots C\ell_{IV}$	3.601
$N\ldots C(3)_{IV}$	3.612
$C(6)\ldots C\ell_{IV}$	3.630
$N\ldots N_{II}$	3.650
$C(5)\ldots C(2)_{IV}$	3.670
$O(3)\ldots C(1)_{IV}$	3.679
$N\ldots O(4)_{II}$	3.680
$O(3)\ldots C\ell_{V}$	3.699
$O(3)\ldots C(5)_{II}$	3.728

- Cont'd -

TABLE 23.

(Cont'd)

The subscripts refer to the following positions:

I	$-x$, $-y$, $-z$	IV	x, $1+y$ z
II	$-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$	V	$1+x$, $1+y$ z
III	$-x$, $1-y$, $-z$	VI	$x-1$, y, z

Intramolecular non-bonded distances:

C(7)...Cℓ	3.173	O(3)...C(6)	2.715
O(1)...Cℓ	2.896	O(4)...C(4)	2.709
O(2)...C(6)	2.685	O(1)...C(2)	2.951

TABLE 24.

Standard deviations of the final atomic coordinates (Å).

	(x)	(y)	(z)
C(1)	0.0055	0.0076	0.0054
C(2)	0.0058	0.0079	0.0058
C(3)	0.0058	0.0082	0.0057
C(4)	0.0057	0.0078	0.0058
C(5)	0.0056	0.0080	0.0055
C(6)	0.0057	0.0078	0.0058
C(7)	0.0057	0.0073	0.0058
O(1)	0.0042	0.0055	0.0041
O(2)	0.0044	0.0054	0.0042
O(3)	0.0045	0.0056	0.0046
O(4)	0.0044	0.0053	0.0042
N	0.0049	0.0062	0.0049
Cl	0.0015	0.0022	0.0016

are listed in Table 24. The estimated standard deviations in bond length (in Å) obtained from these values are carbon-carbon = 0.009, carbon-oxygen = 0.008, carbon-nitrogen = 0.008, carbon-chlorine = 0.007 and nitrogen-oxygen = 0.007. The standard deviation in bond angle, calculated by Cruickshank and Robertson's (1953) method, is 0.8°.

4.8. Mean molecular plane calculations.

The best plane through the carbon, nitrogen, chlorine and oxygen atoms calculated by the method of Schomaker et al (1959) has equation

$$0.51574\ X' - 0.66874\ Y + 0.53554\ Z' + 0.13468 = 0.$$

The deviations of the atoms from this plane (Table 25) show that, as in o-chlorobenzoic acid, the molecule is clearly non-planar. The equation of the plane through the benzene ring carbon atoms was then calculated and found to be

$$0.50771\ X' - 0.68389\ Y + 0.52395\ Z' + 0.19423 = 0.$$

The small displacements of the benzene carbon atoms from this plane (Table 25) are not significant, their average value being 0.006 Å. The chlorine atom and the nitrogen atom deviations are similarly not significant. The

TABLE 25.

Deviations (Å) of the atoms from various planes.

(a) Plane through C(1)....C(7), O(1)....O(4), N, Cl.

(b) Plane through the benzene ring atoms C(1)....C(6).

(c) Plane through C(1)....C(7), N, Cl.

(d) Plane through C(1), C(7), O(1), O(2).

(e) Plane through C(5), N, O(3), O(4).

	(a)	(b)	(c)	(d)	(e)
C(1)	-0.025	0.005	-0.010	0.003	-
C(2)	-0.048	-0.006	-0.010	-	-
C(3)	-0.022	0.006	0.014	-	-
C(4)	-0.005	-0.006	0.004	-	-
C(5)	0.019	0.006	0.005	-	0.000
C(6)	-0.006	-0.005	-0.018	-	-
C(7)	0.007	0.051	0.022	-0.009	-
O(1)	0.424	0.492	0.460	0.004	-
O(2)	-0.407	-0.379	-0.416	0.003	-
O(3)	0.180	0.125	0.116	-	0.000
O(4)	-0.080	-0.136	-0.124	-	0.000
N	0.043	0.000	0.000	-	0.001
Cl	-0.080	-0.001	-0.007	-	-

displacement of the exocyclic carbon atom C(7) from the benzene plane is 0.051 Å, implying an out-of-plane bending of the exocyclic carbon-carbon bond of 2.0°. This displacement, although small, is several times greater than the standard deviation in positional parameter and would appear to be significant. A means of testing the significance of the C(7) deviation is by application of the χ^2 test (see Part I, 1.10) to the displacements of the chlorine, nitrogen and the seven carbon atoms from the best plane that can be fitted to them. This plane has equation

$$0.50083\, X' - 0.68361\, Y + 0.53090\, Z' + 0.14758 = 0$$

$$\sum \Delta^2 = 1.28 \times 10^{-3}\ \text{Å}^2$$

$$\text{and} \quad \chi^2 = \sum \Delta^2/\sigma^2 = 26$$

It is found from tables of χ^2(Fisher and Yates,1957) that this corresponds to a probability of less than one in one thousand that no atoms deviate significantly from the calculated plane, i.e. the chlorine, nitrogen and the seven carbon atoms cannot all be regarded as coplanar.

The atoms of the carboxyl group C(7), O(1) and O(2), and carbon atom C(1) of the benzene ring lie on the plane with equation

$$0.72169\,X' - 0.35446\,Y + 0.59458\,Z' + 0.09759 = 0$$

The angle between this plane and that of the aromatic ring is 23.0°. The plane through the atoms of the nitro group N, O(3) and O(4), and carbon atom C(5) of the benzene ring has equation

$$0.41333\,X' - 0.68278\,Y + 0.60247\,Z' - 0.35560 = 0.$$

The angle which this plane makes with the benzene ring is 7.0°.

The equation of the plane through the four oxygen atoms, O(1), O(2), O(1)' and O(2)', of an acid dimer and the centre of symmetry at the origin is required in the computation of Fourier syntheses in the oxygen atom plane. It was found to be

$$0.68048\,X' - 0.33614\,Y + 0.65113\,Z' = 0.$$

4.9. Location of hydrogen atoms.

On completion of the three-dimensional least-squares refinement, a further set of structure factors F_c' was calculated using the final coordinates and temperature factors listed in Tables 21 and 22, omitting the hydrogen atom contributions. Difference Fourier projections on (010) (Fig.22) and (100) (Fig.23) were computed using

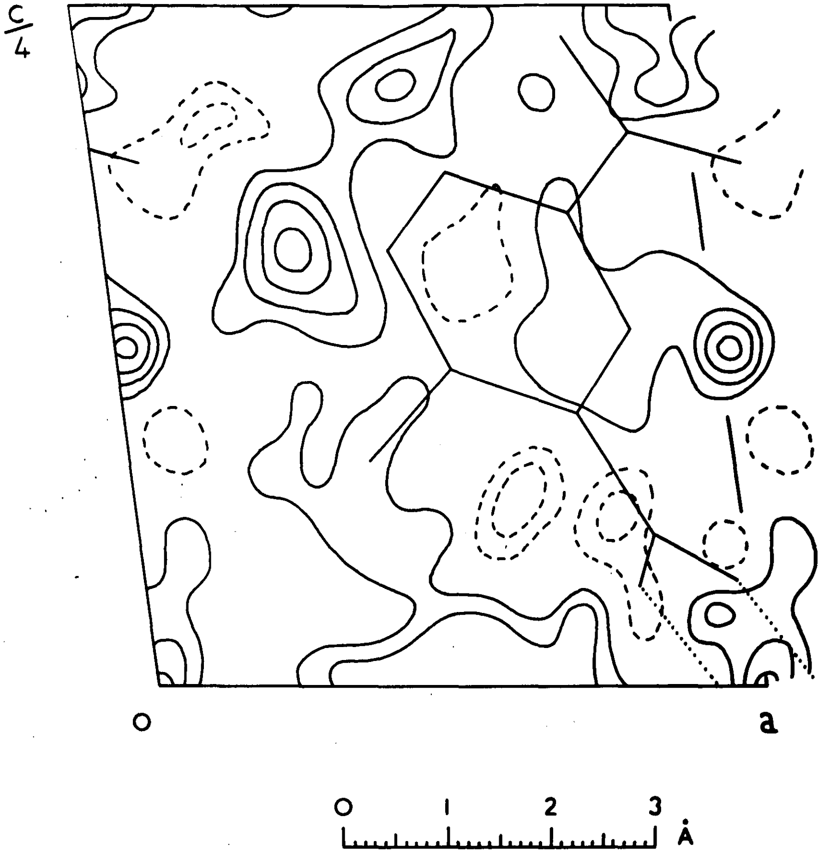


Fig.22. Difference electron-density projection on (010). Contour scale: 0.2 eÅ^{-2}, negative levels broken, zero contours omitted.

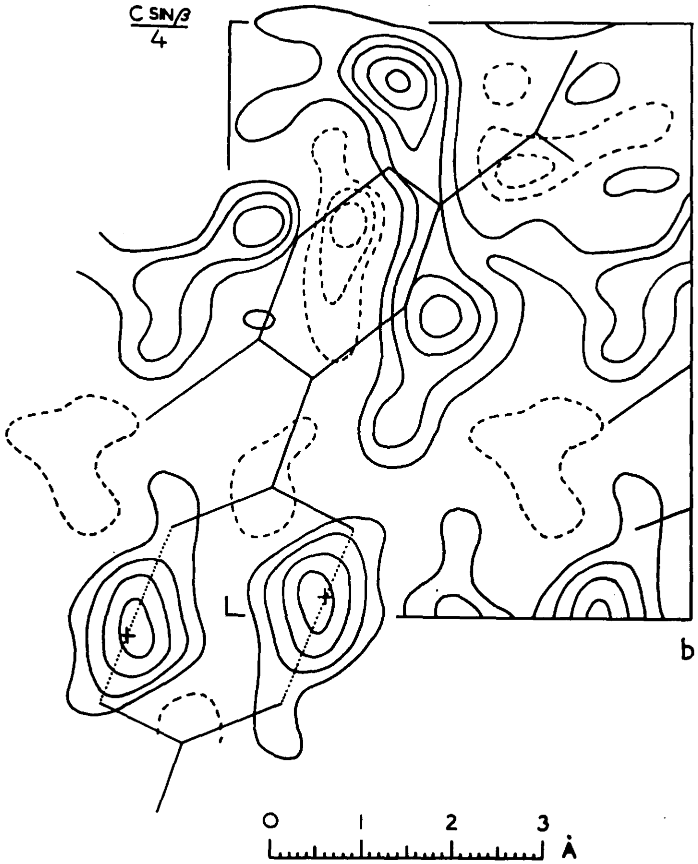


Fig. 23. Difference electron-density projection on (100). Contour scale: 0.2 eÅ^{-2}, negative levels broken, zero contour omitted.

$(F_o - F_c')$ as coefficients, the hydrogen atoms of the benzene ring being clearly visible in these projections. The carboxyl hydrogen atom responsible for the hydrogen bonding between dimers is found as a rather diffuse maximum in the projection on (010) but appears to be better resolved in the (100) projection.

Difference Fourier syntheses using $(F_o - F_c')$ as coefficients were also evaluated in the plane of the aromatic ring (Fig.24), and in the plane of the four oxygen atoms of an acid dimer (Fig.25). In Fig.24 the direction <u>d</u> is the line of intersection of the molecular plane and (010), and <u>e</u> is the direction of the line of intersection of the molecular plane and (100). The lengths of the lines <u>d</u> and <u>e</u> are

$$d = 9.427, \quad e = 9.344 \text{ Å}$$

and the angle between them is 131°12'. The corresponding values for the direction <u>f</u> and <u>g</u> in Fig.25 are

$$f = 9.914, \quad g = 6.008 \text{ Å}$$

the angle between them being 114°58'.

The data used in the Fourier calculations were limited to the planes with $\sin^2\theta < 0.400$ since the effective hydrogen atom contribution to planes with a higher value is small; this also minimises the effects of any errors in the thermal parameters.

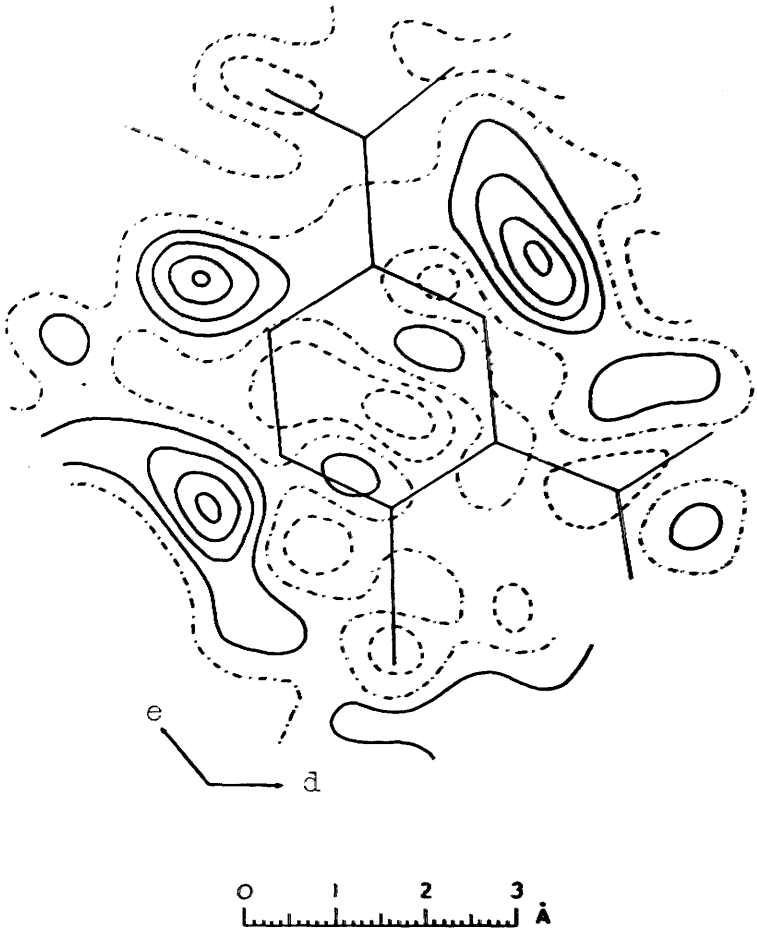


Fig.24. Section through the three-dimensional difference electron-density distribution evaluated in the plane of the benzene ring. Contour scale: 0.1 eÅ^{-3}, negative levels broken, zero contour dot-dashed.

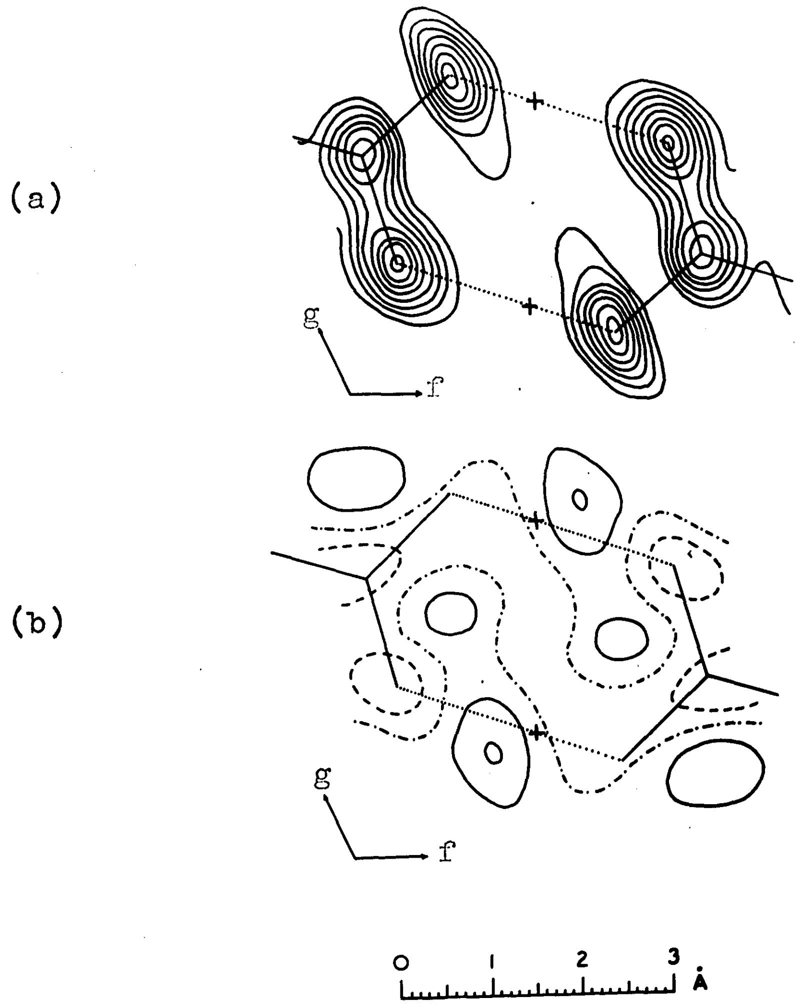


Fig.25. Sections through (a) the three-dimensional electron-density distribution and (b) the three-dimensional difference electron-density distribution evaluated in the plane containing the oxygen atoms of the carboxyl group and the origin of the unit cell. Contour scale (a) 1 eÅ^{-3}, (b) 0.1 eÅ^{-3}, negative levels broken, zero contour dot-dashed.

In Fig.24 the hydrogen atoms of the benzene ring are clearly revealed, the peak heights lying between 0.41 and 0.42 $e\text{Å}^{-3}$. The carbon-hydrogen bond lengths measured directly on this map are

$$C(3) - H = 0.98; \quad C(4) - H = 0.96;$$
$$C(6) - H = 0.88 \text{ Å},$$

the average value being 0.93 Å.

In Fig.25 a triple F_o synthesis in the plane of the oxygen atoms of the acid dimer is shown above the (F_o-F_c') synthesis in the same plane. The hydroxyl hydrogen atom is not nearly as well resolved in this difference synthesis as its benzene ring counterparts in Fig.24. The expected position on the dotted line joining O(2) and O(1)' is indicated by a cross at 1.0 Å from O(2). The maximum of 0.21 $e\text{Å}^{-3}$ situated midway between the oxygen atoms and to one side of the line joining them may be attributed to this hydrogen atom. A comparable lack of resolution was found with o-chlorobenzoic acid.

4.10. Discussion.

The Cl...O(1) (2.896 Å) and Cl...C(7) (3.173 Å) intramolecular separations are appreciably shorter than the sums of the appropriate van der Waal's radii, 3.20 and 3.80 Å respectively. The corresponding distances in o-chlorobenzoic acid are 2.892 and 3.217 Å.

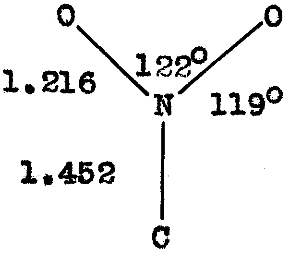
The displacements of the benzene carbon atoms from the plane of the aromatic ring are all about 0.006 Å and are not significant. The displacements of the chlorine and nitrogen atoms are similarly not significant. The displacement of the carboxyl carbon atom C(7) from the benzene plane is 0.051 Å which, being several times greater than the standard deviation in position (Table 24), would appear to be significant (see 4.8). This displacement implies a deflection of the exocyclic carbon-carbon bond of 2.0° from the plane of the benzene ring, a result of the same order of magnitude as that found in o-chlorobenzoic acid (2.2°).

The tilt of the carboxyl group plane to the benzene plane (23.0°) is appreciably greater than that found in o-chlorobenzoic acid (13.7°). This difference may arise from an intramolecular buttressing effect, or intermolecular crystal forces. In o-chlorobenzoic acid it is highly probable in view of the in-plane deflection of the exocyclic carbon-carbon bond that the hydrogen atom adjacent to the carboxyl group is also displaced away from its ideal radial position. In 2-chloro-5-nitrobenzoic acid the bulky nitro group in the 5 position will strictly curtail the in-plane splaying-out of the hydrogen atom at position 6, the resulting increased H...O(2) interaction causing the carboxyl oxygen atoms to be rotated further out of the benzene plane. Similar arguments can be advanced concerning the orientation of the nitro group in 2-chloro-5-nitrobenzoic acid. Nitrobenzene (Trotter, 1959) and p-nitroaniline (Donohue & Trueblood, 1956) are completely planar as would be expected, while on the other hand 2:4-dinitrochlorobenzene (Watson, 1960), m-dinitrobenzene (Trotter, 1961a) and 2-chloro-5-nitrobenzoic acid all have nitro groups adjacent to buttressed hydrogen atoms, the nitro groups being rotated 15°, 11° and 7° respectively out of the benzene planes. These considerations lead to the conclusion that it is intramolecular rather than intermolecular forces which are responsible for the rotation of the nitro group and the increased rotation of the carboxyl group in 2-chloro-5-nitrobenzoic acid as compared with o-chlorobenzoic acid.

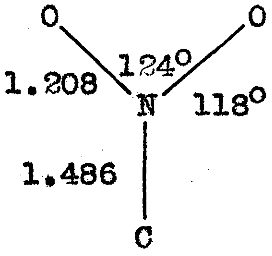
The in-plane displacements of the exocyclic carbon-carbon and carbon-chlorine bonds away from one another (Fig.19) are comparable to those in o-chlorobenzoic acid, the angle between the carbon-carbon and carbon-chlorine vectors being 67.4° (67.2° in o-chlorobenzoic acid).

The bond lengths and valency angles in the carboxyl group conform to the pattern usually found in unionised carboxylic acids. This is exemplified by the angle C-C-OH approaching the tetrahedral value while the angles C-C=O and O=C-OH exceed 120°. As in the case of o-chloro- and o-bromo-benzoic acids the carbon-oxygen bond lengths are indicative of the carboxyl hydrogen atom being bonded to O(2), the oxygen atom remote from the chlorine atom. As has been previously explained (2.10) this allows sufficient clearance between the halogen atom and neighbouring oxygen atom for a smaller tilt than would be required if the opposite conformation were adopted.

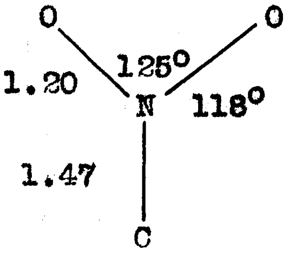
The dimensions of the nitro group do not differ significantly from those reported for nitrobenzene or m-dinitrobenzene.



2-chloro-5-nitro-benzoic acid



nitrobenzene (Trotter,1959)



m-dinitrobenzene (Trotter,1961a)

The pattern of the valency angles (O-N-O exceeding 120° and C-N-O less than 120°) can be attributed to electronic repulsion involving the lone pairs of electrons on oxygen atoms in the sp^2 state of hybridisation, these electrons being situated in the plane of the nitro group. The angular variations found in the carboxyl group can similarly be explained.

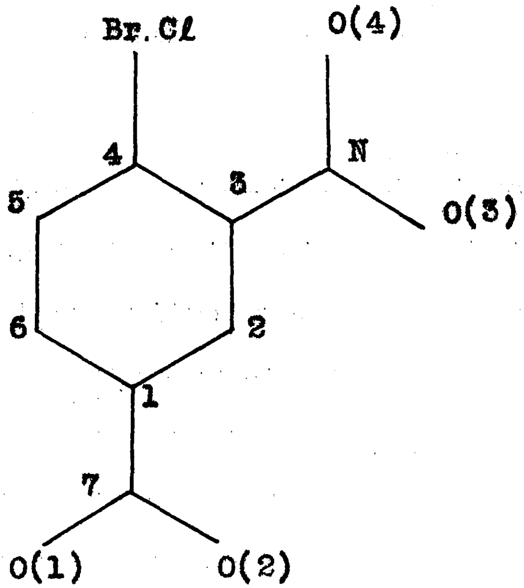
The mean carbon-carbon distance in the aromatic ring is 1.376 Å, which is not significantly different from the mean distance of 1.385 Å in o-chlorobenzoic acid. The carbon-chlorine bond length (1.753 Å) is not significantly longer than that found in o-chlorobenzoic acid (1.737 Å).

5. 4-Chloro-3-nitrobenzoic acid and 4-Bromo-3-nitrobenzoic acid.

The molecules of 4-chloro-3-nitrobenzoic acid and 2-chloro-5-nitrobenzoic acid are related in that only the carboxyl and nitro groups have been interchanged. It was to find the effect of this interchange on the molecular geometry that the analysis of 4-chloro-3-nitrobenzoic acid was undertaken.

At a later date crystals of 4-bromo-3-nitrobenzoic acid were obtained and found to be isomorphous with the 4-chloro-acid. This was put to good use in solving the 4-chloro-acid structure which had been resisting attempts at solution by Patterson and trial-and-error methods. In addition the effect on the stereochemistry of the molecule of replacing a chlorine atom by the bulkier bromine atom could be investigated for comparison with o-chloro- and o-bromo-benzoic acids.

In the calculations involved in the analysis the atoms were numbered as follows:-



5.1. Experimental details:

Crystals of 4-chloro-3-nitrobenzoic acid (43CNBA) and 4-bromo-3-nitrobenzoic acid (43BNBA) suitable for X-ray investigation, obtained by recrystallising the crude commercially available material from alcohol-ether mixtures, are monoclinic laths normally elongated along the <u>b</u> crystal axis, although occasionally along <u>a</u>. The unit-cell dimensions and space group were determined from oscillation and rotation photographs of crystals rotating about the <u>a</u> and <u>b</u> crystal axes, and the $0kl$, $h0l$, $h1l$, $h2l$ and $h3l$ Weissenberg films.

5.2. Crystal data.

	43CNBA	43BNBA
Cell dimension	a = 7.41 ± 0.02 Å	a = 7.48 ± 0.02 Å
	b = 5.70 ± 0.02	b = 5.82 ± 0.02
	c =19.12 ± 0.04	c =19.27 ± 0.04
	β = 100°30' ± 20'	β = 103°3' ± 20'
Unit-cell volume	U = 794 $Å^3$	U = 817 $Å^3$
D_m	1.687	1.990
Z	4	4
D_x	1.686	1.999
Absorption coefficient for X-rays, λ = 1.542 Å	μ = 42.0 $cm.^{-1}$	μ = 70.1 $cm.^{-1}$

Absent spectra:- $h0\ell$ when ℓ is odd and $0k0$ when k is odd. The space group is therefore determined uniquely as $P2_1/c$ (C^5_{2h}).

5.3. Intensity data.

For both acids, the $h0\ell$, $h1\ell$, $h2\ell$ and $h3\ell$ intensities were collected using the multiple-film equi-inclination Weissenberg technique with copper Kα radiation. At the present stage of the analyses only the $h0\ell$ and $h3\ell$ data have been utilised. The intensities were estimated visually and no absorption corrections have been applied. The structure amplitudes were derived by the usual mosaic crystal formula, the absolute scale being established later by comparison with the calculated structure factors.

5.4. 4-Bromo-3-nitrobenzoic acid.

(i) The (010) projection.

The Patterson projection on (010) was computed using the 169 $h0\ell$ terms and is shown in Fig.26. The large peak on this map at a general position corresponds to a bromine-bromine vector between the bromine atoms of an acid dimer. The x and z coordinates of the bromine atom were then deduced to be approximately (0.380, 0.181). The next step was to calculate structure factors on the basis of the bromine atom alone using a temperature factor $B = 4.0 \overset{o}{A}{}^2$ with the bromine scattering curve of Thomas and Fermi (Internationale Tabellen, Vol.II, 1935). The value of the residual R was 0.40. The signs of the bromine atom contributions were then taken with the observed structure amplitudes in evaluating the Fourier projection on (010), in which the positions of the remaining atoms (other than hydrogens) could be clearly distinguished.

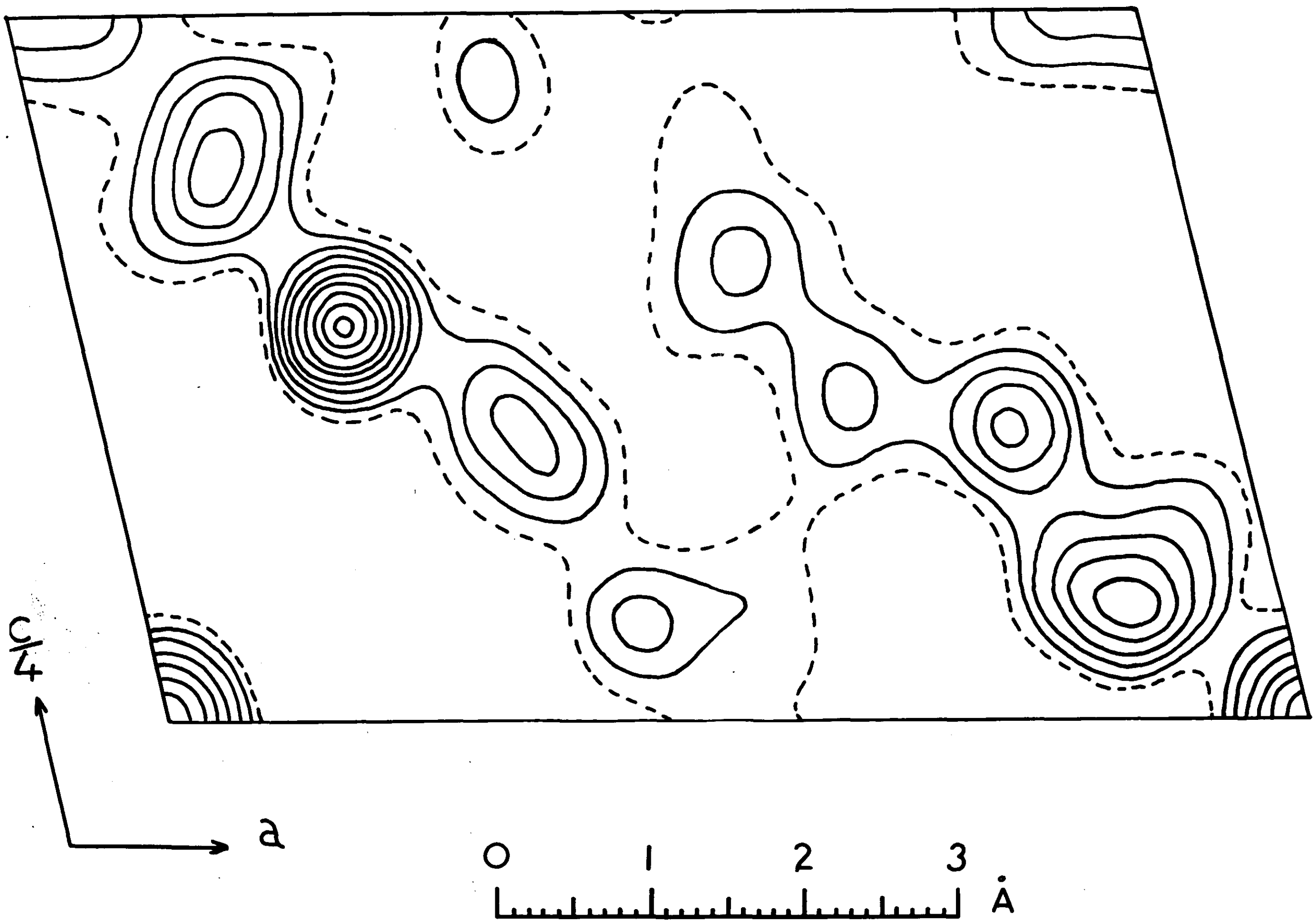


Fig. 26. Patterson projection on (010). Contours at equal arbitrary intervals except around the origin peak.

In this way coordinates for the carbon, nitrogen and oxygen atoms were obtained and those for the bromine atom improved.

In the next structure-factor calculation the scattering curves of Berghuis et al (1955) for carbon, nitrogen and oxygen were used, an isotropic temperature factor B = 4.0 Å^2 was assigned to all the atoms and R fell to 0.29. A further F_o Fourier synthesis was computed, followed by an F_c synthesis which was used to determine back-shift corrections to allow for the effect of termination of series on the Fourier summations, and a new improved set of coordinates was obtained. In the ensuing structure-factor calculation R was 0.21.

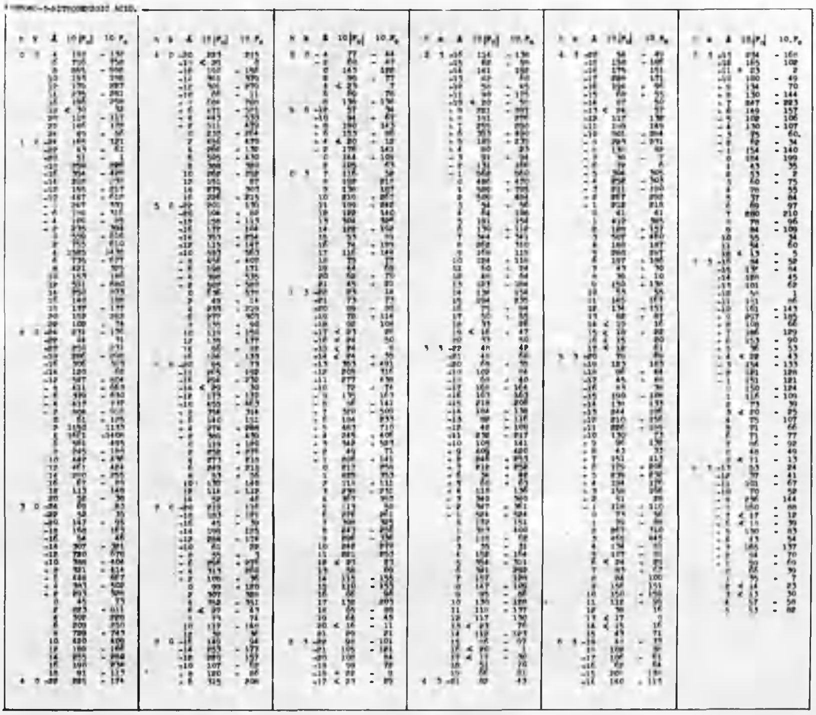
(ii) Determination of y-coordinates and partial three-dimensional refinement.

From considerations of known bond lengths, y-coordinates for the bromine and carbon atoms were deduced in a manner completely analogous to that described for o-bromobenzoic acid (see 3.5), with the advantage that this time there was no ambiguity about molecular centres to complicate the calculation. Using the x and z coordinates from the (010) projection and the calculated y-coordinates, the $h3\ell$ structure factors were calculated on the basis of bromine and carbon atom contributions only. An overall isotropic temperature factor $B = 4.0\ \mathring{A}^2$ was employed and R was 0.42.

Using only the $h3\ell$ data, Fourier line syntheses parallel to the y-direction were computed through the known x and z positions of the atoms. From these, y-coordinates of nitrogen and oxygen atoms were obtained and those of the bromine and carbon atoms improved. In the second $h3\ell$ structure-factor calculation R was 0.28. Two further rounds of refinement by Fourier methods using both F_o and F_c syntheses were completed using the $h0\ell$ and $h3\ell$ data. No attempts were made to refine the temperature parameters and hydrogen atom contributions were neglected. The present values of R are 0.185 for the $h0\ell$ and 0.216 for the $h3\ell$ sets of data. The values of the calculated structure factors at this point are listed in Table 26a along with the observed structure amplitudes, scaled so that $\sum k|F_o| = \sum |F_c|$ for each set of data. The unobserved terms have been included in the list at half the minimum value of $|F_o|$ locally observable.

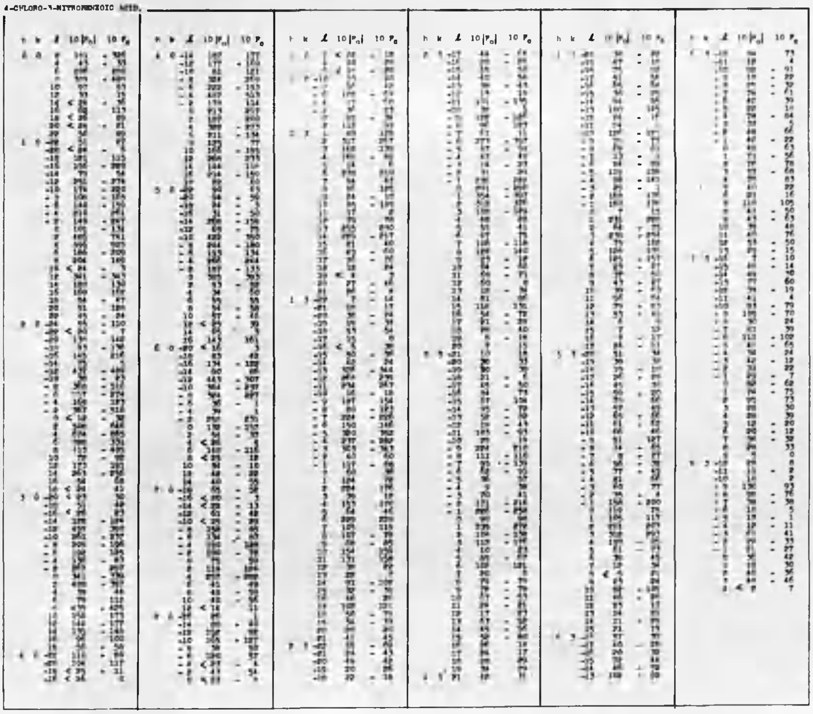
Table 26: Measured and calculated values of the structure factors.

(a)



(b)

4-CHLORO-3-NITROBENZOIC ACID.



(iii) Coordinates and molecular dimensions.

The present atomic coordinates expressed as fractions of the monoclinic cell edges are listed in Table 27. In Fig.27 the bond lengths and valency angles calculated from these coordinates are shown. Since this analysis has still to be completed the lengths and angles in Fig.27 are necessarily of qualitative rather than quantitative significance. No standard deviations have been calculated.

(iv) Mean molecular plane calculations.

The best plane through the carbon atoms of the benzene ring (C(1)...C(6)), found by the method of Schomaker *et al* (1959), has equation

$$-0.06317\ X' - 0.63617\ Y + 0.76896\ Z' + 0.00824 = 0$$

while the best plane through the atoms of the nitro group O(3), O(4) and N, and C(3) has equation

$$0.63849\ X' - 0.67955\ Y + 0.36136\ Z' + 3.34306 = 0$$

The equation of the plane through the atoms of the carboxyl group C(7), O(1) and O(2), and carbon atom C(1) of the benzene ring is

$$0.04063\ X' - 0.53947\ Y + 0.84102\ Z' - 0.01611 = 0$$

TABLE 27.

Interim atomic coordinates.

Coordinates x, y and z are referred to the monoclinic crystal axes and are expressed as fractions of the axial lengths, with origin at the centre of symmetry. Coordinates X', Y and Z' are referred to orthogonal axes a, b and c', c' being taken perpendicular to the a and b crystal axes, and are expressed in Å units.

Atom	x	y	z	X'	Y	Z'
C(1)	-0.263	0.371	0.080	-2.31	2.16	1.51
C(2)	-0.168	0.533	0.129	-1.82	3.10	2.42
C(3)	-0.278	0.671	0.160	-2.78	3.90	3.01
C(4)	-0.468	0.644	0.147	-4.14	3.75	2.75
C(5)	-0.550	0.485	0.101	-4.55	2.83	1.89
C(6)	-0.447	0.325	0.072	-3.66	1.89	1.36
C(7)	-0.140	0.206	0.047	-1.26	1.20	0.89
N	-0.183	0.844	0.215	-2.31	4.91	4.03
O(1)	-0.221	0.033	0.011	-1.70	0.19	0.21
O(2)	0.028	0.256	0.051	-0.01	1.49	0.96
O(3)	-0.061	0.967	0.194	-1.30	5.63	3.64
O(4)	-0.220	0.852	0.270	-2.82	4.96	5.06
Br	-0.619	0.869	0.181	-5.41	5.06	3.39

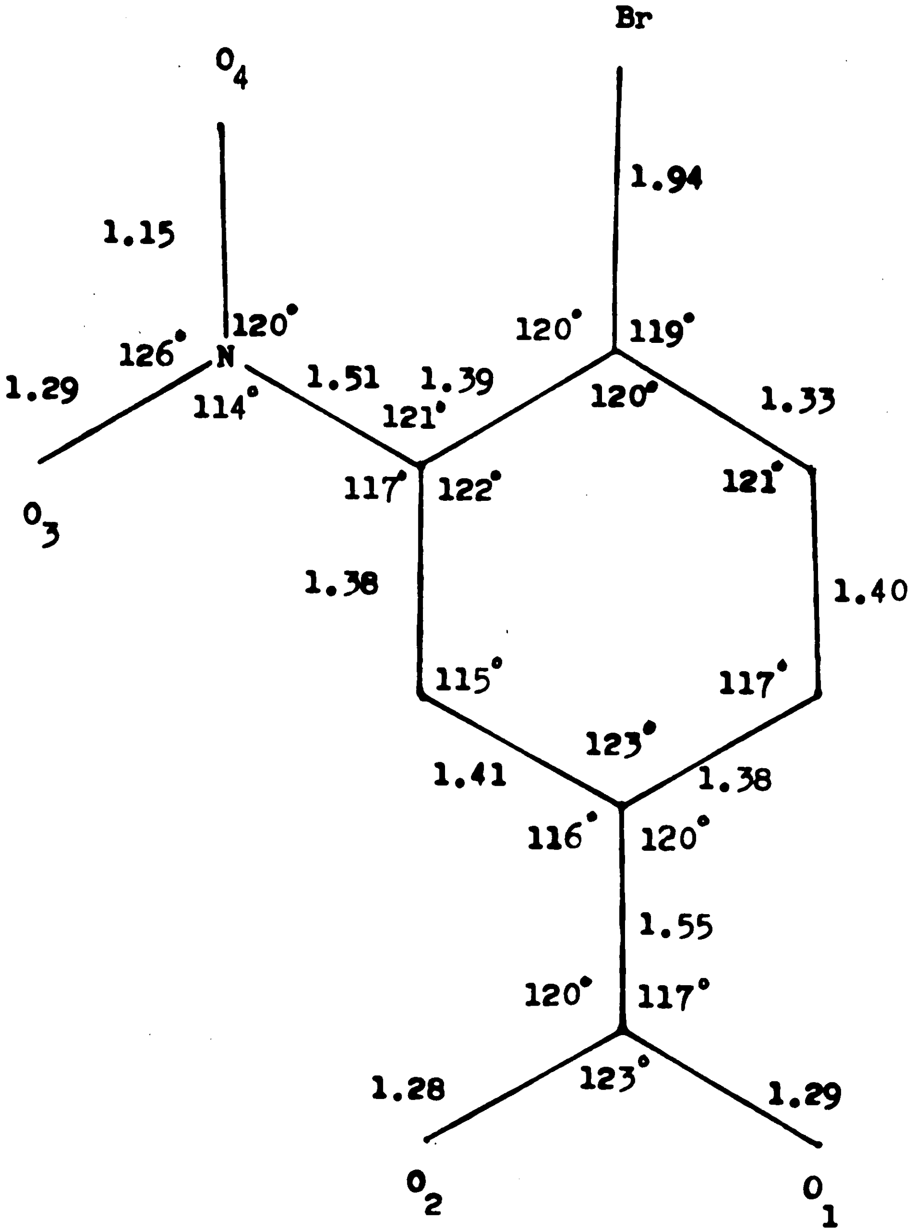


Fig.27. Bond lengths and valency angles in 4-bromo-3-nitrobenzoic acid.

TABLE 28.

Deviations (Å) of the atoms from the various planes.

(a) Plane through the benzene ring atoms C(1)....C(6).

(b) Plane through C(3), N, O(3), O(4).

(c) Plane through C(1), C(7), O(1), O(2).

	(a)	(b)	(c)
C(1)	-0.061	-	-0.009
C(2)	0.013	-	-
C(3)	0.016	0.003	-
C(4)	0.003	-	-
C(5)	-0.050	-	-
C(6)	0.078	-	-
C(7)	0.006	-	0.031
N	0.128	-0.011	-
O(1)	0.156	-	-0.011
O(2)	-0.199	-	-0.011
O(3)	-0.688	0.004	-
O(4)	0.922	0.004	-
Br	-0.260	-	-

The deviations of the atoms from these planes are listed in Table 28.

The plane of the nitro group and C(3) makes an angle of 48.9° with that of the benzene ring, while the tilt of the plane through the carboxyl group and C(1) to the aromatic ring is 9.1°.

5.5. 4-Chloro-3-nitrobenzoic acid.

(i) The (010) projection.

Before the structural analysis of 4-bromo-3-nitrobenzoic acid had been initiated, many fruitless attempts were made at solving the structure of 4-chloro-3-nitrobenzoic acid by means of a systematic study of the peaks in the Patterson projection on (010) (Fig.28). The data used in the Patterson summation were "sharpened" by multiplying each $|F_o|^2$ term by the Lorentz and polarisation factor appropriate to that plane. This proved to be the best of several sharpening functions used on this projection.

Each of the larger peaks in Fig.28 was considered in turn, assuming that it was the chlorine-chlorine vector. On this basis, numerous trial structures involving the chlorine atom and carbon atoms C(1),

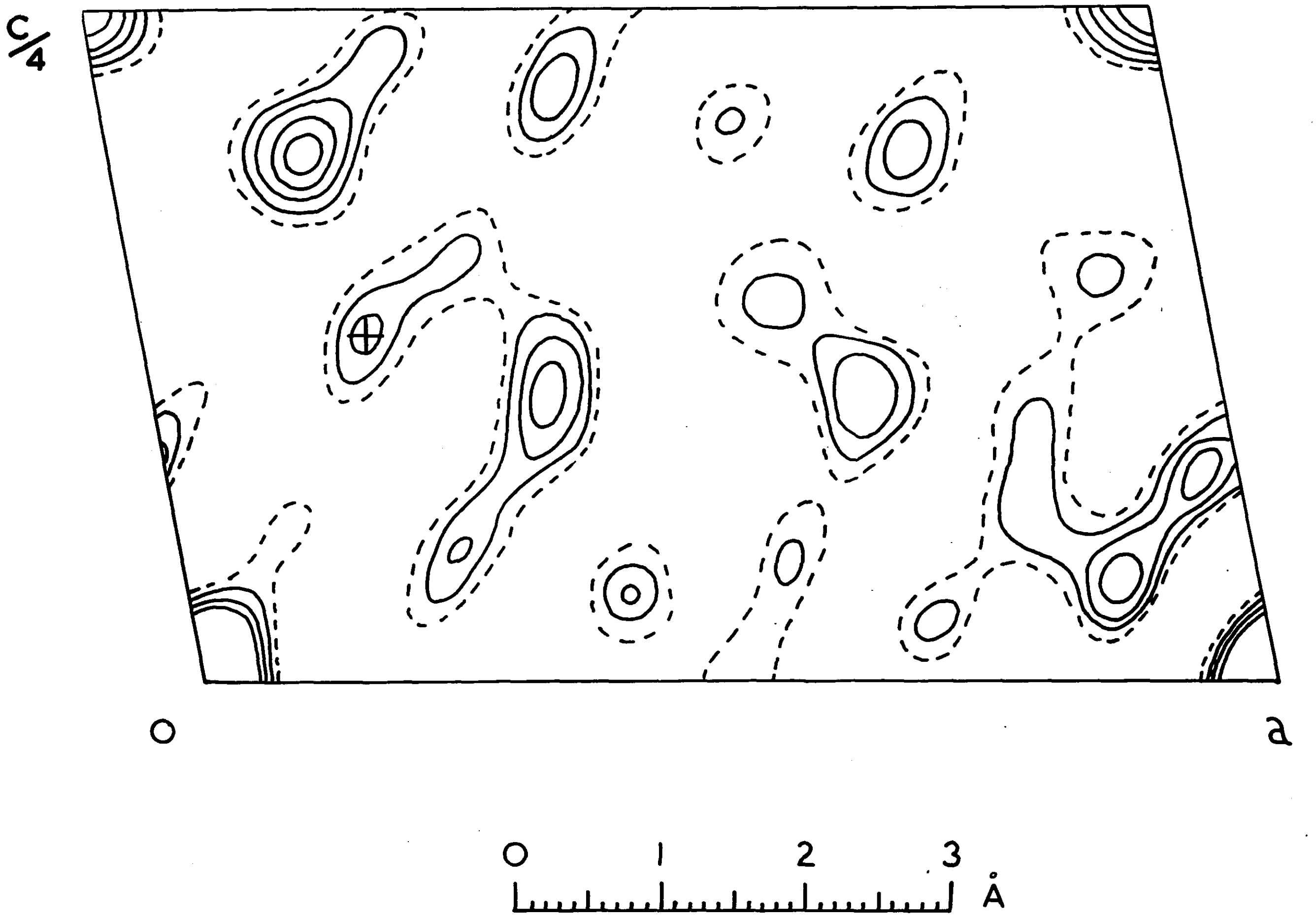


Fig. 28. Patterson projection on (010). Contours at equal arbitrary intervals; origin peak contours omitted. The chlorine-chlorine vector is marked by a cross.

C(4) and C(7) were investigated. In no case did the value of the residual in the structure factor calculations fall below 0.70.

It was during this period of trial structure-factor calculations that work began on 4-bromo-3-nitrobenzoic acid which proved to be isomorphous with the 4-chloro-acid. As has been described previously (5.4.(i)) the bromine-bromine vector was quickly located on the 4-bromo-3-nitrobenzoic acid Patterson projection on (010), which in turn indicated the correct choice of peak for the chlorine-chlorine vector in the 4-chloro-acid Patterson projection on (010). This is shown in Fig.28 by a cross. The correct peak is the ninth largest on the vector map.

Coordinates for the chlorine, carbon, nitrogen and oxygen atoms were then derived and structure factors calculated. A temperature factor $B = 4.0\ \mathring{A}^2$ was assigned to all the atoms (no allowances were made at any stage for hydrogens); for the chlorine atom, the scattering curve of Tomiie and Stam (1958) was used and for the remaining atoms the curves of Berghuis et al (1955) were chosen. The residual R, in the structure factor calculation, had the encouraging value of 0.40. The electron-density projection on (010) was then computed,

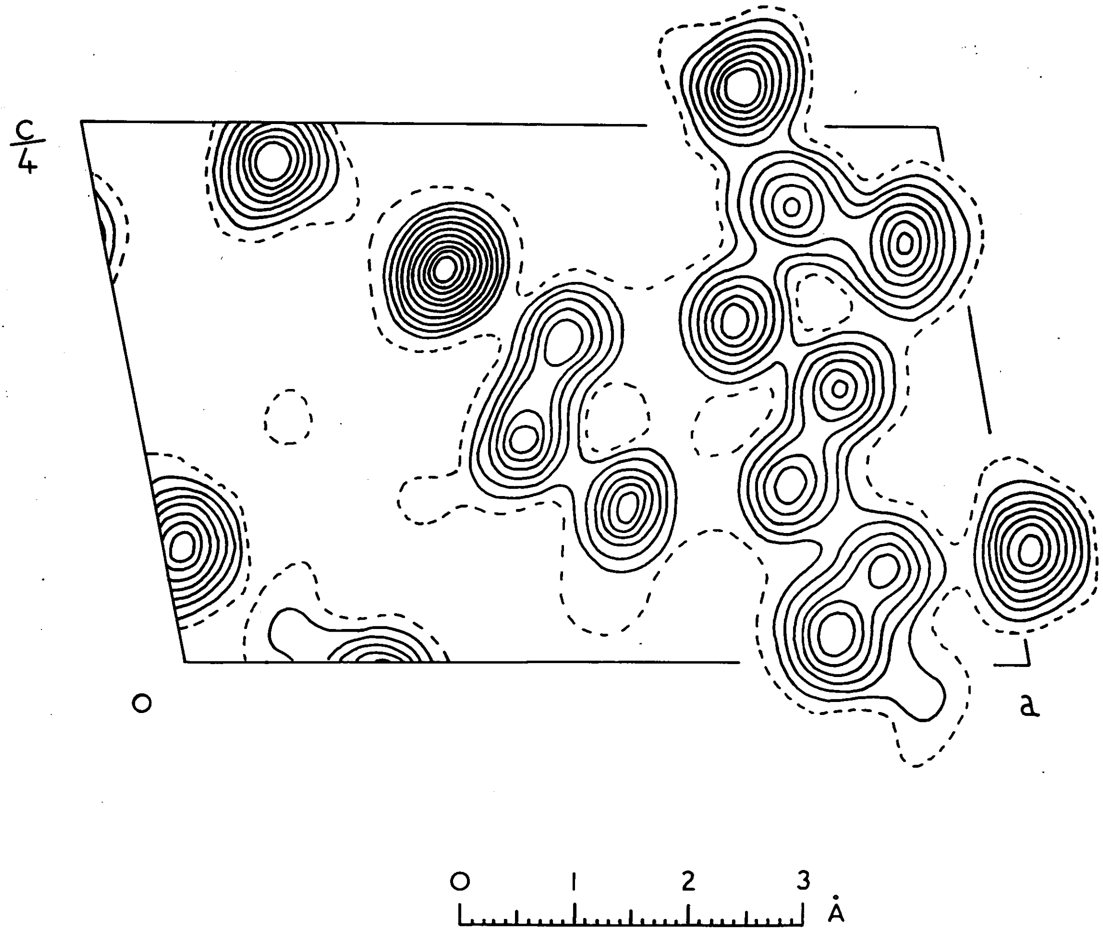


Fig.29. Electron-density projection on (010). Contours at intervals of 1 eÅ^{-2}, except around the chlorine atom (2 eÅ^{-2}). The one-electron contour is broken.

new atomic centres chosen and structure factors recalculated, R falling to 0.29. No more work on the projection alone was done as three-dimensional Fourier syntheses were contemplated. The final electron-density projection on (010) is shown in Fig.29.

(ii) Partial three-dimensional refinement.

The y-coordinates obtained from the 4-bromo-3-nitrobenzoic acid Fourier syntheses were used with the x and z coordinates from the (010) projection in calculating structure factors for the h3ℓ reflexion data. An isotropic temperature parameter B = 4.0 $\mathring{A}^2$ was assumed for all the atoms, the resulting value of R being 0.37. The atomic coordinates were improved by computing F_o and F_c Fourier syntheses in the region of the atomic centres using the h0ℓ and h3ℓ data, in a manner similar to that described for 4-bromo-3-nitrobenzoic acid. After two rounds of structure-factor and Fourier calculations, R was 0.240 for the h0ℓ and 0.224 for the h3ℓ data. The present interim calculated values of the structure factors are shown in Table 26b, along with the scaled observed structure amplitudes; planes too weak to be observed have been included at half the minimum value locally observable.

(iii) Coordinates and molecular dimensions.

The positional parameters of the atoms at the present stage of the analysis are listed in Table 29. The equation of three mean molecular planes were evaluated by the method of Schomaker et al (1959).

That of the benzene ring carbon atoms C(1)...C(6) :

$$-0.06226\,X' - 0.60416\,Y + 0.79443\,Z' + 0.16624 = 0.$$

Carbon atom C(3) and the nitro group N, O(3) and O(4):

$$0.58689\,X' - 0.71597\,Y + 0.37811\,Z' + 3.20739 = 0.$$

Carbon atom C(1) and the carboxyl group C(7), O(1) and O(2):

$$0.06235\,X' - 0.57907\,Y + 0.81288\,Z' + 0.04271 = 0.$$

The angle of tilt for the nitro group plane to the benzene plane is 45.8°; for the carboxyl group plane to the benzene plane the angle becomes 7.4°. The deviation of the atoms from these planes are listed in Table 30.

The bond lengths and valency angles, calculated from the coordinates of Table 29 are shown in Fig.30. As was the case with the 4-bromo-acid the values are of qualitative rather than quantitative significance.

TABLE 29.

Interim atomic coordinates.

Coordinates x, y and z are referred to the monoclinic crystal axes and are expressed as fractions of the axial lengths, with origin at the centre of symmetry. Coordinates X', Y and Z' are referred to orthogonal axes a, b and c', c' being taken perpendicular to the a and b crystal axes, and are expressed in Å units.

Atom	x	y	z	X'	Y	Z'
C(1)	-0.251	0.360	0.084	-2.16	2.05	1.58
C(2)	-0.166	0.541	0.130	-1.68	3.09	2.44
C(3)	-0.279	0.692	0.160	-2.61	3.94	3.01
C(4)	-0.469	0.670	0.148	-4.00	3.82	2.78
C(5)	-0.553	0.490	0.106	-4.47	2.79	2.00
C(6)	-0.447	0.327	0.072	-3.57	1.86	1.35
C(7)	-0.140	0.212	0.047	-1.20	1.21	0.88
N	-0.179	0.851	0.215	-2.08	4.85	4.05
O(1)	-0.219	0.034	0.012	-1.66	0.19	0.22
O(2)	0.027	0.251	0.052	0.01	1.43	0.97
O(3)	-0.052	0.973	0.193	-1.06	5.55	3.63
O(4)	-0.228	0.882	0.271	-2.64	5.03	5.09
Cl	-0.599	0.876	0.182	-5.08	4.99	3.43

TABLE 30.

Deviations (Å) of the atoms from the various planes.

(a) Plane through the benzene ring atoms C(1)....C(6).

(b) Plane through C(3), N, O(3), O(4).

(c) Plane through C(1), C(7), O(1), O(2).

	(a)	(b)	(c)
C(1)	-0.015	-	0.005
C(2)	0.011	-	-
C(3)	0.004	-0.012	-
C(4)	-0.015	-	-
C(5)	0.011	-	-
C(6)	0.004	-	-
C(7)	-0.123	-	-0.018
N	0.248	0.042	-
O(1)	-0.005	-	0.006
O(2)	-0.258	-	0.007
O(3)	-0.566	-0.014	-
O(4)	1.002	-0.016	-
Cl	-0.145	-	-

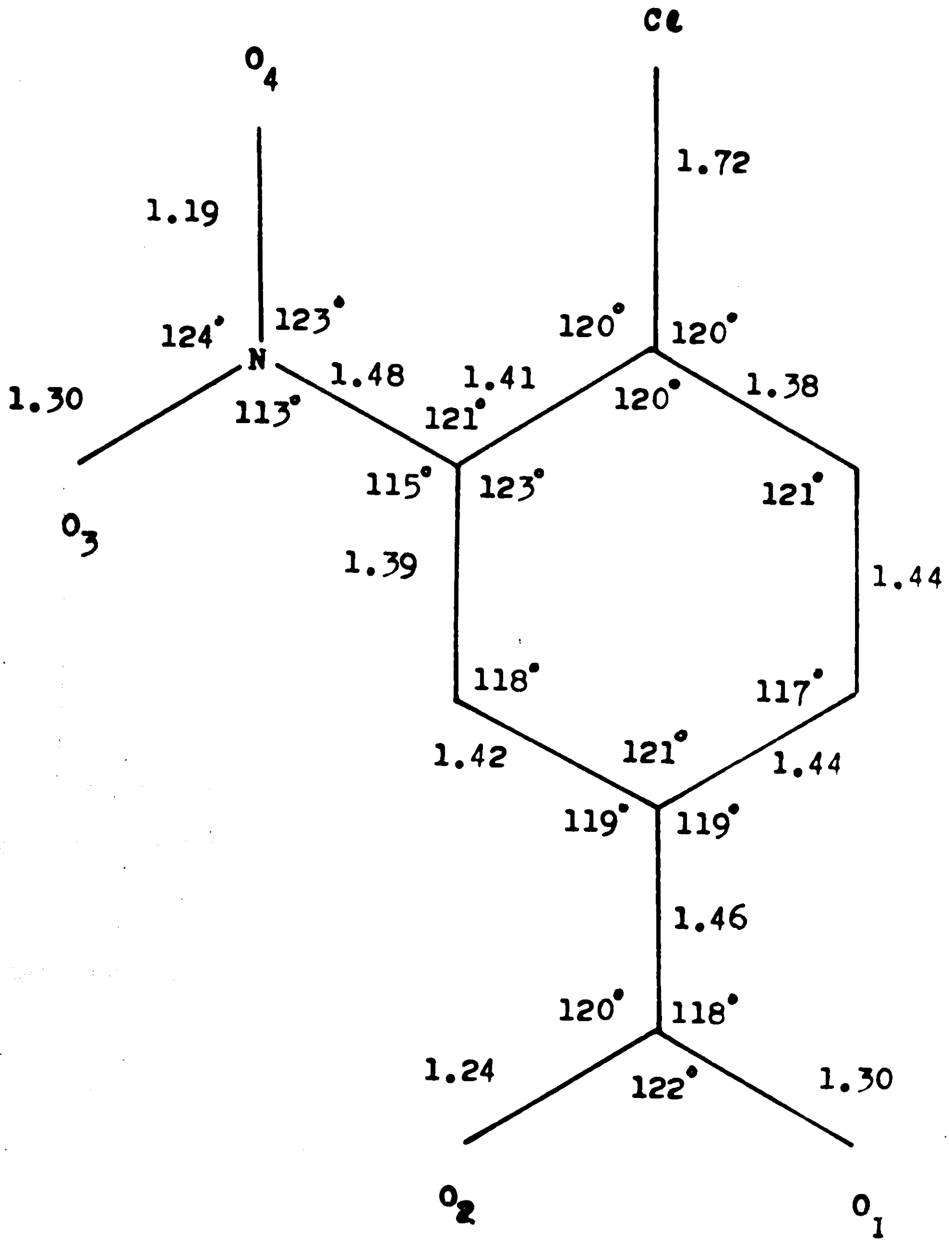


Fig.30. Bond lengths and valency angles in 4-chloro-3-nitrobenzoic acid.

5.6. Discussion.

No great accuracy can be claimed for the results obtained with the limited number of data utilised at the present stage of the analyses. The bond lengths and valency angles shown in Fig.27 and 30 are sufficient to confirm the correctness of the structures, detailed discussion of the bond lengths and angles must await further refinement.

The deviations of the benzene ring carbon atoms from the plane of the aromatic ring vary from -0.06 Å to +0.08 Å (Table 27) in the 4-bromo-acid and from -0.02 Å to +0.01 Å (Table 29) in the 4-chloro-acid, and must be considered insignificant at present. One feature which will be of some interest, if confirmed by further refinement, is the apparently large deviations of the halogen atoms from their respective benzene planes: Br = -0.26 Å, Cℓ = -0.15 Å. These deviations are considerably greater than the corresponding displacements found in o-bromo- and o-chloro-benzoic acids (0.064 Å and 0.036 Å respectively).

The Br...O(4) (3.09 Å) and Cℓ...O(4) (2.95 Å) intramolecular separations are in agreement with the Br...O(1) separation in o-bromobenzoic acid (3.004 Å) and the Cℓ...O(1) separations in o-chlorobenzoic acid

(2.892 Å) and 2-chloro-5-nitrobenzoic acid (2.896 Å) all of which are less than the sums of the appropriate van der Waal's radii. The Br...N(3.17 Å) and Cl...N (3.06 Å) intramolecular contacts are also appreciably shorter than the sums of the respective van der Waal's radii (3.45 Å and 3.30 Å), consequently the molecules, if planar, would be under considerably steric strain. With the accuracy attained at present, only the rotations of the nitro and carboxyl groups, about their respective exocyclic valency bonds with respect to the benzene rings, may be considered as being definitely significant in relieving imposed steric strain.

The unsubstituted aromatic acids, benzoic acid (Sim, 1955) and 2-naphthoic acid (Trotter, 1961b) are planar in the solid state as would be expected. The fact that in 4-bromo-3-nitrobenzoic acid and 4-chloro-3-nitrobenzoic acid, the carboxyl groups are rotated about the exocyclic carbon-carbon bonds can be explained by invoking an identical buttressing effect as was used to explain the tilt of the nitro group in 2-chloro-5-nitrobenzoic acid. The much larger inclination of the nitro group planes to the aromatic rings in 4-bromo-3-nitrobenzoic acid (48.9°) and 4-chloro-3-nitrobenzoic acid (45.8°) over a carboxyl group in a comparable situation in 2-chloro-5-nitrobenzoic acid (23.0°), is of some interest. To clarify this situation, and to confirm if this effect is genuine, the crystal structures of o-bromonitrobenzene and o-chloronitrobenzene are being investigated by Asher and Sim (1961) and should provide interesting information, since they bear the same relationship to 4-bromo- and 4-chloro-3-nitrobenzoic acids as o-chlorobenzoic acid does to 2-chloro-5-nitrobenzoic acid.

6. Final Discussion.

It is well known that crystal forces can be important in conformation effects; diphenyl, for example, is centrosymmetrical and hence planar in the solid state (Dhar,1932; Hargreaves et al, (1961), while in the gas-phase, electron-diffraction studies (Karle and Brockway, 1944; Bastiansen, 1949) indicate that the two rings are inclined at about 45° to one another . A similar discrepancy exists between X-ray crystallographic and electron-diffraction results in polyhalogenobenzenes. In the carboxylic acids described in this thesis, it is likely that the deviations from planarity which are found arise from intramolecular, rather than intermolecular or crystal, forces. This can be inferred from the fact that the unsubstituted parent molecules, benzoic acid and nitrobenzene, are, as would be expected, planar in the solid state.

One of the interesting features which emerges from the analyses of o-chloro- and o-bromo-benzoic acids and of 2-chloro-5-nitrobenzoic acid is that small but significant deviations of the carboxyl carbon atoms (0.058, 0.057 and 0.051 Å respectively) from the benzene planes do occur. These displacements correspond to significant out-of-plane bending of the exocyclic carbon-carbon bonds through approximately 2°. Out-of-plane deviations of the carbon-halogen bonds are also found in o-chlorobenzoic acid (1.2°) and in o-bromobenzoic acid (1.9°). However, no significant out-of-plane deviation of the carbon-chlorine bond was found for 2-chloro-5-nitrobenzoic acid.

In addition to out-of-plane bending, significant in-plane splaying-out of the exocyclic valency bonds has been found in the acids investigated. Thus the angle between exocyclic carbon-carbon and carbon-halogen vectors is increased beyond the value of 60° appropriate to a regular planar model to 67.4° in o-chlorobenzoic acid, to 68.3° in o-bromobenzoic acid and to 67.2° in 2-chloro-5-nitrobenzoic acid. In o-phthalic acid (Nowacki and Jaggi, 1957), the angle between exocyclic carbon-carbon vectors is 65.4°; in ammonium acid phthalate (Okaya and Pepinsky, 1957) the corresponding angle is 65°. No reliable figures can be quoted for the angles between carbon-nitrogen and carbon-halogen vectors in 4-chloro- and 4-bromo-3-nitrobenzoic acids as full three-dimensional refinement has still to be completed.

The angles, through which the carboxyl and nitro groups are rotated with respect to the appropriate aromatic ring planes, follow a regular understandable pattern. The angle of tilt of the carboxyl group in o-bromobenzoic acid (18.3°) is larger than that found in o-chlorobenzoic acid (13.7°) while in 2-chloro-5-nitrobenzoic acid the corresponding angle is 23.0°. The increase in inclination angle of 9.3° in 2-chloro-5-nitrobenzoic acid over that found in o-chlorobenzoic acid has been attributed to the buttressing effect of the nitro group which as a direct consequence is also inclined (7°) to the benzene plane; the carbon-nitrogen bond lies in the aromatic plane, only the oxygen atoms being displaced from it. A similar buttressing effect is almost certainly present in 4-chloro- and 4-bromo-3-nitrobenzoic acids, where the tilts of the nitro groups to the benzene rings are 46° and 49° respectively, with much smaller rotations (7° and 9°) of the corresponding carboxyl groups. It will be interesting to find what deviations occur in o-chloro- and o-bromo-nitrobenzene which are at present being investigated (Asher and Sim, 1961).

The refinement of o-phthalic acid by Nowacki and Jaggi was limited to two rounds of structure-factor and Fourier calculations; no mean molecular plane equations are given in their paper. These have accordingly been calculated using the method of Schomaker _et al_, with

Nowacki and Jaggi's coordinates suitably transformed so that they relate to one molecule. From the equation of the benzene plane and that of a carboxyl group it was deduced that the carboxyl groups are rotated through 33° about the exocyclic carbon-carbon bonds. In ammonium acid phthalate, on the other hand, the angles between the plane of the benzene ring and those of the carboxyl groups are 21° and 65°.

In mellitic acid (benzene hexacarboxylic acid) (Darlow, 1961), two crystallographically independent molecules are found in the asymmetric crystal unit. Of the eight independent carboxyl groups, four lie on diads and four have no symmetry restraints upon them. The angles which the carboxyl group planes make with the respective benzene rings range from 25.7° to 80.7°, and constitute the main difference between the two molecules. The value of the inclination angle, averaged over both molecules, is 52°.

The bond lengths found in the carboxyl groups of o-chlorobenzoic acid, o-bromobenzoic acid and 2-chloro-5-nitrobenzoic acid are compared with the values found for some other acids in Table 31. In each molecule the differences in lengths of the carbon-oxygen bonds serve to indicate to which oxygen atom the hydrogen atom

TABLE 31.

Comparison of some carboxyl group bond lengths.

Acid	C—C	C—O	C=O	mean C—O
o-chlorobenzoic	1.521	1.295	1.208	1.252
o-bromobenzoic	1.487	1.346	1.201	1.274
2-chloro-5-nitrobenzoic	1.489	1.294	1.220	1.257
β-succinic	1.485	1.322	1.252	1.287
salicylic	1.458	1.333	1.241	1.287
L-serine phosphate	1.541	1.321	1.201	1.261
α-oxalic	1.560	1.289	1.194	1.241
oxalic (dihydrate)	1.529	1.285	1.187	1.236
mellitic (mean value)	1.521	-	-	1.257

is attached. The mean carbon-oxygen distances in o-chlorobenzoic acid (1.252 Å) and 2-chloro-5-nitrobenzoic acid (1.257 Å) are shorter than the means of 1.287 Å in β-succinic acid (Broadley <u>et al</u>, 1959) and in salicylic acid, and are closer to the means of 1.261 Å in L-serine phosphate (McCallum <u>et al</u>, 1959), 1.241 Å in α-oxalic acid (Cox <u>et al</u>, 1952) and 1.236 Å in oxalic acid dihydrate (Ahmed and Cruickshank, 1953).

A factor common to o-chlorobenzoic acid, o-bromobenzoic acid and 2-chloro-5-nitrobenzoic acid arises from the conformation of the carboxyl group. In particular, the carbonyl oxygen atom is invariably adjacent to the more sterically hindered position with the hydroxyl oxygen atom remote. The reasons for this preference are easily found. The angle CC(OH) is approximately tetrahedral, whereas the angles CCO and OC(OH) exceed 120°, this being the pattern observed in other carboxylic acids (Table 32); further, the length of a carbon-oxygen double bond is less than that of a single bond. A sufficient clearance between the oxygen atom and the halogen atom is thus ensured for a smaller inclination of the carboxyl group plane to the benzene ring plane than would be required if the carbonyl and hydroxyl

TABLE 32.

Angles about the carbon atom of the carboxyl group in some carboxylic acids.

Acid	CCO	CC(OH)	OC(OH)
o-chlorobenzoic	122.2°	113.3°	124.4°
o-bromobenzoic	126.6	113.7	120.4
2-chloro-5-nitrobenzoic	121.3	114.0	124.8
β-succinic	124.4	112.9	122.7
salicylic	122.7	117.0	120.2
L-serine phosphate	121.1	113.5	125.3
α-oxalic	122.7	109.1	128.1
oxalic (dihydrate)	121.6	112.6	125.8

oxygen atoms were interchanged. The conformation adopted in o-phthalic acid is that with the carbonyl oxygen atoms adjacent and the hydroxyl oxygen atoms remote.

Without having the results of a larger number of di- and tri- substituted benzene derivatives available for correlation purposes, it would be unwise to forecast what deviations from planarity will occur in any given benzene derivative, although no doubt this will be possible when a sufficient number of suitable model compounds have been examined. It is clear, however, that the large out-of-plane displacements reported from electron-diffraction studies on polyhalogenobenzenes are suspect and a reinvestigation seems desirable. In o-phthalic acid, the exocyclic carbon-carbon bonds are bent out of the benzene plane through 10°. This value must also be regarded with some suspicion and a completion of the refinement appears to be called for.

A rather unexpected property of substituted benzoic acids which has been brought to my notice recently (Wain, 1961) is that they can act as plant-growth regulators in concentrations as low as a few parts per million. It appears that the potency of a substituted benzoic acid is a direct function of the angle of inclination of the carboxyl group to the benzene plane, the activity increasing in the series, o-chlorobenzoic acid, o-bromobenzoic acid and 2-chloro-5-nitrobenzoic acid. In 2:6-dichlorobenzoic acid and 2:3:6-trichlorobenzoic acid, where presumably the carboxyl groups are even more steeply inclined to the benzene planes, still greater activity is found.

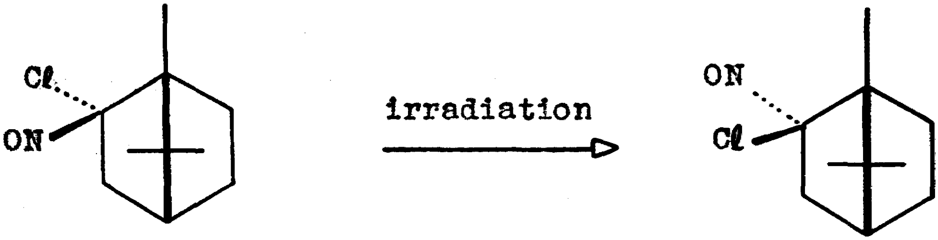
PART III.

The crystal and molecular structure of (+)-10-Bromo-2-chloro-2-nitrosocamphane.

1.1. Introduction.

A number of monomeric nitroso compounds have been prepared by Dr. Mitchell and co-workers in this department as part of a search for substances suitable for asymmetric photolysis.

It was found that irradiation of an alcoholic solution of (–)-2-chloro-2-nitrosocamphane (Mitchell, Watson and Dunlop, 1950) with red light produced a gradual inversion of the Cotton effect (Cotton, 1896; Mitchell, 1933). This was attributed to an inversion of configuration at C(2) (Hope and Mitchell, 1953) thus:



I

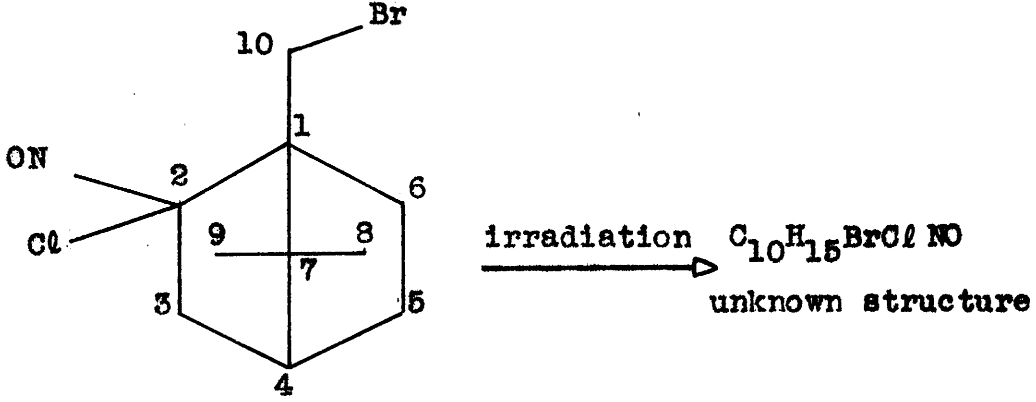
II

(–)-2-chloro-2-nitroso-
camphane.

(+)-2-chloro-2-nitroso-
camphane.

A quantitative X-ray analysis of compounds I and II was suggested as a method of determining the stereochemistry precisely. This has not yet been possible because of the poor quality of the available crystalline material.

Photolysis studies with (+)-10-bromo-2-chloro-2-nitrosocamphane (III) (Davidson, 1958) indicated that this molecule behaved rather differently on irradiation with red light. In particular, although the Cotton effect is altered, its sign remains unchanged and there is a marked shift in the absorption maximum, suggesting that the change in the molecular structure may not be a simple inversion of configuration at C(2).



III

IV

(+)-10-bromo-2-chloro-2-nitroso-camphane.

To discover what was happening in this reaction and to obtain details of the stereochemistry of molecule III, X-ray structure determination was desirable. Crystals of compound III were supplied by Dr. Mitchell. Compound IV has not yet been obtained in a crystalline form suitable for X-ray analysis.

The structure investigation by X-rays was initially undertaken by C.J.Fritchie, who worked in this department during his one year tenure of a Fulbright scholarship. I took over the analysis on Fritchie's departure from Glasgow. Our individual contributions to the structure analysis are shown in Table 33.

The work described in this chapter has since been published (Ferguson, Fritchie, Robertson and Sim, 1961).

1.2. Crystal Data.

As the blue crystals of (+)-10-bromo-2-chloro-2-nitrosocamphane obtained from Dr. Mitchell were somewhat sensitive to light, all experimental work with them was carried out in subdued light. X-rays appeared to have no adverse effects on the crystals; no signs of decomposition were detected on the X-ray photographs.

Rotation, oscillation and Weissenberg photographs were taken, using copper Kα radiation, with crystals rotating about the three crystallographic axes. The crystals are orthorhombic with unit-cell dimensions $a = 23.11 \pm 0.05$ Å, $b = 11.32 \pm 0.03$ Å, $c = 9.03 \pm 0.03$ Å.

The volume of the unit cell is 2362 Å^3. The density measured by flotation in aqueous zinc chloride is 1.562 g.cm.$^{-3}$, hence there are eight molecules of $C_{10}H_{15}BrClNO$ in the unit cell and the calculated density is 1.578 $g.cm.^{-3}$ The number of electrons in the unit cell is 1136. The absorption coefficient for X-rays ($\lambda = 1.542$ Å) is $\mu = 66.7$ $cm.^{-1}$

The systematic absences detected on the various Weissenberg films are

$h00$ when h is odd
$0k0$ when k is odd
00ℓ when ℓ is odd

The space group is therefore $P2_12_12_1$ (D_2^4).

1.3. Intensity Data.

Small crystals of (+)-10-bromo-2-chloro-2-nitrosocamphane were selected for collection of intensity data and no corrections for absorption were applied. The three-dimensional data utilised in the analysis were obtained from multiple-film equi-inclination Weissenberg photographs of the $hk0$ ... $hk7$ and $h0\ell$ layers. The intensities were measured visually and corrected for Lorentz, polarisation, and Tunell (1939) factors. They were put on the same relative scale by means of the $h0\ell$ set of data, the absolute scale being found later by comparison with the calculated structure amplitudes. A total of 1233 intensities were estimated, no allowances being made for planes too weak to be observed.

1.4. Structure Determination.

The crystal data show that there are eight molecules in a unit cell of space group $P2_12_12_1$. The asymmetric crystal unit consists therefore of two crystallographically independent molecules, necessitating the location of 28 atoms other than hydrogens.

The first attempts to solve the structure were with two-dimensional data. A study of the $h0l$ and $hk0$ Patterson projections (Figs. 31 and 32 respectively) yielded coordinates for the two bromine atoms. Elucidation of the structure by means of Fourier projections on (010) and (001) using the phases of the bromine atoms was not possible owing to the extensive overlap of atoms, thereby making essential the collection of three-dimensional data.

When the intensity data were available, the three-dimensional Patterson function was computed and the coordinates for the bromine atoms, derived from the two-dimensional work, confirmed.

In the sequence of structure-factor calculations required to solve the structure, the Thomas-Fermi scattering curve for bromine was chosen along with that of Tomiie and Stam for chlorine and those of

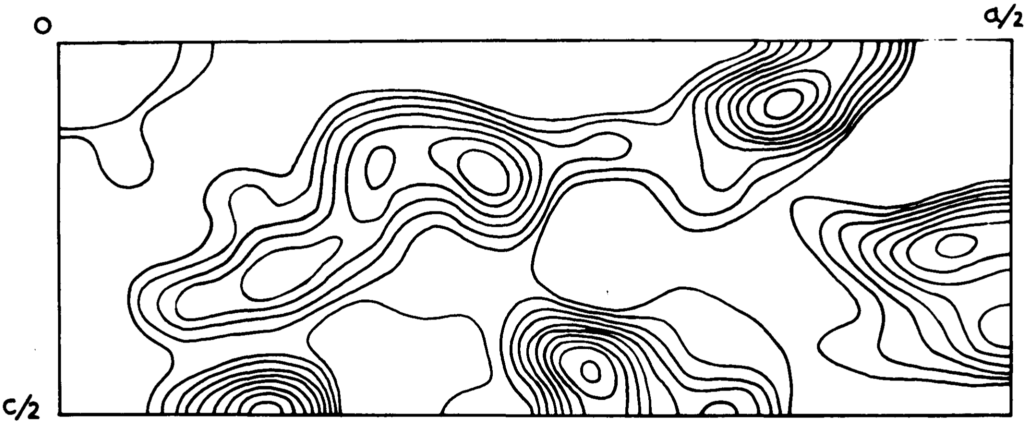


Fig.31. Patterson projection on (010). Contours at equal arbitrary intervals; origin peak contours omitted.

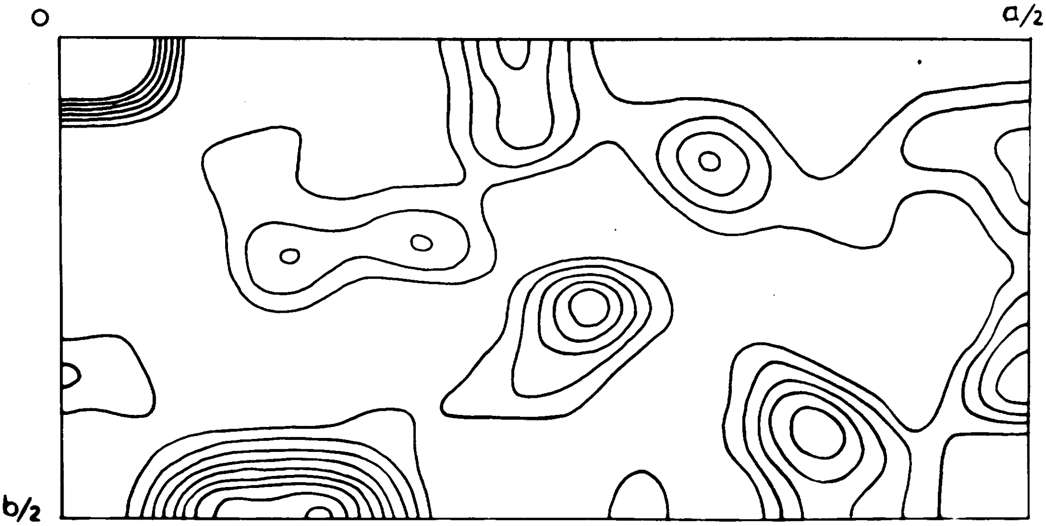


Fig.32. Patterson projection on (001). Contours at equal arbitrary intervals; origin peak contours omitted.

Berghuis et al for carbon, oxygen and nitrogen. Application of Wilson's method (Wilson, 1942) indicated that an overall thermal parameter B = 5.4 $\mathring{A}^2$ should be employed.

The first three-dimensional Fourier summation was computed with the phase angles calculated for the bromine atoms alone. The two largest peaks in this Fourier map other than those of the bromine atoms had peak heights of 4.8 and 4.5e$\mathring{A}^{-3}$. These were assumed to be the chlorine atoms. When the vectors to be expected from these positions were compared with the three dimensional Patterson function, an excellent measure of agreement was obtained. A number of smaller peaks, all less than 3e$\mathring{A}^{-3}$ in height, were visible in the Fourier synthesis, but as it was not possible to identify these atoms chemically, with certainty, only the bromine and chlorine atoms were used in the next phase angle calculation.

In the second structure-factor calculation the value of the residual R was 0.364, the resulting improved phase angles being employed in computing the second three-dimensional F_o synthesis. The value of having two crystallographically unrelated molecules in the asymmetric crystal unit soon became apparent. Only those atoms which could be distinguished in both molecules were chosen for inclusion in the third structure-factor calculation. By adopting this procedure the possibility of a spurious peak being chosen as an atomic site was effectively minimised. Carbon atoms 1, 2, 3, 4 and 10, and the nitroso group were in this way located.

In the third phase angle calculation, R was 0.296 and in the subsequent Fourier synthesis all the atoms in the asymmetric unit (with the exception of hydrogens) were located. When all 28 atoms were included in the structure-factor calculations, R decreased to 0.246.

1.5. Refinement.

With the phase angles from the fourth F_c calculation, the fourth F_o Fourier synthesis was computed, Booth's method (Booth, 1948b) being used to locate the atomic centres accurately. On recalculation of structure factors, R was 0.218.

Up to this stage in the analysis no attempts had been made to refine the temperature parameters (all atoms had $B = 5.4\ \text{Å}^2$). To remedy this situation one cycle of least-squares calculations, in which new positional and anisotropic thermal parameters for the bromine, chlorine, oxygen and nitrogen atoms were obtained, was computed.

In the next (sixth) structure-factor calculation R was 0.164. The refinement was terminated by computing an F_o synthesis followed by an F_c synthesis to allow for the correction of termination-of-series errors (Booth, 1946,1947). The final average discrepancy between observed and calculated structure amplitudes is 0.155. Superimposed contour sections parallel to (001) illustrating the final electron-density distribution over the two molecules in the asymmetric crystal unit are shown in Fig.33. The atomic arrangement corresponding to this electron-density distribution is shown in Fig.34, which also shows the convention adopted for the numbering of the two molecules. Details of the progress of the analysis are summarised in Table 33. The final atomic coordinates are listed in Table 34 and the corresponding thermal parameters in Table 35. The final set of observed and calculated structure amplitudes is given in Table 36.

The final electron-density distribution shown in Fig.33 is dependent to a large extent on the correct choice of atomic centres for the lighter atoms, it being

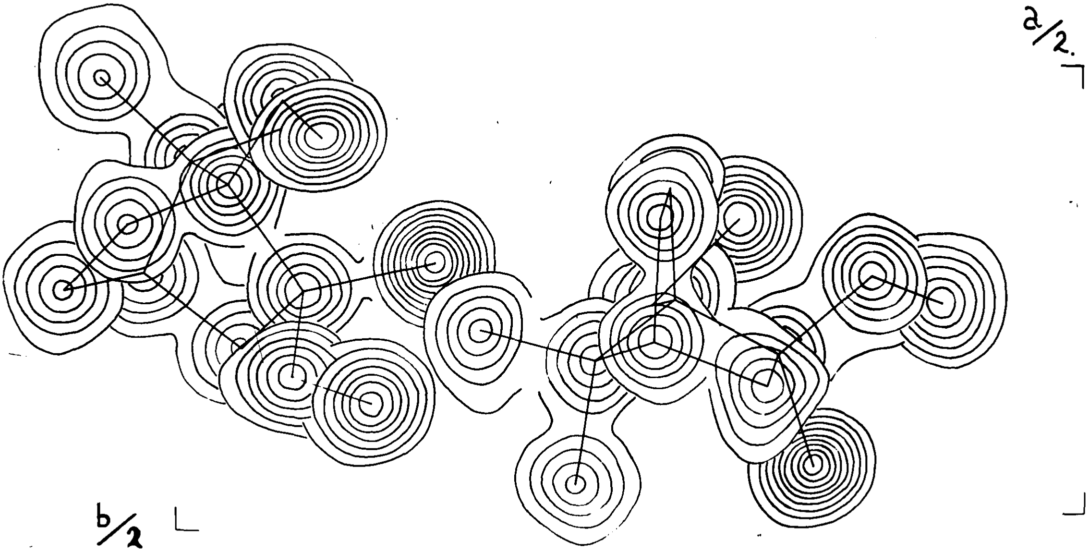


Fig. 33. Final three-dimensional electron-density distribution for (+)-10-bromo-2-chloro-2-nitrosocamphane shown by means of superimposed contour sections parallel to (001). Contour interval 1 eÅ^{-3} except around the chlorine and bromine atoms where it is 2 eÅ^{-3} and 5 eÅ^{-3}, respectively.

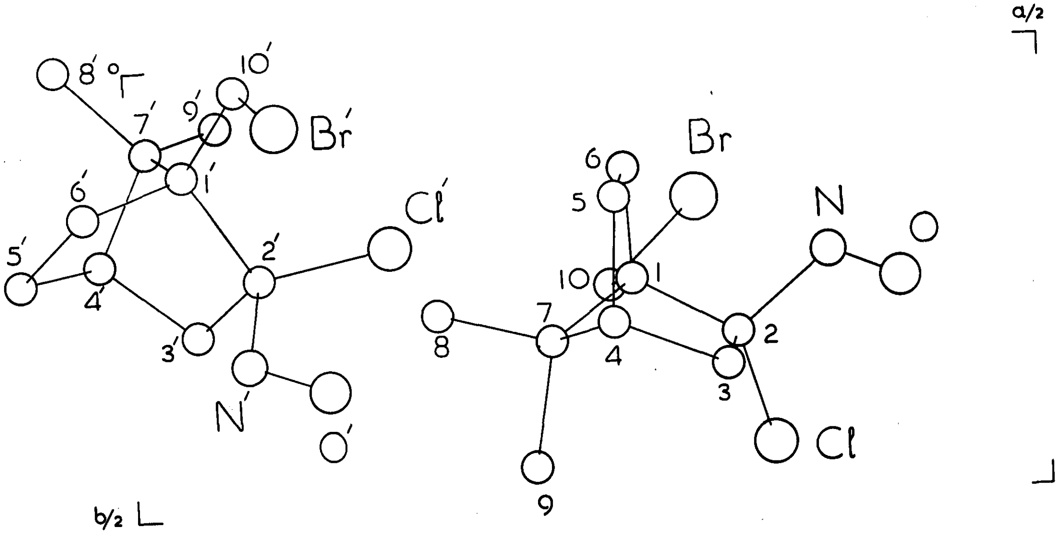


Fig.34. Atomic arrangement corresponding to Fig.33.

TABLE 33.

Progress of analysis and Division of Work.

Cell Dimensions and Space Group.

Solution of $hk0$ and $h0\ell$ Patterson projections.

↓

Initial two-dimensional work

↓

Collection and estimation of three-dimensional data.

↓

Three-dimensional Patterson function.

↓

Br (2 atoms).

↓

1st F_c calculation

1st three-dimensional F_o synthesis.

↓

Br, Cℓ, (4 atoms).

↓

2nd F_c calculation. ($R = 0.364$)

C. J. F.

- Cont'd -

TABLE 33.

(Cont'd)

Progress of analysis and Division of Work.

2nd three-dimensional F_o synthesis.

↓

Br, Cℓ, N, O, C(1), C(2), C(3), C(4), C(10). (18 atoms)

↓

3rd F_c calculation. (R = 0.296)
3rd three-dimensional F_o synthesis.

↓

Br, Cℓ, N, O, C(1)...C(10). (28 atoms)

↓

4th F_c calculation. (R = 0.246)
4th three-dimensional F_o synthesis.

↓

5th F_c calculation.
Least squares refinement of Br, Cℓ, N, O.

↓

6th F_c calculation. (R = 0.164)
5th three-dimensional F_o synthesis.
1st three-dimensional F_c synthesis.

↓

7th F_c calculation. (R = 0.155)

↓

Final bond lengths, angles, deviations.

G. F.

TABLE 34.

Final coordinates of the atoms in the asymmetric crystal unit expressed as fractions of the axial lengths. Origin of coordinates as in International Tables, midway between non-intersecting pairs of screw axes.

Atom (c.f.Fig.34)	x	y	z
C(1)	0.2741	0.2545	0.0246
C(2)	0.3311	0.3163	-0.0216
C(3)	0.3232	0.3574	-0.1848
C(4)	0.2643	0.2998	-0.2209
C(5)	0.2662	0.1599	-0.2217
C(6)	0.2723	0.1296	-0.0549
C(7)	0.2296	0.3198	-0.0800
C(8)	0.1653	0.2850	-0.0766
C(9)	0.2182	0.4556	-0.0368
C(10)	0.2616	0.2578	0.1905
O	0.4239	0.2620	0.0355
N	0.3807	0.2288	-0.0153
Br	0.3095	0.1662	0.3075
Cl	0.3503	0.4429	0.0899

- Cont'd -

TABLE 34.

(Cont'd)

Atom (c.f.Fig.34)	X	Y	Z
C(1)'	0.0317	0.1241	0.4058
C(2)'	0.0703	0.2348	0.4350
C(3)'	0.0373	0.2962	0.5685
C(4)'	-0.0154	0.2191	0.5938
C(5)'	-0.0607	0.2319	0.4679
C(6)'	-0.0272	0.1662	0.3450
C(7)'	0.0102	0.0897	0.5691
C(8)'	-0.0366	-0.0026	0.5710
C(9)'	0.0591	0.0582	0.6787
C(10)'	0.0607	0.0243	0.3240
O'	0.1060	0.3646	0.2634
N'	0.0638	0.3307	0.3314
Br'	0.0817	0.0664	0.1290
Cl'	0.1437	0.2090	0.4727

TABLE 35.

Final Thermal parameters.

For all carbon atoms B = 5.4 Å^2.

For O, N, Br, and Cl the average isotropic values derived from the least-squares produced anisotropic parameters are:-

Atom	B	atom	B
O	7.1	O'	6.8
N	5.7	N'	7.1
Br	6.2	Br'	6.5
Cl	6.0	Cl'	6.0

Table 36: Measured and calculated values of the structure factors.

h	k	l	$\lvert F_o \rvert$	$\lvert F_c \rvert$	α°
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

comparatively easy to select spurious sites for light atoms from a three-dimensional Fourier synthesis based on heavy atom phases alone (see, for example, Hodgkin _et al_, 1959). Crystals of (+)-10-bromo-2-chloro-2-nitrosocamphane, being of space group $P2_12_12_1$, afford centrosymmetrical electron-density projections. Such projections will be much less dependent on the correct choice of sites for the lighter atoms because the signs of the structure factors are largely determined by the bromine and chlorine contributions. Accordingly the Fourier projection on (001) was computed and on it the final atomic coordinates were plotted. The result is shown in Fig.35 where it is seen that the coordinates obtained from the three-dimensional Fourier syntheses fit the projected electron density very closely, providing additional proof of the correctness of the structure. In Fig.35 the contour interval is $1e\text{Å}^{-2}$ (the $1e\text{Å}^{-2}$ line being broken), except around the chlorine atoms above $6e\text{Å}^{-2}$ where the interval becomes $2e\text{Å}^{-2}$, and around the bromine atoms above $5e\text{Å}^{-2}$ where the interval becomes $5e\text{Å}^{-2}$.

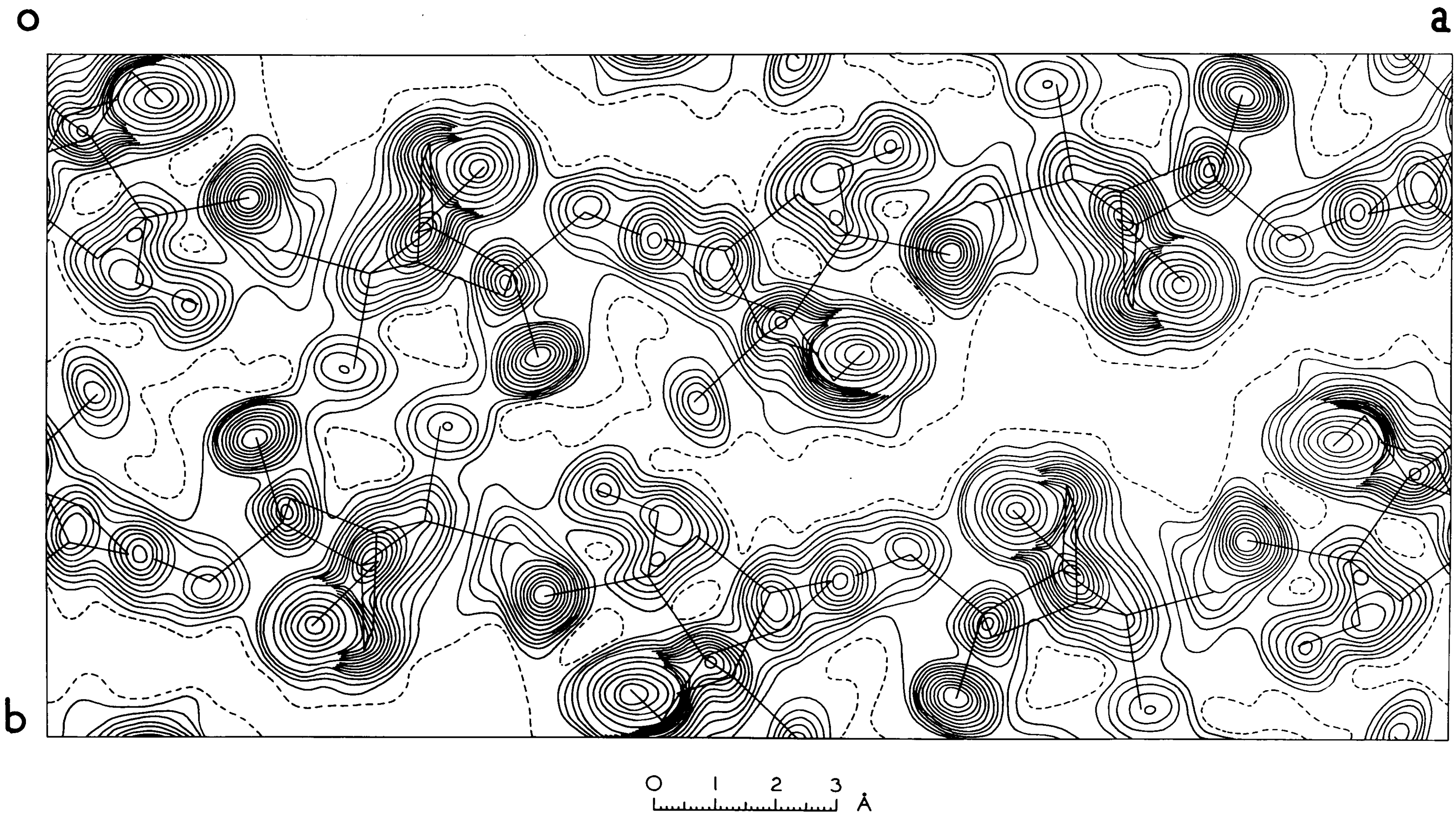


Fig. 35. Electron-density projection on (001).

1.6. Molecular Geometry.

The bond lengths and inter-bond angles calculated from the coordinates listed in Table 34 are given in Tables 37 and 38 respectively. The shorter intramolecular contacts are listed in Table 39, and the intermolecular approach distances ≤ 4.0 Å in Table 40. None of these appears to be abnormal. Examination of the distances between bromine and oxygen atoms, and bromine and carbon atoms in each molecule indicates that the atoms, which might have been expected to take up different orientations in the two molecules, appear to adopt positions with respect to the remaining molecular framework that are very similar. In particular the distances d(Br...C(n)) and d(Br'...C(n)') are comparable, as are also the distances d(O...C(n)) and d(O'...C(n)'). This would appear to indicate that the two crystallographically independent molecules are conformationally identical. In view of this identity, averaged dimensions for the molecule of (+)-10-bromo-2-chloro-2-nitrosocamphane are also given in Tables 37, 38 and 39.

The estimated standard deviation in bond length calculated from the differences between the two molecules is 0.044 Å. The corresponding value deduced from the

TABLE 37.

Final Bond Lengths.

				Average
C(1)-C(2)	1.55	C(1')-C(2')	1.56	1.56
C(2)-C(3)	1.56	C(2')-C(3')	1.59	1.57
C(3)-C(4)	1.54	C(3')-C(4')	1.52	1.53
C(4)-C(5)	1.58	C(4')-C(5')	1.55	1.57
C(5)-C(6)	1.55	C(5')-C(6')	1.54	1.55
C(6)-C(1)	1.59	C(6')-C(1')	1.54	1.56
C(1)-C(10)	1.53	C(1')-C(10')	1.51	1.52
C(1)-C(7)	1.58	C(1')-C(7')	1.60	1.59
C(7)-C(8)	1.54	C(7')-C(8')	1.50	1.52
C(7)-C(9)	1.61	C(7')-C(9')	1.55	1.58
C(7)-C(4)	1.52	C(7')-C(4')	1.59	1.56
C(10)-Br	1.85	C(10')-Br'	1.89	1.87
C(2)-Cℓ	1.81	C(2')- Cℓ'	1.75	1.78
C(2)-N	1.52	C(2')-N'	1.44	1.48
N-O	1.16	N'-O'	1.21	1.19

TABLE 38.

Final Interbond Angles.

	molecule I	molecule II	Average
C(1)C(2)C(3)	107°	102°	104°
C(2)C(3)C(4)	100	104	102
C(3)C(4)C(5)	114	112	113
C(4)C(5)C(6)	103	98	101
C(5)C(6)C(1)	104	110	107
C(6)C(1)C(2)	108	108	108
C(2)C(1)C(7)	100	103	102
C(6)C(1)C(7)	97	97	97
C(3)C(4)C(7)	103	102	103
C(5)C(4)C(7)	100	103	102
C(1)C(7)C(8)	120	114	117
C(1)C(7)C(9)	114	115	114
C(4)C(7)C(8)	119	112	116

-Cont'd-

TABLE 38

Final Interbond Angles.

(Cont'd)

	molecule I	molecule II	**Average**
C(4)C(7)C(9)	116°	113°	114°
C(10)C(1)C(2)	115	115	115
C(10)C(1)C(6)	118	117	117
C(10)C(1)C(7)	117	114	115
C(1)C(7)C(4)	95	91	93
C(1)C(10)Br	116	113	114
C(1)C(2)N	110	116	113
C(3)C(2)N	109	97	103
C(1)C(2)Cℓ	115	117	116
C(3)C(2)Cℓ	109	113	111
Cℓ C(2)N	108	111	109
C(2)N O	117	119	118
C(8)C(7)C(9)	95	111	103

TABLE 39.

Intramolecular non-bonded distances in Å.

	molecule I	molecule II	Average
C(1)...C(4)	2.29	2.28	2.29
C(1)...C(8)	2.70	2.60	2.65
C(1)...C(9)	2.68	2.65	2.66
C(1)...C(5)	2.48	2.52	2.50
C(1)...C(3)	2.49	2.44	2.47
C(1)...Br	2.86	2.83	2.85
C(1)...Cℓ	2.83	2.83	2.83
C(1)...O	3.47	3.47	3.47
C(2)...C(4)	2.38	2.45	2.42
C(2)...C(6)	2.53	2.52	2.53
C(2)...C(7)	2.41	2.47	2.44
C(2)...C(9)	3.05	2.99	3.02
C(2)...C(10)	2.59	2.59	2.59
C(2)...Br	3.46	3.37	3.41
C(3)...C(5)	2.62	2.55	2.58
C(3)...C(7)	2.40	2.42	2.41
C(3)...C(9)	2.99	2.92	2.95
C(3)...Cℓ	2.74	2.79	2.76
C(3)...O	3.25	3.27	3.26

- Cont'd -

TABLE 39.

(Cont'd)

Intramolecular non-bonded distances in Å.

	molecule I	molecule II	Average
C(4)...C(6)	2.45	2.34	2.40
C(4)...C(8)	2.64	2.57	2.60
C(4)...C(9)	2.65	2.62	2.64
C(5)...C(7)	2.37	2.47	2.42
C(5)...C(8)	3.03	2.87	2.95
C(6)...C(7)	2.38	2.36	2.37
C(6)...C(8)	3.04	2.80	2.92
C(6)...C(10)	2.66	2.60	2.63
C(7)...C(10)	2.65	2.61	2.63
C(8)...C(10)	3.30	3.18	3.24
C(9)...C(10)	3.20	3.22	3.21
N...Cℓ	2.70	2.63	2.66
N...Br	3.42	3.53	3.48
O...Cℓ	2.71	2.73	2.72
O...Br	3.77	3.63	3.70
Cℓ...Br	3.82	3.78	3.80
Cℓ...C(9)	3.26	3.19	3.23
Cℓ...C(7)	3.48	3.48	3.48

TABLE 40.

The Intermolecular Contacts ≤ 4.0 Å.

C(8)...O'	3.48	C(10)...O'	3.85
C(10')...N$_{\mathrm{I}}$	3.49	C(9')...O$_{\mathrm{I}}$	3.87
O'...C(3)$_{\mathrm{II}}$	3.58	C(10')...N'$_{\mathrm{V}}$	3.88
C(4')...O$_{\mathrm{III}}$	3.64	C(9)...O'	3.89
C(8)...Br'	3.65	Cl...C(9)$_{\mathrm{II}}$	3.90
C(6')...O$_{\mathrm{IV}}$	3.71	Br'...C(5')$_{\mathrm{V}}$	3.92
C(8')...O'$_{\mathrm{V}}$	3.74	C(9)...C(3)$_{\mathrm{II}}$	3.94
C(6')...C(3)$_{\mathrm{IV}}$	3.76	C(3')...Cl$_{\mathrm{II}}$	3.94
C(10)...Cl'	3.77	C(8')...O$_{\mathrm{I}}$	3.94
C(10')...O$_{\mathrm{I}}$	3.78	C(9')...N$_{\mathrm{I}}$	3.94
C(5')...Br$_{\mathrm{III}}$	3.80	C(8')...C(3')$_{\mathrm{VI}}$	3.97
O'...Cl$_{\mathrm{II}}$	3.80	C(6')...O'$_{\mathrm{V}}$	3.99
C(8')...C(8)$_{\mathrm{V}}$	3.83	Cl'...C(5)$_{\mathrm{VII}}$	3.99
C(5')...C(3)$_{\mathrm{IV}}$	3.84	N'...Cl$_{\mathrm{II}}$	4.00
C(6')...N$_{\mathrm{IV}}$	3.85	C(9)...C(4)$_{\mathrm{II}}$	4.00

The subscripts refer to the following positions:

I. $\frac{1}{2} - x,\ -y,\ \frac{1}{2} + z.$

II. $\frac{1}{2} - x,\ 1 - y,\ \frac{1}{2} + z.$

III. $x - \frac{1}{2},\ \frac{1}{2} - y,\ 1 - z.$

IV. $x - \frac{1}{2},\ \frac{1}{2} - y,\ -z.$

V. $-x,\ y - \frac{1}{2},\ \frac{1}{2} - z.$

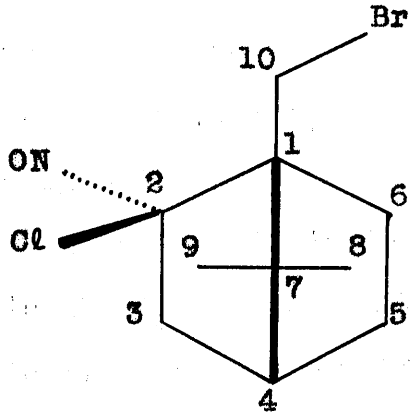
VI. $-x,\ y - \frac{1}{2},\ 1\frac{1}{2} - z.$

VII. $x,\ y,\ 1 + z.$

earlier least-squares refinement was 0.080Å. For the averaged dimensions in Tables 37, 38 and 39, it is reasonable to take $0.064/\sqrt{2} = 0.045$Å as the standard deviation in bond length. The standard deviation in bond angle is 3°.

1.7. Discussion.

The establishing of the stereochemistry of (+)-10-bromo-2-chloro-2-nitrosocamphane was the primary objective of the analysis. The chlorine atom is shown to be *cis* to the CMe_2 bridge, thus:-



This arrangement of the chloro- and nitroso- groups is the opposite of that assigned to (−)-2-chloro-2-nitrosocamphane by Hope and Mitchell. It is perhaps of some significance that the two compounds have Cotton effects of opposite sign. A detailed crystal structure analysis of (–)-2-bromo-2-nitrocamphane has recently been carried out (Brueckner _et al_, 1961) and it is found that in this molecule also, the halogen atom is _cis_ to the CMe_2 bridge.

The mean length of a carbon-carbon bond in (+)-10-bromo-2-chloro-2-nitrosocamphane, averaged over the two crystallographically independent molecules, is 1.554 Å which is not significantly different from the value of 1.545 Å found in diamond. The average carbon-bromine (1.87 Å) and carbon-chlorine (1.78 Å) bond lengths are in fair agreement with values of 1.93 Å and 1.77Å respectively given in Tables of Interatomic Distances (1958).

The mean carbon-nitrogen bond length is 1.48 Å, which is that accepted for a carbon-nitrogen single bond. The mean nitrogen-oxygen distance of 1.19 Å is not significantly different from the value of 1.21 Å accepted for the nitrogen-oxygen separation in a nitro group. It is however distinctly shorter than the accepted value of 1.36 Å for a nitrogen-oxygen single bond, implying that in this case the nitrogen-oxygen bond has a large amount of double-bond character comparable with that of a pure double bond. The

C-N-O group is not linear, the angle CNO being 118°. In p-iodonitrosobenzene (Webster, 1956) the molecule is planar with a carbon-nitrogen distance of 1.28 Å and a nitrogen-oxygen distance of 1.24 Å, while the angle CNO was found to be 125°. The shortening of the carbon-nitrogen bond in this molecule was attributed to conjugation, but as relatively few (projection) data were used in the analysis the light atom positions may be considerably in error.

In (+)-10-bromo-2-chloro-2-nitrosocamphane the camphane skeleton appears to be buckled slightly, distortion from the regular camphane skeleton being caused by the bulky chlorine atom cis to the CMe_2 bridge. This is illustrated by the angle C(2)C(1)C(7) (102°) being greater than the angle C(6)C(1)C(7) (97°); further, the distances C(2)...C(7) (2.44 Å) and C(2)...C(9) (3.02 Å) are larger than the distances C(6)...C(7) (2.37 Å) and C(6)...C(8) (2.92 Å). The angle C(1)C(7)C(4) (93°) is much smaller than the normal tetrahedral angle. An identical value is found for the corresponding angle in (—)-2-bromo-2-nitrocamphane, which would appear to confirm that in the camphane molecular framework, this angle is indeed significantly reduced.

APPENDIX.

This appendix contains brief details of the programs written by the author for the Glasgow University DEUCE computer.

DEUCE - the initials stand for Digital Electronic Universal Computing Engine - is a serial machine with numbers and instructions consisting of 32 binary digits, the digit rate being 1 million per second. DEUCE has two types of storage units: a fast (immediate access) store of 402 words in mercury delay lines (access time 32 - 1024 micro-seconds), and a slow (backing) store of 8192 words on a magnetic drum (access time 13 - 48 milliseconds). Both punched cards and paper tape can be used for input and output.

Programs may be written in the basic machine language or with the help of a number of translation schemes. One of these, Alphacode, has been used by the author; it allows programs to be written for DEUCE fairly quickly at the expense of the speed of the subsequent calculation.

Program 1.

Structure factor program for the plane group P2. This program was written at an Alphacode programming course before the Rollett programs became available and was made obsolete by their arrival.

Input. Lattice constants, the total number of atoms, the atomic coordinates, an overall isotropic temperature factor, the number of chemical types, the number of atoms of each chemical type, scattering factor curve data, and the maximum and minimum values of the indices h and ℓ.

Output. Sets of h, ℓ and F_c, 3 cards per reflexion, for every $h0\ell$ structure factor possible for copper Kα radiation within the range specified.

Time. With o-chlorobenzoic acid, approximately 30 seconds per structure factor.

Program 2.

This Alphacode program corrects intensity data from zero layer Weissenberg photographs of triclinic crystals for Lorentz and polarisation factors. It was used successfully until Dr. J.G.Sime's basic program was operational.

Input. Lattice constants, wavelength of X-rays used and sets of h, ℓ, I_o, 3 cards per reflexion.

Output. Sets of h, ℓ, $|F_o|^2$ and $|F_o|$, 4 cards per reflexion.

Time. Approximately 6 seconds per reflexion.

Program 3.

Scaling program: This program was written in the basic machine language for scaling hkℓ F_o data by any 5 decimal digit (four decimal place) number. Simple facilities are available for index rearrangement, for reading a variety of decimal input data apart from simply hkℓ F_o cards, and for punching out $k|F_o|$ in place of kF_o if required.

Input. Scale factor card followed by hkℓ F_o cards (one card per reflexion).

Output. hkℓ kF_o one card per reflexion. After a batch of hkℓ F_o cards have been read, scaled and punched out, the program calls for the next scale factor card and the next set of hkℓ F_o data.

Time. Reading and punching time (DEUCE can read 200 cards per minute and punch 100 cards per minute).

Program 4.

This basic program converts the output from the Rollett structure factor program into a convenient form for publication. This program is for use with centrosymmetrical structures. A companion program for non-centrosymmetrical structures has been written by Dr. Sime.

Input. The program accepts the Rollett structure factor "α-form" output, i.e. $hk\ell$, $\sin^2\theta$, $\Delta = |F_o| - |F_c|$, $|F_c|$, $\cos\alpha$, $\sin\alpha$, one card per reflexion. The set of structure factor cards is preceeded by a scale-factor card.

Output. The program evaluates $|F_o|$, applies the scale factor and punches out on cards $hk\ell$, $k|F_o|$ and F_c, one card per reflexion. Both $|F_o|$ and F_c have one decimal place; h and k are only punched when either h or k changes, ℓ being punched with $|F_o|$ and F_c on every card.

Time. Reading and punching time.

This output is in a form suitable for automatic tabulation by the English Electric card-operated typewriter. In this way approximately 1200 reflexion data can be typed on strips of paper which can be glued together to produce one large sheet of paper. Photographic reduction to quarto size then produces a convenient record of the structure factor data. Tables 12, 20 and 26 were prepared in this way.

Program 5.

This basic program (written in collaboration with Dr. J.G.Sime) accepts the Rollett "α-form" structure factor output on cards and converts it to punched paper tape which can be more conveniently stored.

Input. Atomic coordinates and temperature factors in the Rollett form (Rollett 1961) followed by the Rollett "α-form" structure factor output.

Output. The same data on paper tape for storage. A complimentary program has been written by Dr. Sime to convert the tape into cards if, at some later date, further structure factor or Fourier calculations are required.

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