

X-RAY CRYSTALLOGRAPHIC STUDIES OF  
FOUR ORGANIC COMPOUNDS

by

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## ABSTRACT

Supervisor: Professor James Trotter

Single crystal X-ray diffraction methods have been used to investigate four organic compounds, two monosaccharide derivatives and two nitrobenzene compounds:

1. methyl 3-C-(carbomethoxymethyl)-4,6-di-O-p-chlorobenzoyl-2,3-dideoxy- $\alpha$ -D-ribo-hexopyranoside,  $C_{24}H_{24}Cl_2O_8$ .
2. 5-O-(p-bromobenzenesulphonyl)-2,2'-O-cyclohexylidene-3-deoxy-2-C-hydroxymethyl-D-erythro-pentono-1,4-lactone,  $C_{18}H_{21}BrO_7S$ .
3. 2,6-dichloro-4-nitroaniline,  $C_6H_4Cl_2N_2O_2$ .
4. ethyl 3,5-dinitrobenzoate,  $C_9H_8N_2O_6$ .

Crystals of the di-(p-chlorobenzoate) derivative of a novel branched-chain sugar, methyl 3-C-(carbomethoxymethyl)-2,3-dideoxy- $\alpha$ -D-ribo-hexopyranoside, are monoclinic, space group  $P2_1$ ,  $a = 5.752$ ,  $b = 15.436$ ,  $c = 13.698$  Å.,  $\beta = 93.74^\circ$  and  $Z = 2$ . Intensity data have been measured on an automatic diffractometer, firstly with Mo- $K_\alpha$  radiation, then more accurately with Cu- $K_\alpha$  radiation. Efforts to confirm the molecular structure of the derivative have been unsuccessful, although various methods of analysis have been employed; the principal approaches have been the examination of the Patterson and sharpened Patterson maps, and by direct methods, the application of the tangent formula in the phase determination procedures for noncentrosymmetric space groups. None of the methods has produced any encouraging, distinctive portions of the molecule, and at present, the investigation has been halted.

The structure of " $\alpha$ "-D-isosaccharinic acid has been determined by crystal structure analysis of a derivative which was shown to be 5-O-(p-bromo-

benzenesulphonyl)-2,2'-O-cyclohexylidene-3-deoxy-2-C-hydroxymethyl-D-erythro-pentono-1,4-lactone. Crystals are monoclinic,  $a = 5.757$ ,  $b = 10.586$ ,  $c = 16.021$  Å.,  $\beta = 98.85^\circ$ ,  $Z = 2$ , space group  $P2_1$ . The intensities of 1319 reflections were measured with a scintillation counter and  $\text{Cu-K}_\alpha$  radiation, the structure was derived from Patterson and electron-density maps, and refined by least-squares methods, the final  $R$  being 0.10 for 1140 observed reflections. The absolute configuration is established, since the compound was obtained by degradation of cellulose.

Each of the two five-membered rings in the derivative has an envelope conformation, with one atom displaced from the plane of the other four. In the 1,3-dioxolane ring, the displacement is 0.49 Å.; the  $\gamma$ -lactone ring is less prominently bent, with displacement only 0.14 Å. The bond distances and valency angles in the molecule do not differ significantly from the usual values, and the intermolecular distances correspond to van der Waals' interactions.

Crystals of 2,6-dichloro-4-nitroaniline are generally twinned; they are monoclinic, space group  $P2_1/c$ ,  $a = 3.723$ ,  $b = 17.833$ ,  $c = 11.834$  Å.,  $\beta = 94.12^\circ$ ,  $Z = 4$ . Intensity data were collected for one of the twins on an automatic diffractometer. The coordinates of the two chlorine atoms were found in a Patterson map and all the other atoms in electron-density and difference Fourier maps. The structure was refined by full-matrix least-squares methods to  $R = 0.038$ .

There are only slight deviations from overall planarity of the molecule, the amino and nitro groups being rotated by  $6.3$  and  $7.2^\circ$  respectively out of coplanarity with the benzene ring. The amino group appears to be held nearly coplanar with the benzene ring by intermolecular  $\text{N-H}\cdots\text{O}$  and intramolecular  $\text{N-H}\cdots\text{Cl}$  hydrogen bonds. The intermolecular hydrogen bonding also connects the molecules in long chains in the crystal.



It is thought that the twins are congruent, related by a twin axis parallel to a; a possible arrangement of molecules at the twinning plane is suggested.

Crystals of ethyl 3,5-dinitrobenzoate are colourless needles of monoclinic space group  $P2_1/c$  ;  $a = 13.856$ ,  $b = 4.770$ ,  $c = 18.354 \text{ \AA}$ .,  $\beta = 119.59^\circ$  and  $Z = 4$ . The structure of this compound was determined from diffractometer data by direct methods, and was refined by full-matrix least-squares methods to  $R = 0.061$ .

The substituent nitro groups are rotated  $1.6$  and  $11.5^\circ$ , and the carboxyl group  $2.2^\circ$ , out of coplanarity with the benzene ring; the molecular packing arrangement appears to determine that the rotation of one nitro group is considerably more than that of the other.

The ethyl group is disordered randomly in the crystal in two orientations, with a ratio of populations approximately 7:3.

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## GENERAL INTRODUCTION

In 1912, von Laue proposed that X-rays might be diffracted by crystals, and shortly afterwards Friedrich and Knipping confirmed this experimentally. The next year, W.L. Bragg gave a mathematical explanation for the patterns and positions of the X-ray beams diffracted by a crystal, and the solution of simple crystal structures soon followed. Since that time, the science of X-ray crystallography has advanced rapidly. The development of computers and the automation of measurement of X-ray diffraction intensities have assisted the crystallographer greatly in recent years so that now the solutions of many structures, including several complex biological structures, are being reported annually.

This thesis is concerned primarily with the crystallographic studies of four organic compounds, two monosaccharide derivatives and two nitrobenzene compounds. The structures of three of these have been determined, but that of one of the carbohydrate derivatives remains as yet unsolved. A description of the methods of structure analysis, and of the resulting molecular and crystal structures form the main parts of the thesis, Parts I-IV. Part V describes the up-dating of a program for the generation of diffractometer settings for a crystal mounted along a reciprocal axis, and the modification of this program to calculate the settings for a twinned crystal.

The principles of X-ray crystallography are well established and are discussed in several standard texts <sup>1-4</sup>. However, some of the symbols and formulae used and quoted in this thesis should perhaps be mentioned here; in general, all the crystallographic nomenclature found in this thesis has its conventional meaning as described in "International Tables for X-ray Crystallography" <sup>5</sup>.

The diffraction of an X-ray beam may be considered as reflection in a crystal plane. A crystal plane has indices  $hkl$ , and the spacing between planes of the same indices,  $d_{hkl}$ , is related by the Bragg Law to the diffraction angle  $\theta$ , the angle between the incident beam and the reflecting plane:

$$2.d_{hkl}.\sin \theta = n \lambda$$

where  $n$  is an integer, and  $\lambda$  is the wavelength of the X-radiation.

The intensity,  $I_{hkl}$ , of a diffracted beam is corrected by Lorentz and polarisation factors - these, respectively, allow for the method of intensity measurement (the scanning through a diffracted beam), and for the loss of beam intensity due to polarisation of the beam in the reflection; these are both geometrical factors, depending on the angle  $\theta$ . The corrected  $I_{hkl}$  is, in general, related to the structure amplitude,  $|F|$  :

$$I_{hkl} \propto |F_{hkl}|^2$$

and this represents the measurable part of the structure factor,  $F_{hkl}$ , which may be written:

$$F_{hkl} = \sum_j f_j . \exp[2\pi i(hx_j + ky_j + lz_j)]$$

where  $f_j$  is the scattering factor for atom  $j$ , with fractional coordinates  $(x_j, y_j, z_j)$  in the unit cell; and the summation is over all the atoms in the unit cell.

Thus the structure factor is a complex number and may also be written:

$$F = A + iB \quad \text{or} \quad F = |F|(\cos \phi + i.\sin \phi)$$

where  $|F|^2 = A^2 + B^2$ , and  $\phi$  is the phase of the structure factor.

The atomic scattering factor,  $f_{0,j}$ , represents the scattering power of the stationary atom,  $j$ . Its value is characteristic of the type of

atom, and varies with  $(\sin \theta)/\lambda$ . Calculated values of  $f_0$  for many atoms are tabulated in "International Tables", vol. III <sup>5c</sup> and in more recent literature. These values of  $f_0$  should, however, be corrected for thermal motion - the atoms are always vibrating, and the scattering factors used in structure factor calculations have the form:

$$f_j = f_{0,j} \cdot \exp[(-B_j \cdot \sin^2 \theta)/\lambda^2]$$

where  $B_j$  is the temperature factor and is related to the mean square displacement,  $U_j^2$ , of the atom  $j$  from its mean position:

$$B_j = 8 \pi^2 U_j^2 .$$

In recent and more accurate structure determinations, it has been possible to describe the anisotropic vibrations of the atoms more fully, by means of thermal ellipsoids of electron distribution. These are determined from the squared amplitudes,  $U$ 's, of vibration, in the general temperature factor expression:

$$\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}\ell^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}h\ell a^*c^* + 2U_{23}k\ell b^*c^*)]$$

The electron density,  $\rho$ , at a point  $(x, y, z)$  in the unit cell can be calculated to be:

$$\rho(x,y,z) = \frac{1}{V} \sum_h \sum_k \sum_\ell F_{hkl} \cdot \exp[-2\pi i(hx + ky + \ell z)]$$

i.e. the periodic electron density in a crystal can be represented by a three-dimensional Fourier series; the triple summation is over all values  $(-\infty$  to  $+\infty)$  of each of  $h$ ,  $k$  and  $\ell$ . The electron density at all points in the unit cell (hence the location of all the atoms) can be determined if the structure factors,  $F_{hkl}$ , are known. But only the amplitudes  $|F_{hkl}|$  can be measured; the phases,  $\phi_{hkl}$ , of the structure factors cannot be measured. This lack of data constitutes the phase problem, and the art of crystallography is in finding these phases.

Various methods have been used to solve the problem. One of the earliest was introduced by Patterson, who found that the expression:

$$\rho'(x,y,z) = \frac{1}{V} \sum_h \sum_k \sum_l |F|^2 \cdot \exp[-2\pi i(hx + ky + lz)]$$

(in which all the coefficients can be measured), represents the distribution of interatomic vectors in the unit cell, and in it, each vector peak is weighted according to the electron densities of the atoms involved. For simple structures, the whole molecule may be discernible in a Patterson map, but for larger structures the map becomes too complex. However, the Patterson map may be useful in determining the coordinates of one or two heavy atoms in a molecule containing many lighter atoms.

In the first case, where an approximate solution has been determined, structure amplitudes may be calculated from the coordinates of the atoms in this structure and the results compared with the observed values. If the agreement is good, then the phase problem has been overcome and the structure is solved.

In the second case, part of a structure has been determined, and phases can be calculated from the heavy atoms alone. In the heavy atom method, it is hoped that the heavy atom(s) dominate in the structure factors and that the magnitudes and phases due to the heavy atom(s) are an approximation to those of the whole structure. Then using the observed magnitudes, and the phases from the heavy atoms, an electron-density map is calculated, and it is hoped that the phases are a close enough approximation to show the positions of more of the atoms in the molecule. These new atom positions can be used to improve the phase calculations and another electron-density map can be drawn. This process is repeated until all the non-hydrogen atoms have been located.

A more recent method of phase determination derives the phases directly by mathematical means from a consideration of the structure ampli-

tudes <sup>6</sup>. Rather than working with the usual structure factors,  $F_{hkl}$ , it is common to use unitary structure factors,  $U_{hkl}$ , or normalised structure factors,  $E_{hkl}$ ; these latter put the structure factors on scales of relative importance after correction according to the diffraction angle,  $\theta$ , for each reflection - the scattering matter is effectively concentrated at the atomic coordinates. The normalised structure amplitude,  $|E|$ , is defined <sup>7</sup>:

$$|E_{hkl}|^2 = \frac{|F_{hkl}|^2}{\epsilon \sum_j f_{j,hkl}^2}$$

where (i)  $f_{j,hkl}$  is the atomic scattering factor for the  $j$ th atom in the unit cell for the value of  $\theta$  for the reflection  $hkl$ ; it is corrected by the temperature factor;

(ii) the summation is over all atoms in the unit cell;

(iii)  $\epsilon$  is a symmetry factor which corrects for space group extinctions; normally  $\epsilon = 1$ , except e.g.:

(a) in space group  $P2_1$  for  $0k0$  reflections,  $\epsilon = 2$ ,

(b) in space group  $P2_1/c$  for  $0k0$  and  $h0l$  reflections,  $\epsilon = 2$ .

Both  $U_{hkl}$  and  $E_{hkl}$  are complex numbers, and have the same phase as the corresponding  $F_{hkl}$ .

In 1948, Harker and Kasper showed that inequality relationships existed between the structure factors, and that sometimes one could obtain information on the phases of the structure factors from these inequalities. From considerations of symmetry elements, inequalities for various groups of reflections in many space groups have been derived, but in larger structures, the number of phases that can be determined from these relationships is limited. However, Sayre and others, in about 1952, developed probability expressions, by which a phase can be calculated and will be correct within a certain probability.

Most of the earlier work in these direct methods was concentrated on the solution of structures in centrosymmetric space groups, but more recently, attention has been paid, particularly by the Karles, to noncentrosymmetric space groups, and several phase-determining formulae have now been proposed for use in either case. The Karles have developed the determination of phases into a routine known as the symbolic addition procedure <sup>7</sup>, which appears capable of solving fairly complex structures.

Other methods of structure analysis include

(i) trial and error methods - for simple structures in which, normally, the molecule is rigid, and

(ii) the multiple isomorphous replacement method, particularly applicable to the large protein molecules. Crystals are prepared of the protein itself and of several heavy atom derivatives of the protein, all of which are isostructural. The heavy atom coordinates are calculated from a Patterson series of the difference between the structure amplitudes,  $(|F_A| - |F_B|)^2$ , of the native protein crystals and their heavy atom derivatives. From a comparison of the data of at least two heavy atom derivatives and the native protein, the phases of all the structure factors can be determined unambiguously.

When all the non-hydrogen atoms of a molecule have been found, and their parameters partly refined (see below), it might be possible to locate any hydrogen atoms in the molecule. The best means of searching for these atoms, and for confirming that there are no other regions of residual electron density (perhaps solvent molecules), is by the computation of a Fourier difference synthesis:

$$\Delta\rho = \frac{1}{V} \sum_h \sum_k \sum_l (|F_{\text{obs}}| - |F_{\text{calc}}|) \cdot \exp(i\phi_c) \cdot \exp[-2\pi i(hx + ky + lz)]$$

where  $\phi_c$  is the phase of  $F_{\text{calc}}$ .

The positional and thermal parameters of an approximate solution are refined, i.e. adjusted, normally by least-squares methods, until the calculated structure amplitudes agree as well as possible with the observed values. A measure of the average agreement between the amplitudes is the R factor:

$$R = \frac{\sum ||F_{\text{obs}}| - |F_{\text{calc}}||}{\sum |F_{\text{obs}}|}$$

Other measurements of accuracy of structural details are found in the standard deviations, statistically determined, for each of the atomic parameters. An analysis has been described as complete if a final difference synthesis shows nothing but random fluctuations.

PART I. CRYSTALLOGRAPHIC STUDIES OF METHYL 3-C-  
(CARBOMETHOXYMETHYL)-4,6-DI-O-p-CHLORO-  
BENZOYL-2,3-DIDEOXY- $\alpha$ -D-RIBO-HEXOPYRANOSIDE.



## A. INTRODUCTION.

The title compound was prepared by Rosenthal and Catsoulacos <sup>8</sup> as a derivative of the product of a Wittig reaction on a 2-deoxy-3-ketose. The application of Wittig's reaction in this way provided another method of preparation of branched-chain sugars; these compounds were of great interest after some antibiotics were found having branched-chain sugar substituent groups.

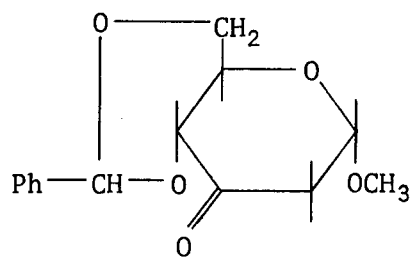
The ketose I was mixed with phosphonoacetic acid trimethyl ester and potassium t-butoxide in anhydrous N,N-dimethyl formamide at room temperature for 20 hours. The product was II, in good yield; only one of the two expected unsaturated (cis/trans) isomers was produced, and p.m.r. studies indicated that the product was probably trans methyl 4,6-O-benzylidene-3-C-(carbomethoxymethylene)-2,3-dideoxy- $\alpha$ -D-erythro-hexopyranoside (as shown).

Hydrogenation of II, using palladium on charcoal as catalyst, gave the reduced, and debenzylidated, product III. This was an oil and could not be crystallised, and its p.m.r. spectrum was indecipherable; therefore the di-(p-chlorobenzoate) derivative was prepared. Examination of the p.m.r. spectrum for this product indicated the structure IV. Microanalyses on compound IV gave the following results:

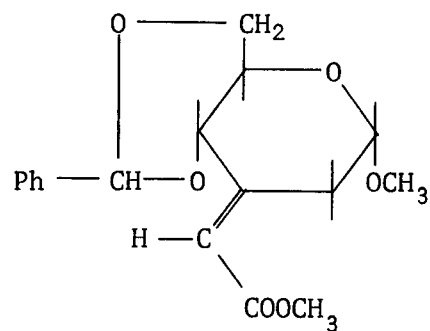
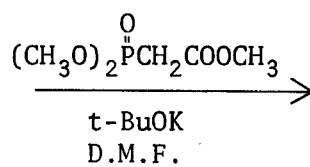
Calcd. for  $C_{24}H_{24}O_8Cl_2$  : C, 56.36 ; H, 4.69 %

Found : C, 56.35 ; H, 4.70 %.

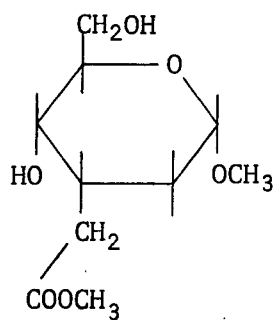
For confirmation that the di-(p-chlorobenzoate) indeed has the structure IV, crystals of the compound were submitted for analysis by X-ray crystallographic methods. An account of the attempts made to determine the molecular structure of this compound is given below.



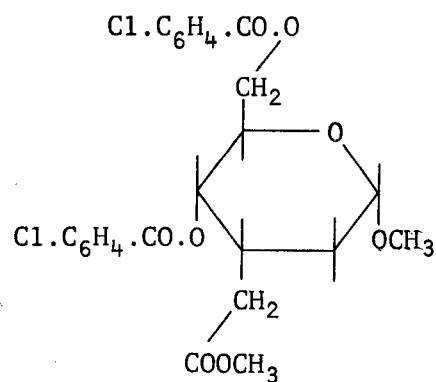
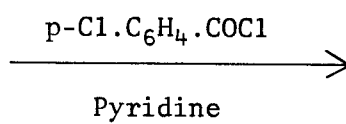
I.



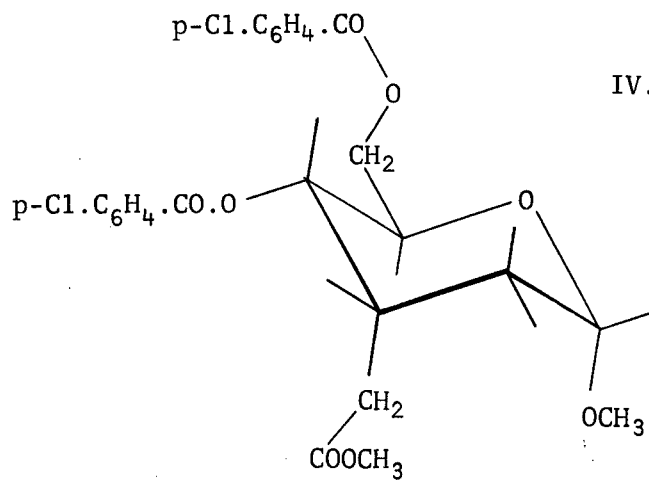
II.



III.



IV.



## B. X-RAY ANALYSIS.

The crystals of the title compound IV, from the laboratory of Drs. Rosenthal and Catsoulacos, had been recrystallised from ethanol, and were minute, colourless needles. Diffraction photographs were recorded on Weissenberg and precession cameras to determine the space group and approximate cell dimensions of the crystal. The cell dimensions were obtained more accurately later from a least-squares refinement based on the  $2\theta$  values of about 30 reflections measured on the diffractometer with Cu-K $_{\alpha}$  ( $\lambda = 1.5418 \text{ \AA}$ .) radiation.

### Crystal data:

Methyl 3-C-(carbomethoxymethyl)-4,6-di-O-p-chlorobenzoyl-2,3-dideoxy- $\alpha$ -D-ribo-hexopyranoside, (compound IV),  $C_{24}H_{24}Cl_2O_8$ .

$M = 511.26$

Monoclinic,  $a = 5.752(3)$ ,  $b = 15.436(3)$ ,  $c = 13.698(3) \text{ \AA}$ .,  $\beta = 93.74(3)^{\circ}$ ,  
(standard deviations in parentheses).

$V_c = 1213.6 \text{ \AA}^3$ .

$D_m = 1.43$  (by flotation in aqueous KI),  $D_c = 1.40 \text{ g.cm}^{-3}$ . with  $Z = 2$ .

$F(000) = 532$ .

Absorption coefficients,  $\mu(\text{Cu-K}_{\alpha}) = 28.1$  ;  $\mu(\text{Mo-K}_{\alpha}, \lambda = 0.7107 \text{ \AA}.) = 3.2 \text{ cm}^{-1}$ .

Reflections absent:  $0k0$  when  $k$  is odd; hence space group is  $P2_1$  or  $P2_1/m$   
(but the latter is not possible since the compound is optically active).

The X-ray photographs were not encouraging; even after many hours' exposure, the spots for reflections at angles corresponding to crystal plane spacings of  $1.7 \text{ \AA}$ . were not visible, whereas, for example, ethyl 3,5- dinitrobenzoate (see part IV) gave patterns for spacings down to  $0.9 \text{ \AA}$ .

Two sets of intensity data were collected on a G.E. XRD-6 automatic diffractometer, with scintillation counter, pulse-height analyser, and a

0-20 scan. The first collection was measured with Mo-K $\alpha$  radiation (with Zr filter), since the absorption of Mo-radiation is considerably less than that of Cu-radiation; the measurements were made at a scanning speed of 4°/minute, and counting backgrounds for 10 seconds before and after the scan. The second collection was taken with Cu-K $\alpha$  radiation (and Ni filter), which is the cleaner radiation; also the scanning speed was now 1°/minute, and the background measurements were taken over 40 seconds.

All the crystals of the sample examined were very small; the crystal mounted for the second collection of data had dimensions 0.25 × 0.05 × 0.04 mm<sup>3</sup>. Since this crystal was so small and approximately cylindrical, the absorption corrections would be small, and were therefore not applied.

Lorentz and polarisation factors were applied to the measured intensities, and the structure amplitudes were calculated. The Mo-data was not very satisfactory; the intensities of 566 reflections were measured, and of these, 255 were considered unobserved. The second set of data, measured with Cu-K $\alpha$  radiation, comprised 1028 independent reflections (i.e. for  $2\theta \leq 90.0^\circ$ , corresponding to a minimum interplanar spacing of 1.09 Å.), of which 130 were classified as unobserved, having  $I/\sigma_I < 2.0$ , where  $\sigma_I^2$  was defined:

$$\sigma_I^2 = S + B + (0.02.S)^2$$

where S = scan count, and B = background count over the same range.

A list of the observed structure amplitudes, scaled from the measured intensities by Wilson's method <sup>9</sup>, is given in Table I.



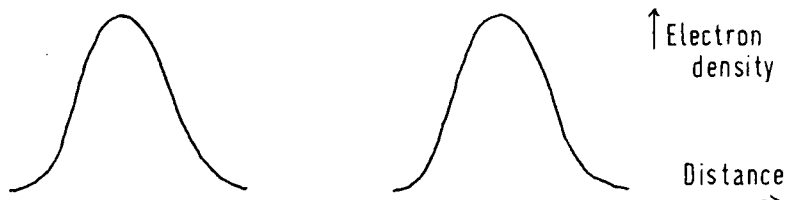
### C. ATTEMPTS AT STRUCTURE ANALYSIS.

From the structure amplitudes, a three-dimensional Patterson map was calculated. In the first instance, with the Mo-data, this map consisted of several large, diffuse peaks; there were no small, sharp, discrete peaks. The Patterson map from the Cu-data showed little improvement over that of the Mo-data.

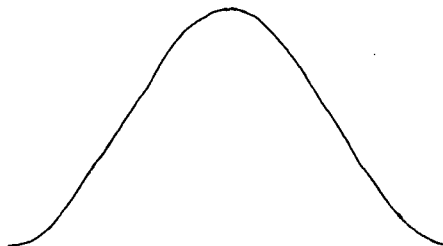
A peak in a Patterson map can be regarded as representing an inter-atomic vector, each such vector in the unit cell being removed so that one end lies at the origin of the map, the other end appearing as the peak. If there are  $n$  atoms in the unit cell, there will be  $n^2 - n$  peaks in the unit cell of the Patterson map, plus a large peak at the origin representing the sum of vectors between each atom and itself. Since either end of each inter-atomic vector can be removed to the origin, there is increased symmetry in the Patterson map ( $P2/m$  in our case) and this results in the asymmetric unit, which occupies half the unit cell in the molecular arrangement, now being only one quarter of the unit cell. Hence the Patterson map contains many more peaks and more symmetry than the fundamental unit cell, and it is from this more complex map that we wish to determine at least the coordinates of the chlorine atoms.

The magnitude of the vector peaks depends upon the numbers of electrons in the atoms responsible for that vector. If the atoms were point-size, the peak heights would be directly proportional to the product of the atomic numbers of the two atoms, e.g. a Cl...Cl peak would stand clearly above a C...C peak by a ratio of 289:36.

However, the atoms are not point-size, and two atoms with electron densities:



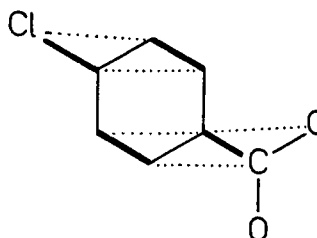
will produce a vector peak:



since vectors between all parts of the atoms are summed to give the vector peaks.

Thermal motion also has the effect of spreading the electron density over wide regions, so that vector peaks involving atoms which are vibrating to any extent will appear smeared, and of much lower magnitude than the product of atomic numbers would indicate. In our di-(p-chlorobenzoate) compound, the chlorine atoms are located furthest from the centre of the molecule; both of the p-chlorobenzoyl groups are probably free to vibrate, and will vibrate considerably, so that the Cl...Cl vectors could be very smeared and unrecognisable above the mass of vectors between the lighter atoms.

A further complication arises from the presence of fairly rigid and symmetric groups in the molecule. For example, in the p-chlorobenzoyl groups, there are several vectors of approximately equal length and nearly parallel, e.g. the thickened bonds and the dotted lines show two sets of similar vectors:



Thus, large peaks, the sums of several vectors, will appear in the map. These are often most prominent around the origin, but may occur elsewhere when there are parallel groups or groups related by a centre of symmetry in the molecule or between molecules.

Hence the location of Cl...Cl vectors in the Patterson map was not straightforward; there were no outstanding peaks in the map - the chlorine

atoms (i) were not heavy enough to stand out above the lighter atom vectors, and (ii) were far from the centre of the molecule and probably vibrating considerably.

However, regions of high intensity in the Patterson map were investigated as containing possible Cl...Cl vectors. There are two chlorine atoms in the molecule, and two molecules per unit cell. Let the two chlorine atoms in the molecule have coordinates  $(x_1, y_1, z_1)$  and  $(x_2, y_2, z_2)$ ; then, according to the symmetry of the space group  $P2_1$ , there are chlorine atoms also at  $(\bar{x}_1, y_1+\frac{1}{2}, \bar{z}_1)$  and  $(\bar{x}_2, y_2+\frac{1}{2}, \bar{z}_2)$ . Hence there are Cl...Cl vectors at:

$$\left. \begin{array}{l} 2x_1, \frac{1}{2}, 2z_1 \\ 2x_2, \frac{1}{2}, 2z_2 \end{array} \right\} \begin{array}{l} \text{These are Harker peaks, found on the Harker} \\ \text{section at } y = \frac{1}{2} \end{array}$$

$$x_1-x_2, y_1-y_2, z_1-z_2$$

$$x_1+x_2, y_1-y_2+\frac{1}{2}, z_1+z_2$$

and in positions related to these by the symmetry of the vector map,  $P2/m$ .

Several pairs of possible coordinates were determined for the chlorine atoms from the Mo-data Patterson map, and the best possibilities appeared to be:

	Cl(1)	Cl(2)
Pair A	(0.03, 0.0, 0.16)	(0.09, 0.48, 0.14)
Pair B	(0.0, 0.0, 0.0)	(0.08, 0.07, 0.65)

Each of these pairs was used in the calculations of structure factors and electron-density maps, but neither map produced any encouraging results. A further problem encountered here was that the chlorine atoms, in each case, have similar y-coordinates, and this feature gives rise to pseudo mirror-plane symmetry in the electron-density maps.

Although no part of the molecule was really obvious in these maps, certain groups were found in not unreasonable positions, and these were used



in phasing further electron-density maps. In these, certain peaks persisted, but no definite signs of the molecular structure were apparent. One would have thought that if the Cl-atoms were in approximately the correct positions, then at least the atoms close to the Cl-atoms would have appeared in the maps, but no complete benzene ring was ever seen. However, the computation of electron-density maps continued, using the persistent atoms (with scattering factors of oxygen atoms), the original chlorine atoms and some possible benzene ring atoms; but no real progress was made.

There is one outstandingly strong reflection in the data, the 103 reflection. The interplanar spacing for the (103) plane is  $3.53 \text{ \AA}$ , and it seems reasonable that both the p-chlorobenzoyl groups should lie in this plane. The Patterson function in this plane was examined and some peaks were found to correspond with possible interatomic vectors of the groups lying in this plane; there appeared to be peaks corresponding to only one orientation of the group, and it is therefore possible that if the two groups are in this plane, then they are either parallel or related by a centre of symmetry. An electron-density map was computed, based on two chlorine atoms in this plane at  $(0.0, 0.0, 0.0)$  and  $(0.124, 0.0, 0.292)$ , and a benzoyl group from the first chlorine atom. But there were no other recognizable features in the map.

Two attempts were made to "sharpen" the Patterson map. In this process, the scattering factors,  $f$ , for the atoms are adjusted so that they approximately represent point-atoms-at-rest, rather than atoms of finite size having some thermal motion. In a crystal containing only one kind of atom, the problem is quite easily overcome, but for most crystals, containing several types of atoms, the problem is not so straightforward. In our examples, the Mo-data was sharpened using a factor of

$$\left( \frac{z_{\text{Cl}}}{f_{\text{Cl},0} \cdot \exp[-B(\sin^2\theta)/\lambda^2]} \right)^2$$

on the intensity data. This factor assumes that the chlorine atoms are the dominating atoms in the molecule, and that their vibrations are characteristic of the other atoms in the molecule. This is only a rough approximation but a map of more discrete peaks was obtained.

This map was superseded by an  $(|E|^2 - 1)$  Patterson of the Cu-data. This function multiplies the intensities by the sharpening factor:

$$\frac{k}{\sum_j f_j^2}$$

where  $k$  is a constant which puts the data on an absolute scale, and is determined by Wilson's method <sup>9</sup>; and where  $f_j$  is the scattering factor, corrected for thermal motion, for the  $j$ th atom in the unit cell, and the summation is over all the atoms in the unit cell. In this Patterson map, the origin peak has been removed, and the resolution of peaks which previously appeared as shoulders in the origin peak is now much improved.

Investigation of the last map led to the computing of a series of electron-density maps which will be outlined here. Three pairs of possible chlorine atom coordinates were first determined:

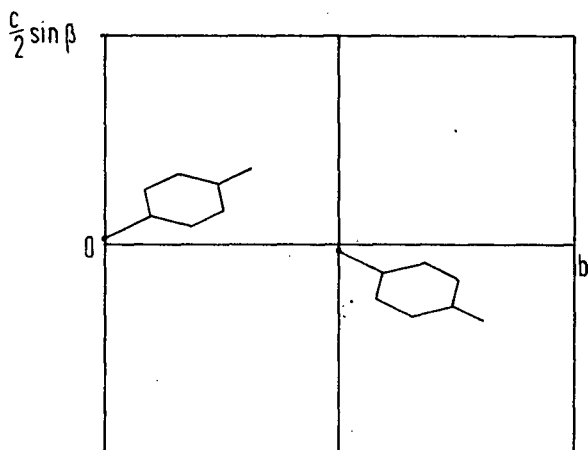
	Cl(1)	Cl(2)
(i)	(0.013, 0.0, 0.013)	(0.14, 0.04, 0.297)
(ii)	(0.045, 0.48, 0.161)	(0.225, 0.0, 0.136)
(iii)	(0.04, 0.02, 0.009)	(0.31, 0.0, 0.306)

Pairs (i) and (iii) have one chlorine atom with almost identical  $x$ - and  $z$ -coordinates, while the second chlorines of each pair are separated by about 1 Å.

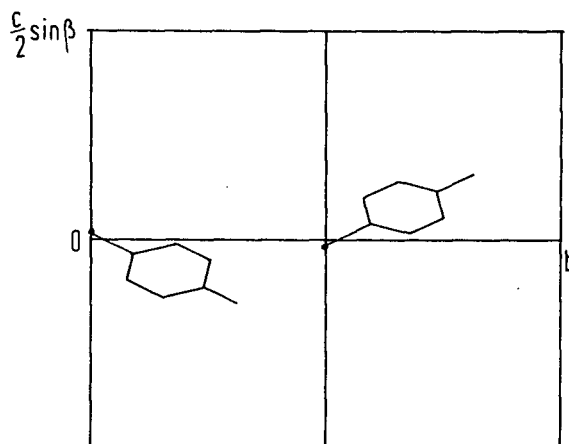
The peaks close to the origin indicated several vectors in a single plane, and the coordinates of all the carbon atoms in a benzoyl group were determined from these and other peaks in this plane. Since there was only

one prominent plane of peaks in the Patterson map, it was assumed that both of the benzoyl groups lay in this plane (which was close to the (103) plane).

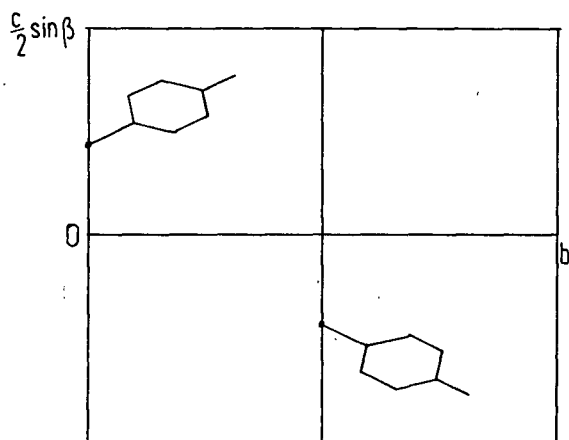
Initially, electron-density maps were calculated using the seven carbon atoms attached to a chlorine atom in each of the two possible ways, with the chlorine atoms at (0.013, 0.0, 0.013) and then (0.225, 0.0, 0.136):



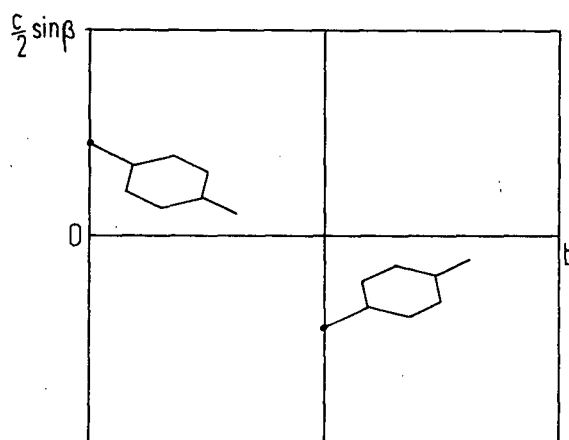
Group A



Group B



Group C

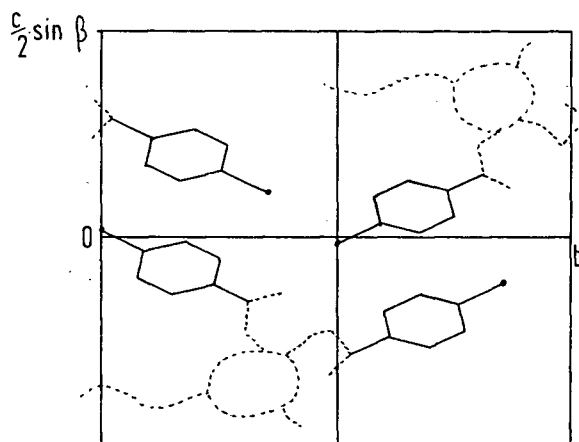


Group D

Group A's map had the strongest new peak appearing, as hoped, at (0.15, -0.004, 0.298), but at only  $1.7 \text{ e}\text{\AA}^{-3}$ . The map of group B also showed its strongest new peak in the anticipated second chlorine position (0.12, 0.020, 0.297), at  $1.9 \text{ e}\text{\AA}^{-3}$ . Similarly for group C, the second chlorine showed at  $2.2 \text{ e}\text{\AA}^{-3}$ , at (0.040, 0.495, 0.160).

However, when second electron-density maps were computed using, to determine the  $F_0$  phases, the two chlorine atoms plus the seven carbon atoms in arrangements A, B and C, there were negligible improvements in the R-factors, and no further parts of the molecule obvious in the electron-density maps.

The initial map for group B (using one chlorine atom) showed the possibility of a second ring system starting from the second chlorine atom, but there was no sign of this ring in the second electron-density map. Also, having the second ring in that position appeared geometrically impossible - there was no way in which the rest of the molecule could reasonably be fitted into the system. After a comparison of the first maps of groups B and C, another map was calculated which had group B as before, with the second ring related by a centre of symmetry at (0.32, 0.178, 0.070), i.e. with the chlorine atom at (0.62, 0.355, 0.114), and the anticipated second chlorine of group B and a peak at (0.29, -0.005, 0.312) as the C=O atoms of the carboxyl group. This arrangement looked geometrically feasible:



Also favouring this type of arrangement, in which there is a certain amount of centrosymmetry, are the "E-statistics" which are shown in Table II. Although the space group is undoubtedly  $P2_1$ , and therefore noncentrosymmetric, the statistics show values which indicate some centrosymmetry, e.g. the mean

Table II.

Results from the Wilson Plot, for the Cu-data.

Overall temperature factor,  $B = 5.42 \text{ \AA}^2$ .

E-Statistics:

	Observed	Theoretical	
		Centro-	Noncentro-symmetric
Mean $ E $	0.860	0.798	0.886
Mean $ E ^2$	1.028	1.000	1.000
Mean $  E ^2 - 1 $	0.844	0.968	0.736
Percentage of reflections			
with $ E  > 3$	0.29	0.30	0.01
" " $ E  > 2$	3.60	5.0	1.80
" " $ E  > 1$	33.7	32.0	37.0

$||E|^2 - 1|$  value is close to the mean of the theoretical centrosymmetric and noncentrosymmetric values, and the proportions of the reflections with higher  $|E|$ 's correspond more to the centrosymmetry values. The relation of two p-chlorobenzoate groups by a centre of symmetry would probably help to explain the statistics' deviation from the theoretical values.

However, again, the R-factor and structure factors appeared negligibly improved, and the electron-density map seemed to have peaks (about  $1 \text{ e}\text{\AA}^{-3}$ .) scattered randomly with no obvious pyranose (or furanose) rings.

Here the analysis by examination of the Patterson maps ended. The heavy atoms, the two chlorine atoms, were not sufficiently heavy. Even if we had, at some stage, determined the coordinates of the chlorine atoms fairly accurately, it is possible that these atoms were not sufficiently dominating in the structure, i.e. the phases based on the chlorine atoms alone were not a good enough approximation to the actual phases, and the electron-density maps therefore could not indicate the rest of the molecule.

A convenient guide as to how heavy the dominating atoms should be is the  $z^2$  ratio. A problem should be easily soluble by the heavy atom method if

$$\frac{\sum z_{\text{heavy}}^2}{\sum z_{\text{light}}^2} \approx 1$$

In our case, the ratio is 0.41, when the chlorines were considered the heavy atoms. This result is low, but far higher than for some cases in which the problem has been solved (if with difficulty), e.g. vitamin B<sub>12</sub>, where the ratio was 0.17. The major problem in our case is probably that the coordinates of the chlorine atoms cannot be determined accurately enough from the Patterson map, and this is primarily because these atoms are both located at the ends of large, vibrating groups.

An alternative approach to solution was then attempted using direct methods, the statistical determination of the phases of the structure factors directly from the structure amplitudes. The procedures for structure determination in the centrosymmetric case are well established <sup>6</sup> and fairly easy to apply; essentially, one determines the phases (which must be either 0 or  $\pi$ ) of the structure factors by consideration of the phases of reflections with related indices. The phases of 0 and  $\pi$  correspond to the signs + and - of the structure factors.

But in the noncentrosymmetric case, the phase determination is more complicated since each phase can take any value between  $-\pi$  and  $+\pi$ . In the last few years, J. Karle, H. Hauptman and I. Karle have developed the Symbolic Addition Procedure <sup>7</sup> for the phase determination for both centrosymmetric and noncentrosymmetric crystals, and it was by using a computer program <sup>10</sup> based on this procedure, that we tried to solve the structure of our sugar derivative.

The intensity data (with Cu-K $\alpha$  radiation) of our compound were scaled to the absolute values of the structure amplitudes by Wilson's method <sup>9</sup>. The normalised structure amplitudes,  $|E|$ 's <sup>7</sup>, were then determined, and the E-statistics for the data were compared with theoretical values <sup>11</sup>. These statistics are shown in Table II. A list of  $\Sigma$ -2 relationships amongst the reflections with  $|E| > 1.3$  was prepared; for every reflection  $hkl$ , pairs of reflections  $h'k'l'$  and  $h-h', k-k', l-l'$  were recorded when  $|E|$  for each of the three reflections was greater than 1.3.

The next step was the selection of three origin-determining reflections. In the space group  $P2_1$ , the origin may be put on any of the four lines  $(0, y, 0)$ ,  $(0, y, \frac{1}{2})$ ,  $(\frac{1}{2}, y, 0)$  or  $(\frac{1}{2}, y, \frac{1}{2})$ . One of these lines is chosen by selecting, and assigning phases to, two  $h0l$  reflections in which the (odd-even) parities of  $h_1l_1$  are different from  $h_2l_2$ , and neither have  $h$  and  $l$  both even. From a consideration of the real and imaginary terms

of the structure factors in the space group  $P2_1$ , the phases of the  $h0\ell$  structure factors must be chosen as 0 or  $\pi$ . The origin is then fixed at a point on the selected line by assigning any phase to any  $hkl$  reflection in which the index  $k$  is not zero; for convenience in the phase-determination procedure, it is suggested that  $h$  and  $\ell$  are both even, and that  $k=1$  for this third reflection.

Having selected three origin-determining reflections, a further three (or more) reflections are chosen and assigned symbols  $a$ ,  $b$ ,  $c$  (etc.) for their phases. Reflections with high  $|E|$  values and with indices entering into as many  $\Sigma$ -2 relationships as possible are chosen here. The symbolic addition procedure calculates the phases of other reflections which have  $\Sigma$ -2 relationships with the reflections of known phase; and the phases are calculated in terms of the three assigned values for the origin-specifying reflections, and of the three (or more) symbols. In our examples, several triplets of reflections were used to specify the origin, e.g.  $(103, 20\bar{1}, 216)$ ,  $(103, 20\bar{1}, 136)$ ,  $(103, 106, 310)$ ,  $(103, 102, 310)$ ,  $(103, 20\bar{1}, 113)$  and  $(103, 20\bar{1}, 016)$ . Reflections selected to have symbols in the procedure included those with indices  $023$ ,  $16\bar{4}$ ,  $20\bar{1}$ ,  $102$  and others mentioned above.

The computer program written to calculate the phases, determined sets of phases; the symbols  $a$ ,  $b$ , and  $c$  were each given several values between  $-\pi$  and  $+\pi$  in the program and a series of computations was made, giving one set of phases for each combination of starting values of  $a$ ,  $b$ , and  $c$ .

One of the symbols was allowed starting values restricted to the range 0 to  $\pi$ ; this had the effect of selecting one of the two possible enantiomorphs allowed in the space group and by the data.

The program had provision for the determination of phases for about 200 of the largest  $|E|$  reflections in the data. For our compound, the program was used several times, generally with the 182 reflections for which  $|E| > 1.3$  (in the Cu-data). The phases for these reflections were calculated



using the tangent formula of Karle and Hauptman <sup>12</sup>:

$$\tan \phi_h \sim \frac{A}{B}$$

where:

$$A = \sum_k |E_k| |E_{h-k}| \cdot \sin (\phi_k + \phi_{h-k})$$

$$B = \sum_k |E_k| |E_{h-k}| \cdot \cos (\phi_k + \phi_{h-k})$$

and the subscripts h, k and h-k correspond to the indices hkl, h'k'l', and h-h', k-k', l-l';

$\phi_h$  is the phase of reflection hkl, etc.;

"~" means "probably equal to".

Each reflection, h, in the list is examined in turn, and a phase is determined for it from the previously known phases of pairs of  $\Sigma$ -2 related reflections. After this initial examination of each reflection, the process is repeated, using, in the second cycle, those phases calculated in the first cycle. This is continued through several cycles until most of the phases have been determined and there is little change from cycle to cycle in the values of the calculated phases.

There are various criteria which must be satisfied for a new phase to be accepted - the consistencies  $t_h$  and  $\alpha$  of the new angle have to exceed certain arbitrary values, normally 0.25 and  $1.25\sqrt{N}$  respectively (N is the number of atoms in the unit cell); the consistencies are defined:

$$t_h = \frac{\sqrt{A^2 + B^2}}{\sum_k |E_k| \cdot |E_{h-k}|} \quad \alpha = |E_h| \cdot \sqrt{A^2 + B^2}$$

$t_h$  must have a value between 0 and 1. The consistency  $\alpha$  is related to the variance V of Karle and Karle <sup>7</sup>, and is derived from the probability distribution of addition pairs of phases,  $\phi_k + \phi_{h-k}$ .

If a new phase angle satisfies these criteria, it is used in the determination of phases of other reflections in the following cycle. Should the calculation of a phase angle in successive cycles differ by more than a certain amount (usually 125 millicycles, i.e.  $\pi/4$ ), the phase is considered

unknown in the following cycle, i.e. it is not used in the determination of further phases, but will be recalculated during that following cycle.

At the end of each cycle, the program computed average values of the consistencies, and an R-factor:

$$R' = \frac{\sum_h |E_h| \cdot (1 - t_h)}{\sum_h |E_h|}$$

and these values were compared in the several sets of phases produced by the program, to select the most likely correct set.

Then, using the calculated phases of the most likely set, an E-map was computed; an E-map is a Fourier synthesis in which the coefficients are E's rather than the usual structure factors, F's. It is hoped that some recognizable parts of the molecule will be apparent in the E-map, and that the more prominent peaks correspond to atoms. Sometimes, however, the first E-map computed does not show anything of sense, and it is recommended that one calculate E-maps using other sets of phases until the molecule is apparent.

In each series of sets of phases calculated for our sugar derivative, there was never one set which stood out as being more consistent than the others, and there was often a choice between two or three sets as to which one might be most likely the correct set of phases. Consequently, several E-maps were computed and examined. In some maps, parts of p-chlorobenzoate groups could be discerned, and in others, pyranose rings were more obvious; but in no cases were there any real indications of the molecule. Some peaks were persistent from one map to another, and these were used, with possible ring fragments of the molecule, in subsequent structure factor and electron-density map calculations.

The most probable position for one of the p-chlorobenzoate groups appeared to be very similar to that of group B of page 19, but the other p-chlorobenzoate group and the pyranose ring were never apparent in any

geometrically suitable position relative to the first group.

After considerable investigation by these methods, the structure determination of the branched-chain sugar derivative IV was halted for the present time.

#### D. CONCLUSIONS.

At the time of writing, the structure of the title compound, IV, has not been determined. Since considerable time and computing funds have already been spent on this analysis without any significant progress visible, alternative approaches to the problem of confirming the branch-chain configuration and the pyranose conformation of the compound are required.

It was wondered, quite early in the investigation, whether an alternative derivative of the sugar was available. The di-(p-chlorobenzoate) was the end product of a series of reactions, and had been produced in minute quantities; the synthesis of, say, the di-(p-iodobenzoate), or the replacement of the two p-chlorobenzoate groups by some other group, was not feasible at the time.

The removal of the huge p-chlorobenzoate groups and the preparation of crystals of a smaller, "equal atom" derivative molecule (the parent sugar was an oil), would possibly allow solution more easily by direct methods. One of the problems of using the direct methods as outlined in previous pages, was that the formulae used in the symbolic addition procedure had been developed for use in equal-atom structures (here the hydrogen atoms are ignored, and the carbon and oxygen atoms are considered to be equal). It has been argued <sup>13</sup> that, in general, the phase-determination amongst the reflections of high  $|E|$ 's should not be affected by the presence of unequal atoms; probability and consistency formulae will be affected a little, but this should not upset the actual calculation of phases.

Other possible reasons why the structure has not been solved have

been suggested in previous parts of this discussion.

A further outstanding possibility is that there is disorder in the crystal. There is no overall rigidity in the molecular model of our compound, and one can readily suggest that there may be more than one arrangement of one or both of the large p-chlorobenzoate groups. If there is disorder involving the chlorine atoms, then, of course, one cannot expect to find Cl...Cl vectors nor indeed any part of the p-chlorobenzoate group in the Patterson map. And in the E-maps, the search would be for several weak groups, some groups possibly overlapping others - very difficult to decipher.

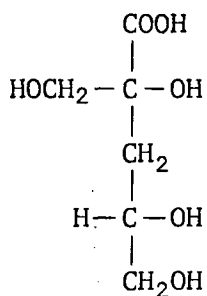
It has been assumed through most of this work that the monosaccharide unit has the pyranose ring configuration; however, the possibility of a furanose ring configuration has not been disregarded and in electron-density and E-maps, any obvious five-member ring was considered as the basis of a furanose compound.

Crystallographic investigation on the present derivative has been suspended; it is recommended that the structure of the branched-chain sugar be confirmed from an alternative derivative, or by some other method.

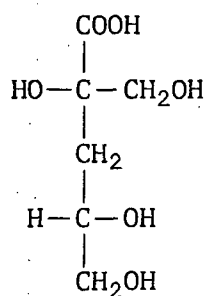
PART II. THE STRUCTURE DETERMINATION OF  
5-O- (p-BROMOBENZENESULPHONYL)-2,2'-O-  
CYCLOHEXYLIDENE-3-DEOXY-2-C-HYDROXYMETHYL-  
D-ERYTHRO-PENTONO-1,4-LACTONE.

## A. INTRODUCTION.

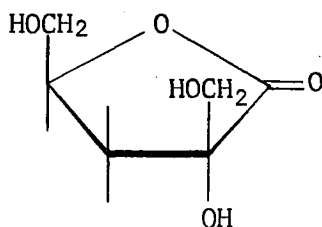
The saccharinic acids are formed by treatment of reducing sugars with alkali, and their formation and chemistry have been reviewed <sup>14,15</sup>. Since their preparation involves a rearrangement during which a new asymmetric centre is produced, there are two possible isomers of each type of saccharinic acid. Reaction of 4-O-substituted D-glucoses with alkali <sup>16</sup> yields " $\alpha$ "-D-isosaccharinic acid, 3-deoxy-2-C-hydroxymethyl-(D-erythro or D-threo)-pentonic acid (I or II), the configuration at C-2 being uncertain. The present crystal structure analysis of a derivative of the lactone of this acid, obtained by alkaline degradation of cellulose, was undertaken to determine the molecular structure, with particular interest in the configuration at C-2. The compound studied has been shown to be 5-O-(p-bromobenzenesulphonyl)-2,2'-O-cyclohexylidene-3-deoxy-2-C-hydroxymethyl-D-erythro-pentono-1,4-lactone, so that " $\alpha$ "-D-isosaccharino-1,4-lactone has structure III, and " $\alpha$ "-D-isosaccharinic acid has the D-erythro configuration I. While this work was in progress the D-erythro configuration was established independently by crystal structure analyses of calcium and strontium " $\alpha$ "-D-isosaccharates <sup>17,18</sup>.



I.



II.



III.

## B. X-RAY ANALYSIS.

$\alpha$ -D-isosaccharinic acid was obtained by alkaline degradation of cellulose, and a p-bromobenzenesulphonyl cyclohexylidene derivative of the  $\gamma$ -lactone was prepared for X-ray analysis. Crystals of the derivative are colourless plates with (001) developed. Unit cell and space group data were determined from rotation, Weissenberg, and precession photographs, and the lattice parameters were obtained more accurately by least-squares refinement based on the  $2\theta$  values for thirty reflections measured on the diffractometer with Cu-K $_{\alpha}$  ( $\lambda = 1.5418 \text{ \AA}$ .) radiation.

### Crystal data:

5-O-(p-bromobenzenesulphonyl)-2,2'-O-cyclohexylidene-3-deoxy-2-C-hydroxy-methyl-D-erythro-pentono-1,4-lactone,  $C_{18}H_{21}BrO_7S$ .

$M = 461.3$

Monoclinic,  $a = 5.757(2)$ ,  $b = 10.586(3)$ ,  $c = 16.021(6) \text{ \AA}$ .,  $\beta = 98.85(3)^{\circ}$ ,  
(standard deviations in parentheses).

$V_c = 964.7 \text{ \AA}^3$ .

$D_m = 1.58$  (by flotation in aqueous KI),  $D_c = 1.59 \text{ g.cm}^{-3}$ . with  $Z = 2$ .

$F(000) = 472$ .

Absorption coefficient,  $\mu(\text{Cu-K}_{\alpha}) = 45 \text{ cm}^{-1}$ .

Absent reflections:  $0k0$  when  $k$  is odd. Space group is  $P2_1$  ( $P2_1/m$  is excluded since the crystals are optically active).

The intensities of the reflections were measured on a Datex-automated G.E. XRD-6 Diffractometer, with a scintillation counter, Cu-K $_{\alpha}$  radiation (Ni filter and pulse-height analyser), and a  $\theta$ - $2\theta$  scan. Of 1319 reflections with  $2\theta(\text{Cu-K}_{\alpha}) \leq 111^{\circ}$  (minimum interplanar spacing  $0.94 \text{ \AA}$ .), 1140 (86.4%) had net intensities greater than half the minimum background, and these were treated as observed; the remaining 179 reflections were

classified as unobserved, and were included in the analysis with  $|F_0| = 0.6.F(\text{threshold})$ . The crystal used was a plate, elongated along a with cross-section  $0.2 \times 0.03 \text{ mm}^2$ , and it was mounted with a\* parallel to the  $\phi$ -axis of the goniostat. It was not possible to grow thicker specimens. Since the crystal is very thin, absorption errors are not serious, except in a few narrow regions of reciprocal space where errors of up to about 20% in  $|F_0|$  are possible. Since the errors for most reflections are much smaller, no absorption correction was made. Lorentz and polarisation factors were applied and the structure amplitudes were derived.

### C. STRUCTURE ANALYSIS.

The bromine and sulphur atom positions were determined from the three-dimensional Patterson function, and all the carbon and oxygen atoms were located on an electron-density map. The structure was refined by block-diagonal least-squares methods, with minimisation of  $\sum w(|F_0| - |F_c|)^2$ , with  $\sqrt{w} = 1$  for the unobserved reflections and when  $|F_0| \leq F^*$ , and  $\sqrt{w} = F^*/|F_0|$  when  $|F_0| > F^*$ .  $F^*$  was initially taken as 30, but examination of  $w\Delta^2$  in the final stages of refinement indicated that  $F^* = 20$  was appropriate. The scattering factors of the International Tables <sup>5c</sup> were used. Refinement with isotropic thermal parameters gave  $R = 0.14$ , and anisotropic refinement of all atoms gave a final  $R$  of 0.10.

During the refinement, the isotropic temperature factors of two carbon atoms, C(14) and C(15) - see figure 1. - were noted to be abnormally low; these values were adjusted to  $4.0 \text{ \AA}^2$ , but in subsequent least-squares cycles, they decreased again. The temperature factor for C(14) did increase before the refinement was complete, but that for C(15) remained low.

A final difference synthesis revealed some of the hydrogen atoms, but these were not introduced into the refinement since many of them could not be positioned accurately, and other areas of equally high electron-



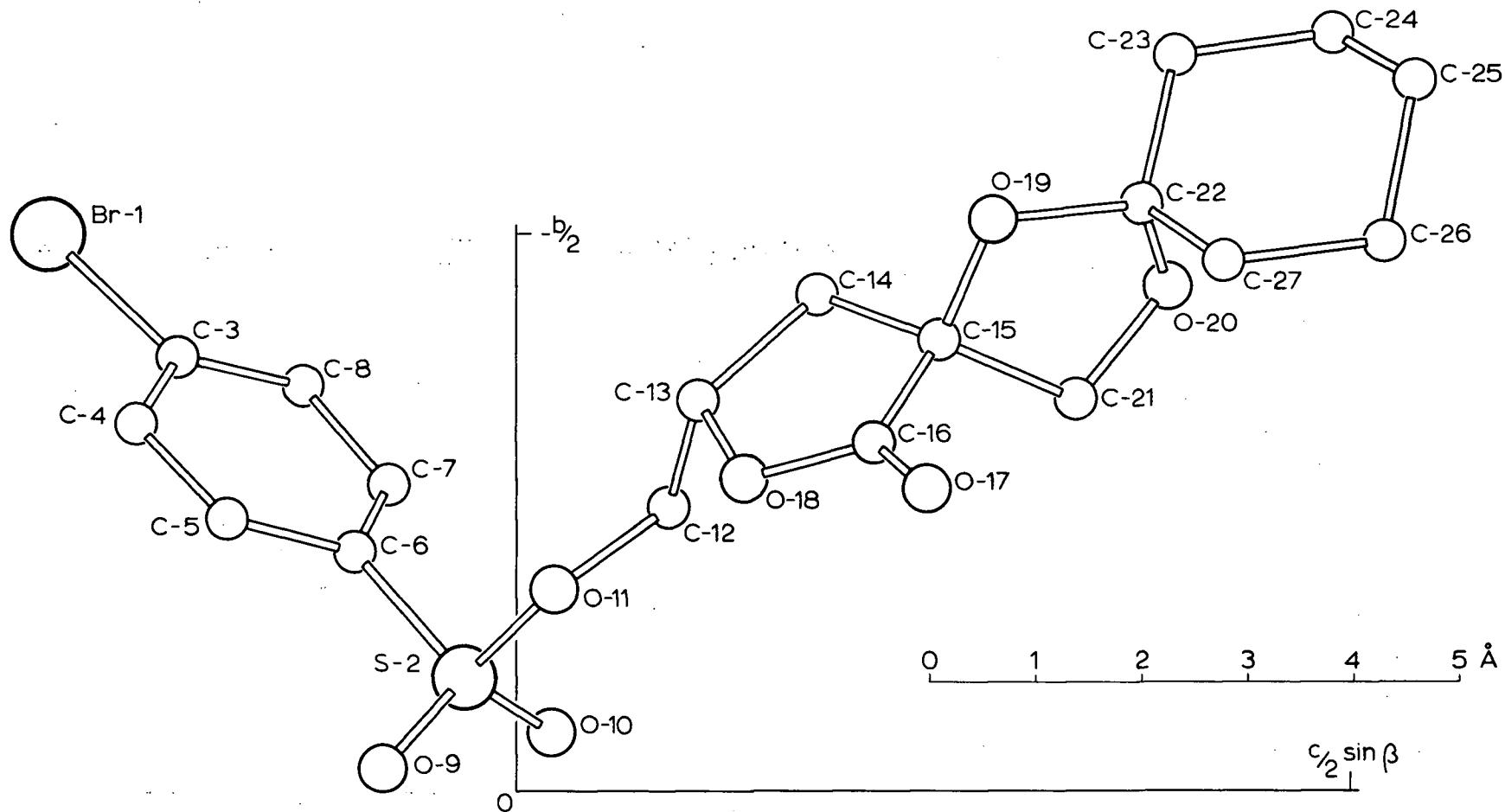


Figure 1. View of the molecule. The positive direction of the a axis is towards the viewer, and the correct absolute configuration is shown. The atom numbering is for convenience in the crystal analysis.

density ( $\sim 0.6 \text{ e}\text{\AA}^{-3}$ .) appeared spuriously in the difference map.

The final positional and thermal parameters are in Table III, and the measured and calculated structure factors are recorded in Table IV.

#### D. DISCUSSION.

A view of the molecule is shown in Figure 1., where the atom numbering is for convenience in the crystal analysis. The compound was prepared by alkaline degradation of cellulose, via a series of reactions <sup>14,15</sup> which involves no change in the configuration at C(13) of Figure 1. The absolute configuration of the molecule is therefore established, and is correctly depicted in Figure 1., and in the parameters of Table III referred to a right-handed set. The derivative studied is 5-O-(p-bromobenzene-sulphonyl)-2,2'-O-cyclohexylidene-3-deoxy-2-C-hydroxymethyl-D-erythro-pentono-1,4-lactone. Of particular interest is the configuration at C(15) of Figure 1. (C-2 in the chemical numbering system), and the analysis has established structure III for " $\alpha$ "-D-isosaccharino-1,4-lactone, and the D-erythro configuration, I, for " $\alpha$ "-D-isosaccharinic acid. This result is in agreement with the configuration determined by crystal structure analyses of calcium and strontium " $\alpha$ "-D-isosaccharates <sup>17,18</sup>.

Both of the five-membered rings in the molecule have envelope conformations, four of the atoms in each ring being approximately coplanar, with the fifth atom displaced. The relevant information about the planes is given in Table V. The envelope conformation of the 1,3-dioxolane ring is similar to that found in various cyclopentane derivatives, with atom O(20) deviating by  $0.49 \text{ \AA}$ . from the plane of the other four atoms of the ring. In the  $\gamma$ -lactone ring, C(15) [C-2 in the chemical numbering], is displaced by  $0.14 \text{ \AA}$ . from the plane of the other four atoms - a less prominent envelope conformation; O(17) is displaced by  $0.12 \text{ \AA}$ . in the opposite direction, the configuration around C(16) being planar. The dihedral angle between the two

Table III.

Final atomic parameters.

(a) Fractional atomic coordinates, (standard deviations in parentheses):

	x	y	z
Br(1)	-0.5089(6)	0.4976(4)	-0.2814(2)
S(2)	0.0615(7)	0.8985(5)	-0.0324(3)
C(3)	-0.3281(32)	0.6091(19)	-0.2042(11)
C(4)	-0.1389(42)	0.6691(22)	-0.2289(14)
C(5)	-0.0072(36)	0.7552(22)	-0.1751(12)
C(6)	-0.0893(26)	0.7848(16)	-0.0981(10)
C(7)	-0.2826(29)	0.7253(20)	-0.0777(12)
C(8)	-0.4105(29)	0.6357(16)	-0.1290(11)
O(9)	0.1784(22)	0.9796(15)	-0.0811(8)
O(10)	-0.0928(23)	0.9474(12)	0.0204(8)
O(11)	0.2670(19)	0.8198(13)	0.0225(7)
C(12)	0.2075(29)	0.7467(21)	0.0916(10)
C(13)	0.4142(28)	0.6504(16)	0.1095(10)
C(14)	0.3795(29)	0.5557(19)	0.1812(10)
C(15)	0.5810(22)	0.5969(16)	0.2545(9)
C(16)	0.7250(25)	0.6892(16)	0.2155(9)
O(17)	0.9129(20)	0.7307(14)	0.2469(7)
O(18)	0.6233(18)	0.7203(11)	0.1373(6)
O(19)	0.7142(19)	0.4884(13)	0.2865(7)
O(20)	0.5130(21)	0.5496(13)	0.3900(7)
C(21)	0.5011(31)	0.6501(22)	0.3356(12)
C(22)	0.7138(27)	0.4754(17)	0.3748(8)
C(23)	0.6696(35)	0.3411(20)	0.3952(12)
C(24)	0.6717(41)	0.3224(19)	0.4894(15)
C(25)	0.9109(44)	0.3658(23)	0.5378(12)
C(26)	0.9424(42)	0.5089(30)	0.5194(13)
C(27)	0.9404(35)	0.5262(20)	0.4235(12)

(b) Anisotropic thermal parameters, in the form:

$$\exp [-2\pi^2 \cdot 10^{-4} (U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}\ell^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}h\ell a^*c^* + 2U_{23}k\ell b^*c^*)]$$

	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>12</sub>	U <sub>13</sub>	U <sub>23</sub>
Br(1)	1232	592	842	-226	-310	- 83
S(2)	244	282	401	- 13	- 11	103
C(3)	510	394	366	51	-304	- 62
C(4)	821	382	689	-169	139	45
C(5)	586	508	453	- 63	-144	109
C(6)	243	270	336	42	- 5	113
C(7)	297	560	574	13	5	228
C(8)	403	257	446	147	- 14	-128
O(9)	450	564	618	- 22	- 76	305
O(10)	568	301	555	60	- 8	- 38
O(11)	342	542	338	70	83	239
C(12)	357	595	305	84	49	15
C(13)	340	256	413	-136	-139	132
C(14)	396	479	314	-165	- 87	159
C(15)	82	395	249	51	- 17	- 9
C(16)	252	256	333	30	74	- 93
O(17)	366	638	385	- 82	28	- 24
O(18)	291	307	287	80	- 38	8
O(19)	409	335	422	61	- 39	- 57
O(20)	554	465	410	116	136	127
C(21)	397	555	524	73	45	46
C(22)	386	411	156	- 44	125	- 28
C(23)	691	441	527	-323	77	178
C(24)	760	241	928	- 60	111	291
C(25)	1079	592	306	-265	-154	160
C(26)	838	808	503	- 76	-149	- 87
C(27)	580	421	527	- 17	-291	95

Table IV.

Measured and calculated structure amplitudes. Measured values with negative sign indicate unobserved reflections.

k l		F <sub>obs</sub> F <sub>calc</sub>		h = 0		h = 1		h = 2		h = 3		h = 4		h = 5	
0	1	36.0	52.4	11	1	15.5	10.4	8	-4	13.0	12.2	6	0	12.2	11.6
0	2	15.5	10.4	9	2	15.5	10.4	8	-4	13.0	12.2	6	0	12.2	11.6
0	3	11.6	10.4	7	3	11.6	10.4	6	-3	11.6	10.4	5	-1	11.6	10.4
0	4	10.4	10.4	6	4	10.4	10.4	5	-2	10.4	10.4	4	-2	10.4	10.4
0	5	10.4	10.4	5	5	10.4	10.4	4	-1	10.4	10.4	3	-3	10.4	10.4
0	6	10.4	10.4	4	6	10.4	10.4	3	-2	10.4	10.4	2	-4	10.4	10.4
0	7	10.4	10.4	3	7	10.4	10.4	2	-3	10.4	10.4	1	-5	10.4	10.4
0	8	10.4	10.4	2	8	10.4	10.4	1	-4	10.4	10.4	0	-6	10.4	10.4
0	9	10.4	10.4	1	9	10.4	10.4	0	-5	10.4	10.4	-1	-7	10.4	10.4
0	10	10.4	10.4	0	10	10.4	10.4	-1	-6	10.4	10.4	-2	-8	10.4	10.4
0	11	10.4	10.4	-1	11	10.4	10.4	-2	-7	10.4	10.4	-3	-9	10.4	10.4
0	12	10.4	10.4	-2	12	10.4	10.4	-3	-8	10.4	10.4	-4	-10	10.4	10.4
0	13	10.4	10.4	-3	13	10.4	10.4	-4	-9	10.4	10.4	-5	-11	10.4	10.4
0	14	10.4	10.4	-4	14	10.4	10.4	-5	-10	10.4	10.4	-6	-12	10.4	10.4
0	15	10.4	10.4	-5	15	10.4	10.4	-6	-11	10.4	10.4	-7	-13	10.4	10.4
0	16	10.4	10.4	-6	16	10.4	10.4	-7	-12	10.4	10.4	-8	-14	10.4	10.4
0	17	10.4	10.4	-7	17	10.4	10.4	-8	-13	10.4	10.4	-9	-15	10.4	10.4
0	18	10.4	10.4	-8	18	10.4	10.4	-9	-14	10.4	10.4	-10	-16	10.4	10.4
0	19	10.4	10.4	-9	19	10.4	10.4	-10	-15	10.4	10.4	-11	-17	10.4	10.4
0	20	10.4	10.4	-10	20	10.4	10.4	-11	-16	10.4	10.4	-12	-18	10.4	10.4
0	21	10.4	10.4	-11	21	10.4	10.4	-12	-17	10.4	10.4	-13	-19	10.4	10.4
0	22	10.4	10.4	-12	22	10.4	10.4	-13	-18	10.4	10.4	-14	-20	10.4	10.4
0	23	10.4	10.4	-13	23	10.4	10.4	-14	-19	10.4	10.4	-15	-21	10.4	10.4
0	24	10.4	10.4	-14	24	10.4	10.4	-15	-20	10.4	10.4	-16	-22	10.4	10.4
0	25	10.4	10.4	-15	25	10.4	10.4	-16	-21	10.4	10.4	-17	-23	10.4	10.4
0	26	10.4	10.4	-16	26	10.4	10.4	-17	-22	10.4	10.4	-18	-24	10.4	10.4
0	27	10.4	10.4	-17	27	10.4	10.4	-18	-23	10.4	10.4	-19	-25	10.4	10.4
0	28	10.4	10.4	-18	28	10.4	10.4	-19	-24	10.4	10.4	-20	-26	10.4	10.4
0	29	10.4	10.4	-19	29	10.4	10.4	-20	-25	10.4	10.4	-21	-27	10.4	10.4
0	30	10.4	10.4	-20	30	10.4	10.4	-21	-26	10.4	10.4	-22	-28	10.4	10.4
0	31	10.4	10.4	-21	31	10.4	10.4	-22	-27	10.4	10.4	-23	-29	10.4	10.4
0	32	10.4	10.4	-22	32	10.4	10.4	-23	-28	10.4	10.4	-24	-30	10.4	10.4
0	33	10.4	10.4	-23	33	10.4	10.4	-24	-29	10.4	10.4	-25	-31	10.4	10.4
0	34	10.4	10.4	-24	34	10.4	10.4	-25	-30	10.4	10.4	-26	-32	10.4	10.4
0	35	10.4	10.4	-25	35	10.4	10.4	-26	-31	10.4	10.4	-27	-33	10.4	10.4
0	36	10.4	10.4	-26	36	10.4	10.4	-27	-32	10.4	10.4	-28	-34	10.4	10.4
0	37	10.4	10.4	-27	37	10.4	10.4	-28	-33	10.4	10.4	-29	-35	10.4	10.4
0	38	10.4	10.4	-28	38	10.4	10.4	-29	-34	10.4	10.4	-30	-36	10.4	10.4
0	39	10.4	10.4	-29	39	10.4	10.4	-30	-35	10.4	10.4	-31	-37	10.4	10.4
0	40	10.4	10.4	-30	40	10.4	10.4	-31	-36	10.4	10.4	-32	-38	10.4	10.4
0	41	10.4	10.4	-31	41	10.4	10.4	-32	-37	10.4	10.4	-33	-39	10.4	10.4
0	42	10.4	10.4	-32	42	10.4	10.4	-33	-38	10.4	10.4	-34	-40	10.4	10.4
0	43	10.4	10.4	-33	43	10.4	10.4	-34	-39	10.4	10.4	-35	-41	10.4	10.4
0	44	10.4	10.4	-34	44	10.4	10.4	-35	-40	10.4	10.4	-36	-42	10.4	10.4
0	45	10.4	10.4	-35	45	10.4	10.4	-36	-41	10.4	10.4	-37	-43	10.4	10.4
0	46	10.4	10.4	-36	46	10.4	10.4	-37	-42	10.4	10.4	-38	-44	10.4	10.4
0	47	10.4	10.4	-37	47	10.4	10.4	-38	-43	10.4	10.4	-39	-45	10.4	10.4
0	48	10.4	10.4	-38	48	10.4	10.4	-39	-44	10.4	10.4	-40	-46	10.4	10.4
0	49	10.4	10.4	-39	49	10.4	10.4	-40	-45	10.4	10.4	-41	-47	10.4	10.4
0	50	10.4	10.4	-40	50	10.4	10.4	-41	-46	10.4	10.4	-42	-48	10.4	10.4
0	51	10.4	10.4	-41	51	10.4	10.4	-42	-47	10.4	10.4	-43	-49	10.4	10.4
0	52	10.4	10.4	-42	52	10.4	10.4	-43	-48	10.4	10.4	-44	-50	10.4	10.4
0	53	10.4	10.4	-43	53	10.4	10.4	-44	-49	10.4	10.4	-45	-51	10.4	10.4
0	54	10.4	10.4	-44	54	10.4	10.4	-45	-50	10.4	10.4	-46	-52	10.4	10.4
0	55	10.4	10.4	-45	55	10.4	10.4	-46	-51	10.4	10.4	-47	-53	10.4	10.4
0	56	10.4	10.4	-46	56	10.4	10.4	-47	-52	10.4	10.4	-48	-54	10.4	10.4
0	57	10.4	10.4	-47	57	10.4	10.4	-48	-53	10.4	10.4	-49	-55	10.4	10.4
0	58	10.4	10.4	-48	58	10.4	10.4	-49	-54	10.4	10.4	-50	-56	10.4	10.4
0	59	10.4	10.4	-49	59	10.4	10.4	-50	-55	10.4	10.4	-51	-57	10.4	10.4
0	60	10.4	10.4	-50	60	10.4	10.4	-51	-56	10.4	10.4	-52	-58	10.4	10.4
0	61	10.4	10.4	-51	61	10.4	10.4	-52	-57	10.4	10.4	-53	-59	10.4	10.4
0	62	10.4	10.4	-52	62	10.4	10.4	-53	-58	10.4	10.4	-54	-60	10.4	10.4
0	63	10.4	10.4	-53	63	10.4	10.4	-54	-59	10.4	10.4	-55	-61	10.4	10.4
0	64	10.4	10.4	-54	64	10.4	10.4	-55	-60	10.4	10.4	-56	-62	10.4	10.4
0	65	10.4	10.4	-55	65	10.4	10.4	-56	-61	10.4	10.4	-57	-63	10.4	10.4
0	66	10.4	10.4	-56	66	10.4	10.4	-57	-62	10.4	10.4	-58	-64	10.4	10.4
0	67	10.4	10.4	-57	67	10.4	10.4	-58	-63	10.4	10.4	-59	-65	10.4	10.4
0	68	10.4	10.4	-58	68	10.4	10.4	-59	-64	10.4	10.4	-60	-66	10.4	10.4
0	69	10.4	10.4	-59	69	10.4	10.4	-60	-65	10.4	10.4	-61	-67	10.4	10.4
0	70	10.4	10.4	-60	70	10.4	10.4	-61	-66	10.4	10.4	-62	-68	10.4	10.4
0	71	10.4	10.4	-61	71	10.4	10.4	-62	-67	10.4	10.4	-63	-69	10.4	10.4
0	72	10.4	10.4	-62	72	10.4	10.4	-63	-68	10.4	10.4	-64	-70	10.4	10.4
0	73	10.4	10.4	-63	73	10.4	10.4	-64	-69	10.4	10.4	-65	-71	10.4	10.4
0	74	10.4	10.4	-64	74	10.4	10.4	-65	-70	10.4	10.4	-66	-72	10.4	10.4
0	75	10.4	10.4	-65	75	10.4	10.4	-66	-71	10.4	10.4	-67	-73	10.4	10.4
0	76	10.4	10.4	-66	76	10.4	10.4	-67	-72	10.4	10.4	-68	-74	10.4	10.4
0	77	10.4	10.4	-67	77	10.4	10.4	-68	-73	10.4	10.4	-69	-75	10.4	10.4
0	78	10.4	10.4	-68	78	10.4	10.4	-69	-74	10.4	10.4	-70	-76	10.4	10.4
0	79	10.4	10.4	-69	79	10.4	10.4	-70	-75	10.4	10.4	-71	-77	10.4	10.4
0	80	10.4	10.4	-70	80	10.4	10.4	-71	-76	10.4	10.4	-72	-78	10.4	10.4
0	81	10.4	10.4	-71	81	10.4	10.4	-72	-77	10.4	10.4	-73	-79	10.4	10.4
0	82	10.4	10.4	-72	82	10.4	10.4	-73	-78	10.4	10.4	-74	-80	10.4	10.4
0	83	10.4	10.4	-73	83	10.4	10.4	-74	-79	10.4	10.4	-75	-81	10.4	10.4
0	84	10.4	10.4	-74	84	10.4	10.4	-75	-80	10.4	10.4	-76	-82	10.4	10.4
0	85	10.4	10.4	-75	85	10.4	10.4	-76	-81	10.4	10.4	-77	-83	10.4	10.4
0	86	10.4	10.4	-76	86	10.4	10.4	-77	-82	10.4	10.4	-78	-84	10.4	10.4
0	87	10.4	10.4	-77	87	10.4	10.4	-78	-83	10.4	10.4	-79	-85	10.4	10.4
0	88	10.4	10.4	-78	88	10.4	10.4	-79	-84	10.4	10.4	-80	-86	10.4	10.4
0	89	10.4	10.4	-79	89	10.4	10.4	-80	-85	10.4	10.4	-81	-87	10.4	10.4
0	90	10.4	10.4	-80	90	10.4	10.4	-81	-86	10.4	10.4	-82	-88	10.4	10.4
0	91	10.4	10.4	-81	91	10.4	10.4	-82	-87	10.4	10.4	-83	-89	10.4	10.4
0	92	10.4	10.4	-82	92	10.4	10.4	-83	-88	10.4	10.4	-84	-90	10.4	10.4
0	93	10.4	10.4	-83	93	10.4	10.4	-84	-89	10.4	10.4	-85	-91	10.4	10.4
0	94	10.4	10.4	-84	94	10.4	10.4	-85	-90	10.4	10.4	-86	-92	10.4	10.4
0	95	10.4	10.4												

Table V.

Mean planes in the molecule.

(a) Equations of mean planes.

These are given in the form:

$$lX' + mY' + nZ' = p$$

where  $X'$ ,  $Y'$  and  $Z'$  are coordinates in Å. referred to orthogonal axes  $a$ ,  $b$  and  $c^*$ .

Ring	$l$	$m$	$n$	$p$
Lactone	-0.6137	0.6880	0.3873	4.0990
1,3-dioxolane	0.8104	0.5582	0.1782	6.4505
Cyclohexylidene	0.7923	-0.6088	0.0399	0.3369
Aromatic	-0.5197	0.7256	-0.4511	6.8673

(b) Displacements of the atoms from the planes; those underlined indicate the atoms included in calculating the equations of the planes.

Atom	Aromatic ring	Lactone ring	1,3-dioxolane ring	Cyclohexylidene ring
Br(1)	0.126			
S(2)	0.040			
C(3)	-0.011			
C(4)	<u>0.029</u>			
C(5)	<u>-0.019</u>			
C(6)	<u>0.003</u>			
C(7)	<u>0.004</u>			
C(8)	<u>-0.001</u>			
C(13)		0.012		
C(14)		<u>-0.008</u>		
C(15)		<u>0.141</u>		
C(16)		0.007		
O(17)		<u>-0.116</u>		
O(18)		<u>-0.005</u>		
O(19)			0.003	
O(20)			<u>-0.489</u>	
C(21)			0.005	
C(22)			<u>-0.003</u>	
C(23)				-0.639
C(24)				<u>-0.002</u>
C(25)				<u>0.003</u>
C(26)				0.751
C(27)				<u>-0.004</u>
				<u>0.002</u>

four-atom planes is  $88^\circ$  (the angle between three-atom planes at C(15) is negligibly different). The cyclohexylidene six-membered ring has a normal chair conformation (Table V); the dihedral angles within the ring vary from  $55^\circ$  to  $61^\circ$ . The aromatic ring and the attached bromine and sulphur atoms are approximately planar (Table V).

The bond distances and valency angles are in Table VI. None of the lengths or angles differ significantly from normal values. The mean dimensions are:

Br - C <sub>ar</sub>	1.90 Å.
C <sub>ar</sub> - C <sub>ar</sub>	1.39
S - C <sub>ar</sub>	1.74
S - O	1.59
S = O	1.41
C - C	1.54
C - O	1.42
C = O	1.20
Angle in aromatic ring	120°
Angle in cyclohexane ring	110°

The bonds and angles at the sulphur atoms are close to previously reported values; in particular, the O=S=O angle ( $120.5^\circ$ ) is significantly larger than the other angles at the sulphur atom.

A projection of the structure is shown in Figure 2. All the intermolecular distances correspond to van der Waals' interactions. The shortest contacts are O...O, 2.99 Å., and O...C, 3.05 Å.

Table VI.

Bond lengths and valency angles.

(a) Bond lengths (in Å.;  $\sigma = 0.02 - 0.04$  Å.):

i	j	Length ij	i	j	ij	i	j	ij
Br(1)	— C(3)	1.90	C(7)	— C(8)	1.39	C(16)	— O(18)	1.34
S(2)	— C(6)	1.74	O(11)	— C(12)	1.44	O(19)	— C(22)	1.42
S(2)	— O(9)	1.40	C(12)	— C(13)	1.56	O(20)	— C(21)	1.37
S(2)	— O(10)	1.42	C(13)	— C(14)	1.56	O(20)	— C(22)	1.45
S(2)	— O(11)	1.60	C(13)	— O(18)	1.43	C(22)	— C(23)	1.49
C(3)	— C(4)	1.37	C(14)	— C(15)	1.58	C(22)	— C(27)	1.51
C(3)	— C(8)	1.39	C(15)	— C(16)	1.48	C(23)	— C(24)	1.52
C(4)	— C(5)	1.40	C(15)	— O(19)	1.43	C(24)	— C(25)	1.54
C(5)	— C(6)	1.42	C(15)	— C(21)	1.55	C(25)	— C(26)	1.56
C(6)	— C(7)	1.36	C(16)	— O(17)	1.20	C(26)	— C(27)	1.55

(b) Valency angles (in degrees;  $\sigma = 0.07 - 2.1^\circ$ ):

i	j	k	Angle (ijk)	i	j	k	Angle (ijk)
C(6)	— S(2)	— O(9)	109.0	C(14)	— C(15)	— O(19)	109.7
C(6)	— S(2)	— O(10)	108.3	C(14)	— C(15)	— C(21)	116.4
C(6)	— S(2)	— O(11)	103.4	C(16)	— C(15)	— O(19)	112.1
O(9)	— S(2)	— O(10)	120.6	C(16)	— C(15)	— C(21)	111.8
O(9)	— S(2)	— O(11)	104.4	O(19)	— C(15)	— C(21)	101.7
O(10)	— S(2)	— O(11)	109.9	C(15)	— C(16)	— O(17)	126.2
Br(1)	— C(3)	— C(4)	118.7	C(15)	— C(16)	— O(18)	111.4
Br(1)	— C(3)	— C(8)	117.6	O(17)	— C(16)	— O(18)	122.4
C(4)	— C(3)	— C(8)	123.3	C(13)	— O(18)	— C(16)	113.0
C(3)	— C(4)	— C(5)	120.3	C(15)	— O(19)	— C(22)	110.6
C(4)	— C(5)	— C(6)	117.3	C(21)	— O(20)	— C(22)	106.1
S(2)	— C(6)	— C(5)	118.4	C(15)	— C(21)	— O(20)	105.0
S(2)	— C(6)	— C(7)	121.7	O(19)	— C(22)	— O(20)	103.8
C(5)	— C(6)	— C(7)	119.9	O(19)	— C(22)	— C(23)	109.7
C(6)	— C(7)	— C(8)	123.5	O(19)	— C(22)	— C(27)	110.2
C(3)	— C(8)	— C(7)	115.5	O(20)	— C(22)	— C(23)	108.2
S(2)	— O(11)	— C(12)	117.5	O(20)	— C(22)	— C(27)	111.6
O(11)	— C(12)	— C(13)	103.2	C(23)	— C(22)	— C(27)	112.9
C(12)	— C(13)	— C(14)	112.0	C(22)	— C(23)	— C(24)	111.5
C(12)	— C(13)	— O(18)	107.6	C(23)	— C(24)	— C(25)	109.3
C(14)	— C(13)	— O(18)	107.5	C(24)	— C(25)	— C(26)	108.4
C(13)	— C(14)	— C(15)	102.0	C(25)	— C(26)	— C(27)	108.6
C(14)	— C(15)	— C(16)	105.3	C(22)	— C(27)	— C(26)	110.2



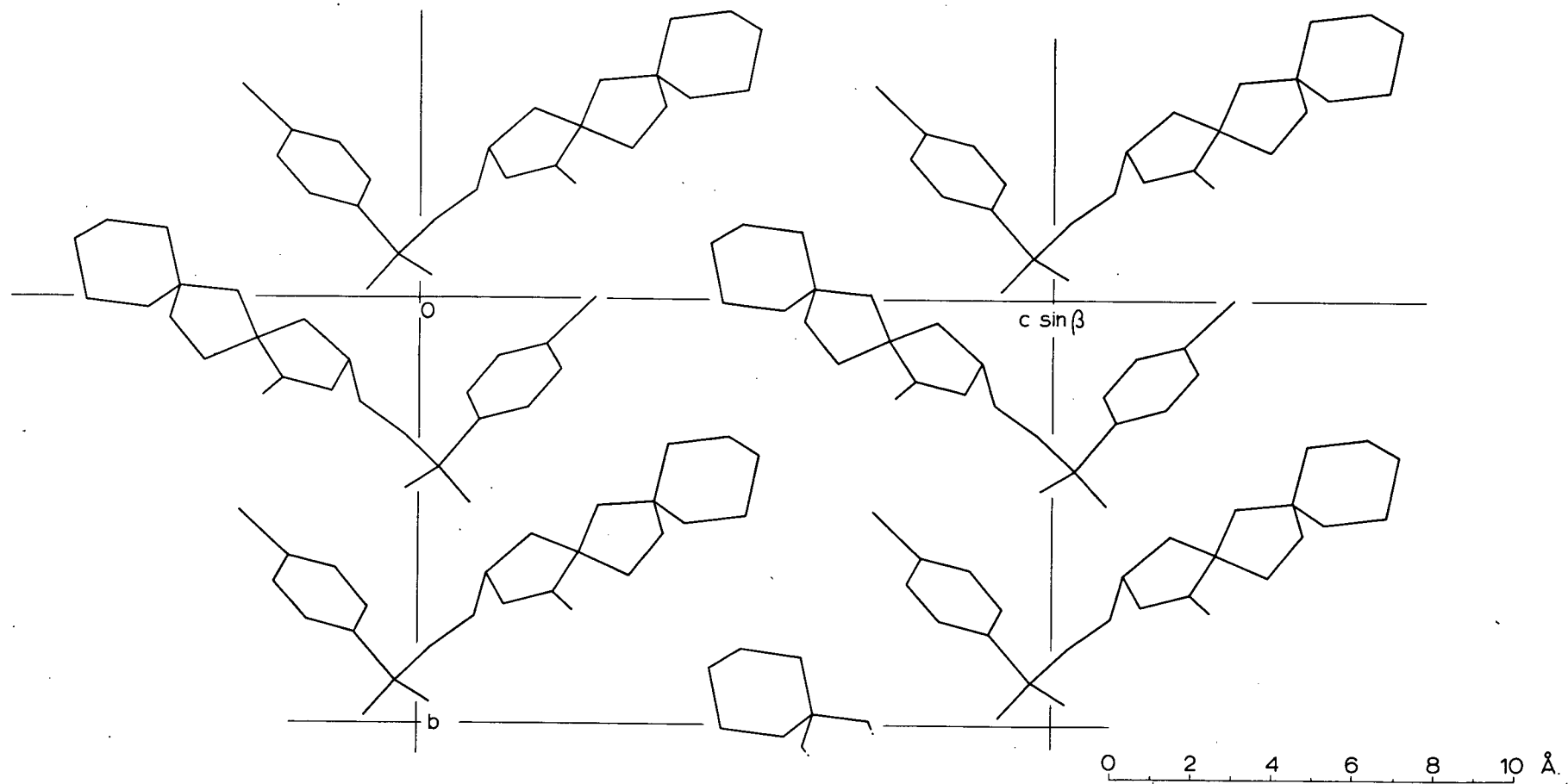


Figure 2. Projection of the structure along  $\underline{a}$ .

PART III. THE STRUCTURE DETERMINATION OF  
2,6-DICHLORO-4-NITROANILINE.

## A. INTRODUCTION.

The determination of the structure of 2,6-dichloro-4-nitroaniline was carried out to investigate further the conformation of substituent groups in benzene derivatives. This molecule contains a nitro group whose orientation with respect to the benzene ring should not be affected by its ortho neighbours. The effect of the formation of hydrogen bonds or the proximity of other molecules might, however, rotate the group out of coplanarity with the benzene ring. The orientation of the amino group should be decided by the formation of hydrogen bonds with the neighbouring chlorine atoms and/or the oxygen atoms of nitro groups of other molecules.

The dimensions of the benzene ring are also of interest; these, with the C-N bond distances, should provide more information on the relevance of resonance forms and of hybridisation of carbon  $\sigma$  orbitals in benzene derivatives.

## B. X-RAY ANALYSIS.

The sample of 2,6-dichloro-4-nitroaniline, supplied by Eastman Organic Chemicals (Eastman Kodak Co.), was recrystallised from 95% ethanol to yield fine yellow needles. The unit cell and space group data were determined initially from rotation, Weissenberg and precession photographs; the cell dimensions were later obtained more accurately from least-squares refinement methods based on the  $2\theta$  values of 30 reflections measured on the diffractometer with  $\text{Cu-K}_\beta$  ( $\lambda = 1.3922 \text{ \AA.}$ ) or  $\text{Cu-K}_{\alpha_1}$  ( $\lambda = 1.5405 \text{ \AA.}$ ) radiations.

### Crystal data:

2,6-dichloro-4-nitroaniline,  $\text{C}_6\text{H}_4\text{Cl}_2\text{N}_2\text{O}_2$ .  $M = 207.02$ .

Monoclinic,  $a = 3.723(0_5)$ ,  $b = 17.833(1)$ ,  $c = 11.834(1) \text{ \AA.}$ ,  $\beta = 94.12(1)^\circ$ ,

(standard deviations in parentheses).

$$V_c = 783.57 \text{ \AA}^3.$$

$$D_m = 1.74 \text{ (flotation in aqueous zinc chloride)}, D_c = 1.755 \text{ g.cm}^{-3} \text{ with } Z = 4.$$

$$F(000) = 416.$$

Absorption coefficient,  $\text{Cu-K}_{\alpha}$  ( $\lambda = 1.5418 \text{ \AA}$ ),  $\mu = 71 \text{ cm}^{-1}$ .

Reflections absent:  $0k0$  when  $k$  is odd,  $h0\ell$  when  $\ell$  odd; hence space group is  $P2_1/c$ .

The upper-level Weissenberg and the precession photographs showed that the crystal selected was twinned. The unit cells of the two twins had a common  $\underline{a}$  axis, and  $c_1^* = -c_2^*$ ; it was shown in the course of this work that the twins are probably congruent so that the  $b$  axes are colinear but opposite in direction, and this arrangement is assumed in the following description.

Optical examination of a sample of the crystals, using polarised light, indicated that all the crystals were twinned, and that there might be only one twinning plane in each crystal, i.e. the crystal could, theoretically, be cut in two to yield two single crystals. The only examples of single crystals in the sample were minute, probably fragments of larger crystals. It was not possible to cut a crystal to provide a good single crystal and therefore a twinned crystal was used for the data collection.

This crystal was a needle with  $\underline{a}$  as major axis and length  $0.4 \text{ mm.}$ , cross-section  $0.08 \times 0.05 \text{ mm}^2$ . It was mounted with  $a^*$  of one of the twins parallel to the goniostat  $\phi$ -axis. The intensities of the reflections were measured on a Datex-automated G.E. XRD-6 diffractometer with a scintillation counter,  $\text{Cu-K}_{\alpha}$  radiation (Ni filter and pulse-height analyser), and a  $\theta$ - $2\theta$  scan. The intensities of 1160 reflections of one twin, with  $2\theta(\text{Cu-K}_{\alpha}) \leq 120^\circ$  (i.e. minimum interplanar spacing of  $0.89 \text{ \AA}$ .) were measured. The 323 reflections with indices  $2k\ell$  were removed since these reflections included varying, unknown amounts of diffracted beams from  $(2\overline{k}\ell+1)$  planes of the second twin. Weissenberg photographs first showed this possibility of over-

lap in spots, and a chart recording of the collection of intensity data confirmed that often there were two diffracted beams measured in the  $\theta$ - $2\theta$  scan.

The 837 remaining reflections were corrected for Lorentz and polarisation factors. There were 110 reflections (i.e. 13.2%) with  $I/\sigma_I < 2.0$ , where  $\sigma_I^2$  is defined:

$$\sigma_I^2 = S + B + (0.02.S)^2$$

where  $S$  = scan count, and  $B$  = background count over the same scan range; these reflections were treated as unobserved.

The  $0kl$  intensities were then scaled down to correspond with those of other layers; the  $0kl$  reflections of one twin were coincident with the  $0k\bar{l}$  reflections of the other twin, and the intensity measured was thus the sum from the two twins. The required scale factor was determined by comparing intensities of several general reflections in both twins; the first twin was found to be 1.034 stronger than the second, hence the scaling factor is 0.508.

No corrections for absorption were made. The structure amplitudes were then derived.

### C. STRUCTURE ANALYSIS.

A map of the Patterson function was calculated, and this indicated the coordinates of the two chlorine atoms. The other ten non-hydrogen atoms were found in an electron-density map. Scattering factors for chlorine, oxygen, nitrogen and carbon were taken from International Tables<sup>5c</sup>, and for hydrogen from the values of Stewart, Davidson and Simpson<sup>19</sup>.

The structure was refined by a full-matrix least-squares procedure which minimised  $\sum w(|F_o| - |F_c|)^2$ , initially with  $w = 1$  for all reflections. Refinement with isotropic thermal parameters gave  $R = 0.124$ . Further refinement with anisotropic thermal parameters gave  $R = 0.060$ . A difference

Fourier at this stage showed the four hydrogen atoms clearly at 0.47 to 0.53 eÅ<sup>-3</sup>. above a maximum background of 0.42 eÅ<sup>-3</sup>.

Final refinement of the coordinates of all atoms, anisotropic thermal parameters of all non-hydrogen atoms and isotropic thermal parameters of the hydrogen atoms, reduced R to 0.038. In the last stages of refinement, the strongest reflection, 10 $\bar{2}$ , suspected of extinction errors, was removed from the data and not included in any calculations. Also at this stage, a weighting scheme of the type:

$$\sqrt{w} = \frac{1}{\sqrt{1 + \left( \frac{|F_o| - F^*}{G^*} \right)^2}}$$

was found to be most suitable, from examination of the average values of  $w(|F_o| - |F_c|)^2$  in ranges of  $|F_o|$ ;  $F^*$  was put as 13.0 and  $G^*$  as 8.0. Unobserved reflections were given a weight  $\sqrt{w} = 0.6$ . Reflections with indices 2k $\bar{l}$  were not included in any calculations.

The resulting atomic parameters are listed in Table VII, and a list of structure factors,  $|F_o|$  and  $|F_c|$ , (not including the 2k $\bar{l}$  reflections), is given in Table VIII.

A view of the molecule is given in Figure 3.

The bond lengths and valence angles, calculated from the atomic coordinates of Table VII, are given in Table IX, and the angles are shown in Figure 4(b). Thermal motion corrections have been applied to the bond lengths (except to those bonds involving hydrogen atoms), and the corrected values are recorded also in Table IX and in Figure 4(a).

In the determination of the thermal motion corrections, the thermal parameters of the atoms were converted to the thermal ellipsoids which describe the atomic vibrations in a molecule. Oscillation of the molecule in the molecule plane appears minimal - intermolecular hydrogen-bonding (see below) and other short intermolecular interactions restrict motion of this type; the ellipsoids of the carbon atoms indicate very little oscillation

Table VII.

## Final atomic parameters.

(a) Fractional atomic coordinates; standard deviations are in parentheses:

	x	y	z
C(1)	0.5098(12)	0.3375(2)	0.3014(3)
C(2)	0.3591(12)	0.3571(2)	0.1932(3)
C(3)	0.3431(12)	0.4296(2)	0.1545(3)
C(4)	0.4766(13)	0.4856(2)	0.2249(3)
C(5)	0.6248(12)	0.4712(2)	0.3330(3)
C(6)	0.6414(12)	0.3984(2)	0.3694(3)
Cl(7)	0.1942(4)	0.2852(1)	0.1060(1)
Cl(8)	0.8261(3)	0.3783(1)	0.5049(1)
N(9)	0.5298(13)	0.2667(2)	0.3390(4)
N(10)	0.4657(12)	0.5632(2)	0.1867(3)
O(11)	0.3037(14)	0.5778(2)	0.0953(3)
O(12)	0.6228(14)	0.6107(2)	0.2474(3)
H(13)	0.251(13)	0.4419(23)	0.0805(35)
H(14)	0.738(11)	0.5098(20)	0.3821(30)
H(15)	0.599(16)	0.2557(29)	0.4124(46)
H(16)	0.459(15)	0.2326(28)	0.2909(39)

(b) Thermal parameters of the atoms. Anisotropic thermal parameters are in the form:

$$\exp [-2\pi^2 \cdot 10^{-4} (U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^{*}b^{*} + 2U_{13}hla^{*}c^{*} + 2U_{23}klb^{*}c^{*})]$$

Standard deviations are given in parentheses; the value for the anisotropic thermal parameters is the mean for the six values.

	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>12</sub>	U <sub>13</sub>	U <sub>23</sub>	Mean e.s.d.
C(1)	331	292	351	30	40	-53	(20)
C(2)	386	372	337	- 8	40	-133	(21)
C(3)	365	430	304	53	36	-21	(21)
C(4)	439	317	359	66	66	19	(21)
C(5)	389	280	332	3	69	-47	(20)
C(6)	338	296	315	3	10	- 4	(19)
Cl(7)	529	491	459	-85	-24	-239	(6)
Cl(8)	502	346	302	12	-50	13	(6)
N(9)	700	274	481	-82	10	-52	(23)
N(10)	631	380	439	112	88	67	(22)
O(11)	995	603	514	126	-73	199	(23)
O(12)	1052	293	656	-57	-16	54	(23)

B (Å<sup>2</sup>.)

H(13)	3.0(9)
H(14)	2.0(8)
H(15)	5.8(14)
H(16)	4.2(11)

Table VIII.

Measured and calculated structure amplitudes. Measured values with negative sign indicate unobserved reflections. (N.B.  $10\bar{2}$  reflection, omitted from final calculations and list has  $|F_0| = 173.8$  and  $|F_c| = 223.2$ ).

h k l	$F_{obs}$	$F_{calc}$	h k l	$F_{obs}$	$F_{calc}$	h k l	$F_{obs}$	$F_{calc}$	h k l	$F_{obs}$	$F_{calc}$	h k l	$F_{obs}$	$F_{calc}$	h k l	$F_{obs}$	$F_{calc}$	
0 0 2	36.4	41.5	0 4 1	17.5	17.3	1 1 1	-8	4.4	3.7	1 13 -6	11.1	11.0	3 12 2	15.4	15.5	3 12 -2	26.3	16.4
0 0 4	14.4	18.7	0 4 3	20.3	28.4	1 1 10	-2.4	0.9	1 13 -8	6.1	6.1	3 12 4	3.5	1.7	3 12 -4	2.9	1.9	
0 0 6	29.3	28.4	0 4 5	10.5	18.8	1 1 12	-2.1	3.3	1 14 -1	15.7	25.8	3 12 6	5.5	4.6	3 12 -6	5.5	4.6	
0 0 8	32.1	32.3	0 4 7	17.9	18.1	1 1 14	-1.2	15.3	1 14 -3	14.0	14.5	3 12 8	1.7	3.5	3 12 -8	17.6	17.9	
0 0 10	35.8	36.4	0 4 9	12.7	12.7	1 1 16	-1.1	57.5	1 14 -5	12.6	12.5	3 12 10	6.5	7.7	3 12 -10	6.5	7.7	
0 0 12	17.7	17.7	0 4 11	11.7	11.8	1 1 18	-1.1	76.4	1 14 -7	10.9	10.9	3 12 12	8.4	8.6	3 12 -12	8.4	8.6	
0 0 14	11.7	11.8	0 4 13	13.3	12.8	1 1 20	-1.1	48.0	1 14 -9	-3.0	25.3	3 12 14	6.7	6.1	3 12 -14	6.7	6.1	
0 0 16	35.5	61.6	0 4 15	6.7	6.4	1 1 22	-1.1	13.5	1 14 -11	13.5	14.1	3 12 16	21.6	29.1	3 12 -16	21.6	29.1	
0 0 18	29.1	29.7	0 4 17	9.3	8.8	1 1 24	-1.1	48.5	1 15 -1	25.1	25.3	3 12 18	1.6	14.4	3 12 -18	1.6	14.4	
0 0 20	44.2	43.7	0 4 19	3.1	3.4	1 1 26	-1.1	16.6	1 15 -3	19.5	18.9	3 12 20	11.3	11.4	3 12 -20	11.3	11.4	
0 0 22	6.3	6.5	0 4 21	14.1	13.0	1 1 28	-1.1	21.5	1 15 -5	13.5	13.4	3 12 22	5.0	4.9	3 12 -22	5.0	4.9	
0 0 24	6.3	6.0	0 4 23	11.3	11.0	1 1 30	-1.1	5.2	1 15 -7	5.4	5.1	3 12 24	1.8	1.2	3 12 -24	1.8	1.2	
0 0 26	8.0	7.4	0 4 25	2.4	2.4	1 1 32	-1.1	16.4	1 15 -9	4.1	3.8	3 12 26	0.0	0.3	3 12 -26	0.0	0.3	
0 0 28	7.4	7.2	0 4 27	13.4	12.8	1 1 34	-1.1	70.1	1 15 -11	15.6	16.3	3 12 28	7.3	7.1	3 12 -28	7.3	7.1	
0 0 30	2.4	31.8	0 4 29	9.4	9.8	1 1 36	-1.1	63.0	1 15 -13	13.8	13.8	3 12 30	5.4	5.7	3 12 -30	5.4	5.7	
0 0 32	11.7	12.2	0 4 31	2.4	2.4	1 1 38	-1.1	21.8	1 15 -15	0.0	1.7	3 12 32	6.3	5.5	3 12 -32	6.3	5.5	
0 0 34	14.4	13.2	0 4 33	26.6	26.0	1 1 40	-1.1	18.6	1 16 -1	3.1	5.7	3 12 34	10.4	10.2	3 12 -34	10.4	10.2	
0 0 36	14.4	13.2	0 4 35	20.3	20.1	1 1 42	-1.1	17.0	1 16 -3	17.0	15.6	3 12 36	11.3	11.0	3 12 -36	11.3	11.0	
0 0 38	14.4	13.2	0 4 37	7.5	7.4	1 1 44	-1.1	10.5	1 16 -5	9.6	8.1	3 12 38	7.2	7.1	3 12 -38	7.2	7.1	
0 0 40	5.0	6.0	0 4 39	11.4	4.4	1 1 46	-1.1	25.9	1 16 -7	6.6	5.7	3 12 40	12.4	9.3	3 12 -40	12.4	9.3	
0 0 42	5.0	6.0	0 4 41	8.5	5.3	1 1 48	-1.1	26.7	1 16 -9	6.2	5.7	3 12 42	4.5	8.0	3 12 -42	4.5	8.0	
0 0 44	3.3	33.0	0 4 43	1.4	0.8	1 1 50	-1.1	28.6	1 16 -11	9.9	9.9	3 12 44	1.1	1.1	3 12 -44	1.1	1.1	
0 0 46	5.2	54.9	0 4 45	11.1	11.2	1 1 52	-1.1	28.6	1 17 -1	12.6	12.2	3 12 46	3.4	3.2	3 12 -46	3.4	3.2	
0 0 48	14.4	13.2	0 4 47	7.8	8.0	1 1 54	-1.1	3.2	1 17 -3	17.0	16.7	3 12 48	4.2	0.3	3 12 -48	4.2	0.3	
0 0 50	11.3	10.7	0 4 49	11.7	11.3	1 1 56	-1.1	1.2	1 17 -5	1.9	1.9	3 12 50	1.3	1.3	3 12 -50	1.3	1.3	
0 0 52	11.3	10.7	0 4 51	33.0	31.7	1 1 58	-1.1	2.3	1 17 -7	5.8	5.4	3 12 52	1.4	1.8	3 12 -52	1.4	1.8	
0 0 54	11.3	10.7	0 4 53	12.8	13.3	1 1 60	-1.1	4.8	1 17 -9	5.9	5.8	3 12 54	3.3	3.4	3 12 -54	3.3	3.4	
0 0 56	11.3	10.7	0 4 55	26.0	26.5	1 1 62	-1.1	35.7	1 17 -11	15.4	15.4	3 12 56	11.0	10.5	3 12 -56	11.0	10.5	
0 0 58	11.3	10.7	0 4 57	26.0	26.5	1 1 64	-1.1	20.1	1 17 -13	25.8	25.8	3 12 58	22.6	21.9	3 12 -58	22.6	21.9	
0 0 60	11.3	10.7	0 4 59	12.4	12.4	1 1 66	-1.1	9.8	1 17 -15	2.0	0.6	3 12 60	11.6	11.4	3 12 -60	11.6	11.4	
0 0 62	11.3	10.7	0 4 61	12.4	12.4	1 1 68	-1.1	25.8	1 17 -17	2.0	0.6	3 12 62	11.6	11.4	3 12 -62	11.6	11.4	
0 0 64	11.3	10.7	0 4 63	12.4	12.4	1 1 70	-1.1	25.8	1 17 -19	2.0	0.6	3 12 64	11.6	11.4	3 12 -64	11.6	11.4	
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0 0 68	11.3	10.7	0 4 67	12.4	12.4	1 1 74	-1.1	25.8	1 17 -23	2.0	0.6	3 12 68	11.6	11.4	3 12 -68	11.6	11.4	
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0 0 72	11.3	10.7	0 4 71	12.4	12.4	1 1 78	-1.1	25.8	1 17 -27	2.0	0.6	3 12 72	11.6	11.4	3 12 -72	11.6	11.4	
0 0 74	11.3	10.7	0 4 73	12.4	12.4	1 1 80	-1.1	25.8	1 17 -29	2.0	0.6	3 12 74	11.6	11.4	3 12 -74	11.6	11.4	
0 0 76	11.3	10.7	0 4 75	12.4	12.4	1 1 82	-1.1	25.8	1 17 -31	2.0	0.6	3 12 76	11.6	11.4	3 12 -76	11.6	11.4	
0 0 78	11.3	10.7	0 4 77	12.4	12.4	1 1 84	-1.1	25.8	1 17 -33	2.0	0.6	3 12 78	11.6	11.4	3 12 -78	11.6	11.4	
0 0 80	11.3	10.7	0 4 79	12.4	12.4	1 1 86	-1.1	25.8	1 17 -35	2.0	0.6	3 12 80	11.6	11.4	3 12 -80	11.6	11.4	
0 0 82	11.3	10.7	0 4 81	12.4	12.4	1 1 88	-1.1	25.8	1 17 -37	2.0	0.6	3 12 82	11.6	11.4	3 12 -82	11.6	11.4	
0 0 84	11.3	10.7	0 4 83	12.4	12.4	1 1 90	-1.1	25.8	1 17 -39	2.0	0.6	3 12 84	11.6	11.4	3 12 -84	11.6	11.4	
0 0 86	11.3	10.7	0 4 85	12.4	12.4	1 1 92	-1.1	25.8	1 17 -41	2.0	0.6	3 12 86	11.6	11.4	3 12 -86	11.6	11.4	
0 0 88	11.3	10.7	0 4 87	12.4	12.4	1 1 94	-1.1	25.8	1 17 -43	2.0	0.6	3 12 88	11.6	11.4	3 12 -88	11.6	11.4	
0 0 90	11.3	10.7	0 4 89	12.4	12.4	1 1 96	-1.1	25.8	1 17 -45	2.0	0.6	3 12 90	11.6	11.4	3 12 -90	11.6	11.4	
0 0 92	11.3	10.7	0 4 91	12.4	12.4	1 1 98	-1.1	25.8	1 17 -47	2.0	0.6	3 12 92	11.6	11.4	3 12 -92	11.6	11.4	
0 0 94	11.3	10.7	0 4 93	12.4	12.4	1 1 100	-1.1	25.8	1 17 -49	2.0	0.6	3 12 94	11.6	11.4	3 12 -94	11.6	11.4	
0 0 96	11.3	10.7	0 4 95	12.4	12.4	1 1 102	-1.1	25.8	1 17 -51	2.0	0.6	3 12 96	11.6	11.4	3 12 -96	11.6	11.4	
0 0 98	11.3	10.7	0 4 97	12.4	12.4	1 1 104	-1.1	25.8	1 17 -53	2.0	0.6	3 12 98	11.6	11.4	3 12 -98	11.6	11.4	
0 0 100	11.3	10.7	0 4 99	12.4	12.4	1 1 106	-1.1	25.8	1 17 -55	2.0	0.6	3 12 100	11.6	11.4	3 12 -100	11.6	11.4	
0 0 102	11.3	10.7	0 4 101	12.4	12.4	1 1 108	-1.1	25.8	1 17 -57	2.0	0.6	3 12 102	11.6	11.4	3 12 -102	11.6	11.4	
0 0 104	11.3	10.7	0 4 103	12.4	12.4	1 1 110	-1.1	25.8	1 17 -59	2.0	0.6	3 12 104	11.6	11.4	3 12 -104	11.6	11.4	
0 0 106	11.3	10.7	0 4 105	12.4	12.4	1 1 112	-1.1	25.8	1 17 -61	2.0	0.6	3 12 106	11.6	11.4	3 12 -106	11.6	11.4	
0 0 108	11.3	10.7	0 4 107	12.4	12.4	1 1 114	-1.1	25.8	1 17 -63	2.0	0.6	3 12 108	11.6	11.4	3 12 -108	11.6	11.4	
0 0 110	11.3	10.7	0 4 109	12.4	12.4	1 1 116	-1.1	25.8	1 17 -65	2.0	0.6	3 12 110	11.6	11.4	3 12 -110	11.6	11.4	
0 0 112	11.3	10.7	0 4 111	12.4	12.4	1 1 118	-1.1	25.8	1 17 -67	2.0	0.6	3 12 112	11.6	11.4	3 12 -112	11.6	11.4	
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0 0 116	11.3	10.7	0 4 115	12.4	12.4	1 1 122	-1.1	25.8	1 17 -71	2.0	0.6	3 12 116	11.6	11.4	3 12 -116	11.6	11.4	
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0 0 130	11.3	10.7	0 4 129	12.4	12.4	1 1 136	-1.1	25.8	1 17 -85	2.0	0.6	3 12 130	11.6	11.4	3 12 -130	11.6	11.4	
0 0 132	11.3	10.7	0 4 131	12.4	12.4	1 1 138	-1.1	25.8	1 17 -87	2.0	0.6	3 12 132	11.6	11.4	3 12 -132	11.6	11.4	
0 0 134	11.3	10.7	0 4 133	12.4	12.4	1 1 140	-1.1	25.8	1 17 -89	2.0	0.6	3 12 134	11.6	11.4	3 12 -134	11.6	11.4	
0 0 136	11.3	10.7																



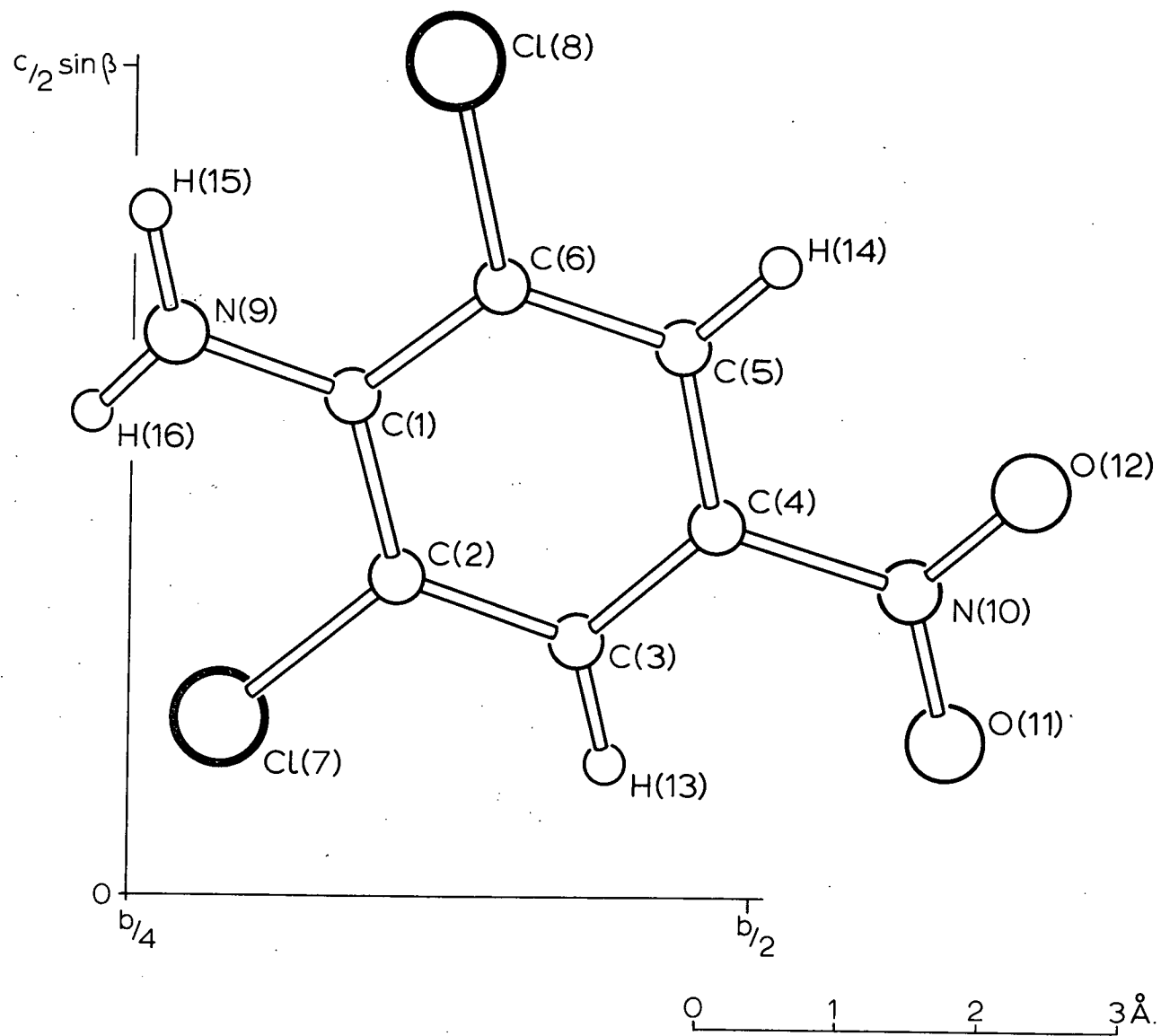


Figure 3. View of the molecule. The positive direction of the a axis is towards the viewer

Table IX.

## Bond lengths and valency angles.

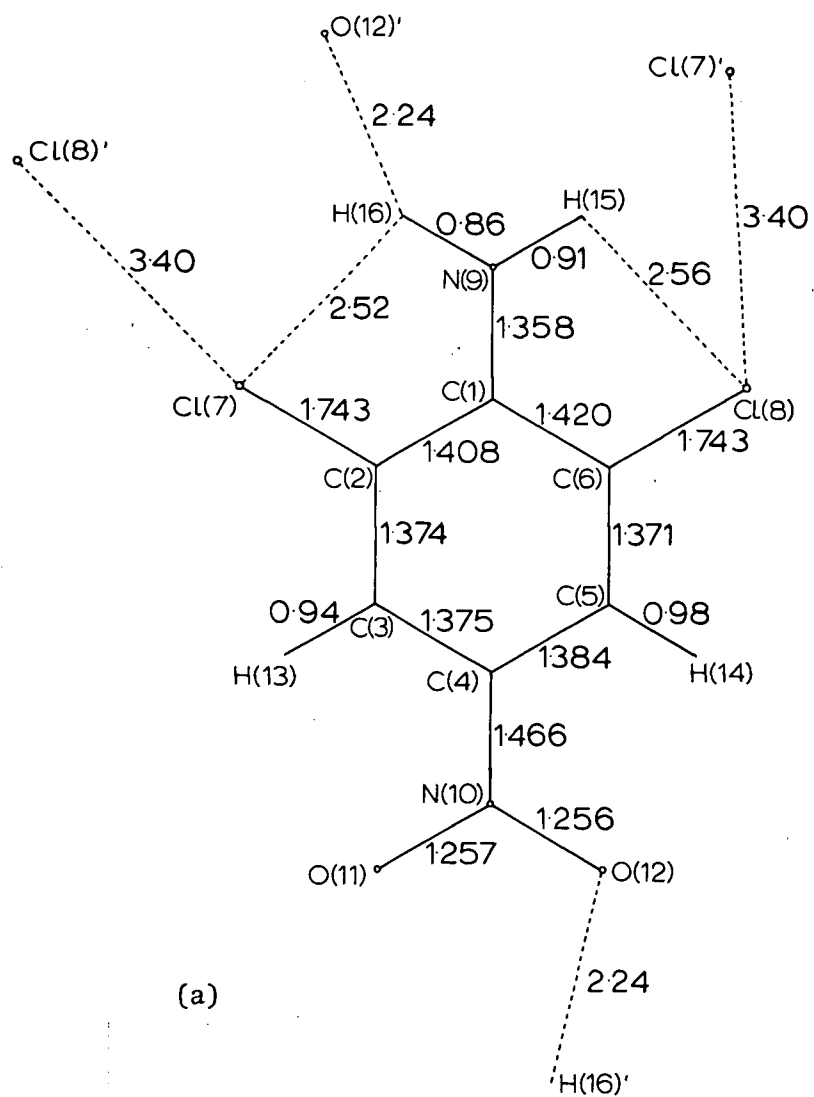
(a) Bond distances (in Å.). For bonds not involving a hydrogen atom,  $\sigma = 0.004 - 0.006$ ; for C-H bonds,  $\sigma = 0.04$ ; for N-H bonds,  $\sigma = 0.05$  Å.

Atoms	Bond length		Atoms	Bond length	
	Uncorr.	Corr.*		Uncorr.	Corr.*
C(1) — C(2)	1.405	1.408	C(4) — N(10)	1.456	1.466
C(1) — C(6)	1.417	1.420	C(5) — C(6)	1.368	1.371
C(1) — N(9)	1.339	1.358	C(5) — H(14)	0.98	
C(2) — C(3)	1.371	1.374	C(6) — Cl(8)	1.736	1.743
C(2) — Cl(7)	1.731	1.743	N(9) — H(15)	0.91	
C(3) — C(4)	1.372	1.375	N(9) — H(16)	0.86	
C(3) — H(13)	0.94		N(10) — O(11)	1.227	1.257
C(4) — C(5)	1.381	1.384	N(10) — O(12)	1.231	1.256

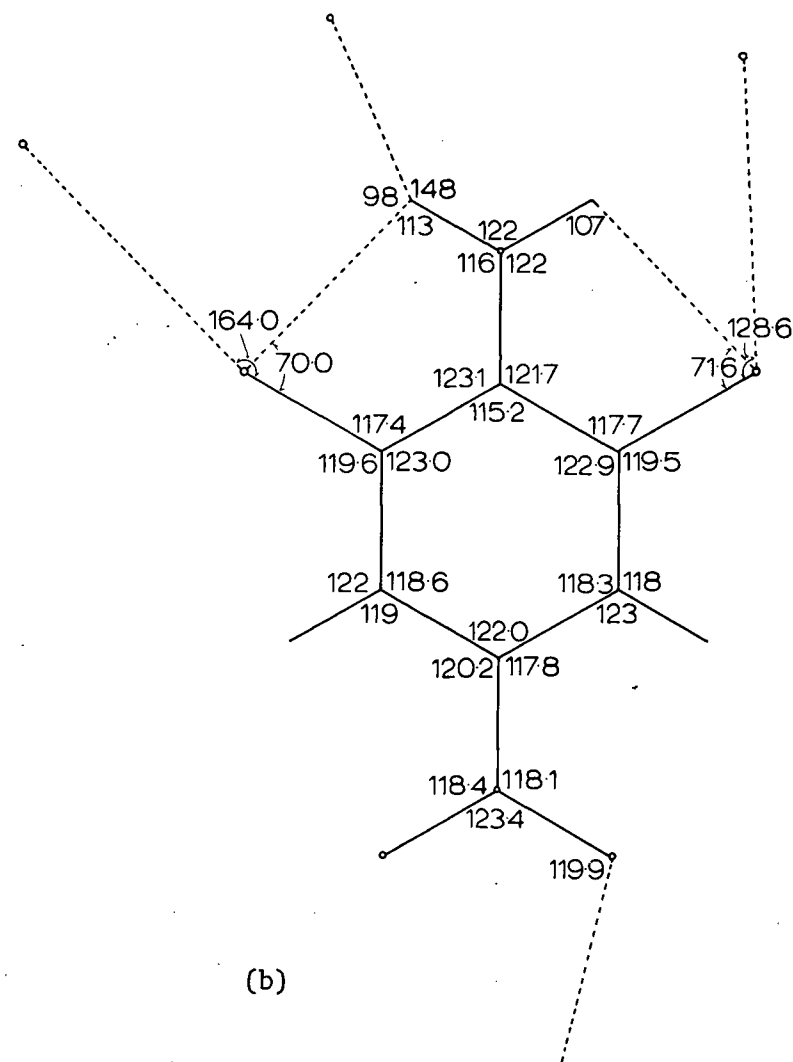
\* Bond lengths corrected for thermal motion.

(b) Valence angles (in degrees). In angles involving (i) no hydrogen atoms  $\sigma \approx 0.35$ , (ii) a ring hydrogen,  $\sigma \approx 2.3$ , (iii) one amino hydrogen,  $\sigma \approx 3.3$ , (iv) two amino hydrogens,  $\sigma \approx 4.6^\circ$ .

i	j	k	Angle (ijk)	i	j	k	Angle (ijk)
C(2)	— C(1)	— C(6)	115.2	C(4)	— C(5)	— C(6)	118.3
C(2)	— C(1)	— N(9)	123.1	C(4)	— C(5)	— H(14)	123
C(6)	— C(1)	— N(9)	121.7	C(6)	— C(5)	— H(14)	118
C(1)	— C(2)	— C(3)	123.0	C(1)	— C(6)	— C(5)	122.9
C(1)	— C(2)	— Cl(7)	117.4	C(1)	— C(6)	— Cl(8)	117.7
C(3)	— C(2)	— Cl(7)	119.6	C(5)	— C(6)	— Cl(8)	119.5
C(2)	— C(3)	— C(4)	118.6	C(1)	— N(9)	— H(15)	122
C(2)	— C(3)	— H(13)	122	C(1)	— N(9)	— H(16)	116
C(4)	— C(3)	— H(13)	119	H(15)	— N(9)	— H(16)	122
C(3)	— C(4)	— C(5)	122.0	C(4)	— N(10)	— O(11)	118.4
C(3)	— C(4)	— N(10)	120.2	C(4)	— N(10)	— O(12)	118.1
C(5)	— C(4)	— N(10)	117.8	O(11)	— N(10)	— O(12)	123.4



(a)



(b)

Figure 4. Molecular dimensions, (a) bond lengths, hydrogen-bond distances, and some shorter intermolecular interactions, and (b) valency angles.

in the plane of the benzene ring and the correction to the C-C ring distances is  $0.003 \text{ \AA}$ .<sup>20</sup> As can be seen from Figure 5., the shortest principal axis of the ellipsoid of each of the atoms C1(7), C1(8), N(9), N(10), O(11) and O(12) is directed approximately along the bond connecting the atom to the centre of the molecule, and the component of vibration in the direction of the bond is approximately equal to that of the atom at the other end of the bond. There is considerably more vibration perpendicular to these bonds. This indicates that an appropriate model for the determination of thermal motion corrections to the bonds is the riding model of Busing and Levy<sup>21</sup>.

The standard deviations in Table IX are for the uncorrected dimensions, and they indicate the precision in the determination of the centres of the scattering masses. Since the model for the estimation of thermal motion corrections is an approximation, the accuracy of the corrected bond lengths must be assumed to be less than that of the uncorrected values, and the standard deviations are probably of the order of twice those quoted for the uncorrected values.

The equations of several atomic planes, and the angles between the planes are given in Table X.

The distances and angles in the hydrogen-bonding systems of 2,6-dichloro-4-nitroaniline are given in Table XI.

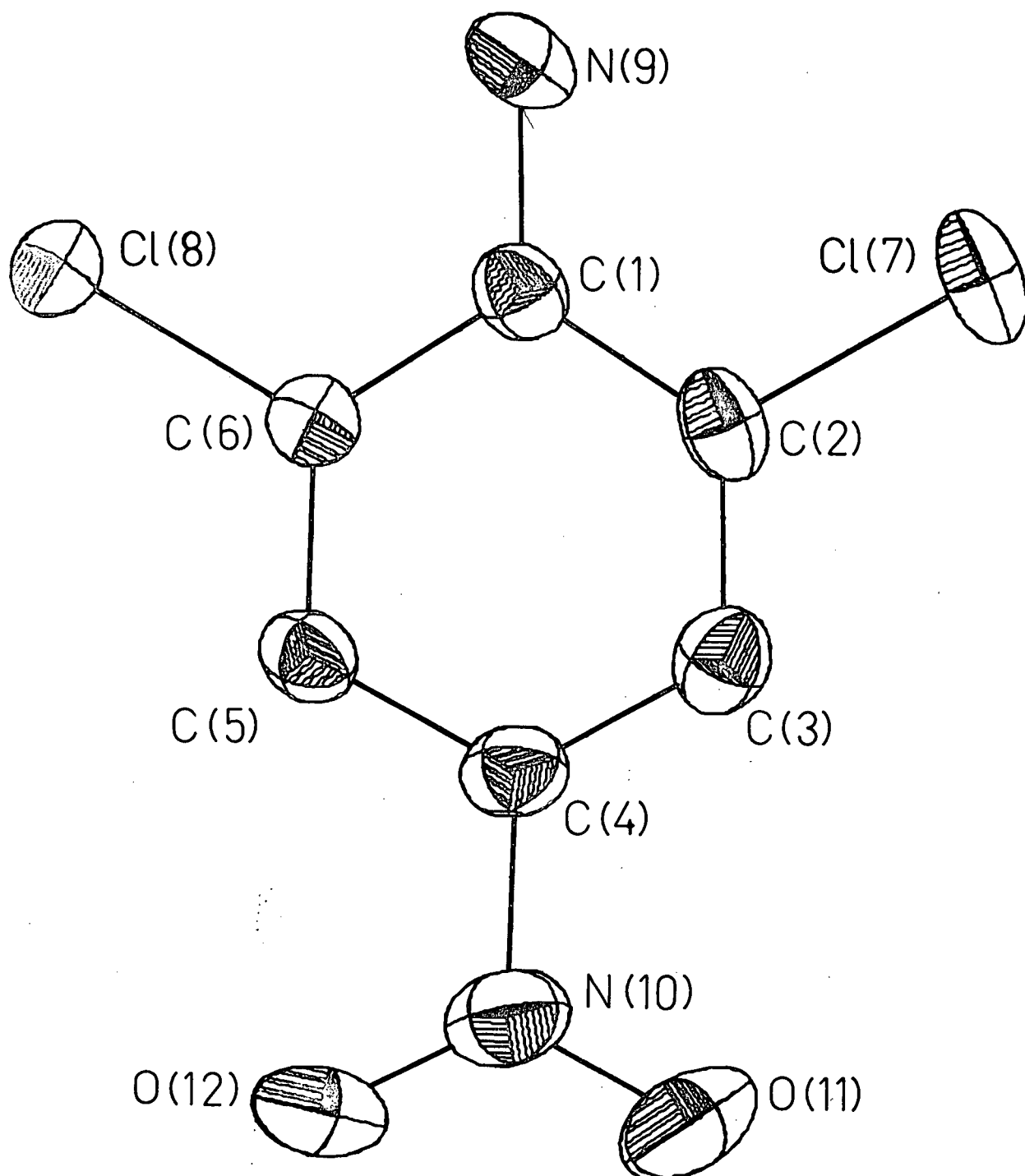


Figure 5. The thermal ellipsoids of the non-hydrogen atoms projected on to the plane of the benzene ring.

Table X.

Mean planes.

(a) Equations of mean planes, given in the form:

$$\ell X' + mY' + nZ' = p$$

where  $X'$ ,  $Y'$  and  $Z'$  are coordinates in Å., referred to the orthogonal axes  $a$ ,  $b$  and  $c^*$ .

Plane no.	Plane	$\ell$	$m$	$n$	$p$
1.	Benzene ring	-0.9265	0.1030	0.3618	0.3890
2.	C-nitro group	-0.8722	0.1499	0.4655	1.1545
3.	Amino group	-0.9615	0.1266	0.2440	-0.0405
4.	C-amino group	-0.9617	0.0619	0.2670	-0.2564
5.	Bifurcated H-bond	-0.9322	0.0336	0.3604	0.0321

(b) Angles between the planes:

Plane	$q$	$r$	Angle ( $qr$ )
	1	2	7.2°
	1	3	7.2
	1	4	6.3
	2	4	13.5

(c) Displacements from the planes; those underlined are the atoms used in calculating the equations of the plane.

Atom	Plane no.	1	2	3	4	5
C(1)		<u>0.003</u>		-0.093	<u>-0.000</u>	
C(2)		<u>-0.006</u>				
C(3)		<u>0.002</u>				
C(4)		<u>0.004</u>	<u>0.001</u>			
C(5)		<u>-0.005</u>				
C(6)		<u>0.002</u>				
Cl(7)		<u>-0.001</u>				<u>0</u>
Cl(8)		-0.010				
N(9)		0.012		<u>0</u>	<u>0.001</u>	<u>0</u>
N(10)		0.017	-0.003			
O(11)		-0.107	<u>0.001</u>			
O(12)		0.165	<u>0.001</u>			<u>0†</u>
H(13)		0.037				
H(14)		0.066				
H(15)		-0.102		<u>0</u>	<u>-0.032</u>	
H(16)		0.072		<u>0</u>	<u>-0.026</u>	0.016

† Actually O(12) of a neighbouring molecule, coordinates  $(1-x, y-\frac{1}{2}, \frac{1}{2}-z)$ .

Table XI.

Hydrogen bond distances and angles;  
standard deviations in parentheses.

Atoms s	t	u	v	Distances (Å.)		Angles (°)	
				su	tu	stu	tuv
N(9) — H(15)...Cl(8) — C(6)				2.953(4)	2.56(5)	107(4)	71.6(12)
N(9) — H(16)...Cl(7) — C(2)				2.963(4)	2.52(5)	113(4)	70.0(11)
N(9) — H(16)...O(12)' — N(10)'				3.004(5)	2.24(5)	148(4)	119.9(12)

#### D. DISCUSSION.

The plane of the benzene ring of the molecule of 2,6-dichloro-4-nitroaniline lies inclined at  $26.1^\circ$  to the (100) plane. The chlorine atoms are displaced 0.001 and 0.010 Å. from the benzene ring plane, and the substituted amino and nitro groups are rotated by small angles,  $6.3^\circ$  and  $7.2^\circ$  respectively, out of coplanarity with the benzene ring.

Table XII contains a comparison of bond lengths and angles in molecules similar to 2,6-dichloro-4-nitroaniline. For the benzene ring C-C distances, an average value is given for equal pairs of bonds; the maximum discrepancy of any of the recorded bond lengths from their mean value is  $1.2 \sigma$ . The precision of the final coordinates in these examples varies widely, but many similarities in the results can be seen.

In the results for 2,6-dichloro-4-nitroaniline, there is a definite shortening and lengthening of the C-C bonds in the benzene ring; the angles at C(1) and C(4) are significantly different from  $120^\circ$  - smaller at the amino C(1) and larger at the nitro C(4); the C-N bonds both differ from the sum of single-bond covalent radii,  $1.47 \text{ Å}$ . But all these results agree well with those of similar compounds.

The two principal factors affecting bond lengths and angles in

Table XII.

## Nitroaniline derivatives and related compounds.

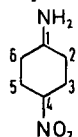
Compound	C-N <sub>amino</sub> distance		Mean of C <sub>1</sub> -C <sub>2</sub> , C <sub>1</sub> -C <sub>6</sub>		Mean of C <sub>2</sub> -C <sub>3</sub> , C <sub>5</sub> -C <sub>6</sub>		Mean of C <sub>3</sub> -C <sub>4</sub> , C <sub>4</sub> -C <sub>5</sub>		C-N <sub>nitro</sub> distance		Mean $\sigma_L^*$	Ring angle at C <sub>1</sub>	Ring angle at C <sub>4</sub>	Mean $\sigma_A^*$	Rotn. ang. of C-NH <sub>2</sub>	Rotn. ang. of C-NO <sub>2</sub>	C-Cl distance		Ref.
	Unc <sup>d</sup> .	Corr. <sup>†</sup>	Unc <sup>d</sup> .	Corr.	Unc <sup>d</sup> .	Corr.	Unc <sup>d</sup> .	Corr.	Unc <sup>d</sup> .	Corr.							Unc <sup>d</sup> .	Corr.	
2,6-dichloro-4-nitroaniline	1.339	1.358	1.411	1.414	1.369	1.372	1.377	1.380	1.456	1.466	0.005	115.2	122.0	0.4	6.3	7.2	1.733	1.743	This work
p-nitroaniline	1.353	1.371	1.409	1.412	1.372	1.375	1.389	1.392	1.454	1.460	0.007	118.9	121.2	0.4	16	1.9	-	-	22.
2,5-dichloroaniline	1.395	1.407	1.405	1.411	1.367	1.374	1.379	1.389	-	-	0.017	117.8	-	1.1	?	-	1.737	1.744	23.
2-chloro-4-nitroaniline	1.382	1.386	1.407	1.412	1.393	1.398	1.394	1.399	1.466	1.471	0.013	116.7	122.9	1.1	~0 ?	4.3	1.760	1.766	24.
N,N-dimethyl-4-nitroaniline	1.352	1.358	1.432	1.435	1.372	1.375	1.397	1.400	1.400	1.405	0.019	117.1	121.0	1.2	7.3 §	2.8	-	-	25.
2,6-dichloro-4-nitro-N,N-dimethylaniline	1.40	-	1.39	-	1.38	-	1.38	-	1.44	-	0.01	120	123	2	60.5 §	6	1.72	-	26.
nitrobenzene (at -30°C.)	-	-	1.363	-	1.426	-	1.367	-	1.486	-	0.014	-	125	-	-	0	-	-	27.
p-nitrophenol (at 90°K.)	-	-	1.390	-	1.379	-	1.385	-	1.442	-	0.006	-	122.3	0.4	-	1.5	-	-	28.
1-(dinitro-2',4'-phenyl)-4-chloro-pyrazole	1.390	-	1.392	-	1.390	-	1.375 1.393	-	1.470 1.482	-	0.012	118.0	123.2 122.1	0.6	21.6	2.3 65.3	-	-	29.
1-(trans-bicyclo[4.2.0]-octyl)-3,5-dinitrobenzoate	-	-	-	-	1.377	-	1.380 1.372	-	1.474 1.489	-	0.004	-	122.8 122.6	0.2	-	1.4 4.3	-	-	30.

Bond distances are in Å., angles in degrees.

† bond lengths corrected for thermal motion.

§ Rotation angle of C-NMe<sub>2</sub> group.\*  $\sigma_L$  - mean e.s.d. of bonds quoted involving C and N atoms. (N.B.  $\sigma$  for uncorrected values). $\sigma_A$  - mean e.s.d. of ring angles quoted.

The compounds are numbered as derivatives of p-nitroaniline:

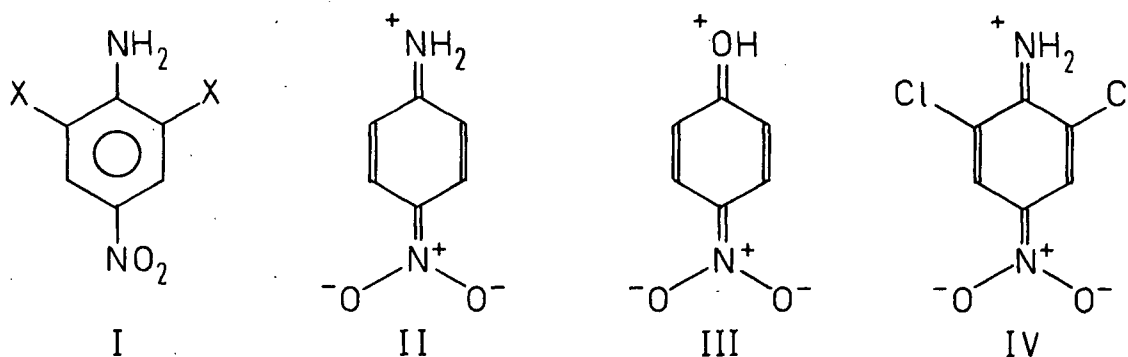


i.e. the nitro group is always at C<sub>4</sub>. In the last two compounds, each nitro group is considered, in turn, as being at C<sub>4</sub>.



benzene derivatives are resonance and hybridisation. The latter effect, in particular the non-equivalent or second-order hybridisation theories of Coulson <sup>31</sup>, Trotter <sup>27</sup>, Bent <sup>32</sup> and Carter, McPhail and Sim <sup>33</sup>, have helped to explain many of the benzene ring distortions, especially the bond lengths and angles adjacent to a substituent group. The theories of  $\pi$ -electron resonance can explain shortening of bonds in molecules capable of conjugation; in benzene derivatives, it is, of course, necessary for the substituent groups to be coplanar (or very nearly so) with the benzene ring if excited, resonance structures are to make any contribution to the overall structure.

In molecules of type I, there are often several excited, resonance



forms possible, and it was concluded by Trueblood, Goldish and Donohue <sup>22</sup> that the quinoidal structure II has considerable importance in the overall structure of p-nitroaniline. The p-nitrophenol results <sup>28</sup> show that, similarly, structure III has importance. Our present study of 2,6-dichloro-4-nitroaniline shows the same characteristics, and an important contributor to the overall structure must be form IV. In these compounds, the C-N<sub>nitro</sub> and C(2)-C(3) bonds are shorter than in nitrobenzene, and it is thus concluded that the introduction of an electron-donating substituent in the para position to the nitro group does enhance the formation of excited, resonance forms as II - IV, and does shorten the C-N<sub>nitro</sub> bond slightly, and the C(2)-C(3) bond considerably.

The C(1)-N(9) bond in 2,6-dichloro-4-nitroaniline is similar to

other C-N<sub>amino</sub> bonds and considerably shorter than the C-N<sub>nitro</sub> distances. It is, at 1.358 Å. (amongst the shortest of recorded C-N<sub>amino</sub> bonds), slightly shorter than that in p-nitroaniline. This is perhaps a result of the more coplanar amino group in our example, allowing increased ease of formation of the resonance structure IV.

The benzene ring C-C distances in these two compounds are similar, and the shortening of the two bonds, C(2)-C(3) and C(5)-C(6) can be explained by the resonance theories above. The two other pairs of bonds - which the resonance theories say should be similar in length - are influenced more by "non-equivalent" hybridisation; for an atom using hybridised orbitals for bonding, the s-character of an atomic orbital is more concentrated in orbitals the atom uses towards electropositive substituents, and these bonds with more s-character are shorter and stronger than strictly equivalent hybridised bonds. Thus the nitro group, strongly electronegative, tends to attract the more diffuse 2p orbitals of the C(4) atom and the resulting hybridised bonding orbital has less s-character, giving a long C-N bond; the adjacent ring C-C bonds have correspondingly more s-character, i.e. are shorter (i.e. opposing the resonance effect), with a ring angle of more than 120°. The less electronegative amine group at C(1) shows the opposite effect - a shortened C-N bond, longer ring C-C bonds and a ring angle of less than 120°. The electronegative effects of the two chlorine atoms ortho to the amine group will tend to shorten the ring C-C bonds adjacent to the C-Cl groups, i.e. opposing the amino group's effect on the C(1)-C(2) and C(1)-C(6) bonds, and enhancing the resonance effects on the C(2)-C(3) and C(5)-C(6) bonds; the ring angles at C(2) and C(6) are, as at C(4), greater than 120°.

These resonance and hybridisation effects are found in most of the compounds of Table XII. Those molecules in which conjugation does not or cannot occur to any significant extent, e.g. nitrobenzene, 2,6-dichloro-4-nitro-N,N-dimethylaniline (in which the -NMe<sub>2</sub> group is rotated through 61°

from coplanarity with the benzene ring), the pyrazole example (where the angle of rotation is  $21.6^\circ$ ) and the dinitrobenzoate, have  $C-N_{\text{amino}}$  distances of approximately  $1.40 \text{ \AA}$ , adjacent  $C-C(-N_{\text{amino}})$  distances of  $\sim 1.40 \text{ \AA}$ ,  $C-N_{\text{nitro}}$  distances between  $1.44$  and  $1.49 \text{ \AA}$  (but mainly  $\sim 1.48 \text{ \AA}$ ), and adjacent  $C-C(-N_{\text{nitro}})$  distances of  $\sim 1.38 \text{ \AA}$ . The possibility of conjugation, as in p-nitrophenol, p-nitroaniline, 2,6-dichloro-4-nitroaniline, etc., adjusts the  $C-N_{\text{amino}}$  length to  $\sim 1.36 \text{ \AA}$  and the other bond lengths less markedly; significant differences can be observed only in the more accurate structure determinations. The ring angles at  $C-N_{\text{amino}}$  and  $C-N_{\text{nitro}}$  are approximately  $117$  and  $122^\circ$  respectively for all the examples.

The C-H, N-H and C-Cl bond distances in 2,6-dichloro-4-nitroaniline all appear to be normal, within experimental error. Similarly, in the nitro group, the N-O distances of  $1.257 \text{ \AA}$  and the O-N-O angle,  $123.4^\circ$ , are normal and similar to those in p-nitroaniline ( $1.247 \text{ \AA}$  and  $123.3^\circ$  respectively).

A summary showing how various bonds and angles in 2,6-dichloro-4-nitroaniline are affected by the resonance and hybridisation effects is given in Table XIII.

In Table X, planes nos. 3 and 4 describe the  $C-NH_2$  group, showing it to be planar within the accuracy of the measurement of the hydrogen atom coordinates. This amino group should be approximately coplanar with the benzene ring if it is to be allowed to contribute to the formation of resonance structures; it is, in fact,  $6.3^\circ$  out of coplanarity with the benzene ring plane. Hence the amino hydrogen atoms are only  $2.56$  and  $2.52 \text{ \AA}$  ( $\sigma = 0.05 \text{ \AA}$ ) from the neighbouring chlorine atoms. It seems likely, therefore, that there is intramolecular hydrogen bonding between H(15) and Cl(8), and H(16) and Cl(7); if there was to be no bonding between the hydrogen and chlorine atoms, the amino group would have to be rotated much further about the C(1)-N(9) bond so that the Cl...H distances were approximately  $3.0 \text{ \AA}$ ,

Table XIII.

Summary of the effects of resonance and hybridisation on normal benzene

ring, C-N<sub>2</sub>, and C-Cl dimensions in 2,6-dichloro-4-nitroaniline.

	C-N <sub>amino</sub> bond	C <sub>1</sub> -C <sub>2</sub> C <sub>1</sub> -C <sub>6</sub>	C <sub>2</sub> -C <sub>3</sub> C <sub>5</sub> -C <sub>6</sub>	C <sub>3</sub> -C <sub>4</sub> C <sub>4</sub> -C <sub>5</sub>	C-N <sub>nitro</sub>	C-Cl	Ring angle at C <sub>1</sub>	Ring angles at C <sub>2</sub> ,C <sub>6</sub>	Ring angle at C <sub>4</sub>
Resonance	shorten	lengthen	shorten	lengthen	shorten	-	-	-	-
Hybridisation at <u>C</u> -NO	-	-	-	shorten	lengthen	-	-	-	increase
" " <u>C</u> -NH	shorten	lengthen	-	-	-	-	decrease	-	-
" " <u>C</u> -Cl	-	shorten	shorten	-	-	lengthen	-	increase	-
"Normal" dimensions	1.475 *	1.395 †	1.395 †	1.395 †	1.475 *	1.7 *	120° †	120° †	120° †
2,6-dichloro-4-nitro- aniline	1.358	1.411	1.372	1.380	1.466	1.743	115.2	122.9	122.0

The "normal" dimensions are taken from:

\* empirical sum of covalent radii, with allowances for differences  
in electronegativities.

† dimensions of the benzene ring in benzene.

the sum of van der Waals' radii.

Additional evidence, indicating that this short H...Cl distance is a hydrogen bond, is found in the angles at the C(2) and C(6) atoms; the chlorine atoms appear to be pulled slightly towards the amino group, rather than being pushed away by merely steric interactions. Any possible intermolecular interactions of the chlorine atoms, e.g. Cl(7)...Cl(8)', Cl(7)...H(15)', Cl(8)...Cl(7)', and Cl(8)...H(14)', would tend to push the chlorine atoms away from the amino group. The formation of a hydrogen bond, however, has the reverse, stronger effect.

A similar type of intramolecular hydrogen bond has been noted for o-chlorophenol and other o-substituted phenols and anilines, etc.<sup>34</sup>; the evidence was found in spectroscopic studies, in particular in the O-H and N-H stretching frequencies. Pimentel and McClellan<sup>35</sup> note that five-membered rings containing an intramolecular hydrogen bond are common and will normally be formed when two adjacent positions of a benzene ring have the proper substituents.

The hydrogen atom, H(16), is also hydrogen-bonded to an oxygen atom, O(12)', of a neighbouring molecule. Thus, H(16) is involved in a bifurcated hydrogen bond system - it is bonded intramolecularly with Cl(7), and intermolecularly with O(12)'; the hydrogen atom is located only 0.02 Å out of the plane through N(9), Cl(7) and O(12)'. The angles at H(16) - 148, 113 and 98° - are similar in range to those of several examples of bifurcated hydrogen bonds, e.g. those quoted by Parthasarathy<sup>36</sup>, particularly the examples in glycylglycine hydrochloride monohydrate<sup>36</sup>.

The nitro group is rotated through 7.2° from coplanarity with the benzene ring; this rotation brings the O(12) atom closer to the H(16)' atom of a neighbouring molecule, and allows the formation of the hydrogen bond O(12)...H(16)' described above, connecting the molecules in long chains parallel to the b-axis. This is illustrated in Figure 6., which shows the

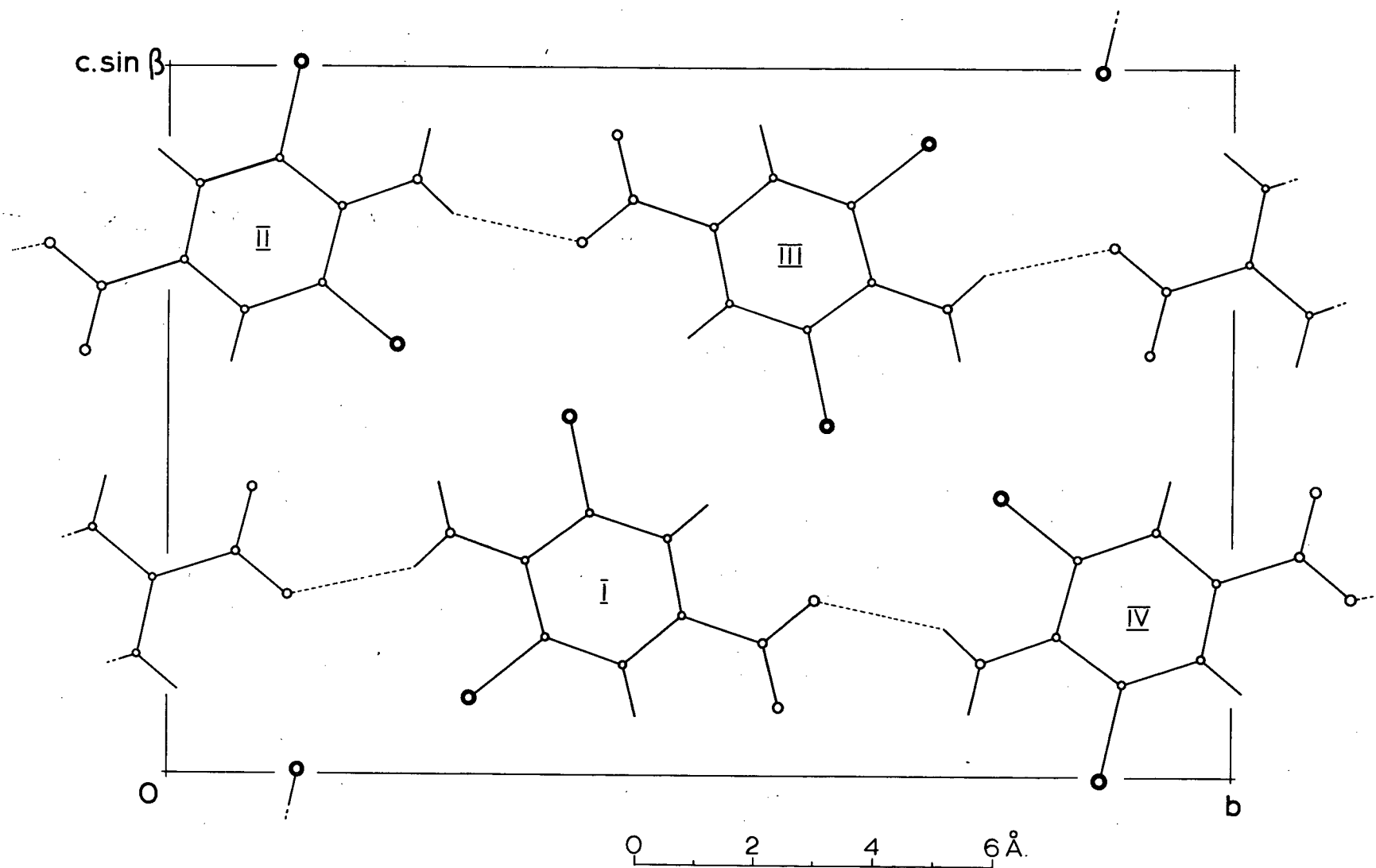


Figure 6. Molecular packing arrangement, showing also the intermolecular hydrogen bonds.

molecular packing arrangement in the crystal, looking down the very short a axis.

There are no other very short intermolecular distances; a list of the shorter distances is given in Table XIV. The Cl(7)...Cl(8)' distance of 3.40 Å. is somewhat shorter than the sum of van der Waals' radii, but appears to correspond well with the Cl...Cl distances in similar compounds, e.g. those quoted by Sakurai, Sundaralingam and Jeffrey <sup>23</sup>. The C(2)-Cl(7)...Cl(8)' angle is 164.0°, and this is also within the normal range for this type of interaction, but the angle at the other chlorine atom, i.e. C(6)-Cl(8)...Cl(7)' is quite different, at 128.6°.

Table XIV.

Shorter intermolecular distances.

Cl(7) <sub>I</sub> ...Cl(8) <sub>II</sub>	3.40 Å.	O(11) <sub>I</sub> ...H(13) <sub>III'</sub>	2.77 Å.
Cl(7) <sub>I</sub> ...H(15) <sub>II'</sub>	2.92	O(11) <sub>I</sub> ...H(13) <sub>III''</sub>	2.85
Cl(8) <sub>I</sub> ...H(14) <sub>III'</sub>	2.84	O(12) <sub>I</sub> ...H(16) <sub>IV'</sub>	2.24 *
N(9) <sub>I</sub> ...O(12) <sub>IV</sub>	3.00 *		

\* Involved in a hydrogen bond.

The Roman numerals refer to symmetry related molecules:

I.	x, y, z.		
II.	x-1, $\frac{1}{2}$ -y, z- $\frac{1}{2}$ ;	II'.	x, $\frac{1}{2}$ -y, z- $\frac{1}{2}$ .
III.	2-x, 1-y, 1-z;	III'.	1-x, 1-y, -z;
IV.	1-x, y- $\frac{1}{2}$ , $\frac{1}{2}$ -z;	IV'.	1-x, $\frac{1}{2}$ +y, $\frac{1}{2}$ -z.
		III''.	-x, 1-y, -z.

## Twinning.

It will be observed from Figure 6. that the a-b plane seems sparsely populated - only the two Cl(8) atoms are close to this plane. This sparseness led to a consideration of the twinning in this crystal. In a monoclinic crystal, there are two possible ways in which the twins may be related <sup>5b</sup> - either by a twin axis or a twin plane. The preliminary photographs for 2,6-dichloro-4-nitroaniline indicated that the twin axis would be [100], and the twin plane (001). Both possibilities were examined here and it was found that only by rotation about the twin axis (followed by a translation along a) could one twin fit reasonably on to the other. The suggested arrangement about the (001) plane is shown in Figure 7., and the shortest estimated intermolecular distances are recorded thereon.

To achieve this system of congruent twins, the unit cell of one twin was rotated through 180° about the a axis and then shifted parallel to a until the position of Cl(8) at the boundary plane (molecule II') coincides with that of Cl(8) in the original system. In the twinned cell, the y- and z-coordinates of the atoms are the same as those in the original cell. The Cl(7)<sub>III'</sub> atom is also found to be very close (within 0.09 Å.) to the position of Cl(7) in the original arrangement.

Some of the estimated intermolecular distances seem short, but none impossibly so. Hydrogen bonding probably controls the twinning across this plane, e.g. it seems likely that hydrogen bonds are formed between Cl(7)<sub>I</sub> and H(15)<sub>II'</sub>, (2.43 Å.), and that there is some kind of hydrogen "liaison" between O(11)<sub>III'</sub> and H(13)<sub>I</sub>, (2.33 Å.), O(11)<sub>I</sub> and H(13)<sub>III'</sub>, (2.52 Å.), Cl(8)<sub>IV</sub> and H(14)<sub>II'</sub>, (2.58 Å.).

The alternative mode of twinning, the formation of enantiomorphous twins by reflection through the twin plane (001), seems less likely. The best arrangement again seemed to have Cl(8)<sub>II'</sub> on the boundary plane coincid-



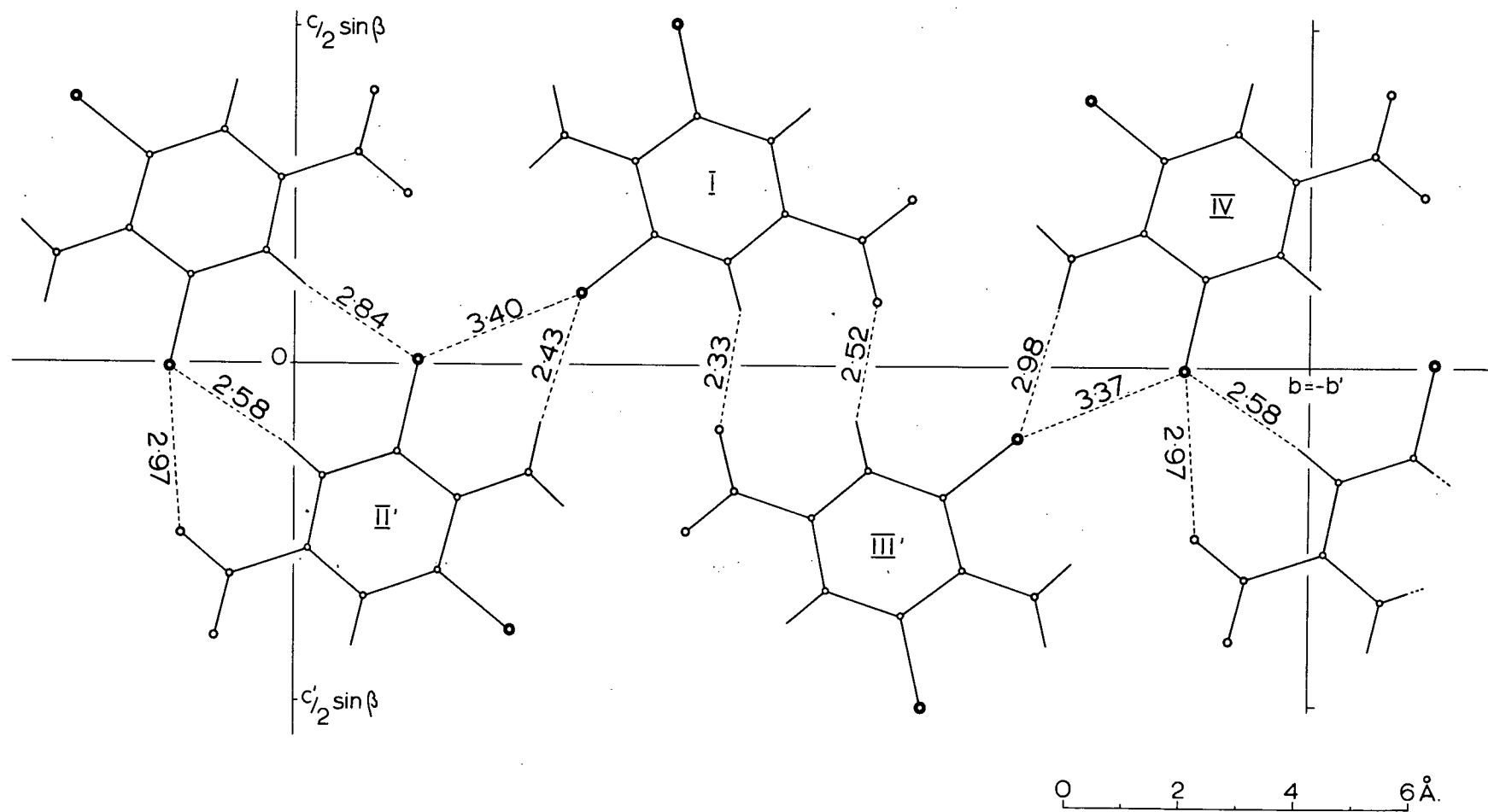


Figure 7. The suggested arrangement about the boundary plane (001) between the two twins.

ent with Cl(8) of the original system, (this involved translations parallel to a and to b), but this resulted in one impossibly short Cl(8)<sub>IV</sub>...

O(11)<sub>III</sub>, (1.67 Å.) distance across the twin plane.

PART IV. THE STRUCTURE DETERMINATION OF  
ETHYL 3,5-DINITROBENZOATE.

## A. INTRODUCTION.

In 1961, Camerman and Trotter <sup>37</sup> recorded the crystallographic data for ethyl 3,5-dinitrobenzoate, but were unable to complete the determination of the structure at that time. A recent reinvestigation into this problem has produced an accurate solution of the molecular structure and is described here.

This compound is of interest in that it has two nitro groups with almost identical intramolecular surroundings. The atoms in positions ortho to both the nitro groups are hydrogen atoms so that steric effects on the nitro group are minimal and equal. Hence we now have an opportunity to examine the orientation of the two nitro groups with respect to the benzene ring, and observe the effects of neighbouring molecules on the orientations.

The C-N bond lengths and benzene ring dimensions in nitrobenzene compounds, and the relative importances of resonance and hybridisation theories in these compounds, have been discussed for a decade, and it was hoped that the results of this investigation might add some more accurate data for this discussion.

## B. X-RAY ANALYSIS.

The crystals of ethyl 3,5-dinitrobenzoate, recrystallised from ethanol, are colourless needles elongated along the b axis and having a well-developed (100) face and lesser (001) face. The crystal selected had dimensions  $0.07 \times 0.8 \times 0.2$  mm. and was mounted with the b axis parallel to the  $\phi$ -axis of the goniostat.

The unit cell dimensions and the space group were determined initially from rotation, Weissenberg and precession films, and the cell dimensions were later found more accurately from a least-squares refinement based on the diffractometer values of  $2\theta$  for 30 reflections, determined with

Cu-K $_{\beta}$  ( $\lambda = 1.3922 \text{ \AA.}$ ) or Cu-K $_{\alpha_1}$  ( $\lambda = 1.5405 \text{ \AA.}$ ) radiation.

Crystal data:

Ethyl 3,5-dinitrobenzoate,  $\text{C}_9\text{H}_8\text{N}_2\text{O}_6$ .  $M = 240.17$ .

Monoclinic,  $a = 13.856(4)$ ,  $b = 4.770(1)$ ,  $c = 18.354(5) \text{ \AA.}$ ,  $\beta = 119.59(2)^\circ$ ,

(standard deviations in parentheses).

$V_c = 1054.75 \text{ \AA}^3$ .

$D_m = 1.511$  (flotation in aqueous KI),  $D_c = 1.512 \text{ g.cm}^{-3}$ . with  $Z = 4$ .

$F(000) = 496$ .

Absorption coefficient,  $\mu$  (Cu-K $_{\alpha}$ ,  $\lambda = 1.5418 \text{ \AA.}$ ) =  $11.4 \text{ cm}^{-1}$ .

Reflections absent:  $0k0$  when  $k$  is odd,  $h0l$  when  $l$  is odd; hence space group is  $P2_1/c$ .

The intensity measurements were made on a Datex-automated G.E. XRD-6 diffractometer with a scintillation counter and a  $\theta$ - $2\theta$  scan. Cu-K $_{\alpha}$  radiation (Ni filter and pulse-height analyser) was used. The intensities of 1466 independent reflections with  $2\theta \leq 120^\circ$  (i.e. minimum interplanar spacing =  $0.89 \text{ \AA.}$ ) were measured. Of these, 166 (i.e. 11.3%) were treated as unobserved reflections, having  $I/\sigma_I < 2.0$ , where  $I$  is the corrected intensity count, and  $\sigma_I^2$  is defined:

$$\sigma_I^2 = S + B + (0.02.S)^2$$

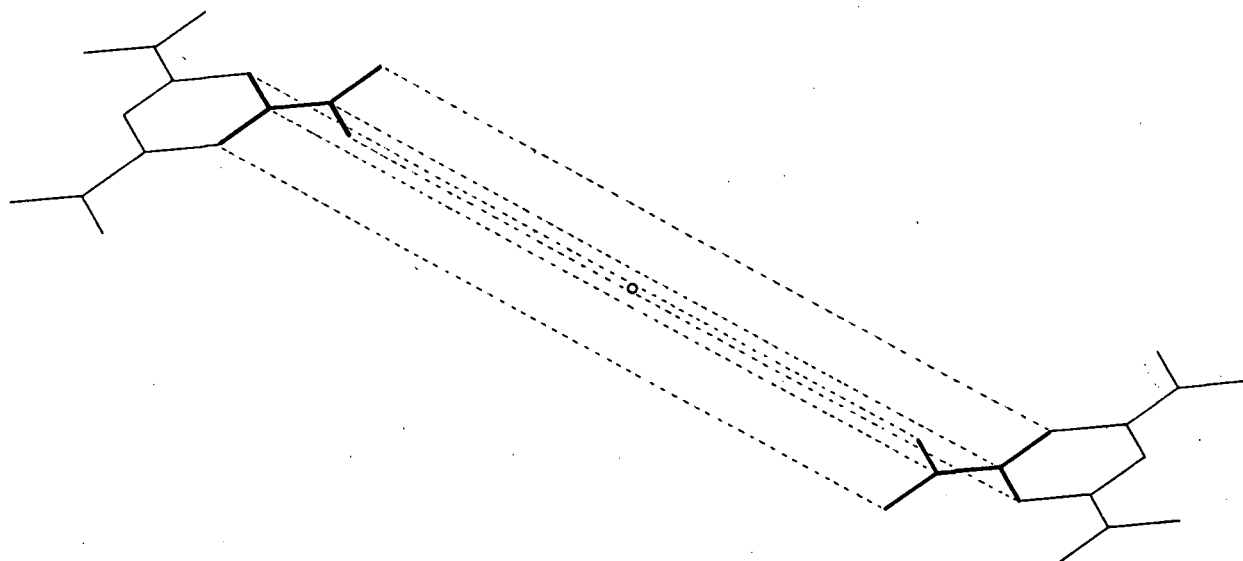
where  $S$  = scan count, and  $B$  = background count over the same scan range.

Lorentz and polarisation corrections were applied. No absorption corrections were made. The structure amplitudes were then calculated.

### C. STRUCTURE ANALYSIS.

A Patterson map was drawn from the diffractometer data. Theoretically, there should have been four outstanding peaks in this map, resulting from the sums of vectors between roughly centred portions of the molecule

and their like portions related by a centre of symmetry, e.g.



and similarly for the other two  $\begin{array}{c} \text{C} \\ \diagup \\ \text{C}-\text{X} \\ \diagdown \\ \text{C} \end{array} \begin{array}{c} \text{O} \\ \diagup \\ \text{O} \end{array}$  groups and for the benzene ring atoms. This assumes, of course, that the illustrated part of the molecule is approximately planar. A set of four possible peaks was found in the Patterson map, and the coordinates of nine atoms - the six carbons of the benzene ring, and three atoms (each taken as a nitrogen) attached to the ring in the 1,3,5 positions - were estimated, and used in a structure factor calculation and a Fourier synthesis. The resulting electron-density map was not encouraging, and indicated that the set of four chosen peaks was not the correct set.

No alternative set of peaks was apparent and another means of approach was required.

All the atoms of ethyl 3,5-dinitrobenzoate are light atoms and similar in size (not including the hydrogen atoms). The space group,  $P2_1/c$ , is a centrosymmetric one. Therefore the problem was a good candidate for solution by direct methods.

Solution by direct methods:

Wilson's method <sup>9</sup> was used to scale the structure amplitudes from their measured values to absolute values, and to determine an overall temperature factor for the structure. The structure amplitudes were then converted to the normalised structure amplitudes,  $|E|$ 's <sup>7</sup>. The scattering factors for oxygen, nitrogen and carbon were taken from International Tables <sup>5c</sup>, and for hydrogen from the values of Stewart, Davidson and Simpson <sup>19</sup>.

The results of the Wilson Plot and the E-statistics for ethyl 3,5-dinitrobenzoate, together with some theoretical values, are recorded in Table XV.

There were 169 reflections with  $|E| > 1.50$ , and these were used in

Table XV.

Results from the Wilson Plot, and the E-statistics.

	Observed	Theoretical	
		Centro-	Noncentro-symmetric
Overall temperature factor	3.98		
Mean $ E $	0.787	0.798	0.886
Mean $ E ^2$	1.022	1.000	1.000
Mean $  E ^2 - 1 $	1.032	0.968	0.736
Percentage of reflections			
with $ E  > 3$	1.02	0.30	0.01
"      " $ E  > 2$	5.46	5.00	1.80
"      " $ E  > 1$	27.42	32.00	37.00

Long's program <sup>38</sup> for phase-determination in the centrosymmetric case. This program determines the signs (phases) of the normalised structure factors by applying Sayre's equation <sup>39</sup>:

$$s_h = s_{h'} \cdot s_{h-h'}$$

where  $s$  means "the sign of", and  $h$  is the reflection  $hkl$ , etc. For this equation to hold, the normalised structure amplitudes of the reflections  $h$ ,  $h'$  and  $h-h'$  must all be large. More generally:

$$s_h \sim s(\sum E_{h'} \cdot E_{h-h'})$$

where the symbol  $\sim$  means "probably equal to". This is known as the  $\Sigma$ -2 relationship.

The probability,  $P$ , of the sign  $s_h$  being correct is given for each reflection, and is determined from:

$$P = 0.5 + 0.5 \cdot \tanh \left| \frac{\epsilon_3}{\epsilon_2^{3/4}} \cdot E_h \cdot \sum E_{h'} \cdot E_{h-h'} \right|$$

where  $\frac{\epsilon_3}{\epsilon_2^{3/4}}$  is a constant depending on the contents of the unit cell, and is equal to  $\sqrt{N}$ , where  $N$  is the number of atoms in the unit cell.

The program prepares a list of reflections for the  $\Sigma$ -2 relationships, i.e. combinations of  $h'$  and  $h-h'$  for each reflection  $h$  in the input data. One of the eight centres of symmetry in the unit cell is then chosen as the origin by selecting, and arbitrarily assigning positive signs to, three reflections. The selection is made from the reflections with the highest  $|E|$ 's and with indices conforming to rules derived from the space group symmetry; here the indices of each reflection, the sums of indices of any pair, and the sum of indices of the three, must have odd-even parities other than (even, even, even). Four more reflections, each having large  $|E|$ 's and many  $\Sigma$ -2 relationships, are then selected and assigned each sign in turn so that there are sixteen ( $2^4$ ) starting sets of signs. The seven starting



reflections selected by the program were:

h	k	l	E
1	1	-4	3.27
0	1	3	3.35
0	2	11	3.65
2	2	-9	3.85
1	4	4	3.41
10	1	-13	3.59
9	0	2	3.41

In each of the sixteen sets, the signs of these seven reflections were not allowed to change. The program predicts the sign of each of the remaining reflections,  $h$ , by the application of Sayre's relationship to all the possible combinations of  $h'$  and  $h-h'$ , using the general equation above. After examining each reflection, and determining the signs of some, the program starts a second cycle, redetermining the signs and determining signs of additional reflections. There are various iteration procedures available in the program; in our case, newly determined signs were not used to determine signs of additional reflections until the next cycle. This procedure was continued through several cycles until there were no further changes in the signs of any of the reflections, and no new signs determined.

A summary of the results of the sixteen sets of determinations is given in Table XVI. The consistency index,  $C$ , is defined as:

$$C = \frac{\langle |E_h| \sum_{h'} |E_{h'}| |E_{h-h'}| \rangle}{\langle |E_h| \cdot \sum_{h'} |E_{h'}| |E_{h-h'}| \rangle}$$

where  $\langle \rangle$  means the average over all  $h$ .

The high consistency index of set no. 1, together with the results that only six cycles of iteration were required to complete the determination of all the signs, and that the numbers of positive and negative structure

Table XVI.

Comparison of the 16 sets of phases  
generated by the Phase Determining program.

Set no.	No. of cycles	No. of pluses	No. of minuses	Consistency, C
1	6	84	85	0.901
2	9	103	66	0.694
3	8	94	75	0.673
4	6	79	90	0.879
5	8	116	53	0.660
6	9	83	86	0.806
7	>12	90	79	0.720
8	11	89	80	0.681
9	9	97	72	0.860
10	9	89	80	0.656
11	7	98	71	0.624
12	7	80	89	0.866
13	7	85	84	0.702
14	12	87	82	0.757
15	10	68	101	0.774
16	7	91	78	0.682

factors were almost equal, indicated that this set was most probably the correct set of signs. It was shown later that all 169 reflections had been assigned the correct signs.

The normalised structure factors, with the phases of set no. 1, were then used in the calculation of an "E-map", a three-dimensional Fourier synthesis. The major part of the molecule of ethyl 3,5-dinitrobenzoate - the benzene ring and the three major substituent groups,  $-XO_2$ , at the 1,3,5 positions - was outstanding in the E-map. These fifteen atoms, with X designated as nitrogen in the three substituent groups, were used to calculate an electron-density map, and this showed, roughly, the positions of the ethyl group carbon atoms, and hence distinguished the carboxyl group from the two nitro groups.

The structure was refined by full-matrix least-squares methods,

with minimisation of the sum  $\sum w(|F_o| - |F_c|)^2$ , initially with  $w=1$  for all reflections. The structure refined rapidly to  $R = 0.164$  for the seventeen non-hydrogen atoms with isotropic temperature factors, and to  $R = 0.100$  when all seventeen atoms were refined anisotropically. The thermal parameters and the standard deviations of the ethyl group carbon atoms were not satisfactory at this stage, and the C-C bond length was very short. A difference Fourier map, computed to locate the hydrogen atoms, showed the three benzene ring hydrogen atoms clearly at  $0.39 - 0.55 \text{ e}\text{\AA}^{-3}$ ; and in the region of the ethyl group, there were two major peaks of  $0.78$  and  $0.39 \text{ e}\text{\AA}^{-3}$ . The high peak here led to the realisation that the ethyl group was randomly disordered in the crystal, and better refinement results were achieved when two ethyl group orientations were considered with a ratio of populations of  $7/3$ .

The occupancy ratio was determined from a consideration of the temperature factors of the ethyl group carbon atoms. If it is assumed that the pairs of carbon atoms, C(16) and C(16'), C(17) and C(17'), are in similar surroundings and are allowed to vibrate to similar extents, then the temperature factors of the atoms of each pair should be approximately the same. The occupancies were varied until this equivalence was achieved. The presence of hydrogen atoms was not considered in the determination of this ratio.

A later difference Fourier map indicated the positions of the five hydrogen atoms of the major ethyl group.

In the last stages of refinement, 15 non-hydrogen atoms (all except the ethyl group carbon atoms) were refined anisotropically, and the ethyl carbon atoms and all the hydrogen atoms were refined isotropically. A Hughes-type weighting scheme was applied to the data, viz. for reflections with  $|F_{\text{obs}}| \leq 10.0$ ,  $\sqrt{w} = 1$ ; with  $|F_{\text{obs}}| > 10.0$ ,  $\sqrt{w} = 10.0/|F_{\text{obs}}|$ ; and for unobserved reflections,  $\sqrt{w} = 0.6$ .

The 013 reflection was omitted from the final calculations since it was suspected of serious extinction errors. The refinement was complete with  $R = 0.061$  for 1299 observed reflections, and 0.068 for all the reflections (except the 013).

A list of the structure factors,  $|F_o|$  and  $|F_c|$ , is given in Table XVII. The final atomic parameters are recorded in Table XVIII, and a view of the molecule is shown in Figure 8.

Corrections for thermal motion have been estimated from an examination of the thermal ellipsoids of the atoms with nos. 1 - 15, (Figure 9.). There seems to be very little oscillation in the plane of the ring, and this results in a correction of approximately  $0.003 \text{ \AA}$ . to the C-C ring bond lengths <sup>20</sup>. The riding model of Busing and Levy <sup>21</sup> appears to be an appropriate model for the determination of corrections to the bond lengths of the nitro groups. Similar corrections have been applied to the carboxyl group, but these results are perhaps not so reliable as for the nitro groups since the ellipsoid of the O(13) atom is modified by the bonding of that atom to the ethyl group in one of two possible positions.

Table XIX shows the bond lengths and valence angles as calculated from the final atomic coordinates, and some bond lengths after correction for thermal motion. Standard deviations are quoted for the uncorrected values in Table XIX; since the thermal motion corrections were estimated from an approximate model, the final bond lengths probably have less precision than the uncorrected lengths. Figures 10(a). and 10(b). show the estimated final bond lengths and the valence angles.

The equations of several planes through the molecule are in Table XX(a); in part (b), the distances of atoms from the benzene ring plane are recorded, and part (c) shows the angles between the normals of the benzene ring plane and the substituent group planes.

Table XVII.

Measured and calculated structure amplitudes. Measured

values with negative sign indicate unobserved reflections.

h k l			F <sub>obs.</sub>			F <sub>calc.</sub>													
1	0	0	2.3	1.4	3	1	6	7.6	7.5	5	1	-11	13.8	13.4	13	2	-6	5.4	6.0
2	0	0	10.6	15.5	4	1	6	4.6	5.4	7	1	-1	10.6	10.3	14	2	-4	1.7	1.9
3	0	0	20.6	21.4	5	1	6	4.6	5.4	7	1	-1	10.6	10.3	14	2	8	12.3	13.4
4	0	0	10.6	15.5	6	1	6	4.6	5.4	8	1	-1	14.8	14.8	15	2	8	12.3	13.4
5	0	0	2.3	1.4	7	1	6	4.6	5.4	9	1	-1	7.4	6.8	16	2	8	6.6	6.6
6	0	0	10.6	15.5	8	1	6	4.6	5.4	10	1	-1	13.1	12.9	17	2	-8	37.2	37.4
7	0	0	2.3	1.4	9	1	6	4.6	5.4	11	1	-1	9.8	9.8	18	2	-8	11.7	11.7
8	0	0	10.6	15.5	10	1	6	4.6	5.4	12	1	-1	11.0	11.3	19	2	-8	11.7	11.7
9	0	0	2.3	1.4	11	1	6	4.6	5.4	13	1	-1	11.6	10.6	20	2	-8	5.4	5.4
10	0	0	10.6	15.5	12	1	6	4.6	5.4	14	1	-1	11.6	10.6	21	2	-8	5.4	5.4
11	0	0	2.3	1.4	13	1	6	4.6	5.4	15	1	-1	11.6	10.6	22	2	-8	5.4	5.4
12	0	0	10.6	15.5	14	1	6	4.6	5.4	16	1	-1	11.6	10.6	23	2	-8	5.4	5.4
13	0	0	2.3	1.4	15	1	6	4.6	5.4	17	1	-1	11.6	10.6	24	2	-8	5.4	5.4
14	0	0	10.6	15.5	16	1	6	4.6	5.4	18	1	-1	11.6	10.6	25	2	-8	5.4	5.4
15	0	0	2.3	1.4	17	1	6	4.6	5.4	19	1	-1	11.6	10.6	26	2	-8	5.4	5.4
16	0	0	10.6	15.5	18	1	6	4.6	5.4	20	1	-1	11.6	10.6	27	2	-8	5.4	5.4
17	0	0	2.3	1.4	19	1	6	4.6	5.4	21	1	-1	11.6	10.6	28	2	-8	5.4	5.4
18	0	0	10.6	15.5	20	1	6	4.6	5.4	22	1	-1	11.6	10.6	29	2	-8	5.4	5.4
19	0	0	2.3	1.4	21	1	6	4.6	5.4	23	1	-1	11.6	10.6	30	2	-8	5.4	5.4
20	0	0	10.6	15.5	22	1	6	4.6	5.4	24	1	-1	11.6	10.6	31	2	-8	5.4	5.4
21	0	0	2.3	1.4	23	1	6	4.6	5.4	25	1	-1	11.6	10.6	32	2	-8	5.4	5.4
22	0	0	10.6	15.5	24	1	6	4.6	5.4	26	1	-1	11.6	10.6	33	2	-8	5.4	5.4
23	0	0	2.3	1.4	25	1	6	4.6	5.4	27	1	-1	11.6	10.6	34	2	-8	5.4	5.4
24	0	0	10.6	15.5	26	1	6	4.6	5.4	28	1	-1	11.6	10.6	35	2	-8	5.4	5.4
25	0	0	2.3	1.4	27	1	6	4.6	5.4	29	1	-1	11.6	10.6	36	2	-8	5.4	5.4
26	0	0	10.6	15.5	28	1	6	4.6	5.4	30	1	-1	11.6	10.6	37	2	-8	5.4	5.4
27	0	0	2.3	1.4	29	1	6	4.6	5.4	31	1	-1	11.6	10.6	38	2	-8	5.4	5.4
28	0	0	10.6	15.5	30	1	6	4.6	5.4	32	1	-1	11.6	10.6	39	2	-8	5.4	5.4
29	0	0	2.3	1.4	31	1	6	4.6	5.4	33	1	-1	11.6	10.6	40	2	-8	5.4	5.4
30	0	0	10.6	15.5	32	1	6	4.6	5.4	34	1	-1	11.6	10.6	41	2	-8	5.4	5.4
31	0	0	2.3	1.4	33	1	6	4.6	5.4	35	1	-1	11.6	10.6	42	2	-8	5.4	5.4
32	0	0	10.6	15.5	34	1	6	4.6	5.4	36	1	-1	11.6	10.6	43	2	-8	5.4	5.4
33	0	0	2.3	1.4	35	1	6	4.6	5.4	37	1	-1	11.6	10.6	44	2	-8	5.4	5.4
34	0	0	10.6	15.5	36	1	6	4.6	5.4	38	1	-1	11.6	10.6	45	2	-8	5.4	5.4
35	0	0	2.3	1.4	37	1	6	4.6	5.4	39	1	-1	11.6	10.6	46	2	-8	5.4	5.4
36	0	0	10.6	15.5	38	1	6	4.6	5.4	40	1	-1	11.6	10.6	47	2	-8	5.4	5.4
37	0	0	2.3	1.4	39	1	6	4.6	5.4	41	1	-1	11.6	10.6	48	2	-8	5.4	5.4
38	0	0	10.6	15.5	40	1	6	4.6	5.4	42	1	-1	11.6	10.6	49	2	-8	5.4	5.4
39	0	0	2.3	1.4	41	1	6	4.6	5.4	43	1	-1	11.6	10.6	50	2	-8	5.4	5.4
40	0	0	10.6	15.5	42	1	6	4.6	5.4	44	1	-1	11.6	10.6	51	2	-8	5.4	5.4
41	0	0	2.3	1.4	43	1	6	4.6	5.4	45	1	-1	11.6	10.6	52	2	-8	5.4	5.4
42	0	0	10.6	15.5	44	1	6	4.6	5.4	46	1	-1	11.6	10.6	53	2	-8	5.4	5.4
43	0	0	2.3	1.4	45	1	6	4.6	5.4	47	1	-1	11.6	10.6	54	2	-8	5.4	5.4
44	0	0	10.6	15.5	46	1	6	4.6	5.4	48	1	-1	11.6	10.6	55	2	-8	5.4	5.4
45	0	0	2.3	1.4	47	1	6	4.6	5.4	49	1	-1	11.6	10.6	56	2	-8	5.4	5.4
46	0	0	10.6	15.5	48	1	6	4.6	5.4	50	1	-1	11.6	10.6	57	2	-8	5.4	5.4
47	0	0	2.3	1.4	49	1	6	4.6	5.4	51	1	-1	11.6	10.6	58	2	-8	5.4	5.4
48	0	0	10.6	15.5	50	1	6	4.6	5.4	52	1	-1	11.6	10.6	59	2	-8	5.4	5.4
49	0	0	2.3	1.4	51	1	6	4.6	5.4	53	1	-1	11.6	10.6	60	2	-8	5.4	5.4
50	0	0	10.6	15.5	52	1	6	4.6	5.4	54	1	-1	11.6	10.6	61	2	-8	5.4	5.4
51	0	0	2.3	1.4	53	1	6	4.6	5.4	55	1	-1	11.6	10.6	62	2	-8	5.4	5.4
52	0	0	10.6	15.5	54	1	6	4.6	5.4	56	1	-1	11.6	10.6	63	2	-8	5.4	5.4
53	0	0	2.3	1.4	55	1	6	4.6	5.4	57	1	-1	11.6	10.6	64	2	-8	5.4	5.4
54	0	0	10.6	15.5	56	1	6	4.6	5.4	58	1	-1	11.6	10.6	65	2	-8	5.4	5.4
55	0	0	2.3	1.4	57	1	6	4.6	5.4	59	1	-1	11.6	10.6	66	2	-8	5.4	5.4
56	0	0	10.6	15.5	58	1	6	4.6	5.4	60	1	-1	11.6	10.6	67	2	-8	5.4	5.4
57	0	0	2.3	1.4	59	1	6	4.6	5.4	61	1	-1	11.6	10.6	68	2	-8	5.4	5.4
58	0	0	10.6	15.5	60	1	6	4.6	5.4	62	1	-1	11.6	10.6	69	2	-8	5.4	5.4
59	0	0	2.3	1.4	61	1	6	4.6	5.4	63	1	-1	11.6	10.6	70	2	-8	5.4	5.4
60	0	0	10.6	15.5	62	1	6	4.6	5.4	64	1	-1	11.6	10.6	71	2	-8	5.4	5.4
61	0	0	2.3	1.4	63	1	6	4.6	5.4	65	1	-1	11.6	10.6	72	2	-8	5.4	5.4
62	0	0	10.6	15.5	64	1	6	4.6	5.4	66	1	-1	11.6	10.6	73	2	-8	5.4	5.4
63	0	0	2.3	1.4	65	1	6	4.6	5.4	67	1	-1	11.6	10.6	74	2	-8	5.4	5.4
64	0	0	10.6	15.5	66	1	6	4.6	5.4	68	1	-1	11.6	10.6	75	2	-8	5.4	5.4
65	0	0	2.3	1.4	67	1	6	4.6	5.4	69	1	-1	11.6	10.6	76	2	-8	5.4	5.4
66	0	0	10.6	15.5	68	1	6	4.6	5.4	70	1	-1	11.6	10.6	77	2	-8	5.4	5.4
67	0	0	2.3	1.4	69	1	6	4.6	5.4	71	1	-1	11.6	10.6	78	2	-8	5.4	5.4
68	0	0	10.6	15.5	70	1	6	4.6	5.4	72	1	-1	11.6	10.6	79	2	-8	5.4	5.4
69	0	0	2.3	1.4	71	1	6	4.6	5.4	73	1	-1	11.6	10.6	80	2	-8	5.4	5.4
70	0	0	10.6	15.5	72	1	6	4.6	5.4	74	1	-1	11.6	10.6	81	2	-8	5.4	5.4
71	0	0	2.3	1.4	73	1	6	4.6	5.4	75	1	-1	11.6	10.6	82	2	-8	5.4	5.4
72	0	0	10.6	15.5	74	1	6	4.6	5.4	76	1	-1	11.6	10.6	83	2	-8	5.4	5.4
73	0	0	2.3	1.4</															

[illegible]

Table XVIII.

## Final atomic parameters.

(a) Atomic fractional coordinates, (standard deviations in parentheses):

	x	y	z
C(1)	0.1902(2)	0.3676(6)	0.1210(2)
C(2)	0.2814(3)	0.5167(6)	0.1794(2)
C(3)	0.2659(2)	0.7092(6)	0.2291(2)
C(4)	0.1643(3)	0.7619(6)	0.2222(2)
C(5)	0.0758(2)	0.6081(6)	0.1633(2)
C(6)	0.0865(3)	0.4120(6)	0.1128(2)
C(7)	0.1995(3)	0.1549(7)	0.0642(2)
N(8)	0.3628(2)	0.8728(7)	0.2902(2)
N(9)	-0.0341(2)	0.6555(6)	0.1545(2)
O(10)	-0.0452(2)	0.8580(5)	0.1904(1)
O(11)	-0.1078(2)	0.4906(5)	0.1128(2)
O(12)	0.1227(2)	0.0269(5)	0.0126(2)
O(13)	0.3022(2)	0.1242(6)	0.0815(2)
O(14)	0.4507(2)	0.8324(8)	0.2941(2)
O(15)	0.3488(3)	1.0433(7)	0.3328(2)
C(16)	0.3336(6)	-0.1078(15)	0.0429(5)
C(16')	0.2986(12)	-0.0303(32)	0.0053(11)
C(17)	0.3401(10)	0.0450(23)	-0.0238(6)
C(17')	0.4157(18)	-0.0512(51)	0.0290(15)
H(18)	0.158(3)	0.894(9)	0.261(3)
H(19)	0.028(3)	0.326(7)	0.075(2)
H(20)	0.354(3)	0.488(7)	0.189(2)
H(21)	0.277(3)	-0.252(10)	0.022(3)
H(22)	0.414(4)	-0.177(11)	0.071(3)
H(23)	0.400(3)	0.152(9)	0.001(2)
H(24)	0.369(8)	-0.139(20)	-0.036(6)
H(25)	0.255(6)	0.063(14)	-0.064(5)

(b) Thermal parameters; anisotropic thermal parameters are in the form:

$$\exp [-2\pi^2 \cdot 10^{-4} (U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^{*}b^{*} + 2U_{13}hla^{*}c^{*} + 2U_{23}k\ell b^{*}c^{*})]$$

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$	Mean e.s.d.
C(1)	513	388	459	4	234	42	(14)
C(2)	497	484	539	14	242	53	(16)
C(3)	530	458	454	-63	176	6	(15)
C(4)	648	419	436	-21	256	20	(16)
C(5)	505	410	437	28	245	63	(14)
C(6)	518	368	431	0	212	48	(15)
C(7)	564	513	594	-26	324	-19	(17)
N(8)	631	687	592	-128	191	-88	(17)
N(9)	597	510	520	39	295	25	(14)
O(10)	738	724	715	148	348	-165	(14)
O(11)	578	698	911	-91	395	-157	(14)
O(12)	705	769	728	-121	389	-263	(14)
O(13)	685	943	1222	-110	589	-490	(17)
O(14)	566	1354	1289	-254	297	-520	(21)
O(15)	964	1066	934	-306	399	-507	(20)

B.

C(16)	6.43(13)
C(16')	5.19(26)
C(17)	9.02(19)
C(17')	8.68(44)
H(18)	6.4(10)
H(19)	4.6(7)
H(20)	4.7(7)
H(21)	4.0(9)
H(22)	4.9(11)
H(23)	3.2(8)
H(24)	14.1(26)
H(25)	9.0(17)



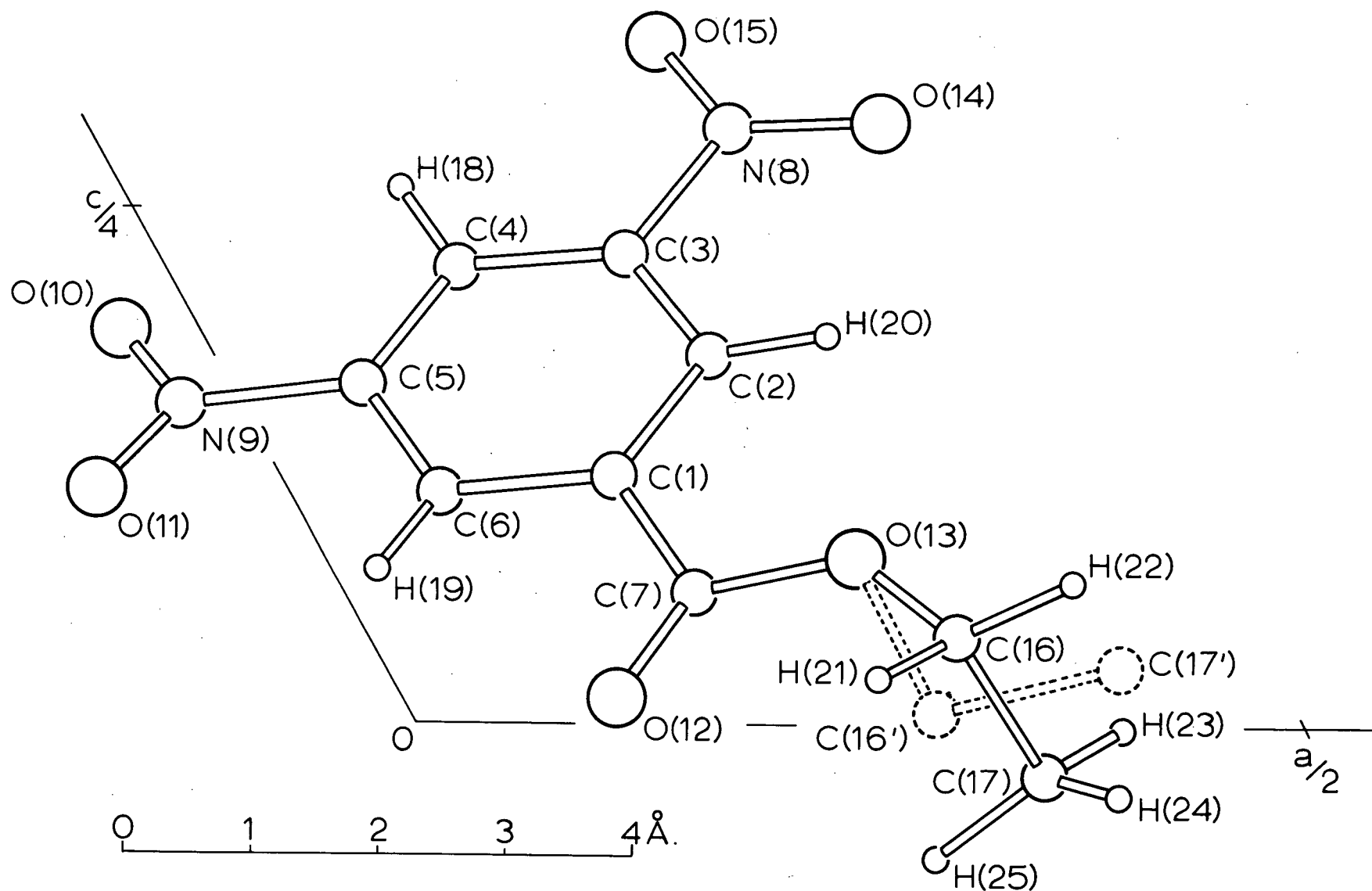


Figure 8. View of the molecule. The positive direction of the b-axis is away from the viewer.

Figure 9. The thermal ellipsoids of atoms nos. 1-15, projected on to the plane of the benzene ring.

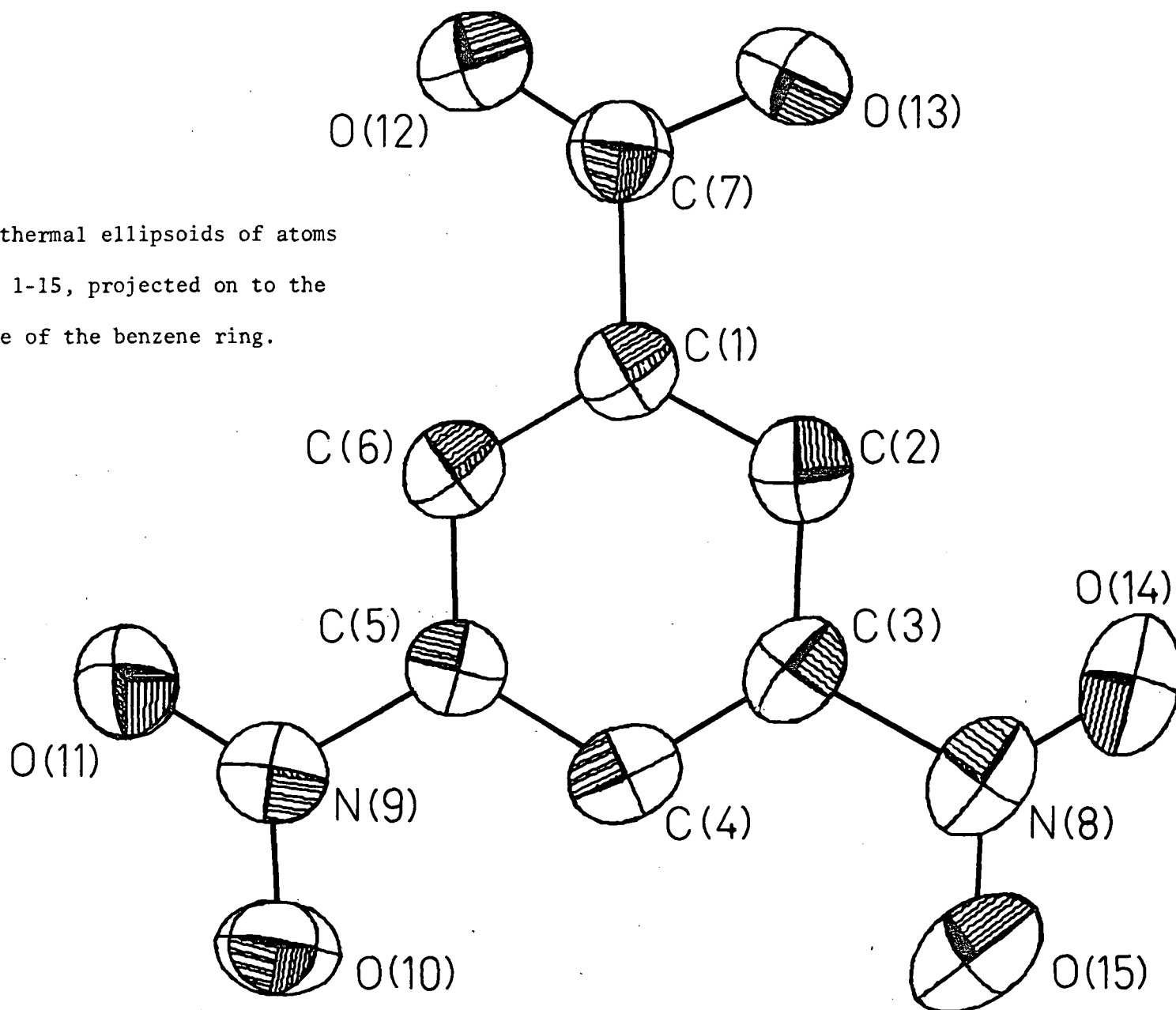


Table XIX.

Molecular dimensions of ethyl 3,5-dinitrobenzoate;

(standard deviations in parentheses).

## (a) Bond distances (in Å.):

Bond	Uncorrected distance	Corrected distance	Bond	Uncorrected distance	Corrected distance
C(1) — C(2)	1.383(4)	1.386	N(9) — O(11)	1.215(3)	1.239
C(1) — C(6)	1.384(4)	1.387	O(13) — C(16)	1.490(7)	
C(1) — C(7)	1.506(4)	1.513	O(13) — C(16')	1.560(15)	
C(2) — C(3)	1.384(4)	1.387	C(16) — C(17)	1.465(12)	
C(3) — C(4)	1.372(4)	1.375	C(16') — C(17')	1.461(26)	
C(3) — N(8)	1.478(4)	1.494	C(2) — H(20)	0.94(3)	
C(4) — C(5)	1.379(4)	1.382	C(4) — H(18)	0.98(4)	
C(5) — C(6)	1.376(4)	1.379	C(6) — H(19)	0.87(3)	
C(5) — N(9)	1.467(4)	1.473	C(16) — H(21)	0.97(4)	
C(7) — O(12)	1.186(4)	1.208	C(16) — H(22)	1.02(5)	
C(7) — O(13)	1.305(4)	1.346	C(17) — H(23)	0.89(4)	
N(8) — O(14)	1.199(4)	1.257	C(17) — H(24)	1.03(9)	
N(8) — O(15)	1.209(4)	1.251	C(17) — H(25)	1.04(7)	
N(9) — O(10)	1.222(3)	1.248			

## (b) Valence angles (in degrees):

i	j	k	Angle (ijk)	i	j	k	Angle (ijk)
C(2)	— C(1)	— C(6)	120.5(3)	C(7)	— O(13)	— C(16')	106.7(6)
C(2)	— C(1)	— C(7)	121.7(3)	O(13)	— C(16)	— C(17)	100.4(6)
C(6)	— C(1)	— C(7)	117.8(3)	O(13)	— C(16')	— C(17')	103.0(13)
C(1)	— C(2)	— C(3)	118.2(3)	C(1)	— C(2)	— H(20)	124(2)
C(2)	— C(3)	— C(4)	123.1(3)	C(3)	— C(2)	— H(20)	118(2)
C(2)	— C(3)	— N(8)	118.2(3)	C(3)	— C(4)	— H(18)	120(2)
C(4)	— C(3)	— N(8)	118.7(3)	C(5)	— C(4)	— H(18)	123(2)
C(3)	— C(4)	— C(5)	116.8(3)	C(1)	— C(6)	— H(19)	122(2)
C(4)	— C(5)	— C(6)	122.6(3)	C(5)	— C(6)	— H(19)	119(2)
C(4)	— C(5)	— N(9)	118.6(3)	O(13)	— C(16)	— H(21)	110(3)
C(6)	— C(5)	— N(9)	118.8(3)	O(13)	— C(16)	— H(22)	120(3)
C(1)	— C(6)	— C(5)	118.8(3)	C(17)	— C(16)	— H(21)	113(3)
C(1)	— C(7)	— O(12)	123.4(3)	C(17)	— C(16)	— H(22)	95(3)
C(1)	— C(7)	— O(13)	111.3(3)	H(21)	— C(16)	— H(22)	116(4)
O(12)	— C(7)	— O(13)	125.3(3)	C(16)	— C(17)	— H(23)	107(3)
C(3)	— N(8)	— O(14)	118.4(3)	C(16)	— C(17)	— H(24)	87(5)
C(3)	— N(8)	— O(15)	118.0(3)	C(16)	— C(17)	— H(25)	97(4)
O(14)	— N(8)	— O(15)	123.6(3)	H(23)	— C(17)	— H(24)	103(6)
C(5)	— N(9)	— O(10)	117.5(3)	H(23)	— C(17)	— H(25)	140(5)
C(5)	— N(9)	— O(11)	118.3(2)	H(24)	— C(17)	— H(25)	110(6)
O(10)	— N(9)	— O(11)	124.2(3)				
C(7)	— O(13)	— C(16)	120.5(4)				



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Table XX.

## Mean planes.

(a) Equations of mean planes, in the form:

$$lX + mY + nZ = p$$

where X, Y and Z are coordinates in Å. referred to orthogonal axes a, b and c\*.

Plane no.	Plane	<i>l</i>	<i>m</i>	<i>n</i>	<i>p</i>
1.	Benzene ring	0.1800	0.7089	-0.6819	0.2008
2.	Carboxyl group, C-COO	0.2141	0.7151	-0.6654	0.3004
3.	N(8) nitro group, C-NO <sub>2</sub>	0.1573	0.7016	-0.6950	0.0841
4.	N(9) nitro group, C-NO <sub>2</sub>	0.1638	0.5592	-0.8127	-0.5656

(b) Displacements of atoms from the plane of the benzene ring. Underlined values indicate atoms included in the calculation of the equation of that plane.

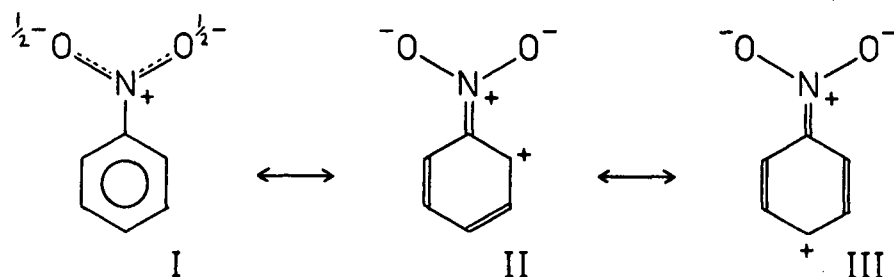
Atom	Displacement	Atom	Displacement
C(1)	0.002 Å.	O(12)	0.038 Å.
C(2)	<u>0.004</u>	O(13)	-0.046
C(3)	<u>-0.007</u>	O(14)	0.057
C(4)	<u>0.005</u>	O(15)	0.032
C(5)	<u>0.001</u>	C(16)	-0.270
C(6)	<u>-0.004</u>	C(16')	0.376
C(7)	<u>0.017</u>	C(17)	1.098
N(8)	0.023	C(17')	0.300
N(9)	-0.003	H(18)	-0.045
O(10)	0.204	H(19)	0.027
O(11)	-0.223	H(20)	-0.037

(c) Angles between the normals to the benzene ring plane and the substituent group planes:

Plane	<i>q</i>	<i>r</i>	Angle ( <i>qr</i> )°
	1	2	2.2
	1	3	1.6
	1	4	11.5

## D. DISCUSSION.

It has been concluded <sup>22,27</sup> that there is negligible contribution from excited resonance structures such as II and III in nitrobenzene comp-



ounds, except when there is an electron-donating group in the ortho or para position to the nitro group.

Table XXI shows the dimensions of nitro groups in several nitrobenzene derivatives. Where there are appreciable contributions from resonance structures, as in p-nitrophenol and p-nitroaniline derivatives, the C-N<sub>nitro</sub> bond distance,  $\sim 1.46$  Å., is generally shorter than in compounds not readily forming resonance structures, (C-N<sub>nitro</sub> now  $1.46 - 1.49$  Å.). Our results conform with the latter, but there is a significant difference between the C-N bond lengths in the two nitro groups in our molecule.

The nitro group of N(8), O(14) and O(15) is rotated  $1.6^\circ$  out of the plane of the benzene ring, and the group of N(9), O(10) and O(11) is rotated  $11.5^\circ$ . The N-O bonds are approximately equal in the two groups, with mean values  $1.254$  Å. in the first group and  $1.244$  Å. in the second group. But the C-N bond length in the first group,  $1.494$  Å., is significantly longer than that in the second group,  $1.473$  Å. This is the opposite effect to that expected from the rotations of the nitro groups out of coplanarity with the benzene ring since one of the requirements for the formation of resonance structures is that the planes of the nitro group and the benzene ring should be closely aligned; hence if any resonance effects are to be observed, they should be found in the N(8) nitro group.

Table XXI.

A comparison of the dimensions of nitro groups in nitrobenzene derivatives which have no substituted ortho groups.

Compound		C-N <sub>nitro</sub>		N-O <sub>1</sub>		N-O <sub>2</sub>		Mean $\sigma_L^*$	Angle O-N-O	Angle C-N-O <sub>1</sub>	Angle C-N-O <sub>2</sub>	Ang. in benzene ring	Mean $\sigma_A^*$	Rotn. ang. of C-NO <sub>2</sub>	Ref.
		Unc. <sup>d</sup>	Corr. <sup>d</sup>	Unc. <sup>d</sup>	Corr. <sup>d</sup>	Unc. <sup>d</sup>	Corr. <sup>d</sup>								
Ethyl 3,5-dinitro- benzoate	1.	1.478	1.494	1.199	1.257	1.209	1.251	0.004	123.6	118.4	118.0	123.1	0.3	1.6	This work
	2.	1.467	1.473	1.215	1.239	1.222	1.248	0.003	124.2	118.3	117.5	122.6	0.3	11.5	
Trans-bicyclo-[4.2.0]- octyl 3,5-dinitro- benzoate	1.	1.489		1.218		1.213		0.004	125.4	117.4	117.2	122.6	0.2	4.3	30.
	2.	1.474		1.207		1.216		0.004	123.4	117.7	118.8	122.8	0.2	1.4	
p-Nitrobenzoic acid		1.480		1.228		1.203		0.006	124.1	118.3	117.3	122.8	0.4	13.7	40.
2,6-Dichloro-4-nitro- aniline		1.456	1.466	1.227	1.257	1.231	1.256	0.005	123.4	118.4	118.1	122.0	0.4	7.3	Part III.
1:1 complex of s-trinitro- benzene and s-triaminobenzene		1.462	1.463	1.232	1.247	1.207	1.222	0.006	124.0	117.1	118.9	122.6	0.4	9.9	41.
	2.	1.464	1.466	1.222	1.233	1.238	1.247	0.006	122.9	118.5	118.6	122.8	0.4	0.9	
	3.	1.472	1.474	1.219	1.228	1.213	1.220	0.005	124.9	116.7	118.4	122.2	0.4	5.9	
p-Nitroaniline		1.454	1.460	1.227	1.246	1.229	1.247	0.007	123.3	117.7	119.0	121.2	0.4	1.9	22.
p-Nitrophenol (at 90°K.)		1.442		1.232		1.236		0.006	122.0	119.3	118.8	122.3	0.4	1.5	28.
m-Dinitrobenzene	1.	1.484	1.491	1.243	1.276	1.197	1.220	0.009	125.1	116.6	118.3	123.1	0.6	13	42.
	2.	1.487	1.494	1.214	1.230	1.227	1.266	0.009	126.5	116.8	116.1	124.0	0.6	13	

\*  $\sigma_L$ ,  $\sigma_A$  - e.s.d's of uncorrected bond lengths and valence angles.

The larger rotation of the N(9) group appears to result from packing forces - see Figures 11. and 12.; if this nitro group were rotated through a smaller angle, the N(9)...O(10)' distance would be shorter than the sum of van der Waals' radii, and other interactions, e.g. O(10)...O(10)', O(11)...O(12)' and O(11)...C(7) would approach the minimum non-bonding distances.

The angles around both the nitro groups compare well with those in other nitro compounds. In all cases, the O-N-O angle is larger than  $120^\circ$ .

The angles in the benzene ring are similar to those in other compounds and as expected from second-order hybridisation effects <sup>31-33</sup>, viz.  $\sim 123^\circ$  at the carbons of -NO<sub>2</sub> substituents, three with a mean of  $117.9^\circ$  at the carbons bonded to hydrogens, and  $120.5^\circ$  at the carboxyl group carbon. Similarly, the ring C-C distances about C(1), mean length  $1.387 \text{ \AA}$ ., are perhaps slightly longer than those about C(3) and C(5), mean length  $1.381 \text{ \AA}$ .

The plane of C(1) and the -CO.O- part of the carboxylic ester group is rotated  $2.2^\circ$  out of coplanarity with the benzene ring. The (uncorrected) dimensions of this group appear quite normal and are compared with those of other molecules in Table XXII. The angles about C(7) result from the repulsions between bonding electrons about the C(7) atom.

The coordinates of the three hydrogen atoms on the benzene ring refined well, and these atoms are not significantly out of the plane of the ring. Their C-H bond lengths and the angles about their bonded carbon atoms are normal.

The outer parts of the disordered ethyl group are not well defined and the lengths and angles are not very reliable. The hydrogen atoms H(21) and H(22) are well removed from the minor ethyl group, and their positions are thus reasonably well determined, but the methyl groups of C(17) and C(17') are overlapping and hence there is some confusion and a lack of definition. It is therefore not reasonable to discuss critically the dimensions of the



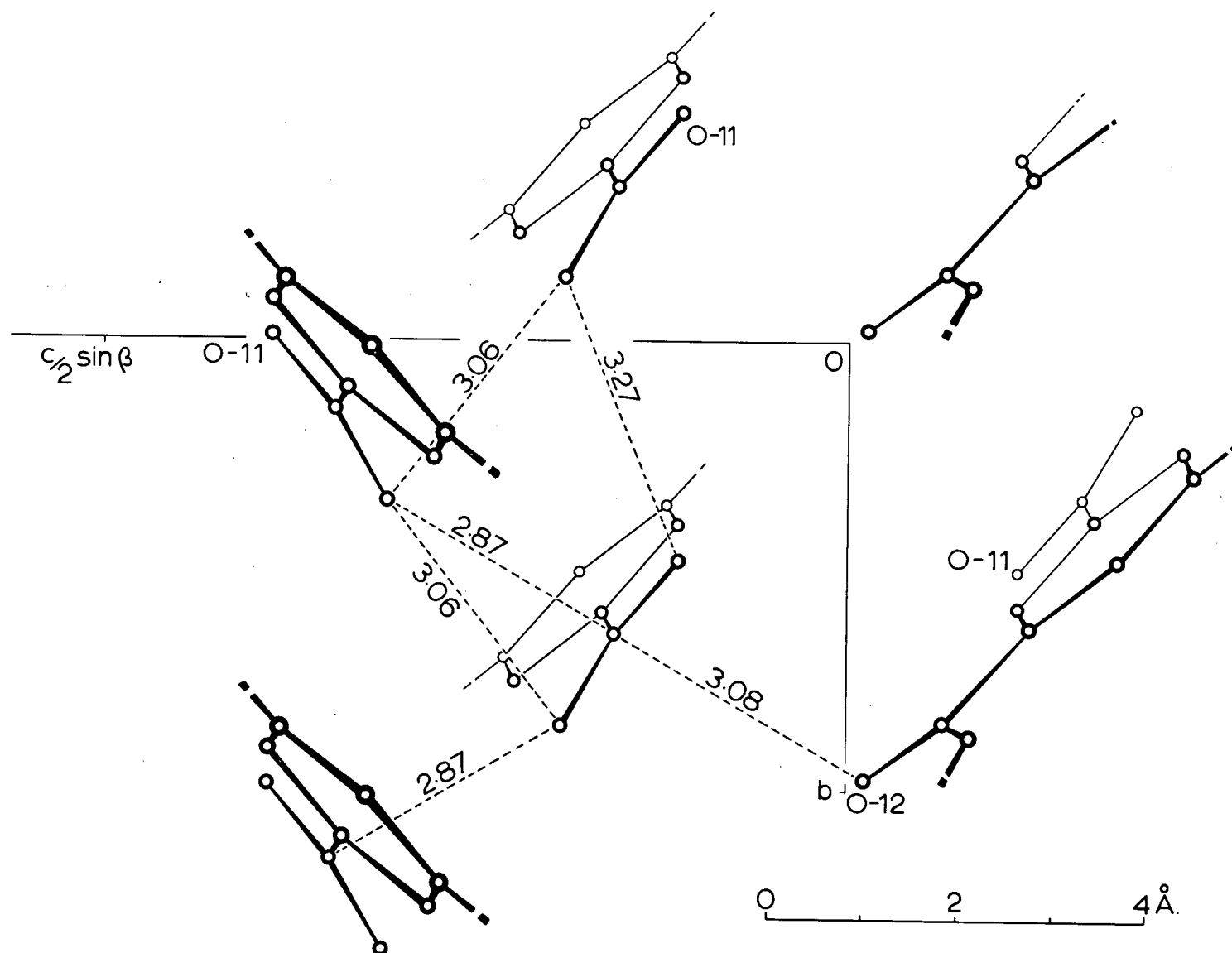


Figure 11. The close neighbours of the N(9) nitro group. The positive direction of the a axis is away from the viewer.

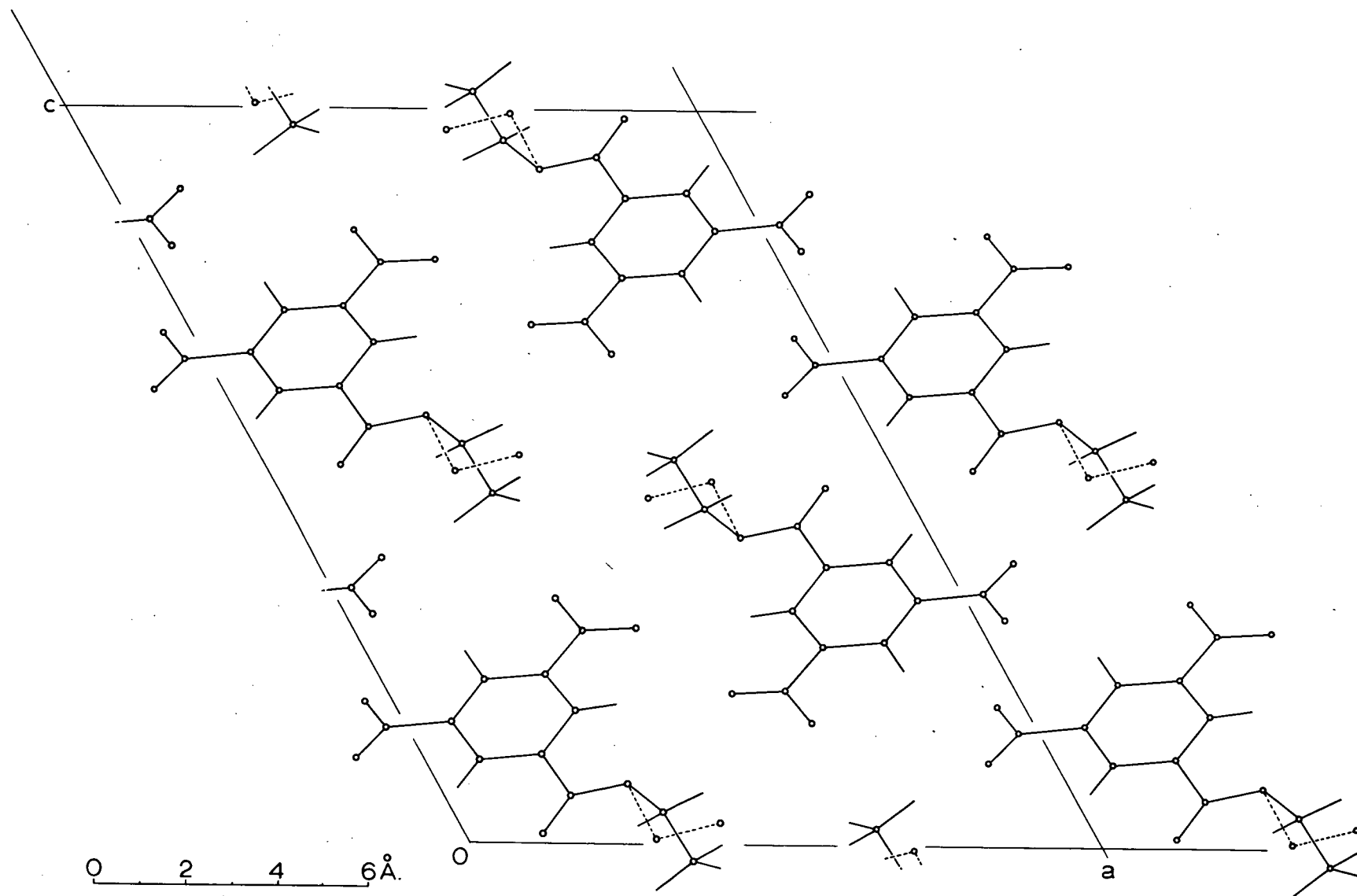


Figure 12. The molecular packing arrangement; a projection along  $\underline{b}$ .

Table XXII.

A comparison of the dimensions of the carboxyl group  
in benzoic acids and esters, and in related compounds.

Compound	C-C <sub>COO</sub>	C=O	C-O	Mean $\sigma_L^*$	C-C=O	C-C-O	O=C-O	Ang. in benzene ring	Mean $\sigma_A^*$	Rotn. ang. of C-CO.O	Ref.
Benzoic acid derivatives:											
p-nitrobenzoic acid	1.501	1.222	1.319	0.007	121.1	115.0	123.9	121.2	0.5	3.3	40.
2-chloro-5-nitrobenzoic acid	1.489	1.220	1.294	0.008	121.3	114.0	124.8	117.7	0.6	23.0	43.
o-chlorobenzoic acid	1.521	1.208	1.295	0.008	122.2	113.3	124.5	120.5	0.6	13.7	44.
p-aminobenzoic acid, mol. A	1.455	1.236	1.315	0.006	123.5	115.6	120.8	118.1	0.4	1.5	45.
" " , mol. B	1.464	1.248	1.293	0.006	121.4	116.5	122.1	118.5	0.4	2.5	45.
Benzoic ester derivatives:											
ethyl 3,5-dinitrobenzoate	1.506	1.186	1.305	0.004	123.4	111.3	125.3	120.5	0.3	2.2	This work
trans-bicyclo-[4.2.0]-octyl 3,5-dinitrobenzoate	1.507	1.200	1.323	0.004	122.0	111.1	126.9	119.8	0.2	8.9	30.
complex of tricarbonyl- chromium:methyl benzoate	1.49	1.19	1.35	0.013	124	111	126	119	0.9	very small	46.
Related compounds:											
o-nitroperoxybenzoic acid	1.495	1.214	1.337	0.007	125.1	109.9	124.7	118.6	0.5	58	47.
2-thio-amidopyridine	1.505	-	-	0.005	122.9	113.9	123.0	123.3	0.3	10.5	48.

ethyl groups.

The molecular packing arrangement is shown in Figure 12. The perpendicular distance between the planes of rings is  $3.38 \text{ \AA}$ , which appears general in benzene derivative crystals, and similar to the interplanar distance of  $3.35 \text{ \AA}$  in graphite.

There are several short intermolecular distances and these are given in Table XXIII. The distances recorded (maximum  $4.0 \text{ \AA}$ .) are less than  $0.3 \text{ \AA}$  greater than the sum of van der Waals' radii, which were taken as:

hydrogen	$1.2 \text{ \AA}$ .
oxygen	$1.4$
nitrogen	$1.5$
carbons of ethyl group	$2.0 \text{ \AA}$ .
other carbons:	(a) radius in plane of benzene ring $2.0 \text{ \AA}$ .
	(b) radius perpendicular to plane of benzene ring $1.7 \text{ \AA}$ .

The  $N(9) \dots O(10)'$  distance of  $2.870 \text{ \AA}$  and the  $O(12) \dots H(19)'$  distance of  $2.54 \text{ \AA}$  correspond to van der Waals' interactions. The first nine interactions recorded of those involving carbons of the ethyl group have distances less than or equal to the sum of van der Waals' radii. The  $C(17') \dots C(17')'$  distance of  $3.049 \text{ \AA}$  seems prohibitively short, but it must be remembered that the  $C(17')$  atoms may not be perfectly defined. It seems improbable, however, that two molecules each containing the minor ethyl group will be able to lie adjacent.

When only one molecule of an adjacent pair contains the minor ethyl group, the  $C(17')$  to  $C(17)'$ ,  $H(23)'$  and  $H(24)'$  distances are still short but more reasonable; the  $C(17') \dots O(14)'$  and  $C(16') \dots O(11)'$  distances are slightly less than the sum of van der Waals' radii, but this is allowable at certain orientations of the ethyl group bonds. The same applies to the

Table XXIII.

## Short intermolecular distances.

(a) Distances from the ethyl group carbon atoms.

Atom i is in molecule I \*.

i	j	Molecule of j *	ij	i	j	Molecule of j	ij
C(17')...H(23)		IIIc	2.90 Å.	C(16)....O(11)		IIIa	3.530 Å.
C(17')...H(24)		IIIc	3.06	C(17')...O(15)		IIf	3.556
C(17')...C(17')		IIIc	3.049	C(16')...O(11)		IIIb	3.557
C(16)....H(20)		Ib	3.21	C(17)....O(11)		IIIb	3.570
C(16')...O(11)		IIIa	3.293	C(16')...O(10)		IIIb	3.667
C(17)....O(15)		IVa	3.333	C(16)....O(14)		IId	3.669
C(17')...O(14)		IId	3.373	C(16)....C(1)		Ib	3.884
C(17)....C(17')		IIIc	3.432	C(16')...C(2)		Ib	3.961
C(16)....C(2)		Ib	3.434				

(b) Distances involving hydrogen atoms:

i	j	Molecule of j	ij	i	j	Molecule of j	ij
O(12)...H(19)		IIIa	2.54 Å.	O(11)...H(25)		IIIb	2.77 Å.
O(14)...H(20)		IIf	2.68	O(11)...H(18)		IIf	2.78
O(11)...H(21)		IIIa	2.68	N(9)....H(25)		IIIb	2.98
O(10)...H(25)		IIIb	2.70	C(2)....H(21)		Ia	3.06

(c) Distances between non-hydrogen atoms:

i	j	Molecule of j	ij	i	j	Molecule of j	ij
N(9)....O(10)		IIf	2.870 Å.	C(7)...O(11)		IIIb	3.310 Å.
O(10)...O(10)		IIf, b	3.055	C(2)...O(15)		Ib	3.362
N(9)....O(12)		IIIb	3.080	C(6)...O(12)		IIIa	3.390
C(5)....O(10)		IIf	3.151	C(3)...C(7)		Ia	3.431

\* Coordinates of adjacent molecules:

I        x,    y,    z  
 Ia       x,    1+y,    z  
 Ib       x,    y-1,    z  
 IIf       -x,    y- $\frac{1}{2}$ ,     $\frac{1}{2}$ -z  
 IIf       -x,    y+ $\frac{1}{2}$ ,     $\frac{1}{2}$ -z  
 IIf       1-x,    y+ $\frac{1}{2}$ ,     $\frac{1}{2}$ -z  
 IId       1-x,    y- $\frac{1}{2}$ ,     $\frac{1}{2}$ -z  
 IIf       1-x,    y- $\frac{3}{2}$ ,     $\frac{1}{2}$ -z

IIIa       -x,    -y,    -z  
 IIIb       -x,    1-y,    -z  
 IIIc       1-x,    -y,    -z  
 IIId       1-x,    1-y,    -z  
 IVa       x,     $\frac{3}{2}$ -y,    z- $\frac{1}{2}$

C(17)...O(15)' distance - the only really short intermolecular interaction of two adjacent, major ethyl group molecules.

If, in fact, two molecules with minor ethyl groups are not able to lie adjacent, and there is no preference between major-major and major-minor pairs, then it is expected that the ratio of major to minor group molecules would be 67/33. Our results indicate approximately 30% occupancy of the minor group's sites.

PART V. THE COMPUTER PROGRAM "GESTAR".

## A. INTRODUCTION.

In collecting the intensity data of the twinned crystal, 2,6-dichloro-4-nitroaniline, data from both the twins was required. The crystal was mounted so that the  $a^*$ -axis of one of the twins (the first twin) was parallel to the goniostat  $\phi$ -axis. A computer program which would calculate all the diffractometer settings for this twin, and which would punch out the instrument instructions on cards for use in the diffractometer, was available.

It was considered that the best comparison between the intensity data of the first twin and that of the second twin would be obtained if the measurements could be made without altering the arcs of the goniometer head. But the second twin had neither a reciprocal axis nor a real axis parallel to the goniostat  $\phi$ -axis; therefore, a short computer program would have to be written to calculate the diffractometer settings for the collection of the second twin data.

It was then thought worthwhile to bring the old program for the calculation of diffractometer settings - part one of the DATAPR program written for the IBM 1620 computer some years ago - more up-to-date, and to write a subprogram, which could be incorporated into the more general program, to calculate the second twin settings. The new version of DATAPR is named GESTAR, and the subprogram for second-twin calculations is named TWIN.

The program GESTAR will be described first, in section B, and the subprogram TWIN (and the slight modifications in the main GESTAR program) will then be described in section C.



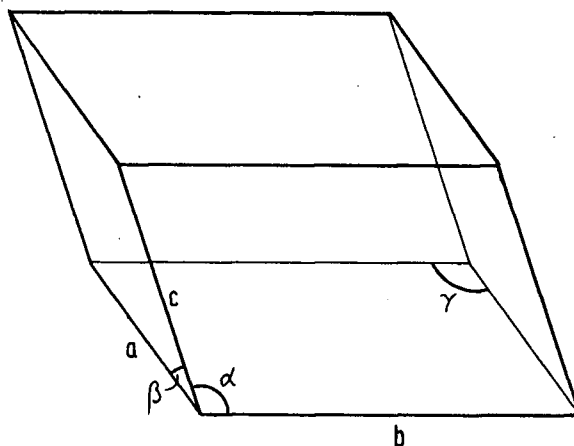
## B. THE PROGRAM "GESTAR".

### 1. Diffractometer geometry used in GESTAR.

The basic diffractometer geometry used in the program DATAPR was used with little alteration in GESTAR, and is described below.

A crystal has periodicity in the arrangement of its atoms and molecules in three dimensions. The small repeating unit is the "unit cell" which has edges of length  $a$ ,  $b$  and  $c$ , and angles between the edges  $\alpha$ ,  $\beta$  and  $\gamma$  as shown in Figure 13.

Figure 13.  
The unit cell.



Related to the unit cell is the Reciprocal Lattice which is a three-dimensional array of points with its origin placed at the centre of the crystal. The three major axes of the reciprocal lattice are the  $a^*$ -,  $b^*$ - and  $c^*$ -axes, whose directions are defined as being:

the  $a^*$ -axis is normal to the  $b$ - $c$  plane of the unit cell,

"  $b^*$ - " " " " "  $a$ - $c$  " " " " " , and

"  $c^*$ - " " " " "  $a$ - $b$  " " " " " .

The angles between these axes are  $\alpha^*$ ,  $\beta^*$  and  $\gamma^*$ , and their values are related to those of  $\alpha$ ,  $\beta$  and  $\gamma$ .

The points in the reciprocal lattice are indexed  $hkl$ , and they are

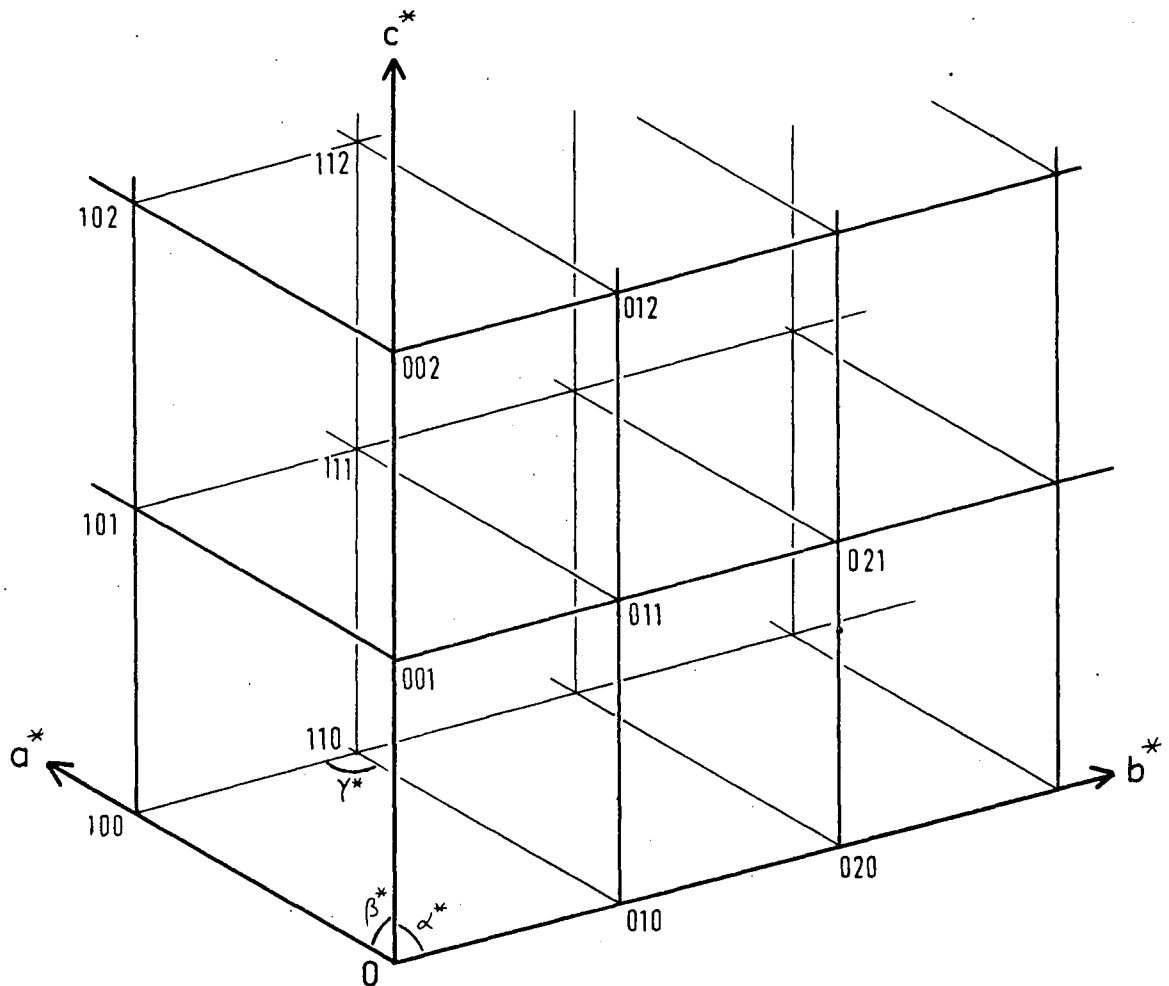


Figure 14. A portion of the reciprocal lattice.

related to planes in the unit cell having Miller indices  $hkl$ . The mode of indexing the reciprocal lattice points is shown in Figure 14.

The distances from the origin 0 to the points 100, 010 and 001 are  $a^*$ ,  $b^*$  and  $c^*$  respectively, and these lengths are defined:

$$a^* = \frac{b \cdot c \cdot \sin \alpha}{V} ; \quad b^* = \frac{a \cdot c \cdot \sin \beta}{V} ; \quad c^* = \frac{a \cdot b \cdot \sin \gamma}{V}$$

where  $V$  is the volume of the real unit cell and is calculated to be:

$$V = a \cdot b \cdot c \cdot \sqrt{1 + 2 \cdot \cos \alpha \cdot \cos \beta \cdot \cos \gamma - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma}$$

The angles  $\alpha^*$ ,  $\beta^*$  and  $\gamma^*$  are, in the general case:

$$\cos \alpha^* = \frac{\cos \beta \cdot \cos \gamma - \cos \alpha}{\sin \beta \cdot \sin \gamma}$$

and similarly for  $\cos \beta^*$  and  $\cos \gamma^*$ .

It should be noted that all these expressions simplify considerably in crystal systems of higher symmetry than the triclinic system.

The distance from the origin 0 to any reciprocal lattice point  $hkl$  is  $d_{hkl}^*$ , and

$$d_{hkl}^* = \frac{1}{d_{hkl}}$$

where  $d_{hkl}$  is the perpendicular distance between  $(hkl)$  planes in the real cell. Hence:

$$d_{100}^* = a^* = \frac{1}{d_{100}}$$

$$d_{300}^* = \frac{1}{d_{300}} = 3a^*$$

$$d_{040}^* = 4b^* \quad \text{etc.}$$

and the distance  $d_{hkl}^*$  for any point  $hkl$  can be calculated from the dimensions of the reciprocal unit cell.

Just as the  $a^*$ -axis is perpendicular to the  $b$ - $c$  plane, i.e. the  $(h00)$  planes, and the distance of, say, the 200 point from the origin is the reciprocal of the distance between  $(200)$  planes in the real cell, so any vector  $hkl$ , from the origin of the reciprocal lattice to the point  $hkl$ , is normal to the planes  $(hkl)$  in the real cell, and its length is the reciprocal of the interplanar spacing.

The G.E. XRD-6 diffractometer employs the "Normal-beam Equatorial" method of diffraction geometry - the incident X-ray beam, the crystal and the X-ray detector for the diffracted beam, all lie in the equatorial plane of the instrument, and the incident beam is normal to the crystal oscillation axis  $\omega (\equiv \theta)$ . The instrument geometry is illustrated in Figures 15. and 16.

For a diffracted beam to be recorded, the crystal plane  $(hkl)$  must be perpendicular to the equatorial plane and inclined at  $\theta$  to the incident

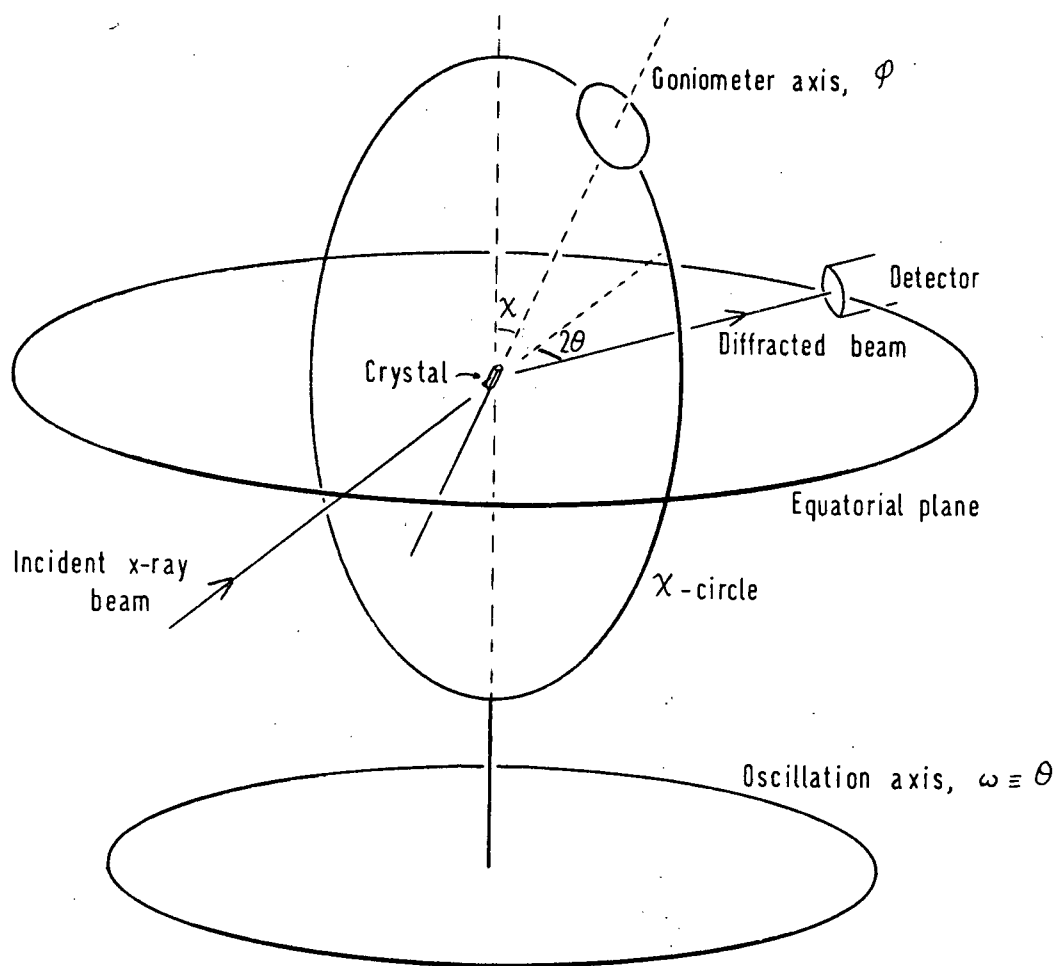


Figure 15. Diffractometer "normal-beam equatorial" geometry.

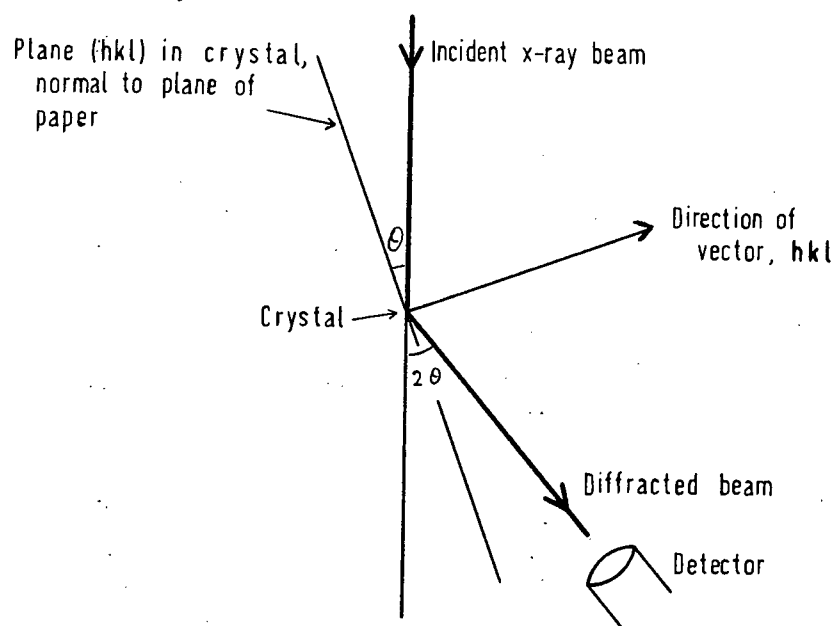


Figure 16. In the equatorial plane.

beam, and the detector must be at  $2\theta$  from the emergent non-diffracted beam. The  $\theta$  and  $2\theta$  circles in the instrument are coordinated, and the required  $2\theta$  value can be calculated from Bragg's Law (see below).

The reciprocal lattice vector  $hkl$ , normal to the  $(hkl)$  plane, is in the equatorial plane; if  $\theta$  and  $2\theta$  are turned to 0, this vector is perpendicular to the incident X-ray beam. The diffractometer settings are thus calculated to bring the vector  $hkl$  initially into the equatorial plane and perpendicular to the incident X-ray beam; the  $2\theta$  setting rotates the vector through  $\theta$  and the detector through  $2\theta$  in the equatorial plane, to the correct diffracting position.

The calculation of the  $2\theta$  setting is made from the Bragg Law which expresses the condition under which a crystal plane will diffract an X-ray beam; the Law is:

$$\lambda = 2d \cdot \sin \theta$$

where  $\lambda$  is the wavelength of the radiation to be used, and  $d$  is the interplanar spacing. Hence:

$$\begin{aligned} 2\theta &= 2 \cdot \sin^{-1} \left( \frac{\lambda}{2d} \right) \\ &= 2 \cdot \sin^{-1} \left( \frac{\lambda d^*}{2} \right) \end{aligned}$$

The program GESTAR calculates the instrument settings for crystals mounted with a reciprocal axis parallel to the  $\phi$ -axis of the goniostat. After the crystal is correctly aligned to the "initial" position - the settings of  $\chi$  and  $2\theta$  at 0, and of  $\phi$  at the value of  $\phi_0$  (so that the projection on the equatorial plane of one of the reciprocal axes,  $a_1^*$ , is normal to the incident beam) - the situation is as in Figures 17(a). and 17(b).

In order that the  $(hkl)$  planes might be in the correct diffracting orientation, the vector  $hkl$  (Figure 17(b).) must be rotated through  $\chi$  into the equatorial plane, and then through  $\phi$  into the  $\phi_0$  position normal to the incident beam, (and then through  $\theta$  in the equatorial plane). To determine

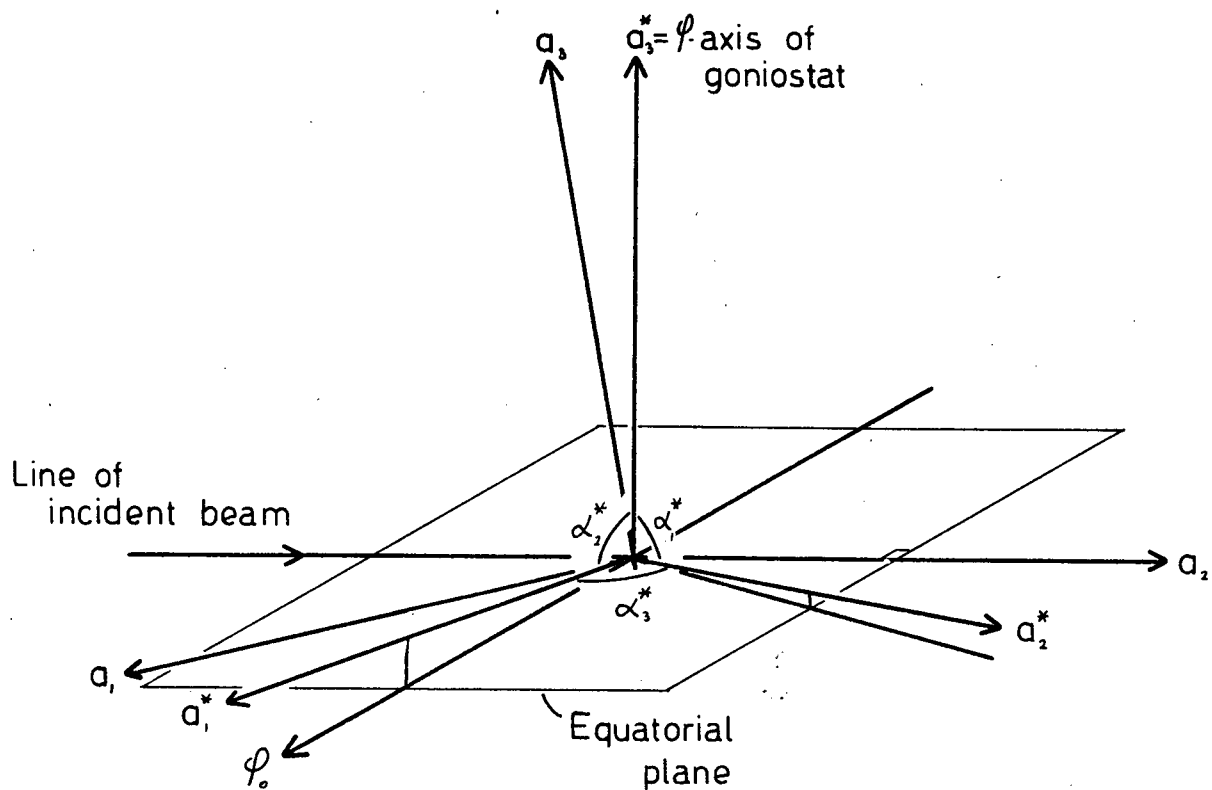


Figure 17(a). Positions of real and reciprocal axes in a reciprocal axis mounting.

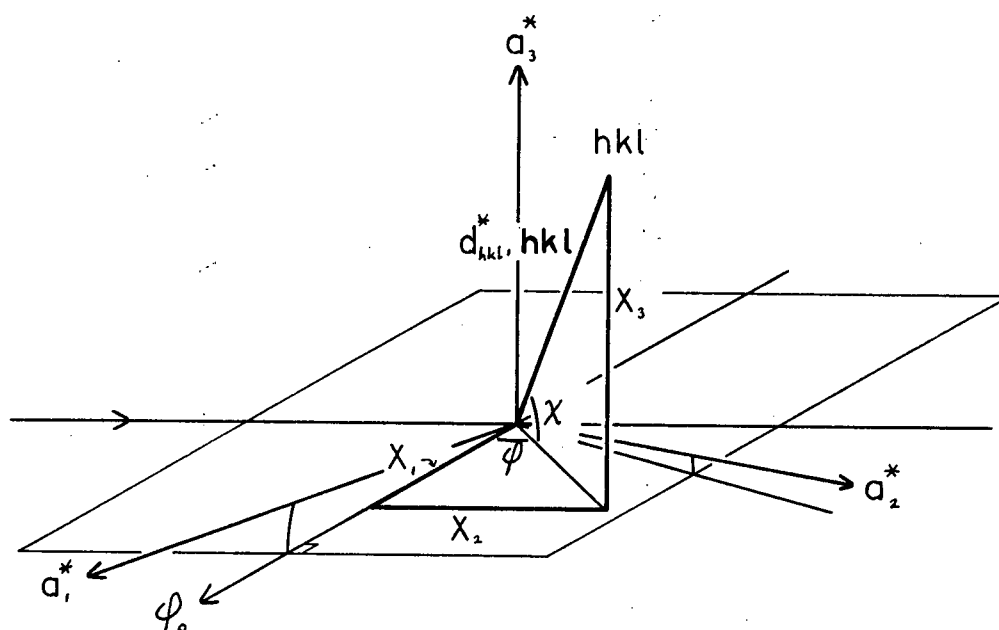


Figure 17(b). The coordinates of a point  $hkl$  in reciprocal space.

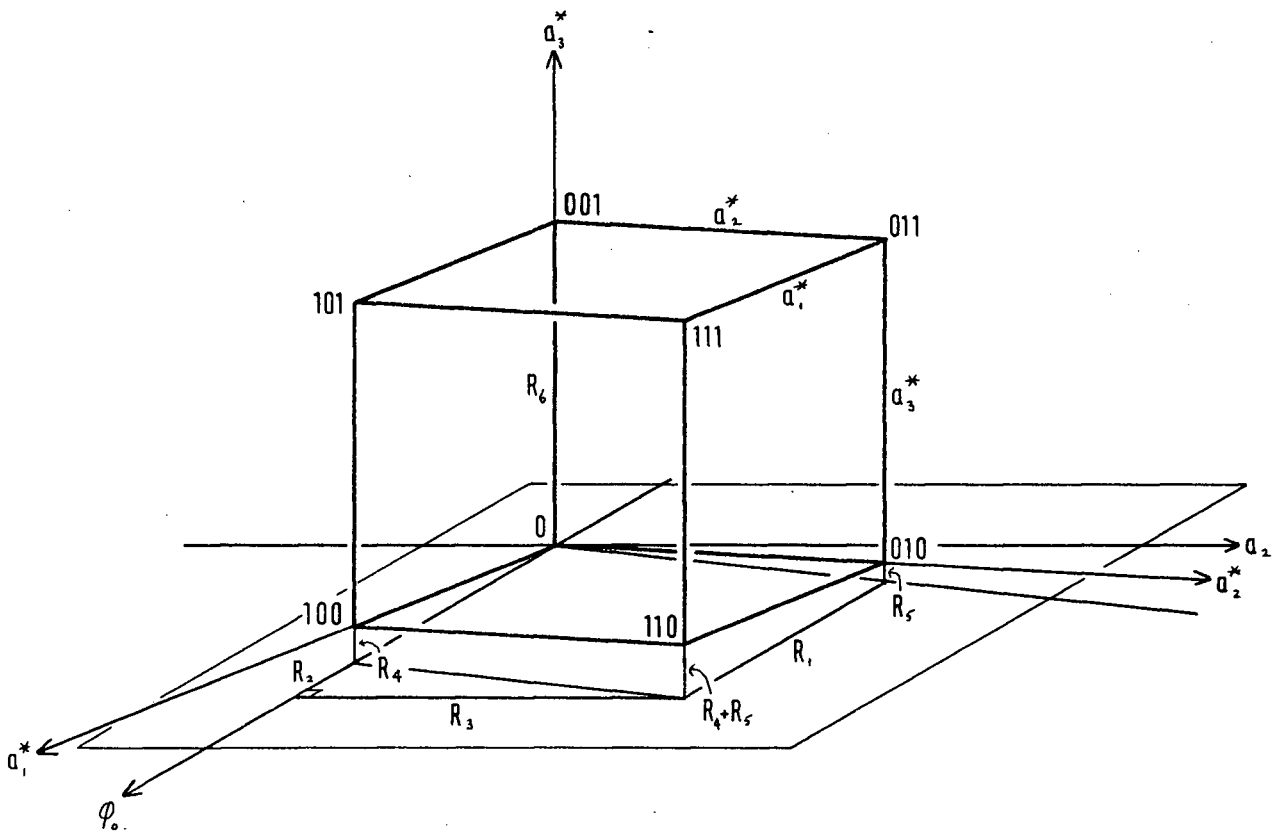


Figure 18. The reciprocal unit cell. N.B. the indices of the corners of the cell are  $h_1 h_2 h_3$ , where  $h_1$  is in the direction of  $a_1^*$ , etc.

$\chi$  and  $\phi$ , we shall calculate  $X_1$ ,  $X_2$  and  $X_3$ , the distances parallel to the orthogonal axes - the  $\phi_0$ -,  $a_2$ - and  $a_3^*$ -axes, respectively.

Consider a reciprocal unit cell, dimensions  $a_1^*$ ,  $a_2^*$ ,  $a_3^*$  and  $\alpha_1^*$ ,  $\alpha_2^*$ ,  $\alpha_3^*$ , as in Figure 18., shown in the same orientation as in Figure 17(a). The indices of the lattice points in Figure 18. are  $h_1 h_2 h_3$ , where  $h_1$  is in the direction of  $a_1^*$ , etc.

The six values  $R_1 - R_6$  can be calculated, by simple trigonometry, to be:

In the  $X_1$  direction:

$$R_1 = a_1^* \cdot \sin \alpha_2^*$$

$$R_2 = \frac{a_2^*}{\sin \alpha_2^*} \cdot (\cos \alpha_3^* - \cos \alpha_1^* \cdot \cos \alpha_2^*)$$

In the  $X_2$  direction:

$$R_3 = \frac{a_2^*}{\sin \alpha_2^*} \cdot \sqrt{1 - \cos^2 \alpha_1^* - \cos^2 \alpha_2^* - \cos^2 \alpha_3^* + 2 \cdot \cos \alpha_1^* \cdot \cos \alpha_2^* \cdot \cos \alpha_3^*}$$

In the  $X_3$  direction:

$$R_4 = a_1^* \cdot \cos \alpha_2^*$$

$$R_5 = a_2^* \cdot \cos \alpha_1^*$$

$$R_6 = a_3^*$$

The values of  $X_1$ ,  $X_2$  and  $X_3$  for the general reflection  $hkl$  are then determined from the increments  $R_1 - R_6$  in the reciprocal unit cell:

$$X_1 = h_1 R_1 + h_2 R_2$$

$$X_2 = h_2 R_3$$

$$X_3 = h_1 R_4 + h_2 R_5 + h_3 R_6$$

where  $h_1$ ,  $h_2$  and  $h_3$  are the indices of the point in reciprocal space,  $h_1$  in the direction of  $a_1^*$ , etc.

The diffractometer settings are then calculated:

$$\chi = \tan^{-1} \left( \frac{X_3}{\sqrt{X_1^2 + X_2^2}} \right)$$

$$\phi = \tan^{-1} \left( \frac{X_2}{X_1} \right)$$

Also:

$$d_{hkl}^* = \sqrt{X_1^2 + X_2^2 + X_3^2}$$

Hence:

$$2\theta = 2 \cdot \sin^{-1} \left( \frac{\lambda}{2} \cdot \sqrt{X_1^2 + X_2^2 + X_3^2} \right)$$

## 2. Outline of the program GESTAR.

The main program of GESTAR may be divided into several sections, and there is one subprogram (named ANGSRRT); several library subroutines



are also called.

An outline of the main program is:

- (i) The cell dimensions, either real or reciprocal, are read in and all the other dimensions are calculated.
- (ii) The values of  $R_1 - R_6$  are calculated for the reciprocal unit cell (see subsection 1. above).
- (iii) The indices  $hkl$  are generated, and if they are within the required ranges (see subsection 3. below for the options available in the generation of  $hkl$  indices), values of  $X_1$ ,  $X_2$  and  $X_3$ , the coordinates of the point  $hkl$  in reciprocal space, are calculated for each reflection. The results are written on file 3.
- (iv) The file 3 is read, selecting reflections according to their positive and negative indices, and the  $2\theta$ ,  $\chi$  and  $\phi$  values for each reflection are calculated, printed out and written on file 8.
- (v) If " $\phi$ -scaling" is required, the sorting subroutine ANGSR is called and the values of  $\phi$ ,  $\chi$  and  $2\theta$  for the sorted reflections are listed.
- (vi) If required, the diffractometer instructions for each reflection are printed out and/or punched on cards; this section requires the "packing" of results, and some of the UBC CHAR character handling routines are called here.

The subroutine ANGSR is a sorting subprogram which sorts reflections on their values of  $2\theta$ ,  $\chi$  and  $\phi$  so that  $\phi$  decreases slowest,  $2\theta$  fastest. The program calls the library routine ASORT which sorts partially complete arrays. The version of ASORT used here is new and its machine language deck is included with the deck of GESTAR.

### 3. Data cards for program GESTAR.

The input instructions for the program GESTAR are given below, and

the various options available in the program are included here.

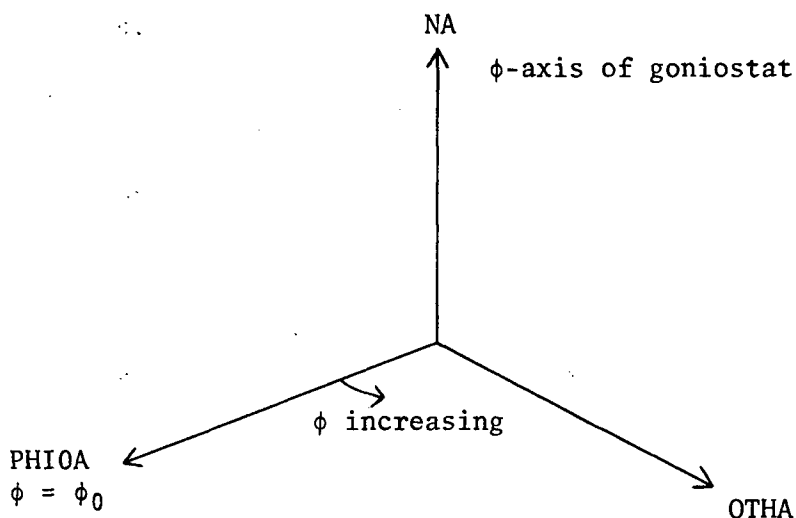
# PROGRAM GESTAR.

Scratch files on units 3 and 8 must be named; if cards are to be punched, unit 7 must be assigned to the punch device. The program should therefore be called:

```
$RUN XRAY:GESTAR 3=-A 7=*PUNCH* 8=-B
```

or, if running the program from the source deck:

```
$RUN -LOAD#+-SORT 3=-A 7=*PUNCH* 8=-B
```



CARD 1. (20A4)

Title.

CARD 2. (3I3)

Col. 3 IPRG Type of output required:

0 - goniostat settings only.

1 - automatic diffractometer instructions, cards  
punched plus listing of cards.

2 - A. D. instructions, listing only.

3 - A. D. instructions, cards punched only.

6 WRORC Cell dimensions as supplied on Card 3:

0 - real dimensions.  
1 - reciprocal dimensions.

9 ISRT Sorting for " $\phi$ -scaling" (reflections sorted for  $2\theta$   
changing most rapidly, then  $\chi$ ,  $\phi$  slowest):

0 - sorting required.  
1 - sorting not required.

CARD 3. (6F10.0)

Cell dimensions, as for BUCILS2:

a, b, c,  $\alpha$ ,  $\beta$ ,  $\gamma$ , or  $a^*$ ,  $b^*$ ,  $c^*$ ,  $\alpha^*$ ,  $\beta^*$ ,  $\gamma^*$ .

CARD 4. (5I3, 5X, 5F10.0)

Col. 3	NA	Goniostat axis	} 1 for $a^*$ ; 2 for $b^*$ ; 3 for $c^*$ .
6	PHIOA	Axis along $\phi_0$	
9	OTHA	Third axis	

12 CENTT No. of tests to be made for centred cells; reflections  
for which  $\Sigma H_i = 2n+1$ , ( $H = h, k, l$ ), will be omitted,  
e.g. for A, B, C and I type cells, CENTT=1 and test  
 $k+l$ ,  $h+l$ ,  $h+k$ , or  $h+k+l$ , respectively; for F cells,  
CENTT=2 and test  $h+k$  and  $k+l$ .

15 SCSP Scan speed required in data collection:

1 -  $\frac{1}{4}$  degree per minute.  
2 -  $\frac{1}{2}$  " " "  
3 - 1 " " "  
4 - 2 " " "  
5 - 4 " " "  
6 - Slew.

21-30 MINTTH Minimum  $2\theta$  value (in degrees) for reflections for data  
collection; if blank,  $2\theta_{\min}$  taken as  $4.0^\circ$ .

31-40 MAXTTH Maximum  $2\theta$  value (in degrees) for reflections; if blank,  
 $2\theta_{\max}$  taken as  $160.0^\circ$ .

41-50 PHIO Value of  $\phi_0$ , (in degrees).

51-60 SCAN Constant  $k$  in calculation of scan range:

$2\theta_{\text{scan}} = 1.80 + k \cdot \tan \theta$  ; if blank,  $k = 0.86$ .

61-70 WAVE Wavelength of radiation to be used, (in Å.).

CARD 5. (12I3)

Values of h, k,  $\ell$  required.

Col. 1-3	Lowest absolute value of h	}	N.B. 000 reflection not generated.	
4-6	" " " " k			
7-9	" " " " $\ell$			
-12	No. of layers of h	}	if blank, there is no restriction on the no. of layers.	
-15	" " " " k			
-18	" " " " $\ell$			
-21	}	+1 indicates positive values only	{	in h
-24		0 indicates both positive and negative values		in k
-27		-1 indicates negative values only		in $\ell$
-30	Interval in h	}	if blank, unit increments in h, k, $\ell$ are assumed.	
-33	Interval in k			
-36	Interval in $\ell$			

CARD 6. (6I3). Required only if CENTT > 0.

Col.	3	1 - if h, ( $H_1$ )	} is to be included in the test:
	6	1 - if k, ( $H_2$ )	
	9	1 - if l, ( $H_3$ )	
			$\sum_i H_i = 2n + 1$
	12	} ditto for second test, (if CENTT = 2).	
	15		
	18		

N.B. when CENTT = 2, both sums must have  
odd totals if the reflection is to be omitted.

#### 4. A listing and an example output of GESTAR.

A listing of the program GESTAR, followed by an example set of input data cards and the output for this test run are shown below:



```

0001 SUBROUTINE ANGSRG (N)
C
C SORTING SUBROUTINE, SORTING 2-THETA, CHI, & PHI SO THAT PHI
C DECREASES SLOWEST, 2-THETA FASTEST
C
0002 INTEGER N
0003 INTEGER ANGLE(5000,6), BANGL(500,6), EANGL(50,6)
0004 REAL ANGLE(5000,3)
0005 ILL = 9
0006 DO 120 I=1,N
0007 READ (111,END=121) (ANGLE(I,J), J=6,5), (BANGL(I,J), J=1,3)
0008 DO 163 J=1,3
0009 ANGLE(I,J) = 100.0*ANGLE(I,J)+0.1
0010 CONTINUE
0011 IF=IND 111
0012 CALL ASORT (ANGLE, 6, -5000, N, 6)
0013 JJ = 1
0014 DO 123 J=2,N
0015 IF (BANGL(I,J),FJ,BANGL(I,J-1)) JJ = JJ+1
0016 IF (BANGL(I,J),FJ,BANGL(I,J-1),AND,JJ,GE,2) GO TO 124
0017 IF (J,FJ,N,AND,JJ,GF,2) GO TO 132
0018 GO TO 123
0019 KJ = J+1
0020 GO TO 135
0021 KJ = J
0022 DO 125 K=1,JJ
0023 BANGL(K,1) = ANGLE(I,J-J+K,2)
0024 BANGL(K,2) = ANGLE(I,J-J+K,1)
0025 DO 126 H=1,6
0026 BANGL(K,H) = ANGLE(I,J-J+K,H)
0027 CALL ASORT (BANGL, 6, -500, JJ, 6)
0028 KK = 1
0029 DO 127 K=2,JJ
0030 IF (BANGL(K,1),FJ,BANGL(K-1,1)) KK = KK+1
0031 IF (BANGL(K,1),FJ,BANGL(K-1,1),AND,KK,GE,2) GO TO 127
0032 IF (K,FJ,N,AND,KK,GE,2) GO TO 131
0033 GO TO 126
0034 JK = K+1
0035 GO TO 136
0036 JK = K
0037 DO 128 L=1,KK
0038 BANGL(L,1) = BANGL(JK-KK+1,L,3)
0039 BANGL(L,2) = BANGL(JK-KK+1,L,2)
0040 BANGL(L,3) = BANGL(JK-KK+1,L,1)
0041 DO 129 H=1,6
0042 BANGL(L,H) = BANGL(JK-KK+1,L,H)
0043 CALL ASORT (BANGL, 6, -50, KK, 6)
0044 DO 129 L=1,KK
0045 BANGL(JK-KK+1,L,1) = BANGL(L,3)
0046 BANGL(JK-KK+1,L,2) = BANGL(L,2)
0047 BANGL(JK-KK+1,L,3) = BANGL(L,1)
0048 DO 129 H=1,6
0049 BANGL(JK-KK+1,L,H) = BANGL(L,H)
0050 IF (JK,GF,N) GO TO 134
0051 KK = 1
0052 CONTINUE
0053 DO 130 K=1,JJ
0054 ANGLE(I,J-J+K,1) = BANGL(K,2)
0055 ANGLE(I,J-J+K,2) = BANGL(K,1)
0056 DO 130 H=1,6
0057 ANGLE(I,J-J+K,H) = BANGL(K,H)
0058 IF (KJ,GF,N) GO TO 133
0059 JJ = 1
0060 CONTINUE
0061 DO 132 I=1,N
0062 DO 164 J=1,3
0063 ANGLE(I,J) = ANGLE(I,J)
0064 ANGLE(I,J) = 0.01*ANGLE(I,J)
0065 WRITE (111) (ANGLE(I,J), J=6,5), (BANGL(I,J), J=1,3)
0066 CONTINUE
0067 ENDFILE 111
0068 RETURN
0069 END

```

EXECUTION TERMINATED

BRUN / ASMC SPUNCH=32RT SPRINT=0JMMV

EXECUTION BEGINS

EXECUTION TERMINATED

## Input data cards

```

SPUN=LOAD*+SORT 3=A 7=PUNCH* 8=B
Card 1. TRIAL RUN OF "GESTAR" PROGRAM
2. 2
3. 3.7277 17.8335 11.9335 90.00 94.11852 90.00
4. 1 2 3 4 22.50 27.00 26.14 1.5418
5. +1 +1

```

## Printed output

```

SPUN=LOAD*+SORT 3=A 7=PUNCH* 8=B
EXECUTION BEGINS
TRIAL RUN OF "GESTAR" PROGRAM
REAL CELL: A = 3.723 B = 17.833 C = 11.834 ALPHA = 90.000 BETA = 94.119 GAMMA = 90.000
RECIP. CELL: A* = 0.26932 B* = 0.05608 C* = 0.08472 ALPHA* = 90.000 BETA* = 85.981 GAMMA* = 90.000
UNIT CELL VOLUME = 783.57CU. A.
MIN. 2-THETA = 22.50, MAX. 2-THETA = 27.00

```

H	K	L	PHI	CHI	TWO THETA
0	0	1	110.14	4.12	22.60
0	1	3	97.67	4.02	23.15
0	2	3	86.28	3.77	24.73
0	4	2	57.14	2.49	25.73
0	5	0	20.14	0.00	26.97
0	5	1	36.91	1.19	26.10
1	0	0	20.14	00.00	23.87
1	0	1	110.14	72.94	25.66
1	1	0	20.14	78.24	26.49
1	1	1	76.57	69.78	26.15
1	2	0	20.14	67.39	25.99
0	0	-3	280.14	-4.17	22.60
0	1	-3	32.01	-4.02	23.15
0	2	-3	314.00	-3.77	24.73
0	4	-2	343.14	-2.48	25.03
0	5	-1	32.87	-1.19	26.10
1	0	-1	20.14	72.92	26.61
1	1	-1	324.71	68.93	25.12
1	2	-1	343.14	61.92	26.59

NO. OF REFLECTIONS = 19

H	K	L	PHI	CHI	TWO THETA
1	2	-1	343.14	61.92	26.59
0	4	-2	343.14	-2.48	25.03
1	1	-1	324.71	68.93	25.12
0	2	-3	314.00	-3.77	24.73
0	1	-3	32.01	-4.02	23.15
1	0	-1	20.14	72.92	26.61
0	0	-3	280.14	-4.17	22.60
1	0	1	110.14	72.94	25.66
1	0	0	20.14	00.00	23.87
1	1	0	20.14	78.24	26.49
1	1	1	76.57	69.78	26.15
1	2	0	20.14	67.39	25.99
0	5	1	36.91	1.19	26.10
1	0	0	20.14	00.00	23.87
1	0	1	110.14	72.94	25.66
1	1	1	76.57	69.78	26.15
1	2	1	36.91	1.19	26.10
0	5	0	20.14	0.00	26.97
0	5	-1	36.91	-1.19	26.10

DIFFRACTOMETER INSTRUCTIONS

W001C02101/6006343144600606192520060255855004027595200602759

W001C04102/6006343144600635752520060240355004026025200602602

W001C01101/6006323704600606893520060241255004026115200602611

W001C02103/6006314004600635624520060237355004025725200602572

W001C01103/6006302614600635598520060221655004024135200602413

W001C00101/600629014600607220520060236155004025605200602560

W001C00103/60062901460063558520060216155004023585200602358

W001C00001/60061101460060729452006024665500402665200602665

W001C00003/6006110146006060411520060216155004023585200602358

W001C00100/6006097646006060402520060221655004024135200602413

W001C02003/600608627460060376520060237355004025725200602572

W001C01001/60060676574600606978520060251555004027145200602714

W001C04002/6006057134600600248520060240355004026025200602602

W001C00100/6006036914600603119320060251055004027095200602709

W001C00000/600602014600609000520060229855004024955200602495

W001C01100/600602014600607823520060234855004025475200602547

W001C02000/600602014600606739520060249955004026985200602698

W001C005000/600602014600600000520060239655004025955200602595

W001C05101/600601364600635882520060251055004027095200602709

## C. THE SUBROUTINE "TWIN".

### 1. Introduction.

This subprogram can be incorporated into the GESTAR program with only minor modifications in the latter parts of the main program. It was written specifically for the determination of the diffractometer settings for the reflections of the second twin of 2,6-dichloro-4-nitroaniline, a monoclinic crystal, mounted with the  $a^*$ -axis of the first twin parallel to the goniostat  $\phi$ -axis; it may, however, be adapted for similar modes of twinning.

The subprogram TWIN is called after the  $\phi$ ,  $\chi$  and  $2\theta$  values for each reflection of the first twin have been determined in GESTAR; it uses these results and calculates the  $\phi$  and  $\chi$  settings (the  $2\theta$  setting is unchanged) for the corresponding reflection in the second twin.

The output of results in the main program has been altered a little from that described for GESTAR, section B.4 above. A listing of the subprogram TWIN and of the latter part of the main program, and an example of the output, are shown below in subsection 3. The input data cards for the modified GESTAR/TWIN program are the same as for GESTAR, (section B.3), except that an extra card is required if diffractometer instructions are required for one or both of the twins:

CARD 7. (I3). Required only if IPROG is not zero.

Col. 3	ITW	0 - if diffractometer instructions are required for both twins.
		1 - for second twin only.
		2 - for first twin only.

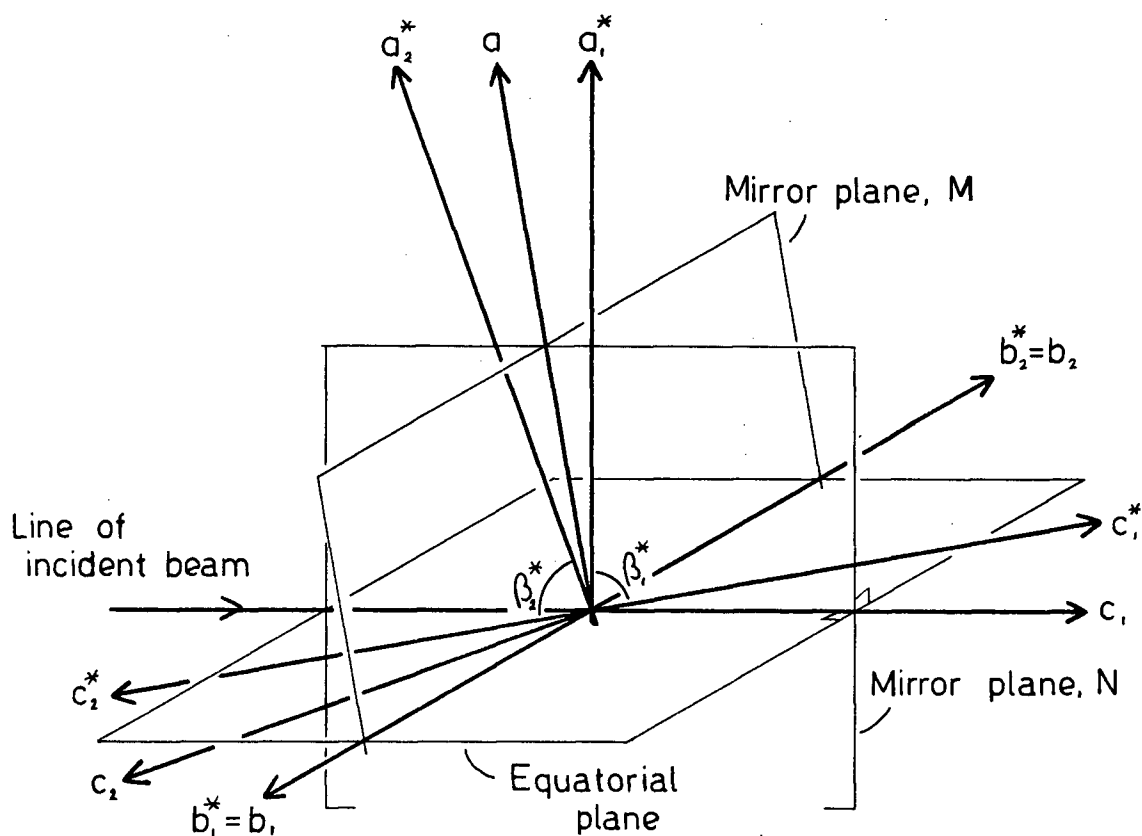


Figure 19. The axes of the twins of 2,6-dichloro-4-nitroaniline.

## 2. Geometry of the second twin system.

In Figure 19., the major axes of the reciprocal lattices of the two twins of 2,6-dichloro-4-nitroaniline crystals are shown. The orientation of the diagram is the same as in Figure 17(a). and since the crystal system is monoclinic, the angles  $\alpha_2^*$  and  $\alpha_3^*$  of Figure 17(a). are  $90^\circ$  and the  $a_1^*$ -axis of Figure 17(a). is now in the equatorial plane.

In the labelling of the axes in Figure 19., the subscript refers to the twin number, i.e.  $a_1^*$  is the  $a^*$ -axis of the first twin. The  $a$ -axis is common to both twins and is therefore not given a subscript.

It will be seen from Figures 19. and 20. that, in general, a reciprocal lattice point  $(hkl)_1$  of the first twin has a corresponding lattice



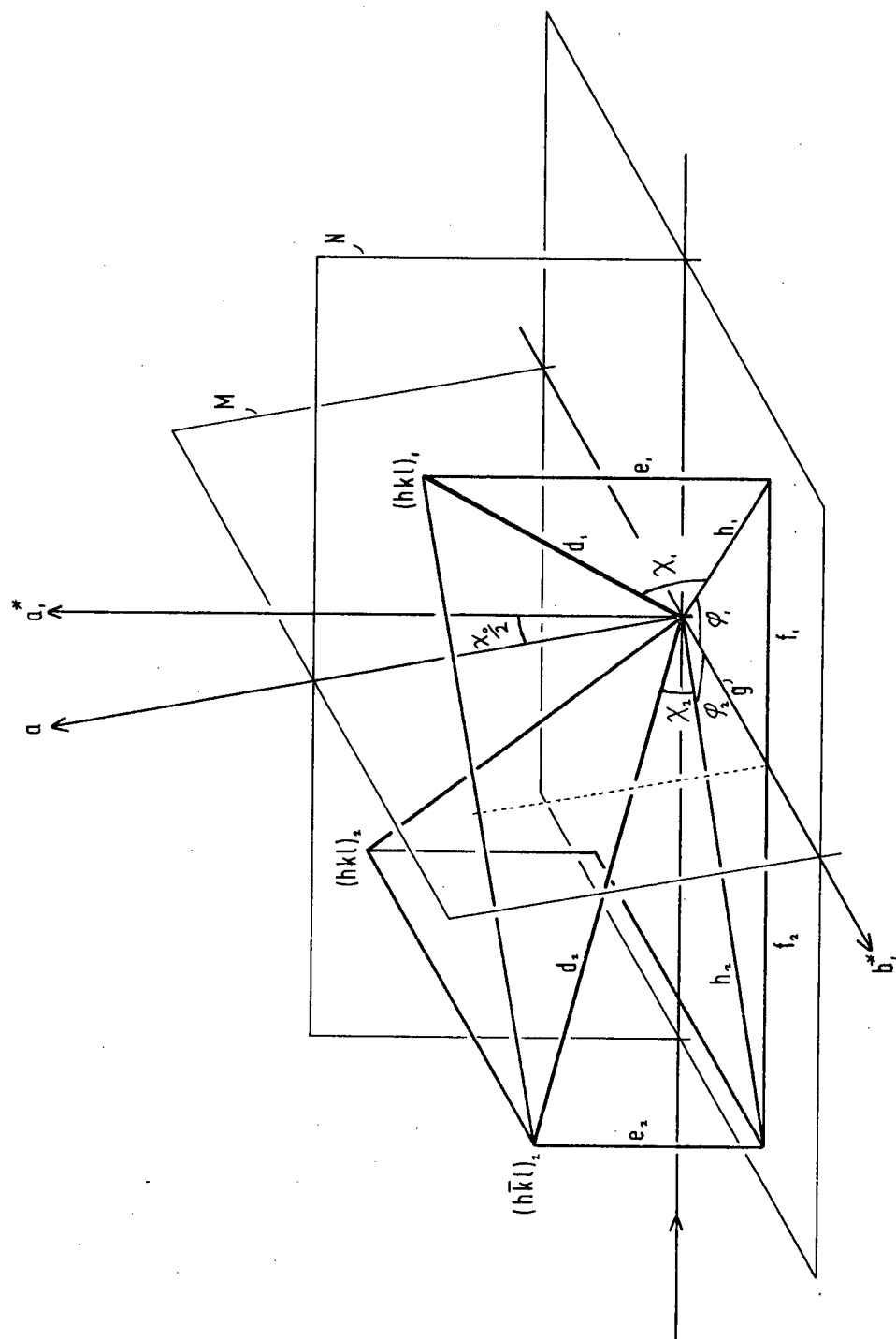


Figure 20. Corresponding lattice points in the two twins of 2,6-dichloro-4-nitroaniline.

point  $(hkl)_2$  of the second twin in the opposite quadrant on the same side of the equatorial plane. In order to calculate the  $\chi$  and  $\phi$  settings for the  $(hkl)_2$  point, the subprogram TWIN first calculates the settings for the  $(h\bar{k}l)_2$  point; this latter point is equidistant with the  $(hkl)_1$  point from the a-b plane (the mirror plane M) and is on a line from  $(hkl)_1$  perpendicular to the plane M. The points  $(hkl)_2$  and  $(h\bar{k}l)_2$  are related by the mirror plane N through the a- and c-axes - see Figure 20.

The angles  $\phi_1$  and  $\chi_1$  (Figure 20.) are the settings determined in GESTAR for the point  $(hkl)_1$ . We wish to calculate, first, the angles  $\chi_2$  and  $\phi_2$ . The angle  $\chi_0$  is defined as the angle between the  $a^*$ -axes of the two twins in the plane N, i.e.

$$\chi_0 = 2(90 - \beta^*)^\circ$$

Since the two twins' real unit cells, (and therefore also reciprocal unit cells), have identical dimensions, the distances  $d_1$  and  $d_2$  are equal:

$$d_1 = d_2 = d$$

Then:

$$e_1 = d \cdot \sin \chi_1$$

$$e_2 = d \cdot \sin \chi_2$$

$$h_1 = d \cdot \cos \chi_1$$

$$h_2 = d \cdot \cos \chi_2$$

$$f_1 = h_1 \cdot \sin \phi_1$$

$$f_2 = h_2 \cdot \sin \phi_2$$

$$= d \cdot \cos \chi_1 \cdot \sin \phi_1$$

$$g = h_1 \cdot \cos \phi_1$$

$$= d \cdot \cos \chi_1 \cdot \cos \phi_1$$

Figure 21. shows the points  $(hkl)_1$  and  $(h\bar{k}l)_2$  in the plane that contains both points and which is normal to the  $b^*$ -axes; this plane cuts the mirror plane M perpendicularly.

About the plane M:

$$j_1 = j_2 = j$$

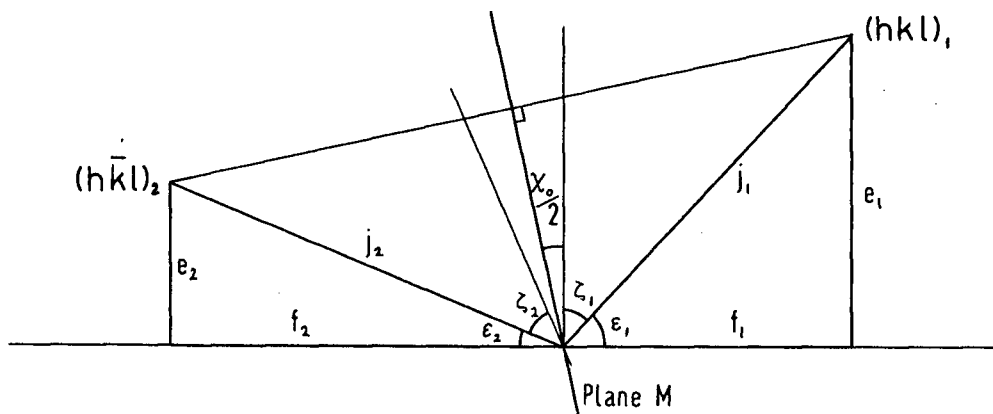


Figure 21. The plane, normal to the  $b^*$  axes,  
containing the points  $(hkl)_1$  and  $(h\bar{k}l)_2$ .

$$\text{Angle } \zeta_1 = \zeta_2 = \zeta$$

Also:

$$\epsilon_1 + \zeta = 90^\circ$$

$$\chi_0 + \zeta + \epsilon_2 = 90^\circ$$

$$\underline{\epsilon_2 = \epsilon_1 - \chi_0}$$

Now:

$$\begin{aligned} e_2 &= j \cdot \sin \epsilon_2 \\ &= j \cdot \sin (\epsilon_1 - \chi_0) \\ &= j \cdot (\sin \epsilon_1 \cdot \cos \chi_0 - \sin \chi_0 \cdot \cos \epsilon_1) \\ &= j \cdot \left( \frac{e_1}{j} \cdot \cos \chi_0 - \frac{f_1}{j} \cdot \sin \chi_0 \right) \\ &= \underline{d \cdot \sin \chi_1 \cdot \cos \chi_0 - d \cdot \cos \chi_1 \cdot \sin \phi_1 \cdot \sin \chi_0} \end{aligned}$$

And:

$$\begin{aligned} f_2 &= j \cdot \cos \epsilon_2 \\ &= j \cdot \cos (\epsilon_1 - \chi_0) \\ &= j \cdot (\cos \epsilon_1 \cdot \cos \chi_0 + \sin \epsilon_1 \cdot \sin \chi_0) \\ &= j \cdot \left( \frac{f_1}{j} \cdot \cos \chi_0 + \frac{e_1}{j} \cdot \sin \chi_0 \right) \\ &= \underline{d \cdot \cos \chi_1 \cdot \sin \phi_1 \cdot \cos \chi_0 + d \cdot \sin \chi_1 \cdot \sin \chi_0} \end{aligned}$$

Hence;

$$\begin{aligned}\sin \chi_2 &= \frac{e_2}{d} \\ &= \frac{\sin \chi_1 \cdot \cos \chi_0 - \cos \chi_1 \cdot \sin \phi_1 \cdot \sin \chi_0}{d}\end{aligned}$$

And:

$$\begin{aligned}\tan \phi_2 &= \frac{f_2}{g} \\ &= \frac{d \cdot (\cos \chi_1 \cdot \sin \phi_1 \cdot \cos \chi_0 + \sin \chi_1 \cdot \sin \chi_0)}{d \cdot \cos \chi_1 \cdot \cos \phi_1} \\ &= \cos \chi_0 \cdot \tan \phi_1 + \frac{\tan \chi_1 \cdot \sin \chi_0}{\cos \phi_1}\end{aligned}$$

The  $\chi$  settings are the same for the  $(hkl)_2$  and  $(h\bar{k}l)_2$  reflections. The  $\phi$  setting for  $(hkl)_2$  is calculated from the  $\phi_2$  result above, and the three values,  $\phi$ ,  $\chi$  and  $2\theta$ , for the second twin reflection,  $hkl$ , are returned to the main program.

For reflections with indices  $h00$  and  $h0l$ , calculations of  $\phi_2$  are much simpler and are made separately from the general case; this avoids calculations of  $\tan 90^\circ (= \infty)$  values in the computer.

### 3. A listing and example output of GESTAR/TWIN.

The first parts of the main program are as listed in section B.3, except for line 94. This line and the latter parts of the main program, and the subroutine TWIN are shown below; minor alterations in the subroutine ANGSR are also shown. The library program ASORT is unchanged from section B.3. A listing of a sample set of input data cards, and the printed output, follow the program listing.

## Program listing

```

0001  SUBROUTINE ANGSR4 (I1,N)
0002  SORTING SUBROUTINE, SORTING 2-THETA, CHI, L PHI SO THAT PHI
0003  DECREASES SLOWEST, 2-THETA FASTEST
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## Input data cards

```

SKIN-LODGE-SHET 3-A 7-PUNCH B-H 9-C
Card 1. TVAL RIN OF REGISTRATION PROGRAM
2. 2
3. 217276 17.0310 11.43152 90.30 46.1142 90.00
4. 1 2 3 4 25.14 1.5418
5. 2 7 2 1
6. (blank)

```



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