THE CRYSTAL STRUCTURE AND CONSTITUTION OF SOME MOLECULAR COMPLEXES OF 4:4'-DINITRODIPHENYL.

by D. H. Saunder, M.Sc.
(Beit Railway Trust Rhodesian Fellow).

Thesis presented to the University of Cape Town
for the degree of Doctor of Philosophy, 1947.

SUMMARY.

The crystal structures of a number of molecular complexes formed by 4:4'-dinitrodiphenyl with various diphenyl derivatives are described. The general type of structure is undoubtedly the same for all the complexes examined and the typical arrangement may be taken as that in the complex of 4:4'-dinitrodiphenyl with 4-hydroxydiphenyl, the structure of which has been fully determined. As shown in fig. 7 the dinitrodiphenyl molecules form layers in face-centred array and lie one above the other with a spacing of about 3·7 A. The arrangement of these molecules alone is such that a set of tubular cavities, also in face-centred array, run through the structure. In the complexes these cavities are occupied by the other component molecules, the hydroxydiphenyl molecules in the case considered, which thus lie nearly normal to the planes containing the dinitrodiphenyl molecules and are seen end-on in fig. 7. In the other structures examined geometrical and symmetry conditions require that the individual molecules should be tilted in varying degrees, but the type of structure still remains essentially the same.

It is shown that the ratio of the components in these complexes is determined by the length of the molecule other than dinitrodiphenyl, and that in no case is it necessary for the intermolecular distances to be shorter than those found in crystals of ordinary aromatic nitro-compounds.

A bonding mechanism in terms of dipole attraction between the component molecules is shown to be consistent with all the observed data.

Of interest are the periodic distortions which appear to occur in the crystal lattices of the complexes of 4:4'-dinitrodiphenyl with 4-iodo-, 4-bromo- and 4-chlorodiphenyl.

INDEX OF CONTENTS.

APPENDICES.

INDEX OF FIGURES AND TABLES.

INTRODUCTION.

The problem of the constitution of molecular complexes derived from nitro-compounds and certain unsaturated hydrocarbons and their derivatives has, in recent years, attracted considerable attention and many hypotheses have been advanced with regard to the nature of the bonding.

Thus Bennett (15) and Hammick (16) have suggested that the components are united by covalent bonds while Weiss (17) has attributed complex formation to "a complex molecule, essentially ionic in character, which is formed from the two components by an electron transfer from the unsaturated hydrocarbon to the nitro-compound." In more recent years, however, the tendency has been to regard complex formation as being due to the interaction of dipoles (18-22), and this idea has been supported by the crystallographic studies of Powell and Huse (12).

In the present work a crystallographic study of a series of complexes formed by 4:4'-dinitrodiphenyl is described and a possible bonding mechanism for these complexes is discussed in terms of the interaction of dipoles.

THE MOLECULAR COMPLEXES OF 4:4'-DINITRODIPHENYL.

A large number of molecular complexes of 4:4'-dinitrodiphenyl with various diphenyl derivatives have been prepared and analyzed by Dr. W.S. Rapson and Mr. E. Theal Stewart (1) of the University Chemistry Department, and are listed in table 1.

4:4'-Dinitrodiphenyl has been found to exhibit great selectivity in the formation of molecular complexes, which have been isolated only with 4-substituted and 4:4'-disubstituted diphenyls. Diphenyl derivatives with strong electron-donating substituents such as $-NH_2$ or -OH in one or both of the ortho positions have failed even to generate colour on admixture with 4:4'-dinitrodiphenyl in solution. No evidence has been obtained of compound formation between 2:2'-dinitrodiphenyl and any of a large number of simple diphenyl derivatives which have been applied to it.

The compounds of 4:4'-dinitrodiphenyl with benzidine and its tetramethyl derivative appear to be by far the most stable of those studied. They are much more intensely coloured (table 1) than those with 4-aminodiphenyl, 4:4'-dihydroxydiphenyl, 4-hydroxydiphenyl, and 4:4'-dimethoxydiphenyl. These in turn are much more deeply coloured than the remaining complexes listed, all of which have approximately the same colours as the substances from which they are derived.

[page 4

TABLE 1.

PROPERTIES OF SOME MOLECULAR COMPLEXES DERIVED FROM 4:4'-DINITRODIPHENYL.

Molecular complex of 4:4'-dinitrodiphenyl with:	Colour	Molecular ratio of 4:4'-dinitrodiphenyl to the other component.	M.P. °C
NN:N'N'-Tetramethylbenzidine.	Dark-red.	4:1	233°
	Steel-grey	1:1	224°
Benzidine	Red	4:1	240°
4-Aminodiphenyl	Orange	3:1	220°
4:4'-Dihydroxydiphenyl.	Orange-yellow	3:1	249°
4-Hydroxydiphenyl	Yellow	3:1	229°
4:4'-Dimethoxydiphenyl.	Canary-yellow	7:2	217°
4:4'-Diacetoxydiphenyl	Cream	5:1	225°
4-Acetoxydiphenyl	Cream	4:1	191°-221°
4-Iododiphenyl	Pale-yellow	7:2	192°-220°
4-Bromodiphenyl	Pale-cream	?	192°-220°
4-Chlorodiphenyl	Pale-cream	?	-
4-Fluorodiphenyl	Cream	3:1	-
Diphenyl	Pale-yellow	3:1	191°-221°

In almost every case, these lightly coloured complexes melt with decomposition (over approximately the same range of temperature), indicating that they are less stable than their more deeply coloured analogues. In the cases studied, no complex formation has been observed between 4:4'-dinitrodiphenyl and diphenyl derivatives with electron-accepting groups in *para* position. In this para series, therefore, it appears that electron-donating substituents favour, and electron-accepting substituents inhibit, compound formation. Of interest from this point of view is the formation of a highly coloured and stable compound from 4-nitrodiphenyl and N:N:N':N'-tetramethylbenzidine (which contains strongly electron-donating dimethylamino groups). This compound is the only known stable and easily prepared molecular complex formed by a simple mononitro derivative, and is the only compound formed by 4-nitrodiphenyl which was isolated.

The crystal structures of most of the molecular complexes listed in table 1 have been examined, and suitable crystals were grown by slowly cooling a solution of the complex in acetone containing a slight excess of the more soluble component. Many attempts were generally necessary before a suitable batch was obtained.

CRYSTALLOGRAPHY.

The optical properties.

It was generally possible to select crystals that were clear and free from flaws and in most cases a very complete optical examination was possible.

With one exception all the complexes examined are monoclinic and show straight extinction on the (100) face. Wherever possible the monoclinic angle, β, was determined from goniometer measurements; in many cases, however, no crystals developing a (001) face could be found and the monoclinic angle was then determined from a Weissenberg photograph taken with the crystal rotating about the symmetrical axis.

The complex with tetramethylbenzidine is triclinic and the axes were chosen so that the angles between the reciprocal axes, $\alpha^* = 49°42'$, $\beta^* = 68°9'$, $\gamma^* = 71°50'$, could be measured directly on the goniometer, and the angles of the actual crystal cell were calculated from the relations

$$\cos\alpha = \frac{\cos\beta^*\cos\gamma^* - \cos\alpha^*}{\sin\beta^*\sin\gamma^*} \qquad \text{etc.}$$

All the crystals are very strongly doubly refracting and are optically positive. In most cases under the polarizing microscope a biaxial figure containing the acute bisectrix, which is nearly perpendicular to (100), may be obtained. By measuring the separation, 2D, of the poles of the figures, it

TABLE 2.

OPTICAL PROPERTIES OF SOME OF THE MOLECULAR COMPLEXES OF 4:4'-DINITRODIPHENYL.

Complex of 4:4'-dinitrodiphenyl with:	System and prominent faces.	Cell angles.	Optic axial angle (2V)	Principal refractive indices.
4:4'-Dihydroxydiphenyl	Monoclinic {100} {110}	$\beta = 95^\circ$	29°	$\alpha = 1.62$ $\beta = 1.63$ $\gamma = 1.99$
4-Hydroxydiphenyl	Monoclinic {100} {110} {001}	$\beta = 99^\circ 39'$	45°	$\alpha = 1.59$ $\beta = 1.64$ $\gamma = 2.03$
4-Iododiphenyl	Monoclinic {100} {110}	$\beta = 100^\circ$	34°	$\alpha = 1.62$ $\beta = 1.65$ $\gamma = 2.13$
4-Bromodiphenyl	Monoclinic {100} {110}	$\beta \approx 100^\circ$	37°	$\alpha = 1.60$ $\beta = 1.64$ $\gamma = 2.39$
4-Chlorodiphenyl	Monoclinic {100} {110}	$\beta \approx 100^\circ$	-	-
Diphenyl	Monoclinic {100} {110}	$\beta = 99^\circ 30'$	-	-
Benzidine	Monoclinic {100} {110} (001) {101}	$\beta = 120^\circ 28'$	-	-
NN:N'N'-Tetramethyl-benzidine	Triclinic {100} {010} {001}	$\alpha = 127^\circ 0'$ $\beta = 103^\circ 39'$ $\gamma = 95^\circ 45'$	-	-

The complex with hydroxydiphenyl.

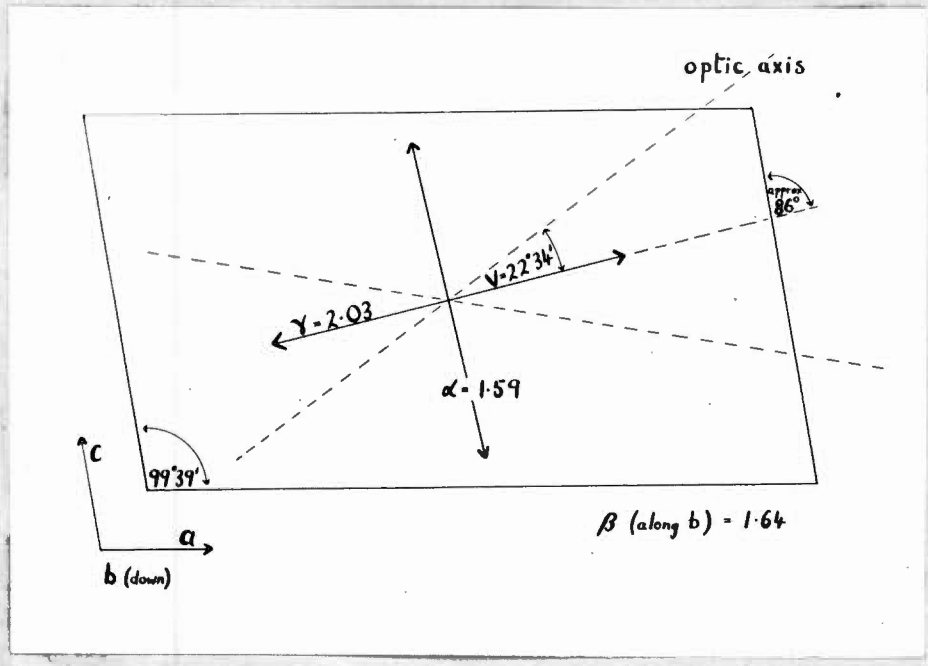


Fig. 1.

Directions of the refractive indices and the optic axes in the unit cell.

was possible to calculate the optic axial angle, 2V, from

$$\sin V = \frac{D}{K\beta}$$

where K is a constant for the microscope and can be determined using a known biaxial mineral, and β is the intermediate refractive index.

The principal refractive indices α and β were determined by the immersion method in solutions of methylene iodide and sulphur and using sodium light. Since solutions of refractive index high enough to determine γ in this way were not available, it was calculated from the relation

$$\tan V = \frac{\gamma}{\alpha}\sqrt{\frac{\alpha^2 - \beta^2}{\beta^2 - \gamma^2}}$$

For the complex with hydroxydiphenyl the directions of the principal refractive indices are shown in fig. 1. For the other complexes whose refractive indices are listed in table 2, the corresponding directions are very similar to those shown in fig. 1, with the exception that α is parallel to and γ is perpendicular to c in each case.

The unit cells.

The axial lengths were determined from oscillation photographs taken about the various axes and are listed in table 3.

The density, ρ , of each crystal was measured by the method of flotation, using a mixture of chloroform and carbon tetrachloride, and the number, n, of complex groups per unit cell was then calculated from

$$n = \frac{\rho \times \text{vol. of unit cell}}{\text{mass of hydrogen atom} \times \text{M.W.}}$$

[page 10

TABLE 3.

UNIT CELLS OF SOME OF THE MOLECULAR COMPLEXES OF 4:4'-DINITRODIPHENYL.

Complex of 4:4'-dinitrodiphenyl with:	Cell dimensions in A. a	b	c	Density in gm./c.c.	Calculated number of complex groups in the unit cell.
4:4'-Dihydroxydiphenyl	20.0	18.65	11.3	1.45	3.98
4-Hydroxydiphenyl	20.06	9.46	11.13	1.43	1.99
4-Iododiphenyl	20.0	9.5	25.8	1.56	2.04
4-Bromodiphenyl	20.0	9.5	?	1.52	?
4-Chlorodiphenyl	20.0	9.5	?	-	?
Diphenyl	19.9	9.50	11.0	1.43	1.98
Benzidine	30.2	11.15	11.5	1.44	4.05
NN:N'N'-Tetramethyl-benzidine	19.1	14.8	22.0	1.43	2.02

The space-groups will be discussed together with the structures, since in only one case was the space-group determined uniquely from the systematic absences. The routine methods and the apparatus used in the determination of the unit cells and space-groups are described in Appendix 1.

DESCRIPTION OF THE STRUCTURES.

As it was not practicable to undertake Fourier analyses for all the complexes prepared, the structure of only one of them, the complex between 4:4'-dinitrodiphenyl and 4-hydroxydiphenyl, was determined in detail; and approximate structures were worked out for the complexes of 4:4'-dinitrodiphenyl with diphenyl, NN:N'N'-tetramethylbenzidine, benzidine, 4:4'-dihydroxydiphenyl, 4-iododiphenyl, 4-bromodiphenyl and 4-chlorodiphenyl. Comparative photographs have also been taken for the complex of 4:4'-dinitrodiphenyl with 4-fluorodiphenyl, but an approximate structure has not been worked out for it.

The structures of all these complexes are closely similar and the typical arrangement may be taken as that in the complex of 4:4'-dinitrodiphenyl with 4-hydroxydiphenyl. As shown in fig. 7 the dinitrodiphenyl molecules form layers in face-centred array and lie one above the other with a spacing of about 3·7 A. The arrangement of these molecules alone is such that a set of tubular cavities, also in face-centred array, run through the structure. These cavities are occupied by the other component molecules, the hydroxydiphenyl molecules in the case considered, which thus lie nearly normal to the planes containing the dinitrodiphenyl molecules and are seen end-on in fig. 7. In the other complexes geometrical and symmetry considerations require that the individual molecules should be tilted in varying degrees, but the type of structure still remains essentially the same.

In all these complexes there is no evidence for localized bonding between the units in the crystal structure; there is sufficient space in the unit cell in each case for the molecules to pack without intermolecular approaches closer than those observed in crystals of ordinary aromatic nitro-compounds. This is reflected in the densities of the complexes (table 3), which are all of the same order as those recorded for nitro-compounds such as *p*-dinitrobenzene (1·64), *m*-dinitrobenzene (1·57) and 4:4'-dinitrodiphenyl (1·45).

1. DETAILED ANALYSIS OF THE COMPLEX OF 4:4'-DINITRODIPHENYL WITH 4-HYDROXYDIPHENYL.

The space-group.

The dimensions of the unit cell are $\underline{a} = 20{\cdot}06$ A, $\underline{b} = 9{\cdot}46$ A, $\underline{c} = 11{\cdot}13$ A, $\beta = 99^\circ 39'$, and this cell contains two of the complex groups $(C_6H_5C_6H_4OH)(O_2N\text{-}C_6H_4C_6H_4NO_2)_3$.

Reflections of type hkl occur only with h+k even. The cell, therefore, has the c-face centred. Reflections of type 0k0 occur only with k even, and reflections of type h0l only with h even. The space-group may, therefore, be either C_2, $C_{2/m}$, or C_m. There are only two of the complex groups in the unit cell, and each such group contains only one molecule of hydroxydiphenyl and an odd number of molecules of dinitrodiphenyl. The general position is four-fold in the space-group C_2 and eight-fold in $C_{2/m}$, so that each molecule of hydroxydiphenyl, and at least one molecule of dinitrodiphenyl in each group, must lie in a special position. In the space-group C_2 this special position can only be a two-fold axis. Each of the molecules concerned might have a two-fold axis, but in the case of the polar molecule of hydroxydiphenyl this can only be the long axis of the molecule. The length of this molecule, allowing for the approach of the next molecule along the two-fold axis, can hardly be less than 11·8A; and, since the length of the *b* axis of the cell, parallel to which the two-fold axes of the spcae-group C_2 lie, is only 9·46 Å, this would appear to exclude the possibility of this space-group. In the space-group $C_{2/m}$, since the general position is eight-fold, the odd molecules in the complex group must lie both on a two-fold axis and a mirror plane. In the case of the hydroxydiphenyl molecule this is impossible; for its only possible two-fold axis lies in its only possible mirror planes of symmetry, while in the space-group the two-fold axes are perpendicular to the mirror planes. The space-group must therefore be C_m (C_s^3).

Packing considerations lead, as will be shown in the next section, to the conclusion that the hydroxydiphenyl molecule has itself to lie completely in a mirror plane; and, as there appears so far to be no case in which a benzene ring has been definitely shown to lie in a mirror plane, it was decided to test the crystal for pyro-electricity. The method used was substantially the same as that described by Orelkin and Lonsdale (2), except that instead of an electroscope an electrometer valve, the circuit for which is described in Appendix 2, was used. The sensitivity of the apparatus was tested using rochelle salt and *m*-dinitrobenzene, which are known to be polar, and, on introduction of the liquid air, the galvanometer spot was thrown off the scale in each case, Using rock-salt as a control, maximum deflections of about ½ cm. were observed.

When a crystal of the complex of dinitrodiphenyl with hydroxydiphenyl was gripped across the *b* axis maximum deflections of the order of 1 cm. were observed on introduction of the liquid air in repeated experiments. This small deflection, when the difficulty of holding the crystal in exactly the right direction is taken into account, may be taken as showing an absence of polarity in the *b* direction, which is consistent with the existence of a mirror plane perpendicular to the *b* axis. When the crystal was gripped across the *c* axis, under similar conditions, deflections of about 10 cms. were observed, whilst across the *a* axis the deflections were about 20 cms. These small, but positive, results indicate that the *a* and *c* directions are polar, and that there is no centre of symmetry; which is consistent with the space-group C_m.

Preliminary estimate of the structure.

In the space-group C_m the general position is fourfold; it is therefore necessary so to arrange the complex groups that each has a mirror plane of symmetry, thus reducing the number of groups in the unit cell to two, and at the same time to pack the molecules into the available space. Each molecule of 4-hydroxydiphenyl and at least one of the molecules of 4:4'dinitrodiphenyl must now lie on a mirror plane in such a way that this plane is also a symmetry plane of the molecule. In the case of the hydroxydiphenyl molecule, the OH group must lie in a mirror plane, but the plane of the benzene rings themselves may be either in the mirror plane or at right angles to it. Three-dimensional cardboard models were made of the two types of component molecule and these were packed into the unit cell with due regard to the symmetry conditions. A coplanar configuration of the benzene rings in diphenyl was assumed for these models and the dimensions were taken from previous work on p-dinitrobenzene (3), 4:4'-dinitrodiphenyl (4) and resorcinol(5). With normal distances of approach between adjacent benzene rings in neighbouring molecules only one arrangement was found to be possible. The hydroxydiphenyl molecules have to lie completely in the mirror planes with their greatest lengths approximately in the direction of the c axis; whilst the dinitrodiphenyl molecules have to lie across the mirror planes, so that the terminal carbon atoms of the benzene rings and the nitrogen atoms are in the mirror planes and the other carbon atoms and the oxygen atoms are reflected across these planes. In order to get the most economical packing, the dinitrodiphenyl molecules must lie with their greatest lengths inclined at about 11° to the a axis, thus interleaving with one another. The type of arrangement arrived at will easily be understood on reference to figs. 5 and 7, and was indeed very close to the final structure. Confirmation of this type of arrangement is given by the refractive indices, and by the diffuse spectra due to thermal vibrations.

The direction of vibration of the light vector for the largest refractive index (γ in fig. 1) is nearly parallel to the planes of all the benzene rings (see fig. 5). The direction of vibration for the intermediate refractive index, β , is parallel to the planes of the benzene rings of the three dinitrodiphenyl molecules but is perpendicular to the planes of the benzene rings of the hydroxydiphenyl molecule; while the direction of vibration for the smallest refractive index, α, is parallel to the planes of the benzene rings of the one hydroxydiphenyl molecule but nearly perpendicular to the planes of the benzene rings of the three dinitrodiphenyl molecules.

Lonsdale (6) has shown that the shape of the diffuse spectra, due to thermal vibrations in the crystal, depends on the type of structure. In Appendix 3 it is described how with a layer-lattice structure the spectra from planes parallel to the layers of atoms are accompanied by large and nearly circular diffuse reflections, while with a chain-like structure the spectra from planes perpendicular to the direction of the chains are accompanied by diffuse streaks. It is possible for a structure containing long flat molecules to produce both types of diffuse spectra, and this is the case for the complex between dinitrodiphenyl and hydroxydiphenyl. The dinitrodiphenyl molecules all lie in planes approximately parallel to one another thus producing a layer-lattice type of structure while they are also sufficiently long to have a chain-like nature.

It is found that the spectra 003, $20\bar{3}$, $11\bar{3}$, and $1\bar{1}\bar{3}$ have very pronounced, and more or less circular, diffuse reflections accompanying them, indicating that the dinitrodiphenyl molecules are not greatly inclined to these planes. It is also found that the spectra $10,0\bar{1}$, 802, $91\bar{1}$ and $9\bar{1}\bar{1}$ have very pronounced diffuse streaks accompanying them, indicating that the lengths of the dinitrodiphenyl molecules are nearly perpendicular to

The complex with hydroxydiphenyl.

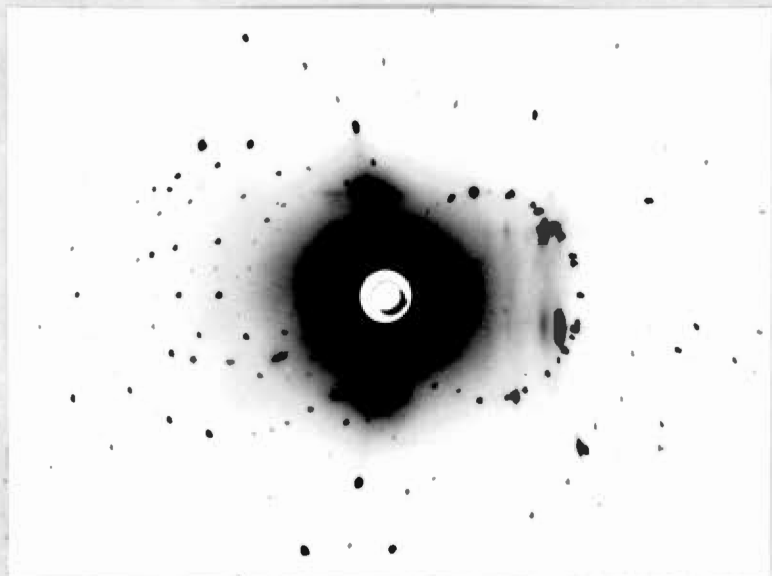


Fig. 2.

Laue photograph taken in a cylindrical camera, with the crystal mounted with the c axis vertical, and using unfiltered copper radiation incident at 65° to a^*.

The two broad diffuse areas accompany the spectra $\bar{1}\bar{1}3$ and $1\bar{1}\bar{3}$. The strongest streaks accompany the spectra 802 and $10,0\bar{1}$. $10,0\bar{1}$ shows streaks due to both the α and β radiation.

The complex with hydroxydiphenyl.

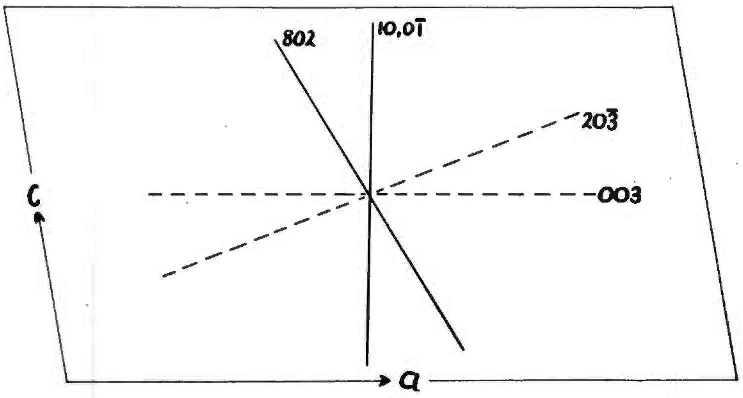


__Fig. 3.__

The broken lines indicate the directions in the unit cell of the planes producing broad diffuse reflections, and are thus approximately parallel to the molecules lying in layers.

The continuous lines indicate the directions in the unit cell of planes producing diffuse streaks, and are thus approximately perpendicular to the chain lengths of the molecules.

these planes. A number of less pronounced ghosts corresponding to similar directions in the unit cell have been observed. The directions in the unit cell of some of the planes giving pronounced diffuse spectra are shown in fig. 3 and may be compared with the actual structure as shown in fig. 5. A photograph showing both types of ghost is reproduced in fig. 2. It is also significant that the spectrum from the planes (020), in which lie all the hydroxydiphenyl molecules (see fig. 7), also has a pronounced diffuse reflection accompanying it, which is not circular but is considerably elongated owing to the influence of the dinitrodiphenyl molecules.

The Fourier synthesis of the structure.

For the accurate determination of the structure the method of double Fourier series first developed by Bragg (7) was used. The preliminary structure promised a reasonable resolution of many of the atoms when projected on the *ac* plane, whilst a projection on the *ab* plane, although offering no actual resolution of the atoms, promised sufficient information to fix the *y* coordinates.

In neither case is there a centre of symmetry, and, putting the summation equations in such a form that only positive values of *h*, *k* and *l* need be considered, we get, for the space-group C_m

$$\rho(xz) = \frac{1}{ac\sin\beta}\Big[F(000) + 2\sum_{0}^{H}\sum_{0}^{L}\Big\{|F(h0l)|\cos\Big[2\pi\Big(\frac{hx}{a}+\frac{lz}{c}\Big) - \delta(h0l)\Big] + |F(\bar{h}0l)|\cos\Big[2\pi\Big(-\frac{hx}{a}+\frac{lz}{c}\Big) - \delta(\bar{h}0l)\Big]\Big\}\Big] \qquad \text{— (1)}$$

where $\rho(xz)$ is the density of the projection parallel to b on the ac plane, and

$$\rho(xy) = \frac{1}{ab}\left[F(000) + 4\sum_{0}^{H}\sum_{0}^{K}\left\{|F(hk0)\cos\left[2\pi\left(\frac{hx}{a}\right) - \delta(hk0)\right]\right\}\cos 2\pi\left(\frac{ky}{b}\right)\right] \quad \text{---}(2)$$

where $\rho(xy)$ is the density of the projection parallel to c on the ab plane. The numerical factor in front of the summation signs must be halved if either h or l are zero in equation (1) and if either h or k are zero in equation (2). $|F(h0l)|$ and $|F(hk0)|$ are observable quantities but the phase differences δ have to be calculated using the positions of the atoms assumed in the preliminary structure.

In the space-group C_m the coordinates of equivalent point positions are

$$\begin{array}{lcl} xyz & : & x+\tfrac{1}{2},\ y+\tfrac{1}{2},\ z \\ x\bar{y}z & : & x+\tfrac{1}{2},\ \bar{y}+\tfrac{1}{2},\ z \end{array}$$

Since there are only two complex groups in the unit cell this means that not all the atoms in a group are symmetrically independent of one another. For the purposes of structure factor calculations, only those atoms in a complex group which are not connected by symmetry relationships need be considered.

The Structure Factors for atoms in general positions are given by

$$F = A + iB$$

where

$$\left.\begin{array}{l} A(h0l) = 4\sum\left\{f\cos 2\pi\left(\frac{hx}{a} + \frac{lz}{c}\right)\right\} \\ B(h0l) = 4\sum\left\{f\sin 2\pi\left(\frac{hx}{a} + \frac{lz}{c}\right)\right\} \end{array}\right\} \quad \text{---}(3)$$

$$\left.\begin{array}{l} A(hk0) = 4\sum\left\{f\cos 2\pi\left(\frac{hx}{a}\right)\cos 2\pi\left(\frac{ky}{b}\right)\right\} \\ B(hk0) = 4\sum\left\{f\sin 2\pi\left(\frac{hx}{a}\right)\cos 2\pi\left(\frac{ky}{b}\right)\right\} \end{array}\right\} \quad \text{---}(4)$$

f is the appropriate atomic scattering factor of the atom whose coordinates are (xyz) and the sum is to be taken over all the independent atoms in the complex group. In the case of atoms lying in the mirror planes the factor of 4 in equations (3) and (4) must be halved in order to avoid counting such atoms twice.

The phase differences are calculated from

$$\delta = \tan^{-1}\frac{B}{A} \quad — \quad (5)$$

<u>Intensity measurements</u>.

In order to evaluate the Fourier series it was necessary to determine the structure factors $|F(h0l)|$ and $|F(hk0)|$ for all spectra of appreciable strength. For this purpose two crystal specimens were cut to approximately cubic dimensions with a side of 0·2 - 0·3 mm., and were set for rotation about the b and c axes, the crystals being completely immersed in the beam of Cu K_α radiation. For such small crystals corrections for absorption may be nearly neglected.

As no ionisation spectrometer was available, the relative intensities of the spectra were measured by means of a microphotometer as described in Appendix 4(a), and an attempt was made to put these relative values on an approximately absolute scale by comparison with a known crystal, p-dinitrobenzene, as described in Appendix 4(b).

There is in this case, however, a more reliable means of standardisation. The y-coordinates of a large number of atoms are fixed from space-group and packing considerations.

Since the hydroxydiphenyl molecules lie in the mirror planes, and the dinitrodiphenyl molecules across the mirror planes, the only atoms whose coordinates are not fixed are the oxygens of the nitro-groups and some of the carbons of the dinitrodiphenyl molecules, which are reflected, however, across the mirror planes. The dimensions of the benzene ring and the nitro-group are known from previous work, and thus the y coordinates of these few atoms can also be fixed without making many assumptions. This means that the structure factors $|F(0k0)|$ can be calculated with considerable accuracy. (A rough temperature correction for the various atomic scattering factors was made as described in Appendix 5 and used in all subsequent structure factor calculations). If the observed values for $|F(0k0)|$ are then adjusted to fit these, a correction factor to reduce all F values to an approximately absolute scale can be obtained.

Agreement between the absolute F values as calculated by both methods was almost exact; this is satisfactory, but the closeness of the agreement must be considered as largely fortuitous. The calculated and adjusted observed values of $|F(0k0)|$ are shown in table 4.

Evaluation of the Fourier series for the projection on the ac plane.

Since the calculation of structure factors according to equations (3) promised to be a very laborious process, for the first approximation the following assumptions were made:

(a) That, if the OH group be left out of account, the structure has a centre of symmetry at the origin. This assumption is consistent with a reasonable packing, and the relatively small polarity observed in the *a* and *c* directions suggests that it may not be far from the truth.

(b) That the dinitrodiphenyl molecules lie parallel to one another and are evenly spaced with a separation of ~~1/3c~~ $c/3$ in the *c* direction. This is borne out by the strength of the 003, $20\bar{3}$ and particularly the $20\bar{6}$ spectra.

(c) That the dinitrodiphenyl molecules are completely planar, although to get the best packing it is necessary to tilt the nitro-groups slightly away from the plane of the benzene rings.

The structure factor calculations were thus considerably simplified, while the agreement between $|F(\text{obs.})|$ and $|F(\text{calc.})|$ was on the whole quite good.

The phase relationships for the various spectra were calculated as follows: since a centre of symmetry had been assumed for the whole structure, excepting the OH group, the value of *B* was given by the position of this group alone. The *magnitude* of *A* was taken from

$$A = \sqrt{F^2_{(\text{obs.})} - B^2}$$

while the *sign* of *A* was taken as being that of its calculated value. The phases were then calculated according to the expression (5).

TABLE 4.

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR THE COMPLEX WITH HYDROXYDIPHENYL.

hkl	$\lvert F(\text{obs.})\rvert$	$\lvert F(\text{calc.})\rvert$
200	60	60
400	113	103
600	97	65
800	54	33
10,00	35	27
12,00	8	7
14,00	27	16
020	300	318
040	35	42
060	80	76
080	149	134
0,10,0	66	56
110	68	55
130	139	112
150	81	51
170	27	26
190	30	4
220	27	12
240	99	85
260	68	55
280	23	4
310	89	52
330	52	41
350	58	55
370	47	38
390	20	5
420	130	120
440	102	74
460	39	12
4,10,0	15	29
510	112	86
530	95	86
550	100	82
590	16	18
620	41	22
640	29	19
710	115	80
730	9	9
750	27	25
820	27	16
840	11	6
910	43	43
930	21	20
950	18	19
990	12	12
10,20	19	18
10,40	10	12
10,60	12	15
11,10	11	13
11,30	12	13
13.10	10	7
13,30	13	7
14,40	33	15
14,60	13	4
15,30	21	15
15,50	17	13
16,20	10	7
16,40	17	13
16,60	10	10
17,10	12	8
19,10	8	12
001	14	25
002	24	28
003	213	181
004	20	10
005	47	29
006	36	60
007	32	14
00,12	24	5
201	42	18
202	63	25
203	22	33
204	17	17
205	39	18
206	18	15
208	19	7
209	37	54
20,10	19	4
$20\bar{1}$	35	13
$20\bar{2}$	41	26
$20\bar{3}$	180	151
$20\bar{4}$	37	59
$20\bar{5}$	53	64
$20\bar{6}$	107	241
$20\bar{7}$	14	47
401	26	14
402	22	28
403	90	126
404	28	28
405	34	59
406	14	28
408	13	14
$40\bar{1}$	91	79
$40\bar{2}$	42	33
$40\bar{3}$	24	24
$40\bar{4}$	52	33
$40\bar{5}$	29	30
$40\bar{6}$	25	104
$40\bar{8}$	12	12
$40\bar{9}$	17	23
$40,\overline{12}$	—	55

TABLE 4. (continued).

hkl	|*F*(obs.)|	|*F*(calc.)|	*hkl*	|*F*(obs.)|	|*F*(calc.)|
601	12	11	10,0$\bar{1}$	190	123
602	114	91	10,0$\bar{4}$	85	106
603	56	73	10,0$\bar{8}$	15	13
604	18	32	10,0$\bar{9}$	26	14
607	21	11	12,01	19	15
60$\bar{1}$	113	97	12,05	16	42
60$\bar{2}$	59	44	12,07	26	12
60$\bar{3}$	14	43	12,08	28	29
60$\bar{6}$	28	46	12,0$\bar{1}$	59	21
60$\bar{7}$	14	30	12,0$\bar{2}$	19	7
60$\bar{8}$	28	30	12,0$\bar{4}$	15	44
801	74	58	12,0$\bar{7}$	42	67
802	148	105	14,01	40	14
803	60	79	14,02	39	52
804	27	42	14,0$\bar{1}$	81	68
805	75	58	14,0$\bar{2}$	37	26
806	21	27	16,01	28	11
807	30	28	16,02	17	7
808	17	2	16,04	19	10
80$\bar{1}$	50	35	16,0$\bar{1}$	15	3
80$\bar{2}$	52	48	16,0$\bar{2}$	47	33
80$\bar{3}$	90	83	16,0$\bar{7}$	53	12
80$\bar{4}$	55	65	16,0$\bar{8}$	20	3
80$\bar{7}$	17	52	16,0,$\overline{10}$	17	2
80$\bar{8}$	32	4	18,01	23	17
80,$\overline{10}$	37	4	18,02	18	26
10,01	42	26	18,04	26	28
10,02	47	36	18,0$\bar{2}$	34	20
10,05	20	4	18,0,$\overline{10}$	20	16
10,06	21	20	20,0$\bar{2}$	18	19
10,07	16	18	20,0$\bar{5}$	23	13

The series (1) was now evaluated using the method of Lipson and Beevers (8) and taking the precaution mentioned in Appendix 6. The projection so obtained was fairly clean with little false detail, except around the position of the hydroxydiphenyl molecule. From this projection, improved values of the x and z coordinates were estimated. For most atoms there was little change, but a tilt of the nitro-groups away from the plane of their benzene rings had appeared. Except for the OH group, there was no departure from a centre of symmetry at the origin for the structure.

The structure factors were recalculated, still assuming this approximation to a centre of symmetry, but without other simplification. The values of A and B used in determining the phase relationships for the summation were obtained in the same way as before, and the series was again evaluated. The projection so obtained was much cleaner, and showed better resolution than the first, but there was little appreciable change in the positions of the peaks, even those of the nitro-groups.

The observed and calculated structure factors are shown in table 4. The agreement on the whole is excellent and generally it is only for spectra with sin θ greater than 0·5 that any serious discrepancies are found. As no <u>differential</u> corrections for the temperature motion were made for the different spectra, one would expect the observed values for those spectra, particularly the higher orders, which are most affected by thermal vibration, to be somewhat lower than the calculated values. Such spectra will be produced by those planes which most nearly contain the dinitrodiphenyl molecules and so have the largest vibrations approximately perpendicular to them. These spectra are mainly 003, 006, $20\bar{3}$, $40\bar{6}$, $20\bar{6}$ and $40,\overline{12}$, and it is found that the calculated values for 006, $40\bar{6}$ and $40,\overline{12}$ are far too high.

The contour diagram drawn from the final values of $\rho(xz)$ for the projection on the *ac* face viewed parallel to *b* is shown in fig. 4. This contour diagram may be interpreted with the aid of the key diagram shown in fig. 5.

In all projections where there is no centre of symmetry the observed coefficients $|F|$ must be combined with phase differences δ that have to be calculated, according to equation (5), from assumed data. In the present instance the assumptions made have led to no inconsistencies, and there is no reason to believe that they can represent any marked deviation from the truth. Only the position of the OH group has been used to determine *B*, since a centre of symmetry was assumed for the rest of the structure. B^2 is generally very small compared with F^2(obs.), the *magnitude* of *A* thus depends mainly on observation, the *sign* only being determined from the assumed positions of the atoms. It is significant that the benzene rings of the hydroxydiphenyl molecule appear in the projection as clearly as can be expected, although their position rarely affected the sign of *A* which was determined almost

[page 31

The complex with hydroxydiphenyl.

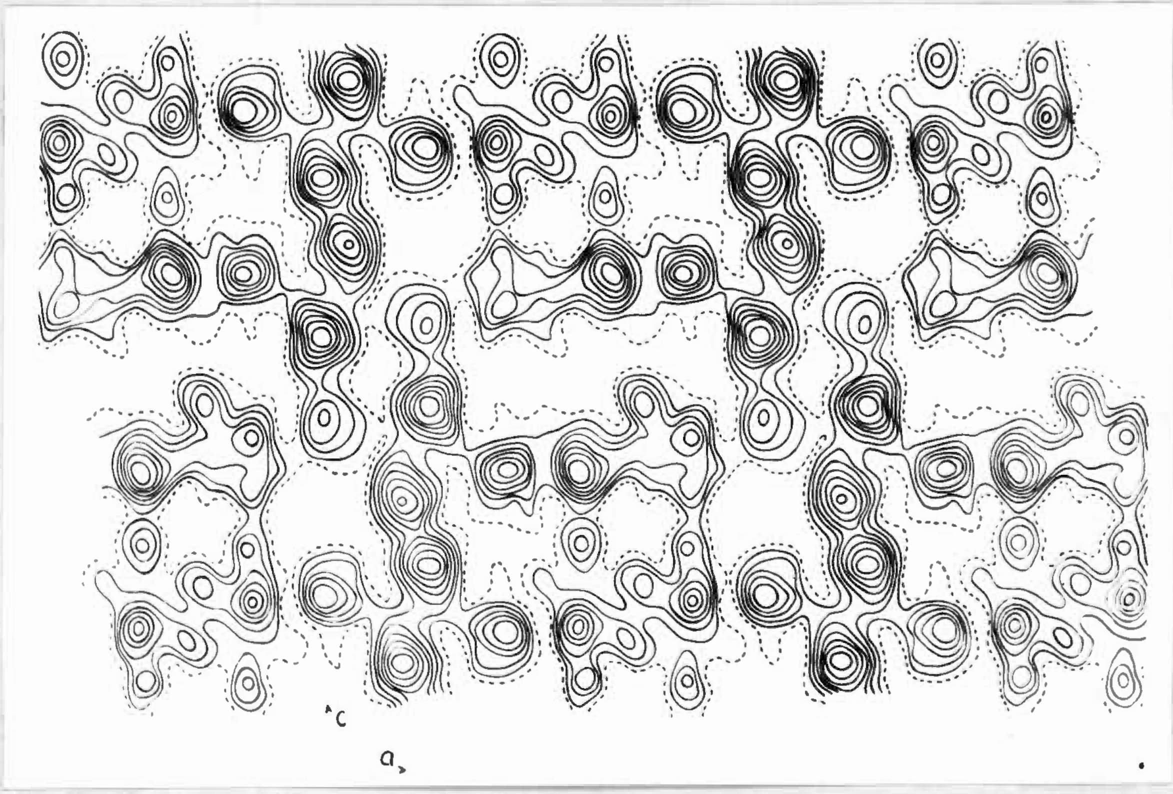


__Fig. 4.__

Fourier projection of the structure in the direction of the __b__ axis on to the __ac__ plane. Contours at intervals of approximately 2 electrons per A^2. The dotted line is the 2 electron contour.

The complex with hydroxydiphenyl.

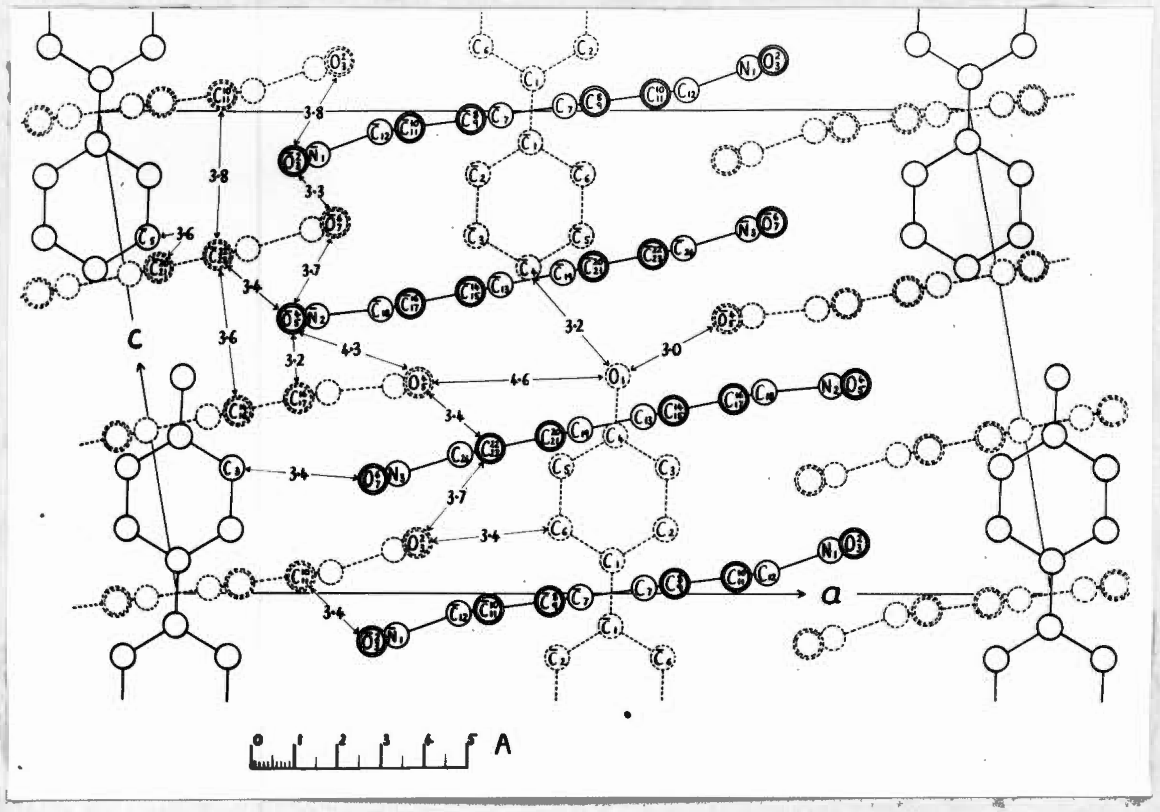


Fig. 5.

Projection of the structure in the direction of the b axis on to the ac plane. The molecules denoted by broken lines lie b/2 above or below those denoted by unbroken lines. Double circles indicate two atoms superimposed upon one another by reflection across the mirror planes.

entirely by the dinitrodiphenyl molecules. It is also satisfactory that the tilt of the nitro-groups to the plane of the molecules has emerged in the course of the summations and was not assumed initially. Probably the most convincing confirmation of the proposed structure, however, is the excellent agreement between $|F(\text{obs.})|$ and $|F(\text{calc.})|$.

Evaluation of the Fourier series for the projection on the *ab* plane.

From the previous projection the *x* coordinates of the atoms can be estimated while, as has already been shown, the *y* coordinates can be fixed from the preliminary structure with some accuracy.

The structure factors F(*hk*0) were calculated according to the expression (4) assuming as before a centre of symmetry for the structure, with the exception of the OH group. The values of $|F(\text{obs.})|$ and $|F(\text{calc.})|$ are included in Table ~~X~~4. The agreement is excellent. The phase relationships were calculated in the same way as for the *ac* projection; thus the value of *B* was given by the OH group alone, and the sign of *A* was taken as being that of its calculated value while its magnitude was calculated from

$$|A| = \sqrt{F^2_{(obs.)} - B^2}$$

The series (2) was then evaluated using, as before, the method of Lipson and Beevers. The contour diagram and key diagram corresponding to values of $\rho(xy)$ are given in figs. 6 and 7.

The complex with hydroxydiphenyl.

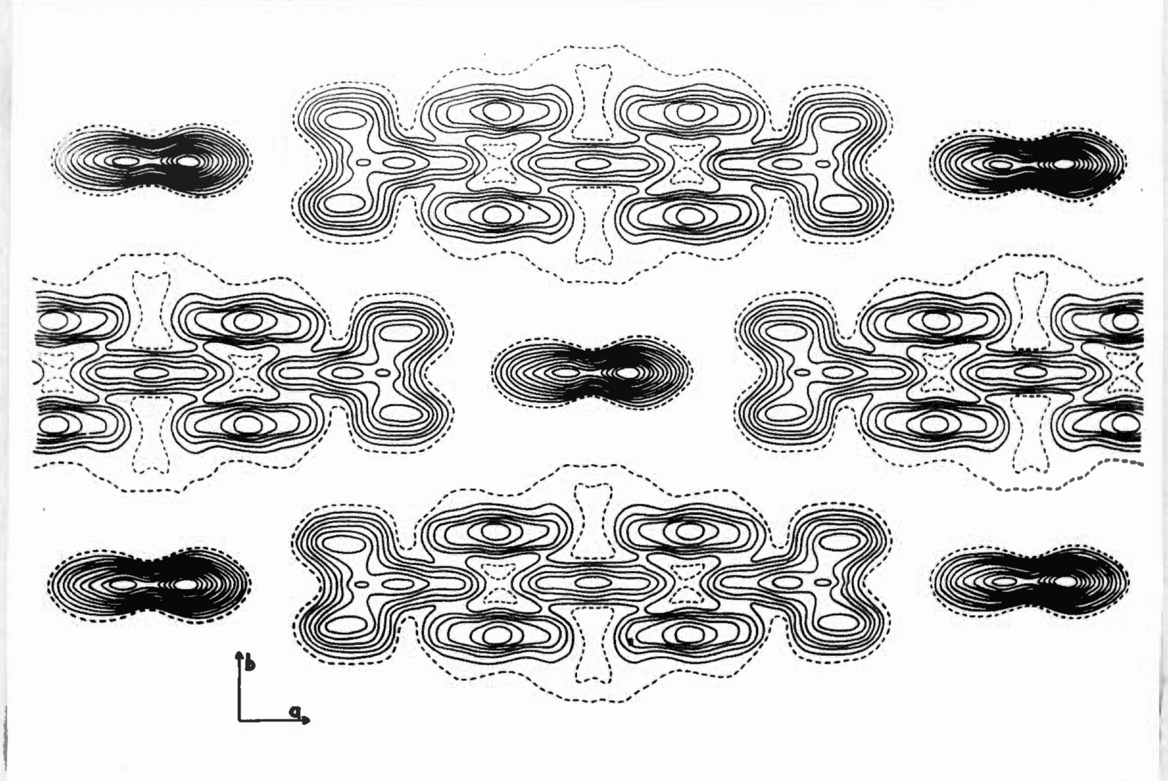


Fig. 6.

Fourier projection of the structure in the direction of the c axis on to the ab plane. Contours at intervals of approximately 2 electrons per A^2. The dotted line is the 2 electron contour.

The complex with hydroxydiphenyl.

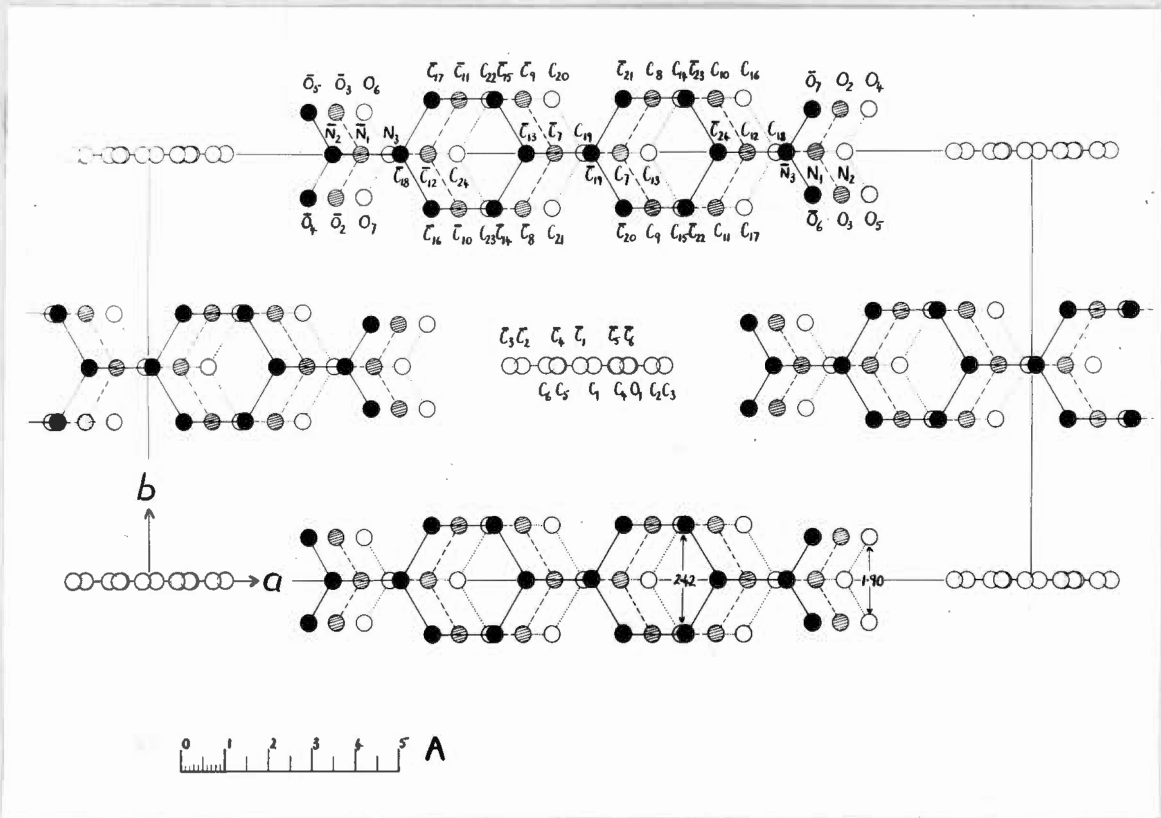


Fig. 7.

Projection of the structure in the direction of the c axis on to the ab plane. The dinitrodiphenyl molecules denoted by black circles are at height 2c/3, those denoted by plain circles are at height c/3, and those denoted by shaded circles at height 0c.

Estimation of parameters.

From the ac projection the x and z parameters were estimated as follows:

(a) The dinitrodiphenyl molecules. The displacement of the position of $C_{8,9}$ from the centre of the peak in which they are unresolved from C_7 was assumed to be the same as the displacement of $C_{10,11}$ from the centre of the peak in which they are unresolved from C_{12}. If the side of the benzene ring is 1·40A this displacement is approximately 0·13A, and assuming the benzene ring to be a regular hexagon, the positions of all the carbon atoms in this ring can be fixed. An estimate was made of the sort of displacement to be expected, taking into account the height of the peaks produced by the separate atoms, 0.7A apart, and the approximate resolving power shown in the projection, and agreement was good. A similar displacement was calculated for the unresolved $O_{2,3}$ - N_1 peak and the position of the two oxygen atoms fixed at about 0.20A from the centre of the peak, and directly away from C_{12}. The position of the nitrogen atom was then fixed by assuming a C - N distance of 1.53A, as found by James et.al. (3), and placing the nitrogen along the line joining C_{12} to $O_{2,3}$. This procedure was repeated for the other benzene rings and nitro-groups. The benzene rings in each dinitrodiphenyl molecule were assumed to be coplanar and the slight deviations from this shown by the projection were neglected.

(b) The hydroxydiphenyl molecule. Here two benzene rings, regular hexagons of side 1.40A, were adjusted so as to

[page 36

TABLE 5.

PARAMETERS OF THE ATOMS IN THE COMPLEX WITH HYDROXY-DIPHENYL EXPRESSED AS FRACTIONS OF THE CORRESPONDING LATTICE TRANSLATIONS.

The atoms denoted by bars in the figures 5 and 7 are to be taken as derived from their corresponding atoms listed below by the operation of a centre of symmetry at the origin. The actual deviation from this was very small and has been neglected.

Atom.	x/a.	y/b.	z/c.
C_1	.007	0	.068
C_2	.073	0	.131
C_3	.088	0	.258
C_4	.034	0	.323
C_5	-.032	0	.260
C_6	-.047	0	.132
C_7	.038	.500	.010
C_8	.073	.628	.018
C_9	.073	.372	.018
C_{10}	.144	.628	.036
C_{11}	.144	.372	.036
C_{12}	.179	.500	.045
C_{13}	.069	.500	.363
C_{14}	.105	.628	.376
C_{15}	.105	.372	.376
C_{16}	.176	.628	.402
C_{17}	.176	.372	.402
C_{18}	.211	.500	.414
C_{19}	-.006	.500	.337
C_{20}	-.041	.628	.324
C_{21}	-.041	.372	.324
C_{22}	-.112	.628	.298
C_{23}	-.112	.372	.298
C_{24}	-.147	.500	.286
O_1	.048	0	.445
O_2	.285	.600	.103
O_3	.285	.400	.103
O_4	.317	.600	.430
O_5	.317	.400	.430
O_6	-.253	.600	.235
O_7	-.253	.400	.235
N_1	.256	.500	.088
N_2	.288	.500	.427
N_3	-.224	.500	.247

give the best fit with the resolved peaks C_1, C_2, C_6, and $\overline{C}_1$, $\overline{C}_2$, $\overline{C}_6$, while having a linear arrangement of the atoms C_4, C_1, $\overline{C}_1$, $\overline{C}_4$. The OH peak is resolved.

The estimation of the <u>y</u> parameters from the <u>ab</u> projection presented no difficulties.

A list of parameters is given in table 5.

<u>Description of the Structure</u>.

The packing of the molecules in this structure is best illustrated by fig. 7. It may be described as a face centred arrangement of dinitrodiphenyl molecules all lying across the mirror planes (020) and nearly in the planes (20$\bar{6}$), thus interleaving with one another (as shown in fig. 5); the long holes thus left in the structure are filled by the hydroxydiphenyl molecules lying nearly end to end in the mirror planes with their lengths nearly normal to the planes containing the dinitrodiphenyl molecules. Each hydroxydiphenyl molecule is thus surrounded by twelve dinitrodiphenyl molecules all approximately equally spaced from it. In these circumstances it is impossible to choose any particular group of individual molecules as representing the 'complex molecule', the discrete existence of which must be doubted. With a view to illustrating the molecular dimensions of the individual components in the structure, however, a group of three dinitrodiphenyl molecules and one hydroxydiphenyl molecule, which may be taken as representing the repeating unit of structure, is shown in fig. 8.

[page 38

The complex with hydroxydiphenyl.

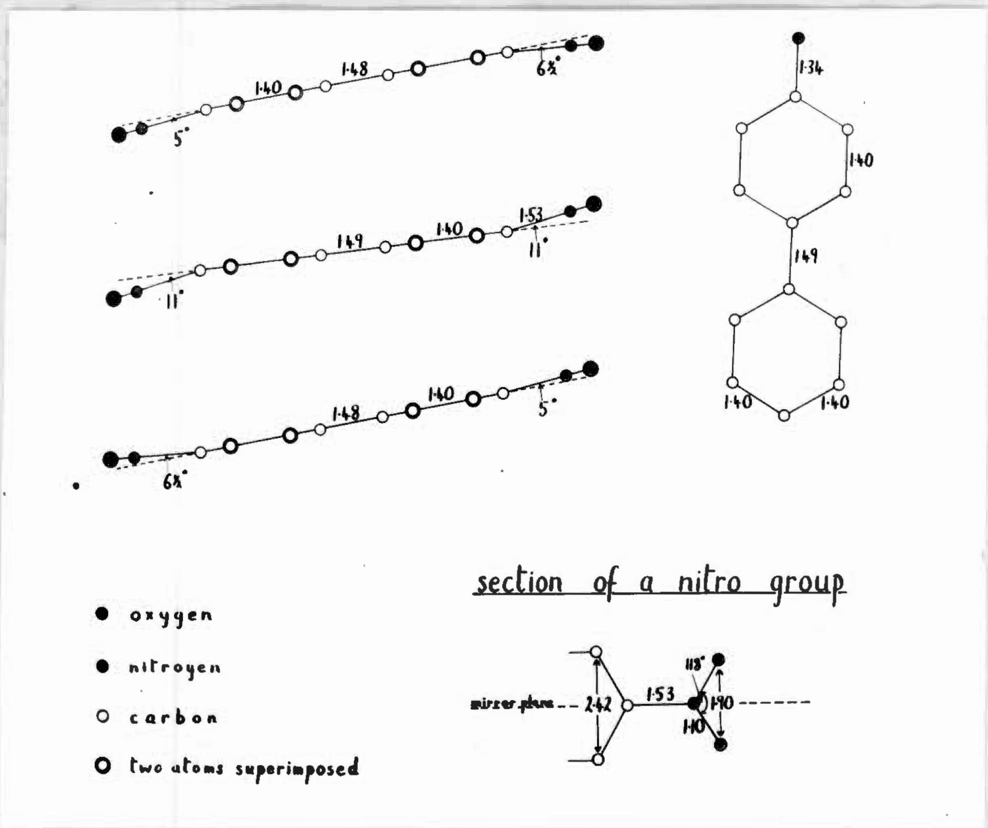


Fig. 8.

The repeating unit of structure projected on to one of the mirror planes.

An unusual and striking feature of this structure is that certain groupings must be perfectly symmetrical. Thus the benzene rings of the hydroxydiphenyl molecules have a plane of symmetry in the plane of the rings and the benzene rings of the dinitrodiphenyl molecules have a mirror plane passing through the terminal carbon atoms and perpendicular to the plane of the rings. It, therefore, seems reasonable to infer that each benzene ring possesses both types of mirror plane. The nitro-groups must also possess a plane of symmetry, passing through the nitrogen atom, and across which the two oxygen atoms are reflected; this suggests that the unequal N - O distances observed by James et al. (3) and by van Niekerk (4) in p-dinitrobenzene and 4:4'-dinitrodiphenyl respectively, may not have been a real effect.

The molecular dimensions of greatest interest are those of the nitro-group. A distance of 1.90A is found between the two oxygen atoms which are reflected across the mirror plane; and, since the distance between the carbon atoms of the benzene ring, similarly reflected across the mirror plane, is 2.42A (which agrees well with the corresponding dimension, 2.425A, for a regular hexagon of side 1.40A), this is probably a fairly accurate determination. This distance of 1.90A is somewhat less than the O - O distance in the nitro-group found by other workers, namely 2.14A in p-dinitro benzene (3), 2.00A in 4:4'-dinitrodiphenyl (4), and 2.17A in m-dinitro benzene (9). Unfortunately the positions of the nitrogen atoms cannot be fixed with accuracy, but by assuming a C - N distance of 1.53A a value of 1.10A is obtained for the N - O distance in the nitro-groups.

This may be compared with the values 1.25 and 1.10 A for p-dinitrobenzene (3), 1.21 and 1.14 A for 4:4'-dinitrodiphenyl (4) and 1.20A for m-dinitrobenzene (9). The tilt of the nitro-groups away from the plane of the benzene rings, varying from 5° to 11°, seems to be due to packing considerations, and is such as to give a reasonable balance between the O to O and O to CH distances between interleaving molecules, without making any of these distances abnormally short.

Also of interest are the C - C distances, between the benzene rings in the diphenyl part of the molecules, of 1.48 - 1.49 A; these may be compared with the values of 1.48A obtained by Dhar (10), and 1.42A by van Niekerk (4). The present values are not very accurate but suggest that the diphenyl link is nearer 1.5 than 1.4 A.

None of the intermolecular distances, the most important of which are shown in fig. 5, are abnormally short. The distances between oxygens in neighbouring nitro-groups are 3.8, 3.3, 3.7, 4.3 A between O_3 and $\bar{O}_3$ $\bar{O}_3$ and $\bar{O}_6$, $\bar{O}_6$ and $\bar{O}_5$, $\bar{O}_5$ and O_5, respectively. Some of the O to CH links between neighbouring dinitrodiphenyl molecules are 3.2, 3.4, 3.4, 3.6, 3.7, 3.8 A between $\bar{O}_5$ and C_{17}, O_5 and C_{22}, $\bar{O}_3$ and C_{11}, O_6 and C_{17}, O_3 and C_{22}, O_6 and C_{11}, respectively; while some similar links between nitro-groups and hydroxydiphenyl molecules are 3.4, 3.4, 3.8, 3.6, 3.7, 3.8 A between O_6 and C_3, O_2 and C_6, O_3 and C_5, O_6 and C_2, O_4 and C_5, O_4 and $\bar{C}_4$, respectively. The closest C to C distances are quite normal, namely 3.6, 3.6, 3.8 A between

$\bar{C}_5$ and $\bar{C}_{20}$, C_{15} and $\bar{C}_{22}$, C_{11} and $\bar{C}_{22}$, respectively. The closest intermolecular approach of all is that between the OH group and one of the nitro-groups, i.e. 3.0A between O_1 and $\bar{O}_5^4$.

The short intermolecular distances are thus those between oxygen atoms of nitro-groups and carbon atoms of benzene rings, but it is unlikely that these would provide a mechanism for the formation of the complex, since the approach of the nitro-groups to the benzene rings of the hydroxydiphenyl molecule is no closer than their approach to the benzene rings of the dinitrodiphenyl molecules; in fact the latter values are, on the whole, smaller. Moreover, as shown in table 8, these distances are of the same order as those observed in crystals of ordinary aromatic nitro compounds such as *p*-dinitrobenzene (3), *m*-dinitrobenzene (9), 4:4'-dinitrodiphenyl (4) and picryliodide (11), and are all, therefore, compatible with ordinary van der Waal's forces. These results are thus in agreement with those obtained by Powell and Huse (12a) for the complex between *s*-trinitrobenzene and *p*-iodoaniline.

There is a possibility of weak hydrogen bonding between the OH group and the oxygen atoms of one of the nitro-groups. The OH to O distance is 3.0A, and corresponding NH to O distances in urea have been attributed to hydrogen bonding. This, however, cannot provide a bonding mechanism in this complex where the ratio of dinitrodiphenyl to hydroxydiphenyl is 3:1.

2. THE COMPLEX OF 4:4'-DINITRODIPHENYL WITH DIPHENYL.

As shown in table 3 the unit cell dimensions for this complex are almost identical with those for the similar complex with 4-hydroxydiphenyl just described; and this unit cell also contains two of the complex groups $(C_6H_5C_6H_5)(O_2NC_6H_4C_6H_4NO_2)_3$. Since comparative photographs for these two complexes are very nearly identical and the thermal vibrations in each produce diffuse reflections accompanying corresponding spectra it seems probable that they both have very closely similar structures. This is confirmed by the very close agreement shown in table 6 between the observed values of F(*h*0*l*) after allowance has been made for the extra OH group.

The *h*0*l* spectra for the diphenyl complex were recorded by Dr. J.M. van Niekerk of the University Physics Department on a Weissenberg photograph taken with a crystal mounted about the *b* axis, and the intensities of these spectra were measured by him on the microphotometer. The values of F(*h*0*l*) thus obtained are compared in table 6 with the corresponding values of F(*h*0*l*) observed for the complex with hydroxydiphenyl, from which the calculated contribution of the OH group has been subtracted.

In this diphenyl complex reflections of type *hkl* occur only with *h* + *k* even, *h*00 only with *h* even and 0*k*0 only with *k* even. The space-group may therefore be $C2$, Cm or $C2/m$, and all these space-groups are spatially possible. It should be possible to distinguish between the space-group possibilities from observation

[page 43

TABLE 6.

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR THE COMPLEX WITH DIPHENYL.

h0l	$\lvert F(\text{obs.})\rvert$ (observed for the complex with diphenyl)	$\lvert F(\text{calc.})\rvert$ (observed for the complex with hydroxy-diphenyl but with the calculated contribution of the OH group subtracted).
200	80	72
400	120	109
600	82	93
800	41	46
1000	14	27
1400	17	26
001	25	28
002	27	35
003	270	219
004	20	22
005	29	49
006	23	32
007	20	28
201	60	56
202	74	76
204	23	24
205	21	35
20$\bar{1}$	37	29
20$\bar{2}$	53	40
20$\bar{3}$	240	177
20$\bar{4}$	36	41
20$\bar{5}$	71	59
20$\bar{6}$	155	114
402	43	32
403	70	80
404	20	19
405	20	28
40$\bar{1}$	110	88
40$\bar{2}$	36	35
40$\bar{3}$	14	14
40$\bar{4}$	44	42
40$\bar{5}$	16	21
602	120	110
603	56	62
604	22	25
605	15	-
606	17	-
60$\bar{1}$	176	120
60$\bar{2}$	80	68
60$\bar{3}$	23	24
60$\bar{6}$	21	32
60$\bar{8}$	25	28
801	60	69
802	160	146
803	31	59
804	15	24
805	47	71
806	21	25
807	23	26
80$\bar{1}$	27	41
80$\bar{2}$	26	43
80$\bar{3}$	79	81
80$\bar{4}$	58	59
80$\bar{5}$	14	-
80$\bar{8}$	22	31
80,$\overline{10}$	24	34
1001	22	35
1002	44	52
1005	22	21
1006	23	23
100$\bar{1}$	220	197
100$\bar{3}$	19	-
100$\bar{4}$	106	84
120$\bar{1}$	39	55
120$\bar{2}$	19	20
120$\bar{7}$	33	38
1401	37	37
1402	36	42
140$\bar{1}$	82	81
140$\bar{2}$	27	35
1601	33	27
160$\bar{1}$	13	16
160$\bar{2}$	27	44
160$\bar{7}$	37	54

of the pyro-electric effect but single crystals large enough to make satisfactory measurements have not been obtained. However, whichever space-group is correct, only the finer details of structure can be affected.

If the space-group is either Cm or $C2/m$ it should be noted that, since there are only two complex groups in the unit cell, it is then necessary for the diphenyl molecules to lie completely in the mirror planes and for the dinitrodiphenyl molecules to lie across the mirror planes, as was found to be the case for the hydroxydiphenyl complex.

Assuming the space-group $C2/m$ a Fourier projection of the unit cell along *b* onto the *ac* plane was made by Dr. van Niekerk, and the contour diagram thus obtained was found to be closely similar to the corresponding contour diagram for the complex with hydroxydiphenyl, the only significant difference being that there was no peak corresponding to the position of the OH group.

3. THE COMPLEXES OF 4:4'-DINITRODIPHENYL WITH NN:N'N'-TETRAMETHYLBENZIDINE, BENZIDINE, 4:4'-DIHYDROXYDIPHENYL, AND WITH 4-IODO-, 4-BROMO- AND 4-CHLORODIPHENYL.

A comparison of the unit cell dimensions (table 3) for all these complexes suggested that the structures might be similar to that of the complex with 4-hydroxydiphenyl. Assuming this similarity, and taking into account the symmetry elements of the possible space-groups, it was found that the molecules could be packed into the unit cells so as to give reasonable structures. These approximate structures were then tested by observation of the strength of the more important spectra and by observation of the diffuse reflections due to thermal vibrations. Further confirmation was then obtained by taking photographs for the various complexes about <u>structurally</u> equivalent directions; these photographs show very striking similarity.

In this section the approximate structures will first be described and then compared with that of the complex with hydroxydiphenyl.

The complex with tetramethylbenzidine.

Spectra of all types occur and the space-group may be either $P1$ or $P\bar{1}$. The unit cell contains two of the complex groups $[O_2NC_6H_4C_6H_4NO_2]_4[(CH_3)_2NC_6H_4C_6H_4N(CH_3)_2]$. The approximate structure described here neither specifically contains nor excludes a centre of symmetry; it need not be materially altered to fit either space-group. Fig 9 shows a projection of the unit cell along *a* onto the *bc* plane. The tetramethylbenzidine molecules, seen end-on, are shown lying along *a* and there are two such molecules, one above the other, in the distance *a*. Since there is no halving of the unit cell there must, however, be some difference in orientation between successive tetramethylbenzidine molecules in the *a* direction. These successive molecules, therefore, are probably inclined differently to the *a* axis; they must, however, still lie very nearly in the (011) plane in order to account for the very great strength of the spectrum 011.

Each dinitrodiphenyl molecule shown on the projection (fig. 9) represents eight molecules lying parallel to one another and separated by 1/8 *a* or 3.78A. Of course, if the tetramethylbenzidine molecules are inclined to the *a* axis, then the eight dinitrodiphenyl molecules will not lie exactly above one another as shown. In order to account for the great strength of the 011 spectrum they must, however, all lie with the long axes of the molecules very nearly in the (011) plane as shown. If the planes of the benzene rings of these molecules are very nearly perpendicular to the (011) plane the dinitrodiphenyl molecules will interleave with one another as shown in fig. 10, which is a projection of the structure along the axis $[01\bar{1}]$ onto the plane $(01\bar{1})$. In this projection the dinitrodiphenyl molecules, lying across the (011) planes, are seen end-on, and the tetramethylbenzidine molecules are seen sideways-on. It will be seen that the dinitrodiphenyl molecules lie in the $(\overline{16},11)$ planes; and,

[page 47

The complex with tetramethylbenzidine. (B).

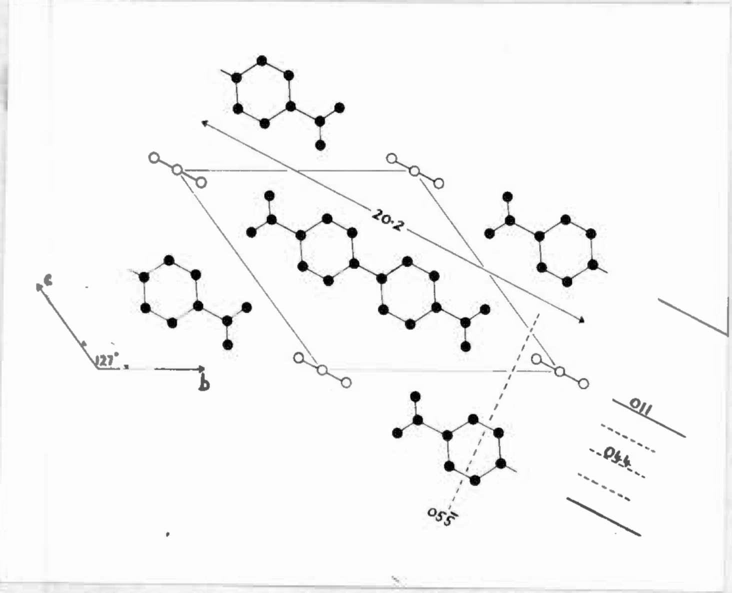


Fig. 9.

Projection of the structure in the direction of the a axis onto the bc plane. There are 2 tetramethylbenzidine molecules, seen end-on, in the distance a. Each dinitrodiphenyl molecule represents 8 such molecules in the distance a.

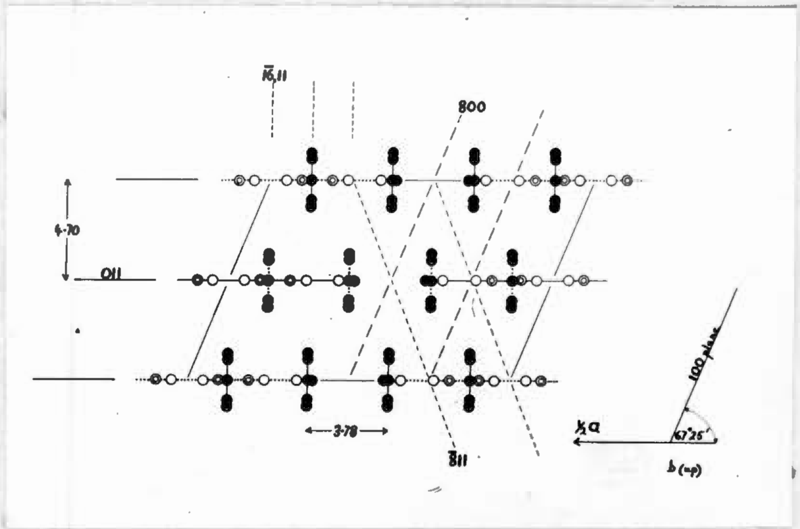


Fig. 10.

Projection of the structure in the direction of the [01$\bar{1}$] axis onto the (01$\bar{1}$) plane. The dinitrodiphenyl molecules are seen end-on and the tetramethylbenzidine molecules sideways-on.

as would be expected from such an arrangement, the spectrum $\overline{16},11$ and the spectra 800 and $\bar{8}11$ are found to be very strong.

The complex with benzidine.

Spectra *hkl* occur only with *h* + *k* even, and *h*0*l* occur only with *h* and *l* even; the space-groups $\underline{C}_c$ and $\underline{C}_{2/c}$ are therefore possible, but it will be shown that $\underline{C}_c$ is the more probable. The unit cell contains four of the complex groups $[O_2NC_6H_4C_6H_4NO_2]_4[H_2NC_6H_4C_6H_4NH_2]$. Fig. 11 shows a projection of the unit cell, which is *c* face-centred, along *b* onto the *ac* plane, which is also a glide plane with translation ½*c*. The benzidine molecules lie along *b* and are thus seen end-on. Each dinitrodiphenyl molecule shown on the projection represents four molecules lying parallel to one another and separated by ¼*b* or 3.71A. These dinitrodiphenyl molecules must all lie with their long axes very nearly in the (40$\bar{2}$) planes, while the benzidine molecules must lie almost wholly in these planes; this is necessary in order to account for the very great strength of the 40$\bar{2}$ spectrum.

It will be seen from fig. 12, which is a projection of the structure along the axis [102] onto the *ab* plane, that the dinitrodiphenyl molecules lie parallel to the *ac* plane and are contained by the planes midway between the planes (080); this is necessary in order to account for the great strength observed for the spectrum 080, as well as for the spectra 24$\bar{1}$ and 2$\bar{4}\bar{1}$. With this arrangement, which is consistent with the space-group $\underline{C}_c$, it will be observed (fig.12) that the dinitrodiphenyl

The complex with benzidine (C).

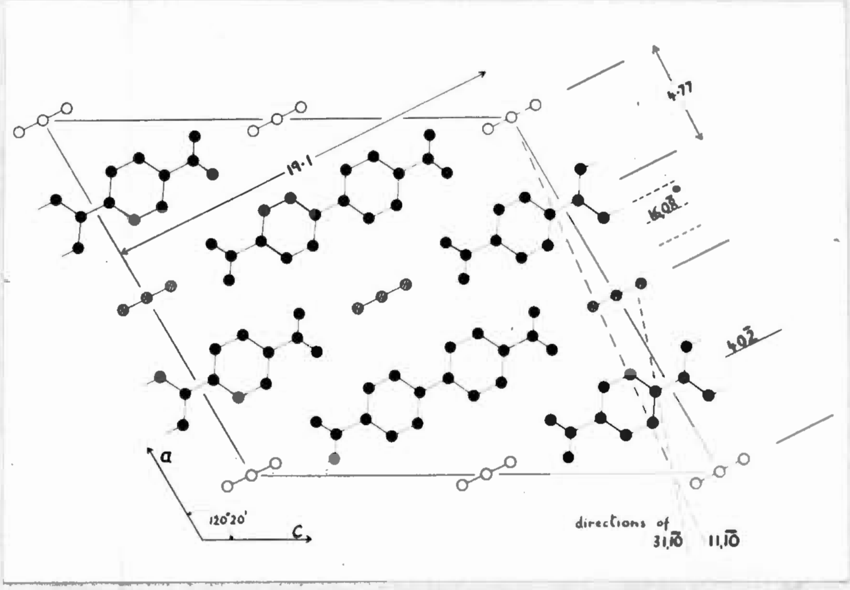


Fig. 11.

Projection of the structure in the direction of the b axis onto the ac plane. The benzidine molecules are seen end-on. Each dinitrodiphenyl molecule represents 4 such molecules in the distance b.

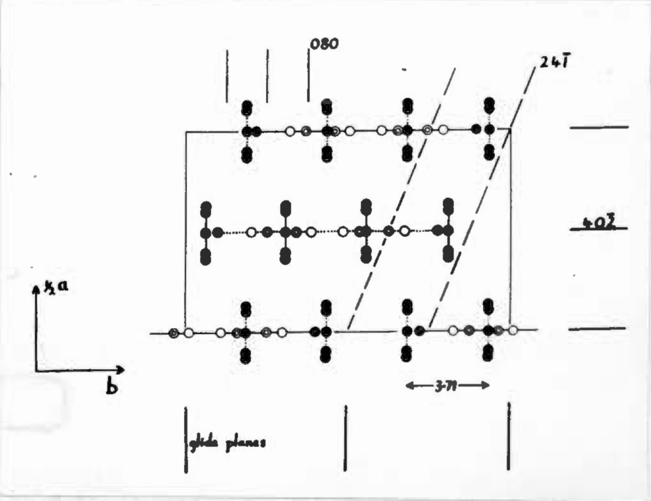


Fig. 12.

Projection of the structure in the direction of the [102] axis onto the ab plane. The dinitrodiphenyl molecules are seen end-on and the benzidine molecules sideways-on.

molecules in adjacent $(40\bar{2})$ planes interleave with one another. If the space-group were $C2/c$ the two-fold axis parallel to b would make it necessary for adjacent dinitrodiphenyl molecules in adjacent $(40\bar{2})$ planes to have the same b coordinates, and no interleaving of the molecules is then possible. This would mean a closer than normal approach of the molecules to one another, and the spectrum 040 should then be strong, whereas it is actually very weak indeed as would be expected from the arrangement shown in fig. 12.

The complex with dihydroxydiphenyl.

Spectra hkl of all types occur, while h0l occur only with h even and 0k0 with k even; the space-group is therefore fixed uniquely as $P2_1/a$. The unit cell contains four of the complex groups $[O_2NC_6H_4C_6H_4NO_2]_3\,[OHC_6H_4C_6H_4OH]$. Fig. 13 shows a projection of the unit cell along c onto the ab plane; the symmetry elements are included in the diagram. The special positions given to the molecules are the only ones which satisfy the symmetry conditions and at the same time give a structure closely similar to that of the complex with hydroxydiphenyl shown in fig. 7. The dihydroxydiphenyl molecules seen end-on are shown lying directly along c, but the length of this axis (11.3A) is not sufficient for this, since the length of a dihydroxydiphenyl molecule, allowing for the approach of the next molecule and even assuming hydrogen bonding between adjacent OH groups, is approximately 12.8A. These molecules must, therefore, be inclined to c, but, in order to account for the very great strength of the 040 spectrum, they must lie almost wholly in the planes midway between the (040) planes, as shown.

Each dinitrodiphenyl molecule shown in fig. 13 represents three molecules lying parallel to one another and separated by 1/3 *c* or 3.76A. Since the dihydroxydiphenyl molecules are inclined to *c*, the dinitrodiphenyl molecules cannot lie, as shown, directly one above the other; in order to account for the great strength of the spectrum 040, however, they must lie with their long axes very nearly midway between the (040) planes. These molecules do not lie parallel to the *ab* plane, but, as for the complex with hydroxydiphenyl, are probably inclined to it so that their lengths lie in the $(20\bar{6})$ planes. This is shown in fig. 14, which is a projection of the structure along the axis [301] onto the *bc* plane; the dinitrodiphenyl molecules are then seen end-on and the dihydroxydiphenyl molecules sideways-on. The *c* coordinates of the dinitrodiphenyl molecules were chosen in the only possible way to account for the great strength of the spectra $11\bar{3}$ and $\bar{1}\bar{1}\bar{3}$; it was then found that in order to get interleaving of the molecules, and consequently better packing, it was necessary that they should be inclined to the $(20\bar{6})$ planes as shown in fig.14. The spectrum $20\bar{6}$ should then be very much weaker for this complex than it was for the complex with hydroxydiphenyl where the dinitrodiphenyl molecules are practically contained by the $(20\bar{6})$ planes, and this was found to be the case. This arrangement is not very satisfactory but, in spite of many trials, it is the only one which could be found to fit the observed data.

The complex with dihydroxydiphenyl (D).

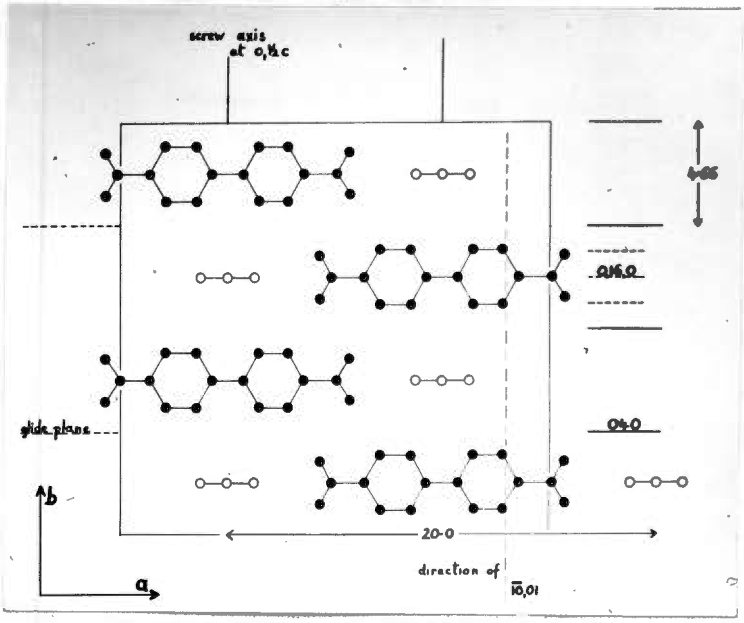


Fig. 13.

Projection of the structure in the direction of the c axis onto the ab plane. The dihydroxydiphenyl molecules are seen end-on. Each dinitrodiphenyl molecule represents 3 such molecules in the distance c.

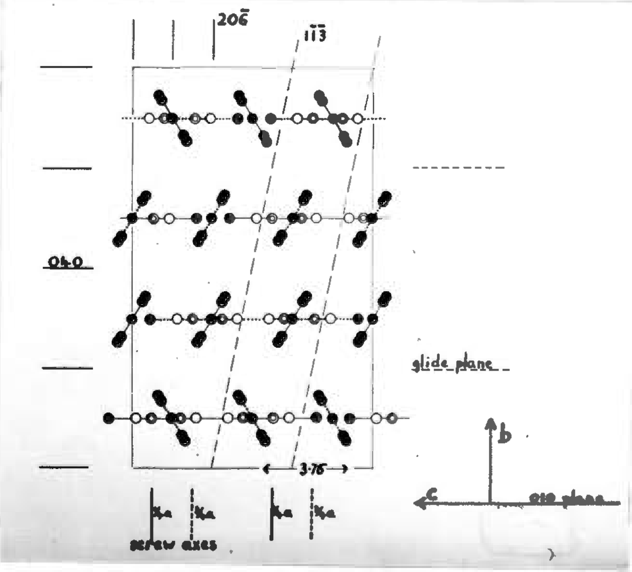


Fig. 14.

Projection of the structure in the direction of the [301] axis onto the bc plane. The dinitrodiphenyl molecules are seen end-on and the dihydroxydiphenyl molecules sideways-on.

The complexes with iodo-, bromo- and chlorodiphenyl.

The oscillation photographs for these complexes are abnormal and a large number of spots on these photographs are diffuse and elongated in the *b* direction instead of being sharply defined. These diffuse spectra are probably the result of periodic errors in the structure, the nature of which will be discussed in the next section. In oscillation photographs about the *c* axis for these complexes only the 0th, 7th and 14th layer lines consist of sharply defined spectra; all the other layer lines consist of diffuse spectra. The layer lines are evenly spaced for the iodo complex, but irregularly spaced for the bromo and chloro complexes. Only an approximate value can therefore be assigned to the *c* spacing for the complexes with bromo- and chlorodiphenyl and there is of course no true unit cell for these complexes. In this section, however, these abnormalities have been disregarded and the diffuse spectra have been treated as normal spectra and indexed in the usual manner.

Except for the irregularity in the spacing of the layer-lines about the *c* axis for the bromo- and chloro- complexes, the dimensions of the crystal cells are the same within the errors of measurement. The unit cells contain two of the complex groups $[O_2NC_6H_4C_6H_4NO_2]_7[XC_6H_4C_6H_5]_2$, where X represents the halogen atom. The space-groups may be $C2$, Cm or $C2/m$. The face-centring of the structure already accounts for the presence of two complex groups in the unit cell; if there were to be a two-fold axis as well, the molecules would have to lie in special positions in order to avoid a further doubling. We need consider only the polar halogen molecules. As these molecules lie with their lengths nearly along c and with two molecules in the distance c, they must be so arranged that the one molecule is derived from its neighbour by operation of the two-fold axis, which must be parallel to b. This means that the molecules must lie so that the halogen atoms are alternately adjacent to and opposed to one another; pairs of halogen atoms are then spaced along c at intervals of approximately 25.8A instead of being spaced singly at intervals of 12.3 - 12.9A as they would be if the molecules lay end to end. Now, the arrangement of the layer-lines on rotation photographs for the bromo- and chloro-complexes about the c axis is such as would appear if a set of planes of spacing 3.69A (probably corresponding to the dinitrodiphenyl molecules) had been modified by some periodic distribution (probably corresponding to the halogen molecules) repeating itself in a distance 12.3 - 12.7A in the direction of the c axis. A similar arrangement involving a modifying distribution with a repeat of 12.9A, will explain corresponding photographs for the iodo complex. This question is further discussed in the next section. It appears likely, therefore, that in all these complexes the halogen molecules lie end to end approximately along c; the possibility of a two-fold axis is then excluded, and the space-groups are probably C_m.

Fig. 15 shows a projection of the structure of these

[page 55

The complex with iododiphenyl (E).

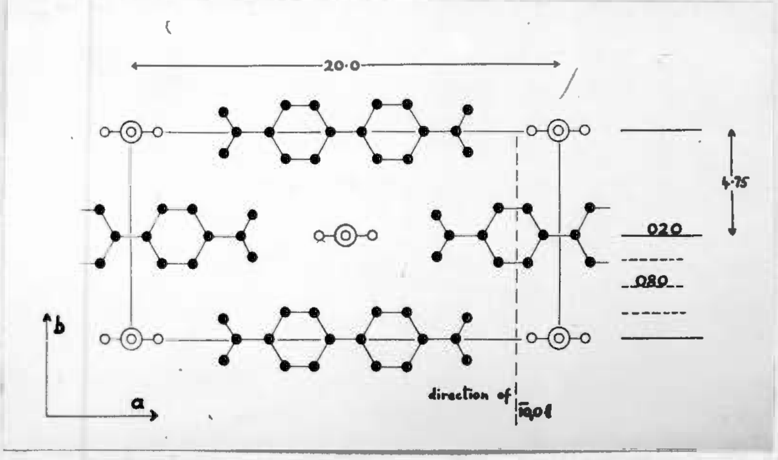


Fig. 15.

Projection of the structure in the direction of the c axis onto the ab plane. There are 2 iododiphenyl molecules seen end-on, in the distance c. Each dinitrodiphenyl molecule represents 7 such molecules in the distance c.

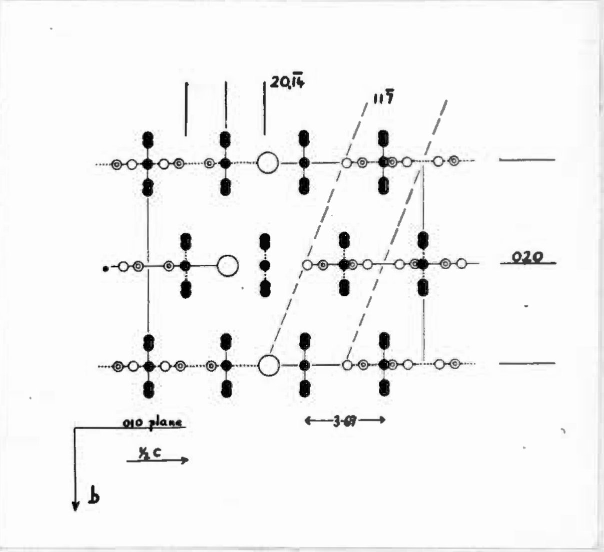


Fig. 16.

Projection of the structure in the direction of the [701] axis onto the bc plane. The dinitrodiphenyl molecules are seen end-on and the iododiphenyl molecules sideways-on.

complexes along $\underline{c}$ onto the $\underline{ab}$ plane. The halogen molecules lying along $\underline{c}$ are seen end-on, and there are two molecules in the distance $\underline{c}$. Each dinitrodiphenyl molecule represents seven molecules lying parallel to one another and separated by 1/7 $\underline{c}$ or 3.69A. If the space-group is $\underline{C}_m$, in order to avoid doubling the number of complex groups in the unit cell, it is necessary for the halogen molecules to lie exactly in the mirror planes (020) and for the dinitrodiphenyl molecules to lie across these mirror planes as shown. This is supported by the very great strength of the spectrum 020. It will be seen from fig. 16, which is a projection of the structure along the axis [701] onto the $\underline{bc}$ plane, that the dinitrodiphenyl molecules lie practically in the planes $(20,\overline{14})$; this is necessary in order to account for the great strength of the spectra $20,\overline{14}$, $11\bar{7}$ and $1\bar{1}\bar{7}$.

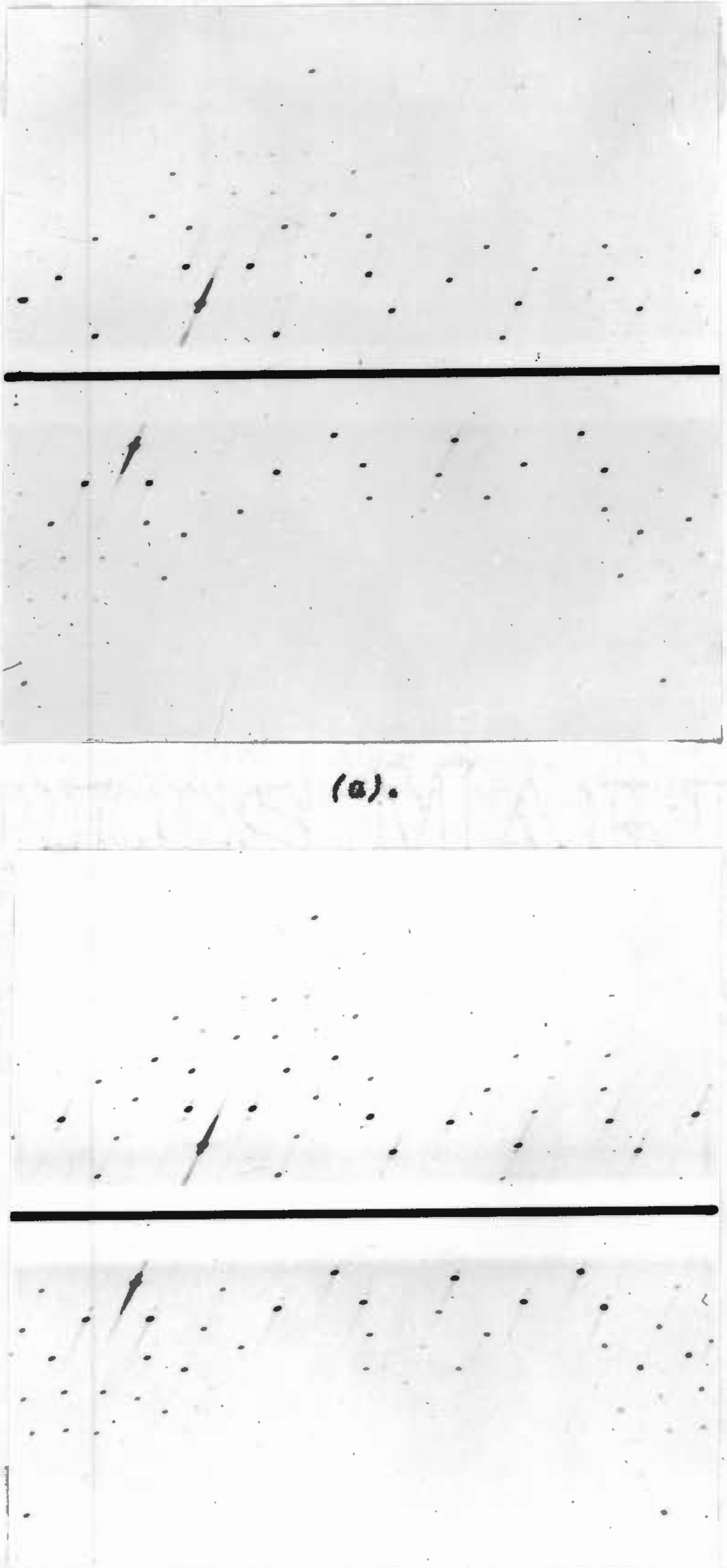
General comparison and confirmation of the structures.

For the sake of brevity it is convenient here to refer to the complexes of dinitrodiphenyl with hydroxydiphenyl (A), tetramethylbenzidine (B), benzidine (C), dihydroxydiphenyl (D), and the halogenated diphenyls (iodo-, bromo- and chlorodiphenyl) (E), by the letters in brackets.

The great similarity between the fully determined structure of the complex (A) and the approximate structures just described for the complexes (B), (C), (D) and (E) is particularly apparent if fig. 7 is compared with figs. 9, 11, 13 and 15. Comparative photographs taken with the crystals mounted about the vertical axes of these figures show very

[page 59

Comparative photographs.

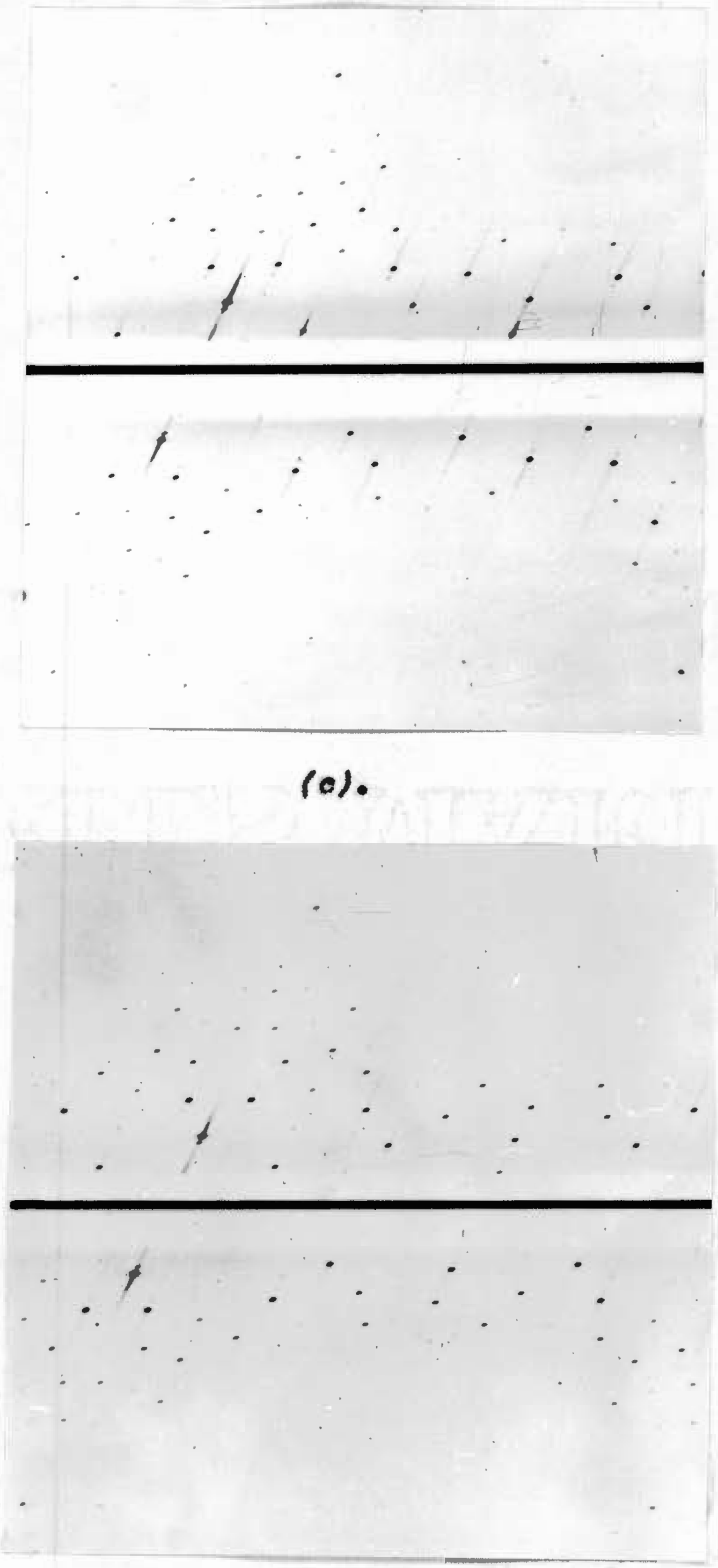


(a).

(b).

Fig. 17.

Comparative photographs (continued).

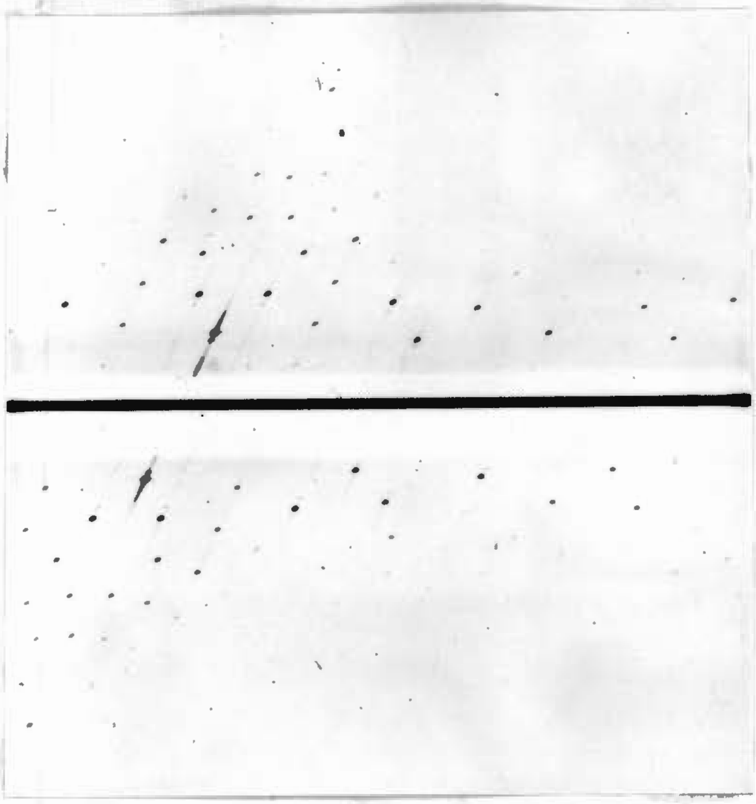


(c).

(d).

Fig. 17.

Comparative photographs (continued).



(e).

Weissenberg zero-layer level photographs taken for :

(a) The complex with hydroxydiphenyl (A), rotating about the c axis.

(b) The complex with tetramethylbenzidine (B), rotating about the a axis.

(c) The complex with benzidine (C), rotating about the b axis.

(d) The complex with dihydroxydiphenyl (D), rotating about the c axis.

(e) The complex with iododiphenyl (E), rotating about the c axis.

Fig. 17.

great similarity indeed; Weissenberg photographs, showing only the zero layer-line, and taken with the crystals rotating about these axes, are reproduced in fig. 17. Further photographs taken with the crystals rotating about other structurally equivalent axes also show considerable similarity.

In all these structures the dinitrodiphenyl molecules lie *across* one of the crystal planes while the other component molecules lie *in* this plane with their lengths nearly normal to the planes of the benzene rings of the dinitrodiphenyl molecules. These crystal planes are, for the complexes (A), (B), (C), (D), and (E) respectively, the planes (020), (011), (40$\bar{2}$), the planes midway between (040), and the planes (020), (see figs. 7, 9, 11, 13 and 15). These planes contain, therefore, a very large number of atoms, namely four carbon and two nitrogen atoms for each dinitrodiphenyl molecule, and *all* the atoms in the other component molecule. It is found that in every case the spectrum arising from these planes is exceedingly strong, and is the strongest spectrum appearing in each photograph of fig. 17. The fourth order spectrum for these planes, namely the spectrum 080, 044, 16,0$\bar{8}$, 0,16,0 and 080 for the complexes (A), (B), (C), (D) and (E) respectively, is also found to be very strong indeed; this is to be expected since *all* the atoms of the dinitrodiphenyl molecules now have a nearly meximum contribution (see figs. 9, 11, 13 and 15).

The separation of the equivalent planes (020), (011), (40$\bar{2}$), (040) and (020), in the complexes (A), (B), (C), (D) and

[page 61

TABLE 7.

COMPARISON OF THE DIMENSIONS OF THE VARIOUS COMPLEXES.

(dimensions in A)

	Complex of dinitrodiphenyl with				
	hydroxy-diphenyl	tetramethyl- benzidine	~~tetramethyl-~~ benzidine.	dihydroxy-diphenyl	iodo-, bromo- or chloro-diphenyl.
Separation (d) of the planes containing the molecules other than dinitrodiphenyl.	d(020) 4.73	d(011) 4.70	d(40$\bar{2}$) 4.77	d(040) 4.66	d(020) 4.75
Separation of like molecules in the above planes.	20.1	20.2	19.1	20.0	20.0
Length of the axis along which the molecules other than dinitrodiphenyl lie.	<u>c</u> 11.13	<u>a</u> 30.2	<u>b</u> 14.8	<u>c</u> 11.3	<u>c</u> approx. 25.8
Approximate length of the above molecules.	11.7	15.2	14.0	12.8	12.9(iodo) 12.7(bromo) 12.3(chloro)
Separation of the dinitrodiphenyl molecules along the above axis.	3.71	3.78	3.71	3.76	3.69

(E) respectively, should be very similar and is found to be always about 4.7A. (see Table 7) The distance between the molecules, lying *in* these planes, which are separated from one another by dinitrodiphenyl molecules should also be similar and is found to be always about 20A (again see Table 7).

In all these complexes the molecules other than dinitrodiphenyl lie approximately along one of the principal axes, namely the *c*, *a*, *b*, *c* and *c* axes, for the complexes (A), (B), (C), (D) and (E) respectively and are nearly normal to all the dinitrodiphenyl molecules, which are separated by approximately 3.7A in this direction. The length of this axis must, therefore, be sufficient to accommodate the right number of dinitrodiphenyl molecules and should be comparable with the length of the other component molecule. This is shown to be the case in Table 7.

As with the complex (A) pronounced diffuse reflections, some of which are reproduced in figs. 18 - 20, have been observed for all these complexes and provide a useful check on the proposed structures. The strongest *circular* diffuse reflections are found to accompany the spectra 800 and $\bar{8}11$, $24\bar{1}$ and $2\bar{4}\bar{1}$, $11\bar{3}$ and $1\bar{1}\bar{3}$, and $11\bar{7}$ and $1\bar{1}\bar{7}$ for the complexes (B), (C), (D) and (E) respectively. The directions of the planes corresponding to these spectra have been drawn in on figs. 10, 12, 14 and 16 and will be seen to be nearly parallel to the planes of the benzene rings of the dinitrodiphenyl molecules. The strongest diffuse *streaks* are found to accompany the spectra $05\bar{5}$, $11,\overline{10}$, $\overline{10},01$ and $\overline{10},01$ for the complexes (B), (C), (D) and (E) respectively. The

The complex with tetramethylbenzidine (B).

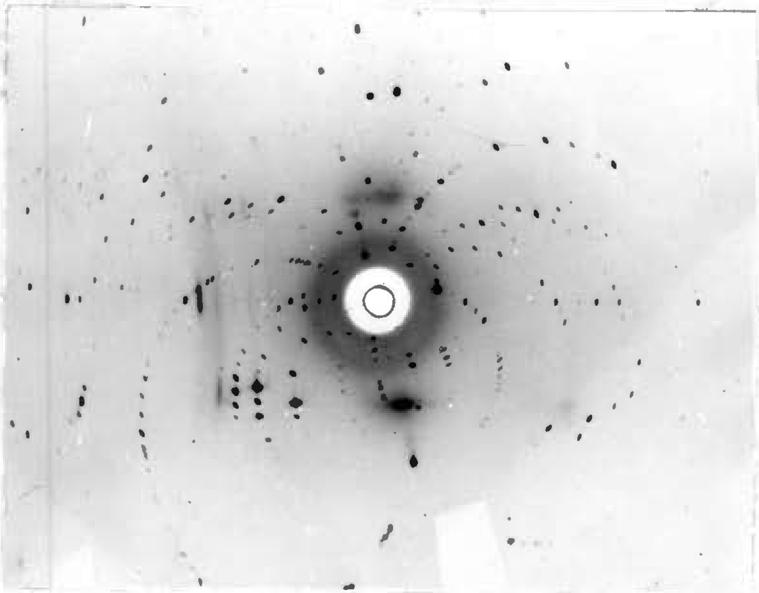


Fig. 18.

Laue photograph, taken in a cylindrical camera, with the crystal mounted with the $\underline{a}$ axis vertical, and using unfiltered copper radiation incident perpendicular to $\underline{c}^*$.

The strongest diffuse streak accompanies the spectrum $05\bar{5}$.

The broad diffuse areas accompany the spectra 800 and $\bar{8}11$.

The complex with benzidine (C).

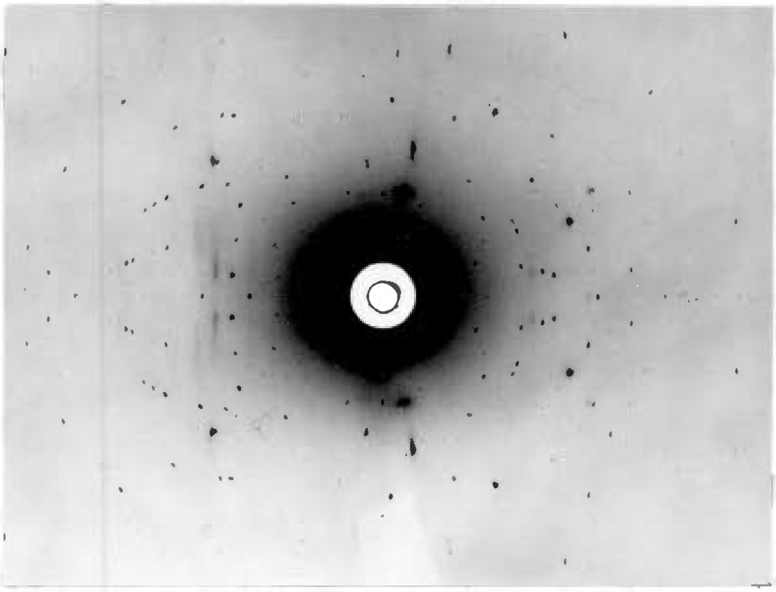


Fig. 19.

Laue photograph, taken in a cylindrical camera, with the crystal mounted with the $\underline{b}$ axis vertical, and using unfiltered copper radiation incident at 10° to $\underline{a}^*$.

The strongest diffuse streaks accompany the spectra $11,\overline{10}$ and $1\bar{1},\overline{10}$.

The broad diffuse areas accompany the spectra $24\bar{1}$ and $2\overline{41}$.

The complex with dihydroxydiphenyl (D).

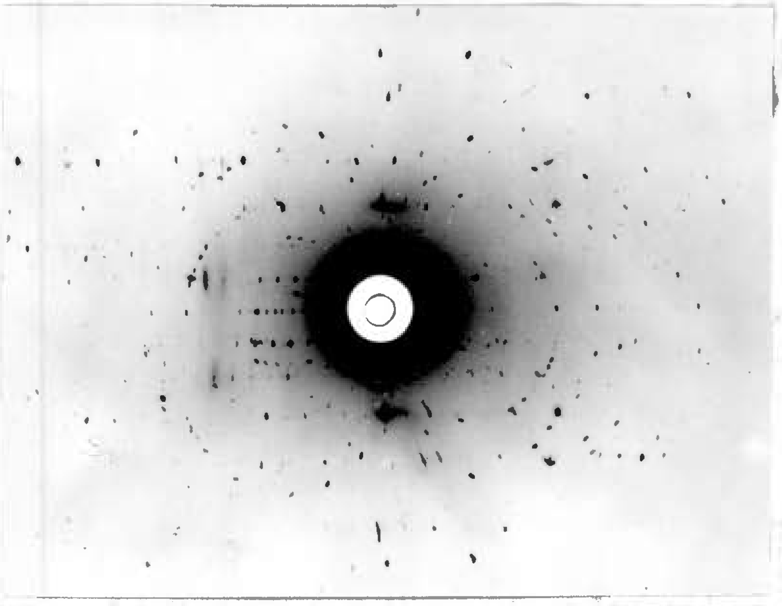


Fig. 20.

Laue photograph, taken in a cylindrical camera, with the crystal mounted with the c axis vertical, and using unfiltered copper radiation incident at 65° to a^{*}.

The strongest diffuse streak accompanies the spectrum $\overline{1}\overline{0},01$.

The broad diffuse areas accompany the spectra $\overline{1}13$ and $11\overline{3}$.

direction of the planes producing these spectra have been drawn in on figs. 9, 11, 13 and 15 and will be seen to be nearly perpendicular to the lengths of the dinitrodiphenyl molecules.

Further confirmation of the relation between the structures of the complexes (A), (D) and (E) is given by the similarity both in direction and magnitude, of the principal refractive indices (see Table 2).

The complex with hydroxydiphenyl.

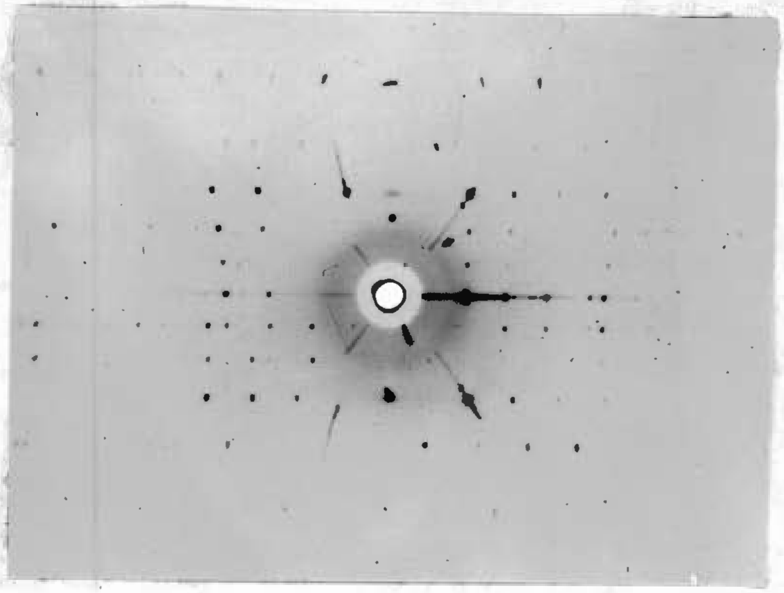


Fig. 21.

15° oscillation photograph, with the crystal mounted with the c axis vertical, and using CuK$_\alpha$ radiation incident initially parallel to a^*.

The complex with iododiphenyl.

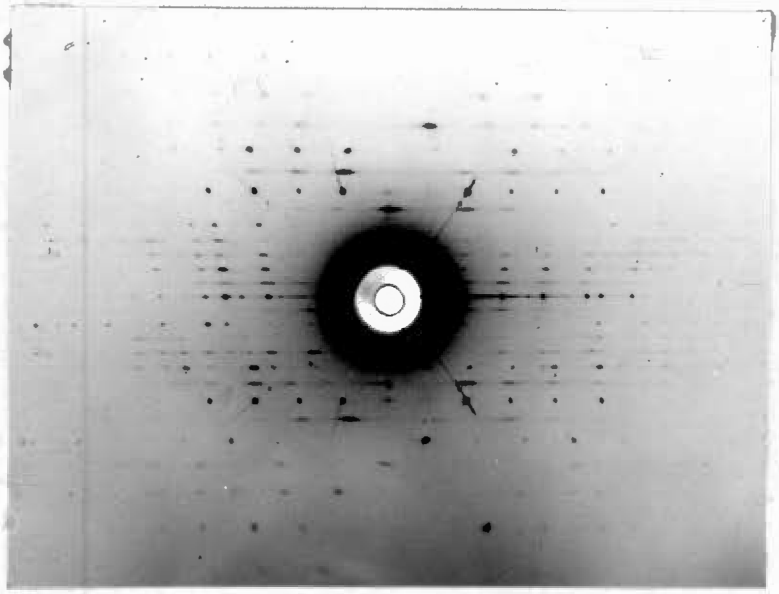


Fig. 22.

15° oscillation photograph, with the crystal mounted with the c axis vertical, and using CuK$_\alpha$ radiation incident initially parallel to a*.

The complex with bromodiphenyl.

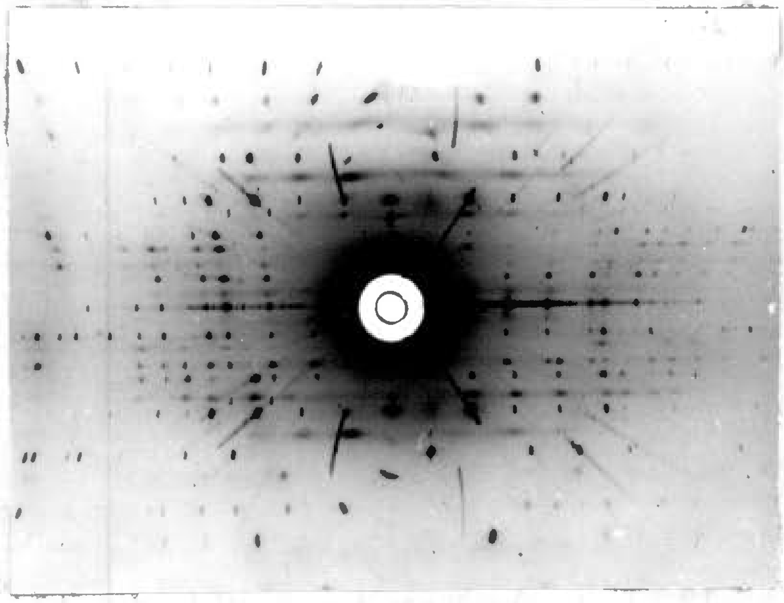


Fig. 23.

15° oscillation photograph, with the crystal mounted with the <u>c</u> axis vertical, and using CuK$_\alpha$ radiation incident initially parallel to <u>a</u>*.

The complex with chlorodiphenyl.

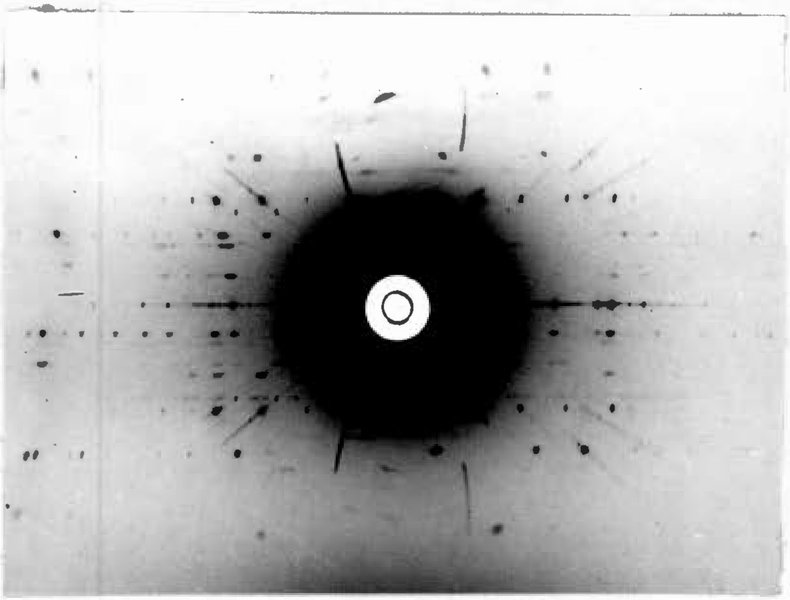


Fig. 24.

15° oscillation photograph, with the crystal mounted with the c axis vertical, and using CuK_{α} radiation incident initially parallel to a^*.

The complex with hydroxydiphenyl.

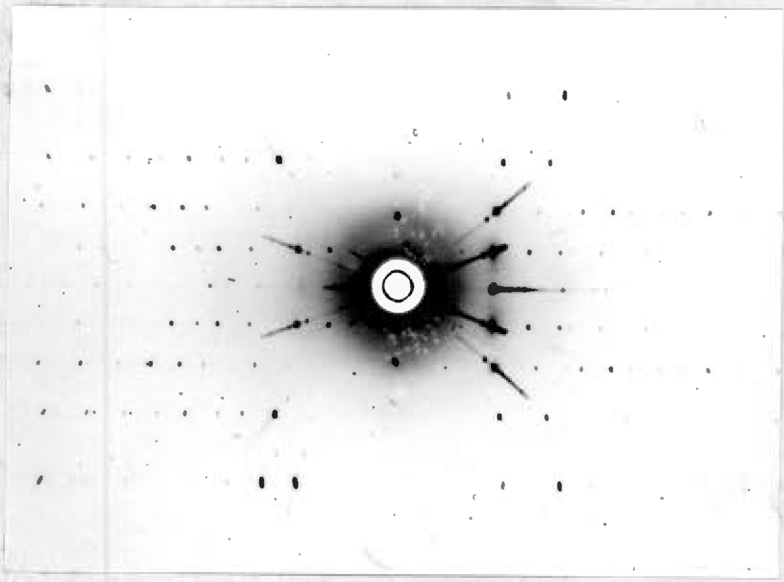


Fig. 25.

15° oscillation photograph, with the crystal mounted with the <u>b</u> axis vertical, and using CuK_α radiation incident initially parallel to $\underline{a}^*$.

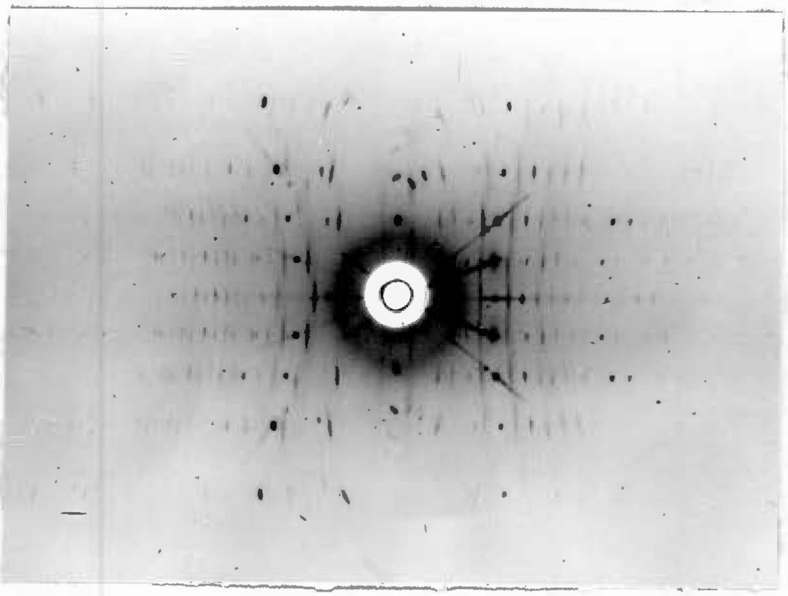


Fig. 26.

15° oscillation photograph, with the crystal mounted with the **b** axis vertical, and using CuK_{α} radiation incident initially parallel to $\underline{a}^*$.

4. PERIODIC ERRORS IN THE CRYSTAL LATTICES OF THE MOLECULAR COMPLEXES OF 4:4'-DINITRODIPHENYL WITH 4-IODO-, 4-BROMO- AND 4-CHLORODIPHENYL.

In the previous section, where the approximate structure to which these complexes conformed was described, it was mentioned that the oscillation photographs are abnormal, showing alternation of sharp and diffuse spectra. Some photographs are reproduced in figs. 22, 23 and 24 and fig. 26. In figs. 21 and 25 are reproduced corresponding photographs for the complex with 4-hydroxydiphenyl, showing the similarity in the two types of structure.

Description of the oscillation photographs.

Photographs taken with oscillations about the c axis show sharp and clear 0th, 7th and 14th layer-lines but all the intermediate layer-lines show spots that are more or less diffuse, with elongations along the layer lines. The diffuseness of the spots on any one line appears to be about the same, but it varies markedly from line to line. Careful inspection shows that in the photograph from the iodo complex (fig. 22) the spacing of the layer-lines is quite uniform; with the bromo complex (fig. 23) and particularly with the chloro complex (fig. 24) the spacing of the diffuse intermediate layer-lines is not uniform, but the lines are arranged in groups, themselves evenly spaced about the sharp layer-lines.

Oscillation photographs about the b axis show sharp and diffuse spots also (fig. 26) and in every case the diffuse spots are those that would lie on the intermediate layer-lines in photographs about the c axis. The diffuse spots are not, however, always centred exactly on the layer lines, but show marked displacements above and below them; the degree of this displacement appears to be a property of the individual crystal, since it varies in photographs obtained from different specimens.

A careful study of photographs taken with oscillations about different axes shows the elongation of the diffuse spectra to be always parallel to b ; this is very apparent in fig. 26. There is no marked elongation in other directions.

Interpretation of the photographs.

In the approximate structure of these complexes the dinitrodiphenyl molecules lie parallel to one another and separated by 3.69A in the direction of the c axis (see fig. 15). If the structure consisted only of such regularly spaced molecules a rotation photograph taken about the c axis would show widely spaced layer-lines corresponding to this distance. In the actual complexes the pattern repeats itself nearly every seven layers of the dinitrodiphenyl molecules, there being approximately two halogen molecules in this distance, so that intermediate layer-lines make their appearance.

So far as the irregular spacing of the intermediate layer-lines in the photographs about the c axis is concerned, the arrangement is exactly that to be expected of a series of optical ghosts accompanying the sharp layer-lines, such as would appear if a set of planes (consisting of dinitrodiphenyl molecules) of regular spacing 3.69A had been modified by a periodic error of spacing repeating in the direction of the c axis in a distance of 12.7A in the case of the bromo complex and 12.3A in the case of the chloro complex, that is to say, with two repetitions in a distance a little less than that corresponding to seven layers of the dinitrodiphenyl molecules. Had the error repeated itself *exactly* twice in seven layers, that is in a distance of 12.9A, the ghost layer-lines would have exactly divided the spacing between the 0th and 7th layer-lines and between the 7th and 14th layer-lines, as in fact they do within the errors of measurement for the iodo complex.

On the actual photographs for the bromo and chloro complexes the departure from regularity is very plain to the eye. For the chloro complex the measured spacings of the layer-lines in the reciprocal lattice space, as determined by means of the Bernal chart, and using CuK_α radiation, are shown diagrammatically in fig. 27. The notation used in the figure has the following significance. Let n be the order of a spectrum from a series of regularly spaced planes. Suppose these planes to be displaced periodically, a complete period of the displacement occurring every Q planes. Then additional spectra of order $n \pm m/Q$ make their appearance, and these are the optical ghosts. We denote any spectrum by the symbol (n,m), the spectra from the undisturbed planes being those of order $(n,0)$. When the planes are periodically displaced, the spectra of order $(n,0)$ still appear, but those with $m \neq 0$ also appear. In the photographs from the bromo and

[page 76

The complex with chlorodiphenyl.

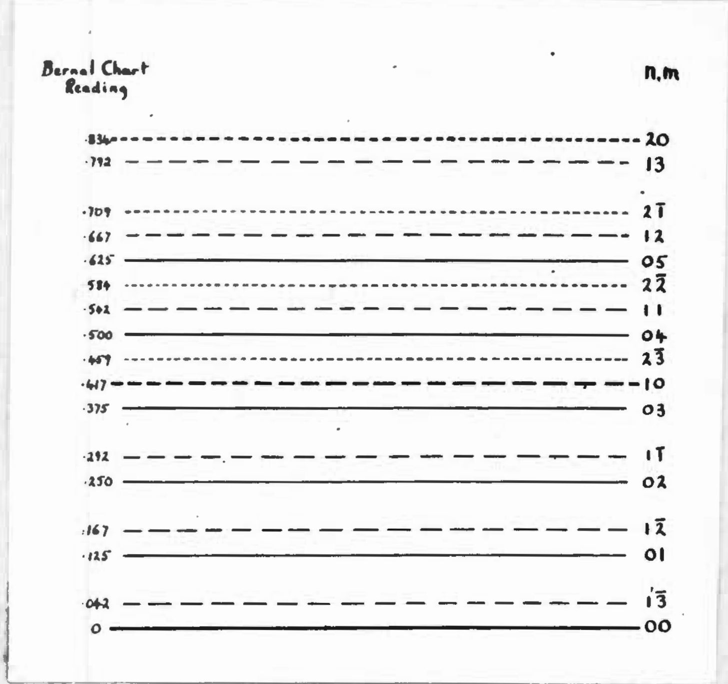


Fig. 27.

Diagrammatic representation of the position of the layer-lines as they appear on an oscillation photograph taken with the crystal mounted with its c axis vertical (fig.24).

chloro complexes the positions of the layer-lines correspond to a value of Q rather less than $3\frac{1}{2}$.

The positions of the layer-lines may thus be explained in detail by the assumption of a periodic error in spacing. As a working hypothesis, the occurrence of the halogen molecules at regular intervals might be supposed to impose a variation of spacing on the sheets of dinitrodiphenyl molecules which are separated by 3.69A. It is significant that the error periods, as determined by direct measurement from the photographs, are 12.9, 12.7 and 12.3, which are the lengths, as closely as can be determined from the available data, to be expected for the molecules of 4-iodo-, 4-bromo- and 4-chlorodiphenyl respectively. If this hypothesis is correct the ratio of dinitrodiphenyl to iodo-, bromo- and chlorodiphenyl in the complexes should be 3.50:1, 3.44:1 and 3.33:1 respectively. Unfortunately it has not been found possible to perform the chemical analyses with sufficient accuracy to confirm this. On the view that the intermediate layer-lines are ghost spectra due to a periodic error in a fundamental spacing, we should expect the ghosts accompanying the zero layer-line, the ghosts ($0 \pm m$), to be very weak, although not in principle absent, while in the actual photographs these spectra are quite strong. It must, however, be remembered that the structure contains the regularly spaced halogen molecules, which, considered alone, would give a set of spectra in the positions of the spectra ($0 \pm m$) so that in any case these would be expected to occur.

Another point requiring consideration is the diffuseness of the lines. An elongation of the spectra along **b** would be produced by a crystal having only a small extension in the **b** direction, but this would make all the spots equally diffuse, which is not observed here where the diffuseness varies with the order, **m**, of the ghost. The explanation of the diffuseness is therefore probably to be sought in random faults occurring in the **b** direction of the nature of those discussed by Wilson (13), which are superposed on the framework of a fundamentally regular lattice structure.

The idealised model.

A simplified model that will give an adequate explanation of the effects actually observed has been produced by Professor R.W. James of the University Physics Department (14).

The crystal is assumed to consist of layers of dinitrodiphenyl molecules, all exactly alike, placed one above the other in the array represented in fig. 15, and this array is assumed to persist coherently throughout the crystal. Through this structure the chains of halogen molecules pass transversely to the dinitrodiphenyl molecules and parallel to the **c** axis of the crystal. The halogen molecules lying in any one chain are assumed to maintain an unchanged regular sequence through the crystal. In any one (020) plane the structure is supposed to be without faults, corresponding atoms in the different halogen chains all having the same **c** coordinates, so that the consequent periodic displacements of the dinitrodiphenyl molecules are all in phase. It is supposed, however, that in different (020) planes there may be relative displacements of the halogen molecules so that in passing from one (020) plane to the next there may be a sudden change in the c coordinates of corresponding halogen molecules. It is assumed that there is a certain probability that within any distance measured parallel to b such a sudden change, or fault, may occur. The simplest possible assumption is made, that there are two possible sets of coordinates for the halogen molecules.

The probability that two (020) planes separated by a given distance shall have the same or different c coordinates is calculated and the interference function for the crystal is worked out, considering the scattering due to the dinitrodiphenyl molecules alone, with the periodic errors imposed on their scattering by the halogen molecules and neglecting for the time being the scattering by the halogen molecules themselves. For this purpose, the model is still further simplified, each unit of the structure being replaced by a scattering point.

It is shown that the diffuseness of the ghost maxima is governed by a factor which is a function of m, the order of the ghost, and the form of this factor suggests that the spots on the ghost layer lines might show sharp nuclei with relatively diffuse wings. On the actual photographs a number of such spots are in fact to be seen, which may be some confirmation of the view that the effects observed are due to an irregularity of the same general nature as that discussed.

The ghosts accompanying the zero layer-line are actually much stronger than would be expected from the analysis of this simple model. It must be remembered, however, that in this model the scattering from the halogen molecules themselves is neglected. It has, however, been further shown by Professor James (14) that scattering from the halogen molecules alone, assuming the same probability of faults in the structure, would produce a set of layer-lines having the same positions, and the same variation of diffuseness with order, as those predicted for the ghost spectra of zero order. The relatively strong spectra actually observed in these positions can therefore be mainly ascribed to this cause, the true ghosts being those accompanying the higher orders.

The nature of the errors.

It is not possible to specify the exact nature of the irregularities in these structures, but it is tempting to associate the distortions which appear to be produced in the regular arrangement of the dinitrodiphenyl molecules with the size of the halogen atom introduced by the other component. Thus the ghost spectra are most intense in the iodo complex and weakest in the chloro complex, which corresponds to large distortions in the iodo complex and small distortions in the chloro complex. In this connection it is interesting to note that oscillation photographs for the complex of 4:4'-dinitrodiphenyl with 4-fluorodiphenyl are perfectly normal with no trace of any diffuse spectra; in fact, the photographs exhibit great

great similarity with corresponding photographs for the complex with dihydroxydiphenyl previously described.

Alternations of sharp and diffuse spectra on the same photograph have also been observed by Powell and Huse (12b) for the molecular complexes of hexamethylbenzene with picryliodide, -bromide and -chloride. They suggest that errors are due to the alternate layers, consisting each of one kind of molecule, not being completely regular so that sometimes two adjacent layers of the same type of molecule may exist. Also, in each layer of picryliodide, -bromide or -chloride there are three ways of packing the molecules and they suggest that all three ways are actually used in a random manner.

THE BONDING MECHANISM.

The crystallographic evidence.

The following are the significant points arising from the x-ray studies:

1. In the detailed analysis of the complex of 4:4'-dinitrodiphenyl with 4-hydroxydiphenyl it was shown that all the molecules are approximately equally spaced from one another, and, as shown in table 8, none of the intermolecular distances are shorter than those normally found in crystals of ordinary aromatic nitro-compounds, bonding in which is generally attributed to van der Waal's forces. These ~~data~~ results are in agreement with those of Powell, Huse and Cooke (12a) who found no evidence for localized bonding in the molecular complex of s-trinitrobenzene with p-iodoaniline. The complex of 4:4'-dinitrodiphenyl with diphenyl has been shown to have an almost identical structure to that of the complex with hydroxydiphenyl, and in all the other complexes examined there is no necessity to assume intermolecular approaches any closer than those listed in table 8; there is sufficient space in the unit cell in each case for the molecules to pack quite normally. This is reflected in the densities of the crystals (table 3) which are all of the same order, and are no higher than those recorded for the aromatic nitro-compounds listed in table 8.

2. In the complexes of 4:4'-dinitrodiphenyl with 4-iodo-, 4-bromo- and 4-chlorodiphenyl periodic distortions appear to be produced in the regular arrangement of the dinitrodiphenyl

[page 83

TABLE 8.

DISTANCES OF CLOSEST INTERMOLECULAR APPROACH OBSERVED IN VARIOUS NITRO-COMPOUNDS.

(dimensions in A).

Compound	O----O (between oxygen atoms of nitro-groups)	O----C (between oxygen atom of nitro-group and carbon atom of benzene ring)	C----C (between carbon atoms of adjacent molecules)
Molecular complex of 4:4'-dinitrodiphenyl with 4-hydroxydiphenyl.	3.3	3.2	3.6
Molecular complex of s-trinitrobenzene with p-iodoaniline (12a).	3.2_5	3.3_5	3.5
4:4'-dinitrodiphenyl (4).	3.4	2.9	3.6
p-dinitrobenzene(3).	3.2	3.3	3.6
m-dinitrobenzene(9).	3.2	3.0	3.6
picryliodide (11).	3.0	3.1	-

molecules. The magnitude of these distortions may depend on the size of the halogen atoms and they are no longer present in the complex with 4-fluorodiphenyl. Further, in these complexes random faults in the positions of the iodo-, bromo- and chlorodiphenyl molecules appear to occur. It is difficult to interpret the significance of these results, but it should be noted that these complexes are amongst the most lightly coloured and least stable of the series of complexes examined. Powell and Huse (12b) have also observed random faults in the complexes of hexamethylbenzene with picryliodide, -bromide and -chloride. Such faults are only possible where there is weak bonding between the two kinds of molecule.

3. In all the complexes examined very pronounced thermal vibrations occur as shown by the strong diffuse reflections accompanying certain spectra. This is an indication of comparatively weak bonding between the "layers" of atoms concerned.

4. In complexes conforming to the type of structure found for all those examined, the number of 4:4'- dinitrodiphenyl molecules that can be accommodated for each molecule of the other component depends on the length of this latter molecule. In table 9 are listed molecular ratios calculated on this basis for a number of complexes, along with the ratios actually observed. The agreement between the observed and calculated values is very striking. The integral ratio observed in the majority of cases is a normal requirement of crystal structure and is preserved by a slight tilting of the molecules. Of particular interest are the complexes with bromo- and chlorodiphenyl

[page 85

TABLE 9.

RELATION BETWEEN THE LENGTHS OF THE MOLECULES AND THE MOLECULAR RATIO OF THE COMPONENTS.

Complex of 4:4'-dinitrodiphenyl with:	Approximate length of the other component molecule. (allowing for the approach of the next molecule in an end-on position). (A)	Number of molecules of 4:4'-dinitrodiphenyl separated by 3.7A that can be accommodated at right angles to each molecule of the other component.	Molecular ratio of the components found by analysis.
4:4'-Diacetoxydiphenyl	17-18	4.6-4.9	5:1
NN:N'N'-Tetramethylbenzidine	15.3	4.1	4:1
4-Acetoxydiphenyl	14.0-14.5	3.8-3.9	4:1
Benzidine	13.9	3.8	4:1
4:4'-Dimethoxydiphenyl	14.8-15.3	4.0-4.1	7:2
4-Iododiphenyl	12.9	3.5	7:2
4-Bromodiphenyl	12.7	3.4	?
4-Chlorodiphenyl	12.3	3.3	?
4:4'-Dihydroxydiphenyl	12.8*	3.5	3:1
4-Aminodiphenyl	12.2	3.3	3:1
4-Hydroxydiphenyl	11.8	3.2	3:1
4-Fluorodiphenyl	11.7	3.2	3:1
Diphenyl	10.7	2.9	3:1

* hydrogen bonding is here assumed between adjacent OH groups.

for which the crystallographic evidence suggests that the molecular ratio of the components is 3.44:1 and 3.33:1 respectively. It seems clear, therefore, that in these complexes the molecular ratios in which the components unite are determined solely by geometrical and not by chemical considerations.

Discussion.

From the crystallographic evidence it is certain that weak intermolecular forces, of the same order as van der Waal's forces, must be operative in these complexes. The possibility of covalent bonding, as advocated by Bennett (15) and Hammick (16), would necessitate localised intermolecular approaches of the order of 1.5A. This is definitely excluded since none of the observed intermolecular distances are less than 3.0A. Similarly the variable ratios, which seem to be determined solely from geometrical considerations, encountered in these complexes are against the hypothesis of integral electron transfer, as advocated by Weiss (17).

It appears, therefore, that the stability of these complexes may be accounted for by the interaction energy due to the mutual polarization of the molecules, a conclusion which has been reached by several workers, namely Briegleb (18), Pauling (19), Gibson and Loeffler (20), Hammick (21) and Sutton (22).

It is well known that the phenomenon of molecular attraction has its origin in three main effects (23). Thus there are attractive forces between the different molecules as a result of : (a) the "orientation" effect, attraction between the permanent dipoles in different molecules; (b) the "induction" effect, attraction between the permanent dipoles of one molecule and the induced dipole in an adjacent molecule, and (c) the "dispersion" effect, statistical attraction arising from the rapidly fluctuating dipoles due to the motion of the electrons and atoms in the molecules. The potential energy, U, arising from interaction of each of the three types may be represented by

$$U_{orientation}\ (U_o) = -\tfrac{2}{3}\,\mu^4/r^6 KT$$
$$U_{induction}\ (U_I) = -2\alpha\mu^2/r^6$$
$$U_{dispersion}\ (U_D) = -\tfrac{3}{4}\,h\nu_0\alpha^2/r^6$$

where μ is the dipole moment of the molecules, α is the polarizability of the molecules, r is the distance between the molecules, h is Planck's constant, K is Boltzmann's constant, ν_0 is the characteristic frequency of the molecules and T is the absolute temperature.

It should be noted that these equations apply only to interaction between identical molecules, but it may be taken that they will have the same form when applied to interaction between the unlike molecules.

For simple compounds, consisting of only one type of molecule, U_D is generally very much greater than U_o or U_I, although U_o may become large for highly polar compounds. U_I is nearly always very small. It is, however, to be expected that if molecules with intense localized dipoles are brought into proximity with highly polarizable molecules, the "inductive" attractive forces may become considerable. The value of $\alpha \mu^2$ for interaction between the two types of molecule will be large, U_I will then become appreciable, and this increase in binding energy may be sufficient to account for the formation of a solid complex.

It must be emphasized that the total binding energy in any molecular crystal is given by the sum of the "orientation", "induction" and "dispersion" effects. It is not envisaged that in these molecular complexes the value of U_I is greater than the others, but merely that it is large enough to account for the existence of the two unlike components in the one compound. The values of U_o and U_D may still be larger than the value of U_I, but they do not depend for their magnitude on the presence of unlike molecules; that is, the values of U_o and U_D are not enhanced by the presence of the two types of molecule, whereas this presence may mean an increase in the value of U_I.

In compounds containing highly polar groups it is to be expected that the value of U_o should be large, since it depends on μ^4/r^6. This is strikingly illustrated by the existence of solid, though non-coloured, complexes obtained between different nitro-compounds (24).

At the present time it is not possible to carry out calculations of the binding energy in molecular complexes with any degree of accuracy. In order to treat the distortion of an electron distribution in the presence of polar reactants it is necessary to have more information about the anisotropy of the polarizability of molecules and bonds. Briegleb (18b) has, however, made calculations of the binding energies in some molecular complexes of s-trinitrobenzene, assuming an approach of 3.0A between the nitro-groups ($\mu = 4$D) and the hydrocarbon whose polarizability was calculated from the molecular refractivity, and has obtained values of the order of 2Kg.-cals. for the gm.-mol. heats of interaction. While these results are in agreement with other experimentally determined heats of interaction (18b, 16b, 21, 15b), which are of the order of 1-5 Kg.-cals. they must be considered as being only very approximate.

The application of the ideas outlined above to the formation of molecular complexes between nitro-compounds and aromatic hydrocarbons is supported by the following data:

1. The nitro-group has one of the highest group dipole moments. In this connection it is very significant that similar complexes are formed by nitroso-compounds (25), quinones (17b, 25, 26), liquid SO_2 (27), aromatic acid chlorides and nitriles (15c). It will be observed from table 10 that all these components contain highly polar groups.

It is of interest to note that a highly coloured complex has recently been obtained with 4:4'-dicyanodiphenyl and benzidine. It is hoped to obtain further complexes of 4:4'-dicyanodiphenyl, and perhaps of 4:4'-diisocyanodiphenyl (the group moment of the -NC grouping is 3.9D).

[page 90

TABLE 10.

GROUP DIPOLE MOMENTS.

GROUP	Dipole moment (debye units) When group attached to aliphatic nucleus.	When group attached to aromatic nucleus.
$>SO_2$	4.4	5.1
$-NO_2$	3.2	4.0
$-NO$	-	3.2
$-CN$	3.5	3.9
$>C=O$*	2.8	3.0

*The dipole of the $>C=O$ grouping is not very large but it has been observed that in quinones the dipole moment is much larger than can be calculated using a value of 3.0D for the $>C=O$ grouping.

Also in acid chlorides ($-COCl$) the effect of the $C-Cl$ linkage, which has a moment of 1.7D, is to reinforce the effect of the $C=O$ link.

Anderson (26) has investigated the crystal structures of some molecular complexes involving quinones and the evidence is that in these complexes also there are no abnormally short intermolecular distqnces.

2. Aromatic hydrocarbons contain a conjugated double bond system and so have a disperse distribution of electrons in the $\pi\pi$ bonds; such an electron distribution should be comparatively mobile and so easily polarized. Polarizability may be roughly determined (28) from measurements of refractivity, according to the Lorentz-Lorenz relation. It is found that compounds containing conjugated double bonds show optical exaltation, that is they have unusually high molecular refractivities. This is regarded as indicating the increased polarizability of the electron system.

The aromatic nucleus itself, however, does not show optical exaltation, probably for reasons of symmetry since exaltation appears again in aromatic compounds with unsaturated side chains and in condensed ring systems. It is, however, emphasized by Sutton (22) that values for the polarizability obtained by using ordinary macroscopic fields, such as light fields, may not always be applicable to the discussion of short range intermolecular attractions where the fields are very intense. For instance, the field at 3A axially from a mathematical dipole of 3D is 67×10^6 volts/cm. It is possible therefore, as Sutton suggests, that the unsaturated aromatic-ring system may have abnormally high polarizability in very strong localized fields.

Of interest are the results of Briegleb (18a) who has found that the binding energy in complexes of *s*-trinitrobenzene with various hydrocarbons depends in a marked way on the structure of the hydrocarbon, and these binding energies are greater the greater the optical exaltation shown by the hydrocarbon. The binding energy of the complex is high if the hydrocarbon system is completely conjugated but decreases as soon as the conjugation is interrupted.

When considering the question of the polarizability of the aromatic hydrocarbon it is interesting to note that ~~the~~ in general complexes with nitro-compounds are apparently more stable if electron-repelling groups are introduced into the hydrocarbon and less stable if electron-attracting groups are introduced, indeed in the latter case it is generally impossible to isolate a crystalline complex. It is tempting to suggest that the introduction of an electron-repelling group into the hydrocarbon leads to a greater availability of electrons in the aromatic nucleus, implying a greater polarizability of the molecule. Considerable care must, however, be exercised in interpreting the effect of substituents on the stability of these complexes since geometrical effects depending on the size of these substituents will undoubtedly be of importance in determining the approach of the molecules to one another. *

As far as the production of colour in these complexes is concerned, it is not possible, without a quantum mechanical treatment, methods for which are not yet fully developed, to attempt to describe the mechanism involved. The production of colour depends on the existence of suitable intervals between the available electron energy-levels, and it is to be expected that variations in these energy levels will accompany the distortions in the electron systems of the molecules which must occur during the formation of these molecular complexes, or when the unlike molecules approach closely in solution. It is not necessary, as was suggested by Gibson and Loeffler (20), to postulate incipient "chemical" action in order to account for the production of colour either in solution or in the solid state.

To summarise, it may be said that the tendency to formation of these complexes is probably determined by the increase in the "inductive" attractive forces, with a consequent increase in binding energy, as the highly polar groups of the one component approach the polarizable nucleus of the other component. The final stability, however, of the solid complex, if one is formed at all, and the molecular ratio of the components, must depend largely on geometrical considerations, that is, on the nature of the crystal structure the complex is able to assume.

APPENDIX 1.

X-RAY METHODS AND APPARATUS.

Two Machlett x-ray tubes emitting CuK_α radiation were used throughout this work and were supplied by the circuit shown diagrammatically in fig. 28. They are rated to operate at 50 KVP. and 15 mA. but were generally operated at about 35 KVP. and 10-12 mA. The CuK_β radiation was partly absorbed by a filter of Nickel foil. The presence of Nickel as an impurity in both anticathodes was shown by the appearance of extra spots on the films corresponding to the NiK_α wavelength, and it was therefore necessary to exercise care in indexing the spectra.

The rotation camera, made by Unicam Instruments Cambridge, had a diameter of 60.0 mm. and was equipped with goniometer arcs and a collimator and telescope system. In addition to the 5°, 10° and 15° cams originally fitted to the camera, extra cams of 30° and 50° were constructed and adapted for use with the camera.

The Weissenberg camera, constructed in the workshops of the University Physics Department, was of undistorted scale, having a diameter of 57.3 mm. and a travel of 2°/mm. It was also equipped with goniometer arcs and a telescope system and gave a total rotation of 190°.

[page 95

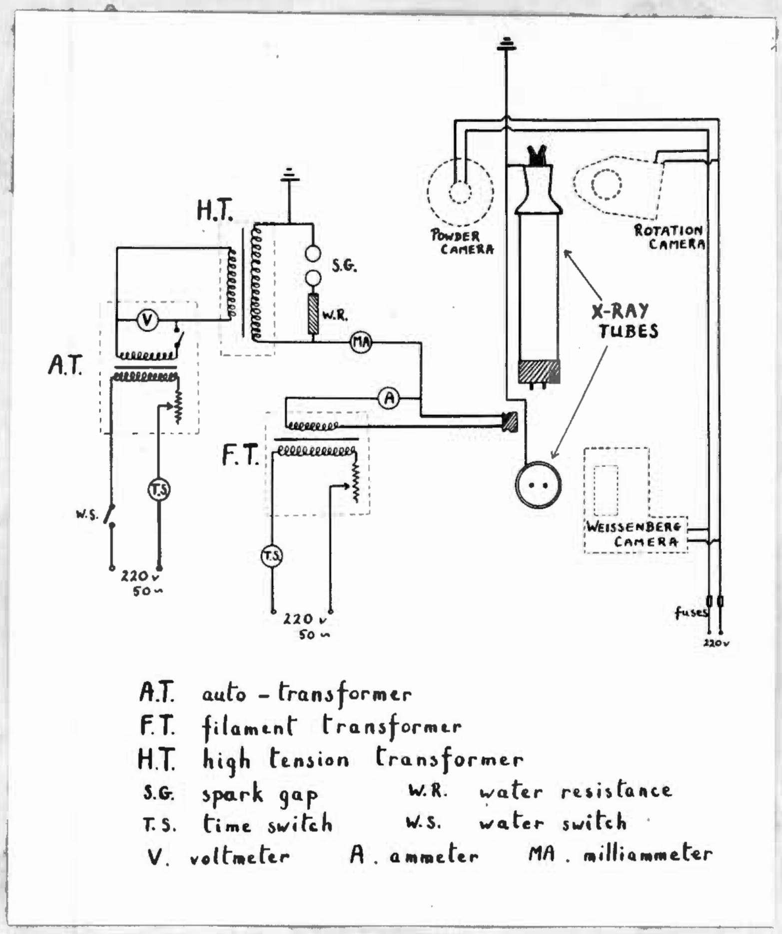


Fig. 28.

Diagrammatic representation of the X-ray circuit used.

Considerable care was always exercised in choosing good crystal specimens. Single crystals of suitable size were first selected under a binocular microscope and in general had to be cut to approximately uniform cross section (about 0.2 mm.) about the desired axes; the final selection was made under a polarizing microscope where flaws show up very clearly. The crystals were mounted on the sharp point of a bakelite holder with a speck of Canada balsam. The setting of the crystals was generally done using reflections from faces about the zone axes; when no faces were available, however, the setting was adjusted by trial and error from the slope of the layer lines on the photographs.

The unit cells of the crystals and the indices of the spectra were determined using the standard reciprocal-lattice methods developed by Ewald (29) and applied by Bernal (30) to graphical indexing. The reciprocal-lattice point *hkl* is regarded as being located by the cylindrical coordinates $\zeta \xi \varphi$ where ζ is parallel to the rotation axis, ξ is perpendicular to the rotation axis and φ is the angular coordinate. The unit cells and general indices *hkl* may then be determined by measurement of the $\zeta\xi$ coordinates of the spectra on *rotation* photographs using a Bernal chart. The reciprocal-lattice points having the same $\zeta\xi$ coordinates may be determined graphically. The indices of particular spectra of the type *h*00, *h*0*l*, etc., may best be determined by measurement of the $\xi\varphi$ coordinates of the spectra on *Weissenberg* photographs using the $\xi\varphi$ scales described by Buerger (31) and employing a similar graphical method.

Where it was not possible to determine the monoclinic angle, β, from goniometer measurements, Weissenberg photographs were taken with a crystal rotating about the *b* axis and the angular separation of the *h*00 and 00*l* spectra measured.

APPENDIX 2.

APPARATUS FOR MEASURING THE PYRO-ELECTRIC EFFECT.

The crystal was gripped between copper terminals in a manner similar to that described by Orelkin and Lonsdale (2). Changes in potential may be produced across the crystal when it is immersed in liquid air; if the crystal is contained in the grid circuit of an electrometer valve, changes in the anode current may then be produced which will cause deflections of a balanced galvanometer in the anode circuit. The circuit which was used was self-compensating to allow for changes in the filament current and is shown in fig. 29. The electrometer valve used, when operated with the grid at -3V and the anode +4V with respect to the filament, and using a filament current of 0·1 amp., passed a grid current of only 10^{-14} amps. A negligible current was therefore passed through the crystal. For efficient operation it was necessary to shield both the electrometer valve and the grid circuit. It was also necessary for a drying agent such as P_2O_5 to be introduced into the tube containing the crystal.

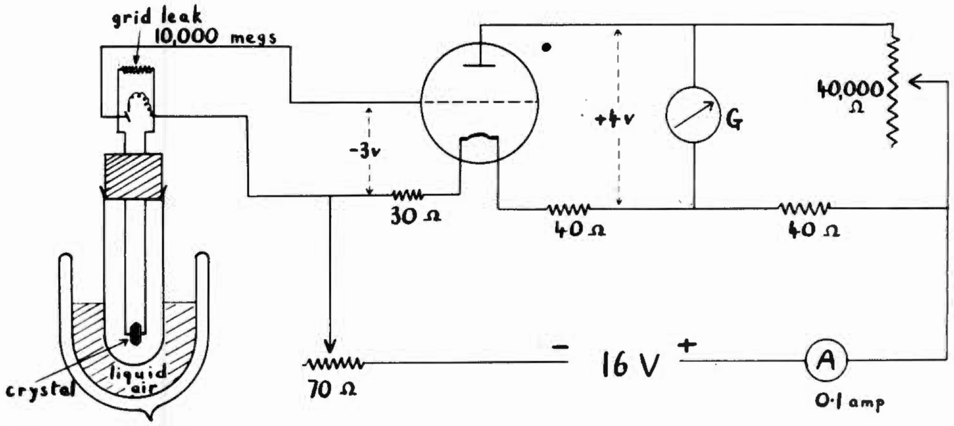


Fig. 29.

Diagrammatic representation of the apparatus used for measuring the pyro-electric effect in crystals.

APPENDIX 3.

THE DIFFUSE REFLECTIONS DUE TO THERMAL VIBRATIONS.

The thermal vibrations which occur in crystals at ordinary temperatures cause random irregularities in the structure which diminish the intensities of the main spectra but leave their sharpness unaltered. At the same time the general scattering is increased.

It was first predicted by Faxén (32) and Waller (33), who treated thermal vibrations as displacements due to a series of elastic waves in the crystal, that the effect of these thermal vibrations would be to produce an extension of reflecting power of the reciprocal-lattice points. The reciprocal-lattice points would then be surrounded by a cloud of weak reflecting power, the shape of which depends on the velocity of the elastic waves in various directions in the crystal. The effect of this extension of reflecting power is to produce diffuse extra reflections accompanying the Bragg maxima on x-ray photographs. This was first studied by Laval (34) and has recently been extensively studied by Lonsdale (6).

The dependence of the extra intensity in the neighbourhood of the reciprocal-lattice points upon the nature of the crystal is of great importance. Although it is possible to calculate the detailed distribution of the intensity function about the reciprocal-lattice points for only very simple crystals, it is possible to reach qualitative conclusions using the following data:

1. Elastic waves propagated along a given direction in a crystal will cause extension of the reflecting power of each reciprocal-lattice point along the direction of propagation.

2. The intensity of reflecting power at any given point depends on the square of the cosine of the angle between the radius vector of that point in reciprocal-lattice space and ~~on~~ the direction of the atomic movements, that is on the polarization of the waves.

From these simple considerations it is possible to arrive at general conclusions concerning the extra reflections from "layer" and "chain" structures (6a).

Layer structures.

The atoms in the layer planes of a structure such as graphite, mica, etc., are more firmly linked than in other crystal planes. Such structures will yield most readily to displacements perpendicular to the layer planes and the preferred modes of vibration of the atoms are therefore perpendicular to these planes.

Suppose the layer planes to be the planes (100), then the vector from the origin to the reciprocal-lattice point 100 is always parallel to the direction of maximum vibration whatever the direction of the wave. For instance, maximum contributions will be given by longitudinal waves travelling along [100] and also by transverse waves travelling along [001] and [010] , but which are polarised along [100].

The reciprocal-lattice point 100 will thus show a maximum extension of reflecting power in every direction in reciprocal space and will be nearly spherical. The reciprocal-lattice point 100 will then be cut by the sphere of reflection in a circular section and, on a Laue photograph, the spectrum 100 will be accompanied by a large nearly circular diffuse reflection.

Chain structures.

In long chain compounds the compressibility along the length of the chains is much smaller than that at right angles to the chains. Therefore longitudinal vibrations along the chain axis cannot occur to any marked extent. If the chain axis is the axis [100] then no extension of reflecting power along [100] for the reciprocal-lattice points 100 is to be expected.

Transverse vibrations perpendicular to the chain lengths are however permitted, and if such waves are polarised along [100] they will give maximum contributions. There will thus be a disc-shaped extension of reflecting power, in all directions perpendicular to the chain lengths, about the reciprocal-lattice point 100. The intersection of this by the sphere of reflection will be more or less linear and the spectrum 100 will be accompanied by a diffuse streak.

It has been shown (35) that with a structure containing long flat molecules both types of diffuse reflection may be observed, and useful information as to the orientation of the molecules is thus obtainable.

APPENDIX 4.

INTENSITY MEASUREMENTS.

(a) Relative intensity determination.

As no ionization spectrometer or integrating photometer was available the relative intensities of the spectra were determined by measuring the density or amount of blackening of the spots on the rotation photographs with a travelling microphotometer. A typical photometer trace of one of the films is shown in fig. 30. The zero-line is the trace obtained when no illumination falls on the photoelectric cell. The indexing of the peaks on the traces was done by taking a trace of a Bernal chart and transferring it to tracing paper; by placing this over the traces of the films, the value of ξ for the various peaks could be read off directly, and the corresponding indices assigned to the peaks.

The variation in intensity with the height of the peak was determined by Dr. J.N. van Niekerk of the University Physics Department (36). The method used was to make a series of standard wedges of known exposure from the direct x-ray beam; these were then photometered and the relationship between h (the distance from the zero-line to the trace) and I (the intensity in secs. of exposure) obtained. A graph of I against h was drawn using these values and from this intensity curve the relative intensities of the spectra, appearing on the photometer curves for the films, were determined as follows:

[page 104

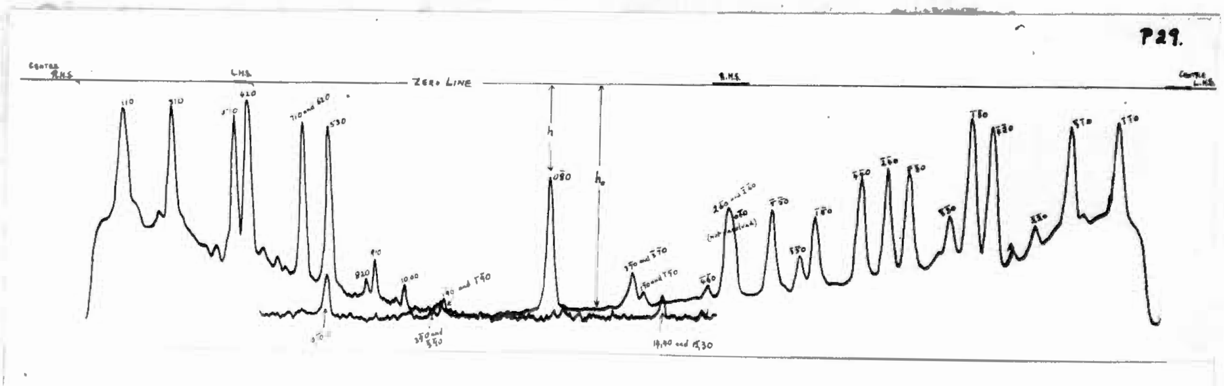


Fig. 30.

A typical microphotometer trace, showing the spectra appearing on the zero layer-line of film P29, which is an oscillation photograph taken with a crystal of the complex with hydroxydiphenyl rotating about the <u>c</u> axis.

Values of h_o and h were measured, where h is the distance from the zero-line to the top of the peak and h_o is the distance from the zero-line to the background on which the peak occurs. The corresponding values of I_o and I were found from the intensity curve and the relative intensity of the spectrum is $(I - I_o)$. The relative intensities of the spectra appearing on the trace shown in fig. 30 are given in table 11.

Since no Weissenberg camera was available at this stage, many oscillation photographs were necessary in order to get the full rotation required for the crystal (90° or 180°), and, although care was taken to expose and develop the films for the same length of time, it was impossible to record each film under exactly the same conditions. For each film, therefore, oscillations of 15° were given to the crystal, which was then turned through 10° for successive films until the full rotation had been obtained. In this way some spectra were common to each successive pair of films and these spectra were used to standardize the films in terms of one another. The standardization of two successive films in this way is shown in table 12.

When making these intensity observations many low order spectra were overexposed; any peaks with $h < 0.5$ cm. were assumed to be overexposed. It was therefore necessary to take further films with reduced exposure times to include these strong spectra as well as other spectra of determined intensity, by comparison with which the strong spectra could be expressed on the same scale.

TABLE 11.

INTENSITIES OF THE SPECTRA APPEARING ON PHOTOMETER TRACE P29 SHOWN IN FIG. 30.

Index.		h_o (cms.)	h (cms.)	I_o (secs.)	I (secs.)	$(I-I_o)$ (secs.)
L.H.S.	$\bar{1}\bar{1}0$	4.7	1.15	15	73	58
	$\bar{3}\bar{1}0$	4.7	1.2	15	71	56
	$\bar{2}\bar{2}0$	5.65	4.8	8	14	6
	$\bar{4}\bar{2}0$	6.05	1.4	6	64	58
	$\bar{1}\bar{3}0$	5.85	1.1	7	75	68
	$\bar{3}\bar{3}0$	5.7	4.45	8	17	9
	$\bar{5}\bar{3}0$	6.25	3.0	4.5	31.5	27
	$\bar{2}\bar{4}0$	6.35	2.8	4	34	30
	$\bar{4}\bar{4}0$	6.6	3.15	2.5	29.5	27
	$\bar{1}\bar{5}0$	6.75	4.5	1.5	16.5	15
	$\bar{3}\bar{5}0$	6.9	5.85	1	7	6
	$\bar{5}\bar{5}0$	7.1	4.25	0	19	19
	$\bar{4}\bar{6}0$	7.3	6.9	-1.5	1	2.5
	$0\bar{8}0$	7.7	3.25	-3.5	28.5	32
	$0,\overline{10},0$	7.95	6.55	-4.5	3	7.5
R.H.S.	110	4.5	1.0	17	79	62
	310	4.5	0.95	17	82	65
	510	6.1	1.2	6	71	65
	420	6.0	0.66	7	106	99
	530	6.9	1.6	1	58	59 ?
	820	7.3	6.75	-1.5	1.5	3
	910	7.4	6.2	-2	5	7
	10,00	7.4	6.7	-2	2	4

N.B. $\bar{1}\bar{1}0$ and 110, $\bar{3}\bar{1}0$ and 310, $\bar{5}\bar{3}0$ and 530 should, of course, have the same intensity. 530 is however far stronger than $\bar{5}\bar{3}0$ and is also stronger than the value of this spectrum on other films; it has probably therefore coincided in position with a β spot of some other spectrum.

TABLE 12.

STANDARDIZATION OF FILM P30 IN TERMS OF FILM P29.

Spectra common to P29 and P30	Intensity on P29 (secs.)	Intensity on P30 (secs.)	Factor P29/P30.
$\bar{3}\bar{1}0$	mean value 60	55	1.1
510	65	57	1.2
820	3	2.5	1.2
910	7	6.5	1.1
10,00	4	4	1.0
		mean	1.1

(b) Absolute intensity determination.

It is possible to reduce the relative intensities to an approximately absolute scale by comparison with a known crystal; p-dinitrobenzene was chosen as the standard since crystals of convenient shape are easily obtained, the absorption coefficient for this is nearly the same as that for the complex of dinitrodiphenyl with hydroxydiphenyl, and the absolute intensities of its spectra have already been measured (3). A photograph with a crystal of the complex rotating about the c axis and set to include a representative set of spectra was taken, one side of the film being shielded by lead. A crystal of p-dinitrobenzene, having approximately the same size as the complex crystal, was then set to rotate about the b axis; the other side of the film was then exposed under as nearly as possible the same conditions for the same length of time. This procedure was repeated using different spectra and the films were measured up on the microphotometer. In comparing the intensities of the two sets of spectra, absorption effects may be neglected since $e^{-\mu t}$ was virtually the same for the two different crystals. The main difficulty is to make the necessary correction for the size of the two crystals. Owing to the manner in which the intensities were measured they are probably not proportional to the volumes of the crystals, as would be the case had integrated intensities been used; since only peak intensities were measured it seems probable that an increase in cross section of the crystal, as presented to the x-ray beam, would result mainly in an increase in the size of the reflected spots without any great increase in their peak intensity. The intensities may, therefore, be assumed to be proportional to the mean thickness, *t*, of the crystals. Neglecting absorption, the expression for *I*, the intensity as measured on the microphotometer, thus becomes

$$I = \left[\left(\frac{e^2}{mc^2}\right)^2 \lambda^3 \left(\frac{1+\cos 2\theta}{2\sin\theta}\right)\right] F^2_{(hkl)} \, \frac{t}{V_c^2}$$

$$\text{i.e.} \quad I \sim \frac{F^2 \phi \, t}{V_c^2}$$

where V_c is the volume of the unit cell.

The ratio *I* (complex) / *I* (*p*-dinitrobenzene) may then be calculated and a factor is obtained by which the observed relative intensities may be multiplied in order to place them on an absolute scale.

APPENDIX 5.

TEMPERATURE CORRECTION FOR THE ATOMIC SCATTERING FACTORS.

The theoretical values of f calculated by James and Brindley (37) are for atoms at rest. There is, however, considerable thermal motion in soft organic crystals so that it is necessary to reduce the theoretical value of f to allow for this. Values of f for carbon have been obtained experimentally from the accurately known structures graphite, hexamethylbenzene and anthracene and are quoted, for various values of $\sin\theta/\lambda$ by Robertson (38). If these experimental values of f for carbon are compared with the theoretical values obtained by James and Brindley it is found that

$$f_{\text{experimental}} \approx f_{\text{theoretical}} \times e^{-3\cdot 1\left(\frac{\sin\theta}{\lambda}\right)^2}$$

Thus in all calculations of structure factors in the present work the f values obtained experimentally for carbon were used, whilst for oxygen and nitrogen the f values of James and Brindley were reduced by the factor $e^{-3\cdot 1\left(\frac{\sin\theta}{\lambda}\right)^2}$.

APPENDIX 6.

NOTE ON THE SUMMATION METHOD OF LIPSON AND BEEVERS.

When using the method of summing double Fourier series described by Lipson and Beevers (8), care must be taken to see that the summation equations have the right form.

The equations worked out by Lipson and Beevers have the form

$$\sum\sum F(hk)\, e^{+i(hx+ky)}$$

which means that the structure factors would have to be calculated in the form

$$F(hk) = \sum f\, e^{-i(hx+ky)} \qquad \text{or} \qquad F = A - iB$$

It is more usual, however, to calculate structure factors in the form

$$F(hk) = \sum f\, e^{+i(hx+ky)} \qquad \text{or} \qquad F = A + iB$$

and that is the method which has been adopted in this work. The summation equations must then have the form

$$\sum\sum F(hk)\, e^{-i(hx+ky)}$$

and will therefore be somewhat different to those given by Lipson and Beevers, in the case of a crystal which has no centre of symmetry, although the method of summation remains exactly the same.

ACKNOWLEDGEMENTS.

I wish particularly to thank Professor R.W. James and Dr. W.S. Rapson for their constant personal interest and invaluable advice throughout the course of this work. To Professor James I am further indebted for the use of his as yet unpublished manuscript of the second volume to "The Crystalline State"; and to Dr. Rapson and Mr. E. Theal Stewart I am in debt for the preparation and analysis of most of the complexes.

I also wish to thank Dr. P.C. Carman for the helpful discussions I have had with him on the question of bonding in these complexes. I am grateful to Professor F. Walker for the use of apparatus in the Geology Department, and to Mrs. F.C.M. Mathias for help in the measurement of the optical properties of the crystals. I am also grateful to Mr. R.D. Linton for being ever ready to undertake the construction of new apparatus.

To the Beit Railway Trust Board of S. Rhodesia I am indebted for a research fellowship, which enabled me to complete the major portion of this work.

BIBLIOGRAPHY.

(1) Rapson, Saunder & Stewart, J.C.S. (1946) 1110.

(2) Orelkin & Lonsdale, Proc. Roy. Soc. (1934) A**144**, 633.

(3) James, King & Horrocks, Proc. Roy. Soc. (1935) A**153**, 225.

(4) van Niekerk, Proc. Roy. Soc. (1943) A**181**, 314.

(5) Robertson, Proc. Roy. Soc. (1936) A**157**, 79.

(6)a. Lonsdale, Proc. Phys. Soc. (1942) **54**, 314.

b. Lonsdale & Smith, Proc. Roy. Soc. (1941) A**179**, 8.

(7) Bragg W. L., Proc. Roy. Soc. (1929) A**123**, 537.

(8) Lipson & Beevers, Proc. Phys. Soc. (1936) **48**, 772.

(9) Archer, Proc. Roy. Soc. (1946) A**188**, 51.

(10) Dhar, Ind. J. Phys. (1932) **7**, 43.

(11) Huse & Powell, J.C.S. (1940) 1398.

(12)a. Powell, Huse & Cooke, J.C.S. (1943) 153.

b. Powell & Huse, J.C.S. (1943) 435.

(13) Wilson, Proc. Roy. Soc. (1943) A**181**, 360.

(14) James & Saunder, Proc. Roy. Soc. (1947) series A, in the press.

(15)a. Bennett & Willis, J.C.S. (1929) 258.

b. Baker & Bennett, Ann. Rep. Chem. Soc. (1932) **28**, 138.

c. Bennett & Wain, J.C.S. (1936) 1108.

(16)a. Hammick & Sixsmuth, J.C.S. (1935) 580.

b. Hammick & Young, J.C.S. (1936) 1463.

c. Hammick & Hellican, J.C.S. (1938) 761.

d. Davies & Hammick, J.C.S. (1938) 763.

(17)a. Weiss, Nature (1941) **147**, 512.

b. Weiss, J.C.S. (1942) 245.

(18)a. Briegleb, Z. Phys. Chem. (1935) B31, 58.

b. Briegleb & Kambeitz, Z. Phys. Chem. (1936) B32, 305.

c. Briegleb, "Ahrens Sammlung Newsens" (1937) part 37.

(19) Pauling, Proc. Nat. Acad. Sc. (1939) 25, 577.

(20) Gibson & Loeffler, J.A.C.S. (1940) 62, 1324.

(21)a. Hamilton & Hammick, J.C.S. (1938) 1352.

b. Hammick & Yule, J.C.S. (1940) 1540.

(22) Sutton, Trans. Far. Soc. (1946) - "On the application of dielectric measurements to chemistry"- in the press.

(23) Melwyn-Hughes, "Physical Chemistry", Cambridge University Press (1940), 363-368.

(24) Hammick, Andrew & Hampson, J.C.S. (1932) 171.

(25) Pfeiffer, "Organische Molekulverbindungen" (1927).

(26) Anderson, Nature (1937) 140, 583.

(27)a. Hill, J.A.C.S. (1931) 53, 2598.

b. Foote & Fleischer, J.A.C.S. (1934) 56, 870.

(28) Douglas Clark, "The Fine Structure of Matter", Chapman & Hall (1938), part 2

(29) Ewald, Z. Kryst. (1921) A56, 148.

(30) Bernal, Proc. Roy. Soc. (1926) A113, 118.

(31) Buerger, "X-Ray Crystallography", Wiley & Sons.(1942).

(32) Faxén, Z. Phys. (1923) 17, 266.

(33) Waller, "Dissertation Uppsala" (1925).

(34) Laval, Bull. Soc. Franç. Min. (1939) 62, 137.

(35) Lonsdale, Robertson & Woodward, Proc. Roy. Soc. (1941) A178, 43.

(36) van Niekerk, "An x-ray Study of the Internal Structure of Certain Crystals, with Special Reference to 4:4'-Dinitrodiphenyl", Thesis presented to the University of Cape Town (1941).

(37) James & Brindley, Phil Mag. (1931) 12, 81.

(38) Robertson, Proc. Roy. Soc. (1935) A150, 110.

General references.

Bragg, W.H. & W.L., "The Crystalline State", Bell & Sons (1933), Vol. 1.

James, R.W., "The Crystalline State", Vol. 2, in preparation.

Buerger, M.J., "X-Ray Crystallography", Wiley & Sons (1942).

"Internationale Tabellen zur Bestimmung von Kristallstrukturen", Gebrüder Borntraeger (1935).

Lonsdale, K., "Structure Factor Tables", Bell & Sons (1936).