the Darwin formula is obtained (see Zachariasen, 1945, p. 142, Table 3·2). This is

$$R^y_H = \tfrac{8}{3}.$$

Consider now the case of a reflexion for which $|g| \gg 1$ and $|k| \ll |g|$. Then

$$L = \{(y^2+g^2) + |\sqrt{[(y^2-g^2)^2+4y^2g^2]}|\}/(1+k^2)$$
$$= 2(y^2+g^2)/(1+k^2)$$

so that $L \gg 1$. Consequently,

$$P_H/P_0 = L - \sqrt{(L^2-1)} = 1/2L = (1+k^2)/[4(y^2+g^2)].$$

This can be integrated and gives

$$R^y_H = \int_{-\infty}^{+\infty} \frac{P_H}{P_0}\,dy = \frac{\pi}{4}\frac{(1+k^2)}{|g|}. \qquad (22)$$

Hence

$$\rho_H = \frac{1}{4\mu}\frac{N^2e^4\lambda^3}{m^2c^4}\frac{K^2}{\sin\theta_B\cos\theta_B}|F_H|^2\frac{1}{\frac{1}{2}(1-b)}, \qquad (23)$$

which is exactly the expression for an asymmetric Bragg reflexion from a mosaic crystal.

The assumption made in the above derivation that $|g|$ is large may be secured in either of two possible ways: (i) if $|\psi''_0| \gg |\psi'_H|$; or (ii) if $(1-b)/\sqrt{|b|}$ is large, which happens if $b \to 0$ or $\to \infty$, i.e. when either the incident or reflected beam is very oblique to the surface. In such a case, a perfect crystal gives the same integrated reflexion as a mosaic crystal.

The integration was done graphically from the curves shown in Figs. 4, 5 and 6 for the range $-3{\cdot}0 < y < 3{\cdot}0$. Outside this range the value of the integral was found by using an approximate formula with a correction. The numerical values of R^y_H are probably correct to 2%. They are plotted in Fig. 1 together with the corresponding values for a mosaic crystal. These results are discussed in detail in § 2.

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The Crystal Structure of *p*-Dinitrobenzene

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The previous two reports on the crystal structure of *p*-dinitrobenzene are shown to be correct in essence, but to possess serious internal inconsistencies. The earlier of these investigations apparently ceased before the Fourier series was completely refined, while the later determination gives a set of atomic co-ordinates which is not in accord with the given description of the molecule. These co-ordinates show that the molecule is not coplanar, the plane of the nitro group making an angle of 11½° with the plane of the benzene ring. A further structure is proposed, based upon a new double Fourier series investigation, in which the molecule remains non-coplanar, the angle between the two planes being 9½°. The C–N distance is changed from 1·41 to 1·48 A.; the other bond distances and angles remain unaltered.

Introduction

The first complete crystal-structure investigation of *p*-dinitrobenzene was reported by James, King & Horrocks (1935), who employed the double Fourier series method, based upon the absolute intensities from the zonal planes, and using Mo $K\alpha$ radiation. The result was a very distorted molecule, which became the object of considerable criticism, especially by Pauling (1938,

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p. 201). The most important source of error in this work appears to lie in the incomplete refinement of the Fourier series, although it is also likely that the range of observed intensities was insufficient, resulting in the omission of several small terms from the summation.

A measure of the accuracy of a structure is given by the discrepancy $\Delta = \frac{\Sigma\{\,||F_{\text{calc.}}| - |F_{\text{obs.}}||\,\}}{\Sigma|F_{\text{obs.}}|}$, and this has the value of 35 % for the $(h0l)$ zone when the two sets of structure factors are placed upon the same scale. (In the paper, $\Sigma|F_{\text{obs.}}| \neq \Sigma|F_{\text{calc.}}|$.) When the value of Δ is much greater than 20 % for light organic molecules, this may often be taken as an indication of an unfinished or incorrect structure.

A feature of special interest in this projection is the non-parallelism of O_1O_2 and C_2C_3 (see Fig. 2), and the same effect was observed in a subsequent double Fourier synthesis (Abrahams & Robertson, 1947). It is clear that if the molecule is coplanar, and if the nitro group and benzene ring are both truly symmetrical, then these two lines should always be parallel. An examination of the electron contour diagrams of the later work (Llewellyn, 1947), both of the projection on to the (010) plane and the composite picture obtained by three-dimensional sections parallel to (010), showed that this non-parallelism was still very evident, although the molecule was described as coplanar, and as possessing a strictly symmetrical nitro group and benzene ring.

Discussion of the structure

If the new co-ordinates obtained by Llewellyn are expressed on the basis of a set of rectangular axes, in which a new c' axis is used, normal to the original a and b axes, Table 1 is produced.

Table 1. *Co-ordinates in Ångström units*

Atom	x'	y	z'
C_1	0·75	1·04	0·51
C_2	0·40	−0·63	−1·16
C_3	1·15	0·41	−0·65
N	1·53	2·10	1·04
O_1	2·42	2·56	0·32
O_2	1·28	2·49	2·17

These co-ordinates correspond very closely to the bond lengths and angles given in the paper, but on deriving the equation of the planes containing NO_1O_2 and $C_1C_2C_3$, we obtain

$$x' - 1{\cdot}04y + 0{\cdot}58z' + 0{\cdot}05 = 0,$$

and

$$x' - 1{\cdot}23y + 1{\cdot}01z' + 0{\cdot}01 = 0,$$

respectively. These two planes are inclined at an angle of 11° 42′ to each other.

On the establishment of a non-coplanar molecule from Llewellyn's co-ordinates, we resumed our two-dimensional survey, and after complete refinement of the Fourier series in the $(h0l)$ and $(hk0)$ zones was effected, the co-ordinates in Table 2 were obtained.

Table 2. *Co-ordinates in Ångström units*

Values expressed both with respect to the crystallographic axes, and to a set of orthogonal axes as in Table 1.

Atom	x	x'	y	$z = z'$
C_1	0·76	0·74	1·01	0·50
C_2	0·35	0·40	−0·66	−1·19
C_3	1·11	1·14	0·39	−0·67
N	1·59	1·55	2·12	1·05
O_1	2·45	2·44	2·58	0·36
O_2	1·36	1·27	2·52	2·16

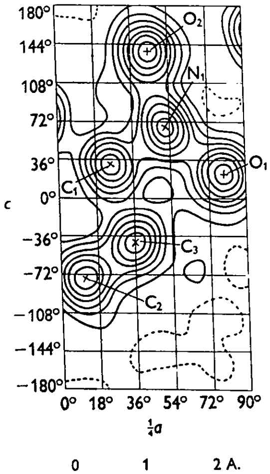

Fig. 1. Projection of the *p*-dinitrobenzene molecule on to the (010) plane, the asymmetric unit only being illustrated. Each contour line represents a density increment of 1 e. A.$^{-2}$, the one-electron line being dotted.

The discrepancies corresponding to these co-ordinates are 15·1 % for the $(h0l)$ zone and 12·1 % for the $(hk0)$ zone, which may be compared with Llewellyn's values of 25·5 % and 17·2 % respectively. These latter values are rather higher than they require to be because of the atomic scattering curve used; thus when the empirical curve we derived (see Table 3) was used with Llewellyn's co-ordinates, the value in the $(h0l)$ zone became 21·5 %. In using this curve, the atoms were weighted in the ratio C:N:O = 6:7:8.

Table 3. *Atomic scattering curve*

(Maximum $f = 100$)

$\sin\theta$ ($\lambda = 1{\cdot}54$ A.)	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9	1·0
f	76	62	49	35	24	17	11	7	4	2

This new set of co-ordinates gives the following bond distances and angles:

C_1–C_2 = 1·38 A. C_1–N = 1·48 A. $\angle O_1$–N–C_1 = 118° 3′
C_2–C_3 = 1·38 A. O_1–N = 1·21 A. $\angle O_2$–N–C_1 = 117° 29′
C_3–C_1 = 1·38 A. O_2–N = 1·21 A. $\angle O_2$–N–O_1 = 124° 28′

and they are probably accurate to ±0·03 A. and ±3°. The equations for the planes defined by NO_1O_2 and $C_1C_2C_3$ are

$$x' - 1{\cdot}00y + 0{\cdot}61z' - 0{\cdot}08 = 0$$

and

$$x' - 1{\cdot}19y + 0{\cdot}97z' + 0{\cdot}03 = 0$$

respectively, and these are inclined to each other at an angle of 9° 25′.

It is of interest to note that the C–N distance has now changed to 1·48 A. from the previous value of 1·41 A. A possible reason for the assignment of this short distance might lie in Llewellyn's method for selecting the positions of the atomic centres. It has been observed both in the case of naphthalene (Abrahams, Robertson & White, 1949) and of anthracene (Sinclair, Robertson & Mathieson, to be published) that if an arbitrary section is taken in the unit cell, which does not happen to pass through the atomic centre, the apparent centre, as given by the section, is not necessarily coincident with the true position. Thus, if the electron cloud as given in electrons per cubic Ångström unit does not represent a truly spherical distribution, then the shift in apparent centre may exceed 0·01 A. at distances of more than 0·1 A. from the true centre. In the same way, arbitrary lines dropped through the unit cell may give a value for that one co-ordinate that is wrong by even larger amounts. Another possible source of error in this three-dimensional determination was the incomplete set of terms used in the summation. Thus, the ($h0l$) zone alone has 17 small terms omitted, which will introduce an appreciable effect into the Fourier series (Robertson & White, 1947).

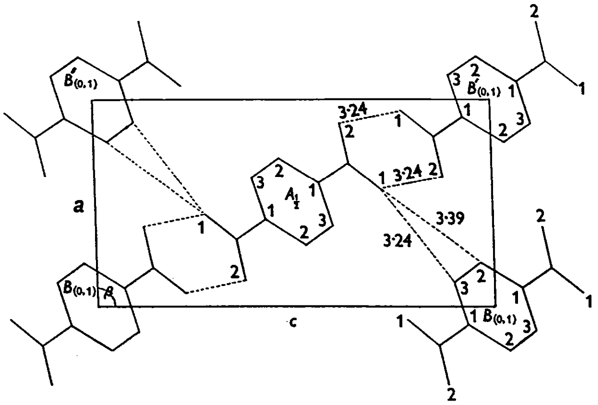

Fig. 2. The relations of five *p*-dinitrobenzene molecules in the *b*-axis projection.

The co-ordinates in Table 2 give the following intermolecular distances:

$O_1(A_{\frac{1}{2}})–C_3(B_0)=3·24$ A. $O_2(B'_0)–C_3(B_0)=3·55$ A.
$O_1(A_{\frac{1}{2}})–C_2(B_0)=3·39$ A. $O_2(B'_0)–C_2(B_0)=4·03$ A.
$C_3(A_{\frac{1}{2}})–C_3(B_0)=4·49$ A. $O_2(B'_0)–C_3(B_1)=3·39$ A.
$O_1(A_{\frac{1}{2}})–O_2(B'_0)=3·24$ A. $O_2(B'_0)–C_2(B_1)=4·32$ A.

There are no very short approach distances between the oxygen atoms and the carbon atoms of adjacent molecules, as in the case of *p*-nitroaniline (Abrahams & Robertson, 1948), although the distance of 3·24 A. between $O_1(A_{\frac{1}{2}})$ and $C_3(B_0)$ suggests a stronger attraction than is usually associated with van der Waals forces. A somewhat similar approach of 3·31 A. between an oxygen atom of a sulphone group and an aromatic carbon atom of an adjacent molecule has also recently been reported (Mathieson & Robertson, 1949).

It is thus clear that the finer details of the *p*-dinitrobenzene structure remain obscure, and will require to await a full three-dimensional determination in which the electron density throughout the whole unit cell is accurately evaluated.

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