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The Crystal Structure of *p*-Nitroaniline, $NO_2.C_6H_4.NH_2$

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p-Nitroaniline forms monoclinic crystals, space group C_{2h}^5–$P2_1/n$, with four asymmetric molecules in the unit cell. A quantitative X-ray investigation based on visual intensity measurements of about 250 reflexions from the axial zones has led to a complete determination of the structure, and the results have been refined by the double Fourier series method, which gives projections of the structure along the three crystal axes. The co-ordinates of the atoms, the molecular dimensions, and the intermolecular distances are given. The nitro-group is symmetrical and lies in the plane of the benzene ring. In addition to rather weak hydrogen bridges connecting the oxygen atoms of the nitro-group to the amino-groups of adjoining molecules, there is a very close approach (2·7–3·0 A.) between one of the nitro-oxygen atoms and three of the aromatic carbon atoms of an adjoining molecule. This appears to be an intermolecular attraction of a new type, and it is suggested that a similar mechanism may be responsible for the formation of a large class of the molecular compounds that are formed between aromatic nitro-compounds and polycyclic hydrocarbons.

Introduction

The structure of the nitro-group in aromatic compounds has been the subject of a number of recent studies, but the results show considerable variation. Thus, the N–O distances have been reported as 1·41 and 1·21 A. in 4:4′-dinitrodiphenyl (van Niekerk, 1942), equal at 1·19 A. and also at 1·20 A. in *m*-dinitrobenzene (Gregory & Lassettre, 1947; Archer, 1946), 1·25 and 1·10 A. in *p*-dinitrobenzene (James, King & Horrocks, 1935), and equal at 1·23 A. in the same compound (Llewellyn, 1947). The values assigned to the O–N–O valency angle vary from 116 to 130° in the same studies, and the C–N distances from 1·41 to 1·54 A. Further work on simple nitro-compounds is therefore required, and the present study is a contribution to this field.

The crystal structure of *p*-nitroaniline is also of special importance in the study of intermolecular attractions and the formation of molecular compounds. It will be shown that the compound displays certain abnormal properties, and that these appear to be explained by a new type of rather powerful attraction between an oxygen atom of the nitro-group and the aromatic carbon atoms of an adjacent molecule in the crystal structure. Judged by the approach distances (2·6–3·0 A.) these attractions are equivalent to the stronger types of hydrogen bridge and probably afford an explanation of the formation of certain large classes of aromatic molecular compounds.

Analysis of the structure

Crystal data. *p*-Nitroaniline, $NO_2.C_6H_4.NH_2$; *M*, 138·1; m.p. 147·5° C.; *d*, calc. 1·422, found 1·418; monoclinic prismatic; $a=12{\cdot}34\pm0{\cdot}02$, $b=6{\cdot}02\pm0{\cdot}02$, $c=8{\cdot}63\pm0{\cdot}02$ A., $\beta=91°\,40'$. Absent spectra, $(h0l)$ when $h+l$ is odd; $(0k0)$ when k is odd. Space group, C_{2h}^5–$P2_1/n$. Four molecules per unit cell. No molecular symmetry required. Volume of the unit cell, 640·7 A.^{3}

Absorption coefficient for X-rays ($\lambda = 1{\cdot}54$ A.), $\mu = 10{\cdot}7$ cm.$^{-1}$ Total number of electrons per unit cell $= F(000) = 288$.

Earlier determinations of the crystal data have been given by Groth (1917) and by Prasad & Merchant (1938). These authors use the orientation $P2_1/c$, while we have adopted $P2_1/n$ to afford more convenient comparison with *p*-dinitrobenzene (Abrahams & Robertson, 1947). When allowance is made for this change of orientation, our results are in quite good agreement with the earlier work.

The analysis of the structure is complicated, as four asymmetric molecules occupy general positions in the unit cell and there are few outstanding features in the intensity distributions among the various spectra. Trial and error methods, based on the known chemical structure and standard covalent radii for the atoms involved, were employed. The strength of the (202) reflexion ($F = 119$, possible maximum about 149) indicates that most of the atoms are concentrated near this plane. This is confirmed by the pronounced cleavage which is displayed by the crystal parallel to this plane. The inclination of the molecular plane to the (010) plane must be fairly high, and considerations based on packing and the observed length of the *b* axis (6·02 A.) indicated values of between 60 and 70° for this angle. Models set up on this basis were found capable of explaining other important intensity features in the higher orders, such as the relatively strong (800), (50$\bar{7}$) and (70$\bar{5}$) reflexions, and some general measure of agreement for the whole ($h0l$) zone of reflexions was soon obtained.

Further refinement of the *x* and *z* atomic co-ordinates was carried out by the Fourier series method, and the results of the final synthesis are given in Fig. 1 as an electron-density map. This covers one molecule in projection on the (010) plane, and the estimated centres of the atoms are indicated by small crosses. The explanatory drawing (upper part) is inverted by the operation of the centre of symmetry.

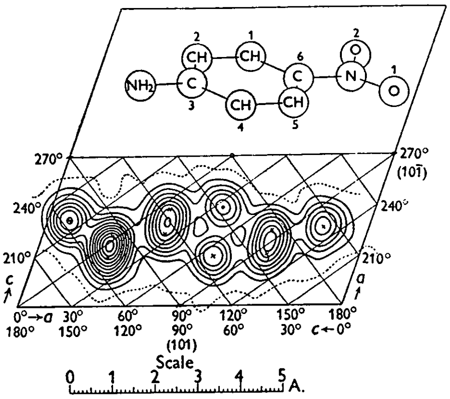

Fig. 1. Projection of the *p*-nitroaniline molecule along the *b* crystal axis on the (010) plane. The boundaries are the *ac* cell diagonals. Each contour line represents a density increment of one electron per A.^{2}, the one-electron line being dotted.

The amino-nitrogen atom, two of the carbon atoms and one oxygen atom are well resolved in this projection, and the centres can be accurately marked. The estimated centres of the other atoms are consistent with the projection of a planar molecule containing a regular hexagonal benzene ring and a symmetrical nitro-group.

A smaller scale drawing is given in Fig. 2, which illustrates the relations of a group of nine molecules in the crystal structure. Hydrogen bonding between the amino- and nitro-groups at the ends of consecutive molecules is clearly one factor which stabilizes the structure, but, in addition, there appear to be strong lateral attractions between the rows of molecules. This has the effect of binding the rows together in pairs, with a larger gap between the next pair. The intermolecular distances involved in these relations are evaluated in the next section (see also Fig. 7).

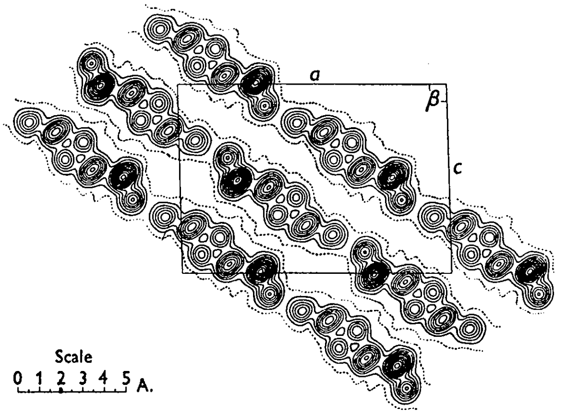

Fig. 2. The relations of a group of nine molecules in the *b*-axis projection. Contour scale as in Fig. 1.

Although satisfactory definition has been achieved in the above projections, and reliable values for the *x* and *z* co-ordinates can be obtained from them, the evaluation of the third co-ordinate of the atoms is a matter of considerable difficulty. Even if a regular planar structure is assumed, there is still a free translation for the molecule as a whole, along the *b* axis, which must be determined from the intensities of the other zones of reflexions. Two of these zones, ($hk0$) and ($0kl$), have been examined in detail. The average values of the structure factors are small, and when the Fourier series method is applied it does not lead rapidly to optimum positions for the atoms as it does for the ($h0l$) zone.

A large number of successive Fourier syntheses were carried out on these two zones of structure factors, leading to projections along the *c* and *a* crystal axes. The final results, with explanatory drawings, are shown in Figs. 3–6. The general definition of the atoms is poor, and they are further obscured by overlap of adjoining molecules lying at different depths in the crystal.

The positions finally assigned to the centres of the atoms in these projections are those which appear to be most consistent with all the data. One method of assessing the reliability of the results is to recalculate the structure factors from the final values of the co-ordinates. The results of this calculation, using a composite empirical atomic scattering curve, are given in Table 4. When the discrepancies are expressed as

$$\frac{\Sigma\{|F_{\text{calc.}}|-|F_{\text{obs.}}|\}}{\Sigma|F_{\text{obs.}}|},$$

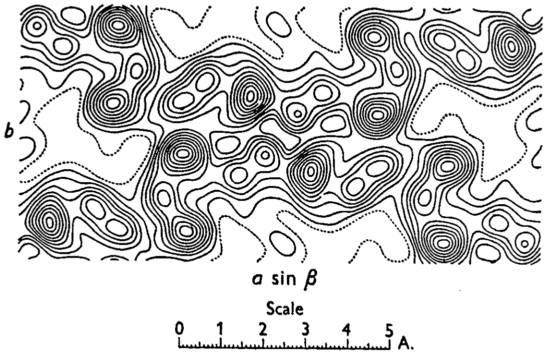

Fig. 3. Normal projection of the unit cell along the c crystal axis. Contour scale: one electron per A.^{2} per line (first line dotted).

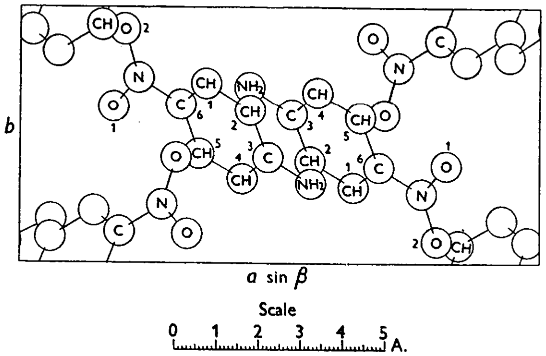

Fig. 4. Arrangement of the molecules in the c-axis projection.

the results for the different zones are found to be 15·2 % for the ($h0l$) structure factors, 22·1 % for the ($hk0$) structure factors, and 26·2 % for the ($0kl$) structure factors, with an average of 19·4 % for all the structure factors taken together. These figures are not very satisfactory, but they are considerably better than those obtained in other recent determinations of similar nitro-compounds (Gregory & Lassettre, 1947; Llewellyn, 1947; Archer, 1946).

The comparatively large values of the discrepancy in the ($hk0$) and ($0kl$) zones mentioned above are probably due more to the small average value of the observed structure factors in these zones than to serious errors in the atomic co-ordinates. This may be demonstrated by expressing the discrepancies as

$$\frac{\Sigma\{|F_{\text{calc.}}|-|F_{\text{obs.}}|\}}{\Sigma|F_{\text{max.}}|},$$

where $F_{\text{max.}}$ represents the maximum value that the structure factor would have if all the atoms made contributions in phase for that particular plane, i.e. if all the atoms lay exactly on the plane. On this basis the discrepancies become 2·68, 3·05 and 3·25 % for the ($h0l$), ($hk0$) and ($0kl$) zones respectively. If these figures are placed on the original scale for the ($h0l$) zone they become 15·2, 17·2 and 18·4 %, showing that the results obtained for the three zones are reasonably comparable.

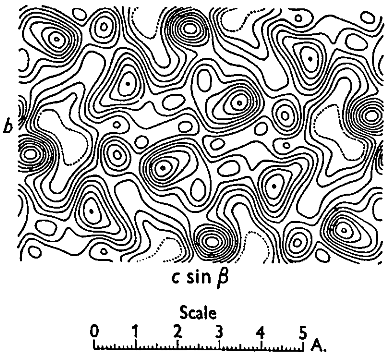

Fig. 5. Normal projection of the unit cell along the a crystal axis. Contour scale: one electron per A.^{2} per line (first line dotted).

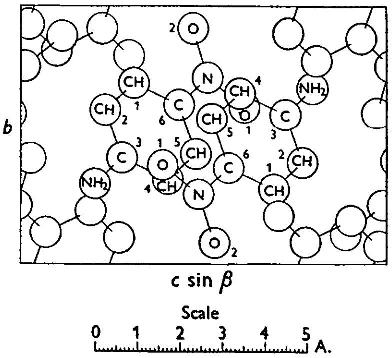

Fig. 6. Arrangement of the molecules in the a-axis projection.

Co-ordinates and dimensions

The x and z co-ordinates obtained from Fig. 1 are probably the most reliable. The y co-ordinates of all the atoms except NH_2, C(5), and C(2), may be obtained directly from Figs. 3 and 5. The other y co-ordinates are deduced by assuming that the figures are projections of regular planar hexagons and that NH_2, C(3), C(6) and N lie on a straight line, an assumption which is justified by the b-axis projection (Fig. 1). The results are given in Table 1, where the co-ordinates are expressed in Ångström units and as fractions of the axial lengths in degrees. The co-ordinates referred to the monoclinic crystal axes are denoted by x, y, z, while x' and z' denote orthogonal co-ordinates referred to the a, b and c' axes, where c' is an axis chosen perpendicular to the a and b crystal axes. These orthogonal co-ordinates are useful for calculating interatomic distances, and are derived from the monoclinic crystal co-ordinates by the relations

$$x' = x + z\cos\beta, \quad z' = z\sin\beta.$$

As β is 91° 40′ in this crystal, z and z' are equal within the limits of measurement.

Table 1. *Co-ordinates referred to crystal axes*

(Origin at centre of symmetry.)

Atom (cf. Fig. 1)	x (A.)	x' (A.)	$\frac{2\pi x}{a}$	y (A.)	$\frac{2\pi y}{b}$	$z=z'$ (A.)	$\frac{2\pi z}{c}$
NH_2	6·90	6·85	201·4°	1·87	111·8°	1·74	72·8°
CH(1)	4·42	4·34	128·8	4·25	254·1	2·66	111·1
CH(2)	5·46	5·40	159·3	3·66	216·7	1·98	82·8
C(3)	5·90	5·83	172·1	2·50	149·4	2·39	99·5
CH(4)	5·28	5·18	154·2	1·99	119·0	3·46	144·3
CH(5)	4·25	4·13	124·1	2·59	154·9	4·13	172·2
C(6)	3·82	3·71	111·4	3·75	224·5	3·73	155·6
N	2·80	2·68	81·8	4·38	261·8	4·41	184·0
O(1)	2·21	2·06	64·6	3·69	220·9	5·28	220·2
O(2)	2·42	2·30	70·6	5·53	329·5	4·06	169·5

The atomic centres given by these co-ordinates are co-planar to within narrow limits (less than 0·04 A.) and they satisfy the equation

$$x' + 0{\cdot}74y + 1{\cdot}30z' - 10{\cdot}30 = 0.$$

The C–C distances within the benzene ring are found to vary from 1·31 to 1·39 A., the shorter distances being CH(2)–C(3), CH(5)–C(6), C(3)–CH(4) and C(6)–CH(1). The two remaining distances, CH(1)–CH(2) and CH(4)–CH(5), give the normal benzene distance of 1·39 A.

The reality of these contractions, however, is felt to be somewhat doubtful, in view of the poor definition of the projections which define the y co-ordinates. It is also significant that the one well-resolved projection (Fig. 1) gives a benzene ring which could be the projection of a regular planar hexagon.

The other interatomic distances within the molecule and the valency angles are listed in Table 2.

Table 2. *Interatomic distances and valency angles*

N–O(1) = 1·26 A.
N–O(2) = 1·26 A.
O(1)...O(2) = 2·22 A.
C(4)–N = 1·39 A.
C(3)–NH_2 = 1·36 A.
O(1)–N–C(6) = 117°
O(2)–N–C(6) = 120°
O(2)–N–O(1) = 123°
C–C distances in the ring = 1·31–1·39 A.

The nitro-group is seen to be symmetrical and lies in the plane of the benzene ring. The O–N–O valency angle appear to be slightly greater than 120°, probably due to mutual repulsion between the oxygen atoms. The bond lengths are probably accurate to within ± 0·04 A. and the angles to within ± 3°, but the precise limits are difficult to estimate.

Intermolecular distances

The approach distances between atoms of adjoining molecules in the crystal structure may be calculated when the atomic co-ordinates (Table 1) are combined with the co-ordinates of the equivalent points for this space group. These are:

$$(A)\ x, y, z; \quad (B)\ \tfrac{1}{2}a - x,\ \tfrac{1}{2}b + y,\ \tfrac{1}{2}c - z;$$
$$(C)\ -x,\ -y,\ -z; \quad (D)\ \tfrac{1}{2}a + x,\ \tfrac{1}{2}b - y,\ \tfrac{1}{2}c + z.$$

Table 3. *Intermolecular distances*

O–N	O(1)*A* ...NH_2(*D*)	3·07 A.
	O(2)*A* ...NH_2(*D*)	3·11
O–C	O(2)*A* ...CH(1)*B*	3·03
	O(2)*A* ...CH(2)*B*	2·66
	O(2)*A* ...C(3)*B*	2·99
	O(2)*A* ...CH(4)*B*	3·55
	O(2)*A* ...CH(5)*B*	3·89
	O(2)*A* ...C(6)*B*	3·69
N–C	N(*A*) ...CH(2)*B*	3·70
	N(*A*) ...C(3)*B*	3·68
C–C	C(3)*A* ...CH(5)*C*	3·38
	C(3)*A* ...C(6)*C*	3·60
	CH(4)*A*...CH(1)*C*	3·60
	CH(4)*A*...CH(4)*C*	3·38
	CH(4)*A*...C(3)*C*	3·38
	CH(4)*A*...CH(5)*C*	3·39
	CH(4)*A*...C(6)*C*	3·49
	CH(4)*A*...CH(2)*C*	3·55
	CH(5)*A*...CH(2)*C*	3·60
	CH(5)*A*...CH(1)*C*	3·69
	CH(5)*A*...C(3)*C*	3·37
	CH(5)*A*...CH(4)*C*	3·42
	C(6)*A* ...CH(1)*C*	3·81
	C(6)*A* ...CH(4)*C*	3·54
	CH(1)*A*...CH(4)*B*	3·96
	CH(1)*A*...CH(5)*B*	3·70
	CH(1)*A*...C(6)*B*	3·82

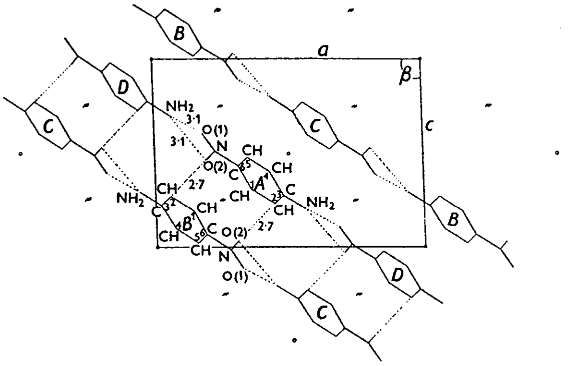

Fig. 7. Intermolecular approach distances. The structure is viewed along the *b*-axis and the drawing is comparable with Fig. 2.

The interesting distances are those which fall below 4 A., and especially those which are less than the normal van der Waals approach of about 3·5 A. The values are collected in Table 3, and the dispositions of the stronger intermolecular attractions are indicated by dotted lines in Fig. 7. The closest approach distances occur between the oxygen atom O(2) and the carbon atoms of one of the adjoining benzene rings.

Three of these distances are between 2·7 and 3·0 A., values which indicate rather powerful bonding forces between the molecules. It should be noted that the centres of the molecules marked *A* and *B* are separated by half a translation along the *b* axis (normal to the plane of the diagram) by the operation of the screw axis, and that the intermolecular bonds between these molecules, indicated by the dotted lines, do not really form a closed circuit as might appear from this diagram but return to another molecule, *A'*, one translation further along the *b* axis and situated vertically above the one drawn. The molecules are therefore not linked in pairs by these bonds, but form a helical arrangement which extends right through the crystal. This kind of arrangement has been observed in other crystals, notably in the hydrogen bonding of the resorcinol structure (Robertson, 1936*a*).

The end-to-end linking of the molecules is maintained by two moderately weak hydrogen bridges (3·1 A.) which extend from the amino-nitrogen to the oxygen atoms of the nitro-group of the next molecule. The helical arrangement referred to in the preceding paragraph also applies to these hydrogen bridges, the two bridges from any one amino-nitrogen atom being directed towards oxygen atoms of nitro-groups at different levels along the *b* axis, although in the projection as drawn in Fig. 7 they appear to form a closed circuit.

The C–C approach distances between the molecules *A* and *C* (Table 3, Fig. 7) are all of the usual van der Waals type and range from the graphite value of 3·4 to about 3·8 A. The carbon-atom approaches in the case of the more closely linked molecules, *A* and *B*, are all greater than 3·7 A.

Discussion

Some caution is necessary in discussing the finer details of this structure because the poor resolution of certain atoms makes the error limits in bond-length determinations rather uncertain. The results (Table 2) are in favour of a symmetrical nitro-group, lying in the plane of the benzene ring, and this is in agreement with the more recent determinations made on other aromatic nitro-compounds. The N–O distances, at 1·26 A., are slightly greater than the values found in *m*- and *p*-dinitrobenzene. On the other hand, our C–N distances, 1·36–1·39 A., are distinctly less than might be expected for the type of groupings involved in this molecule, and are similar to those found in fully conjugated carbon–nitrogen systems, such as the inner ring of the phthalocyanines (Robertson, 1936*b*). It is possible that the distance of the amino-nitrogen atom has been underestimated in this structure, and a final decision on this point as well as on the exact nature of the distortions from the standard 1·39 A. C–C distance in the benzene ring may have to await a more exact three-dimensional determination.

The most important aspect of this structure, however, lies in the intermolecular approach distances (Table 3), and here the general conclusions still hold, even if some atomic positions should be uncertain by as much as 0·1 A. The hydrogen bonding between the amino-groups and the nitro-groups at the ends of the molecules is weak, but the distances (3·07 and 3·11 A.) are of the order to be expected in such a structure, and they correspond closely, for example, to the approach distance of 3·03 A. observed in urea (Wyckoff, 1932).

The dominant feature of the present structure lies in the remarkably close approach distance of 2·66 A. which exists between one of the oxygen atoms of one molecule and an aromatic carbon atom of the next molecule. In all there are three approach distances ranging from 2·66 to 3·03 A. between this oxygen atom and adjoining aromatic carbon atoms (Table 3). All these distances are far below the normal van der Waals approach of 3·4 A., and indicate powerful attractions of a new type. It seems very likely that this type of attraction may be the cause of some of the well-known molecular complexes which are formed between aromatic nitro-compounds and polycyclic aromatic hydrocarbons. Several such complexes have been examined by the X-ray method (Powell, Huse & Cooke, 1943), but no definite evidence of such a close approach between the component molecules has yet been obtained. The complexity of the structures examined may, however, account for the lack of a positive result.

The results obtained by chemical methods show that the stability of molecular complexes of this nature is often increased if an amino-group is substituted in the hydrocarbon. There is also evidence that any molecular linkage must be directly to a carbon atom in the aromatic molecule, because hexamethylbenzene forms a well-defined complex with *s*-trinitrobenzene. This is supported by the present study, which also shows that the intermolecular attachment is between the oxygen atom, and not the nitrogen atom, of the nitro-group and the aromatic carbon atom. With regard to mechanism, it has been suggested (Gibson & Loeffler, 1940) that the linkage is of an electrostatic nature, caused by polarization of an ethylenic linkage in the hydrocarbon by a neighbouring nitro-group and a resultant pairing up of the dipoles.

In the present structure it seems clear that *p*-nitroaniline forms a self-complex, the nitro-group of one molecule acting as the 'acceptor' with the benzene ring of another molecule as the 'donor'. Some early anomalous results of Sudborough & Beard (1910) support this conclusion. These authors found that *s*-trinitrobenzene forms fairly well-defined molecular complexes with a large range of aryl amines, including *o*- and *m*-nitroaniline, but not with *p*-nitroaniline. This result becomes clear if it is realized that the *p*-nitroaniline molecules are already engaged in the formation of a self-complex.

Further evidence of inner molecular complex formation in *p*-nitroaniline has been obtained from the ultraviolet absorption spectra by Dede & Rosenberg (1934). A characteristic band at 3900 A. has been ascribed to some bond resulting from complex formation, and the strength of this bond is greater in *p*-nitroaniline than in the other nitroanilines.

Independent evidence of strong association in *p*-nitroaniline has also been obtained from a study of the entropies of vaporization (Berliner & May, 1925; Berliner, 1928). At an arbitrary concentration of 0·00507 moles per litre the entropy of vaporization for normal liquids is about 13·7 cals. per degree. For *p*-nitroaniline the value is 17·5 cals. per degree, which indicates that the molten substance does not behave as a normal liquid. For the other nitro-anilines a smaller degree of association is detected by the same method, while the nitro-toluenes behave as practically normal liquids.

Experimental

The X-ray work was carried out by means of rotation-, oscillation- and moving-film photographs with Cu $K\alpha$ radiation ($\lambda = 1{\cdot}54$ A.). Suitable crystal specimens were grown from chloroform solution. These were elongated in the direction of the *b* crystal axis, and the (101) and $(10\bar{1})$ faces were usually well developed, the former being a prominent cleavage plane. Detailed exploration of the (0*kl*) (*h*0*l*) and (*hk*0) zones was made by moving-film exposures of the equatorial layer-lines for crystals rotated about the *a*, *b* and *c* axes. The multiple-film technique (Robertson, 1943) was used to obtain accurate correlations between very strong and weak reflexions, the integrated intensities being obtained by careful visual estimation.

For the (0*kl*) zone, two crystal specimens were employed, with cross-sections 0·28 by 0·35 mm. and 0·65 by 0·39 mm., each about 0·80 mm. in length along the *a* axis. The intensity range covered was about 7000 to 1. For the (*h*0*l*) zone, the two crystals employed measured 0·18 by 0·23 mm., and 0·29 by 0·81 mm. in cross-section, and were each about 0·75 mm. in length. The intensity range covered in this zone was about 40,000 to 1. For the (*hk*0) zone, the crystal specimens measured 0·31 by 0·39 mm. and 0·52 by 0·65 mm. and had lengths of about 0·80 mm. The intensity range for this zone was about 3600 to 1.

In all cases the crystals were completely bathed in the X-ray beam, and the intensities of only the weaker reflexions were estimated from the larger specimens. Absorption corrections were not applied in view of the uniformity in cross-section of the smaller of the crystal specimens in each case.

The values of the structure factor *F* were derived from the intensity measurements by the usual formulae for a mosaic crystal, and the results are given in Table 4 under '$F_{\text{meas.}}$'. The calculated values of *F* and the phase constants (or signs) are derived from the final co-ordinates (Table 1). A composite empirical atomic scattering curve was used, derived from a careful correlation of the (*h*0*l*) calculated and observed structure factors. The atoms were then weighted in the ratio C : N : O = 6 : 6 : 9. The composite atomic *f*-values are given below (max. $f = 100$):

$\sin\theta\ (\lambda = 1{\cdot}54)$	0·1	0·2	0·3	0·4	0·5
f	70	55	43	33	23
$\sin\theta\ (\lambda = 1{\cdot}54)$	0·6	0·7	0·8	0·9	1·0
f	15	10	6	4	3

The numerical work of the various Fourier syntheses was carried out by three-figure methods (Robertson, 1948). For this purpose the *a* axis was subdivided into 60 parts (interval 0·205 A.), the *b* axis into 30 parts (interval 0·201 A.) and the *c* axis into 60 parts (interval 0·144 A.). The positions of the contour lines were obtained by graphical interpolation from the summation totals.

In conclusion, one of us (S.C.A.) desires to express his thanks to the Department of Scientific and Industrial Research for a Maintenance Allowance which enabled him to take part in this work.

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Table 4. *Measured and calculated values of the structure factor*

hkl	sin θ (λ = 1·54 A.)	$F_{\text{meas.}}$	$F_{\text{calc.}}$	*hkl*	sin θ (λ = 1·54 A.)	$F_{\text{meas.}}$	$F_{\text{calc.}}$	*hkl*	sin θ (λ = 1·54 Å.)	$F_{\text{meas.}}$	$F_{\text{calc.}}$
200	0·125	23·5	−23·0	107	0·654	8·5	−10·0	$80\bar{8}$	0·868	1·0	− 0·5
400	0·250	1·0	+ 1·0	105	0·475	26·5	−26·5	907	0·863	4·5	− 2·0
600	0·375	16·5	+18·0	103	0·301	< 1·0	− 2·0	905	0·731	1·5	+ 3·0
800	0·500	27·5	−30·0	101	0·116	9·5	− 7·5	903	0·634	< 1·0	− 2·0
10,0,0	0·625	3·5	− 3·5	$10\bar{1}$	0·109	27·0	+26·0	901	0·572	17·0	−13·0
12,0,0	0·750	< 1·0	0	$10\bar{3}$	0·273	10·5	+ 7·5	$90\bar{1}$	0·564	1·0	0
14,0,0	0·875	3·0	+ 1·5	$10\bar{5}$	0·453	15·5	+15·0	$90\bar{3}$	0·615	23·0	−22·5
020	0·257	19·5	−13·0	$10\bar{7}$	0·635	4·0	+ 7·5	$90\bar{5}$	0·709	5·0	− 5·0
040	0·512	22·0	−23·5	$10\bar{9}$	0·821	1·5	− 1·0	$90\bar{7}$	0·885	5·0	− 4·5
060	0·767	7·0	− 7·0	2,0 10	0·923	< 1·0	+ 0·5	$90\bar{9}$	0·974	< 1·0	+ 0·5
002	0·179	13·5	+16·0	208	0·745	2·5	+ 2·5	10,0,8	0·976	< 1·0	− 1·0
004	0·357	27·5	+26·0	206	0·563	15·0	−10·5	10,0,6	0·844	5·0	− 5·0
006	0·536	2·5	− 2·5	204	0·394	< 1·0	0	10,0,4	0·735	1·5	+ 1·5
008	0·714	3·0	+ 2·5	202	0·225	119·0	−114·0	10,0,2	0·652	12·5	+14·5
0,0,10	0·893	3·5	+ 4·0	$20\bar{2}$	0·212	22·5	−22·5	10,0,$\bar{2}$	0·645	< 1·0	+ 1·5
011	0·157	30·0	+28·5	$20\bar{4}$	0·378	4·0	0	10,0,$\bar{4}$	0·711	7·5	− 7·5
012	0·223	5·0	+ 5·0	$20\bar{6}$	0·554	9·5	− 9·5	10,0,$\bar{6}$	0·814	4·0	+ 3·0
013	0·301	20·0	−10·0	$20\bar{8}$	0·728	4·0	− 5·0	10,0,$\bar{8}$	0·939	1·5	+ 1·5
014	0·385	12·0	+12·0	2,0,$\overline{10}$	0·908	1·0	− 0·5	11,0,7	0·954	< 1·0	− 2·0
015	0·472	11·0	−11·0	309	0·842	2·5	+ 2·5	11,0,5	0·837	1·0	+ 0·5
016	0·557	11·5	−11·5	307	0·668	9·0	+11·0	11,0,3	0·748	5·0	+ 3·0
017	0·647	1·0	− 1·0	305	0·502	9·5	−10·5	11,0,1	0·696	< 1·0	− 2·0
018	0·735	1·0	− 2·0	303	0·324	5·0	+ 5·0	11,0,$\bar{1}$	0·687	2·0	+ 1·0
019	0·824	1·0	+ 1·0	301	0·211	8·5	− 8·0	11,0,$\bar{3}$	0·730	2·0	+ 1·5
0,1,10	0·915	3·5	+ 3·5	$30\bar{1}$	0·202	25·5	+30·5	11,0,$\bar{5}$	0·808	2·5	+ 2·5
021	0·271	3·0	+15·0	$30\bar{3}$	0·325	8·0	+ 3·5	11,0,$\bar{7}$	0·921	< 1·0	+ 0·5
022	0·314	5·0	+ 6·5	$30\bar{5}$	0·434	7·0	− 8·5	12,0,6	0·942	< 1·0	+ 1·0
023	0·374	17·0	+17·0	$30\bar{7}$	0·653	< 1·0	− 1·5	12,0,4	0·841	2·0	− 2·5
024	0·443	1·5	+ 4·5	$30\bar{9}$	0·832	5·5	+ 4·5	12,0 2	0·773	1·5	+ 1·5
025	0·521	9·5	+ 2·0	4,0,10	0·949	< 1·0	− 1·0	12,0,$\bar{2}$	0·762	< 1·0	+ 1·0
026	0·600	5·0	− 4·0	408	0·773	3·5	+ 1·0	12,0,$\bar{4}$	0·817	2·0	− 2·5
027	0·684	1·0	− 1·0	406	0·608	1·0	− 6·0	12,0,$\bar{6}$	0·910	1·0	− 3·0
028	0·768	1·0	+ 1·5	404	0·445	16·0	+17·0	13,0,5	0·943	< 1·0	− 0·5
029	0·852	2·5	+ 2·5	402	0·315	9·5	+10·0	13,0,3	0·864	1·0	+ 1·5
0,2,10	0·940	2·5	− 2·5	$40\bar{2}$	0·304	2·5	− 6·0	13,0,1	0·819	2·0	+ 4·0
031	0·394	15·0	−18·0	$40\bar{4}$	0·428	5·5	+ 6·0	13,0,$\bar{1}$	0·814	< 1·0	+ 1·0
032	0·425	3·5	+ 9·0	$40\bar{6}$	0·588	3·5	+ 3·5	13,0,$\bar{3}$	0·845	2·0	− 2·0
033	0·471	4·5	+ 2·0	$40\bar{8}$	0·760	4·0	+ 2·5	13,0,$\bar{5}$	0·913	3·0	+ 0·5
034	0·527	15·0	−15·0	4,0,$\overline{10}$	0·934	1·0	− 0·5	14,0,4	0·953	1·5	+ 1·0
035	0·594	3·0	+ 8·0	509	0·884	2·0	− 2·0	14,0,2	0·898	1·0	− 1·0
036	0·664	3·0	+ 1·0	507	0·720	4·0	+ 4·5	14,0,$\bar{2}$	0·884	1·0	− 0·5
037	0·741	0·5	− 0·5	505	0·559	1·5	+ 3·0	14,0,$\bar{4}$	0·935	2·5	+ 2·5
038	0·820	3·5	− 4·5	503	0·422	11·5	−11·0	15,0,3	0·982	< 1·0	− 0·5
039	0·900	2·0	− 1·0	501	0·328	26·0	−28·5	15,0,1	0·941	< 1·0	− 1·0
0,3,10	0·982	2·0	+ 2·0	$50\bar{1}$	0·409	22·5	−16·0	15,0,$\bar{1}$	0·935	2·5	+ 2·5
041	0·521	8·0	+ 1·5	$50\bar{3}$	0·515	8·5	− 6·0	15 0,$\bar{3}$	0·968	< 1·0	− 0·5
042	0·544	2·0	− 1·5	$50\bar{5}$	0·648	< 1·0	+ 0·5	110	0·144	50·5	+51·0
043	0·581	3·5	+ 2·0	$50\bar{7}$	0·805	21·5	−14·0	120	0·264	20·0	−16·0
044	0·628	1·0	+ 1·0	$50\bar{9}$	0·864	1·0	− 1·0	130	0·390	25·5	−21·5
045	0·685	13·5	+ 2·5	608	0·828	1·0	+ 3·0	140	0·566	3·5	+14·5
046	0·747	6·5	+ 6·5	606	0·674	2·5	+ 4·0	150	0·643	2·0	− 1·0
047	0·815	1·0	+ 2·0	604	0·531	3·0	− 2·5	160	0·771	3·0	+ 2·0
048	0·887	0·5	− 0·5	602	0·419	< 1·0	0	170	0·897	1·5	+ 2·0
049	0·961	1·5	+ 1·5	$60\bar{2}$	0·410	20·5	+19·0	210	0·181	3·5	+ 3·5
051	0·647	1·5	+ 1·0	$60\bar{4}$	0·514	< 1·0	+ 1·0	220	0·285	3·0	− 2·0
052	0·665	1·5	− 1·5	$60\bar{6}$	0·649	5·5	− 4·0	230	0·404	18·0	+20·0
053	0·695	3·5	+ 3·5	$60\bar{8}$	0·805	4·0	− 4·0	240	0·526	< 2·0	+ 0·5
054	0·735	2·0	− 0·5	6,0,$\overline{10}$	0·967	1·5	− 1·5	250	0·652	< 2·0	+ 2·0
055	0·784	4·0	+ 4·0	709	0·938	1·0	0	260	0·777	5·0	+ 4·0
056	0·840	1·0	+ 2·0	707	0·784	1·0	− 4·0	270	0·902	< 1·5	− 1·0
057	0·901	1·0	+ 1·0	705	0·638	7·5	+ 7·5	310	0·228	10·5	− 5·5
058	0·967	< 1·0	+ 1·0	703	0·524	3·5	+ 5·5	320	0·319	2·5	− 2·0
061	0·773	< 0·5	0	701	0·449	10·0	+12·5	330	0·427	2·0	− 4·5
062	0·789	3·0	− 3·0	$70\bar{1}$	0·443	22·0	+21·0	340	0·545	< 2·0	− 2·5
063	0·815	1·0	− 1·0	$70\bar{3}$	0·510	< 1·0	0	350	0·667	2·0	− 1·5
064	0·849	3·5	− 4·0	$70\bar{5}$	0·618	40·5	+36·0	360	0·789	< 2·0	− 0·5
065	0·892	5·5	+ 3·0	$70\bar{7}$	0·759	3·5	+ 4·0	370	0·914	1·5	+ 1·5
066	0·940	1·5	− 1·5	$70\bar{9}$	0·964	5·0	+ 4·0	410	0·282	31·0	−24·0
067	0·996	< 0·5	+ 0·5	808	0·901	1·0	− 1·0	420	0·358	4·5	+ 3·5
071	0·901	2·0	+ 1·0	806	0·754	1·0	+ 1·5	430	0·457	15·0	−15·5
072	0·915	1·0	− 1·0	804	0·631	5·5	+ 5·5	440	0·567	2·0	− 1·0
073	0·937	< 0·5	0	802	0·532	11·5	−13·5	450	0·685	3·0	− 3·0
074	0·967	2·0	+ 2·0	$80\bar{2}$	0·525	< 1·0	+ 0·5	460	0·804	3·0	− 3·0
1,0,11	0·994	1·0	+ 1·0	$80\bar{4}$	0·609	1·5	− 0·5	470	0·926	1·0	+ 2·0
109	0·823	1·0	− 1·0	$80\bar{6}$	0·724	11·0	+10·0	510	0·339	4·5	+10·0

Table 4 (*cont.*)

hkl	$\sin\theta$ ($\lambda = 1{\cdot}54$ A.)	$F_{\text{meas.}}$	$F_{\text{calc.}}$	hkl	$\sin\theta$ ($\lambda = 1{\cdot}54$ A.)	$F_{\text{meas.}}$	$F_{\text{calc.}}$	hkl	$\sin\theta$ ($\lambda = 1{\cdot}54$ A.)	$F_{\text{meas.}}$	$F_{\text{calc.}}$
520	0·403	2·5	+ 2·5	770	0·994	< 1·0	− 1·0	11,1,0	0·698	2·0	− 2·5
530	0·494	1·5	+ 5·0	810	0·516	6·0	− 6·5	11,2,0	0·733	4·0	+ 4·0
540	0·599	< 2·0	− 2·5	820	0·561	3·0	− 3·0	11,3,0	0·786	< 2·0	+ 1·5
550	0·711	3·0	− 6·0	830	0·629	11·0	+ 10·0	11,4,0	0·856	2·0	+ 2·0
560	0·826	< 2·0	− 1·5	840	0·714	10·0	+ 10·0	11,5,0	0·937	< 1·5	+ 0·5
570	0·945	< 1·5	− 1·0	850	0·810	2·0	+ 0·5	12,1,0	0·759	2·5	+ 2·5
610	0·397	15·0	+ 14·0	860	0·914	< 1·5	+ 0·5	12,2,0	0·790	< 2·0	0
620	0·454	16·0	+ 16·0	910	0·575	4·0	− 4·0	12,3,0	0·840	2·5	+ 2·5
630	0·536	2·5	+ 1·0	920	0·616	3·0	+ 3·0	12,4,0	0·956	1·5	− 0·5
640	0·634	7·5	− 7·5	930	0·679	3·0	+ 4·0	12,5,0	0·983	< 1·0	0
650	0·740	7·5	+ 4·0	940	0·759	2·0	+ 2·5	13,1,0	0·821	< 2·0	0
660	0·851	6·0	− 4·5	950	0·850	2·0	− 2·0	13,2,0	0·850	4·0	+ 1·5
670	0·968	1·0	− 1·0	960	0·948	< 1·5	− 2·0	13,3,0	0·897	1·5	− 1·0
710	0·456	15·0	− 9·0	10,1,0	0·637	2·5	+ 1·5	13,4,0	0·958	< 1·0	− 1·0
720	0·507	7·0	− 7·0	10,2,0	0·674	6·0	+ 5·5	14,1,0	0·884	4·5	+ 3·5
730	0·581	3·0	+ 5·0	10,3,0	0·731	< 2·0	− 1·0	14,2,0	0·909	3·0	− 2·0
740	0·672	14·0	+ 5·0	10,4,0	0·805	< 2·0	− 2·0	14,3,0	0·953	< 1·0	+ 0·5
750	0·774	6·5	+ 3·0	10,5,0	0·893	1·5	+ 1·5	15,1,0	0·943	< 1·5	+ 2·0
760	0·881	7·5	+ 4·0	10,6,0	0·987	< 1·0	− 1·0	15,2,0	0·969	1·5	+ 2·0

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The Ambiguity Factor in Implication Theory

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The *implication* is a transformation of a Harker synthesis that has the property of indicating the possible positions of atoms in the crystal structure. The location of the atoms is subject to a certain ambiguity which can be defined by an ambiguity factor, $m = M/q$. M is a basic ambiguity characteristic of the symmetry axis and arising from group products, while q is a degeneracy factor expressing a particular kind of equivalence of these products. The ambiguity factor can also be determined more easily with the aid of missing spectra. It is shown that M is the modulus of the transformation from the implication cell to the crystal cell, and $1/q$ is the fraction of spectra present. The ambiguity factor of any implication synthesis can, therefore, be easily determined from the symmetry and characteristic missing spectra of the space group.

The ambiguity of an implication can be resolved with the aid of m Patterson line syntheses. The implication synthesis, therefore, provides a theoretical device for untangling the Patterson synthesis. This suggests that there should exist a simple relation between the Fourier coefficients in the implication function and the corresponding coefficients in the Fourier expression of the projected electron density. The details of this relation are dealt with in another paper.

Introduction

In an earlier contribution (Buerger, 1946) it was pointed out that the Harker function (Harker, 1936) can be generalized so that it can be applied to any level of the Patterson function (Patterson, 1934, 1935) which represents a translation component of a general screw axis. If the screw is assumed parallel to [001], the generalized Harker function has the form

$$P(xyz_1) = \sum_{h=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} C_{hk} \cos 2\pi(hx+ky) - C'_{hk} \sin 2\pi(hx+ky), \quad (1)$$

where

$$C_{hk} = \sum_{l=-\infty}^{\infty} |F_{hkl}|^2 \cos 2\pi l z_1, \quad (2)$$

$$C'_{hk} = \sum_{l=-\infty}^{\infty} |F_{hkl}|^2 \sin 2\pi l z_1, \quad (3)$$

z_1 is the level of the section in Patterson space, and is equal to 0, $\frac{1}{2}$, $\frac{1}{3}$, $\frac{1}{4}$, or $\frac{1}{6}$.

Because of the antisymmetrical property of the sine, C' vanishes whenever the symmetry provides that $|F_{hkl}|^2 = |F_{hk\bar{l}}|^2$. The condition for this is that the crystal have a plane of symmetry (001) in Patterson