

The Crystal Structure of *p*-Nitroaniline\*

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The structure found by Abrahams & Robertson for *p*-nitroaniline has been re-examined and shown to be incorrect. The correct structure is related to that proposed earlier and may be derived from it by shifting the origin in the projection on (010) from a center of symmetry to a twofold screw axis. The correct structure has been refined with two-dimensional Fourier syntheses and least-squares methods. Within the rather low precision obtainable with the original two-dimensional data, the intra- and inter-molecular geometry is normal. In particular, the abnormally short intermolecular distances characteristic of the structure of Abrahams & Robertson, and often cited in the recent literature as 'polarization bonds', or 'charge-transfer bonds', are completely absent.

## Introduction

Some years ago, Abrahams & Robertson (1948) reported the results of their determination of the crystal structure of *p*-nitroaniline. They found the crystals to be monoclinic, with space group  $C_{2h}^5-P2_1/n$ , the unit cell of four molecules having dimensions  $a = 12.34$ ,  $b = 6.02$ ,  $c = 8.63$  Å,  $\beta = 91^\circ 40'$ . They refined the parameters by use of the three axial Fourier projections calculated with the observed values for  $F_{h0l}$ ,  $F_{hk0}$ , and  $F_{0kl}$ , respectively. Their structure is noteworthy in that there are three remarkably short intermolecular distances of 2.66, 2.99, and 3.03 Å between oxygen and carbon atoms of different molecules which, they stated, 'indicate powerful attractions of a new type'. This feature is rather unusual. Nevertheless, the intrinsic evidence for the correctness of any structure lies in the agreement between the observed and calculated structure factors. Abrahams & Robertson reported an average discrepancy of 15.2% for the (*h*0*l*) zone, 22.1% for the (*h**k*0) zone, and 26.2% for the (0*k**l*) zone. By means of a specious argument which invoked the maximum value that a structure factor would have if all the atoms scattered in phase, they arrived at the conclusion that the agreements for the three zones were 'reasonably comparable'. In spite of the fact that, instead of using a conventional set of form factor curves, they calculated their  $F$  values with a 'composite empirical scattering curve', the atoms being weighted in the curious ratio C:N:O = 6:6:9, there remained more than a few serious discrepancies between  $F_c$  and  $F_o$ , some of the most serious being those shown in Table 1.

Since none of these discrepancies occurred in the

Table 1. Some discrepant structure factors

<i>hkl</i>	$F_o$	$F_c$
(021)	3.0	+15.0
(025)	9.5	+ 2.0
(045)	13.5	+ 2.5
(140)	3.5	+14.5
(510)	4.5	+10.0
(740)	14.0	+ 5.0

zone [010], it seemed reasonable to suppose that the poor agreement in the other two prism zones and the generally poor definition of the atoms in these two corresponding Fourier projections arose from the same cause, namely, that the structure was somewhere in error. Consideration of the data they presented in their Table 4, the observed and calculated structure factors, showed that of the (*h**k*0) reflections with  $h = 2n$  the average discrepancy was 14.7%, while for those with  $h = 2n+1$  the average discrepancy was 34.6%, and similarly, for the (0*k**l*) reflections the values for *l* even and odd were 18.9% and 39.8% respectively. These facts strongly suggest that the origin as chosen by Abrahams & Robertson in the (*h*0*l*) projection lies on the twofold screw axis, rather than on a center of symmetry. Such an interchange would not of course affect the calculated values of  $F_{h0l}$ , nor those of  $F_{hk0}$  or  $F_{0kl}$  where *h* or *l* is even. Practically, this interchange is effected by adding  $\frac{1}{4}$  to the *x* and *z* parameters, while retaining the conventional coordinates for the four equivalent points of  $P2_1/n$ , with the origin on a symmetry center.

## Establishment of the correct structure

A direct test of the correctness of the above idea was made by calculation of the structure factors for the three prism zones, first with the Abrahams & Robertson parameters and then with the parameters altered

\* Editorial note.—See also Short Communications by Abrahams & Robertson (*Acta Cryst.* (1956). 9, 966) and by Ubbelohde & Parry (*Acta Cryst.* (1956). 9, 966).

as described above. In these calculations we used the McWeeny (1951) form factors and, as indicated by some preliminary calculations, an isotropic temperature factor with  $B = 4 \text{ \AA}^2$  and a scale factor of 1.2. Although the comparison of the results with those of Abrahams & Robertson is somewhat less than straightforward, owing to their use of their empirical form factor, there is no doubt that these first calculations, summarized in Table 2, indicate that the new structure is the correct one. It is also apparent from the data of Table 2 that the use of the empirical form factors resulted in misleadingly good average discrepancies for the erroneous structure.

Table 2. Average discrepancies for *p*-nitroaniline

Zone	Original structure, empirical <i>f</i> -curve	Original structure, McWeeny <i>f</i> -curve	Correct structure,* McWeeny <i>f</i> -curve
( <i>h</i> 0 <i>l</i> )	15.2	18.6	18.6
( <i>hk</i> 0), <i>h</i> even	14.7	17.0	17.0
( <i>hk</i> 0), <i>h</i> odd	34.6	48.9	37.2
(0 <i>kl</i> ), <i>l</i> even	18.9	28.7	28.7
(0 <i>kl</i> ), <i>l</i> odd	39.8	50.9	21.8

\* Before refinement.

The signs of the structure factors for the new structure were then used, together with the  $F_o$  of Abrahams & Robertson, to calculate the three Fourier projections. Because the only sign changes in the (*h*0*l*) zone were those for reflections with  $h+l = 4n+2$  (a consequence of the shift in the origin) our projection on (010) is identical with that of Abrahams & Robertson. It is interesting that no sign changes occurred merely as a result of the drastic change from the empirical to the McWeeny form factors. For the other two zones, on the other hand, there were of course numerous sign changes, since the two structures are not the same in these projections. The Fourier projections on (100) and (001), although not completely resolved, show excellent definition of the resolved atoms, and none

of the spurious maxima or irregular peaks characteristic of the projections made with the signs of the original structure (see Figs. 3 and 5 of Abrahams & Robertson).

### Refinement of the parameters

The structure factors for the three zones were then treated by the method of least squares. These calculations, like those described above, were made on the National Bureau of Standards Western Automatic Computer (SWAC) by procedures which have been described elsewhere (Sparks, Prosen, Kruse & Trueblood, 1956). McWeeny's form factors were used throughout.

The least-squares routine, which was devised for analysis of three-dimensional data, calculates in each cycle the shifts in the positional parameters and in the six individual anisotropic temperature factors for each atom, and the change in scale factor. In solving the normal equations, all of the cross-terms among the three positional parameters for each atom and all of the cross-terms among the six temperature factors for each atom are used; all other cross-terms are neglected. Since there are unresolved atoms in the several zones, the neglect of off-diagonal terms probably introduces errors. The three zones were therefore treated separately, since different atoms are unresolved in each. Nine cycles on each zone were performed. During this refinement, there were changes in the parameters averaging 0.023 Å, the largest change being 0.072 Å. None of the shifts in the last two cycles was as much as 0.010 Å; the average shift at this stage was 0.005 Å. A set of best least-squares parameters was then obtained by averaging the two individual results (i.e., for the *x*-parameters, the answers given by the least-squares treatment of  $F_{hk0}$  and  $F_{h0l}$ , and so forth), with the condition, however, that if an atom was resolved in a particular zone, the corresponding least-squares parameter was given triple weight in the averaging.

During the above refinement, the signs of several

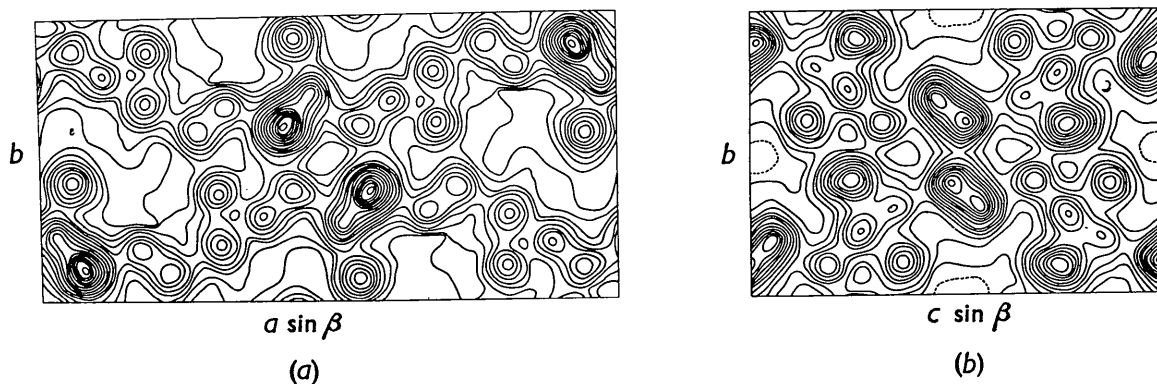


Fig. 1. (a) Fourier projection,  $\rho(x, y)$ . Contours are drawn at intervals of  $1 \text{ e.}\text{\AA}^{-2}$ , starting at  $2.5 \text{ e.}\text{\AA}^{-2}$ . (b) Fourier projection,  $\rho(y, z)$ . Contours are drawn at intervals of  $1 \text{ e.}\text{\AA}^{-2}$ , starting at  $4 \text{ e.}\text{\AA}^{-2}$  (broken).

small structure factors in each zone changed. The three Fourier projections were then recalculated with the new signs. The final projections on (100) and (001) are shown in Fig. 1. The final projection on (010) is not shown because it is virtually identical with that of Abrahams & Robertson; there were only two changes in the signs of  $F_{h0l}$ , those of the weak reflections (109) and (808). The positions of the resolved atoms were located by the Gaussian method (Shoemaker, Donohue, Schomaker & Corey, 1950), and back-shift corrections were obtained and applied in the usual way. Values for twenty-four of the thirty parameters could be obtained from the electron-density maps.

The final parameters (Table 3) were obtained by averaging the least-squares and Fourier values (except for those six parameters which could not be obtained from the Fourier projections). We estimate the average standard error in a final parameter, as obtained from the standard errors given by the least-squares data and from the difference between the Fourier and least-squares results, to be about 0.025 Å. The corresponding limit of error in an interatomic distance is about 0.07 Å, and about 4° for the bond angles.

Table 3. Final positional parameters

Atom	<i>x</i>	<i>y</i>	<i>z</i>
O <sub>1</sub>	0.4292	0.6130	0.8654
O <sub>2</sub>	0.4448	0.9182	0.7187
N <sub>1</sub>	0.4757	0.7300	0.7612
N <sub>2</sub>	0.8133	0.3109	0.4509
C <sub>1</sub>	0.6076	0.7111	0.5578
C <sub>2</sub>	0.6922	0.6198	0.4819
C <sub>3</sub>	0.7283	0.4112	0.5218
C <sub>4</sub>	0.6788	0.3194	0.6509
C <sub>5</sub>	0.5930	0.4154	0.7288
C <sub>6</sub>	0.5562	0.6142	0.6818

The structure factors calculated with the final parameters together with the observed  $F$  values (with a change in the scale factor) reported by Abrahams & Robertson are presented in Table 4. Since we do not feel that much significance attaches to the individual anisotropic temperature factors as obtained in the least-squares procedure with zonal data only, the calculated structure factors include a single isotropic temperature factor with  $B = 4.50 \text{ \AA}^2$ , which is the average of the least-squares values. The average discrepancies for the ( $h0l$ ), ( $hk0$ ), and ( $0kl$ ) zones are 18.2%, 22.1% (15.8% for  $h$  even, 31.6% for  $h$  odd) and 18.5% (20.7% for  $l$  even, 16.0% for  $l$  odd), respectively. ( $R$  for each zone would be decreased by 3–4% if the individual anisotropic temperature factors were used.) All of the serious discrepancies have been removed, and no new ones have been introduced, with the possible exception of (110) and (130), both of which are calculated to be about one-third too small. Although the overall agreement in the case of the ( $hk0$ ) data is apparently satisfactory, and considerably better than for the original structure, the difference between the agreement for reflections with  $h$  even and  $h$  odd remains. The larger discrepancy for  $h$  odd

Table 4. Observed and calculated structure factors.

All  $F_o$  and  $F_c$  have been multiplied by 10.

<i>h</i>	<i>k</i>	<i>l</i>	$F_o$	$F_c$	<i>h</i>	<i>k</i>	<i>l</i>	$F_o$	$F_c$	<i>h</i>	<i>k</i>	<i>l</i>	$F_o$	$F_c$
0	0	0	285	275	0	0	0	18	18					
0	0	1	108	108	0	0	1	18	18					
0	0	2	10	10	0	0	2	18	18					
0	0	3	333	324	0	0	3	18	18					
0	0	4	423	424	0	0	4	18	18					
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0	0	100	336	331	0	0	100	18	18					

is, however, due entirely to the poor agreement for (110) and (130). The agreement for the ( $0kl$ ) data is, on the other hand, entirely comparable for  $l$  even and  $l$  odd.

## Discussion

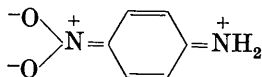
### Intramolecular dimensions

The intramolecular bond lengths and bond angles are listed in Table 5; they are also shown in Fig. 2. The individual variations of the C–C bonds of the benzene ring from the average value of 1.38 Å are not significant, nor is the difference of 0.04 Å between the two N–O bonds of the nitro group. Both C–N bonds are shorter than the standard value 1.47 Å; whether or not these differences are real cannot be definitely decided with the data available at present, but must await the results of a refinement of the complete ( $hkl$ ) data, as the zonal data alone do not afford sufficient resolution for precise parameter determination. Because the exact molecular dimensions might

Table 5. Bond distances and angles

Distance (Å)		Angle (°)	
C <sub>1</sub> -C <sub>2</sub>	1.35	C <sub>6</sub> -C <sub>1</sub> -C <sub>2</sub>	125
C <sub>2</sub> -C <sub>3</sub>	1.37	C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	120
C <sub>3</sub> -C <sub>4</sub>	1.40	C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub>	115
C <sub>4</sub> -C <sub>5</sub>	1.40	C <sub>3</sub> -C <sub>4</sub> -C <sub>5</sub>	125
C <sub>5</sub> -C <sub>6</sub>	1.34	C <sub>4</sub> -C <sub>5</sub> -C <sub>6</sub>	119
C <sub>6</sub> -C <sub>1</sub>	1.39	C <sub>5</sub> -C <sub>6</sub> -C <sub>1</sub>	117
C <sub>6</sub> -N <sub>1</sub>	1.41	C <sub>5</sub> -C <sub>6</sub> -N <sub>1</sub>	122
N <sub>1</sub> -O <sub>1</sub>	1.29	C <sub>1</sub> -C <sub>6</sub> -N <sub>1</sub>	121
N <sub>1</sub> -O <sub>2</sub>	1.25	C <sub>1</sub> -C <sub>6</sub> -O <sub>1</sub>	114
C <sub>3</sub> -N <sub>2</sub>	1.37	C <sub>6</sub> -N <sub>1</sub> -O <sub>1</sub>	121
		C <sub>6</sub> -N <sub>1</sub> -O <sub>2</sub>	121
		O <sub>1</sub> -N <sub>1</sub> -O <sub>2</sub>	124
		C <sub>4</sub> -C <sub>3</sub> -N <sub>2</sub>	123
		C <sub>2</sub> -C <sub>3</sub> -N <sub>2</sub>	123

allow an estimation of the importance of the resonance structure



to the state of the molecule, we have begun the collection of all (*hkl*) reflections accessible to Cu *K*α radiation, and hope to carry out the above refinement soon. This refinement will not, however, affect the discussion below concerning the hydrogen bonding and the molecular packing, since it is unlikely that any

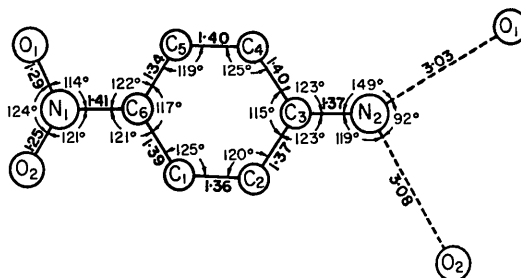


Fig. 2. Intramolecular bond lengths and bond angles.

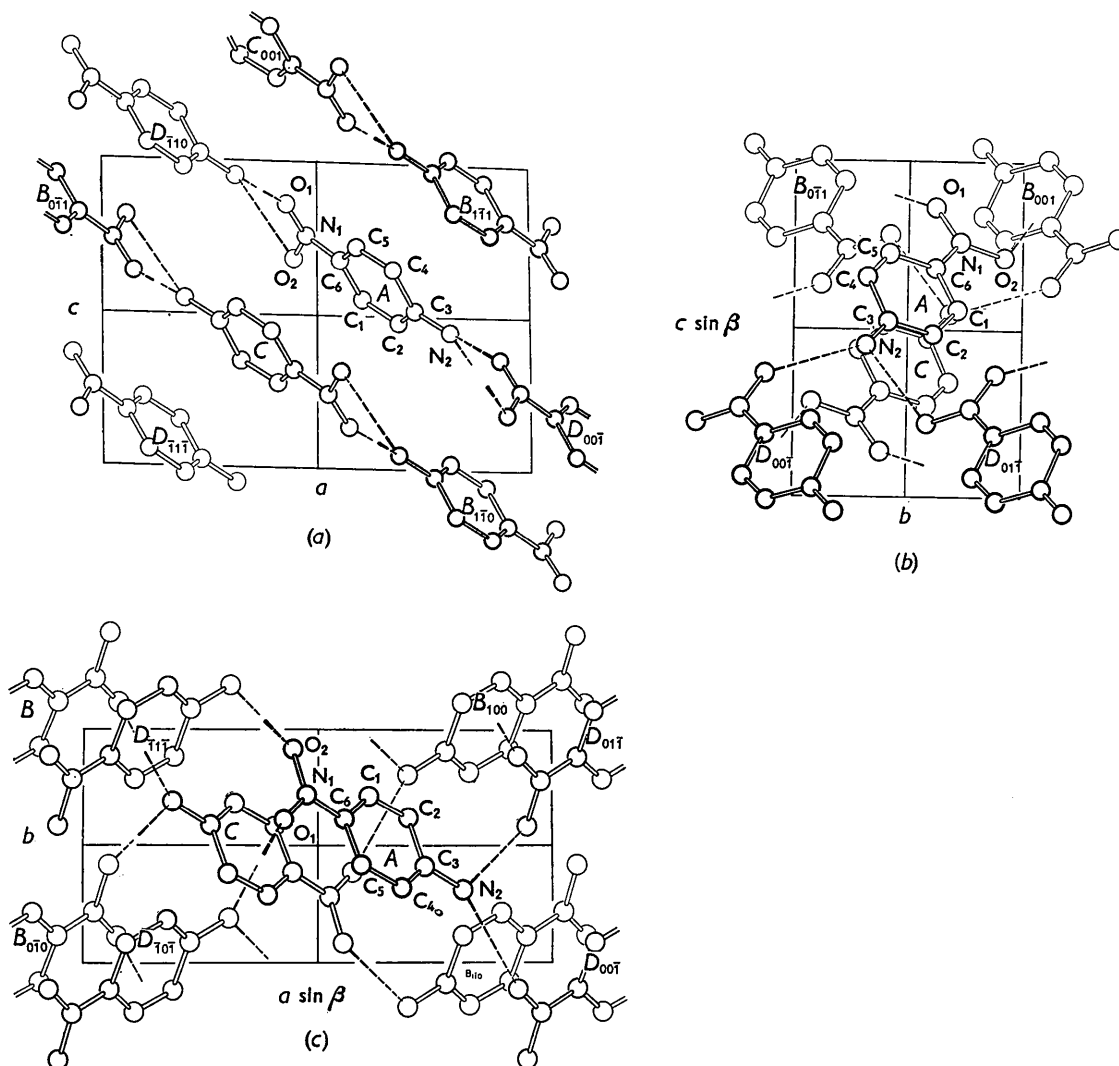


Fig. 3. The structure projected (a) along the *b* axis, (b) along the *a* axis, (c) along the *c* axis. Hydrogen atoms are not shown; dashed lines represent the hydrogen bonds between amino and nitro groups of different molecules.

interatomic distance is in error by as much as 0.07 Å.

The plane of the molecule is defined by the equation

$$0.06680X' + 0.04322Y + 0.06633Z' = 1$$

(where  $X' = X + Z \cos \beta$ , and  $Z' = Z \sin \beta$ ,  $X$ ,  $Y$ , and  $Z$  being expressed in Å). None of the ten atoms of the molecule lies further than 0.06 Å from this plane, the average distance being 0.03 Å.

#### Hydrogen bonding

Fig. 3 shows projections of the structure along the three crystallographic axes. The molecules are labelled according to the four equivalent positions of the space group:

$$\begin{aligned} &A(x, y, z), \\ &B\left(\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z\right), \\ &C(1-x, 1-y, 1-z), \\ &D\left(\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z\right); \end{aligned}$$

molecules equivalent to these by lattice translations are so designated with subscripts.

The amino group forms two hydrogen bonds, to nitro groups of different molecules. The hydrogen bond lengths are 3.03 (to  $O_1$  of molecule  $D_{00\bar{1}}$ ) and 3.08 Å (to  $O_2$  of molecule  $D_{01\bar{1}}$ ). The angle expected for C-N-H is close to 120°, and the two hydrogen atoms are expected to lie in the molecular plane. The observed angles,  $C_3-N_2 \cdots O$  are 149° and 119°, and the respective distances of  $O_1$  of molecule  $D_{00\bar{1}}$  and  $O_2$  of molecule  $D_{01\bar{1}}$  from the plane of molecule  $A$  are -0.47 and 0.57 Å. If we assume that the amino hydrogen atoms lie in the plane defined by  $C_3, N_2, O_1$  ( $D_{00\bar{1}}$ ), and  $O_2$  ( $D_{01\bar{1}}$ ), then a twist of the amino group of 14° from the molecular plane is indicated. The lengths and departures from linearity of these N-H  $\cdots$  O hydrogen bonds are comparable to those in, for example, urea (Vaughan & Donohue, 1952).

#### Packing of molecules

The molecular packing is entirely satisfactory. Intermolecular distances less than 3.9 Å are given in Table 6. Individual distances between molecules  $A$  and  $C$  are not listed because these molecules, which lie in parallel planes—they are related by the center of symmetry at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ —are separated by 3.48 Å. This distance is slightly greater than the separation of 3.34 Å between layers in graphite; consequently there is no reason to believe that the interplanar forces here are even as large as those in graphite. The distances of  $C_4$  to the six carbon atoms of the benzene ring of molecule  $B_{1\bar{1}\bar{1}}$  vary from 3.65 to 3.89 Å, and apparently the situation is similar to that in biphenylene (Waser & Lu, 1944), namely, a hydrogen atom (on  $C_4$ ) pointing in the general direction of the center of an aromatic six-ring. None of the other intermolecular distances is so short as to require any special comment.

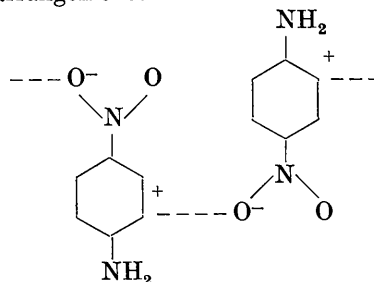
Table 6. Intermolecular distances

From atom $x$ in molecule $A$	To atom $y$ in molecule		Distance $x-y$ (Å)
$N_2$	$O_1$	$D_{00\bar{1}}$	3.03
$N_2$	$O_2$	$D_{01\bar{1}}$	3.08
$C_4$	$C_1$	$B_{1\bar{1}\bar{1}}$	3.65
$C_4$	$C_2$	$B_{1\bar{1}\bar{1}}$	3.71
$C_4$	$C_3$	$B_{1\bar{1}\bar{1}}$	3.89
$C_4$	$C_4$	$B_{1\bar{1}\bar{1}}$	3.86
$C_4$	$C_5$	$B_{1\bar{1}\bar{1}}$	3.84
$C_4$	$C_6$	$B_{1\bar{1}\bar{1}}$	3.75
$O_2$	$C_1$	$C_{010}$	3.32
$O_2$	$C_2$	$C_{010}$	3.66
$O_1$	$O_1$	$C_{001}$	3.17
$N_2$	$O_1$	$D_{01\bar{1}}$	3.83
$O_1$	$N_2$	$B_{101}$	3.71
$N_1$	$N_2$	$B_{101}$	3.58
$C_5$	$N_2$	$B_{101}$	3.79
$C_6$	$N_2$	$B_{101}$	3.71
Plane of $A$	Plane of $C$		3.48

#### The so-called 'polarization bonding'

Since there are no abnormally short intermolecular contacts in crystals of *p*-nitroaniline, the discussion by Abrahams & Robertson of the 'powerful attractions of a new type' in relation to apparently abnormal properties of the substance, and the related discussion by Abrahams (1952) of molecular complex formation between aromatic amines and nitrohydrocarbons, are accordingly without significance. Similarly, Mulliken's (1952) proposal that a covalent bond is formed between a carbon of one ring and a nitro-oxygen of an adjacent molecule as a result of charge transfer, not only in crystalline *p*-nitroaniline but also possibly in solution complexes of aniline with polynitrobenzenes, is unwarranted.

The supported short C  $\cdots$  O distance of 2.66 Å in *p*-nitroaniline was later termed a 'polarization bond' by McKeown, Ubbelohde & Woodward (1951), who studied the anisotropic thermal expansion of *p*-nitroaniline over the range 90–293° K. They concluded that, since the very large  $\alpha_{11}$  expansion of the crystal coincided within 6° with the projection on (010) of the 'polarization bond', the large expansion was due to the presence of this bond in the crystals and, moreover, that at 90° K. the C  $\cdots$  O distance was reduced to 2.44 Å. They made a specific proposal related to that of Mulliken (1952), namely, that the bond arose from actual electron transfer, giving rise to the following arrangement:



This proposal, which has since been cited elsewhere (Harding & Wallwork, 1953), is not only dubious but is not now justified by the structural evidence. The direction of maximum thermal expansion is, moreover, in projection on (010), roughly perpendicular to the plane of the molecule, in the direction in which the intermolecular forces might well be expected to be considerably less than those arising from the N-H...O interactions. This situation thus is somewhat analogous to that in graphite, where the thermal expansion normal to the 'molecular' plane is about ten times as great as that in the plane (Pierrey, 1946).

In his investigation of 1,3-dimethyl-5-iminotetrazole hydrochloride, Bryden (1955) found that the rings lay in parallel planes 3.29 Å apart. This cyclic mesoion would appear to offer very favorable conditions for strong interaction, and yet the distances found correspond to a normal van der Waals separation. Bryden suggested that the interaction between the rings was probably similar to that found by Abrahams & Robertson in *p*-nitroaniline, but concluded that the forces in other directions (mainly hydrogen bonds) were much greater, as shown by the cleavage, and of 'primary importance in determining the structure of the crystal'.

Polarization bonding was also invoked by Harding & Wallwork (1955) in their discussion of the results of their determination of the structure of the chloranil-hexamethylbenzene complex. Their structure, however, contains features much more unusual than the 'slightly less than normal van der Waals separations' which they ascribe to the formation of polarization bonds, to wit, extreme departure from planarity for both the chloranil and hexamethylbenzene molecules. It is difficult to understand how the authors arrived at their estimated standard deviations in the parameters, since the values quoted for  $\sigma_{\text{chlorine}}$  are 20% larger than those for  $\sigma_{\text{carbon}}$ , whereas one would normally expect the errors in the carbon parameters to be almost three times those for chlorine. For this reason, and because only 185 independent reflections were used to determine the 24 positional parameters, their structure cannot be accepted with regard to detail.

The complexes of 1,3,5-trinitrobenzene with naphthalene and aniline in several different solvents have been studied recently by Ross & Labes (1955), who considered that the specific polarization bond O<sup>-</sup>...C<sup>+</sup>

in *p*-nitroaniline was unlikely, but then postulated a structure for their complex with charge transfer at different points. Charge transfer would be expected to lead to distances shorter than the usual van der Waals contacts. The present results show that there are no abnormally short distances in *p*-nitroaniline, nor were any found by Powell, Huse & Cooke (1943) in crystals of the complex formed by *p*-iodoaniline with 1,3,5-trinitrobenzene, the only other structure of this sort which has been investigated.

It would therefore appear that there is not at this time any direct structural evidence for short intermolecular contacts resulting from charge transfer, and the general question of the structural nature of such intermolecular complexes remains open.

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