

The Crystal and Molecular Structure of *N,N*-Dimethyl-*p*-nitroaniline

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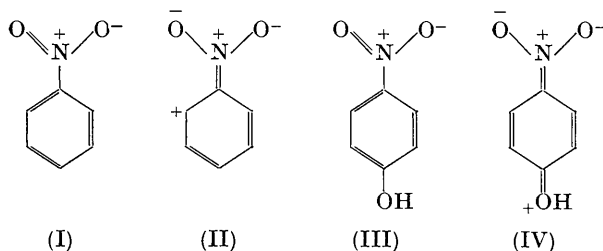
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Crystals of *N,N*-dimethyl-*p*-nitroaniline are monoclinic with two molecules in a unit cell of dimensions $a = 9.73$, $b = 10.56$, $c = 3.96_4$ Å, $\beta = 91^\circ 28'$, space group $P2_1$. The structure was determined with scintillation-counter Cu $K\alpha$ data from the three-dimensional Patterson function, and the positional and anisotropic thermal parameters of the carbon, nitrogen, and oxygen atoms were refined by four cycles of differential syntheses and six cycles of least squares; approximate positions of the four aromatic hydrogen atoms were obtained by Fourier methods. The final R value was 0.116. The aromatic ring, nitro group, and dimethylamino group are each planar, but not coplanar; the nitro group is rotated 2.8° and the Me_2N group 7.3° out of the aromatic plane. The mean bond distances in the molecule are very similar to those in *p*-nitroaniline, but suggest that there is a rather greater contribution of a quinonoid resonance form to the structure of the molecule. The thermal vibrations are similar to those in *p*-nitroaniline, the nitro and the dimethylamino groups showing pronounced torsional oscillation. The intermolecular contacts correspond to normal van der Waals interactions.

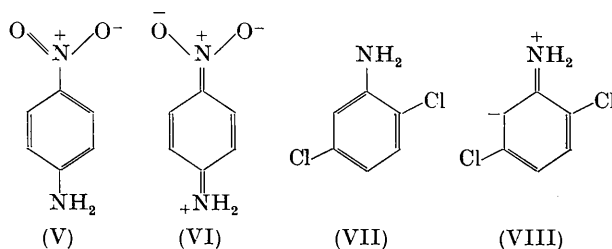
Introduction

The C–N bond distances in aromatic nitro and amino compounds are very markedly different. Study of a number of nitro derivatives indicates that the C–N bond distances are all about 1.48 Å (Trotter, 1960), not significantly different from the single-bond length; this can be accounted for in terms of valence-bond theory by assuming (plausibly) that ‘sacrificial’ structures (such as (II) for nitrobenzene, which is sacrificial relative to (I) since it has one less double bond) make no, or relatively little, contribution to the resonance hybrid molecule (Sakurai, Sundaralingam & Jeffrey, 1963). The carbon–carbon bond length variations are then explicable in terms of differences in hybridization of the carbon σ orbitals (other explanations might of course equally well be advanced).

is, by the criterion described above, comparable in importance to (III), and the measured C–N bond distance is 1.442 and 1.445 Å in the two crystal forms. Similar considerations apply to *p*-nitroaniline, (V) and (VI) (Trueblood, Goldish & Donohue, 1961), where the C–NO₂ length is 1.460 Å. It might be added that the shortenings even in this type of molecule are quite minor in comparison with the values often quoted in textbooks as evidence for resonance interaction between nitro groups and aromatic π -electrons (see *e.g.* Wheland, 1955). The C–C bond distances in molecules of this type are explicable in terms of contributions from structures such as (VI), hybridization differences in *p*-nitroaniline being quite minor (Trueblood, Goldish & Donohue, 1961).



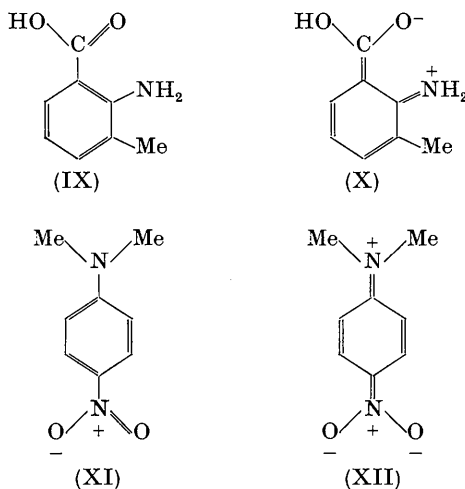
None of the nitro derivatives considered by Trotter (1960) has electron-donating substituents in addition to the nitro groups; when electron-donating groups are introduced, the C–NO₂ bond is shortened to about 1.44–1.46 Å. This again can be rather readily accounted for in valence-bond terms; for 4-nitrophenol for example (Coppens, 1960) the quinonoid structure (IV)



The C–NH₂ bond distances in amino compounds are very significantly shorter than the C–NO₂ lengths in nitro derivatives. No compounds with only NH₂ as substituent appear to have been examined in detail crystallographically, but the C–NH₂ length in 2,5-dichloroaniline (VII), in which contributions from structures like (VIII) are no doubt of importance in contrast to nitro compounds where similar structures are sacrificial, is 1.41 Å (Sakurai, Sundaralingam & Jeffrey, 1963); in 2,2'-dichlorobenzidine the corresponding distance is 1.40 Å (Smare, 1948). In *p*-nitro-

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aniline (V) and 2-amino-3-methylbenzoic acid (IX) where quinonoid forms (VI) and (X) make significant contributions the C-NH₂ distances are still shorter, 1.371 and 1.367 Å (Brown & Marsh, 1963) respectively.



As a further contribution to these studies we have examined the structure of *N,N*-dimethyl-*p*-nitroaniline (XI). Another reason for investigating this structure in detail was to determine whether the bonds from the amino nitrogen atom are strictly coplanar; the NH₂ group has been shown fairly conclusively to be planar in *p*-nitroaniline, but it was felt that more definite information would be obtainable for the NMe₂ group, since the methyl carbon atoms could be located more precisely than the hydrogen atoms in NH₂.

Experimental

Crystals of *N,N*-dimethyl-*p*-nitroaniline grown from ethanol solution are yellow prisms elongated along *c*, with (100) and (010) well developed. The unit-cell dimensions and space group were determined from various rotation, Weissenberg and precession films.

Crystal data (λ , Cu $K\alpha$ = 1.5418, λ , Mo $K\alpha$ = 0.7107 Å)
N,N-Dimethyl-*p*-nitroaniline, C₈H₁₀N₂O₂;
 M.W. 166.2; m.p. 163 °C.

Monoclinic,

$$a = 9.73 \pm 0.01, \quad b = 10.56 \pm 0.01, \\ c = 3.964 \pm 0.005 \text{ \AA}; \quad \beta = 91^\circ 28' \pm 5'. \\ U = 407.2 \text{ \AA}^3.$$

$$D_m = 1.35 \text{ g.cm}^{-3}, \quad Z = 2, \quad D_x = 1.355 \text{ g.cm}^{-3}.$$

Absorption coefficients for X-rays,

$$\lambda = 1.5418 \text{ \AA}, \quad \mu = 9.4 \text{ cm}^{-1}.$$

$$F(000) = 176.$$

Absent spectra: $0k0$ when k is odd.

Space group is $P2_1$ (C_2^2) or $P2_1/m$ (C_{2h}^2).

The intensities of the $hk0$ reflexions were recorded on multiple Weissenberg films and estimated visually;

these data were used in a preliminary study of the *c*-axis projection. Later the intensities of all reflexions with 2θ (Cu $K\alpha$) $\leq 102^\circ$ (corresponding to a minimum interplanar spacing $d = 0.99$ Å) were measured on a General Electric XRD 5 Spectrogoniometer with Single Crystal Orienter, using a scintillation counter and Cu $K\alpha$ radiation (nickel filter and pulse height analyser). The moving-crystal moving-counter technique was used (Furnas, 1957). The intensities were corrected for background, Lorentz and polarization factors were applied, and the structure amplitudes were derived. No absorption corrections were considered necessary. 383 reflexions were observed, 84% of the total number in the range examined; many of the reflexions had weak intensities, and the precision of measurement is probably not high for these planes. There are about 900 reflexions within the copper sphere, but all the higher-order ones were too weak to be observed.

Structure analysis

[001] projection

A trial structure was derived from the *c*-axis Patterson projection, which could be interpreted on the basis of space group $P2_1/m$; assuming a symmetrical model for the molecule at this stage, and using the scattering factors of *International Tables for X-ray Crystallography* (1962) with $B = 5.0$ Å² for all atoms, R , the usual discrepancy index, was 0.38 for the $hk0$ reflexions. A Fourier series was computed and on the resulting electron-density map all the atoms (except hydrogen) were well resolved, although it was not yet possible to distinguish between the dimethyl-amino and nitro groups. A new set of positional parameters was derived with the assumption that two of the end atoms were oxygen and the other two methyl carbon atoms. For this structure R was 0.35, and there were several large differences between F_o and F_c , particularly for the 110 reflexion. On interchanging the methyl carbon and nitro oxygen atoms, R was reduced to 0.28 and all the gross anomalies were removed. Refinement of this projection was then completed by two difference syntheses, which reduced R to 0.18. At no stage was there any indication of deviations from space group $P2_1/m$; the only slight anomaly was that atoms C(2), C(3) C(5), and C(6) seemed a little too close to the mirror plane (giving bond lengths for C(1)-C(2) *etc.* of about 1.35 Å).

Three-dimensional analysis

z Parameters were derived from a consideration of the tilt of the molecule from the plane of the [001] projection, and of the $00l$ structure factors. The resulting structure gave $R(hkl) = 0.49$, and a cycle of differential synthesis reduced this to only 0.47. The three-dimensional Patterson function was therefore computed, and this indicated at once that the space group was $P2_1$, peaks corresponding to inter-

atomic vectors such as C(2)–C(6) for example being considerably displaced from the *y* axis. The previous structure was grossly correct, but when displacements of the atoms were made in accordance with the three-dimensional Patterson map, *R* was markedly reduced to 0.25.

Refinement of positional and isotropic thermal parameters then proceeded by computing successive differential syntheses, with calculated syntheses for temperature factor corrections and for application of series-termination corrections by the 'back-shift' method. One cycle reduced *R* to 0.165; after a second cycle contributions from the four aromatic hydrogen atoms were introduced with $B=6.0 \text{ \AA}^2$ (they had appeared as well-defined peaks on the *c*-axis difference projections) and *R* was reduced to 0.150. A third cycle was carried out, in which the positional and isotropic thermal parameters of the C, N and O atoms, and the positional parameters of the H atoms were refined. The hydrogen atom peak electron densities were in the range 0.46–0.78 e.\AA^{-3} and the shifts in the hydrogen positions were reasonably small, but the curvatures were unrealistic in some cases. *R* was reduced by these changes to 0.146.

Examination of the observed and calculated curvatures of the atoms at this stage indicated that there were significant anisotropic thermal vibrations, and refinement was continued by the least-squares method (block-diagonal approximation). In the first cycle the positional and isotropic temperature factors of all the atoms were refined. However the *B* values for two of the hydrogen atoms increased greatly (to 13 and 26 \AA^2) and in subsequent cycles therefore the hydrogen atoms were not refined; the four aromatic hydrogens were included in all the structure factor calculations with the positional parameters of the third differential cycle and with $B=6.0 \text{ \AA}^2$; and no effort was made to locate the methyl hydrogen atoms. Two further cycles of least squares using anisotropic thermal parameters did not improve the structure factor agreement, but indicated that fudge factors were required to ensure convergence, of 0.5 for positional parameters and scale factor and 0.2 for anisotropic thermal parameters. From this stage third, fourth and fifth least-squares cycle reduced *R* smoothly to 0.125, 0.117, 0.116. Throughout the least-squares refinement $\sum w(|F_o| - |F_c|)^2$ was minimized with $|w| = |F_o|/6$ when $|F_o| < 6$, and $|w| = 6/|F_o|$ when $|F_o| \geq 6$.

A sixth least-squares cycle was computed, but none of the shifts in this cycle (or in the fourth and fifth cycles) was greater than one-quarter of a standard deviation, and refinement was considered to be complete. A fourth set of observed and calculated differential syntheses was then computed; the changes in positional parameters from the least-squares results were all less than one standard deviation (mean differences in *x*, *y* and *z* were 0.005, 0.003 and 0.004 \AA , and maximum changes 0.017, 0.009 and 0.011 \AA). The observed and calculated peak electron-densities

and curvatures are listed in Table 1 (the numbering of the atoms being shown in Fig. 1(a)).

Table 1. Peak electron densities (e.\AA^{-3}) and curvatures (e.\AA^{-5}) in the 4th differential cycle

Atom	ρ		$-\partial^2\rho/\partial x^2$		$-\partial^2\rho/\partial y^2$		$-\partial^2\rho/\partial z^2$	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
C(1)	5.77	5.81	35.9	34.6	35.9	35.9	32.6	31.2
C(2)	5.53	5.63	30.0	30.6	35.6	35.9	30.3	30.2
C(3)	5.58	5.55	31.1	30.3	34.3	34.6	30.2	29.4
C(4)	5.92	6.05	38.5	39.3	34.2	34.6	32.6	33.1
C(5)	5.73	5.83	32.7	32.4	35.8	36.4	32.3	32.0
C(6)	5.62	5.70	31.5	32.5	33.9	34.0	31.7	31.1
C(7)	4.54	4.51	23.5	24.4	25.9	26.8	20.9	21.7
C(8)	4.71	4.89	25.2	27.8	24.7	26.5	24.4	26.3
N(9)	6.83	6.87	41.3	42.2	37.8	38.8	35.4	35.6
N(10)	6.21	6.37	35.6	36.3	29.9	30.6	31.8	32.6
O(11)	6.62	6.67	36.4	36.1	32.9	33.7	31.3	32.4
O(12)	6.21	6.21	32.3	31.7	29.0	28.6	27.2	28.3

The measured structure amplitudes are compared in Table 2 with the values calculated from the final parameters ($R=0.116$ for the observed reflexions).

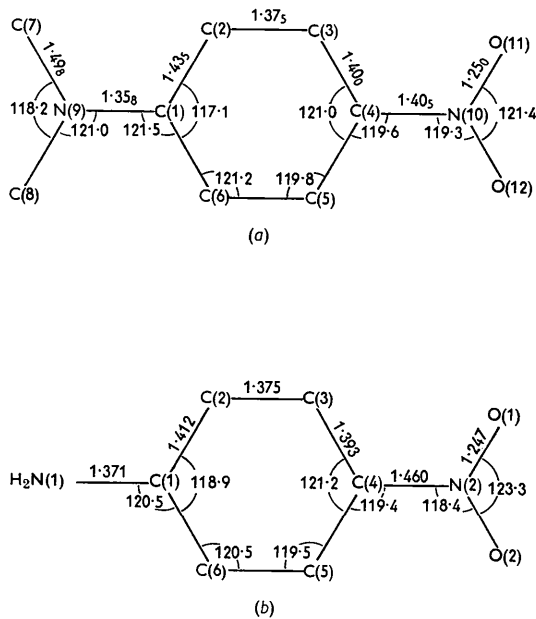


Fig. 1. Mean bond distances (\AA) and valency angles ($^\circ$) in (a) *N,N*-dimethyl-*p*-nitroaniline, and (b) *p*-nitroaniline.

Atomic parameters and molecular dimensions

The final positional parameters are given in Table 3, *x*, *y*, and *z* being coordinates referred to the monoclinic crystal axes and expressed as fractions of the unit cell edges. The carbon, nitrogen and oxygen parameters are those of the fifth least-squares cycle, and those of the hydrogen atoms (which are not considered to be particularly accurate) are from the third differential synthesis. The anisotropic thermal parameters of the fifth least-squares cycle are given in Table 4, the B_{ij}

being the coefficients in the temperature factor expression:

$$\exp - \{B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{23}kl + B_{13}hl + B_{12}hk\},$$

Table 3. *Final positional parameters*

Atom	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	0.3159	0.2490	0.1321
C(2)	0.3744	0.1463	0.3106
C(3)	0.5095	0.1466	0.4127
C(4)	0.5944	0.2473	0.3351
C(5)	0.5429	0.3535	0.1580
C(6)	0.4056	0.3558	0.0625
C(7)	0.0944	0.1354	0.0886
C(8)	0.1153	0.3644	-0.1057
N(9)	0.1815	0.2527	0.0369
N(10)	0.7324	0.2517	0.4429
O(11)	0.7827	0.1562	0.5924
O(12)	0.8014	0.3431	0.3853
H(13)	0.302	0.054	0.332
H(14)	0.541	0.053	0.563
H(15)	0.584	0.428	0.060
H(16)	0.368	0.447	-0.070

Table 4. *Anisotropic thermal parameters*

Atom	$B_{ij} \times 10^4$					
	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
C(1)	145	79	852	-63	48	28
C(2)	153	95	904	9	-61	-24
C(3)	172	91	746	-37	99	12
C(4)	103	92	745	-89	-68	10
C(5)	157	71	773	-92	53	-33
C(6)	154	60	902	20	37	10
C(7)	189	134	1168	-131	-20	-119
C(8)	170	126	886	87	-131	81
N(9)	130	110	785	50	-3	-23
N(10)	160	98	984	-17	-15	10
O(11)	172	146	1307	169	-73	74
O(12)	192	164	1394	158	-68	-114

 $U_{ij} \times 10^3$ (Å²)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1)	6.93	4.46	6.82	-0.67	0.13	0.75
C(2)	7.35	5.37	7.23	0.10	-0.96	-0.63
C(3)	8.21	5.14	5.97	-0.39	0.67	0.32
C(4)	4.95	5.20	5.96	-0.94	-0.96	0.29
C(5)	7.50	4.01	6.18	-0.98	0.21	-0.83
C(6)	7.37	3.39	7.22	0.21	0.00	0.25
C(7)	9.06	7.57	9.34	-1.39	-0.66	-3.05
C(8)	8.18	7.12	7.09	0.92	-1.64	2.08
N(9)	6.23	6.22	6.28	0.53	-0.34	-0.49
N(10)	7.67	5.54	7.87	-0.18	-0.54	0.27
O(11)	8.26	8.25	10.46	1.79	-1.24	1.87
O(12)	9.22	9.27	11.15	1.67	-1.22	-3.01

and U_{ij} the components of the vibration tensors with respect to orthogonal axes *a*, *b*, and *c**.

The bond distances and valency angles in the molecule, before correcting for rotational oscillation errors (Cruickshank, 1956), are given in Table 5, together with their standard deviations calculated from the least-squares residuals.

A calculation of the displacements of the atoms from the best plane through all the carbon, nitrogen and oxygen atoms indicated that the molecule is

Table 5. *Bond distances* (Å) *and valency angles* (°), *before and after correcting for thermal oscillation effects, and their standard deviations*

Bond	<i>l</i>		$\sigma(l)$
	Uncorr.	Corr.	
C(1)-C(2)	1.407	1.410	0.023
C(2)-C(3)	1.365	1.368	0.022
C(3)-C(4)	1.386	1.389	0.023
C(4)-C(5)	1.408	1.411	0.022
C(5)-C(6)	1.379	1.382	0.019
C(6)-C(1)	1.457	1.460	0.022
C(1)-N(9)	1.352	1.358	0.016
C(4)-N(10)	1.400	1.405	0.016
N(9)-C(7)	1.518	1.531	0.022
N(9)-C(8)	1.451	1.464	0.021
N(10)-O(11)	1.262	1.280	0.019
N(10)-O(12)	1.201	1.219	0.019
C(2)-H(13)	1.20		
C(3)-H(14)	1.18		
C(5)-H(15)	0.97		
C(6)-H(16)	1.15		

Angle	θ	$\sigma(\theta)$
C(1)-C(2)-C(3)	121.4	1.4
C(2)-C(3)-C(4)	120.8	1.4
C(3)-C(4)-C(5)	121.0	1.2
C(4)-C(5)-C(6)	118.8	1.3
C(5)-C(6)-C(1)	121.0	1.3
C(2)-C(1)-N(9)	122.6	1.5
C(6)-C(1)-N(9)	120.3	1.5
C(3)-C(4)-N(10)	122.1	1.5
C(5)-C(4)-N(10)	117.1	1.4
C(1)-N(9)-C(7)	118.6	1.5
C(1)-N(9)-C(8)	123.3	1.4
C(7)-N(9)-C(8)	118.2	1.4
C(4)-N(10)-O(11)	118.3	1.4
C(4)-N(10)-O(12)	120.3	1.4
O(11)-N(10)-O(12)	121.4	1.2

significantly non-planar, the nitro group and, more particularly, the dimethylamino group being twisted out of the plane of the aromatic ring. Mean planes were therefore calculated separately for the aromatic ring, for C(1) and the dimethylamino group, and for C(4) and the nitro group; the equations of these planes are given in Table 6, *X'*, *Y*, and *Z'* being coordinates in Å referred to orthogonal axes *a*, *b*, and *c**. The deviations of the atoms from the planes, and the angles between the planes are included in Table 6.

The values of B_{ij} in Table 4 were converted to U_{ij} referred to the orthogonal axes *a*, *b*, and *c**; these U_{ij} were then used with the direction cosines of the mean plane normals and of other molecular axes to compute the mean-square displacements of the atoms in various directions: normal to the molecular plane for all the atoms, radial and tangential in-plane displacements for the aromatic carbon atoms, and parallel and normal to the bonds for the atoms of the substituent groups. These results are summarized in Table 7. The vibrations are very similar to those in *p*-nitroaniline; the aromatic ring can be considered as a rigid body, but there are considerable torsional

Table 6. Mean planes, displacements of atoms from the planes (Å), and angles between the normals

1. Aromatic ring: $0.2546X' - 0.4314Y' - 0.8655Z' + 0.8171 = 0$
 2. C_1-NMe_2 : $0.2484X' - 0.3145Y' - 0.9162Z' + 0.5430 = 0$
 3. C_4-NO_2 : $0.2838X' - 0.3926Y' - 0.8748Z' + 0.5581 = 0$

Atom	Δ_1	Δ_2	Δ_3
C(1)	+0.009	-0.003	
C(2)	+0.006		
C(3)	-0.013		
C(4)	+0.006		+0.004
C(5)	+0.006		
C(6)	-0.014		
C(7)	+0.128	-0.002	
C(8)	-0.192	-0.003	
N(9)	-0.012	+0.008	
N(10)	-0.044		-0.009
O(11)	0		+0.003
O(12)	-0.090		+0.003
H(13)	+0.17		
H(14)	-0.03		
H(15)	+0.11		
H(16)	-0.07		

$$\text{Angle } \widehat{12} = 7.3^\circ$$

$$\text{Angle } \widehat{13} = 2.8^\circ$$

oscillations of both the nitro group and the dimethylamino group about the C-N bonds, with in addition quite large in-plane vibrations of the methyl groups and of the oxygen atoms normal to the N-Me and N-O bonds respectively. The dimethylamino nitrogen atom, N(9), does not have a large vibration normal to the plane as does the corresponding atom in *p*-nitroaniline; this is to be expected since the methyl groups in the dimethyl compound are of course much heavier than the hydrogen atoms of the NH_2 group in *p*-nitroaniline. The corrections to the bond distances for errors due to rotational oscillations (Cruickshank, 1956) were estimated approximately from the atomic displacements of Table 7, and from comparison with the corresponding displacements in *p*-nitroaniline. These corrections increased all the bond distances,

Table 7. Mean-square displacements (\AA^2)

Atom	Normal to molecular plane	In plane			Normal to bond
		Radial	Tangential	Parallel to bond	
C(1)	0.06	0.07	0.06		
C(2)	0.08	0.06	0.07		
C(3)	0.05	0.06	0.08		
C(4)	0.06	0.05	0.06		
C(5)	0.05	0.05	0.08		
C(6)	0.07	0.05	0.07		
C(7)	0.09			0.06	0.11
C(8)	0.08			0.05	0.10
N(9)	0.07			0.06(C1)	
				0.06(C7)	
				0.06(C8)	
N(10)	0.08			0.07(C4)	
				0.06(O11)	
				0.07(O12)	
O(11)	0.11			0.06	0.10
O(12)	0.13			0.06	0.10

by 0.003 Å for C-C bonds, 0.006 Å for C-N bonds, 0.013 Å for N-Me bonds and 0.018 Å for N-O bonds.

All the intermolecular separations less than 3.9 Å were calculated and the more significant distances are given in Table 8; all these contacts correspond to normal van der Waal's interactions. The perpendicular distance between the aromatic planes of molecules related by translation *c* is 3.43 Å (and only distances ≤ 3.6 Å between these molecules are listed in Table 8).

Table 8. Shortest intermolecular contacts

Molecule	1	at	<i>x</i>	<i>y</i>	<i>z</i>
	2		<i>x</i>	<i>y</i>	1 + <i>z</i>
	3		1 - <i>x</i>	$\frac{1}{2} + y$	- <i>z</i>
	4		1 - <i>x</i>	$\frac{1}{2} + y$	1 - <i>z</i>
	5		- <i>x</i>	$\frac{1}{2} + y$	- <i>z</i>
	9		1 + <i>x</i>	<i>y</i>	<i>z</i>
	10		1 + <i>x</i>	<i>y</i>	1 + <i>z</i>

Atom (in molecule 1)	to Atom	in molecule	<i>d</i>
2	1	2	3.49 Å
3	6	2	3.56
4	5	2	3.49
10	5	2	3.58
11	10	2	3.56
5	2	3	3.71
5	3	4	3.57
6	3	3	3.71
6	3	4	3.79
8	7	5	3.52
8	11	3	3.78
12	7	3	3.77
11	7	9	3.68
11	7	10	3.58
12	8	9	3.67
12	8	10	3.62

H-H Contacts			
15	13	3	2.3 ₅
15	14	4	2.3 ₅
16	14	3	2.4 ₄
16	14	4	2.4 ₄

Discussion

In describing the various aspects of the structure of *N,N*-dimethyl-*p*-nitroaniline it is of considerable interest to make comparisons with corresponding features in *p*-nitroaniline (Trueblood, Goldish & Donohue, 1961). Examination of the standard deviations of the bond distance measurements (~ 0.02 Å for *N,N*-dimethyl-*p*-nitroaniline (Table 5) and about 0.007 Å for *p*-nitroaniline) indicates that the results for *N,N*-dimethyl-*p*-nitroaniline are less accurate. There are several possible reasons for this: the space group of *N,N*-dimethyl-*p*-nitroaniline is non-centrosymmetric; the thermal parameters for the *N,N*-dimethyl derivative are somewhat higher, so that the atoms can be located less precisely; the range of reciprocal space explored, and the number of reflexions observed are both less than in *p*-nitroaniline; there

are in the case of *N,N*-dimethyl-*p*-nitroaniline a larger number of weak reflexions for which the intensity measurements are probably not too accurate, and the final structure factor agreement is not quite as good as in *p*-nitroaniline.

The aromatic ring in *N,N*-dimethyl-*p*-nitroaniline is planar within the limits of experimental error, but both the dimethylamino group and the nitro group are twisted out of the aromatic plane about the C-N bonds by 7.3° and 2.8° respectively; viewed from outside the molecule, these twists are in the same direction. The substituent groups and their attached carbon atoms are each planar (the displacements of Table 6 suggest that each group is slightly pyramidal, but none of these deviations is significant); both of the nitrogen atoms are slightly out of the aromatic plane (in the same direction), but the deviations are barely significant. There are further small deviations from a regular model involving slight in-plane displacements of the nitrogen atoms: for example C(2)-C(1)-N(9) = 122.6° and C(6)-C(1)-N(9) = 120.3°; C(3)-C(4)-N(10) = 122.1° and C(5)-C(4)-N(10) = 117.1°. All of these deviations from a regular model are very similar to the corresponding displacements in *p*-nitroaniline; in the latter molecule the amino and nitro groups are twisted 16° and 1.9° respectively out of the plane of the aromatic ring.

Although there are some fairly large differences between chemically equivalent bonds and angles, none of these is significant on the basis of the standard deviations given in Table 5. The mean lengths and angles (standard deviations about 0.01₁-0.01₆ Å, and 0.8°-1.1°) are shown in Fig. 1, where they are compared with the corresponding values in *p*-nitroaniline (the values in both molecules have been corrected for rotational oscillation errors). On the basis of the estimated standard deviations most of the bond length variations in the six-membered ring of *N,N*-dimethyl-*p*-nitroaniline cannot really be considered significant, but the variations do suggest that the quinonoid structure (XII) makes a slightly larger contribution to the hybrid molecule than does the corresponding structure (VI) in *p*-nitroaniline. Bonds C(2)-C(3) and C(5)-C(6) are the same length (1.37₅ Å) in both molecules, the reduction below the length in benzene indicating contributions from the quinonoid forms. In *p*-nitroaniline the two C-C bonds near the nitro group are about the same length as in benzene, while

those near the amino group are significantly longer; this trend is even greater in the *N,N*-dimethyl derivative. Further the C-NMe₂ distance (1.35₈ Å) appears to be shorter than the C-NH₂ length (1.371 Å) in *p*-nitroaniline (the difference is not however statistically significant; it may be noted that the uncorrected lengths were almost identical); the C-NO₂ distance in *N,N*-dimethyl-*p*-nitroaniline is also considerably shorter than the corresponding distance in *p*-nitroaniline (1.40₅ Å as against 1.460 Å, and here the difference is statistically significant). All of these comparisons suggest greater contribution from a quinonoid form in the *N,N*-dimethyl compound, and this can be correlated with the greater electron releasing properties of NMe₂ in comparison with NH₂. The N-Me bond lengths do not differ significantly from the single bond distance.

The bond angle variations in the two molecules are quite similar; the C(2)-C(1)-C(6) angle is less than 120° in each case, and the O-N-O angle is greater than 120°.

None of the intermolecular distances needs special comment, all corresponding to van der Waal's contacts.

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References

- BROWN, G. M. & MARSH, R. E. (1963). *Acta Cryst.* **16**, 191.
 COPPENS, P. (1960). Doctoral Thesis, University of Amsterdam, The Netherlands.
 CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 757.
 FURNAS, T. C. (1957). *Single Crystal Orienter Instruction Manual*. Milwaukee: General Electric Company.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
 SAKURAI, T., SUNDARALINGAM, M. & JEFFREY, G. A. (1963). *Acta Cryst.* **16**, 354.
 SMARE, D. L. (1948). *Acta Cryst.* **1**, 150.
 TROTTER, J. (1960). *Tetrahedron*, **8**, 13.
 TRUEBLOOD, K. N., GOLDISH, E. & DONOHUE, J. (1961) *Acta Cryst.* **14**, 1009.
 WHELAND, G. (1955). *Resonance in Organic Chemistry*. New York: Wiley.