X-Ray Crystal Structure of the Electro-optic Material *meta*-Nitroaniline

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The crystal and molecular structure of the title compound has been determined from three-dimensional *X*-ray data by Patterson methods. Crystals are orthorhombic, $a = 6{\cdot}501(2)$, $b = 19{\cdot}330(4)$, and $c = 5{\cdot}082(2)$ Å, space group $Pbc2_1$, and $Z = 4$. Full-matrix least-squares refinement, using 541 independent reflections, has reached R 0·084. The molecular structure is unexceptional, with mean C–C, C–N, and N–O distances of 1·384, 1·423, and 1·227 Å. The molecule is almost perfectly planar, but some of the exocyclic atoms may be fractionally distorted out of the plane of the benzene ring. The packing of the molecules is quite different from that recently suggested on the basis of packing considerations, and has been shown to correlate well with the linear electro-optic properties.

meta-NITROANILINE is one of a large group of *meta*-disubstituted benzenes crystallising in the *mm*2 point group.[1] As non-centrosymmetric solids these compounds have been investigated electrically, as piezoelectric and linear electro-optic (Pockels effect) materials.[1,2] The electro-optic properties of *m*-nitroaniline are quite unusual and have generated considerable interest, since the ratios of its non-linear optical susceptibilities to the low-field linear constants are markedly anomalous.[2] Previous structural determinations of *m*-dihydroxybenzene [3] (resorcinol) and *m*-dinitrobenzene [4] gave no real clue to the origins of this behaviour. In order to attempt a basic quantitative treatment of both the electro-optic and also the linear electrochromic effect in *m*-nitroaniline we have carried out a three-dimensional *X*-ray structure analysis.

We have already given a preliminary account [2] of the structure and its relation to the electro-optic behaviour. We now report the full details of the structure determination.

EXPERIMENTAL

m-Nitroaniline was recrystallised from acetone as yellow orthorhombic plates.

Crystal Data.—$C_6H_6N_2O_2$, $M = 138{\cdot}13$. Orthorhombic, $a = 6{\cdot}501(2)$, $b = 19{\cdot}330(4)$, $c = 5{\cdot}082(2)$ Å, $U = 638{\cdot}6$ Å^3, $D_m = 1{\cdot}42$, $Z = 4$, $D_c = 1{\cdot}44$, $F(000) = 288$. Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å, $\mu(\text{Cu-}K_\alpha) = 9{\cdot}3$ cm^{-1}. Space group $Pbc2_1$ (No. 29) from systematic absences: $h0l$, $l = 2n + 1$, and $0kl$, $k = 2n + 1$.

The crystals have *b* perpendicular to the plate, and have hemimorphic habit. They are very susceptible to mechanical damage, with easy (010) cleavage. Accurate unit-cell dimensions were obtained by measuring some high-angle α_1 and α_2 reflections on a diffractometer, and they agree reasonably well with previously published values.[5,6] We have retained the non-standard axial notation to facilitate comparison with previous work.

The single crystal used to collect the intensity data was *ca.* 0·23 × 0·13 × 0·05 mm, and was mounted about the *c* axis on a Siemens off-line four-circle diffractometer. Cu-K_α radiation at a take-off angle of 4·5°, a nickel β filter, and a Na(Tl)I scintillation counter were used. The intensities of 541 independent reflections (to θ 60°) were measured by use of the θ—2θ scan technique with a 'five-value' measuring procedure (one side of peak, background, full peak, background on other side of peak, other side of peak). Of these, 40 were judged to be unobserved having a net count $< 2{\cdot}58\sigma$ (*i.e.* below the 99% confidence level). The 130 reflection was measured as a reference every 25 reflections and its net count did not vary noticeably during the data collection (*ca.* 2 days). Data were scaled by use of the reference reflection, and Lorentz and polarisation corrections were applied. At a later stage the data were corrected for absorption according to the method of Busing and Levy,[7] using an 8 × 8 × 8 grid with crystal pathlengths determined by the vector-analysis procedure of Coppens *et al.*[8]

Solution and Refinement of the Structure.—The major programs used to solve and refine the structure were those in the Crystal Structure Calculations System '*X*-Ray '63' [9] and its updated version of July 1970,[10] although in the early stages the least-squares program NUCLS [11] was also used. Calculations were performed on the Imperial College IBM 7094 and CDC 6400 and the University of London CDC 6600 computers.

Since the molecular structure was simple and probably planar we decided to attempt solution by Patterson rather than direct methods. From a three-dimensional origin-removed Patterson synthesis it proved possible to predict the approximate tilt of the molecule, and by use of packing considerations to place the molecules near their true position in the unit cell. The atomic co-ordinates, however, were not sufficiently accurate and several attempts at least-squares refinement were unsuccessful, with some atoms drifting to unacceptable positions. We therefore decided to restrain the individual movement of the atoms and to use the rigid-body refinement facility of the program NUCLS. This had the desired effect, and R dropped to 0·24. Refinement was now transferred to the full-matrix ORFLS program, and isotropic refinement of individual atoms gave R 0·125. In this and all subsequent calculations the z parameter of O(1) was fixed to define the arbitrary origin in this direction. When the atoms were allowed to

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[3] G. E. Bacon and N. A. Curry, *Proc. Roy. Soc.*, 1956, *A*, **235**, 552.

[4] J. Trotter and C. S. Williston, *Acta Cryst.*, 1966, **21**, 285.

[5] K. Hermann and M. Burak, *Z. Krist.*, 1928, **67**, 189.

[6] P. D. Southgate and D. S. Hall, *Appl. Phys. Letters*, 1971, **18**, 456.

[7] W. R. Busing and H. A. Levy, *Acta Cryst.*, 1957, **10**, 180.

[8] P. Coppens, L. Leiserowitz, and D. Rabinovich, *Acta Cryst.*, 1965, **18**, 1035.

[9] '*X*-Ray '63,' system of programs, J. M. Stewart, University of Maryland Technical Report, TR 64 6.

[10] Ref. 9, version of July 1970, ed. J. M. Stewart, F. A. Kundell, and J. C. Baldwin.

[11] NUCLS, full-matrix least-squares program, a revised and rewritten version of the Doedens–Ibers NUGLS, and basically a highly modified version of the Martin–Busing–Levy ORFLS; adapted for use on the University of London CDC 6600 computer by D. Bright and F. A. Stephens.

refine with anisotropic thermal parameters R was reduced to 0·092. From a difference Fourier the six hydrogen atoms were located, and when they were included as a fixed atom contribution, with isotropic temperature factors of their parent atoms, refinement gave R 0·086.

TABLE 1

Fractional co-ordinates with estimated standard deviations in parentheses

Atom	x	y	z
O(1)	0·0948(11)	0·1948(4)	−0·0050(—)
O(2)	−0·0675(10)	0·1025(4)	0·0904(26)
N(1)	0·7102(10)	0·1950(4)	0·5866(26)
N(2)	0·0781(10)	0·1405(4)	0·1240(25)
C(1)	0·5388(12)	0·1522(4)	0·5438(27)
C(2)	0·3959(13)	0·1675(4)	0·3555(28)
C(3)	0·2264(12)	0·1251(4)	0·3260(29)
C(4)	0·2001(13)	0·0643(4)	0·4749(28)
C(5)	0·3443(14)	0·0507(4)	0·6583(28)
C(6)	0·5165(15)	0·0912(5)	0·6965(26)

Data were now corrected for absorption, and, although the R remained virtually unchanged, slightly improved bond lengths resulted. Up to this point, in view of the nearly constant counting statistics in the data collection,[12] each reflection had been assigned unit weight. A weighting scheme of the type suggested by Hughes [13] was now applied, where $w = 1$ for $F < F^*$, $\sqrt{w} = F^*/F$ for $F \geq F^*$, with $F^* = 12$ being the final optimum value. The application of a weighting scheme reduced R to 0·085, and appreciably lower standard deviations were obtained. One very strong reflection thought to be suffering from extinction was removed from refinement to give the final R 0·084. In the last cycle the largest parameter shift was 0·26σ and the mean shift was 0·05σ.

TABLE 2

Final anisotropic thermal parameters and root-mean-square amplitudes of vibration (Å) with estimated standard deviations in parentheses

Atom	$10^4\beta_{11}$	$10^5\beta_{22}$	$10^3\beta_{33}$	$10^4\beta_{13}$	$10^3\beta_{13}$	$10^4\beta_{23}$	Min.	Inter.	Max.
O(1)	455(25)	374(22)	61(4)	−2(6)	−21(3)	30(9)	0·216	0·272	0·357
O(2)	335(20)	503(26)	75(5)	−26(6)	−14(3)	16(11)	0·234	0·298	0·348
N(1)	265(19)	316(21)	53(5)	−8(5)	−13(3)	8(9)	0·201	0·242	0·295
N(2)	199(18)	398(27)	43(4)	1(6)	−9(3)	−5(10)	0·180	0·257	0·276
C(1)	228(20)	286(25)	39(5)	16(6)	−6(3)	−30(9)	0·194	0·203	0·274
C(2)	259(22)	264(22)	33(4)	1(6)	−3(3)	0(9)	0·203	0·224	0·239
C(3)	169(19)	333(27)	40(4)	15(6)	−3(3)	−13(10)	0·181	0·223	0·264
C(4)	293(25)	290(26)	43(5)	−6(6)	1(3)	11(10)	0·221	0·245	0·254
C(5)	308(23)	330(27)	41(5)	2(7)	−6(3)	4(11)	0·218	0·251	0·267
C(6)	302(24)	309(27)	35(4)	10(7)	−8(3)	10(10)	0·191	0·245	0·270

TABLE 3

Fractional co-ordinates of the hydrogen atoms

	x	y	z
H(2)[C(2)]	0·414	0·208	0·259
H(4)[C(4)]	0·060	0·041	0·445
H(5)[C(5)]	0·318	0·006	0·802
H(6)[C(6)]	0·646	0·085	0·837
H(11)[N(1)]	0·814	0·183	0·722
H(12)[N(1)]	0·731	0·239	0·472

The atomic scattering factors for oxygen, nitrogen, and carbon were taken from ref. 14 and for hydrogen from ref. 15. Final fractional co-ordinates of the non-hydrogen atoms and their estimated standard deviations are listed in Table 1, while Table 2 shows the coefficients in the expression for the anisotropic temperature factor $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ and also the root-mean-square amplitudes of vibration along the principal axes of the thermal ellipsoid. Table 3 lists the unrefined co-ordinates of the hydrogen atoms. The observed and the calculated structure amplitudes are listed in Supplementary Publication No. SUP 20692 (7 pp., 1 microfiche).*

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

Figure 1 shows the molecular structure and also the thermal vibration ellipsoids [16] of the non-hydrogen atoms. The more important bond lengths and bond angles are given in Table 4.

The structure of the molecule is as expected, essentially planar, with a mean C–C bond length of 1·384 Å. This is fractionally shorter than the literature mean [17] of 1·394 Å, but our distances have not been corrected for librational movement. The C–N(amino) distance of

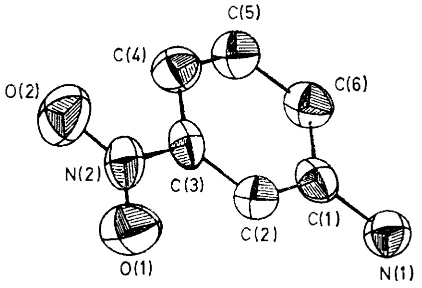

FIGURE 1 The molecular structure; thermal vibration ellipsoids are scaled to enclose 50% probability

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index Issue.

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[14] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[15] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[16] C. K. Johnson, ORTEP Thermal Ellipsoid Plotting Program, Oak Ridge National Laboratory Report, 1965, ORNL 3794.

[17] *Chem. Soc. Special Publ.*, 1965, No. 18.

1·406 † and C–N(nitro) of 1·440 Å may be compared with 1·377 and 1·474 Å in *p,N*-dimethyl-*m*-nitroaniline,[18] 1·371 and 1·460 Å in *p*-nitroaniline,[19] and 1·358 and 1·405 Å in *NN*-dimethyl-*p*-nitroaniline.[20] However, strict comparison is hindered by the likelihood of quinonoid resonance structures in the *p*-nitroanilines, and the generally medium standard of accuracy of these structures (all have $R > 0{\cdot}08$). The average value of the N–O distance (1·227 Å) is very similar to the uncorrected values found in *p*-nitroaniline [19] and *p,N*-dimethyl-*m*-nitroaniline.[18] The oxygen atoms as expected show a higher degree of thermal motion than the other atoms.

TABLE 4

Bond lengths (Å) and angles (°) with standard deviations in parentheses

(*a*) Distances			
C(1)–C(2)	1·366(16)	C(3)–N(2)	1·440(16)
C(1)–C(6)	1·419(15)	C(4)–C(5)	1·348(16)
C(1)–N(1)	1·406(11)	C(5)–C(6)	1·380(13)
C(2)–C(3)	1·381(12)	O(1)–N(2)	1·242(11)
C(3)–C(4)	1·409(15)	O(2)–N(2)	1·211(10)
	Mean C–C	1·384	
	Mean C–N	1·423	
	Mean N–O	1·227	
(*b*) Angles			
C(2)–C(1)–C(6)	119·6(8)	C(3)–C(4)–C(5)	116·7(8)
C(2)–C(1)–N(1)	121·3(9)	C(4)–C(5)–C(6)	123·4(1·0)
C(6)–C(1)–N(1)	119·1(1·0)	C(5)–C(6)–C(1)	118·5(1·0)
C(1)–C(2)–C(3)	119·3(1·0)	C(3)–N(2)–O(1)	119·5(7)
C(2)–C(3)–C(4)	122·3(1·0)	C(3)–N(2)–O(2)	119·9(1·0)
C(2)–C(3)–N(2)	119·3(1·0)	O(1)–N(2)–O(2)	120·5(1·0)
C(4)–C(3)–N(2)	118·3(8)		

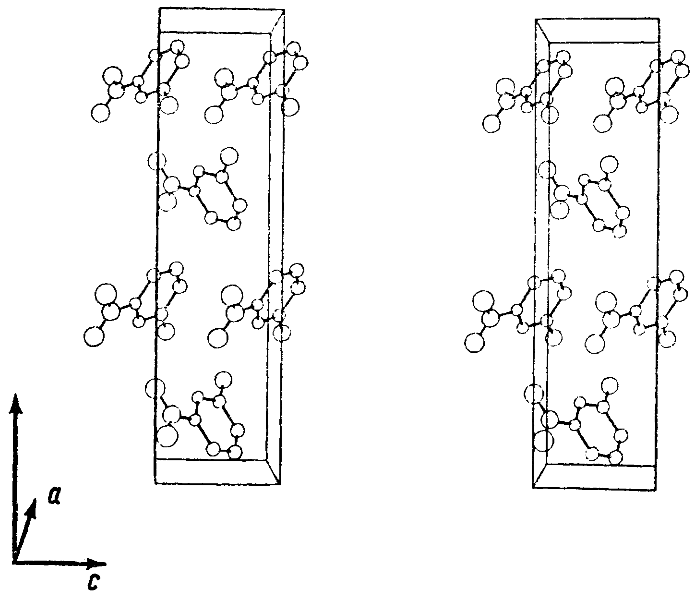

FIGURE 2 A stereoscopic view of the packing

The packing of the molecules is shown in Figure 2 as a stereoscopic pair [16] of drawings. The arrangement of the molecules found is quite different from that recently suggested by Southgate and Hall [6] on the basis of packing considerations. In their structure the molecular plane contained the *b* axis (see Figure 1 in ref. 6), whereas we find that the least-squares plane through the molecule makes angles of *ca.* 59, 58, and 47° with the (100), (010), and (001) planes. The arrangement of the molecules is consistent with the observed (010) cleavage. Figure 2 shows the polar nature of the *c* axis, with all the nitro-groups pointing in the same sense. We stress that no attempt was made to determine the absolute configuration of the crystal by use of the anomalous scattering of oxygen,[21] and the configuration shown in Figure 2 is therefore arbitrary.

The shorter intermolecular distances are shown in Table 5. The shortest of these (3·25 Å) is between an amine nitrogen and a nitro-group oxygen atom. N–H ··· O hydrogen bonds are normally rather shorter, *e.g.* 2·92—2·94 Å for amino-group N–H ··· O bonds in two adenine complexes,[22,23] or 3·07 and 3·14 Å in *p*-nitroaniline.[19] At best, therefore, this distance may represent a very weak interaction. The perpendicular distance between the planes of *m*-nitroaniline molecules stacked in the *c* direction is *ca.* 3·5 Å.

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† *Note added in proof:* In the recent report of the structure of 2,4,6-trinitroaniline (*J. Phys. Chem.*, 1972, **76**, 3597), J. R. Holden, C. Dickinson, and C. M. Bock draw attention (Figure 5) to the inverse relation between the C–N (amino) bond length and the mean length of adjacent C–C bonds in the ring in primary aromatic amines. In *m*-nitroaniline this mean C–C distance is 1·393 Å, and is in excellent agreement with the observed trend.

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[19] K. N. Trueblood, E. Goldish, and J. Donohue, *Acta Cryst.*, 1961, **14**, 1009.

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When a least-squares plane was calculated through all ten non-hydrogen atoms of the molecule it was found that the maximum deviation was 0·03 Å. However, when the calculation was repeated with only the six carbon atoms defining the plane the planarity was now very much better (+0·011 to −0·012 Å), and it does seem likely that at least some of the nitrogen and oxygen atoms are slightly distorted from this plane.

TABLE 5

Intermolecular distances <3·5 Å

$N(1) \cdots O(1^{I})$	3·250	$N(1) \cdots O(1^{V})$	3·317
$N(1) \cdots O(2^{I})$	3·441	$N(1) \cdots N(1^{VI})$	3·312
$C(6) \cdots O(2^{I})$	3·372	$O(1) \cdots O(1^{VI})$	3·317
$N(1) \cdots O(2^{II})$	3·413	$C(2) \cdots O(1^{VI})$	3·378
$C(5) \cdots N(2^{III})$	3·408	$O(2) \cdots C(4^{VII})$	3·388
$C(5) \cdots O(2^{IV})$	3·482		

Superscripts refer to atoms in the following positions:

I $1 + x, y, 1 + z$
II $1 + x, y, z$
III $x, y, 1 + z$
IV $-x, -y, \frac{1}{2} + z$
V $1 + x, \frac{1}{2} - y, \frac{1}{2} + z$
VI $x, \frac{1}{2} - y, \frac{1}{2} + z$
VII $-x, -y, z - \frac{1}{2}$

The full details are given in Table 6. We note that these deviations correspond at best to a rotation of the nitro-group by less than 2°, and that this is quite insignificant compared to a twist of 13° observed for both nitro-groups in *m*-dinitrobenzene.[4]

TABLE 6

Planarity of the molecule

Plane: C(1)—(6)
Equation: $-3{\cdot}29x + 10{\cdot}2y + 3{\cdot}46z = 1{\cdot}65$
Deviations (Å): C(1) 0·011, C(2) −0·012, C(3) 0·011, C(4) −0·010, C(5) 0·010, C(6) −0·011, N(1) 0·033, N(2) −0·042, O(1) 0·012, O(2) −0·067

The implications of this structure to the linear electro-optic and linear electrochromic effects have been discussed,[2,24] and it has been shown that the use of a simple theoretical model, in which *m*-nitroaniline is treated as a molecular solid, gives good correlation between the structure and these properties.

We thank Dr. S. R. Fletcher for assistance in collecting the diffractometer data and for adaptations to the rigid-body refinement program used in the early stages of solution of the structure, Dr. E. A. D. White for discussions, Professor D. Rogers for use of the Siemens diffractometer, and the Post Office for a Postgraduate Award (to J. L. S.).

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