

Structural Basis for the Absence of Thermal Mesomorphism in *p*-[(*p*-Methoxybenzylidene)amino]phenol

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The crystal structure of the title compound (2) has been determined in order to establish the role of hydrogen-bond formation in inhibiting thermal mesomorphism. Hydrogen bonds link the molecules in the crystal in infinite interlocking zig-zag chains with the terminal hydroxy-groups acting as donors and the central nitrogen atoms as acceptors (O—H ··· N 2.756 Å). The angles between the long molecular axes in the chains are alternately 70 and 110°, and the overall molecular packing is of the herring-bone type and unsuited to mesophase formation.

Crystals conform to space group $P2_1/n$ with $a = 11.375(5)$, $b = 17.307(8)$, $c = 6.007(4)$ Å, $\beta = 92.23(3)^\circ$, and $Z = 4$. The structure was solved by direct methods, and least-squares refinement yielded R 0.043 for 1 421 independent significant reflections measured by counter diffractometry.

It is well known that the thermal mesomorphism characteristic of *para*-substituted alkyl- or alkoxy-derivatives of benzylideneanilines and related compounds is suppressed when the counter wing group contains a functional group capable of taking part in intermolecular hydrogen-bond formation,¹ an important exception being for carboxy-groups where intermolecular association normally leads to dimer formation often accompanied by enhancement of nematic or smectic behaviour.² As an example of such inhibition, *p*-[(*p*-methoxybenzylidene)amino]benzotrile (1) shows a nematic phase between 117 and 124° whereas *p*-[(*p*-methoxybenzylidene)amino]phenol (2) melts cleanly to an isotropic liquid at 188 °C.



(1) R = CN

(2) R = OH

Two possible ways in which hydrogen bonding in (2) might act to inhibit mesophase formation suggest themselves. On the one hand, the formation of hydrogen bonds might lead to a mode of molecular packing in the crystal in which the parallel imbricated arrangement of molecules associated with nematic behaviour might be destroyed. Such a situation might be likely if the

¹ G. W. Gray, 'Molecular Structure and the Properties of Liquid Crystals,' Academic Press, London, 1962, p. 162.

hydrogen bonding involved interactions between the terminal donor group of one molecule and the central nitrogen atom of another since steric factors would then favour a T form for the associated pair. On the other hand, the intermolecular association might not destroy an otherwise suitable imbricated or layered arrangement of molecules in the solid, but might act solely to strengthen intermolecular attractions so that the melting point of the substance would be raised above the upper limit of temperature at which a mesophase would remain stable. Such stabilization of an acceptably imbricated structure, albeit involving aromatic–aromatic interactions, has been found in the crystal structures of *p*-methoxy- and *p*-ethoxy-benzoic acids.³ For (2), lateral or terminal intermolecular hydrogen bonding involving the methoxy-oxygen atom as an acceptor might lead to such a situation.

To establish the structural basis by which hydrogen bonding acts to inhibit mesophase formation in (2) we have determined its crystal structure and have found that the association involves molecules related by the space-group glide operations linked in infinite interlocking chains. The terminal hydroxy-groups act as donors and the central nitrogen atoms as acceptors. The

² G. M. Bennett and B. Jones, *J. Chem. Soc.*, 1939, 420.

³ R. F. Bryan, *J. Chem. Soc. (B)*, 1967, 1311; R. F. Bryan and J. J. Jenkins, *J.C.S. Perkin II*, 1975, 1171.

angles between the long molecular axes in the chains are alternately 70 and 110 °C, and the overall arrangement of molecules in the solid is of a herring-bone type unsuited to mesophase formation.

RESULTS AND DISCUSSION

Final positional parameters* with their estimated standard deviations are given in Table 1. Bond lengths and angles and the numbering scheme adopted are shown in Figure 1.⁴

TABLE 1

Positional parameters as fractions of the unit cell edges (O, N, and C $\times 10^4$, H $\times 10^3$). Standard deviations, in parentheses, are applicable to the least significant figure quoted.

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
O(1)	-3 908(1)	-3 060(1)	2 154(2)
C(2)	-2 900(2)	-2 633(1)	2 292(3)
C(3)	-2 649(2)	-2 228(1)	4 221(4)
C(4)	-1 627(2)	-1 809(1)	4 487(3)
C(5)	-837(2)	-1 771(1)	2 764(3)
C(6)	-1 097(2)	-2 170(1)	817(3)
C(7)	-2 116(2)	-2 600(1)	569(3)
N(8)	223(1)	-1 344(1)	3 165(3)
C(9)	616(2)	-934(1)	1 570(4)
C(10)	1 675(2)	-465(1)	1 779(4)
C(11)	2 381(2)	-411(1)	3 717(4)
C(12)	3 363(2)	46(1)	3 828(4)
C(13)	3 682(2)	469(1)	1 959(4)
C(14)	2 987(2)	439(1)	32(4)
C(15)	2 004(2)	-30(1)	-54(4)
O(16)	4 689(1)	886(1)	2 234(3)
C(17)	5 101(2)	1 297(1)	368(5)
H(1)	-415(3)	-324(2)	70(5)
H(3)	-322(2)	-225(1)	539(3)
H(4)	-142(2)	-152(1)	587(3)
H(6)	-52(2)	-215(1)	-36(3)
H(7)	-229(2)	-288(1)	-81(3)
H(9)	13(2)	-93(1)	9(3)
H(11)	218(2)	-68(1)	501(4)
H(12)	392(2)	8(1)	520(4)
H(14)	318(2)	76(1)	-120(4)
H(15)	149(2)	-6(1)	-139(3)
H(17a)	519(2)	98(1)	-95(4)
H(17b)	452(2)	173(2)	-8(4)
H(17c)	586(2)	154(1)	93(4)

A fair number of benzylideneanilines have been studied by X-ray diffraction methods, primarily to confirm the molecular non-planarity suggested by u.v. spectral measurements,⁵ and to test the effects of substitution^{6,7} and of crystal packing forces⁸ on molecular conformation. A fairly consistent pattern of bond lengths and, more especially, bond angles has been found for the central region of these molecules, and their conformations have been described in terms of the angles between the three planar units defined by the phenyl rings and the central four-atom C-N=C-C moiety. Details of previous results are given in Table 2, together with the corresponding results from this analysis.

In the other molecules studied, with the exception of

* Thermal parameters, bond lengths and angles involving hydrogen atoms, and observed and calculated structure amplitudes are listed in Supplementary Publication No. SUP 22176 (13 pp. 1 microfiche). For details see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1977, Index issue.

⁴ C. K. Johnson, Report ORNL 3794, 1965, Oak Ridge National Laboratory, Tennessee, U.S.A.

⁵ H. B. Bürgi and J. D. Dunitz, *Helv. Chim. Acta*, 1970, **52**, 1747; *Chem. Comm.*, 1969, 472.

the metastable form of *p*-[(*p*-chlorobenzylidene)amino]-chlorobenzene, which is apparently planar,⁹ the twist angle τ for the aniline ring lies in the range 15–57° whereas that for the benzylidene ring, ρ , is smaller and in the range 0–15°. These twists may be in the same or in opposite directions. A rationalization of the preferred non-planar conformation, in terms of a balance between π -electron energy and non-bonded interactions, has been offered by Bürgi and Dunitz.¹⁰ Comparison of our results with other work shows that the twist

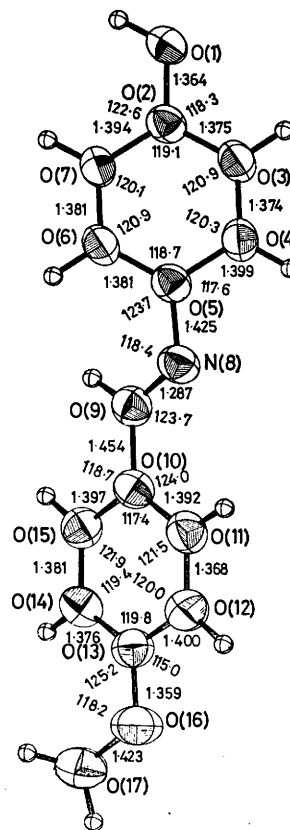


FIGURE 1 ORTEP⁴ drawing of the molecule showing bond lengths (Å), bond angles (°), and the numbering scheme adopted. Thermal ellipsoids for non-hydrogen atoms are drawn with 50% probability level as boundary surface and hydrogen atoms are represented by spheres of arbitrary radius. Estimated standard deviations: distances, 0.003 Å for those not involving H, 0.02–0.03 Å for those involving H; angles, not involving H, 0.2°, involving one H 1.2–2.0°, involving two H 2°

angle (41°) for the aniline ring in (2) lies within the previously observed range, and that the twist for the benzylidene (0.3°) is very small and comparable to those noted for the two other alkoxybenzylidenes listed.

Although, by analogy with stilbene, the potential curve for the benzylidene ring is believed to be fairly flat at low twist angles,¹⁰ the low degree of twist observed

⁶ J. Bernstein, *J.C.S. Perkin II*, 1972, 946.

⁷ D. P. Lesser, A. de Vries, J. W. Reed, and G. H. Brown, *Acta Cryst.*, 1975, **B31**, 653.

⁸ B. T. Blaylock, M. S. Thesis, University of Virginia, U.S.A., 1973.

⁹ J. Bernstein, *J.C.S. Perkin II*, 1972, 651.

¹⁰ H. B. Bürgi and J. D. Dunitz, *Helv. Chim. Acta*, 1971, **54**, 1255.

for the alkoxybenzylidenes suggests enhanced electronic stabilization of a near-planar conformation for the group arising from *p*-alkoxy-substitution. The effect of the electron-donating methoxy-group on the molecular geometry in (2) may be noted in the shortening of the

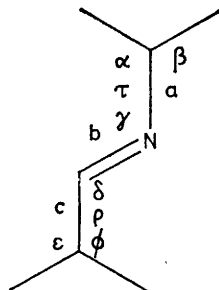
TABLE 2

(a) Bond lengths (Å), and (b) bond and torsion angles (°) in the central region of some related anilines

(a) Distances							
Cpds. ^a	Bond length ^b			Cpds. ^a	Bond length ^b		
	<i>a</i>	<i>b</i>	<i>c</i>		<i>a</i>	<i>b</i>	<i>c</i>
(A)	1.425	1.287	1.454	(G) †	1.41	1.29	1.47
(B)	1.460	1.237	1.496	(H)	1.42	1.29	1.47
(C)	1.431	1.281	1.461	(I)	1.41	1.28	1.46
(D)	1.400	1.269	1.474		1.412	1.269	1.458
(E)	1.407	1.268	1.482				
(F) *	1.421	1.273	1.470				
	1.423	1.269	1.478				

(b) Angles								
Cpds.	Bond angles						Torsion angles ‡	
	α	β	γ	δ	ϵ	ϕ	ρ	τ
(A)	123.7	117.6	118.4	123.7	118.7	124.0	0.3	41.4
(B)	123.7	117.3	119.9	122.7	120.1	122.2	9.9	56.8
(C)	121.7	117.7	116.3	122.4	118.6	122.2	13.8	41.4
(D)	123.3	117.1	120.6	120.2	120.1	122.2	4.2	53.4
(E)	124.8	115.8	118.6	120.3	120.3	122.7	6.7	-37.7
(F)	123.4	116.2	118.7	121.4	118.7	121.5	6.2	33.3
	123.7	115.6	119.3	121.9	118.0	121.6	0.1	-15.2
(G)	124	118	119	121	118	122	4.8	47.0
	124	118	119	124	121	121	10.8	38.7
	123	117	119	122	120	121	6.8	46.1
(I)	124.6	117.1	119.7	122.9	119.5	122.3	0.9	-30.1

^a Compounds: (A) *p*-[*p*-methoxybenzylidene]amino]phenol [present work, cpd. (2)]; (B) benzylideneaniline (ref. 5); (C) benzylideneaniline-*p*-carboxylic acid (ref. 5); (D) *p*-methylbenzylidene-*p*-nitroaniline (ref. 5); (E) *N*-(2,4-dichlorobenzylidene)aniline (ref. 6); (F) 2,2'-dibromo-4,4'-bis(*p*-methoxybenzylideneamino)biphenyl (ref. 7); (G) *N*-benzylidene-*p*-bromoaniline (ref. 8); (H) *N*-naphthylmethylene-*p*-bromoaniline (ref. 8); (I) *p*-[(*p*-ethoxybenzylidene)amino]benzotrile (ref. 11). ^b Key to bond labels:



* Molecule contains two structurally equivalent parts. † Two molecules per asymmetric unit. ‡ Enantiomer chosen to yield a positive sign for ρ .

C(11)-C(12), C(9)-C(10), and C(5)-N(8) bonds, and in the lengthening of the C=N central bond, relative to the comparable values for other compounds listed in Table 2. The aniline ring shows an exact symmetry of bond lengths and angles about the axis C(4)-C(7), not readily interpretable in terms of acceptable resonance structures.

Equations for the least-squares mean planes through the benzylidene moiety, the aniline ring, and the central

¹¹ R. F. Bryan, unpublished data.

¹² R. L. Sass, *Acta Cryst.*, 1960, **13**, 320.

four-atom linkage are given in Table 3. The atoms of the aniline ring are coplanar, maximum and mean deviations of atoms from the plane being 0.01 and 0.005 Å. The phenolic oxygen O(1) is displaced from the plane by 0.04 and the nitrogen atom N(8) by 0.05 Å. For the seven atoms of the benzylidene moiety the corresponding maximum and mean deviations are 0.010 and 0.006 Å, but N(8) is displaced from that plane by 0.03, O(16) by -0.04, and C(17) by -0.13 Å. The slight displacement of the methyl carbon from the plane is most probably associated with the tight intermolecular contacts involving the methyl hydrogen atoms.

The H(6) ··· H(9) separation, important for the twist of the aniline ring, is 2.26, and N(8) ··· H(11) is 2.70 Å. Other intramolecular separations are listed in Table 4.

TABLE 3

Equations of least-squares mean planes for selected groups of atoms in the form $aX + bY + cZ = d$ where X , Y , and Z are orthogonal Å co-ordinates such that $X = x + z\cos\beta$, $Y = y$, $Z = z\sin\beta$

Plane (1) C(2)-(7)	$0.4641X - 0.8016Y + 0.3770Z = -11.262$
Plane (2) C(9)-(15)	$-0.5603X + 0.7678Y + 0.3107Z = 11.965$
Plane (3) C(5), N(8), C(9), C(10)	$-0.5496X + 0.7793Y + 0.3011Z = 12.152$

TABLE 4

Selected intramolecular contact distances (Å)

O(1) ··· H(3)	2.50	O(1) ··· H(7)	2.63
N(8) ··· H(4)	2.55	N(8) ··· H(11)	2.70
H(6) ··· H(9)	2.26	H(9) ··· H(15)	2.35
O(16) ··· H(12)	2.45	O(16) ··· H(14)	2.64
H(14) ··· H(17a)	2.32	H(14) ··· H(17b)	2.35

With increasing coplanarity of the benzylidene ring and the central linkage, increased hydrogen-lone-pair interactions are to be expected and, reflecting this, the bond angles δ and ϕ (see Table 2) in (2) are larger than in the other compounds listed.

The characteristic bond-angle distortion associated with alkoxy substitution is noted in the exocyclic angles at C(13).^{2,11}

Our principal concern, however, is not with these aspects of molecular geometry and conformation, but with the mode of molecular packing in the crystal. The packing adopted is dictated by the formation of hydrogen bonds between molecules related by the space-group glide operations, and is shown in Figure 2. The terminal hydroxy-groups act as donors to the central nitrogen atoms giving an O-H ··· N separation of 2.756 Å, H ··· N 1.81 Å. The hydrogen-bond length is comparable to that found in dimethylglyoxime¹² and indicates a bond of more than average strength for this type.¹³ The molecules are linked by the hydrogen bonds in infinite chains. The detailed structure of a chain may be understood by reference to the molecule marked by an asterisk in the upper left-hand corner of

¹³ W. C. Hamilton and J. A. Ibers, 'Hydrogen Bonding in Solids,' W. A. Benjamin, New York, 1968.

Figure 2. The long axis of this molecule lies almost parallel to the ab plane with $z \approx -0.2$. A hydrogen bond is formed from the hydroxy-group of this molecule

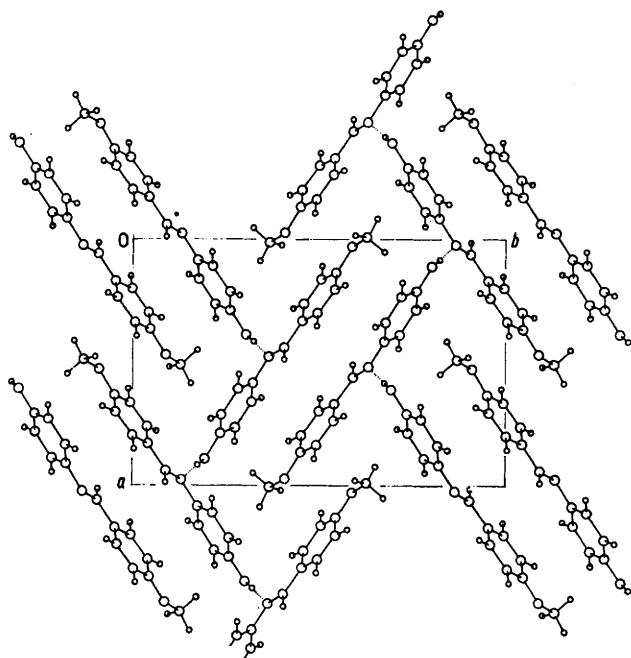


FIGURE 2 View of the molecular packing in the crystal seen in projection down c . Hydrogen bonds are indicated by dotted lines

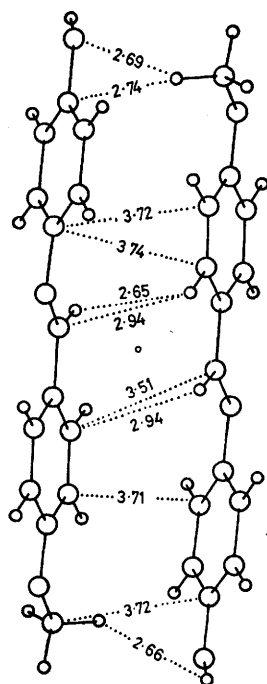


FIGURE 3 Intermolecular contacts (Å) between centrosymmetrically related pairs of molecules

to the nitrogen atom of the molecule related to it by the operation $x + \frac{1}{2}, \frac{1}{2} - y, z + \frac{1}{2}$. The hydroxy-group of this second molecule in turn forms a hydrogen bond to the nitrogen atom of a third molecule related to the first by unit translations in x and z . Repetition of this

pattern creates an infinite zig-zag chain in which the long axes of neighbouring molecules are inclined to one another alternately by 70 and 110°. Identical, but separate, chains are formed by molecules centrosymmetrically related to those of the original set, and these sets of chains interlock to yield an overall molecular packing arrangement of the herring-bone type. Both nematic and smectic mesophases appear to require a more or less parallel orientation of the long molecular axes, and the unsuitability of the packing arrangement found here to act as a precursor for mesophase formation is evident. For this compound, and for related phenols, we may thus be reasonably certain that the principal cause of loss of mesomorphic behaviour stems from the disruption of a near-parallel arrangement of molecules in the crystal rather than from destabilization of a potential mesophase by increase in melting point. It is

TABLE 5

Selected intermolecular approach distances (Å) *

O(1) ... H(6 ^{VI})	2.44	H(6) ... O(1 ^{IVII})
H(1) ... H(11 ^I)	2.45	H(11) ... H(1 ^{II})
H(12) ... H(12 ^{III})	2.50	
H(1) ... C(5 ^I)	2.56	C(5) ... H(1 ^{II})
H(15) ... H(11 ^{IV})	2.57	H(11) ... H(15 ^V)
H(7) ... H(11 ^I)	2.61	H(1) ... H(7 ^{II})
H(1) ... H(4 ^I)	2.62	H(4) ... H(1 ^{II})
H(14) ... H(12 ^{IV})	2.62	H(12) ... H(14 ^V)
H(6) ... H(4 ^{IV})	2.68	H(4) ... H(6 ^V)
H(7) ... H(3 ^{IV})	2.71	H(3) ... H(7 ^V)
O(1) ... H(9 ^{IV})	2.74	H(9) ... O(1 ^{VII})
O(16) ... H(12 ^{III})	2.74	H(12) ... O(16 ^{III})
O(1) ... N(8 ^I)	2.76	N(8) ... O(1 ^{II})
O(1) ... H(11 ^I)	2.84	H(11) ... O(1 ^{II})
H(1) ... C(9 ^I)	2.87	C(9) ... H(1 ^{II})
H(1) ... C(4 ^I)	2.88	C(4) ... H(1 ^{II})
C(13) ... H(17a ^{VIII})	2.89	H(17a) ... C(13 ^{VIII})
C(12) ... H(17c ^{IX})	2.90	H(17c) ... C(2 ^X)
C(7) ... H(17c ^{IX})	2.91	H(17c) ... C(7 ^X)
C(3) ... H(17c ^{IX})	2.95	H(17c) ... C(3 ^X)
C(6) ... H(17c ^{IX})	2.97	H(17c) ... C(6 ^X)
H(7) ... C(11 ^I)	2.99	C(11) ... H(7 ^{II})
C(4) ... H(17c ^{IX})	3.00	H(17c) ... C(4 ^X)
C(12) ... H(17a ^{VIII})	3.01	H(17a) ... C(12 ^{VIII})
C(5) ... H(17c ^{IX})	3.02	H(17c) ... C(5 ^X)
C(7) ... H(11 ^I)	3.10	H(11) ... C(7 ^{II})
O(1) ... C(9 ^{VI})	3.24	C(9) ... O(1 ^{VII})
O(1) ... C(5 ^I)	3.38	C(5) ... O(1 ^{II})
O(1) ... C(6 ^{VI})	3.41	C(6) ... O(1 ^{VII})
C(4) ... O(1 ^{II})	3.44	O(1) ... C(4 ^I)
C(12) ... O(16 ^{III})	3.56	O(16) ... C(12 ^{III})
C(5) ... C(17 ^{IX})	3.61	C(17) ... C(5 ^X)
C(6) ... C(17 ^{IX})	3.66	C(17) ... C(6 ^X)
C(13) ... C(17 ^{VIII})	3.66	C(17) ... C(13 ^{VIII})
C(2) ... N(8 ^I)	3.66	N(8) ... C(2 ^{II})
C(7) ... C(11 ^I)	3.66	C(11) ... C(7 ^{II})
C(4) ... C(17 ^{IX})	3.71	C(17) ... C(4 ^X)
C(14) ... C(17 ^{VIII})	3.72	C(17) ... C(14 ^{VIII})
C(7) ... N(8 ^I)	3.78	N(8) ... C(7 ^{II})
O(16) ... C(14 ^{VIII})	3.79	C(14) ... O(16 ^{VIII})
C(4) ... C(12 ^{XI})	3.80	C(12) ... C(4 ^{XI})
C(7) ... C(17 ^{IX})	3.80	C(17) ... C(7 ^X)

* Because of the centrosymmetric character of the space group, each contact occurs twice. Contacts are given from the first atom in the reference molecule to the second atom at the symmetry-related position denoted by the Roman superscript.

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

not to be excluded, of course, that thermal destabilization may be found in other molecular systems.

Intermolecular separations between pairs of centrosymmetrically related molecules are shown in Figure 3, and Table 5 gives the values for certain other contacts. Most of the shorter contacts involve the phenolic proton, H(1), or the hydrogen atoms of the terminal methyl group. Aside from the hydrogen bonding, there is no evidence of particularly strong interactions between molecules.

EXPERIMENTAL

Crystals of the compound, as small plates directly suited to X-ray study, were obtained by recrystallization of a commercial sample from ethanol.

Crystal Data.— $C_{14}H_{13}NO_2$, $M = 227.3$, m.p. 188 °C. Monoclinic, $a = 11.375(5)$, $b = 17.307(8)$, $c = 6.007(4)$ Å, $\beta = 92.23(3)^\circ$, $U = 1182$ Å³, $D_m = 1.26$, $Z = 4$, $D_c = 1.277$, $F(000) = 480$. Space group $P2_1/n$. Cu- K_α radiation, $\lambda = 1.5418$ Å; $\mu(\text{Cu-}K_\alpha) = 7$ cm⁻¹. Single crystal diffractometry.

Intensity Measurements.—These were made from a single crystal $0.7 \times 0.4 \times 0.1$ mm, mounted with c^* parallel to the ϕ axis of a Picker four-circle diffractometer. Graphite monochromatized Cu- K_α radiation was used, and a single

¹⁴ G. Germain, P. Main, and M. M. Woolfson, *Acta Cryst.*, 1971, **A27**, 368.

¹⁵ P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 1967, **6**, 197.

quadrant of reciprocal space examined to $\theta 60^\circ$ by the θ — 2θ scan technique with scan widths of 3° in 2θ and a scan speed of 2° min^{-1} . Background was measured for 15 s at each end of the scans by the stationary-crystal-stationary-counter method. Scattered intensity was measured by scintillation counting with pulse-height analysis, and 1421 of the 1694 examined had intensity significantly above background [$I > 3\sigma(I)$]. The intensities of two reflections, monitored after every 50 scans, did not vary significantly during data collection, nor did the intensities of symmetry-equivalent $0kl$ and $0k\bar{l}$ reflections measured as a check on crystal orientation.

Structure Determination and Refinement.—The phase problem was solved by use of the program MULTAN,¹⁴ the 185 $E(hkl) > 1.6$ being used. Refinement was by the block-diagonal least-squares method yielding R 0.043 and R' 0.060 at convergence. Anisotropic thermal parameters were adopted for non-hydrogen atoms, and isotropic B values for hydrogen atoms. At convergence the largest shift-to-error ratio was 0.5 and the mean ratio was 0.13. The weighting scheme used was that of ref. 15 with p chosen as 0.025. The scattering functions used were taken from ref. 16. All calculations were carried out using an XDS Sigma 2 computer also used to control the diffractometer, except for MULTAN and ORTEP, where a CDC Cyber 172 computer was used.

[7/1389 Received, 1st August, 1977]

¹⁶ International Tables for X-Ray Crystallography, vol. IV, Kynoch Press, Birmingham, 1974, p. 73; R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.