The Crystal Structure of Ethyl p-Azoxybenzoate

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The low-temperature form (solid I) of the smectogenic compound ethyl p-azoxybenzoate ($C_{18}H_{18}N_2O_5$) is stable below 90 °C. The triclinic unit cell of space group $P\bar{1}$ and dimensions $a = 7\cdot56 \pm 0\cdot02$, $b = 18\cdot35 \pm 0\cdot07$, $c = 6\cdot28 \pm 0\cdot01$ Å, $\alpha = 94\cdot38° \pm 0\cdot30°$, $\beta = 97\cdot21 \pm 0\cdot31°$, and $\gamma = 83\cdot97° \pm 0\cdot25°$ contains two molecules and has a calculated density of $1\cdot325$ g.cm^{-3}. The observed density is $1\cdot315 \pm 0\cdot013$ g.cm^{-3}. Integrated intensities were measured at room temperature by a 2θ–ω scan on a four-circle diffractometer equipped with a post-diffraction monochromator and scintillation detector. The crystal structure was refined by full-matrix least-squares methods with 1460 independent reflections to a final R index of $0\cdot09_3$. The molecules are nearly planar (the normals to the planes of the two benzene rings diverge by only $0\cdot5°$) and are packed in a parallel array, as contrasted with the imbricated structure which has been observed for several nematogenic crystalline solids. The carbonyl and nitroso oxygen atoms are all in the *cis* conformation, resulting in a large dipole component in the plane of the molecule and perpendicular to its long axis. It is speculated that this feature of the molecular structure may be characteristic of smectogenic compounds.

Introduction

Compounds that exhibit liquid crystalline mesomorphism have been known for over 80 years. These materials do not become isotropic immediately upon melting, but varying degrees of molecular order and optical anisotropy persist over a finite temperature above the crystalline melting point. X-ray analysis was undertaken as early as 1921 to obtain a better understanding of the structure and packing of these mesomorphic phases. Hückel (1921) reported that the diffraction patterns from nematic phases resemble those observed for isotropic liquids, indicating an absence of three-dimensional order. Friedel (1925) used diffraction to demonstrate that the smectic phase is composed of equidistant parallel layers. Kast (1927) observed two diffuse diffraction maxima from a magnetically ordered nematic melt. Although only a limited amount of structural information can be obtained by diffraction studies of the mesomorphic phases, crystalline phases of these compounds are sufficiently well ordered to permit the determination of their three-dimensional structures. We have undertaken a study of the crystal structures of mesomorphic compounds with the belief that this information may provide insight into the molecular properties responsible for liquid crystalline behavior. Galigné & Falgueirettes (1968) have determined the crystal structure of the nematogenic compound anisaldehyde azine. Recently Krigbaum, Chatani & Barber (1970), Carlisle & Smith (1969), and others reported the structure of the nematogenic compound, p-azoxyanisole. This paper is concerned with the structure of the low-temperature form (solid I) of the smectogenic compound, ethyl p-azoxybenzoate ($C_{18}H_{18}N_2O_5$):
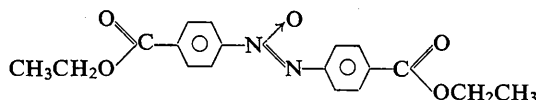
Experimental

Crystalline ethyl p-azoxybenzoate transforms at about 90 °C to a high-temperature polymorph (solid II), melts to a smectic phase at 114 °C, and forms an isotropic liquid at 120 °C. The temperatures of these transitions, particularly those involving the mesophase, are functions of the purity of the material. In an effort to obtain a sample of high purity, we oxidized a commercial sample of ethyl p-azobenzoate with hydrogen peroxide in glacial acetic acid. The yellow material, which was orange before oxidation, was purified by repeated recrystallization from ethanol. Since only flat plates were obtained from the ethanol solutions, the crystals selected for study were large prismatic needles grown from a carbon tetrachloride and isooctane mixed solvent. A 5 mm crystal was cleaved to a $0\cdot3 \times 0\cdot4 \times 0\cdot8$ mm parallelopiped. Observation under a polarizing microscope before mounting indicated that the cleaved crystal was not cracked or twinned. The crystal was mounted with the long axis of the needle (b^* axis of the unit cell) parallel to the φ spindle axis of the diffractometer. Precession and Weissenberg photographs showed no disorder or twinning. These photographs also served to demonstrate that there were no systematic absences, to determine the space group as $P1$ or $P\bar{1}$, and to show that the data are limited to $2\theta < 110°$ for Cu $K\alpha$ radiation. Unit-cell parameters determined from the diffractometer settings for carefully centered axial reflections on three crystals are shown in Table 1.

Table 1. *Unit-cell parameters for ethyl p-azoxybenzoate in space group* $P\bar{1}$

a = 7·56 ± 0·02 Å α = 94·38 ± 0·30°
b = 18·35 ± 0·07 β = 97·21 ± 0·31
c = 6·28 ± 0·01 γ = 83·97 ± 0·25
ϱ_o = 1·315 ± 0·013 g.cm^{-3} ϱ_c = 1·325 g.cm^{-3}
V = 857·71 Å^3
W = 342·36 g.mole
$F(000)$ = 180
z = 2

The density, $1·315 ± 0·013$ g.cm^{-3}, was measured by the flotation method using a sodium iodide solution diluted with deionized and degassed water. This value agrees with that calculated for two molecules in the triclinic unit cell, $1·325$ g.cm^{-3}.

Intensity measurements were made at room temperature ($22° ± 4°C$) with a card-controlled four-circle Picker diffractometer using Cu $K\alpha$ radiation. The diffractometer was equipped with a highly-oriented graphite diffracted beam crystal monochromator, scintillation detector, and pulse-height analyzer. The 1460 independent intensities were collected by a 2θ–ω scan of two degrees plus an allowance for the spectral dispersion of the beam. Scan rate was one degree per minute, and the background was counted on each side of the peak for forty seconds. The data were corrected for background, absorption, polarization, and Lorentz effects. All corrections were customary ones except for polarization. The absorption correction was made by a modification of Furnas's method suggested by North, Phillips & Matthews (1968) in which the line of reflections along the b^* axis in reciprocal space was aligned

at $\chi = 90·00°$ and the intensity was made as independent as possible of rotation about the φ axis. From a normalized plot of the resulting φ dependence, a correction averaging the effects of the entrance and exit paths was applied as shown below.

$$I = \tfrac{1}{2} I'[C(\varphi + \Delta) + C(\varphi - \Delta)] .$$

In this equation the absorption correction factor, C, is a function of angles φ and Δ, where Δ is the increment for the entrance and exit paths, arctan (tan θ cos χ). The relatively small value of the linear absorption coefficient ($8·2$ cm^{-1}), the small maximum difference of 10% between A^*_{min} and A^*_{max}, and the increased expense of further calculations weighed against the use of a more accurate absorption correction.

The polarization correction for an incident beam monochromator is not applicable since the geometries of the two systems are not identical. Correction for the diffracted beam monochromator, which was tested using data collected from a basic beryllium acetate crystal, is discussed elsewhere. The relation is

$$p = \tfrac{1}{2} + \tfrac{1}{2} (\cos^2 2\theta . \cos^2 2\theta_m) ,$$

where θ_m is the Bragg angle of the monochromator crystal. The correction was further tested by collecting 800 reflections from the ethyl p-azoxybenzoate crystal using an $0·175$ mm nickel β-filter and pulse-height analyzer in place of the monochromator. A least-squares scale factor was obtained relating these data

Table 2. *Atomic coordinates and temperature factors for ethyl p-azoxybenzoate*

Temperature factors are multiplied by $\times 10^4$ for the expression exp $[-(b_{11}h^2 + b_{12}hk + \dots)]$
Numbers in parentheses give the standard deviations in the last significant figures calculated from
$\sigma^2(u_i) = \Sigma_j w_j (\Delta F_j)^2 / [(n - s) \Sigma_j w_j (\partial F_j / \partial u_i)^2]$.

	x/a	y/b	z/c	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C(1)	−0·2083 (12)	0·4530 (4)	0·1414 (16)	629 (24)	50 (3)	915 (41)	219 (13)	35 (53)	−1 (20)
C(2)	−0·2294 (11)	0·4124 (3)	−0·0471 (14)	593 (22)	27 (2)	809 (33)	83 (11)	−422 (46)	−5 (14)
O(3)	−0·1392 (6)	0·3383 (2)	−0·0232 (8)	348 (11)	29 (1)	540 (16)	31 (7)	−29 (22)	45 (8)
O(4)	−0·1973 (7)	0·3134 (2)	−0·3767 (7)	483 (13)	55 (2)	524 (14)	55 (8)	−169 (23)	156 (8)
C(5)	−0·1360 (7)	0·2958 (3)	−0·2019 (10)	231 (11)	34 (2)	481 (19)	4 (8)	14 (25)	88 (10)
C(6)	−0·0414 (6)	0·2212 (2)	−0·1619 (8)	178 (9)	29 (2)	368 (16)	−18 (7)	56 (20)	44 (8)
C(7)	−0·0316 (8)	0·1700 (3)	−0·3350 (9)	243 (12)	37 (2)	348 (18)	19 (9)	47 (25)	103 (10)
C(8)	0·0506 (7)	0·1016 (3)	−0·3157 (8)	268 (12)	43 (2)	291 (16)	−12 (8)	−56 (23)	64 (9)
C(9)	0·1209 (6)	0·0842 (2)	−0·1142 (9)	158 (9)	10 (1)	642 (20)	25 (6)	245 (21)	20 (9)
C(10)	0·1160 (7)	0·1308 (3)	0·0688 (9)	213 (10)	27 (2)	374 (16)	31 (7)	41 (22)	64 (9)
C(11)	0·0292 (7)	0·2005 (3)	0·0414 (8)	242 (11)	31 (2)	324 (15)	−2 (7)	3 (22)	37 (9)
N(12)	0·2151 (6)	0·0038 (3)	−0·1072 (7)	303 (10)	96 (2)	307 (14)	−175 (8)	162 (19)	−32 (10)
O(13)	0·2103 (7)	−0·0347 (2)	−0·2883 (6)	549 (13)	49 (2)	272 (11)	62 (8)	−111 (21)	−20 (7)
N(14)	0·2755 (6)	−0·0066 (3)	0·0673 (7)	326 (10)	63 (2)	271 (12)	−134 (7)	198 (18)	−45 (8)
C(15)	0·3729 (6)	−0·0852 (2)	0·0931 (10)	175 (9)	18 (1)	643 (21)	34 (6)	238 (23)	85 (9)
C(16)	0·4367 (7)	−0·0936 (3)	0·3019 (9)	251 (12)	42 (2)	351 (17)	−20 (8)	65 (24)	46 (10)
C(17)	0·5249 (7)	−0·1590 (3)	0·3621 (9)	232 (11)	28 (2)	377 (17)	13 (7)	28 (23)	75 (9)
C(18)	0·5489 (6)	−0·2170 (3)	0·2096 (8)	176 (9)	27 (2)	337 (15)	3 (8)	69 (20)	37 (9)
C(19)	0·4869 (7)	−0·2095 (3)	−0·0028 (9)	242 (11)	41 (2)	324 (16)	10 (8)	82 (23)	25 (10)
C(20)	0·3954 (7)	−0·1424 (3)	−0·0630 (9)	223 (11)	51 (2)	374 (16)	14 (8)	58 (22)	152 (9)
C(21)	0·6445 (7)	−0·2891 (3)	0·2746 (9)	228 (11)	32 (2)	458 (19)	−6 (7)	122 (23)	37 (10)
O(22)	0·6732 (6)	−0·3400 (2)	0·1490 (6)	377 (10)	33 (1)	398 (12)	−6 (6)	−196 (19)	49 (7)
O(23)	0·6910 (6)	−0·2900 (2)	0·4849 (7)	437 (11)	32 (1)	471 (14)	78 (6)	172 (20)	31 (7)
C(24)	0·7797 (10)	−0·3598 (3)	0·5654 (11)	531 (20)	30 (2)	508 (22)	42 (11)	−268 (36)	83 (11)
C(25)	0·6388 (12)	−0·4083 (4)	0·5969 (11)	709 (26)	37 (2)	429 (22)	−17 (13)	−12 (41)	53 (12)

Table 2 (*cont.*)

	x/a	y/b	z/c
H(1A)	−0·246*	0·450	0·302
H(1B)	−0·297	0·495	0·174
H(1C)	−0·098	0·443	0·202
H(2A)	−0·105	0·456	−0·058
H(2B)	−0·302	0·413	−0·149
H(7)	−0·070	0·194	−0·484
H(8)	0·016	0·074	−0·476
H(10)	0·172	0·114	0·229
H(11)	0·031	0·241	0·154
H(16)	0·417	−0·051	0·448
H(17)	0·564	−0·163	0·535
H(19)	0·530	−0·251	−0·114
H(20)	0·371	−0·144	−0·236
H(24A)	0·806	−0·347	0·740
H(24B)	0·848	−0·382	0·450
H(25A)	0·595	0·043	0·450
H(25B)	0·619	−0·378	0·701
H(25C)	0·731	−0·450	0·629

* Estimates of the error in hydrogen positions based on the resolution of the Fourier map are $\Delta_{x/a}=0\cdot020$, $\Delta_{y/b}=0\cdot008$, $\Delta_{z/c}=0\cdot025$. Hydrogen atoms were assigned isotropic temperature factors, $B=3\cdot0$ Å^2.

to the corresponding set collected with the monochromator (after appropriately correcting each set for absorption, Lp, and background). The scale factor plotted as a function of (sin θ/λ) formed a line having a slight positive slope. Application of an empirical correction for this residual slope, which altered the intensities observed at the largest 2θ by only 5%, had the effect of slightly reducing the atomic temperature factors for the final structure.

Of the total number of reflections, 993 had average $|F_o|$ values less than 6 on a scale of 100. Only 109 reflections had average $|F_o|$ values greater than 33. This large proportion of weak reflections became apparent during the determination of the weights to be used during the refinement, which were selected to make $\langle\sum w(|F_o|-|F_c|)^2\rangle$ independent of the value of $|F_o|$. These weights also made the value of $\langle\sum w(|F_o|-|F_c|)^2\rangle$, which is the quantity minimized during refinement, independent of (sin θ/λ). The final weighting scheme used in the refinement was $w=\dfrac{1}{\sigma}$, where

$$\sigma^2=0\cdot522+0\cdot0765\ |F_o|+0\cdot00020\ |F_o|^2.$$

Except for the initial stages of structure determination, all reflections were included. In the initial stages, weak reflections having $|F_o|<2\sigma_F$ were ignored. The estimated standard deviation, σ_F, was calculated from counting statistics by the expression:

$$\sigma_F^2=\tfrac{1}{4}\ (C+k^2B)/|F_o|^2\ (\text{Lp})^2\ ,$$

where C is the total count from the scan, k the ratio of scanning time to total background counting time, and B the total background count (Collins & Hoard, 1970).

Structure analysis

The presence of a center of inversion was indicated by the $N(z)$ test of Howells, Phillips & Rogers (1950),

which showed that the structure is hypersymmetric. Since there are no heavy atoms to cause hypersymmetry, this observation suggests the presence of a molecule with noncrystallographic symmetry, occupying a general position in the centrosymmetric unit cell (Lipson & Cochran, 1966). Thus, parts of the molecule are probably related by a noncrystallographic symmetry operation, which implies that the molecule is nearly planar. The very intense [½,0,0] vector in Patterson space also suggested that the structure consists of planar molecules that are parallel and separated by ½ of the unit-cell dimension in the **a** direction.

From a three-dimensional sharpened Patterson map, the vectors arising from the nitrogen atoms, oxygen atoms, and benzene rings could be identified, yielding a trial structure that gave an R index of 0·59. After two cycles of rigid-body, full-matrix least-squares refinement, R decreased to 0·43. Three-dimensional difference Fourier maps were drawn to locate the azoxy oxygen atom and the ethyl groups. It was expected that the carbonyl oxygen atoms would be in the *trans* conformation; consequently, it was surprising when the difference Fourier map clearly showed them in a *cis* relation to each other and to the azoxy oxygen. Three additional cycles, including these newly located atoms in the rigid-body refinement, decreased R to 0·31. Two further least-square cycles of refinement without the rigid-body restriction reduced the R index to 0·18. Conversion to anisotropic temperature factors for the 25 nonhydrogen atoms reduced R to 0·15 in one cycle. The hydrogen atoms were located in the difference Fourier map, and the introduction of these 18 hydrogen atoms with isotropic temperature factors reduced the R index to 0·12 in two more cycles.

Attempts to achieve further refinement proved futile; a difference Fourier map revealed a fictitious, planar-banded structure appearing exactly midway between the planes of the molecules. Inspection of the list of structure factors revealed three that were in particularly bad agreement with their calculated values, and seven more for which the agreement was poor. Since these were neither exceptionally strong nor located at low 2θ values, the discrepancies could not be ascribed to secondary extinction. Hence, data for a number of reflections were collected using a second crystal mounted about the a^* axis. After replacing these ten structure factors by their new, scaled values, two further cycles of least-squares refinement with anisotropic temperature factors decreased the R index to its final value, $0\cdot09_3$. At this point, the shifts in all position and temperature factors were smaller than the estimated errors. Because of the limited amount of data available and the expense of further calculations, no attempt was made to refine the positions of the hydrogen atoms. Their tabulated positions were calculated by the method of Booth (1948) from the final difference Fourier map in which all hydrogen difference peaks were clearly resolved. Final atomic coordinates

and temperature-factor coefficients are listed in Table 2.

The final difference Fourier showed no anomalous peaks and no hints of disorder. Particular attention was paid to the region around the azoxy group, since spurious peaks in the structure of the related compounds, *p*-azoxyanisole (Krigbaum *et al.*, 1970) and *p*-azotoluene (Brown, 1966), had indicated the presence of disorder.

The least-squares program used in the initial refinement was derived from *ORFLS* (Busing, Martin & Levy, 1962). In this program the atomic form factors used were those of Cromer & Mann (1968). Final stages of refinement were made with a modified version of the Gantzel, Sparks & Trueblood UCLA least-squares program, which used atomic form factors from *International Tables for X-ray Crystallography* (1962).

Description of the structure

The bond lengths and angles with their standard deviations appear in Table 3. Labeled atoms and their temperature ellipsoids at the 50 % probability level are indicated in Fig. 1. All bond lengths accord with those found in similar structures. Average aromatic carbon–carbon bond lengths, and their estimated root-mean-square deviations, are $1\cdot374 \pm 0\cdot016$ and $1\cdot379 \pm 0\cdot019$ Å; average bond angles are $120\cdot0 \pm 3\cdot5$ and $120\cdot0 \pm 0\cdot9°$ for rings C(6) through C(11) and C(15) through C(20), respectively. Clearly, the latter has more uniform bond angles, although the variation in the first ring is consistent with the observation that larger valency angles

occur on aromatic carbon atoms bearing nitro or other electron withdrawing groups (Carter, McPhail & Sim, 1966). The structure of the ester moiety can be compared with that of propargyl 2-bromo-3-nitrobenzoate (PBNB) (Calabrese, McPhail & Sim, 1966). Average carbon–oxygen bond lengths are $1\cdot194 \pm 0\cdot006$ and $1\cdot320 \pm 0\cdot007$ Å in ethyl *p*-azoxybenzoate and $1\cdot18 \pm 0\cdot014$ and $1\cdot32 \pm 0\cdot013$ Å in PBNB; carbonyl bond angles in these two structures are $124\cdot8° \pm 0\cdot5°$ and $124° \pm 1\cdot1°$, respectively. The distance from the carbonyl carbon to the benzene ring is $1\cdot499 \pm 0\cdot007$ Å in the former compound and $1\cdot52 \pm 0\cdot016$ Å in the latter. In both compounds the ester oxygen is tilted about 9° closer to the benzene ring than would be predicted from simple sp^2 hybridization. A comparison of bond lengths and angles about the hydrocarbon portion of the ester groups shows further similarities between the two structures. The structure of the azoxy portion of ethyl *p*-azoxybenzoate may be compared with that of *p*-azoxyanisole. The C–N bond lengths are 0·068 Å longer, the N–N bond length is 0·063 Å shorter, and the N–O distance is 0·012 Å longer in the present structure. The O–N–N bond angle of 134·7° deviates significantly from the value expected for sp^2 hybridization, but a similar deviation was exhibited in the structure of *p*-azoxyanisole (130·3°). The N(14)–C(15)–C(20) angle of 129·0° is similarly larger than predicted, but this agrees with the larger values of 130·6° observed in *p*-azoxyanisole, and $137 \pm 3°$ observed in a mercurichloride adduct of *p*-azoxyanisole determined by McPhail & Sim (1969).
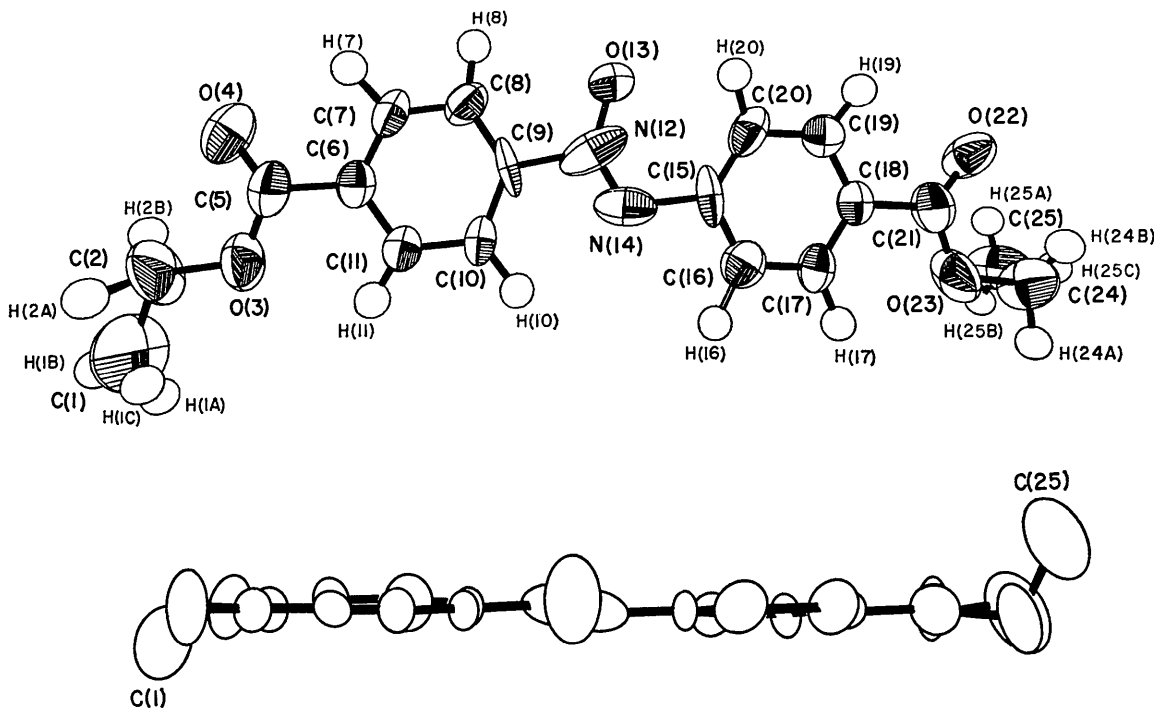

Fig. 1. Perspective drawings of the ethyl *p*-azoxybenzoate molecule showing the thermal ellipsoids.

Table 3. *Bond distances and angles with their standard deviations*

Distance (Å)		Angle (°)	
C(1)—C(2)	1·351 (13)	C(1)—C(2)—O(3)	110·3 (7)
C(2)—O(3)	1·465 (8)	C(2)—O(3)—C(5)	115·7 (5)
O(3)—C(5)	1·318 (7)	O(3)—C(5)—O(4)	125·3 (5)
O(4)—C(5)	1·191 (7)	O(3)—C(5)—C(6)	111·9 (5)
C(5)—C(6)	1·501 (7)	O(4)—C(5)—C(6)	122·8 (5)
C(6)—C(7)	1·385 (8)	C(5)—C(6)—C(7)	118·2 (5)
C(7)—C(8)	1·347 (8)	C(5)—C(6)—C(11)	122·8 (5)
C(8)—C(9)	1·358 (8)	C(6)—C(7)—C(8)	122·7 (5)
C(9)—C(10)	1·381 (7)	C(7)—C(8)—C(9)	116·3 (5)
C(10)—C(11)	1·387 (7)	C(8)—C(9)—C(10)	125·3 (4)
C(11)—C(6)	1·384 (7)	C(9)—C(10)—C(11)	116·3 (5)
C(9)—N(12)	1·570 (7)	C(10)-C(11)—C(6)	120·3 (5)
N(12)—O(13)	1·291 (6)	C(11)—C(6)—C(7)	118·9 (5)
N(12)—N(14)	1·155 (6)	C(8)—C(9)—N(12)	112·8 (5)
N(14)—C(15)	1·559 (7)	C(10)—C(9)—N(12)	121·8 (5)
C(15)-C(16)	1·353 (8)	C(9)—N(12)—O(13)	116·2 (4)
C(16)—C(17)	1·366 (8)	C(9)—N(12)—N(14)	109·1 (5)
C(17)—C(18)	1·390 (7)	O(13)-N(12)—N(14)	134·7 (6)
C(18)—C(19)	1·370 (7)	N(12)-N(14)—C(15)	113·5 (5)
C(19)—C(20)	1·401 (8)	N(14)-C(15)—C(16)	110·0 (4)
C(20)-C(15)	1·393 (8)	N(14)-C(15)—C(20)	129·0 (5)
C(18)-C(21)	1·497 (7)	C(15)-C(16)—C(17)	119·9 (5)
C(21)—O(22)	1·196 (7)	C(16)-C(17)—C(18)	120·2 (5)
C(21)—O(23)	1·324 (7)	C(17)-C(18)—C(19)	120·8 (5)
O(23)—C(24)	1·477 (7)	C(18)-C(19)—C(20)	118·7 (5)
C(24)—C(25)	1·498 (11)	C(19)-C(20)—C(15)	119·3 (5)
		C(20)-C(15)—C(16)	121·1 (5)
		C(17)-C(18)—C(21)	120·5 (5)
		C(19)-C(18)—C(21)	118·7 (5)
		C(18)-C(21)—O(23)	112·6 (5)
		C(18)-C(21)—O(22)	123·2 (5)
		O(22)-C(21)—O(23)	124·2 (5)
		C(21)-O(23)—C(24)	116·5 (4)
		O(23)-C(24)—C(25)	108·7 (6)

The equation for the least-squares best plane representing the benzene ring composed of C(6) through C(11) atoms relative to an orthogonal set of axes is

$$0.9322\, x + 0.3306\, y - 0.1475\, z = 1.7143,$$

and the displacements from this plane are

C(6)	0·0143 Å	C(9)	0·0006 Å
C(7)	−0·0087	C(10)	0·0052
C(8)	0·0012	C(11)	−0·0126.

The best mean plane for the ring C(15) through C(20) has the equation

$$0.9311\, x + 0.3301\, y - 0.1550\, z = 1.7897$$

with displacements

C(15)	−0·0003 Å	C(18)	−0·0048 Å
C(16)	0·0016	C(19)	0·0060
C(17)	0·0010	C(20)	−0·0034.

Respective equations for the mean planes of the azoxy group, and for the two carbonyl groups, O(3) through C(5) and C(21) through O(23), are

$$0.9211\, x + 0.3503\, y - 0.1699\, z = 1.7354$$
$$0.9361\, x + 0.3249\, y - 0.1351\, z = 1.6695$$
$$0.9387\, x + 0.3277\, y - 0.1073\, z = 1.9013.$$

Benzene rings deviate from coplanarity by only 30′, and the angle between the normals to the two carbonyl planes is only 1°27′. These calculations reveal that the ethyl p-azoxybenzoate molecule is nearly planar, as illustrated qualitatively in the lower part of Fig. 1. The p-azoxyanisole molecule deviates much more from planarity, the angle between the benzene rings being 22·6°. The lower portion of Fig. 1 also shows that the two ethyl groups are displaced in opposite directions from the plane of the molecule. Methoxy groups of p-azoxyanisole show a similar displacement, which is probably dictated by packing considerations.

Temperature ellipsoids for the ethyl carbon atoms are much larger than those for the other atoms, but this can be anticipated for atoms near the ends of an elongated molecule. Bond lengths were not corrected for thermal motion, which may explain the discrepancy between the ethyl carbon–carbon bond lengths at the two ends of the molecule.

Also, of concern are the ellipsoids for some of the other atoms, particularly C(9) and C(15), which are quite anisotropic. This might indicate the existence of some disorder in the structure, as was observed for p-azoxyanisole, or the effects of the pseudocenter of inversion at $(\frac{1}{4},0,0.)$ Neither explanation is completely satisfactory, since the final Fourier difference map contained no extraneous peaks to substantiate the presence of disorder; also, the coupling constants for the positional parameters between atoms related by the pseudocenter of inversion were all less than 0·2 at the R index level 0·22. The anisotropy may be due simply to the limited data or to errors in the approximate nature of the absorption correction.

Details of the molecular packing are illustrated in the projection diagrams of Fig. 2. The shortest intermolecular distances are listed in Table 4. The structure of p-azoxyanisole was found to be imbricated and to have the planes of adjacent molecules at right angles to each other. Neither of these features appears in the packing diagram of ethyl p-azoxybenzoate, despite the fact that the latter feature, in particular, is a common arrangement for planar molecules. The planes of the ethyl p-azoxybenzoate molecules make an angle of 17° with the c axis. By translation along this axis, a sheet of aligned molecules is generated. Translation along the a axis shows an alternate (*abab*) stacking of these sheets, with a molecule in one sheet being related to its neighbor in the adjacent one by inversion through a center. The bc projection in Fig. 2 shows that translation along the b axis traverses planar layer boundaries. These layers would be the ones at which slip would most easily occur in passing to the smectic phase.

The unique *cis* arrangement of the azoxy and carbonyl oxygen atoms results in a large dipole moment for the molecule. We estimate this to be 6·95 D from the bond moments given by Smyth (1955). The major component, $m_x = 6·73$ D, lies in the plane of the molecule and perpendicular to its long axis. The other orthogonal components, $m_y = 1·66$ D (along the molec-

Table 4. *Intermolecular distances less than* 3·1 Å

C(17)·····H(20)	2·89 Å	$a \cdots b$
O(23)·····H(19)	2·94	
H(10)·····H(7)	2·93	
H(10)·····H(8)	2·51	
H(11)·····H(7)	2·72	
H(16)·····O(13)	2·40	
H(16)·····H(20)	2·78	
H(17)·····C(20)	2·95	
H(17)·····H(19)	2·88	
H(17)·····H(20)	2·16	
H(24A)···O(22)	2·86	
H(24A)···H(19)	2·78	
H(25B)···O(22)	2·84	
H(25B)···H(19)	2·59	
H(2B)·····H(25A)	2·73	$a \cdots c$
H(1C)·····H(2A)	2·79	$a \cdots d$
H(2A)·····H(2A)	2·40	
O(3)······H(24A)	2·90	$a \cdots e$
O(23)·····H(11)	3·04	
C(24)·····H(1C)	2·99	
C(24)·····H(11)	3·05	
H(1C)·····H(24A)	2·68	
H(1C)·····H(24B)	2·91	
H(1C)·····H(25C)	2·87	
H(10)·····H(17)	2·54	
H(11)·····C(24)	3·05	
H(24A)···H(11)	2·41	

a:	x,	y,	z
b:	x,	y,	$1+z$
c:	$-x$,	$-y$,	$-z$
d:	$-x$,	$1-y$,	$-z$
e:	$1-x$,	$-y$,	$1-z$

ular axis) and $m_z = 0·0$ D, are much smaller. The dipole moment calculated in the same manner for *p*-azoxyanisole is only 4·30 D. Proper quantum mechanical calculations of the charge distribution for a molecule as large as ethyl *p*-azoxybenzoate would be prohibitively expensive. To investigate the intermolecular dipole–dipole interactions qualitatively,[§] we have assigned a fractional formal charge to the appropriate atoms representing the three major dipoles. Consideration of the pair of molecules related by translation along **c**, the direction of closest approach, reveals that the interactions of the three dipole pairs

are all attractive. Dipole interaction between molecules related by a center of inversion, the direction of second closest approach, is neutral or very weakly attractive. These observations imply that dipolar interactions are of major significance in determining molecular packing in the crystalline state of ethyl *p*-azoxybenzoate. Unpublished diffraction studies performed in this laboratory upon a number of compounds in the smectic state have shown that a characteristic feature of this state is the clustering of molecule pairs. The present study strongly suggests that this pairing may have a dipolar origin, in which case the presence of a large dipole component, m_x, in the plane of the molecule and perpendicular to the long axis, may be a structural requirement for smectogenic compounds.

Table 5 lists the observed and final calculated structure factors for ethyl *p*-azoxybenzoate.

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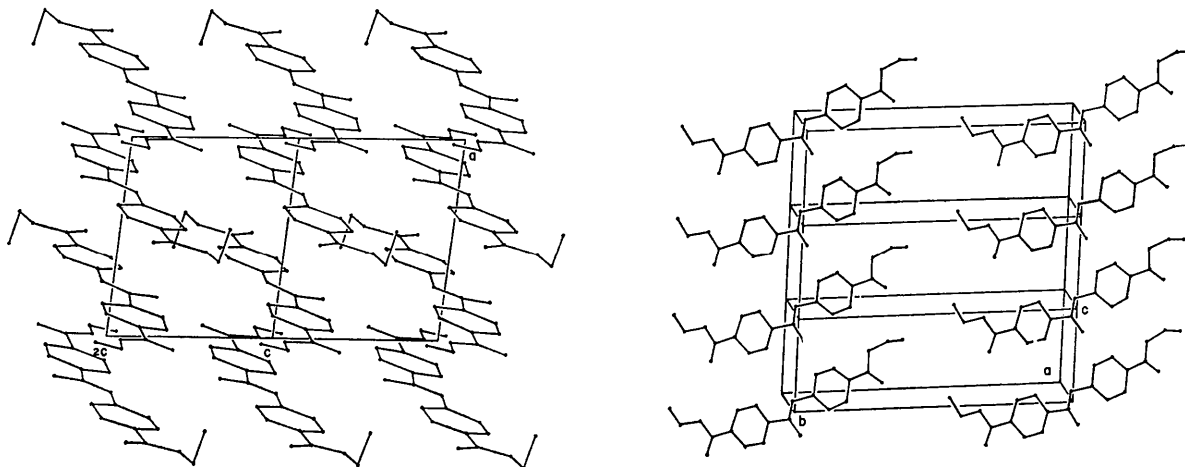
Fig. 2. Projections onto the *ac* and *bc* planes showing the packing of ethyl *p*-azoxybenzoate.

Table 5. *Observed and calculated structure factors* $\times 10$ *for ethyl p-azoxybenzoate.*

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Structure of the Chromophore from the Fluorescent Peptide produced by Iron-deficient *Azotobacter Vinelandii*

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Iron-deficient cultures of *Azotobacter vinelandii* contain a yellow-green fluorescent peptide which, upon hydrolysis, yields several amino acids and a chromophoric moiety that retains the spectral properties of the parent peptide. Crystal-structure analysis by X-ray diffraction has elucidated the molecular formula of the trimethylated derivative of the chromophore to be the zwitterion:
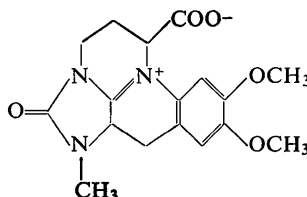
There appears to be an intramolecular attraction between N^+ and O^- since the plane containing the carboxyl ion is perpendicular to the plane containing the three conjugated rings, thus making the $N^+ \cdots O^-$ separation a minimum at 2·64 Å. The compound crystallizes with four molecules of water in the face-centered triclinic space group $F\bar{1}$ with cell parameters: $a = 9·12 \pm 0·02$, $b = 19·94 \pm 0·04$, $c = 21·17 \pm 0·04$ Å, $\alpha = 93·0 \pm 0·3$, $\beta = 92·8 \pm 0·3$, and $\gamma = 98·0 \pm 0·3°$. Visually estimated intensities were obtained from a crystal enclosed in a glass capillary. The final R index for anisotropic refinement was 9·0%. The structure is layered with sheets of hydrogen-bonded water molecules between layers of organic ions. Phases were determined directly from the structure factor magnitudes by the symbolic addition procedure.

Introduction

The presence of yellow-green pigments in cultures of *Azotobacter* was first reported by Beijerinck (1907) in his description of *Azotobacter agile*. The pigment was isolated from iron-deficient cultures of *Azotobacter vinelandii* and the principal component was shown to be a peptide with an attached yellow-green fluorescent chromophore (Bulen & LeComte, 1962). Hydrolysis of the peptide yields the rare amino acids homoserine and β-hydroxyaspartic acid as well as the chromophoric substance which retains the spectral properties of the parent peptide. The chromophore has the formula

$C_{14}H_{11}N_3O_5$, which upon prolonged treatment with diazomethane yields the trimethylated derivative $C_{17}H_{17}N_3O_5$ (Corbin, Karle & Karle, 1970). The purpose of this investigation was to establish the molecular formula of the chromophore. Crystals of the trimethylated derivative were provided by Dr J. L. Corbin of the Charles F. Kettering Research Laboratory. Details of the isolation, properties, and methylation of the chromophore, as well as data on degradation products will be published elsewhere (Corbin, 1970).

During the structure determination, it became apparent that a partial structure was obtained which