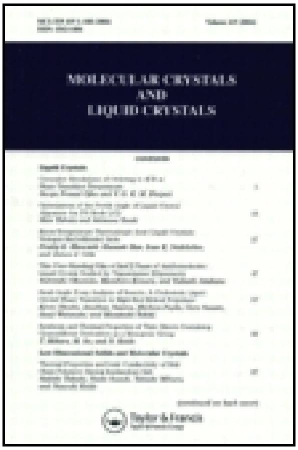


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Crystal Structure of the High Temperature Polymorph of Ethyl p-Azoxybenzoate

W. R. Krigbaum [a] & Tooru Taga [b]
[a] Gross Chemical Laboratory, Duke University, Durham, North Carolina
[b] Faculty of Pharmaceutical Sciences, Kyoto University, Kyoto, Japan

Version of record first published: 21 Mar 2007.

To cite this article: W. R. Krigbaum & Tooru Taga (1974): Crystal Structure of the High Temperature Polymorph of Ethyl p-Azoxybenzoate, Molecular Crystals and Liquid Crystals, 28:1-2, 85-98

To link to this article: http://dx.doi.org/10.1080/15421407408083154

Mol. Cryst. Liq. Cryst., Vol. 28, pp. 85-98
© Gordon and Breach Science Publishers, Ltd.
Printed in Dordrecht, Holland

Crystal Structure of the High Temperature Polymorph of Ethyl p-Azoxybenzoate[†]

W. R. KRIGBAUM and TOORU TAGA[‡]

Gross Chemical Laboratory
Duke University
Durham, North Carolina

(*Received August 20, 1973; in revised form November 12, 1973*)

The high temperature crystal (solid II) of smectogenic ethyl *p*-azoxybenzoate has a monoclinic unit cell of space group C2/c containing eight molecules. Its parameters are: $a = 23.36$ A, $b = 4.58$ A, $c = 32.24$ A and $\beta = 100.0°$. Intensities of 718 independent reflections were estimated visually from Weissenberg photographs, and the structure was solved by direct methods using Sayre's relation. Least-squares refinement using anisotropic temperature factors produced a final R value of 0.14. The molecule is nearly planar in both polymorphs, but solid II is partially disordered due to the presence of both *trans-cis* and *cis-trans* rotational conformers, whereas solid I is predominately in the form of the *cis-cis* conformer. The component of the dipole moment perpendicular to the molecular axis, and in the plane of the molecule, is only 3.1 *D*. for solid II, as contrasted with 6.73 *D*. for solid I. The reduced importance of dipolar interactions in the high temperature crystal is evident upon comparing the molecular packing in solids I and II. This observation makes it less likely that dipolar interactions make a significant contribution to the lateral attractions between molecules of ethyl *p*-azoxybenzoate in the smectic state.

[†] This work was supported in part by Grant GH-32744 from the National Science Foundation. We wish to express our appreciation to Dr. Patrick G. Barber for preliminary work performed in this laboratory which determined the unit cell parameters and established the space group of this crystal.

[‡] Present address: Faculty of Pharmaceutical Sciences, Kyoto University, Kyoto, Japan.

INTRODUCTION

This paper represents a continuation of our efforts to utilize x-ray diffraction to provide structural information at the molecular level concerning compounds which exhibit mesomorphic behavior. We have previously reported the crystal structures of the modifications stable at room temperature for nematogenic *p*-azoxyanisole[1] and smectogenic ethyl *p*-azoxybenzoate.[2] Despite the fact that these molecules share the common azoxybenzene skeleton, they differ substantially (in the crystalline state) in molecular conformation and mode of packing.

It is a significant observation that polymorphic crystalline modifications are quite common among the compounds which form mesophases. Thus, for example, ethyl *p*-azoxybenzoate exhibits a second crystalline polymorph (solid II) above 90°C, while two monotropic crystalline phases have been observed for *p*-azoxyanisole above room temperature.[3] It is reasonable to expect the molecular conformation in the mesophase to resemble more closely that appearing in the crystal which is stable at the highest temperature. Further, the changes in molecular packing on going from the low to high temperature crystalline polymorphs might provide insight into the further changes accompanying melting to the mesophase. For these reasons we believe that the crystal structures of the high temperature modifications merit investigation. We have chosen ethyl *p*-azoxybenzoate for this study because its high temperature crystal is thermodynamically stable, and the solid II → solid I transformation is sufficiently slow to permit the collection of intensity data for solid II at ambient temperature. Further, since bond distances and angles have been rather precisely determined for solid I, our interest can be confined primarily to *differences* in the molecular conformation and packing of the solids. We anticipated that these questions could be answered adequately from a low resolution study, so the reflections were recorded photographically.

EXPERIMENTAL

Several unsuccessful attempts were made to obtain a suitable single crystal of solid II by crystallization from solution at 95°C, or by sublimation at elevated temperature and reduced pressure. Crystallization of the pure material from the smectic phase proved to be more successful. A sample of the solid was sealed in an evacuated tube, and the latter was clamped in an inclined position in an oven and heated until transformation to the isotropic liquid phase occurred. The temperature was lowered to 114°C (slightly below the isotropic → smectic transition) and maintained constant for 3 days, then reduced to 95°C and held there for 3 days. After being slowly cooling to room temperature, the tube was broken and several crystals were picked free from the thin layer of material adhering to its walls. These were examined microscopically, and further selection was based upon x-ray photographs of the best specimens. The crystal chosen for intensity measurements was 0.1 x 0.3 x 1.5 mm in size. Its diffraction photograph showed relatively little streaking, but each spot was accompanied by weaker, sharp spots which were slightly displaced. This indicates that the crystal consists of a number of blocks which are slightly displaced with respect to one another.

Weissenberg photographs revealed that the unit cell is monoclinic with $a = 23.36$ Å, $b = 4.58$ Å, $c = 32.24$ Å and $\beta = 100.0°$. The density calculated for eight molecules per unit cell is 1.339 g/cc, or only slightly larger than the calculated density, 1.325 g/cc, for solid I.[2] The measured density of the solid II crystal, 1.28 g/cc, is significantly lower than the theoretical density, this defect arising from the imperfect character of the crystalline sample. The longest dimension of the sample is along the *b*-axis, as expected from the fact that this is the smallest unit cell dimension. The crystal was mounted along the *b*-axis. Systematic absences of the $hk\ell$ reflections for $h + k$ odd, of $h0\ell$ for h or ℓ odd, and of $0k0$ for k odd, correspond to those expected for space group C2/c or Cc. Since we expected solid II to have high symmetry, initial work was begun with the assumption that the space group was that of higher symmetry, C2/c. Subsequent results demonstrated that this was the correct choice.

Intensity data were collected at ambient temperatures using equi-inclination Weissenberg geometry with nickel-filtered copper K_α radiation. Intensities were estimated visually (using a calibrated standard scale) for 718 independent reflections found on photographs of the zeroth through third layer about the *b*-axis. The intensities decreased quite rapidly with order along this direction, so the total number of reflections which could be measured corresponds to only 19% of those which should theoretically have been observable within the copper K_α sphere. A scale factor for each layer was estimated from no-screen Weissenberg photographs, and Lorentz-polarization and spot shape corrections were applied, but no attempt was made to correct the intensities for absorption. The overall temperature factor 11.1 Å,[2] was estimated from a Wilson plot.

STRUCTURE DETERMINATION

The Patterson map in projection down the *b*-axis consisted of very broad peaks, and only yielded the information that the molecules are arranged with their long axes approximately perpendicular to the *a*-axis. Hence, an attempt was made to solve the structure in projection using direct methods. For this purpose normalized structure factors, $E_{h0\ell}$, were calculated according to the relation:

$$E_{ho\ell} = [\ |F_{ho\ell}|^2 / \epsilon (\sum_{i=1}^{N} f_i^2)\ ]^{1/2} \tag{1}$$

where $|F_{h0\ell}|$ is the structure amplitude for reflection $h0\ell$, f_i is the atomic scattering factor for atom i, and the sum is carried over the N atoms in one asymmetric unit. Here ϵ is an integer (usually 1) which takes into account the symmetry of special sets of reflections. The advantage of normalized structure factors is that they permit all classes of reflection to be compared on a common basis.

Since we are dealing with a centrosymmetric space group, the phase problem reduces to finding the sign of each structure factor. Values can be arbitrarily assigned to the phases of two structure factors (in the present case), thereby specifying the location of the origin of the two-dimensional projection. In practice, however, $E_{40\bar{2}}$ was assigned as positive, and letter assignments were given to represent the signs for three other reflections having large normalized structure amplitudes, (4,0,18), (2,0,12) and (2,0,18). The probable phases of other structure factors were then determined by application of Sayre's relation.[4] A two-dimensional E-map, computed using the phases for 56 reflections having large $|E|$ values, located the x and z coordinates of 21 of the atoms. The two-dimensional Fourier synthesis phased on these positions then located the four remaining atoms in the ester groups. Two cycles of full matrix least-squares reduced R to 0.23 for the two-dimensional projection. Next the y coordinates were sought by applying Sayre's relation to the general $hk\ell$ reflections. Several possible sign combinations were generated for 184 E values, and these possibilities were evaluated by comparison of the Fourier synthesis. The best of these was refined by full matrix least-squares, using isotropic temperature factors, to yield $R = 0.23$ for the full set of 718 reflections.

The fact that least-squares refinement had apparently converged while the R factor was still relatively large implied that the structure under consideration did not offer a totally correct representation of the actual crystal structure. Alternative two-dimensional structures were examined which involved different locations for the atoms of the azoxy group, and some of these gave relatively low R factors. Hence, the three atoms of the azoxy group were removed and a three-dimensional Fourier difference map was computed, phased upon the 22 remaining non-hydrogen atoms. This clearly revealed the presence of disorder in the crystal, as indicated by a second peak corresponding to oxygen on the opposite side of the azoxy nitrogen atoms. A similar type of disorder had previously been reported for azobenzene[5] and p-azoxyanisole,[1] but no evidence for disorder had been detected in the low temperature crystal of ethyl p-azoxybenzoate.[2]

The relative heights of the two peaks corresponding to oxygen were 0.7 and 0.3. Referring to the four possible rotational conformers of ethvl p-azoxvbenzoate and their designated names shown in Figure 1, we recall that solid I was presumed to consist exclusively of the *cis-cis* conformer. Evidently solid II is composed of some mixture of *trans-cis* and *cis-trans* conformers. Unfortunately,

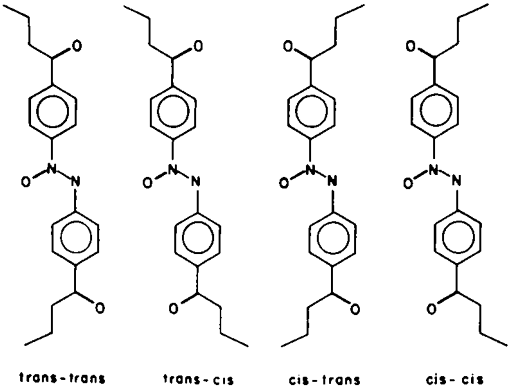


FIGURE 1 Four rotational conformers of ethyl *p*-azoxybenzoate.

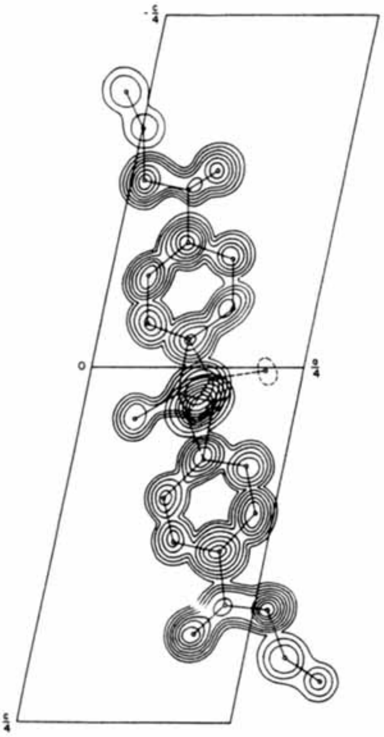


FIGURE 2 Composite electron density map. Full contours are drawn every 0.5 e.A^{-3} beginning at 2.0 e.A^{-3}. The dashed contour for 0(13') is drawn at 1 e.A^{-3}.

each of these conformers might enter a site in the crystal in two different ways, leading to four possible arrangements of each molecule in the crystal. At this point we were unable to assess the contributions of these four arrangements; however, based upon the observation that both oxygen positions appeared to be closer to one of the benzene rings, we could infer that the *trans-cis* conformer predominates.

In order to proceed further, we assigned the two possible oxygen positions the weights, 0.7 and 0.3, as determined from the difference map, and assigned equal weight to the two possible pairs of positions for the azoxy nitrogen atoms (which were not separately resolved in the difference map). Refinement of this model, using the full set of three-dimensional data and isotropic temperature factors, reduced *R* to 0.21. Introduction of anisotropic temperature factors for four of the non-hydrogen atoms in each of the two ester groups reduced *R* to 0.18, and allowing the temperature factors for the remaining atoms to go anisotropic produced the final *R* value, 0.14. In these last stages, refinement was performed by varying the positional and thermal parameters in alternate cycles. No attempt was made to refine the assigned weights of the alternative positions for the *N* and *O* atoms, and alternative sets of aromatic carbon positions were not considered. Figure 2 shows a composite of electron density sections taken through the atomic centers and projected down the *b*-axis. Throughout this work, the ORFLS least-squares program[6] was used with unitary weighting factors, and the atomic form factors were taken from the *International Tables for X-ray Crystallography.*[7] The final atomic coordinates and temperature factors are given in Table 1.

DESCRIPTION OF THE MOLECULAR STRUCTURE

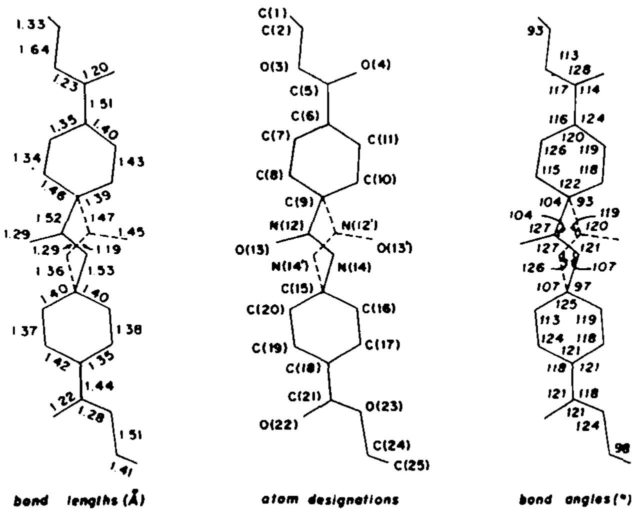
Figure 3 indicates the numbering of the atoms, and shows the bond lengths and angles. Values obtained here for solid II are of lower precision than those previously reported[2] for solid I, both because fewer reflections could be measured in the present case, and also due to the presence of disorder in solid II. Nevertheless, there is reasonable agreement between the bond lengths found here and those reported for solid I and for *p*-azoxyanisole. For example, for these respective structures the *C*(aromatic)-*N* bond lengths average 1.47, 1.56 and 1.50 Å, *N-N* is 1.24, 1.15 and 1.22 Å, *N-O* is 1.37, 1.29 and 1.28 Å, *C=O* is 1.20 and 1.19 Å, *C-O* is 1.26 and 1.32 Å, $O\text{-}CH_2$ is 1.58 and 1.47 Å, and $C\text{-}CH_3$ is 1.37 and 1.43 Å. Of the four possible arrangements, only the two illustrated in Fig. 3 are considered likely, since the other pair would correspond to a N-O bond length of 1.56 Å.

The average bond angle for C(9)-N(12)-N(14) is 112° in solid II, which stands in reasonable agreement with the corresponding values, 109.1° and 111.8° for

TABLE 1.
Atomic Coordinates and Temperature Factors for Ethyl *p*-azoxybenzoate Solid II†

	x/a	y/b	z/c	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C(1)	-339(10)	5078(62)	-1974(6)	92(11)	2919(355)	24(4)	106(51)	-4(5)	-65(32)
C(2)	-9(12)	3374(65)	-1693(7)	119(14)	2626(358)	28(5)	-38(59)	-18(6)	-60(36)
O(3)	131(7)	6022(44)	-1346(5)	64(7)	2687(225)	40(3)	-44(34)	-3(4)	-16(24)
O(4)	1044(7)	5617(43)	-1411(5)	88(8)	2776(250)	37(3)	123(39)	4(4)	-66(24)
C(5)	651(11)	6672(50)	-1266(6)	92(13)	1564(242)	28(4)	114(48)	18(6)	8(27)
C(6)	846(8)	8611(37)	-889(5)	47(7)	1140(173)	19(3)	39(31)	8(4)	-5(19)
C(7)	433(7)	9379(40)	-663(5)	41(6)	1466(189)	21(3)	45(30)	-5(4)	-34(20)
C(8)	511(9)	11146(58)	-327(6)	64(9)	2314(280)	22(4)	82(41)	-10(5)	-37(26)
C(9)	1089(12)	12426(40)	-217(6)	93(13)	911(178)	24(4)	109(40)	1(6)	3(20)
C(10)	1544(9)	11607(46)	-420(6)	70(9)	1431(212)	30(4)	54(36)	-12(5)	-59(24)
C(11)	1408(8)	9750(44)	-780(6)	39(7)	1490(221)	39(4)	-39(34)	1(4)	23(25)
N(12)	1073(17)	14049(81)	192(13)	45(14)	1413(371)	28(9)	-9(69)	14(8)	13(47)
N(12′)	1465(19)	14280(73)	90(9)	42(15)	998(387)	23(6)	7(63)	12(8)	14(37)
O(13)	628(7)	14387(44)	375(5)	46(7)	1889(180)	26(3)	-17(33)	3(4)	-26(21)
O(13′)	2066(15)	14738(92)	49(11)	37(13)	1622(354)	30(7)	28(68)	17(8)	-24(40)
N(14)	1531(17)	15655(107)	240(14)	40(18)	1933(550)	29(11)	18(67)	-8(9)	3(63)
N(14′)	1261(18)	15505(86)	354(12)	55(13)	830(502)	29(7)	20(66)	4(10)	40(49)
C(15)	1545(10)	17352(37)	652(5)	78(11)	952(170)	19(3)	-57(36)	-14(5)	-33(19)
C(16)	2112(9)	18411(44)	689(6)	61(8)	1434(224)	32(4)	-66(36)	-4(5)	-46(25)
C(17)	2326(7)	20260(40)	1018(5)	45(6)	1467(188)	20(3)	48(29)	4(3)	-37(19)
C(18)	1976(7)	20905(36)	1298(5)	36(6)	1050(161)	21(3)	10(27)	-2(4)	2(19)
C(19)	1399(8)	19795(48)	1248(5)	48(7)	1896(237)	28(4)	-28(36)	1(4)	-11(23)
C(20)	1166(9)	17914(51)	933(6)	70(9)	1870(242)	26(4)	64(38)	-3(5)	-40(26)
C(21)	2177(10)	22736(45)	1656(6)	65(10)	1549(228)	23(4)	97(41)	13(5)	9(23)
O(22)	1851(6)	23530(38)	1890(4)	69(6)	2776(210)	24(2)	77(30)	8(3)	-61(19)
O(23)	2694(6)	23726(36)	1698(4)	49(5)	2261(178)	29(2)	-32(27)	3(3)	-54(17)
C(24)	2932(9)	26048(49)	2015(6)	69(9)	1930(256)	34(4)	25(40)	-19(5)	-116(28)
C(25)	3429(9)	24551(66)	2217(5)	68(9)	3470(378)	24(3)	32(49)	-5(4)	-91(31)

† Both fractional coordinates and temperature factors are multiplied by 10^4. Temperature factors are for the expression $\exp[-(b_{11}h^2 + b_{12}hk + ...)]$. Numbers in parentheses give the standard deviations.



bond lengths (Å) atom designations bond angles (°)

FIGURE 3 Atom designations, bond lengths, and bond angles for the high temperature modification of ethyl p-azoxybenzoate. Standard deviations (σ) are: 0.02 A for C-C and C-O and 0.03 A for C-N and N-O bond legths; 1.4° for C-C-C, C-C-O, C-O-C bond angles, 1.8° for C-C-N- and 2.4° for C-N-N and N-N-O.

the other two crystal structures. For solid II, the remaining bond angles within the azoxy portion of the molecule actually correspond more nearly to the expected sp^2 hybridization than do those for the other two structures. Thus, $O(13)$-$N(12)$-$N(14)$ averages 124°, as compared with 134.7° for solid I and 130.8° for p-azoxyanisole. Recalling that alternative molecular positions were not considered for the latter two structures, this suggests the possibility that disorder is present in all three crystals. The difference Fourier maps gave evidence for disorder in p-azoxyanisole, but not in the case of the low temperature polymorph of ethyl p-azoxybenzoate. However, the shapes and directions of the anisotropic thermal ellipsoids for the atoms near the center of the molecule in solid I are at least suggestive of disorder as found in solid II. If the low temperature modification is actually disordered, this would require the presence of some admixture of the *trans-trans* conformer.

Since no account was taken of the possibility of alternate sets of positions for the aromatic carbon atoms, the rather unusual exterior angles at C(9) and C(15) must be discounted. The bond lengths and angles within the benzene rings are surprisingly regular, giving quite acceptable average values: 1.40 Å, 1.39 Å and 120°, 120°. The anisotropic thermal parameters for solid II indicate that the direction of the major thermal vibration is perpendicular to the molecular plane for $O(13)$, while $C(9)$ and $C(15)$ appear to be moving predominately in the plane of the molecule and perpendicular to its long axis. The behavior at C(9) and

C(15) is certainly a reflection of the fact that no cognizance was taken of the possibility of an alternate set of aromatic carbon positions. The two ester groups also appear to be vibrating in the molecular plane, and the rather short average C-CH_3 distance may be due to the fact that the bond distances were not corrected for thermal motion.

The principal difference in molecular conformation between solids I and II is, of course, that solid I is composed of molecules which are at least predominately in the high energy *cis-cis* conformation, while solid II contains a mixture of *trans-cis* and *cis-trans* conformers. In both cases the molecules are remarkably planar, with only the terminal methyl groups protruding from the molecular plane. The equation for the best least-squares plane representing the benzene ring composed of atoms C(6) through C(11), relative to an orthogonal set of axes, is:

$$-0.1463x + 0.7801y - 0.6083z = 4.4312$$

while for the ring C(15) through C(20) the corresponding equation is:

$$-0.2533x + 0.7915y - 0.5563z = 4.3090$$

the angle between the planes representing these two benzene rings is 6.8° for solid II, which may be compared with 0.5° reported for solid I and 22.6° for *p*-azoxyanisole.

Crowding of the azoxy oxygen atom and the ortho hydrogens of the benzene rings appears to be a general characteristic of the azoxy compounds whose crystal structures have been examined. Although no attempt was made to locate the hydrogen atoms in the present structure, approximate positions can be inferred from the known geometry and C-H bond length. These give for $O(13) \cdots H(20)$ and $O(13) \cdots H(8)$ the respective distances 2.1 and 2.2 Å, which may be compared with 2.2_5 and 2.6 Å for solid I, and 2.3 and 2.3 Å for *p*-azoxyanisole. With one exception, these are shorter than the sum of the van der Waals radii given by Pauling,[8] 2.6 Å. We are indebted to Dr. N. J. Bunce of the University of Guelph for revealing his unpublished studies showing that the photochemical transformation of aromatic azoxy compounds to *o*-hydroxyazo compounds, which proceeds by attack of the azoxy oxygen atom upon the ortho carbon atom of the more remote benzene ring, or its hydrogen atom, is a very rapid process. This observation is quite consistent with the short $O \cdots H$ distances which have been deduced from the crystal structure studies of aromatic azoxy derivatives.

DESCRIPTION OF MOLECULAR PACKING

Figures 4 and 5 show the arrangement of molecules in the high temperature crystal of ethyl *p*-azoxybenzoate as projected down the *b* and *a*-axes, respectively. The

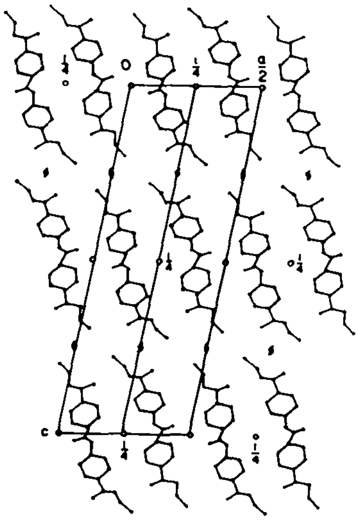


FIGURE 4 The arrangement of molecules in solid II as viewed in projection along the *b*-axis.

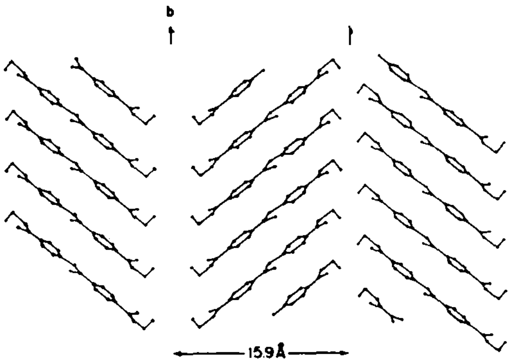


FIGURE 5 Molecular arrangement shown in projection down the *a*-axis. Pairs of molecules related by centers of inversion are not shown for the sake of clarity.

molecules have their long axes approximately perpendicular to the *a*-axis, and are stacked in layers parallel to the *ab* plane. Adjacent layers are related by a 2-fold rotation axis or a 2-fold screw axis, resulting in a herringbone pattern with a layer separation of 15.9 Å. By contrast, the layers in solid I are arranged in a parallel fashion (related by a center of inversion), with a spacing of 18.35 Å.

Using bond moments of 3.3 *D*. and 2.3 *D*. for the *N-0* and *C=0* bonds,

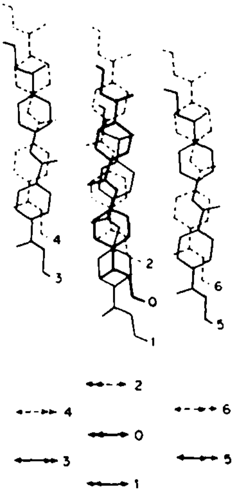


FIGURE 6 Packing diagram showing the relation of one molecule in solid II to its near-neighbors.

respectively, we estimate the dipole moment of the *trans-cis* conformer which predominates in solid II to be 3.4 *D*. This is substantially smaller than the moment, 6.95 *D*., previously estimated for the *cis-cis* conformer which predominates in solid I. Likewise, the component of the moment in the plane of the molecule, and perpendicular to its long axis, is reduced (3.1 *D*. for solid II and 6.73 *D* for solid I). This change is clearly reflected in the molecular packing diagram illustrated in Figure 6. A table of shortest intermolecular vectors reveals no abnormally short distances, but there are a number of contacts at about the sum of the van der Waals' radii involving atoms of molecules labelled 0 with those of either 1 or 2 in Figure 6. Thus the closest approach of molecules in solid II occurs between pairs of molecules stacked face to face, and related by translation along the *b*-axis. The dipolar interactions between these molecules are repulsive for the *trans-cis* conformers. The distance of second closest approach in solid II occurs between pairs of molecules meeting edge to edge, and related by a center of inversion (molecules 0 and 3 Figure 6), and for this pair there is a weakly attractive interaction between the *N-O* and *C=O* dipoles. By contrast, the closest approach in solid I involves molecules packed edge to edge, and related by a translation in the plane of the molecule. For a pair of these molecules the dipolar interactions are attractive. Pairs of molecules making the second closest approach in solid I are stacked face to face, and are related by an inversion center perpendicular to the molecular plane. Their dipolar interactions are either neutral or weakly attractive. Thus, comparison of the molecular packing in the two polymorphs does reveal the reduced importance of dipolar interactions in the high temperature crystal. Returning to the pair of molecules which are closest packed in solid II, we futher note that the dipolar interactions will become attractive if one conformer is followed by the other (*trans-cis* followed by *cis-trans*, or *vice versa*). This would favor an alternating arrangement of the two conformers within a stack, but we have no evidence that such alternation actually occurs in the disordered crystal.

CONCLUSIONS

The determination of the structure of the high temperature crystalline polymorph of ethyl *p*-azoxybenzoate was undertaken because we hoped this might provide further insight into the structure of the smectic *A* phase of this compound. A diffraction study has been previously reported[9] from this laboratory on the mesophases of three compounds showing smetic *A* morphology. It was found that all three exhibited a rapid decrease in structure amplitude with order, even after the intensities were corrected for the presence of distortions of the first and second kinds. The rapidity of this decrease could not be accounted for satisfactorily using a monomeric repeating motif, whereas a dimeric motif was successful. Refinement produced model structures in which the two molecules are displaced 6 to 7 Å along their long axes, and tilted with respect to the smectic planes. For the smectic phases of ethyl *p*-azoxybenzoate and thallium stearate, this produced reasonable agreement between the calculated and observed structure factors (after the latter had been corrected for distortions of the second kind), and also between the calculated and observed thermal parameters. This result was not meant to imply that the molecules actually exist as pairs within the smectic phase, but rather that some type of clustering of the molecules within a layer is required to explain the observed diffraction behavior of these smectic phases. This conclusion is perhaps not surprising, since lateral interactions would appear to be essential to the formation of any smectic phase.

When the crystal structure of the low temperature form of ethyl *p*-azoxybenzoate revealed molecules having the high energy *cis-cis* conformation, with a large component of the dipole perpendicular to the molecular axis, we pointed out the possibility that dipolar interactions might make a significant contribution to the lateral attractions in the smectic phase of this compound. However, since the high temperature crystal is composed of a mixture of *trans-cis* and *cis-trans* conformers, both of which have a dipole moment only half as large, and since dipolar interactions play a smaller role in determining the molecular packing in solid II, it now appears less likely that dipolar interactions will make a significant contribution to the lateral attractions within the smectic phase of ethyl *p*-azoxybenzoate.

We had also hoped that a comparison of the structures of solids I and II might provide hints concerning possible arrangements of the molecules in the smectic state. Both crystalline polymorphs do exhibit a layer structure, as contrasted with the imbricated structure which is characteristic of nematogenic anisaldazin [10] *p*-azophenetole [11] and *p*-azoxyanisole[1] in the crystalline state. This difference may arise simply from the fact that ethyl *p*-azoxybenzoate is very nearly planar in both solids, permitting a face to face closest packing of the molecules in stacked layers, whereas the other molecules are more twisted, and may therefore require an imbricated, face to edge arrangement for efficient packing.

The model structure taken to represent the smectic *A* phase was characterized[9] in terms of three parameters: the relative displacement, *DP* of the centers of the two molecules along their molecular axes, the tilt angle, ϕ, between the molecules and the perpendicular to the smectic layer planes, and the repeat distance, *L*. These parameters for solids I and II are compared in Table 2 with those deduced from refinement of the model for the smectic state. The transition from solid I to solid II involves an increased displacement of nearest-neighbor molecules, an increased tilt angle between the molecular axes and the normal to the planes separating the layers of ethyl groups, and a reduction of the spacing between these layers. The smectic model refined to a still larger displacement, but a smaller tilt angle. The interlayer spacing, *L*, was also larger but in that case a pair of displaced molecules had to be accommodated, rather than a single molecule. Although we might expect the structure of solid II to resemble the smectic state more closely than solid I, particularly since solid II crystallizes readily from the smectic phase, we are unable to draw any further deductions concerning its smectic phase from the structure of solid II.

The *trans-cis* and *cis-trans* conformers found in solid II have lower intramolecular dipolar energy than the *cis-cis* conformer which predominates in solid I. However, one should expect solid II to be stabilized, relative to solid I, by entropy considerations. If disorder is present, we can effectively ignore the azoxy oxygen atom, in which case the conformers appearing in solid II are more symmetrical than the *cis-cis* conformer which predominates in solid I. These two polymorphs do follow the general rule that the high temperature crystal will have a unit cell containing more elements of symmetry.

TABLE 2

Comparison of parameters in solids I and II
with those deducted for the model of the smectic state.

Phase	DP(A)	ϕ(°)	L(A)
Solid I	1.4	32.7	18.4
Solid II	2.8	39.6	15.9
Smectic (model)	6.3	29.7	20.4

References

1. Krigbaum, W.R., Chatani, Y. and Barber, Patrick G., *Acta Cryst.*, B26, 97 (1970).
2. Krigbaum, W.R. and Barber, Patrick G., *Acta Cryst.*, B27, 1884 (1971).
3. Robinder, R.C. and Poirier, J.C., *J. Am. Chem. Soc.*, 90, 4760 (1968).
4. Sayre, D., *Acta Cryst.*, 5 60 (1952).
5. Brown, C. J., *Acta Cryst.*, 21, 153 (1966).
6. Busing, W. R., Martin, K.O. and Levy, H. A., *ORFLS, A Fortran Crystallographic Least-Squares Program*, Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tennessee (1962).
7. *International Tables for X-Ray Crystallography*, Vol. III, Birmingham: Kynoch Press (1962).
8. Pauling, L.C., *The Chemical Bond*, p. 152, Cornell University Press, Ithaca, N. Y. (1967).
9. Krigbaum, W. R., Poirier, J. C. and Costello, M. J., *Mol. Cryst. and Liq. Cryst.*, 20, 133 (1973).
10. Galigné, J. L. and Falgueirettes, J., *Acta Cryst.*, B24, 1523 (1968).
11. Galigné, J. L. and Falgueirettes, J., *C. R. Acad. Sci. Paris* C, 268, 938 (1969).