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The Crystal and Molecular Structure of 4,4′di-*n*-heptyloxyazoxybenzene— A Smectic C Precursor

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The crystal and molecular structure of 4,4′di-*n*-heptyloxyazoxybenzene (HOAB), which melts to give a smectic C phase has been determined by direct methods. The compound crystallizes in space group $P\bar{1}$ with $a = 7.782(2)$, $b = 8.589(2)$, $c = 18.896(3)$ Å, $\alpha = 87.01(2)°$, $\beta = 97.50(2)°$ $\gamma = 96.43(2)°$. The structure was refined by full-matrix least-squares calculations to $R = 0.053$ for 3053 observed reflections. The molecules are in their most extended trans conformation, they are nearly planar and are packed in alternate sheets in which all the molecular long axes are either in head or tail orientation. The packing is also layer-like with the molecules making an angle of approximately 35° relative to the layers, which are the 001 (*ab*) planes. The long axes of the molecules are in a distorted hexagonal arrangement but the orientation of all molecules about these axes is closely similar.

The relationship between the molecular packing in the crystal and smectic C phases is discussed.

INTRODUCTION

Although a considerable amount of direct structural investigation has now been reported on the various liquid crystalline phases, surprisingly few detailed crystal structure determinations have been reported on liquid crystal precursors. The structures which have been determined are primarily those of crystals which melt to give smectic A or nematic phases and while it is widely believed that smectic phases are preceded by layered crystal structures this is based on very meagre evidence. It is nevertheless clear that a full knowledge of the crystal and molecular structure of liquid crystal forming substances is an essential prerequisite for a full and proper understanding of

structure and bonding in the mesophases themselves. It is only in the crystalline phase that enough diffraction data is obtainable to permit a *full* determination of the molecular conformation and packing, so that a determination of these properties for a series of compounds which yield different types of liquid crystal phases on melting must be a powerful starting point for trying to reach an understanding of these phases.

This paper reports the first step in such a programme in which we report the crystal structure of a typical member (heptyl) of the 4,4′-*n*-alkyloxyazoxybenzene series. For the C_1 to C_6 alkyls only a nematic phase is found, for C_7 to C_{10} smectic C and nematic phases are observed while the higher homologues have only smectic C phases.[1] Extensive work has been done on the smectic C structures[1,2,3] and the crystal structure has been determined for the first member of the series PAA.[4,5]

EXPERIMENTAL

Crystals of HOAB were obtained by dissolving the compound in a benzene-petroleum ether (40°C–60°C) mixture at room temperature and then keeping the solution at about 5°C. They were developed in the form of platey discs, the crystallographic *C* axis being normal to the disc. Preliminary cell parameters were derived from Weissenberg and Precession photographs and the space group was determined to be $P\bar{1}$ with $z = 2$. Accurate cell parameters were determined by least-squares calculations from 25θ values measured on an "Enraf Nonius" CAD-4 computer-controlled diffractometer using Nickel filtered CuKα radiation by means of the subroutines Search, Index and Detcel.[6] The diffracted intensities were measured on the same instrument employing ω-2θ step scanning mode. The scan rate used during data collection was variable and determined by a fast (20° min^{-1}) prescan. Backgrounds were collected for 25 % of the total scan time at each end of the range. For any given reflection the width of the scan was determined by the equation:—

Scan range/degs. $2\theta = A + B \tan\theta$, where $A = 0.8°$ and $B = 0.35°$. As a check for reliability of the electronics and of the crystal stability during data collection, two reflections were remeasured every 50 reflections. No significant variations in the intensity of the standard reflections was observed during the entire period of data collection. A total of 3835 reflections were collected in the interval $1.5° < \theta < 70°$, of which 3053 were classified as observed and had intensities greater than $1.5\sigma(I)$. These were corrected for Lorentz and Polarisation factors but no absorption correction (μ(CuKα) = 5.11 cm^{-1}) was made. A complete set of the crystallographically important parameters is given in Table I.

TABLE I

Summary of crystallographic data for HOAB

Molecular formula	$C_{26}H_{38}N_2O_3$
Formula Weight	426.26
Crystal System	Triclinic
Space group	$P\bar{1}$
Form/habit	Platey discs
a =	7.782(2) Å
b =	8.589(2) Å
c =	18.896(3) Å
α =	87.01(2)°
β =	97.50(2)°
γ =	96.43(2)°
V_c =	1243.29 Å^3
D_i =	1.14 g cm^3
Z =	2
$F(000)$ =	464.0
μ(CuKα) =	5.11 cm^{-1}
λ(CuKα) =	1.5418 Å
Number of independent reflections used in the least-squares calculations	3053

STRUCTURE DETERMINATION AND REFINEMENT

The structure was determined by application of the automatic centrosymmetric direct methods routine in the SHELX[7] crystallographic programme system. Normalized structure factors (E-values) were calculated by the modified K-curve methods,[8] and the reflections with $|E| > 1.20$ were used to generate phase sets. The phase set which contains the most probable solution, determined in terms of a reliability index (Parachor) and combination of M(obs) and qt tests,[7] was selected for calculation of an E-map. The 31 highest peaks in the map revealed the positions of all the non-hydrogen atoms in the asymmetric unit. The R index for this trial structure, calculated with isotropic temperature factors for all non-hydrogen atoms of $\bar{U}^2 = 0.05$ Å^2, was 0.28.

Refinement of the trial structure was carried out in a full matrix least-squares analysis using the same programme SHELX.[7] Isotropic refinement of the non-hydrogen parameters converged at $R = 0.153$ for the 3053 reflections with a further reduction to 0.114 with anisotropic temperature factors. A difference electron density map revealed all 38 hydrogen atoms in stereochemically feasible positions. The hydrogen atoms were included in all subsequent structure factor calculations and their positional and isotropic temperature factors were refined. During subsequent refinement cycles the three

TABLE II

Refined atomic parameters for non-hydrogen atoms with e.s.d.'s in parentheses

	x	*y*	*z*
O(1)	0.5356(2)	0.0644(1)	0.3915(1)
O(2)	1.0609(2)	0.3785(2)	0.6357(1)
O(3)	1.2073(2)	1.0208(2)	0.7941(1)
N(1)	0.9402(2)	0.4404(2)	0.5965(1)
N(2)	0.8962(2)	0.5760(2)	0.5999(1)
C(1)	0.2860(4)	−0.7881(3)	0.1480(2)
C(2)	0.2463(3)	−0.6316(3)	0.1710(1)
C(3)	0.3808(3)	−0.5565(2)	0.2265(1)
C(4)	0.3429(3)	−0.3966(2)	0.2469(1)
C(5)	0.4761(3)	−0.3246(2)	0.3063(1)
C(6)	0.4480(3)	−0.1585(2)	0.3213(1)
C(7)	0.5718(3)	−0.0930(2)	0.3815(1)
C(8)	0.6406(2)	0.1502(2)	0.4422(1)
C(9)	0.6050(3)	0.3047(2)	0.4456(1)
C(10)	0.7036(3)	0.4009(2)	0.4948(1)
C(11)	0.8364(2)	0.3437(2)	0.5420(1)
C(12)	0.8702(3)	0.1913(2)	0.5382(1)
C(13)	0.7727(3)	0.0941(2)	0.4887(1)
C(14)	0.9882(2)	0.6800(2)	0.6512(1)
C(15)	0.9084(3)	0.8157(2)	0.6551(1)
C(16)	0.9762(3)	0.9309(2)	0.7010(1)
C(17)	1.1285(2)	0.9144(2)	0.7455(1)
C(18)	1.2129(3)	0.7829(2)	0.7416(1)
C(19)	1.1438(3)	0.6663(2)	0.6959(1)
C(20)	1.1220(3)	1.1553(2)	0.8044(1)
C(21)	1.2325(3)	1.2484(3)	0.8611(1)
C(22)	1.1573(3)	1.3964(3)	0.8762(1)
C(23)	1.2664(4)	1.4925(3)	0.9338(1)
C(24)	1.1969(4)	1.6421(3)	0.9496(1)
C(25)	1.3103(5)	1.7389(3)	1.0036(2)
C(26)	1.2395(6)	1.8856(4)	1.0210(2)

hydrogen atoms attached to C(26) seemed to behave abnormally: their positional and thermal parameters tended to become unstable. A close examination of the difference electron density map showed a probable six local maxima around C(26) suggesting that there were two preferred orientations for that methyl group. In the following refinement cycles, however, rigid group constraints of these hydrogens was applied using known bond lengths and angles to fix the geometry of the methyl group, effectively imposing an ordered configuration but the large thermal parameters (Table III) confirm the presence of some disorder of this group, although it was not possible to make a meaningful refinement of the details of this disorder. After several more refinement cycles the analysis was terminated at $R = 0.053$ and $Rw = 0.060$.† Relative

† Structure factor tables may be obtained from the authors.

TABLE III

Refined anisotropic thermal parameter ($\times 10^4$) for the non-hydrogen atoms with e.s.d.'s in parentheses. The temperature factor is of the form:

$$\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2lhc^*a^*U_{31} + 2hka^*b^*U_{12})]$$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O(1)	762(8)	537(7)	758(8)	−141(6)	−17(7)	155(6)
O(2)	976(10)	687(8)	962(10)	−111(7)	279(8)	302(8)
O(3)	731(9)	654(8)	906(10)	−219(7)	−108(7)	196(7)
N(1)	685(10)	608(9)	669(9)	−6(7)	77(8)	155(8)
N(2)	667(9)	585(9)	707(10)	−31(7)	76(8)	143(8)
C(1)	1043(21)	846(17)	1139(23)	−398(18)	125(19)	84(15)
C(2)	855(16)	693(14)	846(16)	−157(12)	38(13)	89(12)
C(3)	718(13)	608(11)	770(13)	−149(10)	36(10)	125(10)
C(4)	635(13)	631(12)	728(13)	−102(10)	65(10)	121(9)
C(5)	685(13)	616(11)	724(13)	−102(10)	46(10)	142(10)
C(6)	684(13)	562(11)	731(13)	−85(10)	74(10)	137(10)
C(7)	743(13)	512(10)	705(13)	−65(9)	106(10)	160(9)
C(8)	712(12)	568(10)	587(10)	−31(9)	156(9)	107(9)
C(9)	781(13)	547(11)	705(12)	−76(9)	5(10)	137(10)
C(10)	836(14)	516(11)	697(12)	−42(9)	80(10)	169(10)
C(11)	674(11)	603(10)	562(10)	−33(8)	136(9)	97(9)
C(12)	747(12)	650(12)	679(12)	−52(10)	65(10)	219(10)
C(13)	764(13)	561(11)	680(12)	−78(9)	67(10)	192(10)
C(14)	650(11)	571(10)	607(11)	−35(8)	97(9)	75(9)
C(15)	670(12)	611(11)	728(12)	−53(9)	−45(10)	127(9)
C(16)	689(12)	565(11)	797(13)	−85(10)	−5(10)	154(10)
C(17)	603(10)	549(10)	663(11)	−57(9)	69(9)	85(8)
C(18)	605(12)	688(12)	767(13)	−134(10)	−16(10)	164(10)
C(19)	685(12)	604(11)	770(13)	−78(10)	106(10)	159(10)
C(20)	737(14)	564(11)	819(15)	−111(11)	51(11)	120(10)
C(21)	806(15)	621(12)	775(14)	−101(11)	19(12)	108(11)
C(22)	795(15)	657(12)	842(15)	−147(11)	36(12)	63(11)
C(23)	912(17)	726(13)	824(15)	−207(12)	−5(13)	137(12)
C(24)	1099(20)	676(14)	856(16)	−193(12)	62(15)	130(13)
C(25)	1423(26)	827(18)	1161(23)	−382(17)	92(20)	56(18)
C(26)	2230(42)	815(18)	1649(33)	−422(21)	451(30)	165(23)

weights used in calculating Rw were determined by $w = \{1/[\sigma^2(F) + gF^2\}$ where $g = 45 \times 10^{-6}$. With this weighting scheme the mean value of $w(|F_0| - |F_c|)^2$ was approximately constant over ranges of both $\sin\theta$ and (F_0/F_{max}) in the final cycle of least-squares. A final difference electron-density map showed no feature larger than 0.5 $Å^{-3}$ and the largest parameter shifts for the non-hydrogen atoms in the final cycle of refinement were less than 0.02 of their estimated standard deviations. Neutral-atom scattering factors were taken from Stewart, Davidson and Simpson[9] for H and from Cromer and Mann[10] for C, N and O atoms.

Final positional and thermal parameters for all atoms are presented in Tables II, III and IV using the numbering scheme of the molecule in Figure 1.

TABLE IV

Positional and isotropic thermal parameters for the hydrogen atoms (e.s.d.'s in parentheses) located in the structure determination. U^2_{iso} is the isotropic temperature factor in the expression $B_{iso} = 8\pi^2 U^2_{iso}$. The atoms are numbered according to the heavy atoms to which they are bonded.

	x	y	z	U^2_{iso}
H(11)	0.273(5)	−0.858(4)	0.186(2)	0.144(15)
H(12)	0.395(4)	−0.767(3)	0.117(1)	0.115(9)
H(13)	0.179(4)	−0.830(3)	0.112(1)	0.111(8)
H(21)	0.136(4)	−0.634(3)	0.195(1)	0.113(9)
H(22)	0.240(3)	−0.555(3)	0.136(1)	0.113(9)
H(31)	0.411(3)	−0.626(3)	0.271(1)	0.093(7)
H(32)	0.524(3)	−0.545(3)	0.215(1)	0.095(7)
H(41)	0.339(3)	−0.330(3)	0.203(1)	0.086(7)
H(42)	0.223(3)	−0.399(3)	0.257(1)	0.086(7)
H(51)	0.598(3)	−0.320(2)	0.292(1)	0.070(6)
H(52)	0.457(3)	−0.389(3)	0.350(1)	0.084(7)
H(61)	0.456(3)	−0.085(3)	0.280(1)	0.090(7)
H(62)	0.338(3)	−0.154(2)	0.335(1)	0.079(6)
H(71)	0.561(3)	−0.160(3)	0.427(1)	0.093(7)
H(72)	0.687(3)	−0.093(3)	0.370(1)	0.089(7)
H(91)	0.504(3)	0.346(2)	0.412(1)	0.082(6)
H(101)	0.695(3)	0.503(3)	0.502(1)	0.084(7)
H(121)	0.956(3)	0.152(2)	0.570(1)	0.075(6)
H(131)	0.807(2)	−0.009(2)	0.486(1)	0.070(6)
H(151)	0.800(4)	0.817(3)	0.621(1)	0.124(9)
H(161)	0.918(2)	1.023(2)	0.700(1)	0.066(5)
H(181)	1.319(3)	0.779(2)	0.773(1)	0.090(7)
H(191)	1.209(3)	0.586(2)	0.696(1)	0.076(6)
H(201)	1.117(3)	1.216(3)	0.761(1)	0.090(7)
H(202)	0.996(3)	1.122(3)	0.820(1)	0.103(8)
H(211)	1.348(3)	1.277(3)	0.843(1)	0.100(8)
H(212)	1.238(3)	1.183(3)	0.897(1)	0.108(9)
H(221)	1.141(3)	1.467(3)	0.826(2)	0.121(9)
H(222)	1.047(4)	1.365(4)	0.890(2)	0.133(11)
H(231)	1.295(4)	1.417(4)	0.992(2)	0.154(11)
H(232)	1.374(5)	1.522(4)	0.923(2)	0.166(15)
H(241)	1.168(4)	1.708(4)	0.912(2)	0.147(12)
H(242)	1.064(4)	1.621(3)	0.968(1)	0.121(9)
H(251)	1.363(5)	1.671(5)	1.047(2)	0.184(15)
H(252)	1.457(7)	1.765(6)	0.984(3)	0.286(20)
H(261)	1.218	1.948	0.970	0.376
H(262)	1.339	1.953	1.056	0.331
H(263)	1.120	1.870	1.045	0.400

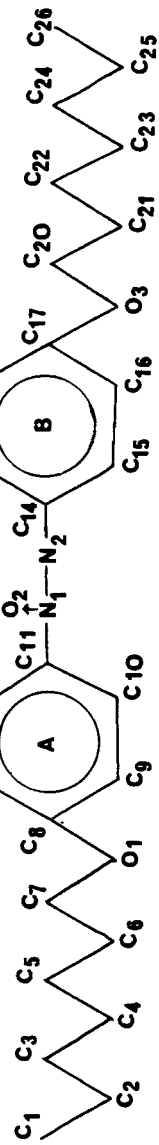

FIGURE 1 Numbering scheme for the non-hydrogen atoms of the molecule of HOAB.

TABLE V

Bond lengths (Å) for non-hydrogen atoms with e.s.d.'s in parentheses

C(1)–C(2)	1.509(4)	N(1)–N(2)	1.257(2)
C(2)–C(3)	1.499(3)	N(2)–C(14)	1.420(2)
C(3)–C(4)	1.516(3)	C(14)–C(15)	1.390(3)
C(4)–C(5)	1.530(3)	C(15)–C(16)	1.365(3)
C(5)–C(6)	1.514(3)	C(16)–C(17)	1.378(3)
C(6)–C(7)	1.482(3)	C(17)–C(18)	1.378(3)
C(7)–O(1)	1.438(2)	C(18)–C(19)	1.373(3)
O(1)–C(8)	1.364(2)	C(19)–C(14)	1.396(3)
C(8)–C(9)	1.392(3)	C(17)–O(3)	1.367(2)
C(9)–C(10)	1.375(3)	O(3)–C(20)	1.429(3)
C(10)–C(11)	1.390(3)	C(20)–C(21)	1.491(3)
C(11)–C(12)	1.372(3)	C(21)–C(22)	1.512(4)
C(12)–C(13)	1.379(3)	C(22)–C(23)	1.511(3)
C(13)–C(8)	1.375(3)	C(23)–C(24)	1.506(4)
C(11)–N(1)	1.458(2)	C(24)–C(25)	1.484(4)
N(1)–O(2)	1.266(2)	C(25)–C(26)	1.499(5)

Bond angles (°) for the non-hydrogen atoms with e.s.d.'s in parentheses

C(1)–C(2)–C(3)	114.4(2)	C(5)–C(6)–C(7)	112.7(2)
C(2)–C(3)–C(4)	113.8(2)	C(6)–C(7)–O(1)	108.6(2)
C(3)–C(4)–C(5)	113.4(2)	O(7)–O(1)–C(8)	118.5(1)
C(4)–C(5)–C(6)	113.2(2)	O(1)–C(8)–C(9)	115.3(2)
O(1)–C(8)–C(13)	124.9(2)	C(14)–C(15)–C(16)	122.2(2)
C(13)–C(8)–C(9)	119.9(2)	C(15)–C(16)–C(17)	119.9(2)
C(8)–C(9)–C(10)	119.8(2)		
C(9)–C(10)–C(11)	120.2(2)	C(16)–C(17)–C(18)	119.2(2)
C(10)–C(11)–C(12)	119.4(2)	C(16)–C(17)–O(3)	125.1(2)
C(10)–C(11)–N(1)	122.0(2)	C(18)–C(17)–O(3)	115.7(2)
C(12)–C(11)–N(1)	118.6(2)	C(17)–C(18)–C(19)	120.9(2)
C(11)–C(12)–C(13)	120.7(2)	C(18)–C(19)–C(14)	120.6(2)
C(12)–C(13)–C(8)	120.0(2)	C(17)–O(3)–C(20)	118.9(2)
C(11)–N(1)–O(2)	117.1(2)	O(3)–C(20)–C(21)	107.8(2)
C(11)–N(1)–N(2)	115.4(1)	C(20)–C(21)–C(22)	113.0(2)
O(2)–N(1)–N(2)	127.5(2)	C(21)–C(22)–C(23)	114.1(2)
N(1)–N(2)–C(14)	120.2(2)	C(22)–C(23)–C(24)	115.6(2)
N(2)–C(14)–C(15)	113.0(2)	C(23)–C(24)–C(25)	114.8(2)
N(2)–C(14)–C(19)	129.8(2)	C(24)–C(25)–C(26)	115.0(3)
C(19)–C(14)–C(15)	117.2(2)		

Bond lengths (Å) involving hydrogen atoms

C(1)–H(11)	0.91(3)	C(7)–H(71)	1.01(2)
C(1)–H(12)	1.09(3)	C(7)–H(72)	0.95(3)
C(1)–H(13)	1.05(3)	C(9)–H(91)	1.03(2)
C(2)–H(21)	1.02(3)	C(10)–H(101)	0.91(2)
C(2)–H(22)	0.92(3)	C(12)–H(121)	0.92(2)
C(3)–H(31)	1.03(2)	C(13)–H(131)	0.96(2)
C(3)–H(32)	1.15(2)	C(15)–H(151)	1.00(3)
C(4)–H(41)	0.98(2)	C(16)–H(161)	0.96(2)
C(4)–H(42)	0.98(3)	C(18)–H(181)	0.95(2)
C(5)–H(51)	1.02(2)	C(19)–H(191)	0.90(2)
C(5)–H(52)	0.98(2)	C(20)–H(201)	0.95(2)
C(6)–H(61)	0.98(2)	C(20)–H(202)	1.06(3)
C(6)–H(62)	0.93(2)		

TABLE V (*continued*)

C(21)–H(211)	1.00(3)	C(24)–H(241)	0.91(3)
C(21)–H(212)	0.85(3)	C(24)–H(242)	1.13(3)
C(22)–H(221)	1.10(3)	C(25)–H(251)	1.05(4)
C(22)–H(222)	0.93(3)	C(25)–H(252)	1.24(6)
C(23)–H(231)	1.25(3)	C(26)–H(261)	1.08
C(23)–H(232)	0.90(4)	C(26)–H(262)	1.08
		C(26)–H(263)	1.08

Bond angles (°) involving hydrogen atoms

C(2)–C(1)–H(11)	107(2)	C(4)–C(5)–H(51)	110(1)
C(2)–C(1)–H(12)	108(1)	C(4)–C(5)–H(52)	105(1)
C(2)–C(1)–H(13)	106(2)	C(6)–C(5)–H(51)	107(1)
H(11)–C(1)–H(12)	128(3)	C(6)–C(5)–H(52)	107(1)
H(11)–C(1)–H(13)	100(3)	H(51)–C(5)–H(52)	115(2)
H(12)–C(1)–H(13)	106(2)	C(5)–C(6)–H(61)	114(1)
C(1)–C(2)–H(21)	115(1)	C(5)–C(6)–H(62)	111(1)
C(1)–C(2)–H(22)	115(2)	C(7)–C(6)–H(61)	108(1)
C(3)–C(2)–H(21)	102(1)	C(7)–C(6)–H(62)	105(1)
C(3)–C(2)–H(22)	102(2)	H(61)–C(6)–H(62)	106(2)
H(21)–C(2)–H(22)	107(2)	C(6)–C(7)–H(71)	111(1)
C(2)–C(3)–H(31)	115(1)	C(6)–C(7)–H(72)	109(1)
C(2)–C(3)–H(32)	117(1)	O(1)–C(7)–H(71)	110(1)
C(4)–C(3)–H(31)	111(1)	O(1)–C(7)–H(72)	110(1)
C(4)–C(3)–H(32)	108(1)	H(71)–C(7)–H(72)	108(2)
H(31)–C(3)–H(32)	91(2)	C(8)–C(9)–H(91)	120(1)
C(3)–C(4)–H(41)	106(1)	C(10)–C(9)–H(91)	120(1)
C(3)–C(4)–H(42)	111(1)	C(9)–C(10)–H(101)	129(1)
C(5)–C(4)–H(41)	111(1)	C(11)–C(10)–H(101)	111(1)
C(5)–C(4)–H(42)	113(1)	C(11)–C(12)–H(121)	120(1)
H(41)–C(4)–H(42)	101(2)	C(13)–C(12)–H(121)	119(1)
C(12)–C(13)–H(131)	117(1)	C(22)–C(23)–H(231)	113(1)
C(8)–C(13)–H(131)	123(1)	C(22)–C(23)–H(232)	112(2)
C(14)–C(15)–H(151)	112(2)	C(24)–C(23)–H(231)	107(2)
C(16)–C(15)–H(151)	126(2)	C(24)–C(23)–H(232)	105(2)
C(15)–C(16)–H(161)	118(1)	H(231)–C(23)–H(232)	102(3)
C(17)–C(16)–H(161)	122(1)	C(23)–C(24)–H(241)	117(2)
C(17)–C(18)–H(181)	116(1)	C(23)–C(24)–H(242)	113(1)
C(19)–C(18)–H(181)	123(1)	C(25)–C(24)–H(241)	107(2)
C(18)–C(19)–H(191)	115(1)	C(25)–C(24)–H(242)	107(1)
C(14)–C(19)–H(191)	125(1)	H(241)–C(24)–H(242)	97(3)
O(3)–C(20)–H(201)	107(2)	C(24)–C(25)–H(251)	112(2)
O(3)–C(20)–H(202)	111(1)	C(24)–C(25)–H(252)	108(3)
C(21)–C(20)–H(201)	109(1)	C(26)–C(25)–H(251)	116(2)
C(21)–C(20)–H(202)	110(1)	C(26)–C(25)–H(252)	113(3)
H(201)–C(20)–H(202)	112(2)	H(251)–C(25)–H(252)	90(3)
C(20)–C(21)–H(211)	106(1)	C(25)–C(26)–H(261)	104
C(20)–C(21)–H(212)	102(2)	C(25)–C(26)–H(262)	108
C(22)–C(21)–H(211)	109(1)	C(25)–C(26)–H(263)	116
C(22)–C(21)–H(212)	113(2)	H(261)–C(26)–H(262)	110
H(211)–C(21)–H(212)	113(2)	H(261)–C(26)–H(263)	110
C(21)–C(22)–H(221)	108(2)	H(262)–C(26)–H(263)	110
C(21)–C(22)–H(222)	106(2)		
C(23)–C(22)–H(221)	110(1)		
C(23)–C(22)–H(222)	110(2)		
H(221)–C(22)–H(222)	109(2)		

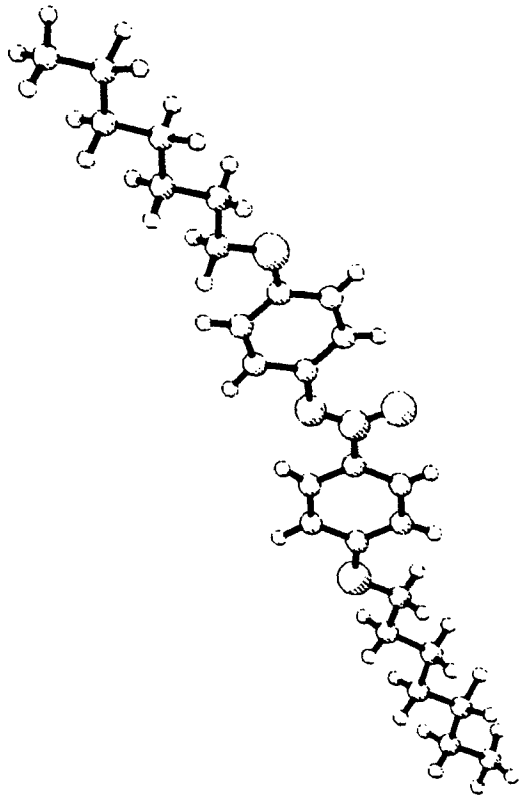

FIGURE 2 Perspective drawing of the HOAB molecule looking down the normal to the plane containing N(1), O(2) and N(2).

Figure 2 shows a perspective drawing of the molecule looking down the normal to the plane containing N(1), O(2) and N(2). Bond lengths and angles are listed in Table V.

DISCUSSION

The average C–C bond lengths in phenyl rings A and B are 1.381 and 1.380 Å respectively (expected value 1.396 Å).[11] In the ring B, C(15)–C(16) has a value of 1.365(3) Å, which is lower than the average of other bond lengths in the ring by 5σ. The average value of all the C–C single bond lengths in the structure is 1.504 Å (expected value 1.541 Å).[11] The C(6)–C(7) and C(24)–C(25) bond lengths are 1.482(3) Å and 1.484(4) Å, respectively. Both are shorter than the average of the other C–C single bond lengths in the structure by 7σ

and 5σ respectively. The two kinds of C–O bond lengths (1.36–1.37 Å and 1.43–1.44 Å) are close to the expected values as are the C–N, N–N and N–O bond lengths, the last two indicating some double bond character.

The average internal C–C–C bond angles in both phenyl rings is 120.0°. Two angles in ring B, C(14)–C(15)–C(16) = 122.2(2) and C(19)–C(14)–C(15) = 117.2(2), both deviate significantly from the mean value. The external non-hydrogen bond angles in the rings ranges from 113.0° to 129.8°, with a wide variation in individual values, depending on environment. The C–C–C bond angles in the side groups ranges from 107.8 to 115.6, with a mean value of 113.03°. The angles at C(7) and C(20), both having an oxygen, are significantly smaller than the mean value. The bond angles at N(1) show a spread of values from 115.4° to 127.5°.

The average C–H bond distance and C–C–H bond angle in phenyl rings are 0.95 Å and 120° respectively. The C–H distances in the alkyl chains range from 0.85 Å to 1.25 Å with a mean value of 1.02 Å. The average C–C–H and H–C–H angles are 107° and 106° respectively.

The molecule is in the trans configuration with the alkyl chains in their most extended all-trans conformation. The length of the molecule as characterized by the largest proton–proton distance is 30.18 Å and using a Van der Waals radius of 1.2 Å this gives an overall length of 32.6 Å. The molecule shows a high degree of planarity and shows no significant tendency to twist at the N—N—group. The degree of planarity may be characterized in terms

of least squares planes calculated for different parts of the molecule (see Figure 1 and Table VI). The equation and r.m.s. displacement for these planes are given in Table VI. Dihedral angles between planes are listed in Table VII. As expected, both the phenyl rings are planar within experimental error (r.m.s.

TABLE VI

Coefficients p, q, r, s, in the equation $(pX' + qY' + rZ' = s)$ of the least-squares planes in HOAB

The equations are defined with respect to orthogonal axes $X'(a^*)$, $Z'(c)$, Y'.

Plane No.	Atoms	p	q	r	s	r.m.s. displacement (Å)
1	Phenyl ring A	0.645	0.217	−0.733	−2.363	0.003
2	Phenyl ring B	0.517	0.400	−0.757	−2.844	0.007
3	N(1), N(2) and O(2)	0.645	0.282	−0.710	−1.970	—
4	C(17), O(3) and C(20)	0.464	0.460	−0.757	−2.904	—
5	C(8), O(1) and C(7)	0.600	0.282	−0.749	−2.656	—
6	C(1) to C(7)	0.548	0.360	−0.755	−2.988	0.042
7	C(20) to C(26)	0.491	0.448	−0.748	−2.668	0.020

TABLE VII

Dihedral angles of different planes of HOAB

Plane	Plane	Dihedral angles (°)
1	2	12.8
1	3	3.9
1	4	17.4
1	5	4.6
1	6	10.0
1	7	15.9
2	3	10.3
2	4	4.6
2	5	8.3
2	6	2.9
2	7	3.2
3	4	14.8
3	5	3.4
3	6	7.6
3	7	13.2
4	5	12.9
4	6	7.5
4	7	1.7
5	6	5.4
5	7	11.4
6	7	6.0

displacements are 0.003 Å and 0.007 Å for rings A and B respectively). The dihedral angles between the rings is 12.8°.

The molecular packing is shown in Figures 3–6 which show respectively drawings of the molecular packing looking down the [100], [010] and [001] directions and a schematic representation of the packing looking down the molecular long axes. Molecules are numbered so that those common to different figures may be readily identified.

No intermolecular atomic contacts shorter than the van der Waals distances are found in the crystal structure. The intermolecular contacts corresponding to van der Waals distances are listed in Table VIII.

The packing consists of pairs of molecules (2, 3 and 4, 5) in an antiparallel head to tail configuration with their N → O dipoles opposed attractively so that the molecules are displaced relative to each other along their long axes by ~3 Å. These pairs are stacked above each other along the *a* direction (Figures 4 and 5) and each molecule of the pair is part of a sheet of identical molecules. Translation along the *a* axis shows alternate sheets with molecules all in head or tail orientation, a molecule in one sheet being related to its neighbour in the next by inversion through a centre. The columns of molecule

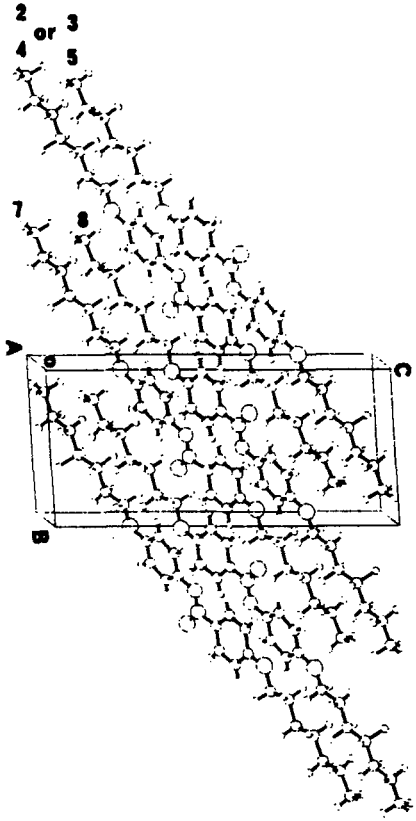

FIGURE 3 Packing of the molecules in crystalline HOAB looking down the [100] direction.

pairs stacked in the *a*-direction are displaced relative to neighbouring pairs, obtained by translation along the *b* axis, so that the oxygen of a heptyloxy group is approximately facing a benzene ring of the next equivalent molecule along the *b* direction (Figure 3). This results in a definite layer structure in which the layers are the 001 (*ab*) planes. The tilt angle of the long axes relative to the layers is $\sim 35°$ (55° to the layer normal). The long axes of the molecules are packed in a distorted and sheared hexagonal arrangement (Figure 6), the approximately planar molecules all having the same orientation of planes.

The relationship of the crystal structure to that in the smectic C phase which forms on melting is not simple but this is not to be expected since the S_c phase has liquid-like layers. Nevertheless, one or two features are worthy of comment. First the crystal structure may certainly be described as a layer structure; this is different from the imbricated structure of crystalline PAA which yields only a nematic phase on melting. Secondly, the tilt angle of the

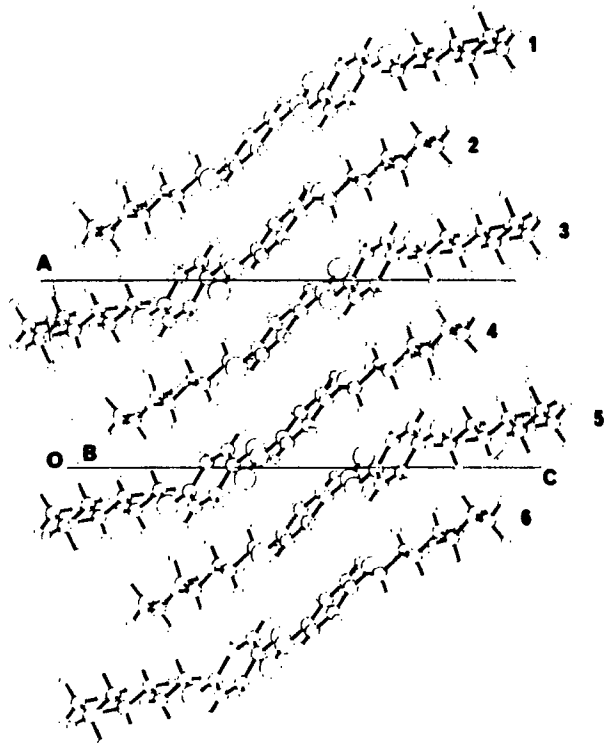

FIGURE 4 Packing of the molecules in crystalline HOAB looking down the [010] direction.

TABLE VIII

Selection of short intermolecular distances (Å)

H(12)–H(252)$^{(i)}$	2.346	C(1)–H(262)$^{(vii)}$	2.996
H(161)–H(62)$^{(ii)}$	2.393	C(17)–H(72)$^{(i)}$	3.022
H(212)–H(261)$^{(iii)}$	2.394	C(9)–H(71)$^{(viii)}$	3.030
H(32)–H(181)$^{(iv)}$	2.451	C(9)–C(19)$^{(i)}$	3.494
H(252)–H(242)$^{(v)}$	2.524	C(8)–C(19)$^{(i)}$	3.497
H(32)–H(191)$^{(iv)}$	2.543	O(1)–C(18)$^{(i)}$	3.499
O(2)–H(201)$^{(vi)}$	2.692	N(1)–C(10)$^{(i)}$	3.561
O(1)–H(151)$^{(ii)}$	2.881	N(2)–C(11)$^{(i)}$	3.597
O(2)–H(51)$^{(iv)}$	2.909	O(2)–C(10)$^{(i)}$	3.599

Symmetry Code

None x, y, z

(i) $2 - x, 1 - y, 1 - z$	(ii) $1 - x, 1 - y, 1 - z$
(iii) $x, y - 1, z$	(iv) $2 - x, -y, 1 - z$
(v) $2 - x, 3 - y, 2 - z$	(vi) $x, 1 + y, z$
(vii) $1 + x, 3 + y, 1 + z$	(viii) $1 - x, -y, 1 - z$

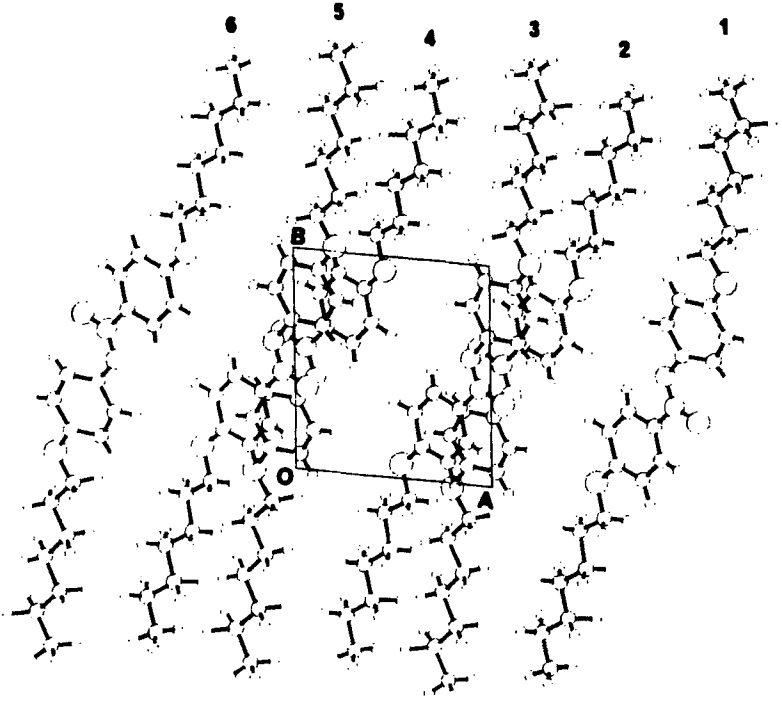

FIGURE 5 Packing of the molecules in crystalline HOAB looking down the [001] direction.

molecules relative to the layer normal in the S_c phase[3] is 32°, which is much smaller than that in the crystal (55°). This shows that on melting not only do the sheets of identical molecules disappear but shear of the columns of pairs occurs to change the layer character. However, it is a striking fact that the tilt angle in the S_c phase corresponds very closely with that between the close pairs of molecules relatively displaced by ~3 Å along their long axes. While

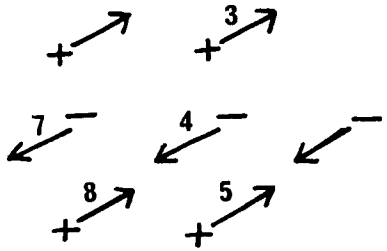

FIGURE 6 Schematic drawing of the molecular packing looking down the molecular long axes. The arrows denote the different directions of the N–O dipoles and the + and − signs the head and tail orientations.

it seems clear that the molecules in S_c phases are rotating about these axes with little bias[12] this result implies that, at least for this compound, the existence of the transverse dipoles in locally antiparallel (but rotating) molecules is still important in locating the relative longitudinal positions of the molecules and hence in determining the tilt angle in the S_c phase.

Acknowledgments

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