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The Crystal and Molecular Structure of Isobutyl 4-(4′-phenylbenzylidene-amino)cinnamate (IBPBAC) - and the Crystal Smectic E Transition

A. J. Leadbetter [a] , M. A. Mazid [a] & K. M. A. Malik [b]
[a] Chemsitry Department, University of Exeter, Exeter, Devon, U.K.
[b] Chemistry Department, Queen Mary College, University of London, Mile End Road, London, El, 4NS, U.K.
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The Crystal and Molecular Structure of Isobutyl 4-(4′-phenylbenzylidene-amino)cinnamate (IBPBAC)—and the Crystal Smectic E Transition

A. J. LEADBETTER and M. A. MAZID

Chemistry Department, University of Exeter, Exeter, Devon, U.K.

and

K. M. A. MALIK

Chemistry Department, Queen Mary College, University of London, Mile End Road, London E1 4NS, U.K.

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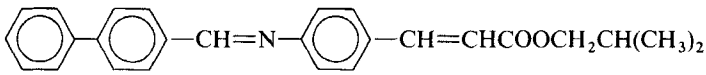
The crystal and molecular structure of isobutyl 4-(4′-phenyl-benzylidene amino) cinnamate (IBPBAC), $C_{26}H_{25}NO_2$, has been determined at room temperature by direct methods. The crystals belong to the monoclinic system with space group Cc, $a = 20.115(2)$, $b = 5.589(1)$, $c = 37.816(4)$Å, $\beta = 97.47\,(1)^\circ$ with eight molecules per unit cell. The structure was refined by full-matrix least-squares calculations to $R = 0.059$ for 1791 observed reflections. The structure is a bilayer with the molecules tilted at $\sim 40^\circ$ to the layer normal and packed in each half layer in a distorted hexagonal arrangement. This substance melts to give a smectic E phase and the relation between the structures of crystal and smectic E phases is described.

INTRODUCTION

As part of a programme to determine the crystal and molecular structure of a variety of liquid crystal precursors[1] we have studied isobutyl-4-(4′-phenyl-benzylidene amino) cinnamate (IBPBAC)



This substance has the following phase behaviour

$$\text{Cr } 86^\circ\text{C } S_E \ 114^\circ\text{C } S_B \ 164^\circ\text{C } S_A \ 207^\circ\text{C N } 214^\circ\text{C I}$$

and (together with the *n*-butyl homologue BPBAC) has been the subject of extensive previous work. The structure of all the liquid crystal phases has been examined in detail by X-ray diffraction[2,4,5] and the molecular dynamics in these phases determined by incoherent quasi elastic neutron scattering experiments.[2,6–8] Distribution functions for the long axis orientations in the S_A and N phases have been determined.[3] The interlayer correlations in the hexagonal S_B phase were also determined together with the detailed structure of the S_E phase. The compound is one of a series for which the first detailed structural study of the S_E phase was reported[9] (although this particular compound was not studied, but it was chosen by us because it possesses a nematic phase which is very helpful in producing aligned specimens of the smectic phases by cooling in a magnetic field). The earlier work showed that the S_E phase is orthorhombic with a chevron-like packing of the molecules in a monolayer structure. However, our very detailed measurements on S_E phases of IBPBAC showed this to be only an approximate description of the structure (at least of this compound) which is very probably an orthorhombic bilayer structure although a monoclinic monolayer structure with a tilt angle of $\sim 5^\circ$ cannot be completely ruled out.

In view of this considerable amount of detailed structural and other work a detailed knowledge of the crystal and molecular structure of this compound is clearly important in attempting to gain as complete an understanding as possible of the phase behaviour. This paper reports this structure and discusses the nature of the changes taking place at the crystal—S_E transition. A preliminary report of the main features of the crystal structure was made in Ref. 4.

EXPERIMENTAL

IBPBAC was supplied by Professor G. W. Gray and was crystallised by slow evaporation from a solution in acetone, in the form of platey needles, *b* being the needle axis. A crystal of dimensions 0.20 × 0.30 × 0.08mm. was mounted with *b* parallel to the goniometer axis. Preliminary cell dimensions and space group information were deduced from oscillation and Weissenberg photographs taken with CuKα radiation. The crystal was found to be monoclinic, with reflections of *hkl*, $h + k = 2n$ and hol, $l = 2n$, defining the space group to be either C2/*c* or C*c*. Space group C*c* rather than C2/*c* was indicated by the intensity statistics and confirmed later by the structure determination. This space group requires two molecules in the assymetric unit. Accurate cell parameters were determined by a least-squares refinement

of the setting angles for 25 reflections on an automatic single crystal 'Enraf Nonius' CAD-4 diffractometer by means of the subroutine Search, Index and Detcel.[10] Nickel filtered Cukα radiation ($\lambda = 1.5418$Å) was used.

The diffracted intensity of the 3531 independent reflections within one quadrant of the Cu sphere limited by $1.5° \leq \theta \leq 60°$ were measured on the same instrument by the $\theta - 2\theta$ step scanning mode. The scan rate used during data collection was variable and determined by a fast (20° min^{-1}) prescan. The background was measured at each end of the scan range and the background time to scan time ratio was 0.25. For any reflection the width of the scan was determined by the equation:

Scan range/degs. $2\theta = A + B \tan\theta$ where $A = 0.75°$ and $B = 0.30°$. The intensity of three reference reflections was monitored after every 50 measure-measurements to check the stability of the crystal during data collection. No significant variations in the intensity of the reference reflections was observed. Of the 3531 measured reflections, 1791 were classified as observed and had intensity greater than $2\sigma(I_h)$. It must be mentioned that even though the crystal used for the data collection was relatively large and optically single, the diffraction pattern was not of high quality, and moreover, did not extend to the high angle region. The data were corrected for Lorentz and Polarisation effects in the usual manner. Since the absorption coefficient was only 5.2 cm^{-1}, the data were not corrected for absorption. A complete set of the crystallographically important parameters is given in Table I.

TABLE I

Crystal data for IBPBAC

Molecular formula	$C_{26}H_{25}NO_2$
Formula weight	383.26
Crystal system	Monoclinic
Form habit	Platey needles
$a = 20.115(2)$Å	
$b = 5.589(1)$Å	
$c = 37.816(4)$Å	
$\beta = 97.47(1)°$	
$V_c = 4214.94$Å^3	
$z = 8$	
$F(000) = 1632e$	
D (calculated) $= 1.21$ g·cm^{-3}	
D (measured) $= 1.19$ g·cm^{-3}	
λ (CuKα) $= 1.541$Å	
μ (CuKα) $= 5.20$ cm^{-1}	
ω axis $= b$	
systematic absences:-	
hkl reflections $h + k = 2n + 1$	
hol reflections $1 = 2n + 1$	
Space group Cc or $C2/c$	
Cc is confirmed by structure determination	

STRUCTURE DETERMINATION AND REFINEMENT

The structure was determined by the application of the Multisolution Tangent Refinement subroutine 'TANG', in the SHELX[11] Crystallographic programme system. Normalised structure factors (E-values) were calculated by the modified K-curve methods.[12] A convergence map[13] was printed using triple phase relations with $|E| > 1.30$. The origin and multisolution phases were chosen by hand from reflections with high estimated α values and high ω values[13] and 512 sets of phase were generated. The phase set (NO 185) which contains the most probable solution, determined in terms of a reliability index, R(Karle) and PSIZERO,[13] was selected for calculation of an E-map. The highests peaks in the E-map revealed only the positions of three phenyl rings of one of the molecules, but there was no indication of the atomic positions of the other crystallographically independent molecule. Using the set of atomic positions obtained from the E-map as the starting point and with the help of a three dimensional sharpened Patterson map the complete asymmetric unit was derived in several stages.

Full matrix least-squares refinement of the trial structure was carried out using the same programme SHELX.[11] Isotropic refinement of the non-hydrogen atoms parameters converged at $R(=\Sigma\Delta F/\Sigma|F|) = 0.187$ for 3531 reflections with a further reduction to 0.147 with anisotropic temperature factors. A difference electron-density map was computed at this stage to locate hydrogen atom positions. The peaks in the map were in agreement with the anticipated locations, particularly those of the aromatic ring systems. But the peaks in the vicinity of terminal carbons were very broad, suggesting that there was considerable disorder associated with the peaks. This was confirmed by the presence of large thermal parameters of the parent carbon atoms. This is expected, since terminal atoms in general have greater thermal motion than other atoms.[14] Also in some other smectogenic compounds[1,15–18] the terminal carbons do indeed exhibit highly anisotropic thermal vibration. It is worth noting in this context that quasi elastic neutron scattering experiments on crystalline BPBAC at $\sim$60°C showed rapid dynamic disorder of the protons attached to the last two or three carbons of the n-butyl tail[2] but similar measurements have not been made for the isobutyl analogue.

The hydrogen atoms were included in the subsequent structure factor calculation in calculated positions (C—H = 1.08Å and C—C—H = 120° for sp^2 carbon and C—H = 1.08Å and H—C—H = 109.5° for sp^3 carbon). The refinement was continued with all non-hydrogen atoms anisotropic, the methyl groups as rigid bodies (C—H = 1.08Å and H—C—H = 109.5°) and one common Uiso (0.1Å^{-2}) for all hydrogen atoms. After several more refinement cycles the analysis was terminated at $R = 0.059$ and

$RW[= \Sigma\omega\Delta F^2/\Sigma\omega|F_0|^2]^{1/2} = 0.069$. The weighting scheme applied was $\omega = 1/[\sigma^2(F_0) + 0.018|F_0|^2]$ and this gave nearly flat analysis of variance with sin θ and $(F_0/F_{max})^{1/2}$ in the final cycle of least-squares.

Unobserved reflections were not included in the last cycle of refinement and a final difference electron-density map showed no anomalous peaks and no hints of disorder. Particular attention was paid to the region around the isobutyl groups as spurious peaks in the structure of related compounds[1,15–18] had indicated the presence of disorder. The largest shifts for the non-hydrogen atoms in the final cycle of refinement were less than 0.02 of their estimated standard deviations. Neutral scattering factors were taken from Stewart, Davidson and Simpson[19] for H and from Cromer and Mann[20] for C, O and N.

Final positional and thermal parameters for the non-hydrogen atoms are listed in Tables II and III and the numbering scheme of the molecule

TABLE II

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

Molecule 1 Atom	x	y	z
C(11)	0.2969(4)	−1.3415(18)	0.4577(2)
C(12)	0.2417(4)	−1.3962(17)	0.4358(2)
C(13)	0.2245(4)	−1.2254(18)	0.4087(2)
C(14)	0.2615(4)	−1.0291(17)	0.4034(2)
C(15)	0.3194(4)	−1.0026(15)	0.4264(2)
C(16)	0.3391(4)	−1.1455(15)	0.4537(2)
C(17)	0.2438(4)	−0.8645(13)	0.3737(2)
C(18)	0.1733(4)	−0.8055(17)	0.3630(2)
C(19)	0.1573(4)	−0.6514(16)	0.3349(2)
C(110)	0.2059(4)	−0.5496(20)	0.3175(2)
C(111)	0.2718(5)	−0.5942(20)	0.3289(3)
C(112)	0.2956(5)	−0.7436(20)	0.3568(2)
C(113)	0.1962(4)	−0.3776(22)	0.2873(3)
N(11)	0.1395(4)	−0.2882(15)	0.2769(2)
C(114)	0.1310(4)	−0.1309(13)	0.2457(2)
C(115)	0.0945(4)	0.0786(15)	0.2476(2)
C(116)	0.0809(4)	0.2247(19)	0.2180(2)
C(117)	0.1100(4)	0.1748(13)	0.1874(2)
C(118)	0.1475(4)	−0.0312(18)	0.1869(2)
C(119)	0.1605(4)	−0.1842(16)	0.2160(2)
C(120)	0.0971(3)	0.3317(17)	0.1544(2)
C(121)	0.0542(4)	0.5074(15)	0.1491(2)
C(122)	0.0555(4)	0.6391(15)	0.1154(2)
O(11)	0.0016(3)	0.7982(14)	0.1143(2)
O(12)	0.0936(3)	0.6229(15)	0.0942(2)
C(123)	−0.0063(5)	0.9632(26)	0.0864(3)
C(124)	−0.0675(5)	0.9902(26)	0.0670(3)
C(125)	−0.0718(5)	1.1887(21)	0.0379(3)
C(126)	−0.1226(4)	0.8578(21)	0.0665(2)

TABLE II (*continued*)

Molecule 2 Atom	*x*	*y*	*z*
C(21)	0.3009(4)	−1.8584(15)	0.6262(2)
C(22)	0.3617(5)	−1.8827(14)	0.6500(2)
C(23)	0.3822(4)	−1.7350(12)	0.6781(2)
C(24)	0.3412(3)	−1.5289(11)	0.6829(2)
C(25)	0.2823(3)	−1.4881(17)	0.6588(2)
C(26)	0.2654(4)	−1.6649(20)	0.6313(2)
C(27)	0.3609(3)	−1.3598(15)	0.7126(2)
C(28)	0.4255(3)	−1.1323(12)	0.7256(2)
C(29)	0.4450(4)	−1.1512(14)	0.7532(2)
C(210)	0.3955(5)	−1.0354(15)	0.7692(2)
C(211)	0.3266(4)	−1.0962(18)	0.7579(3)
C(212)	0.3146(3)	−1.2581(17)	0.7295(2)
C(213)	0.4095(4)	−0.8638(14)	0.7985(2)
N(21)	0.4668(3)	−0.7827(12)	0.8086(1)
C(214)	0.4714(3)	−0.6253(16)	0.8381(2)
C(215)	0.4433(4)	−0.6731(16)	0.8690(2)
C(216)	0.4518(3)	−0.5266(14)	0.8992(2)
C(217)	0.4939(3)	−0.3298(16)	0.8993(2)
C(218)	0.5236(3)	−0.2803(12)	0.8679(2)
C(219)	0.5149(4)	−0.4347(16)	0.8393(2)
C(220)	0.5026(4)	−0.1810(13)	0.9303(2)
C(221)	0.5458(4)	−0.0058(20)	0.9367(2)
C(222)	0.5506(6)	0.1478(21)	0.9689(2)
O(21)	0.6004(3)	0.2911(13)	0.9752(2)
O(22)	0.5110(4)	0.1405(15)	0.9899(2)
C(223)	0.6058(4)	0.4302(17)	1.0099(2)
C(224)	0.6680(3)	0.5540(14)	1.0135(2)
C(225)	0.6663(6)	0.7094(19)	1.0467(3)
C(226)	0.7304(5)	0.3623(21)	1.0178(3)

TABLE III

Refined anisotropic temperature factors ($X10^3$) of the non-hydrogen atoms with e.s.d's in parentheses. The temperature factor is of the form:

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

Molecule 1	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(11)	106(6)	103(7)	52(4)	8(4)	−1(4)	44(6)
C(12)	94(5)	95(6)	69(5)	2(5)	−33(4)	7(5)
C(13)	94(6)	126(7)	36(4)	−17(4)	−14(4)	−49(6)
C(14)	75(4)	118(7)	32(3)	12(4)	7(3)	−2(5)
C(15)	79(5)	65(5)	101(6)	16(5)	15(4)	−11(4)
C(16)	69(5)	64(5)	105(6)	22(5)	−22(4)	1(4)
C(17)	89(5)	52(4)	55(4)	17(3)	−2(3)	−8(4)
C(18)	70(5)	96(6)	82(5)	23(5)	−10(4)	−14(4)
C(19)	46(4)	91(6)	117(7)	16(5)	9(4)	−21(4)

TABLE III (*continued*)

exp $[-2\pi^2 (h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2lhc^*a^*U_{31} + 2hka^*b^*U_{12})]$						
Molecule 1	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(110)	91(6)	130(8)	70(5)	23(5)	−61(5)	16(6)
C(111)	109(7)	145(9)	92(6)	35(6)	24(5)	−77(7)
C(112)	109(7)	126(9)	85(6)	−51(6)	−5(5)	−33(7)
C(113)	43(4)	162(11)	181(11)	−27(9)	15(5)	−50(6)
N(11)	98(5)	104(6)	91(5)	−11(4)	16(4)	−69(5)
C(114)	102(6)	54(4)	64(5)	34(4)	−29(4)	−30(4)
C(115)	89(5)	75(6)	70(5)	15(4)	−2(4)	−11(5)
C(116)	91(5)	129(8)	58(4)	−12(5)	31(4)	−37(6)
C(117)	81(5)	61(4)	60(4)	−10(4)	14(4)	−14(4)
C(118)	99(5)	112(7)	55(4)	−5(5)	18(4)	28(6)
C(119)	79(5)	92(6)	62(5)	−11(4)	17(4)	−7(4)
C(120)	50(3)	121(7)	56(4)	−21(5)	23(3)	−33(4)
C(121)	57(4)	91(6)	72(5)	36(5)	0(3)	13(4)
C(122)	48(4)	84(6)	101(6)	5(5)	−17(4)	22(4)
O(11)	96(4)	137(6)	118(5)	71(5)	−28(4)	−20(4)
O(12)	90(4)	165(7)	106(5)	48(4)	41(4)	44(4)
C(123)	82(6)	199(12)	172(10)	172(10)	−60(6)	−77(8)
C(124)	132(8)	198(13)	116(8)	122(9)	−56(7)	−25(9)
C(125)	74(5)	132(9)	131(8)	39(7)	−1(5)	−7(6)
C(126)	56(4)	147(9)	109(6)	30(7)	−8(4)	−31(7)
Molecule 2						
C(21)	65(4)	73(5)	85(5)	−10(4)	11(4)	19(4)
C(22)	118(7)	59(5)	113(6)	−21(5)	47(6)	30(5)
C(23)	93(5)	41(4)	105(6)	−32(4)	24(5)	−16(4)
C(24)	61(4)	31(3)	111(6)	16(4)	−2(4)	−18(3)
C(25)	63(4)	111(6)	61(5)	1(5)	7(3)	−16(5)
C(26)	75(5)	143(9)	61(5)	11(6)	9(4)	1(6)
C(27)	53(4)	88(6)	97(6)	17(5)	4(4)	−1(4)
C(28)	64(4)	52(4)	63(4)	7(3)	2(3)	−5(3)
C(29)	120(6)	69(5)	38(3)	17(4)	−15(4)	−12(5)
C(210)	117(7)	64(5)	102(6)	−9(5)	49(5)	44(5)
C(211)	58(4)	120(8)	132(8)	−51(7)	−7(5)	−8(5)
C(212)	40(3)	113(7)	102(6)	−29(5)	1(4)	−1(4)
C(213)	108(6)	79(5)	55(4)	−46(4)	−26(4)	3(5)
N(21)	87(4)	86(4)	49(3)	−18(3)	−11(3)	−19(4)
C(214)	60(4)	104(6)	65(5)	24(4)	22(4)	11(5)
C(215)	76(5)	76(5)	110(7)	−32(5)	−12(5)	−5(4)
C(216)	60(4)	61(5)	99(6)	−12(4)	−6(4)	17(4)
C(217)	50(3)	101(6)	51(4)	−16(4)	−14(3)	22(4)
C(218)	67(4)	50(4)	69(4)	−25(4)	−24(3)	−5(3)
C(219)	83(5)	87(6)	59(4)	13(4)	20(4)	−1(5)
C(220)	89(5)	54(4)	70(4)	−25(4)	−20(4)	−5(4)
C(221)	87(5)	121(8)	60(4)	−0(5)	7(4)	17(6)
C(222)	114(7)	137(9)	44(4)	−39(5)	1(5)	37(7)
O(21)	85(4)	122(5)	101(4)	−22(4)	19(3)	−27(4)
O(22)	126(5)	176(7)	68(4)	−50(4)	−3(4)	23(5)
C(223)	126(7)	99(6)	47(4)	−37(4)	33(4)	−30(6)
C(224)	51(4)	75(5)	116(6)	23(5)	8(4)	4(4)
C(225)	135(9)	94(7)	121(8)	−55(6)	11(7)	−18(6)
C(226)	92(6)	129(9)	138(8)	−13(7)	29(6)	−10(6)

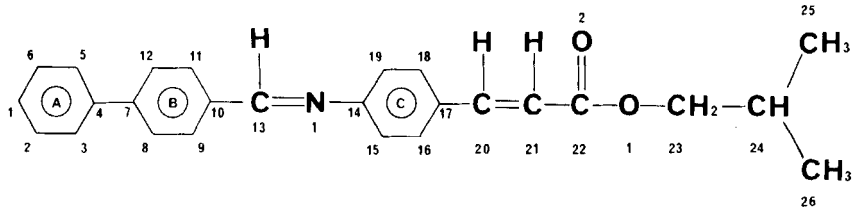


FIGURE 1 Numbering scheme for the atoms of the molecule of IBPBAC.

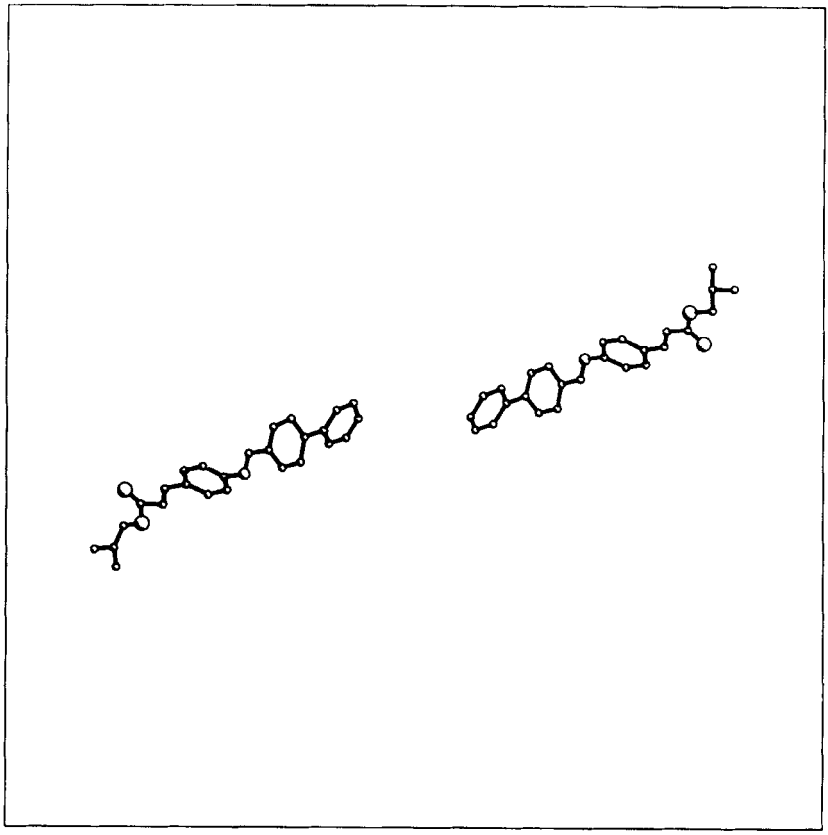


FIGURE 2 Drawing of the IBPBAC molecules in the asymmetric unit looking down the *b* axis.

in Figure 1. Table IV lists the hydrogen atoms coordinates and bond lengths and bond angles are given in Table V. Figure 2 shows a drawing of the molecule looking down the *b* axis.

TABLE IV

Atomic parameters for the hydrogen atoms located in the structure determination. The atoms are numbered according to the heavy atoms to which they are bonded

Molecule 1 Atom	*x*	*y*	*z*
H(111)	0.316	−1.457	0.480
H(121)	0.213	−1.558	0.438
H(131)	0.178	−1.251	0.391
H(151)	0.352	−0.853	0.422
H(161)	0.384	−1.114	0.472
H(181)	0.134	−0.883	0.377
H(191)	0.105	−0.610	0.327
H(1111)	0.309	−0.510	0.315
H(1121)	0.348	−0.766	0.366
H(1131)	0.239	−0.326	0.274
H(1151)	0.075	0.124	0.272
H(1161)	0.051	0.381	0.219
H(1181)	0.167	−0.078	0.163
H(1191)	0.193	−0.339	0.215
H(1201)	0.127	0.296	0.133
H(1211)	0.020	0.551	0.168
H(1231)	0.026	0.905	0.068
H(1232)	0.010	1.137	0.097
H(1241)	−0.077	0.968	0.094
H(1251)	−0.028	1.301	0.036
H(1252)	−0.115	1.292	0.039
H(1253)	−0.078	1.067	0.015
H(1261)	−0.126	0.720	0.087
H(1262)	−0.108	0.777	0.043
H(1263)	−0.170	0.946	0.061
Molecule 2			
H(211)	0.285	−1.989	0.606
H(221)	0.395	−2.028	0.645
H(231)	0.427	−1.772	0.696
H(251)	0.252	−1.332	0.661
H(261)	0.220	−1.636	0.613
H(281)	0.464	−1.406	0.714
H(291)	0.497	−1.116	0.762
H(2111)	0.286	−1.022	0.771
H(2121)	0.263	−1.307	0.721
H(2131)	0.369	−0.807	0.813
H(2151)	0.413	−0.832	0.869
H(2161)	0.426	−0.565	0.922
H(2181)	0.554	−0.122	0.867

TABLE IV (*continued*)

Molecule 2 Atom	*x*	*y*	*z*
H(2191)	0.541	−0.401	0.817
H(2201)	0.471	−0.217	0.951
H(2211)	0.580	0.028	0.917
H(2231)	0.604	0.310	1.032
H(2232)	0.565	0.557	1.009
H(2241)	0.674	0.661	0.990
H(2251)	0.711	0.810	1.043
H(2252)	0.677	0.588	1.069
H(2253)	0.627	0.831	1.052
H(2261)	0.776	0.468	1.021
H(2262)	0.730	0.242	0.996
H(2263)	0.729	0.261	1.042

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

Molecule 1			
C(11)—C(12)	1.33(1)	N(11)—C(114)	1.46(1)
C(12)—C(13)	1.41(1)	C(114)—C(115)	1.39(1)
C(13)—C(14)	1.36(1)	C(115)—C(116)	1.39(1)
C(14)—C(15)	1.37(1)	C(116)—C(117)	1.38(1)
C(15)—C(16)	1.32(1)	C(117)—C(118)	1.38(1)
C(16)—C(11)	1.41(1)	C(118)—C(119)	1.39(1)
C(14)—C(17)	1.46(1)	C(119)—C(114)	1.37(1)
C(17)—C(18)	1.46(1)	C(117)—C(120)	1.52(1)
C(18)—C(19)	1.37(1)	C(120)—C(121)	1.31(1)
C(19)—C(110)	1.37(1)	C(121)—C(122)	1.47(1)
C(110)—C(111)	1.36(1)	C(122)—O(11)	1.40(1)
C(111)—C(112)	1.38(1)	C(122)—O(12)	1.18(1)
C(112)—C(17)	1.46(1)	O(11)—C(123)	1.40(2)
C(110)—C(113)	1.49(2)	C(123)—C(124)	1.36(1)
C(113)—N(11)	1.26(1)	C(124)—C(125)	1.56(2)
		C(124)—C(126)	1.33(2)
Molecule 2			
C(21)—C(22)	1.43(1)	N(21)—C(214)	1.42(1)
C(22)—C(23)	1.37(1)	C(214)—C(215)	1.39(1)
C(23)—C(24)	1.44(1)	C(215)—C(216)	1.40(1)
C(24)—C(25)	1.42(1)	C(216)—C(217)	1.39(1)
C(25)—C(26)	1.44(1)	C(217)—C(218)	1.42(1)
C(26)—C(21)	1.32(1)	C(218)—C(219)	1.38(1)
C(24)—C(27)	1.48(1)	C(219)—C(214)	1.38(1)
C(27)—C(28)	1.35(1)	C(217)—C(220)	1.43(1)
C(28)—C(29)	1.40(1)	C(220)—C(221)	1.31(1)
C(29)—C(210)	1.39(1)	C(221)—C(222)	1.48(1)
C(210)—C(211)	1.44(1)	C(222)—O(21)	1.28(1)
C(211)—C(212)	1.40(1)	C(222)—O(22)	1.20(1)
C(212)—C(27)	1.32(1)	O(21)—C(223)	1.52(1)
C(210)—C(213)	1.47(1)	C(223)—C(224)	1.42(1)
C(213)—N(21)	1.25(1)	C(224)—C(225)	1.53(1)
		C(224)—C(226)	1.64(1)

TABLE V (b)

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

Molecule 1			
C(11)—C(12)—C(13)	114(1)	N(11)—C(114)—C(115)	118(1)
C(12)—C(13)—C(14)	125(1)	N(11)—C(114)—C(119)	121(1)
C(13)—C(14)—C(15)	116(1)	C(119)—C(114)—C(115)	121(1)
C(13)—C(14)—C(17)	123(1)	C(114)—C(115)—C(116)	120(1)
C(15)—C(14)—C(17)	122(1)	C(115)—C(116)—C(117)	121(1)
C(14)—C(15)—C(16)	125(1)	C(116)—C(117)—C(118)	118(1)
C(15)—C(16)—C(11)	116(1)	C(116)—C(117)—C(120)	122(1)
C(16)—C(11)—C(12)	125(1)	C(118)—C(117)—C(120)	120(1)
C(14)—C(17)—C(18)	119(1)	C(117)—C(118)—C(119)	118(1)
C(14)—C(17)—C(112)	121(1)	C(118)—C(119)—C(114)	117(1)
C(112)—C(17)—C(18)	120(1)	C(117)—C(120)—C(121)	127(1)
C(17)—C(18)—C(19)	118(1)	C(120)—C(121)—C(122)	115(1)
C(18)—C(19)—C(110)	122(1)	C(121)—C(122)—O(11)	104(1)
C(19)—C(110)—C(111)	120(1)	C(121)—C(122)—O(12)	129(1)
C(19)—C(110)—C(113)	127(1)	O(12)—C(122)—O(11)	127(1)
C(111)—C(110)—C(113)	113(1)	C(122)—O(11)—C(123)	117(1)
C(110)—C(111)—C(112)	125(1)	O(11)—C(123)—C(124)	119(1)
C(111)—C(112)—C(17)	115(1)	C(123)—C(124)—C(125)	115(1)
C(110)—C(113)—N(11)	121(1)	C(123)—C(124)—C(126)	130(1)
C(113)—N(11)—C(114)	120(1)	C(125)—C(124)—C(126)	116(1)
Molecule 2			
C(21)—C(22)—C(23)	125(1)	N(21)—C(214)—C(215)	124(1)
C(22)—C(23)—C(24)	117(1)	N(21)—C(214)—C(219)	119(1)
C(23)—C(24)—C(25)	120(1)	C(219)—C(214)—C(215)	117(1)
C(23)—C(24)—C(27)	120(1)	C(214)—C(215)—C(216)	124(1)
C(25)—C(24)—C(27)	120(1)	C(215)—C(216)—C(217)	119(1)
C(24)—C(25)—C(26)	117(1)	C(216)—C(217)—C(218)	118(1)
C(25)—C(26)—C(21)	126(1)	C(216)—C(217)—C(220)	118(1)
C(26)—C(21)—C(22)	115(1)	C(218)—C(217)—C(220)	123(1)
C(24)—C(27)—C(28)	123(1)	C(217)—C(218)—C(219)	121(1)
C(24)—C(27)—C(212)	120(1)	C(218)—C(219)—C(214)	122(1)
C(212)—C(27)—C(28)	116(1)	C(217)—C(220)—C(221)	127(1)
C(27)—C(28)—C(29)	124(1)	C(220)—C(221)—C(222)	124(1)
C(28)—C(29)—C(210)	119(1)	C(221)—C(222)—O(21)	119(1)
C(29)—C(210)—C(211)	119(1)	C(221)—C(222)—O(22)	123(1)
C(29)—C(210)—C(213)	124(1)	O(22)—C(222)—O(21)	118(1)
C(211)—C(210)—C(213)	118(1)	C(222)—O(21)—C(223)	117(1)
C(210)—C(211)—C(212)	116(8)	O(21)—C(223)—C(224)	107(1)
C(211)—C(212)—C(27)	126(1)	C(223)—C(224)—C(225)	104(1)
C(210)—C(213)—N(21)	123(1)	C(223)—C(224)—C(226)	110(1)
C(213)—N(21)—C(214)	116(1)	C(225)—C(224)—C(226)	113(1)

RESULTS AND DISCUSSION

Bond lengths and angles

The average C—C lengths in phenyl rings A, B and C for molecule 1 are are 1.37(1), 1.40(1) and 1.38(1) Å respectively. The internal and external C—C—C angles in the phenyl ring system ranges from 113.0° to 127.0° with a mean value of 120.0°. Although there are wide variations in individual values, only a few do differ significantly from the mean values (C(19)—C(110)—C(113) = 127° and C(11)—C(110)—C(113) = 113°). They are also in good agreement with the values found in other smectogenic compounds, 4,4′di-*n*-heptyloxyazoxybenzene,[1] *n*-*p*-methoxybenzylidene-*p*-phenylazoaniline,[15] di-*n*- propyl-*p*-terphenyl-4-4″-carboxylate,[16] ethyl *p*-azoxybenzoate[17] and *p*-azoxyanisol.[18] The C—C lengths between sp^2 carbons of the two molecules are very closely similar to each other with a mean of 1.48(1)Å. All C=C and C=O bonds are normal and very close to the expected values (expected value C=C = 1.34Å and C=O = 1.22Å[21]). The mean C—O bond length is 1.40(1)Å for both molecules, but in molecule 2, they differ significantly from the mean value (C(222)—O(21) = 1.28(1)Å and O(21)—C(223) = 1.52(1)Å). The bond angles at C(20) and C(21) varies from 115° to 127° with a mean value of 123.° The average angle at C(22) is 120° for both molecules but in molecule 1 they differ significantly from the mean value. The N—C and C=N bond lengths and angles at C(13) are normal and close to the expected values (N—C = 1.47Å; C=N = 1.26Å[21]), the latter indicates double bond character. The C—C bond lengths of the isobutyl groups range from 1.33Å (C(124)—C(126) = 1.33(1)Å) to 1.64Å (C(224)—C(226) = 1.64(1)Å) with a mean value of 1.47Å and their corresponding bond angles vary from 104 (C(223)—C(224)—C(226) = 104(1)° to 130° (C(123)—C(124)—C(126) = 130(1)°) with a mean value of 115°. These averages are quite acceptable but some of the individual values are unrealistic. It is quite possible that this is caused by the disorder as discussed above.

Molecular conformation

The two crystallographically independent molecules in the unit cell are in trans configuration with the acrylate and isobutyl groups in their most extended conformation (Figure 2). There is no significant tendency to twist either at amino or carbonyl groups. The equations of the least-squares best planes calculated for different parts of the molecules and r.m.s. displacements for these planes are given in Table VI. As expected, all the phenyl rings for both molecules are planar within experimental error (r.m.s. displacement for rings, A, B and C of molecule 1 are 0.18, 0.021 and 0.018Å respec-

TABLE VI

Coefficients p, q, r and s in the equation ($pX' + qY' + rZ' = s$) of the least square best planes in IBPBAC. The equations are defined with respect to the orthogonal axes X' (a^*), Z' (c), Y'

Plane No.	Atoms	p	q	r	s	r.m.s. displacement (Å)
Molecule 1						
1	Phenyl ring A	−0.517	0.536	0.667	3.930	0.018
2	Phenyl ring B	0.040	0.765	0.643	5.214	0.021
3	Phenyl ring C	0.820	0.520	0.239	3.924	0.018
4	C(110) to C(114)	0.216	0.776	0.593	5.319	0.020
5	C(117), C(120) to O(12)	0.609	0.669	0.426	4.861	0.033
6	C(121) to O(12)	0.595	0.687	0.417	4.883	0.005
Molecule 2						
1	Phenyl ring A	0.512	0.529	−0.677	−17.896	0.017
2	Phenyl ring B	−0.033	0.754	−0.656	−23.066	0.022
3	Phenyl ring C	0.784	−0.559	0.271	17.608	0.023
4	C(210) to C(214)	0.814	−0.767	0.615	23.119	0.012
5	C(217), C(220) to O(22)	0.560	−0.681	0.472	22.215	0.041
6	C(221) to O(22)	0.537	−0.711	0.454	21.286	0.006

tively and for molecule 2 they are 0.017, 0.022 and 0.023Å respectively). The conformation of the two crystallographically independent molecules have remarkable similarity. The phenyl ring A for the first molecule makes an angle of 35.0° with the middle ring B, and this angle is 34.3° for the second molecule. Similarly, ring B of the molecule 1 makes an angle 54.3° with the phenyl ring C and corresponding value is 51.3° for the molecule 2. Both amino and acrylate group adopt a planar conformation within experimental error. The acrylate group makes an angle of 70.8° with the phenyl ring C for the first molecule and this angle is 66.1° for the second molecule. Important dihedral angles are given in Table VII.

Molecular packing

The molecular arrangement of crystalline IBPBAC is shown in Figures 3–5, which show respectively drawings of the molecular packing looking down the [010] and [100] directions, and approximately down the molecular long axis in a half layer. The crystal has a head to tail bilayer structure with the molecular long axes at an angle of ~40° to the layer normal. The packing of the molecules in the layers is approximately hexagonal (cf. the Smectic E and B phases)[4] and alternate rows of molecules in the layers have opposite orientations about the long axes. The layer-like nature of the structure is very

TABLE VII

Dihedral angles of different planes of IBPBAC

Plane	Plane	Dihedral angles (°)
Molecule 1		
1	2	35.0
1	3	89.2
1	4	45.5
1	5	70.8
1	6	70.1
2	3	54.3
2	4	10.5
2	5	35.9
2	6	35.2
3	4	43.8
3	5	18.4
3	6	19.1
4	5	25.4
4	6	24.7
5	6	1.4
Molecule 2		
1	2	34.3
1	3	94.5
1	4	43.3
1	5	66.1
1	6	65.9
2	3	51.3
2	4	9.0
2	5	32.7
2	6	31.6
3	4	42.3
3	5	18.7
3	6	19.7
4	5	23.7
4	6	22.6
5	6	2.4

clearly defined with all the CH=N groups and alternate  groups coplanar, and adjacent molecules are packed with the branched ends of the isobutyl group filling space beyond the end phenyl group of the adjacent molecule. Hence both polar and steric factors tend to promote the planar structure.

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 contacts are listed in Table VIII.

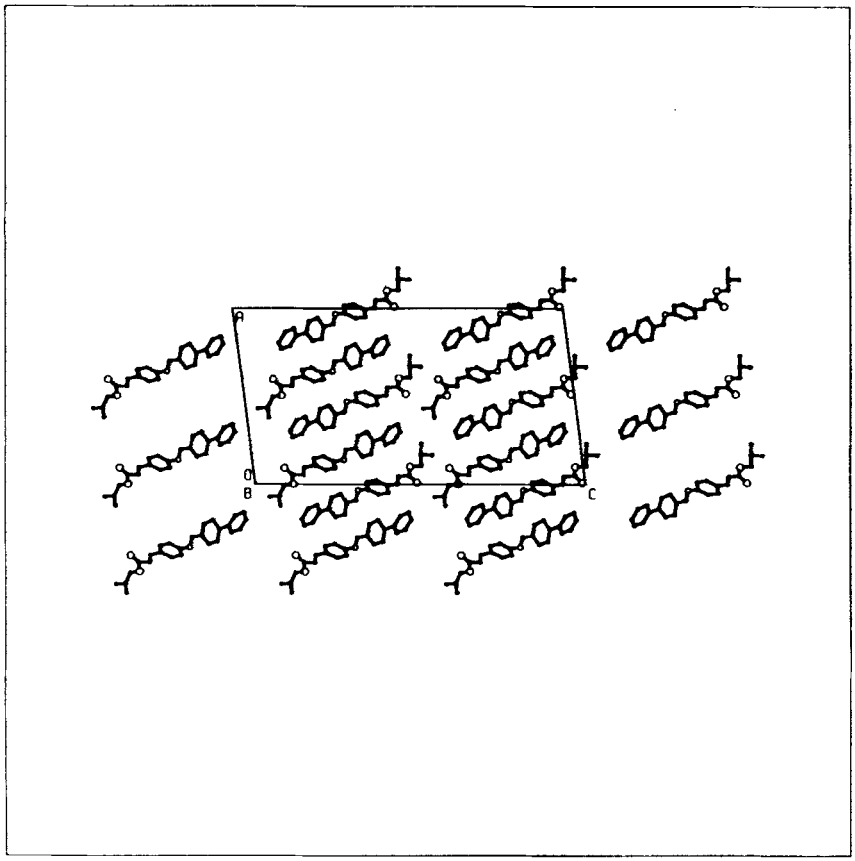


FIGURE 3 Packing of the molecules in crystalline IBPBAC looking down the [010] direction.

TABLE VIII

Selection of short intermolecular distances (Å)

O(12)—C(225)[i]	3.37	O(12)—C(26)[v]	3.56
C(118)—C(121)[ii]	3.39	C(22)—C(27)[v]	3.57
C(216)—C(221)[ii]	3.47	C(118)—C(122)[ii]	3.58
C(111)—C(211)[iii]	3.49	C(216)—C(222)[ii]	3.58
C(18)—C(219)[iv]	3.51	C(215)—C(221)[ii]	3.59
C(12)—C(17)[ii]	3.52	N(11)—C(116)[ii]	3.61
C(119)—C(121)[ii]	3.54	C(125)—O(22)[vi]	3.64
C(16)—O(22)[v]	3.55	O(12)—C(223)[vii]	3.66

Symmetry code

None x,y,z

i) $\frac{1}{2} + x, \frac{1}{2} + y, 1 + z$ ii) $x, 1 + y, z$

iii) $x, 2 - y, \frac{1}{2} + z$ iv) $\frac{1}{2} + x, 1.5 - y, \frac{1}{2} + z$

(v) $x, 1 - y, \frac{1}{2} + z$ vi) $\frac{1}{2} + x, 1.5 + y, 1 + z$

vii) $\frac{1}{2} + x, \frac{1}{2} - y, 1 + z$

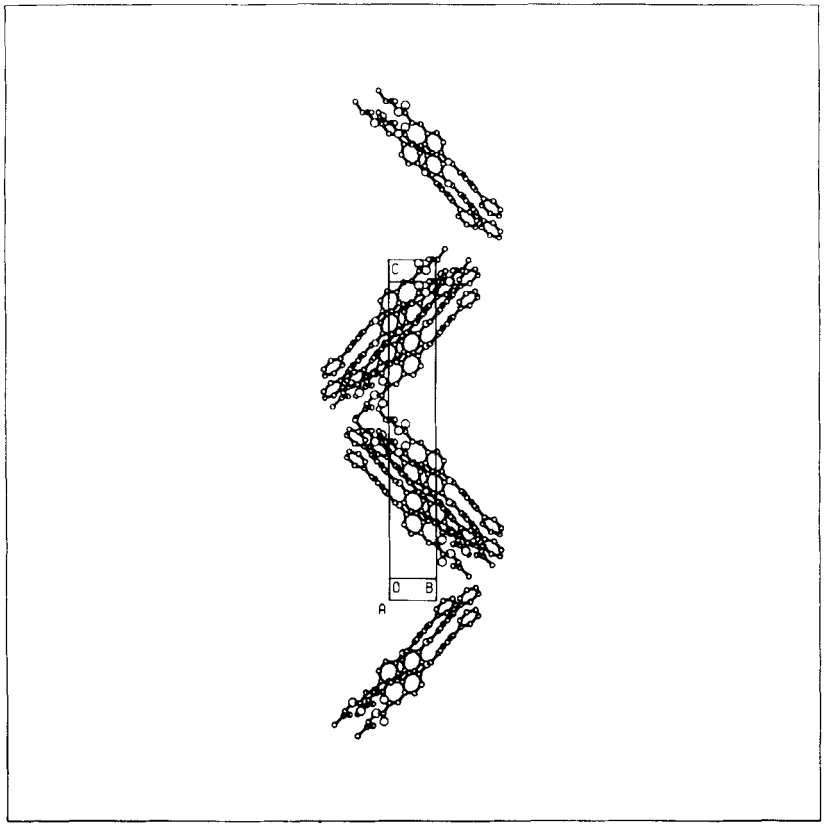


FIGURE 4 Packing of the molecules in crystalline IBPBAC looking down the [100] direction.

The crystal-S_E Transformation

The phase behaviour of IBPBAC has been confirmed using differential scanning calorimetry (DSC) with the following results for the reduced transition entropies:

transition	CR-S_E	S_E-S_B	S_B-S_A	S_A-N	N-I
$\Delta S/R$)	4.1 ± 0.2	0.28 ± 0.06	0.75 ± 0.06	0.63 ± 0.06	0.11 ± 0.02

It was ascertained that there are no crystal-crystal phase transitions between 80K and the mp so that the crystal phase whose structure is reported here is the one which melts to give the S_E phase. The changes occurring at this transition are by far the most important of the 5 distinct transitions which comprise the total melting process in that 70% of the total entropy increase occurs at this first step.

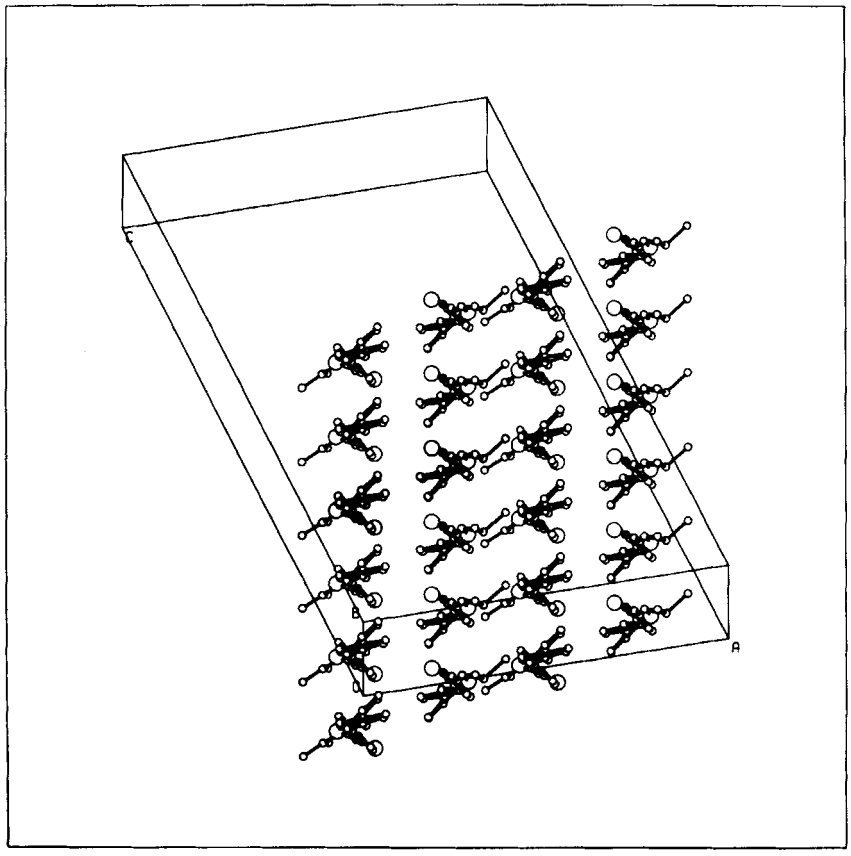


FIGURE 5 Packing of the molecules in a half layer of IBPBAC looking approximately down the molecular long axis in a given half layer.

The details of the S_E structure are not completely resolved as a result of the inaccessibility of true monodomain samples but as will be shown below the essential packing in the layers is well established.

Specimens prepared either by cooling through the nematic phase in a strong magnetic field or by melting a single crystal are always disordered about the layer normal[4]: in the former case almost randomly and in the latter by the formation of domains with 6 (or sometimes only 4) different orientations. Half of these are very well ordered giving sharp Bragg spots and half have some orientational disorder around c giving arc-like reflections. The ab plane of the S_E unit cell is in the plane of the smectic layers and is certainly rectangular, with $a = 5.30$Å and $b = 8.30$Å. However, the diffraction pattern showed clearly that the structure cannot be an orthorhombic monolayer

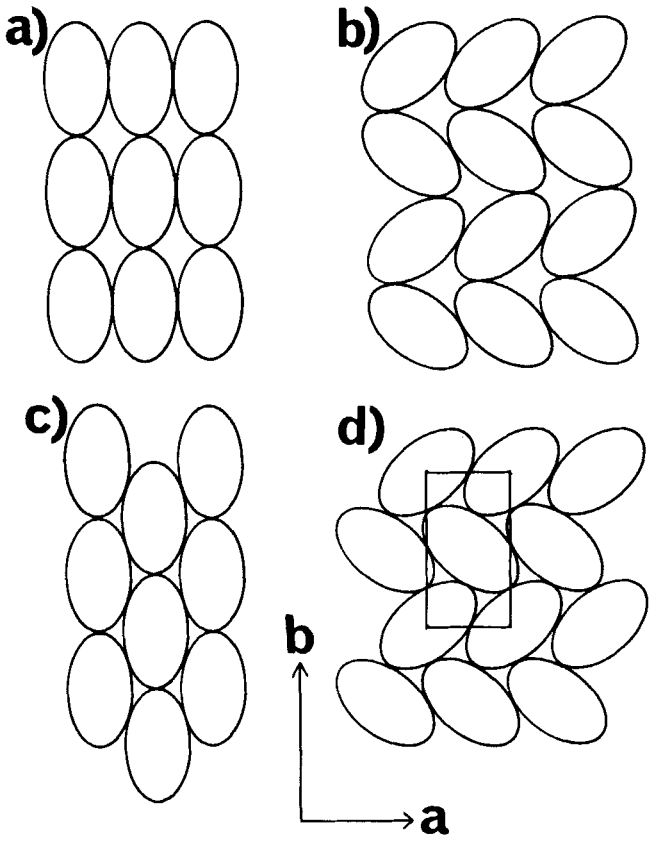


FIGURE 6 Possible packings in $S_E$layers (see text). The actual packing has the symmetry shown in (d) where the *ab* plane of the unit cell is also shown. IBPBAC is a bilayer structure with adjacent half layers related by a translation of *a*/2.

of the type suggested by Doucet *et al.*[9] for homologous compounds. Because of the disorder about the layer-normal and the relatively small number (~ 15) of independent reflections observed, two possible interpretations of the observed pattern are possible. The first is a monoclinic unit cell with a tilt of $\sim 5°$ about the [020] axis. The second is an orthorhombic *bilayer* structure which we believe to be the correct interpretation because a) in the former case the tilt would have to be such as to give reflections by chance at *precisely* the half-layer positions, b) the crystal is a pronounced bilayer structure and c) the S_B phase is a mixture of bi- and tri-layer packings.[5] It should not be inferred that *all* S_E phases have bilayer structures firstly because this interpretation would not give quite such good agreement with Doucet *et al's*[9] high resolution powder data as their assumed monolayer structure, and secondly because it is becoming clear that there might exist different types of inter-

layer correlations in a given type of more ordered smectic phase.[5] Nevertheless it is quite clear that however the details might differ from substance to substance the structure of the S_E phase is 3-dimensional, albeit with considerable disorder.

Taking the S_E phase of IBPBAC to be a bilayer therefore the systematic absences (observed reflections) imply a B-centred cell which describes the bilayer nature of the structure, together with *ab* glide plane. There are a number of possible space groups but they contain essentially only two gross types of molecular packing in the layers (cf Ref. 22). The first comprises rows of molecules along the a and b axes (Figure 6a, b) and the second arises from a relative displacement of these rows by $a/2$ or $b/2$ to give the structures shown in Figure 6c) and 6d). The first two arrangements (6a & b) may be excluded both on the grounds of packing efficiency and because they differ very considerably from the true hexagonal packing found in the adjacent S_B phase at higher temperature and the approximately hexagonal packing of the crystal phase at lower temperature (Figure 5). The packing of 6c) is excluded because it is *c*-centred which leaves the most likely space groups to describe the structure as No. 64 (Bbcm) and No. 68 (Bbcb) and whatever the case a four-fold disorder of the molecules is needed (head-to-tail and side-to-side). This is in accord with the crystal structure where all four configurations are observed, but in an ordered fashion, and it is inconceivable that in the S_E phase the molecules could become more ordered by losing any one of these orientations and hence at least 4 fold disorder must be expected. The molecules in the S_E phase can thus be represented as rods of elliptical cross section and the packing arrangement in each half layer must be like that represented in Figure 6d. This is identical to that proposed by Doucet *et al.* for the monolayer structure and it is remarkable that similar packing is implied even if our data is interpreted in terms of a slightly tilted monoclinic structure.[4] As discussed above we believe the structure of S_E phase of IBPBAC to be a true orthorhombic bilayer not a disordered monoclinic structure and it may be that the bilayer nature is associated with the fact that the (half-) layer spacing (26.8Å) considerably exceeds the molecular length (25.3Å). This is probably associated with dipolar attraction, and packing of the bulky isobutyl groups as discussed for the crystal, and may well give rise to steric factors promoting a bilayer arrangement. The two half layers are of course related to each other by a relative translation of $a/2$.

Note that the crystal and S_E layers remain parallel at least to within a few degrees through the transition[4] and that the macroscopic crystal dimensions only change slightly (the crystal retains its shape) on passing into the S_E phase the structural changes taking place at the transition are now fairly clear.

The molecules straighten from being at $\sim 40°$ to the layer-normal to approximately parallel to it. In each half layer a 3 fold disorder can occur in the

orientation of the ab plane of the orthorhombic S_E cell due to the different ways this can develop from the approximately hexagonal packing in the crystal. The straightening of the molecules must be accompanied by some rearrangement to accomodate the increased space requirement in the c direction and it may be that the observed 6-fold disorder (comprising 3 ordered and 3 disordered orientations) arises from this. The mechanism for the disordering is provided by self diffusion (the diffusion coefficient in the S_E phase $D \sim 2 \times 10^{-14} m^2 s^{-1}$)[23] and by rotation about the long axes, although this is slower than $10^{10} s^{-1}$.[6] Neutron scattering results have shown that on the rapid timescale of these experiments ($< 10^{-10}$s) the molecules in S_E are undergoing large-amplitude overdamped librations about their long axes suggesting a barrier height $V \gtrsim 10kT$, and this motion together with the configurational four fold disorder probably accounts for most of the transition entropy.

The major features of the S_E structure and hence of the crystal-S_E transition are now established but what remains is to determine the *details* of the packing configuration in the S_E phase and a quantitative description of the disorder including the local correlations. We are attempting to do this.

Acknowledgements

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