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A. J. Leadbetter [a] & M. A. Mazid [a]
[a] Deprtment of Chemistry, University of Exeter, Stocker Road, Exeter EX4 4OD, U.K.
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The Crystal and Molecular Structure of N-(4-n-butyloxybenzylidene)-4′-octylaniline (408) and the Crystal-Smectic B Transition

A. J. LEADBETTER and M. A. MAZID

Department of Chemistry, University of Exeter, Stocker Road, Exeter EX4 4QD, U.K.

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The crystal and molecular structure of N-(4-n butyloxybenzylidene)-4′-octyl aniline (408), $C_{25}H_{35}NO$, has been determined at room temperature by direct methods. The crystals belong to the triclinic system with space group $P\bar{1}$, $a = 7.893(1)$, $b = 11.472(2)$, $c = 25.415(4)$Å, $\alpha = 90.41(2)$, $\beta = 97.68(2)$ and $\gamma = 105.95(2)°$ with four molecules per unit cell. The structure was refined by full-matrix least-squares calculations to $R = 0.075$ for 3896 observed reflections. In the two symmetry-independent molecules, the butyloxy and octyl chains are almost fully extended The structure does not comprise a simple layer arrangement but is interdigitated with adjacent molecules in a head to tail configuration with alternate *O* atoms and C = N groups coplanar. The relationship between the crystal structure and that of the hexagonal bilayer smectic B phase to which it melts is also discussed.

INTRODUCTION

The number of compounds showing liquid crystal behaviour for which the crystal structures are known is still rather small, yet this knowledge is of importance for a full understanding of mesophase behaviour. Thus although it remains an open question as to whether there exists any predictive relationship between crystal and mesophase structure the important interactions and steric factors determining the structures are in principle revealed by the crystal structure and the nature of the structural changes at the transition from crystal to first mesophase, which almost invariably has the largest entropy of those which comprise the total melting process, must certainly be important. Most of the crystal structures determined so far are for nematic or smectic A precursors and on the basis of meagre evidence it is sometimes

stated that smectic precursors always have a layer structure while nematic precursors are interdigitated. Certainly this is true of at least the majority of the small number of cases so far known but it is a generalisation which must at this stage be treated with much caution.

The closest relationship between crystal and mesophase structures might be expected when the crystal melts to one of the ordered smectics and only two crystal structures in this category are known. The first is that of TBBA[1] ($C_4H_9PhNCHPhCHNPhC_4H_9$) in which there is a remarkably close similarity in the structure of crystal and smectic *G* ("tilted *B*") phase and the second is IBPBAC.[2] [$PhPhCHNPhCHCHCOOCH_2CH(CH_3)_2$] where the difference between crystal and smectic *E* phase is much greater although the crystal has a very clear layer structure.

This paper reports the first crystal structure determination of one of the n0.m[3,4] compounds, which show such rich mesophase behaviour, and the first of a smectic B precursor. We first describe the crystal structure determination and then consider its relation to the smectic B structure.

EXPERIMENTAL

A sample of *N*-(4n-butyloxybenzylidene)-4′-octylaniline (408) was kindly supplied by Professor G. W. Gray of Hull University. Crystals were obtained by dissolving the sample in a benzene-petroleum ether (40°–60°C) mixture at room temperature and then keeping the solution at about 5°C. The crystals grown from the mixture were big and irregular in shape. A differential scanning calorimeter examination showed that this room temperature phase melts directly to the smectic *B* phase at 33°C.

Oscillation and Weissenberg photographs revealed the crystal to be triclinic. In general the diffracted spots were broad, did not extend to the high angle region and had pronounced smears of diffuse scattering connecting the reflections in the diffraction patterns. The best crystal which had dimensions of $0.22 \times 0.35 \times 0.30$ mm^3 was chosen for intensity measurements and data were collected with the crystal mounted with *b* parallel to the goniometer axis. The space group $P\bar{1}$ rather than $P1$ was selected using information obtained from intensity statistics and later confirmed by the structure determination, requiring two crystallographically independent molecules in the asymmetric unit.

Accurate cell parameters were determined by a least-squares fit of sin θ values of 25 reflections within $10° < \theta < 12°$ measured on an "Enraf Nonius" CAD-4 computer controlled diffractometer. MoK_α ($\lambda = 0.71069$ Å) radiation was used in conjunction with a graphite monochromator. The

procedures for crystal alignment and data collection were identical with those reported previously.[5] The diffracted intensities were collected with the same machine and the only changes were as follows: (a) data were collected over the range $1.5° < \theta < 25°$, (b) an ω scan of 0.25° sec^{-1} was used, (c) standards were collected following every 40 reflections measured and as in the previous case they showed no measurable decay and (d) four octants (hkl, $\bar{h}kl$, $\bar{h}\bar{k}l$, $h\bar{k}l$) were collected plus a few symmetry related reflections. A total of 3896 unique reflections ($I > 3\sigma(I)$) were collected for structure determination and refinement. These were corrected for Lorentz and polarisation effects in the usual manner. Since the absorption coefficient was small (0.34 cm^{-1}) the data were not corrected for absorption. A summary of the important crystallographic data relevant to this structure is given in Table 1.

TABLE I

Summary of crystallographic data for 408

Molecular formula	$C_{25}H_{35}NO$
Formula weight	365.25
Crystal system	Triclinic
Space group	$P\bar{1}$
Form/habit	Platey rectangle
a = 7.893(1)Å	
b = 11.472(2)Å	
c = 25.415(4)Å	
α = 90.41(2)°	
β = 97.68(2)°	
γ = 105.95(2)°	
Vc = 2233.47Å^3	
Dc = 1.09 gm·cm^3	
Z = 4	
$F(000)$ = 800.0	
μ(MoKα) 0.34 cm^{-1}	
λ(MoKα) 0.71069Å	
Number of independent reflections used in the least-squares refinement = 3896	

Structure determination and refinement

An initial attempt to solve the structure was tried using the SHELX 76[6] automatic direct methods. These failed to select an origin despite renormalisation of weak parity group OeO, and a multisolution tangent approach was adopted using MULTAN-78.[7] The reason for the failure of SHELX-76 to give a correct solution probably arises from the layered nature of the structure. The average intensity $\langle I \rangle$, from which E values are calculated, is then obtained from a distribution differing too greatly from an idealised random distribution.

Normalised structure factors (E-values) were calculated by the modified K-curve method.[8] The 400 highest normalized structure factors with $|E| > 2.08$ were used to generate $3382\Sigma_2$ relationships. Origin defining reflections and those constituting the starting set were chosen automatically by the programme. The phases of the seven reflections of the starting set were varied to yield 128 phase sets. Several of the phase sets had similar values of the four figures of merit, COMFOM, ABSFOM, RESID and PSIZERO. The phase set with highest COMFOM (2.45), tenth highest ABSFOM (0.9220), eleventh lowest RESID (22.67) and second smallest PSIZERO (1.31) was selected for calculation of an E-map. The highest peaks in the E-map revealed only the positions of two phenyl rings in each crystallographically independent molecule. These positions were treated as a partial structure in the second stage of phase determination and added as chemical information to the programme part 'NORMAL' in order to allow for a better normalization of structure factors and a correct convergence in the subsequent tangent refinement. The solution with the highest COMFOM produced all the remaining non-hydrogen atoms derived from the positions of the highest peaks in the E-map.

The atomic parameters were refined by least-squares technique using the SHELX-76 programme system. Four cycles of full-matrix unweighted least squares refinement using 3896 observed reflections with individual isotropic temperature factors for O, N and C atoms gave $R(=\Sigma\Delta F/\Sigma|F_0|) = 0.135$. The molecules A and B were refined in alternate cycles. The introduction of anisotropic temperature factors reduced R to 0.114. A difference electron-density map calculated at this stage revealed all the hydrogen atoms in the structure in stereochemically feasible positions. The hydrogen atoms were included in all subsequent structure factor calculations with the constraint that the C—H distances were fixed at 1.08 Å (C—C—H = 120° for sp^2 carbons and H—C—H = 109.5° for sp^3 carbons). The refinement was continued with all non-hydrogen atoms anisotropic, the methyl groups as rigid bodies and one common U_{iso} (0.1 Å)^2 for all hydrogen atoms. After several more refinement cycles the analysis was terminated at $R = 0.075$ and $Rw = [=\Sigma w\Delta F^2/\Sigma w|F_0|^2]^{1/2} = 0.089$. The weighting scheme applied at the latter stage of least-squares refinement was $w = K[\sigma^2|F_0| + g|F_0|^2]$ where K and g refined to 0.989 and 0.0015 respectively. With this weighting scheme the mean value of $w\Delta^2$ was approximately constant over ranges of both $\sin\theta$ and $(F_0/F_{max})^{1/2}$ in the final cycle of least-squares.

A final difference electron density map showed no feature larger than 0.21 eÅ^{-3} and the largest parameter shifts for the non-hydrogen atoms in the final cycle of refinement were less than 0.05 of their estimated standard deviations. Final positional and thermal parameters for the non-hydrogen atoms are listed in Tables II and III and the numbering scheme of the

TABLE II

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

	x	*y*	*z*
Molecule 1			
C(11)	0.9670(6)	0.7258(4)	0.7393(2)
C(12)	0.9667(5)	0.7328(3)	0.7971(1)
C(13)	0.8670(5)	0.6148(3)	0.8179(1)
C(14)	0.8686(5)	0.6270(3)	0.8753(1)
O(11)	0.7693(3)	0.5134(2)	0.8936(1)
C(15)	0.7578(4)	0.5050(3)	0.9457(1)
C(16)	0.8541(5)	0.5948(3)	0.9832(1)
C(17)	0.8331(5)	0.5734(3)	1.0349(1)
C(18)	0.7206(4)	0.4680(3)	1.0504(1)
C(19)	0.6263(5)	0.3810(3)	1.0115(1)
C(110)	0.6440(5)	0.3991(3)	0.9605(1)
C(111)	0.7038(5)	0.4503(3)	1.1053(1)
N(11)	0.6110(4)	0.3574(3)	1.1222(1)
C(112)	0.5979(5)	0.3482(3)	1.1760(1)
C(113)	0.6615(5)	0.4459(3)	1.2132(1)
C(114)	0.6416(5)	0.4287(3)	1.2647(1)
C(115)	0.5571(5)	0.3155(3)	1.2825(1)
C(116)	0.4929(5)	0.2194(3)	1.2452(1)
C(117)	0.5134(5)	0.2350(3)	1.1930(1)
C(118)	0.5378(6)	0.3016(4)	1.3391(1)
C(119)	0.6451(5)	0.2227(3)	1.3663(1)
C(120)	0.6376(5)	0.2220(3)	1.4254(1)
C(121)	0.7375(5)	0.1390(4)	1.4541(1)
C(122)	0.7301(5)	0.1396(3)	1.5124(1)
C(123)	0.8238(5)	0.0550(3)	1.5409(1)
C(124)	0.8175(6)	0.0567(4)	1.5993(1)
C(125)	0.9081(7)	−0.0304(4)	1.6283(2)
Molecule 2			
C(21)	0.0387(7)	−0.2299(5)	1.2597(2)
C(22)	0.0534(5)	−0.2377(4)	1.2013(1)
C(23)	0.1392(5)	−0.1175(3)	1.1792(1)
C(24)	0.1563(5)	−0.1323(3)	1.1225(1)
O(21)	0.2106(3)	−0.0165(2)	1.1018(1)
C(25)	0.2283(4)	−0.0118(3)	1.0510(1)
C(26)	0.2373(5)	−0.1080(3)	1.0193(1)
C(27)	0.2668(5)	−0.0905(3)	0.9683(1)
C(28)	0.2820(4)	0.0214(3)	0.9467(1)
C(29)	0.2679(5)	0.1182(3)	0.9784(1)
C(210)	0.2443(5)	0.1015(3)	1.0295(1)
C(211)	0.3216(4)	0.0387(3)	0.8940(1)
N(21)	0.3414(4)	0.1402(3)	0.8715(1)
C(212)	0.3744(4)	0.1492(3)	0.8193(1)
C(213)	0.3110(5)	0.0519(3)	0.7821(1)
C(214)	0.3400(5)	0.0696(3)	0.7315(1)
C(215)	0.4324(5)	0.1804(3)	0.7148(1)

TABLE II (*continued*)

	x	*y*	*z*
C(216)	0.4979(5)	0.2760(3)	0.7525(1)
C(217)	0.4666(5)	0.2604(3)	0.8033(1)
C(218)	0.4587(5)	0.1981(4)	0.6588(1)
C(219)	0.3509(5)	0.2756(4)	0.6304(1)
C(220)	0.3616(5)	0.2804(3)	0.5725(1)
C(221)	0.2632(5)	0.3611(4)	0.5439(1)
C(222)	0.2715(5)	0.3640(3)	0.4859(1)
C(223)	0.1756(5)	0.4468(4)	0.4578(1)
C(224)	0.1826(6)	0.4483(4)	0.3991(1)
C(225)	0.0868(7)	0.5335(4)	0.3722(2)

TABLE III

Refined anisotropic thermal parameters ($\times 10^3$) 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}
Molecule 1						
C(11)	80(3)	104(4)	66(3)	15(3)	14(2)	27(3)
C(12)	67(2)	60(2)	58(2)	14(2)	16(2)	11(2)
C(13)	62(2)	63(2)	55(2)	4(2)	11(2)	22(2)
C(14)	62(2)	45(2)	59(2)	1(2)	10(2)	13(2)
O(11)	81(2)	44(1)	49(2)	−3(1)	8(1)	6(1)
C(15)	55(2)	38(2)	53(2)	7(2)	5(2)	12(2)
C(16)	66(2)	41(2)	58(2)	−2(2)	4(2)	6(2)
C(17)	79(3)	47(2)	54(2)	−7(2)	4(2)	8(2)
C(18)	51(2)	38(2)	54(2)	−3(2)	2(2)	13(2)
C(19)	61(2)	39(2)	53(2)	3(2)	3(2)	9(2)
C(110)	60(2)	46(2)	59(2)	−4(2)	−3(2)	9(2)
C(111)	64(2)	48(2)	52(2)	−3(2)	1(2)	13(2)
N(11)	70(2)	49(2)	48(2)	−0(1)	3(1)	13(2)
C(112)	57(2)	48(2)	52(2)	−2(2)	3(2)	19(2)
C(113)	80(3)	47(2)	53(2)	−5(2)	10(2)	7(2)
C(114)	74(3)	57(2)	61(3)	−3(2)	8(2)	20(2)
C(115)	61(2)	58(2)	55(2)	3(2)	13(2)	24(2)
C(116)	78(3)	55(2)	61(3)	0(2)	11(2)	14(2)
C(117)	60(2)	50(2)	60(2)	4(2)	12(2)	14(2)
C(118)	88(3)	82(3)	52(2)	12(2)	20(2)	39(2)
C(119)	79(3)	65(2)	52(2)	3(2)	15(2)	24(2)
C(120)	82(3)	70(3)	44(2)	1(2)	13(2)	24(2)
C(121)	77(3)	69(3)	56(2)	−2(2)	13(2)	22(2)
C(122)	86(3)	69(3)	45(2)	−1(2)	7(2)	26(2)
C(123)	75(3)	71(3)	55(2)	−4(2)	8(2)	25(2)
C(124)	96(3)	81(3)	51(2)	3(2)	6(2)	31(3)
C(125)	113(4)	86(3)	74(3)	13(2)	−0(3)	35(3)

TABLE III (*continued*)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Molecule 2						
C(21)	100(4)	114(4)	75(3)	34(3)	22(3)	38(3)
C(22)	70(3)	79(3)	69(3)	13(2)	12(2)	23(3)
C(23)	64(2)	56(2)	56(2)	2(2)	7(2)	8(2)
C(24)	77(3)	42(2)	55(2)	4(2)	9(2)	6(2)
O(21)	88(2)	48(2)	52(2)	−1(1)	10(1)	6(1)
C(25)	48(2)	47(2)	49(2)	−5(2)	2(2)	11(2)
C(26)	66(2)	42(2)	54(2)	3(2)	7(2)	9(2)
C(27)	70(2)	41(2)	59(2)	−2(2)	2(2)	18(2)
C(28)	48(2)	45(2)	47(2)	−1(2)	1(2)	9(2)
C(29)	65(2)	41(2)	54(2)	1(2)	6(2)	16(2)
C(210)	75(3)	41(2)	53(2)	−3(2)	15(2)	14(2)
C(211)	54(2)	48(2)	55(2)	−3(2)	3(2)	16(2)
N(21)	64(2)	48(2)	49(2)	−1(1)	3(1)	17(2)
C(212)	52(2)	47(2)	46(2)	1(2)	2(2)	13(2)
C(213)	66(2)	50(2)	60(2)	−2(2)	4(2)	11(2)
C(214)	77(3)	54(2)	45(2)	−4(2)	6(2)	15(2)
C(215)	60(2)	61(2)	50(2)	1(2)	6(2)	26(2)
C(216)	68(2)	56(2)	59(2)	8(2)	7(2)	14(2)
C(217)	73(3)	49(2)	48(2)	1(2)	1(2)	13(2)
C(218)	77(3)	76(2)	54(2)	7(2)	14(2)	27(2)
C(219)	81(3)	74(3)	47(2)	4(2)	14(2)	33(2)
C(220)	72(3)	67(3)	53(2)	1(2)	13(2)	22(2)
C(221)	81(3)	77(3)	52(2)	5(2)	17(2)	27(2)
C(222)	73(3)	68(3)	55(2)	0(2)	9(2)	22(2)
C(223)	83(3)	72(3)	55(2)	0(2)	12(2)	23(2)
C(224)	93(3)	76(3)	55(2)	2(2)	6(2)	29(2)
C(225)	126(4)	93(7)	68(3)	10(3)	3(3)	36(3)

molecule in Figure 1. Table IV lists the co-ordinates of the H atoms and the bond lengths and bond angles are given in Table V. Figure 2 shows the molecules of the asymmetric unit viewed down the normal to the plane containing the benzene ring C(15)–C(110)(A) of molecule 1.

RESULTS AND DISCUSSION

Bond lengths and angles

Bond lengths and angles in 408 are in close accord with those found in other smectogenic compounds such as isobutyl-4(4-phenylbenzylidene amino cinnamate (IBPBAC),[2] 4,4′-di-n-heptyloxyazoxybenzene,[5] n-*p*-methoxybenzylidene-*p*-phenylazoaniline,[9] di-n-propyl-*p*-terphenyl-4-4′-carboxylate,[10] ethyl p-azoxybenzoate[11] and *p*-azoxyanisole.[12] The two benzene rings A and B in molecule 1 have carbon-carbon bond distances averaging 1.385(5) Å

TABLE IV

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

	x	*y*	*z*
Molecule 1			
H(111)	1.0423	0.8048	0.7216
H(112)	0.8352	0.6939	0.7175
H(113)	1.0335	0.6552	0.7391
H(121)	0.9042	0.8019	0.8058
H(122)	1.1024	0.7575	0.8164
H(131)	0.7307	0.5896	0.7990
H(132)	0.9289	0.5451	0.8094
H(141)	0.8083	0.6972	0.8842
H(142)	1.0042	0.6500	0.8946
H(161)	0.9427	0.6781	0.9725
H(171)	0.9088	0.6420	1.0643
H(191)	0.5369	0.2980	1.0020
H(1101)	0.5696	0.3307	0.9309
H(1111)	0.7764	0.5235	1.1330
H(1131)	0.7248	0.5356	1.2013
H(1141)	0.6926	0.5051	1.2924
H(1161)	0.4274	0.1324	1.2576
H(1171)	0.4611	0.1595	1.1658
H(1181)	0.5820	0.3902	1.3581
H(1182)	0.4001	0.2607	1.3414
H(1191)	0.7835	0.2580	1.3608
H(1192)	0.5936	0.1317	1.3506
H(1201)	0.5016	0.1898	1.4314
H(1202)	0.6961	0.3126	1.4419
H(1211)	0.6825	0.0489	1.4379
H(1212)	0.8766	0.1721	1.4488
H(1221)	0.7891	0.2291	1.5290
H(1222)	0.5906	0.1096	1.5178
H(1231)	0.9612	0.0824	1.5347
H(1232)	0.7616	−0.0363	1.5247
H(1241)	0.8816	0.1464	1.6153
H(1242)	0.6788	0.0306	1.6051
H(1251)	0.9035	−0.0173	1.6680
H(1252)	1.0445	−0.0007	1.6195
H(1253)	0.8534	−0.1257	1.6156
Molecule 2			
H(211)	−0.0079	−0.3189	1.2742
H(212)	−0.0490	−0.1760	1.2672
H(213)	0.1717	−0.1862	1.2788
H(221)	0.1303	−0.2999	1.1950
H(222)	−0.0798	−0.2724	1.1806
H(231)	0.2704	−0.0800	1.2008
H(232)	0.0592	−0.0562	1.1833
H(241)	0.0288	−0.1826	1.1017
H(242)	0.2533	−0.1813	1.1188

TABLE IV (*continued*)

	x	*y*	*z*
H(261)	0.2221	−0.1967	1.0349
H(271)	0.2770	−0.1654	0.9446
H(291)	0.2760	0.2059	0.9624
H(2101)	0.2372	0.1770	1.0535
H(2111)	0.3339	−0.0381	0.8719
H(2131)	0.2378	−0.0359	0.7935
H(2141)	0.2886	−0.0063	0.7035
H(2161)	0.5758	0.3632	0.7418
H(2171)	0.5125	0.3368	0.8311
H(2181)	0.5981	0.2408	0.6572
H(2182)	0.4198	0.1100	0.6387
H(2191)	0.4011	0.3670	0.6472
H(2192)	0.2134	0.2393	0.6360
H(2201)	0.3048	0.1894	0.5556
H(2202)	0.5000	0.3115	0.5672
H(2211)	0.3224	0.4526	0.5600
H(2212)	0.1255	0.3316	0.5501
H(2221)	0.4092	0.3924	0.4796
H(2222)	0.2106	0.2728	0.4696
H(2231)	0.0379	0.4182	0.4640
H(2232)	0.2364	0.5379	0.4742
H(2241)	0.1205	0.3574	0.3827
H(2242)	0.3203	0.4759	0.3929
H(2251)	0.1036	0.5319	0.3315
H(2252)	0.1402	0.6252	0.3886
H(2253)	−0.0531	0.5018	0.3757

TABLE V

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

Molecule 1			
C(11)–C(12)	1.499(5)	C(112)–C(113)	1.407(5)
C(12)–C(13)	1.511(5)	C(113)–C(114)	1.374(5)
C(13)–C(14)	1.492(5)	C(114)–C(115)	1.400(5)
C(14)–O(11)	1.444(4)	C(115)–C(116)	1.399(5)
O(11)–C(15)	1.367(4)	C(116)–C(117)	1.391(5)
C(15)–C(16)	1.394(4)	C(117)–C(112)	1.391(5)
C(16)–C(17)	1.387(5)	C(115)–C(118)	1.500(5)
C(17)–C(18)	1.387(5)	C(118)–C(119)	1.518(6)
C(18)–C(19)	1.394(4)	C(119)–C(120)	1.541(5)
C(19)–C(110)	1.359(5)	C(120)–C(121)	1.533(6)
C(110)–C(15)	1.388(4)	C(121)–C(122)	1.520(5)
C(18)–C(111)	1.457(5)	C(122)–C(123)	1.513(6)
C(111)–N(11)	1.235(4)	C(123)–C(124)	1.523(5)
N(11)–C(113)	1.415(4)	C(124)–C(125)	1.527(7)
Molecule 2			
C(21)–C(22)	1.538(6)	C(212)–C(213)	1.405(5)
C(22)–C(23)	1.513(5)	C(213)–C(214)	1.368(5)

TABLE V (*continued*)

C(23)–C(24)	1.507(5)	C(214)–C(215)	1.385(5)
C(24)–O(21)	1.413(4)	C(215)–C(216)	1.401(5)
O(21)–C(25)	1.341(4)	C(216)–C(217)	1.375(5)
C(25)–C(26)	1.395(5)	C(217)–C(212)	1.382(5)
C(26)–C(27)	1.376(5)	C(215)–C(218)	1.502(5)
C(27)–C(28)	1.387(5)	C(218)–C(219)	1.522(6)
C(28)–C(29)	1.415(5)	C(219)–C(220)	1.513(5)
C(29)–C(210)	1.369(5)	C(220)–C(221)	1.503(6)
C(210)–C(25)	1.398(5)	C(221)–C(222)	1.515(5)
C(28)–C(211)	1.445(5)	C(222)–C(223)	1.504(6)
C(211)–N(21)	1.285(4)	C(223)–C(224)	1.530(5)
N(21)–C(212)	1.410(4)	C(224)–C(225)	1.513(7)

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

Molecule 1

C(11)–C(12)–C(13)	113.1(3)	N(11)–C(112)–C(113)	124.5(3)
C(12)–C(13)–C(14)	111.0(3)	N(11)–C(112)–C(117)	117.4(3)
C(13)–C(14)–O(11)	109.4(3)	C(117)–C(112)–C(113)	118.1(3)
C(14)–O(11)–C(15)	118.6(2)	C(112)–C(113)–C(114)	120.5(3)
O(11)–C(15)–C(16)	123.7(3)	C(113)–C(114)–C(115)	122.3(3)
O(11)–C(15)–C(110)	116.3(3)	C(114)–C(115)–C(116)	116.7(3)
C(15)–C(16)–C(17)	117.7(3)	C(114)–C(115)–C(118)	120.3(3)
C(16)–C(17)–C(18)	122.9(3)	C(116)–C(115)–C(118)	123.1(3)
C(17)–C(18)–C(19)	117.3(3)	C(115)–C(116)–C(117)	121.7(3)
C(17)–C(18)–C(111)	120.6(3)	C(116)–C(117)–C(112)	120.7(3)
C(19)–C(18)–C(111)	122.1(3)	C(115)–C(118)–C(119)	113.5(4)
C(18)–C(19)–C(110)	121.2(3)	C(118)–C(119)–C(120)	111.7(4)
C(19)–C(110)–C(15)	120.8(3)	C(119)–C(120)–C(121)	113.5(4)
C(110)–C(15)–C(16)	120.1(3)	C(120)–C(121)–C(122)	113.0(4)
C(18)–C(111)–N(11)	124.4(3)	C(121)–C(122)–C(123)	113.4(4)
C(111)–N(11)–C(112)	121.0(3)	C(122)–C(123)–C(124)	113.3(4)
		C(123)–C(124)–C(125)	113.7(4)

Molecule 2

C(21)–C(22)–C(23)	114.2(3)	N(21)–C(212)–C(213)	123.3(3)
C(22)–C(23)–C(24)	11.5(3)	N(21)–C(212)–C(217)	118.5(3)
C(23)–C(24)–O(21)	109.2(3)	C(217)–C(212)–C(213)	118.2(3)
C(24)–O(21)–C(25)	117.6(3)	C(212)–C(213)–C(214)	119.8(3)
O(21)–C(25)–C(26)	125.8(3)	C(213)–C(214)–C(215)	122.7(3)
O(21)–C(25)–C(210)	115.7(3)	C(214)–C(215)–C(216)	116.9(3)
C(26)–C(27)–C(28)	121.2(3)	C(216)–C(215)–C(218)	121.4(3)
C(27)–C(28)–C(29)	118.3(3)	C(215)–C(216)–C(217)	121.0(3)
C(27)–C(28)–C(211)	120.0(3)	C(216)–C(217)–C(212)	121.3(2)
C(29)–C(28)–C(211)	121.7(3)	C(215)–C(218)–C(219)	114.2(4)
C(28)–C(29)–C(210)	120.3(3)	C(218)–C(219)–C(220)	113.6(4)
C(29)–C(210)–C(25)	121.1(3)	C(219)–C(220)–C(221)	114.7(4)
C(210)–C(25)–C(26)	118.5(3)	C(220)–C(221)–C(222)	114.5(4)
C(28)–C(211)–N(21)	123.7(3)	C(221)–C(222)–C(223)	114.1(4)
C(211)–N(21)–C(212)	120.5(3)	C(222)–C(223)–C(224)	113.9(4)
		C(223)–C(224)–C(225)	112.6(4)

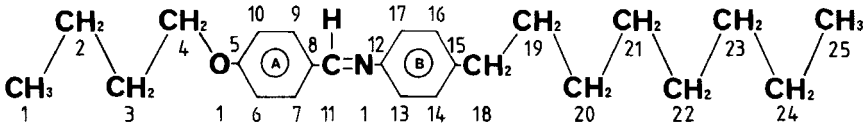

FIGURE 1 Numbering scheme for the atoms of the molecule of 40.8.

and 1.394(5) Å respectively and for molecule 2, they are 1.390(5) Å and 1.386(5) Å respectively. In the ring A of molecule 1 C(19)–C(110) has a value of 1.359(5) Å which is lower than the average of other bond lengths in the ring by 5σ. The internal C—C—C bond angles in rings A and B for both molecules are 120.0(3)°. The following angles for molecule 1 in ring A. C(15)–C(16)–C(17) = 117.7(3), C(16)–C(17)–C(18) = 122.9(3) and C(17)–C(18)–C(19) = 117.3(3),

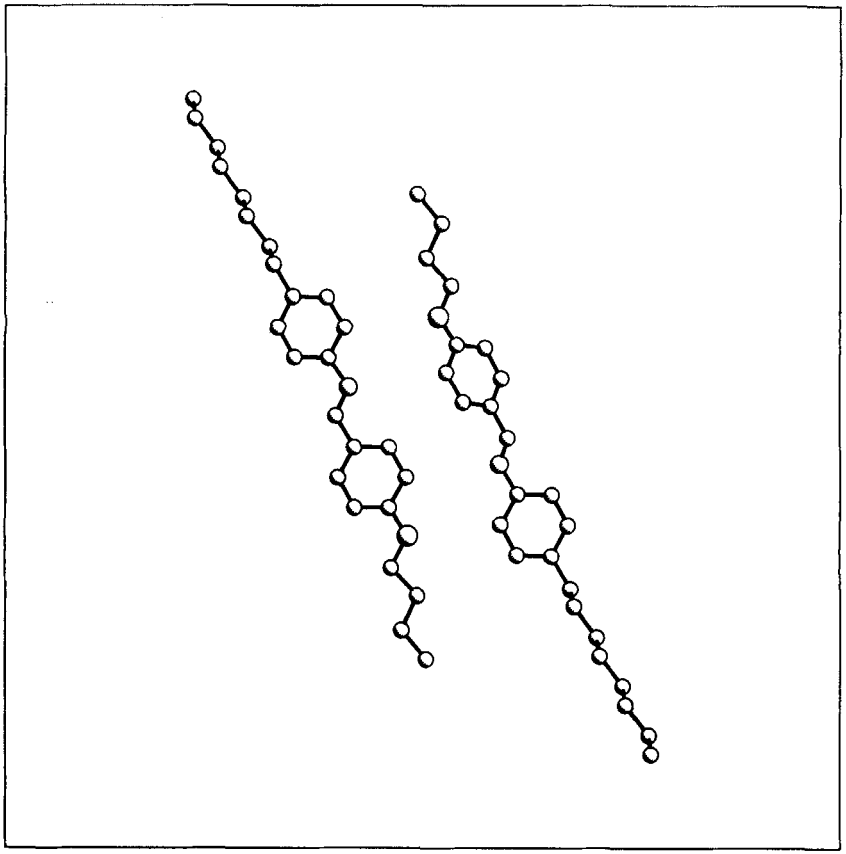

FIGURE 2 Drawing of the 40.8 molecules in the assymetric unit viewed down the normal to the plane containing the benzene ring A of molecule 1.

in ring B, (C(113)–C(114)–C(115) = 122.3(3) and C(114)–C(115)–C(116) = 116.7(3) and for molecule 2 in ring B, C(213)–C(214)–C(215) = 122.7(3) and C(214)–C(215)–C(216) = 116.9(3), deviate significantly from the mean value. The external non-hydrogen bond angles in the rings range from 115.7(3)° to 125.8(3)°, mean 121.0(3)°, with a wide variation in individual values, depending on their environment.

The average value of all the C—C single bond lengths, for both molecules in the structure is 1.515(6) Å (expected value 1.541 Å[13]). None of them differ significantly from this mean value. This average length is somewhat short, perhaps as a result of relatively high thermal motion associated with the side groups. We have not attempted to apply the correction proposed by Cruickshank.[14] The C—C—C bond angles in the side groups range from 109.2(3)° to 114.7(4)°, with a mean value of 112.9(4)°. The angles at C(14) and C(24), both joined to an oxygen, are significantly smaller than the mean value. The two kinds of C—O bond lengths (1.341–1.367(4) Å and 1.413–1.444(4) Å) are close to values reported previously. The C=N-groups can be compared with that of IBPBAC,[2] average C=N and N—C bond lengths are 1.260(4) and 1.413(4) Å respectively in 408 and for IBPBAC they are 1.26(1) and 1.44(1) Å respectively. The angles at C and N in these two structures are 124.1(3) and 120.8(3)° respectively for 408 and for IBPBAC, they are 122(1) and 118(1)°.

Molecular conformation

The two crystallographically independent molecules in the unit cell are in trans configuration with the butyloxy and octyl chains in their most stretched conformation (A–A–A geometry). The conformational features of the two distinct molecules may be described in terms of the least-squares planes calculated for various portions of the molecules (Figure 1). The equations and r.m.s. displacements for these planes are given in Table VI. A selection of distances to these planes from various atoms is given in Table VII. Dihedral angles are in Table VIII. As expected, all the phenyl rings in the two molecules are planar within experimental error (r.m.s. displacements in rings A and B of molecule 1 are 0.002 Å and 0.003 Å respectively and for molecule 2, they are 0.010 Å and 0.007 Å respectively). The dihedral angle between the rings is 13.3° for the first molecule and 29.2° for the second. The CH=N groups are nearly coplanar with the ring A for both molecules (dihedral angles are 2.9° and 2.7° for molecule 1 and 2 respectively), and in the case of ring B the corresponding angles are 10.4° and 29.4° respectively. The twist at the CH=N link is thus appreciably smaller than for IBPBAC. The conformation at the butyloxy linkage is different in the two molecules. The dihedral angle between butyloxy group and ring A has a value of 8.6° in molecule 1 and

TABLE VI

Coefficients p, q, r, s, in the equation $(pX^1 + qY^1 + rZ^1 = s)$ of the least-squares places in 408. The equations are defined with respect to orthogonal axes X^1(**a***), Z^1(**c**), Y^1

Plane Atoms	p	q	r	s	r.m.s. displacement (Å)
Molecule 1					
1. Phenyl ring A	0.750	−0.661	−0.007	1.354	0.002
2. Phenyl ring B	0.878	−0.476	0.047	4.062	0.003
3. C(18), C(111) to C(112)	0.781	−0.624	0.009	2.009	0.009
4. C(11), to O(11)	0.837	−0.546	0.035	3.313	0.009
5. C(118) to C(125)	0.839	0.543	0.026	5.563	0.031
Molecule 2					
6. Phenyl ring A	0.990	−0.027	0.142	5.548	0.010
7. Phenyl ring B	0.855	−0.510	0.093	3.893	0.007
8. C(28), C(211) to C(212)	0.982	−0.029	0.189	6.684	0.011
9. C(21) to O(21)	0.931	−0.340	0.129	5.404	0.045
10. C(218) to C(225)	0.827	0.561	0.045	4.264	0.022

TABLE VII

Deviations (Å) of individual atoms from one or more of the least-squares planes

Molecule 1	Plane 1	Plane 2	Plane 3	Plane 4	Plane 5
C(11)			−0.146	−0.007	
C(12)			−0.185	−0.001	
C(13)			−0.055	0.015	
C(14)			−0.118	0.002	
O(11)	0.031		−0.018	−0.009	
C(15)	0.003		−0.029	0.005	
C(16)	−0.003		0.033		
C(17)	0.001		0.046		
C(18)	0.001		−0.009		
C(19)	0.000		−0.076		
C(110)	−0.002		−0.089		
C(111)	0.006	0.162	0.010		
N(11)	0.050	−0.014	0.008		
C(112)	0.016	0.002	−0.009		
C(113)		−0.004			
C(114)		0.002			
C(115)		0.002			
C(116)		−0.004			
C(117)		0.002			
C(118)		0.001			−0.056
C(119)					0.018
C(120)					0.014
C(121)					0.025
C(122)					0.029
C(123)					−0.001
C(124)					0.016
C(125)					−0.046

TABLE VII (*continued*)

Molecule 2	Plane 6	Plane 7	Plane 8	Plane 9	Plane 10
C(21)				−0.000	
C(22)				−0.053	
C(23)				0.056	
C(24)				0.053	
O(21)	0.065			−0.056	
C(25)	0.006			−0.109	
C(26)	−0.014		0.067		
C(27)	0.009		0.024		
C(28)	0.005		−0.011		
C(29)	−0.013		0.009		
C(210)	0.008		0.095		
C(211)	0.096	0.434	0.012		
N(21)	0.126	−0.068	0.010		
C(212)	0.173	−0.002	−0.011		
C(213)		0.007			
C(214)		−0.003			
C(215)		−0.006			
C(216)		0.011			
C(217)		−0.007			
C(218)		10.050			0.043
C(219)					−0.026
C(220)					−0.009
C(221)					−0.009
C(222)					−0.018
C(223)					0.008
C(224)					−0.016
C(225)					0.027

18.3° in molecule 2. The atoms within the octyl linkage of each molecule are nearly co-planar (dihedral angle between the octyl groups is 1.6°). The plane of the octyl group makes an angle of 61.4° with ring **B** for molecule 1 and the corresponding value is 64.9° for molecule 2.

Molecular packing and relation to smectic B structure

Three views of the molecular packing are shown in Figures 3–5. The packing consists of strongly interdigitated layers which shows immediately that a crystal structure consisting of simple layers, in which Van der Waals contacts between the ends of molecules are confined to a plane, is not a prerequisite for smectic formation.

The molecules may be regarded as forming a distorted hexagonal packing with their long axes tilted by approximately 25° about an axis parallel to **a***. An important feature of the structure appears to be the rows of alternate opposed dipoles in the **a** direction associated with the O atom and the C=N

TABLE VIII

Dihedral angles for various portions of 408

Plane	Plane	Dihedral angle (°)	Plane	Plane	Dihedral angle (°)
1	2	13.3	3	9	19.7
1	3	2.9	3	10	72.8
1	4	8.6	4	5	66.0
1	5	74.4	4	6	32.0
1	6	40.6	4	7	4.1
1	7	12.0	4	8	32.4
1	8	41.1	4	9	14.1
1	9	22.7	4	10	67.2
1	10	75.6	5	6	35.0
2	3	10.4	5	7	63.8
2	4	4.7	5	8	35.7
2	5	61.4	5	9	53.1
2	6	27.3	5	10	1.6
2	7	3.6	6	7	29.2
2	8	27.8	6	8	2.7
2	9	9.6	6	9	18.3
2	10	62.6	6	10	36.0
3	4	5.7	7	8	29.4
3	5	71.5	7	9	10.9
3	6	37.7	7	10	64.9
3	7	9.2	8	9	18.5
3	8	38.1	8	10	36.5
			9	10	54.2

TABLE IX

Selection of short intermolecular contacts (Å) for non-hydrogen atoms

C(15)–C(17)$^{(i)}$	3.558	C(110)–C(26)$^{(iii)}$	3.732
C(18)–C(110)$^{(ii)}$	3.589	C(25)–C(29)$^{(iv)}$	3.738
C(16)–C(17)$^{(i)}$	3.600	C(25)–C(211)$^{(iv)}$	3.742
C(16)–C(16)$^{(i)}$	3.610	O(21)–C(211)$^{(iii)}$	3.758
C(26)–C(28)$^{(iii)}$	3.631	C(22)–C(212)$^{(iv)}$	3.759
O(11)–N(11)$^{(ii)}$	3.674	C(26)–C(211)$^{(iii)}$	3.765
C(19)–C(27)$^{(iii)}$	3.680	C(12)–C(112)$^{(i)}$	3.780
C(14)–C(111)$^{(i)}$	3.691	C(16)–C(210)$^{(ii)}$	3.780
C(19)–C(26)$^{(iii)}$	3.695	C(23)–N(21)$^{(iv)}$	3.783
C(22)–C(216)$^{(iii)}$	3.728	C(113)–C(217)$^{(ii)}$	3.785
		O(11)–C(17)$^{(i)}$	3.803

Symmetry code:
None x, y, z
i) $2 - x, 1 - y, 2 - z$.
ii) $1 - x, 1 - y, 2 - z$.
iii) $1 - x, -y, 2 - z$.
iv) $-x, -y, 2 - z$.

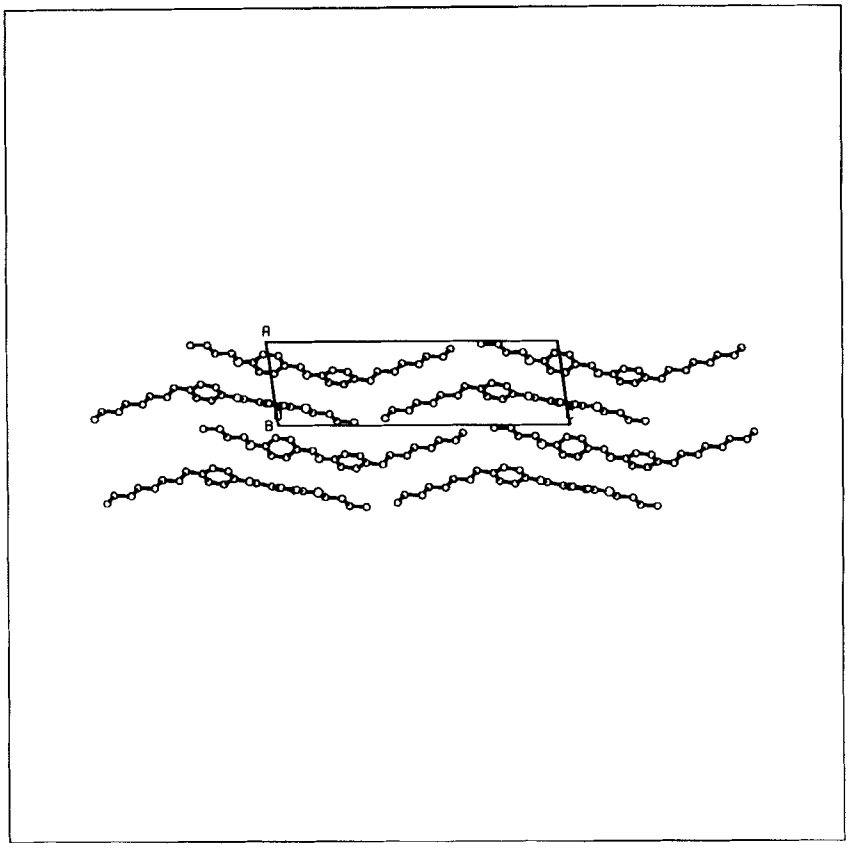

FIGURE 3 Packing of the molecules in crystalline 40.8 looking down the [010] direction.

group (see Figure 4). All the dipoles are essentially co-planar in ab planes and there is essentially complete interdigitation of the octyl chains with alternate molecules pointing up and down.

The smectic B phase has a hexagonal bilayer structure with an ABA... stacking sequence of the layers.[4,15] The molecules are rotating with at least six fold symmetry and executing longitudinal motions of amplitude 1–2 Å, both on a time scale of 10^{-11} s. The distance between the end carbon atoms of the molecule in the crystal is 24.2 Å and assuming a Van der Waals radius for the methyl group of 2.0 Å gives an overall molecular length of 28.2 Å. This is slightly less than the smectic B half layer spacing of 28.6 Å which is the same as that, determined from molecular models, for the maximum possible molecular length. Except for the fact that in the crystal the molecules are

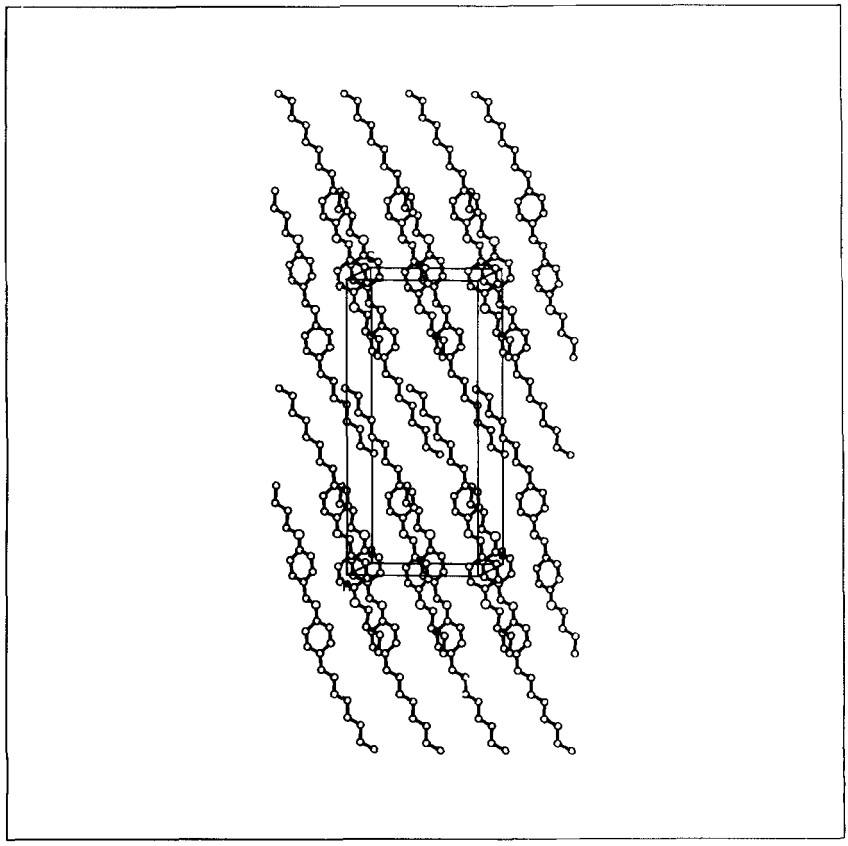

FIGURE 4 Packing of the molecules in crystalline 40.8 looking down the [100] direction.

parallel, head to tail and have a distorted hexagonal packing there is no simple relation between the crystal and smectic B structures. The hexagonal ABA... stacking with the half layer spacing equal to the molecular length shows that at the melting transition the molecules must undergo considerable longitudinal displacement to form simple layers and presumably also lateral exchange within the layers. The ABA... type of stacking could follow from packing considerations of the chain ends but the clear existence of an ordered packing (whether ABA... or ABC...) shows the importance of longer range interactions which are still unexplained.

In conclusion we can say that there seems to be no way in which the type of smectic phase formed on melting could have been predicted from a knowledge of the crystal structure.

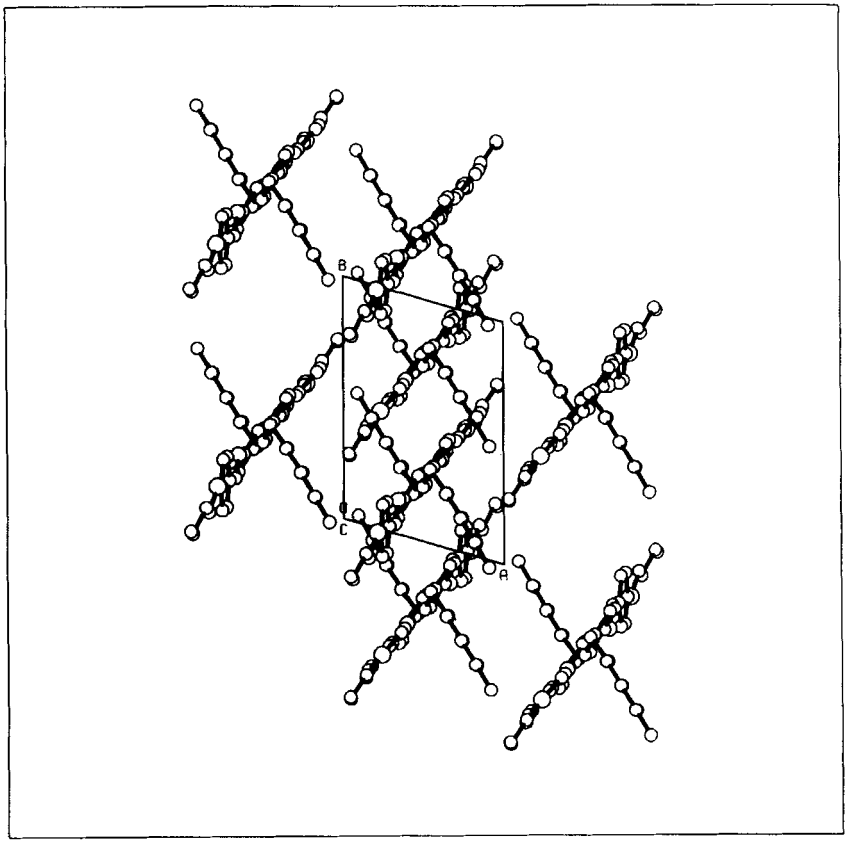

FIGURE 5 Packing of the molecules in crystalline 40.8 looking down the [001] direction.

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