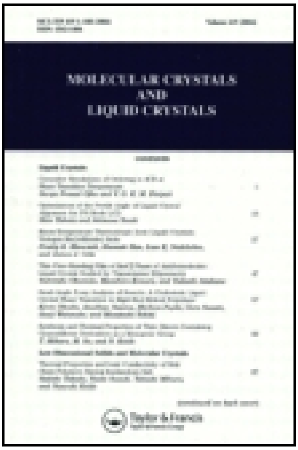

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The Crystal and Molecular Structure of N-(4-n octyloxybenzylidene)-4'-butylaniline (80.4) and the Crystal-Smectic G Transition

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The Crystal and Molecular Structure of N-(4-n octyloxybenzylidene)-4′-butylaniline (80.4) and the Crystal-Smectic G Transition

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The crystal and molecular structure of N-(4-n octyloxybenzylidene)-4′-butylaniline (80.4), $C_{25}H_{35}NO$, has been determined at room temperature partially by direct methods and completed by subsequent Fourier synthesis. The crystals belong to the triclinic system with space group $P\bar{1}$, $a = 5.452(3)$, $b = 7.948(4)$, $c = 27.356(4)$ Å, $\alpha = 90.83(2)$, $\beta = 86.43(2)$ and $\gamma = 108.14(2)^\circ$ with two molecules per unit cell. The structure consists of interdigitated sheets of molecules with alternate sheets in an head-to-tail configuration and displaced in the direction of the long molecular axes so as to give interdigitation of alkyl tails and of cores plus alkoxy tails. It is shown that the superficially very different structure of the homologue 40.8 may be described in a similar way. In neither case is there a close relation with the structure of the liquid crystal phase found in melting.

INTRODUCTION

The structural analysis of the crystalline solid state of 80.4 (N-(4-n octyloxybenzylidene)-4′-butylaniline) is part of a programme[1-3] aimed at investigating whether relations exist between the crystal and liquid crystal structures in compounds which form mesophases. 80.4 has been chosen to complement previously published work on the isomer 40.8[3]. The phase sequences of the two compounds are as follows:

40.8 Cryst 33 S_B48.6 S_A 63.5 N 78.3 I
80.4 Cryst 40 S_G63 S_B 67.5 S_A 82 I

These are typical examples of the nO.m series, which show very rich smectic polymorphism which has been the subject of considerable structural work.[4,5] The two isomers 40.8 and 80.4 thus provide a comparison of structural changes at the Crystal-S_B and Crystal-S_G transitions.

Most liquid crystal precursors whose structures have been determined so far are confined to nematic or S_A precursors with suggested conclusions that nematic precursors demonstrate interdigitation whereas smectic precursors possess a layer structure. The structure described in this paper demonstrates (similarly to that for 40.8) marked interdigitation and contrary to having a layer structure discerned across the molecular long axis, a sheetlike structure is evident with molecular long axes parallel to the sheets.

EXPERIMENTAL

A sample of N-(4-n octyloxybenzylidene)-4'-butylaniline (80.4) was kindly supplied by Professor G. W. Gray of the University of Hull. Suitable platelike crystals were obtained by dissolving the sample in an equal part mixture of ethyl acetate and methanol and evaporating slowly at about 15°C. A differential scanning calorimeter examination showed that this room temperature phase melts directly to the smectic G phase at ~40°C.

Preliminary X-ray investigations by oscillation and Weissenberg photographs revealed the crystal to be triclinic. The diffracted spots were noted to suffer from a severe reduction in intensity at high sin θ. The best crystal of dimensions $0.10 \times 0.25 \times 0.50$ mm^3, was chosen for intensity measurements and data were collected with the crystal mounted with $\underline{\mathbf{a}}$ parallel to the goniometer axis. The centrosymmetric space group $P\bar{1}$ was selected from the E-statistics as a function of $(\sin\theta)/\lambda$, where $\langle|E^2 - 1|\rangle > 0.9$ held true over the range $0 < (\sin\theta)/\lambda < 0.7$, with one molecule in the asymmetric unit.

Accurate cell parameters were determined by a least-squares fit of sin θ values of 25 reflexions within $10° < \theta < 12°$ measured on an "Enraf Nonius" CAD-4 computer controlled diffractometer. Monochromated CuK_α (λ = 1.5418 Å) radiation was used throughout. The procedures for crystal alignment and data collection were identical with those previously reported.[1-3] A total of 3836 unique reflexions were collected for structure determination and refinement and corrected for Lorentz and polarisation effects. The data were not corrected for absorption. A summary of the important crystallographic data is given in Table 1.

Structure determination and refinement

Initial attempts to solve the structure using the SHELX-76[6] automatic direct methods failed to select more than two origin determining reflexions from parity groups eeo and oee respectively. Subsequent renormalisation was performed to reduce the E values, derived by a modified K curve method,[7] which were too strong for k = 2n using the expression

$$[E(hkl)_{\text{new}}]^2 = [E(hkl)_{\text{old}}]^2\ (1.0089\text{-}0.1677 \cos k\pi)$$

TABLE I(a)

Summary of Crystallographic data for 80.4

Molecular formula	$C_{25}H_{35}NO$
Formula weight	365.25
Crystal System	Triclinic
Space Group	P T
Form/habit	Rectangular plates

a = 5.452 (3) Å
b = 7.948 (4) Å
c = 27.356 (4) Å
α = 90.83 (2) °
β = 86.43 (2) °
γ = 108.14 (2) °
$V_c = 1124.41 Å^3$
D_c = 1.08 g cm^{-3}
$Z = 2$
$F(000) = 400.0$
$\mu(CuK_\alpha) = 4240\ m^{-1}$
$\lambda(CuK_\alpha) = 1.5418Å$
Number of independent reflexions used in the least-squares refinement = 3836

TABLE I(b)

List of origin determining (ORIG) and multisolation (MULT) E-values

	h	k	l	E	Sign Relations
1.	−2	4	3	5.617	ORIG +
2.	−1	4	2	5.044	ORIG +
3.	0	2	0	4.914	MULT +−
4.	−1	2	1	4.325	MULT +−
5.	4	2	0	4.330	MULT +−
6.	4	1	1	4.005	ORIG +
7.	−2	0	20	4.099	MULT +−
8.	−6	4	3	4.496	MULT +−
9.	3	−2	18	3.659	MULT +−
10.	3	4	2	3.648	MULT +−
11.	3	0	6	3.852	MULT +−
12.	−1	2	2	4.247	MULT +−
13.	−2	6	3	5.408	MULT +−
14.	−1	0	1	3.985	MULT +−
15.	4	3	1	3.919	MULT +−
16.	3	−1	19	3.331	MULT +−
17.	2	0	20	3.408	MULT +−

Permutations for structures (i) & (ii)

PARACHOR	M(ABS)	NQT	Permutation
(ii) 2.627	0.934	−0.325	++−−++−−−−−−−+−++
(i) 2.355	0.911	−0.234	++−−−+−+++−−−+−−−

where the numerical parameters were determined by least-squares. This resulted in a successful origin determination and the E-map, which followed, revealed the essential features of the rings A and B (see Figure 1), though alternative z coordinates for this partial structure were discernable, separated by the order of a C—C bond. Attempted Fourier synthesis of the remaining structure was successful for only one of these alternatives. However, least-squares refinement of this structure, (i) could not be pursued beyond $R = 0.43$, where

$$R = \Sigma|F_{\mathrm{OBS}} - F_{\mathrm{CALC}}|/\Sigma|F_{\mathrm{OBS}}|$$

An analysis of the isotropic temperature factors arising from this refinement revealed $U_{iso} > 0.1$ for all atoms lying off the molecular axis presented by the octyloxy-chain, which lies about the $y \approx \frac{1}{4}$ plane. A trial refinement was attempted using the operation $x, y, z \rightarrow x, \bar{y}, z$, which essentially reflected the bulk of the molecule in the $y = \frac{1}{4}$ plane, resulting in a rapid fall in R. This structure, (ii), was confirmed when a further use of the SHELX-76 direct methods using renormalised E-values ≥ 1.2, expanded to 574 signs using 5331 relations, resulted in 8 unique E maps with the tests PARACHOR > 2.2, M(ABS) > 0.95 and NQT < -0.13, in which the final structure was revealed in the E-map with third highest PARACHOR and the former structure in the E-map with seventh highest PARACHOR.[6] A list of E's used for the origin determination and multisolution pathway is given in Table 1(b) together with the sign permutations for the two structures.

The atomic parameters for structure (ii) were refined using the full matrix least-squares routine of the SHELX-76 program. Four cycles of unweighted least squares refinement with individual isotropic temperature factors for O, N and C atoms gave $R = 0.17$. The introduction of anisotropic temperature factors reduced R to 0.12. The hydrogen atoms were included in further 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 hydrogen atoms were given isotropic temperature factors fixed at the value of the isotropic temperature factor of the parent carbon atoms after the last cycle of isotropic refinement. A weighting scheme was applied and 3 cycles of accelerated matrix refinement resulted in $Rw = 0.73$, where

$$Rw = [\Sigma w\, \Delta F^2/\Sigma w|F_{\mathrm{OBS}}|^2]^{1/2}$$

and $w = k/\sigma^2\,(F_{\mathrm{OBS}})$. Three further cycles of weighted accelerated matrix refinement, freeing the hydrogen atoms from previous constraints whilst keeping the non-hydrogen atoms fixed, resulted in a final Rw of 0.054, where the weighting factor k refined to 0.034.

Final positional and thermal parameters for the non-hydrogen atoms are listed in Tables 2 and 3; those for the hydrogens are listed in Table 4. The

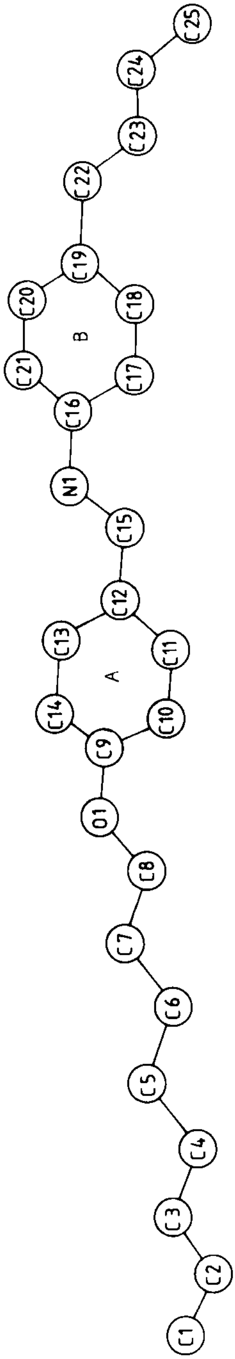


FIGURE 1 80.4 $P\bar{1}$ atomic labelling.

TABLE II

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

Atom	x	y	z
C(1)	−0.3811(10)	0.3121(7)	−0.3512(2)
C(2)	−0.4801(8)	0.2450(6)	−0.3001(2)
C(3)	−0.2740(8)	0.3109(5)	−0.2654(2)
C(4)	−0.3758(7)	0.2444(5)	−0.2107(2)
C(5)	−0.1452(7)	0.2969(5)	−0.1737(2)
C(6)	−0.2337(7)	0.2311(5)	−0.1231(1)
C(7)	−0.0194(7)	0.2949(5)	−0.0884(1)
C(8)	−0.0960(7)	0.2356(6)	−0.0366(1)
O(1)	0.1293(5)	0.3052(4)	−0.0100(1)
C(9)	0.1165(8)	0.2701(5)	0.0392(2)
C(10)	−0.1040(8)	0.1734(5)	0.0665(2)
C(11)	−0.0898(8)	0.1517(6)	0.1157(2)
C(12)	0.1372(8)	0.2239(5)	0.1396(2)
C(13)	0.3563(8)	0.3244(5)	0.1116(2)
C(14)	0.3449(8)	0.3460(5)	0.0625(2)
C(15)	0.1482(8)	0.1994(5)	0.1923(2)
N(1)	0.3549(7)	0.2513(4)	0.2135(1)
C(16)	0.3589(8)	0.2252(6)	0.2645(2)
C(17)	0.1567(8)	0.1248(6)	0.2951(2)
C(18)	0.1847(9)	0.1068(6)	0.3440(2)
C(19)	0.4157(9)	0.1901(6)	0.3653(2)
C(20)	0.6173(8)	0.2894(6)	0.3356(2)
C(21)	0.5932(8)	0.3072(6)	0.2856(2)
C(22)	0.4409(9)	0.1709(6)	0.4196(2)
C(23)	0.2717(9)	0.2517(6)	0.4519(2)
C(24)	0.2966(9)	0.2322(7)	0.5070(2)
C(25)	0.1186(9)	0.3080(7)	0.5384(2)

numbering scheme for the molecule is shown in Figure 1. The bond lengths and bond angles are given in Table 5. Figure 2 shows the structure viewed along the **a** axis, Figure 3 the structure viewed along the **b** axis and Figure 4 the structure viewed along the **c** axis.

RESULTS AND DISCUSSION

Bond lengths and angles in 80.4 are comparable with the structural isomer 40.8[2] and agree closely with those found in other smectogenic compounds such as isobutyl-4(4-phenylbenzylidene amino cinnamate) (IBPBAC),[2] 4,4′-di-n-heptyloxyazoxybenzene,[1] n-p-methoxybenzylidene-p-phenylazoaniline,[8] di-n-propyl-p-terphenyl-4-4′-carboxylate,[9] ethyl p-azoxybenzoate[10] and p-azoxyanisole.[11] The two benzene rings A and B have C—C bond distances averaging 1.384(12) and 1.383(12) Å respectively where the figures in parentheses refer to the standard deviation of the bond distribution. In the ring A, C(13)—C(14) has a value of 1.365(5) Å which is smaller than the average of

TABLE III

Refined anisotropic thermal parameters ($\times 10^4 Å^2$) for the non hydrogen atoms with e.s.d's in parentheses. The temperature factor is of the form:
$\exp[-2\pi^2 (h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2lhc^*a^*U_{31} + 2hka^*b^*U_{12})]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1)	116(44)	1229(47)	1121(45)	−18(37)	−165(36)	305(37)
C(2)	704(30)	822(34)	1059(39)	−111(30)	−158(30)	203(26)
C(3)	780(30)	620(28)	937(34)	−30(25)	−190(27)	262(24)
C(4)	709(28)	708(30)	802(32)	−20(25)	146(25)	134(24)
C(5)	841(31)	721(30)	760(31)	−80(25)	−56(26)	337(26)
C(6)	576(25)	687(29)	911(34)	−65(26)	−46(25)	108(22)
C(7)	551(25)	658(28)	906(34)	−82(25)	8(24)	90(21)
C(8)	538(26)	770(31)	927(35)	−74(27)	−24(25)	100(23)
O(1)	578(18)	989(24)	862(23)	45(19)	−31(17)	15(16)
C(9)	561(26)	596(28)	856(34)	−6(25)	46(25)	176(22)
C(10)	501(25)	712(30)	949(36)	57(27)	−13(24)	49(22)
C(11)	554(27)	801(33)	919(36)	77(28)	65(26)	32(24)
C(12)	592(27)	633(29)	746(32)	21(24)	116(24)	116(23)
C(13)	536(25)	653(30)	908(35)	−22(26)	4(25)	65(22)
C(14)	519(25)	753(31)	923(36)	35(27)	56(25)	67(22)
C(15)	586(27)	625(30)	1079(40)	−44(27)	−108(28)	101(23)
N(1)	627(23)	657(24)	917(29)	48(21)	55(22)	142(19)
C(16)	579(27)	655(30)	935(37)	23(26)	−6(26)	160(23)
C(17)	575(28)	843(34)	1006(39)	134(29)	−101(28)	48(24)
C(18)	681(31)	897(36)	940(39)	141(30)	63(28)	105(27)
C(19)	733(31)	802(34)	923(37)	−18(29)	−113(29)	319(27)
C(20)	587(28)	838(36)	1006(39)	−99(30)	−67(28)	153(25)
C(21)	561(28)	783(33)	1100(41)	−43(30)	28(28)	97(24)
C(22)	803(33)	964(38)	1065(41)	56(32)	−136(30)	319(29)
C(23)	777(32)	1008(38)	897(37)	85(30)	−119(28)	217(28)
C(24)	877(37)	1045(42)	1074(44)	159(34)	−78(33)	119(32)
C(25)	985(40)	1598(55)	949(41)	175(38)	26(33)	273(39)

the other ring bonds by 4σ, where σ is the e.s.d. of each bond, ($\sigma = 0.005$ Å). The same value for the bond C(19)–C(20) in ring B might indicate a degree of 'strain' in the molecular geometry to accommodate the 'arching' appearance of the octyloxy- and butyl chains. Ring A in molecule 1 of 40.8[3] displays a similar distortion with one bond shortened by 5σ. The average internal C—C—C bond angle in rings A and B is 120.0(1.7)°. The angles C(11)—C(12)—C(13) = 117.7(0.4)°, C(10)—C(11)—C(12) = 122.6(0.4)° in ring A and C(17)—C(16)—C(21) = 117.1(0.4)°, C(17)—C(18)—C(19) = 121.8(0.4)° and C(18)—C(19)—C(20) = 117.5(0.5)° in the ring B deviate significantly from the mean value. The external non-hydrogen bond angles in the rings range from 115.3(0.4)° to 126.6(0.4)°, mean 121.0(3.6)° with a wide variation in individual values similar to those found in 40.8.[3]

The average value of all the C—C single bond lengths is 1.519(0.043) Å (expected value 1.541 Å[12]). As indicated by the e.s.d. quoted, none of them differ

TABLE IV

Refined atomic parameters and isotropic thermal parameters ($\times 10^4$ Å^2) for hydrogen atoms with e.s.d.'s in parentheses. The temperature factor is of the form: $\exp[-2\pi^2 (h^2a^{*2} + k^2b^{*2} + l^2c^{*2})U]$

Atom	x	y	z	U
H(C1)(1)	−0.5117(59)	0.2630(40)	−0.3742(10)	1443(120)
H(C1)(2)	−0.2320(56)	0.2773(38)	−0.3620(10)	1180(114)
H(C1)(3)	−0.3397(54)	0.4506(38)	−0.3512(10)	1179(108)
H(C2)(1)	−0.5322(47)	0.1075(32)	−0.2967(8)	1033(89)
H(C2)(2)	−0.6412(42)	0.2886(29)	−0.2853(7)	792(79)
H(C3)(1)	−0.2582(52)	0.4256(36)	−0.2518(8)	1052(110)
H(C3)(2)	−0.1841(47)	0.2590(31)	−0.2670(9)	1019(84)
H(C4)(1)	−0.3059(80)	0.1772(53)	−0.2404(14)	1964(193)
H(C4)(2)	−0.4829(74)	0.1488(49)	−0.1833(15)	1617(163)
H(C5)(1)	−0.0194(49)	0.2358(32)	−0.1940(9)	1327(89)
H(C5)(2)	−0.1368(55)	0.4158(39)	−0.1859(10)	1625(119)
H(C6)(1)	−0.2915(44)	0.1002(29)	−0.1227(8)	767(81)
H(C6)(2)	−0.3792(45)	0.2703(31)	−0.1113(8)	886(85)
H(C7)(1)	0.0303(44)	0.4286(31)	−0.0888(8)	856(81)
H(C7)(2)	0.1210(42)	0.2566(29)	−0.0982(8)	730(76)
H(C8)(1)	−0.1503(44)	0.1043(30)	−0.0343(8)	989(83)
H(C8)(2)	−0.2307(40)	0.2876(27)	−0.0235(7)	676(73)
H(C10)	−0.2695(46)	0.1128(32)	0.0504(9)	1116(86)
H(C11)	−0.2418(44)	0.0836(30)	0.1363(8)	958(83)
H(C13)	0.5143(43)	0.3784(30)	0.1327(8)	824(82)
H(C14)	0.4888(43)	0.4123(29)	0.0429(8)	830(80)
H(C15)	−0.0308(69)	0.1525(47)	0.1936(12)	2655(166)
H(C17)	−0.0041(40)	0.0613(27)	0.2800(8)	691(72)
H(C18)	0.0377(47)	0.0396(32)	0.3669(9)	1134(92)
H(C20)	0.7861(46)	0.3554(32)	0.3516(9)	1022(93)
H(C21)	0.7312(49)	0.3792(33)	0.2626(9)	1283(97)
H(C22)(1)	0.4052(49)	0.0379(34)	0.4336(9)	1097(97)
H(C22)(2)	0.6180(55)	0.2250(37)	0.4260(10)	1450(106)
H(C23)(1)	0.3124(50)	0.3979(35)	0.4416(9)	1112(102)
H(C23)(2)	0.1010(55)	0.2079(37)	0.4430(10)	1350(111)
H(C24)(1)	0.4759(51)	0.2999(35)	0.5146(9)	1171(102)
H(C24)(2)	0.2684(52)	0.1053(37)	0.5133(10)	1237(105)
H(C25)(1)	0.1361(55)	0.2947(37)	0.5740(11)	1498(112)
H(C25)(2)	−0.0570(59)	0.2375(39)	0.5307(10)	1536(125)
H(C25)(3)	0.1381(55)	0.4403(38)	0.5309(10)	1273(110)

significantly from this mean value. A librational analysis, assuming the molecule to be a rigid body, using the method of Schomaker and Trueblood,[13] resulted in a generalised R index for agreement of observed and calculated orthogonalised U_{ij} of 0.134 and an average librationally corrected C—C single bond length of 1.521(0.043) Å exhibiting relatively large thermal motion in the end chains. These calculations were performed using the computer program XANADU.[14] Both the oxtyloxy and butyl chains are in their most ex-

TABLE V(a)

Bond lengths (Å) with e.s.d.'s in parentheses.

C(1)—C(2)	1.510(5)	C(12)—C(13)	1.400(5)
C(1)—H(C1)(1)	0.964(33)	C(12)—C(15)	1.465(5)
C(1)—H(C1)(2)	0.965(32)	C(13)—C(14)	1.365(5)
C(1)—H(C1)(3)	1.052(32)	C(13)—H(C13)	1.041(24)
C(2)—C(3)	1.480(5)	C(14)—C(9)	1.393(5)
C(2)—H(C2)(1)	1.044(27)	C(14)—H(C14)	0.937(24)
C(2)—H(C2)(2)	1.094(25)	C(15)—N(1)	1.250(5)
C(3)—C(4)	1.601(5)	C(15)—H(C15)	0.929(39)
C(3)—H(C3)(1)	0.960(30)	N(1)—C(16)	1.416(5)
C(3)—H(C3)(2)	0.732(26)	C(16)—C(17)	1.382(5)
C(4)—C(5)	1.611(5)	C(17)—C(18)	1.371(5)
C(4)—H(C4)(1)	1.080(44)	C(17)—H(C17)	0.978(23)
C(4)—H(C4)(2)	1.080(42)	C(18)—C(19)	1.388(5)
C(5)—C(6)	1.485(5)	C(18)—H(C18)	1.000(26)
C(5)—H(C5)(1)	1.080(28)	C(19)—C(20)	1.365(5)
C(5)—H(C5)(2)	0.993(32)	C(19)—C(22)	1.514(6)
C(6)—C(7)	1.508(5)	C(20)—C(21)	1.395(5)
C(6)—H(C6)(1)	0.989(25)	C(20)—H(C20)	1.028(27)
C(6)—H(C6)(2)	0.975(26)	C(21)—C(16)	1.397(5)
C(7)—C(8)	1.493(5)	C(21)—H(C21)	0.987(27)
C(7)—H(C7)(1)	1.012(26)	C(22)—C(23)	1.514(5)
C(7)—H(C7)(2)	0.931(25)	C(22)—H(C22)(1)	1.085(28)
C(8)—O(1)	1.423(4)	C(22)—H(C22)(2)	0.953(31)
C(8)—H(C8)(1)	0.994(25)	C(23)—C(24)	1.538(5)
C(8)—H(C8)(2)	0.995(24)	C(23)—H(C23)(1)	1.149(29)
O(1)—C(9)	1.371(4)	C(23)—H(C23)(2)	0.932(31)
C(9)—C(10)	1.387(5)	C(24)—C(25)	1.512(6)
C(10)—C(11)	1.370(5)	C(24)—H(C24)(1)	0.991(29)
C(10)—H(C10)	1.007(26)	C(24)—H(C24)(2)	0.988(31)
C(11)—C(12)	1.390(5)	C(25)—H(C25)(1)	0.994(32)
C(11)—H(C11)	0.983(24)	C(25)—H(C25)(2)	0.981(34)
		C(25)—H(C25)(3)	1.045(32)

tended conformations. The C—C—C bond angles in the side-chains range from 110.4(0.4)° to 114.3(0.4)°, with a mean value of 112.5(1.3)°. The bonds C(8)—0(1) = 1.423(4) Å and 0(1)—C(9) = 1.371(4) Å are close to those reported previously.[3] The C=N—group can be compared with those of IBPBAC and 40.8, C=N and N—C bond lengths are 1.250(5) Å and 1.416(5) Å respectively in 80.4, 1.260(4) Å and 1.413(4) Å respectively in 40.8 and for IBPBAC they are 1.26(1) Å and 1.44(1) Å respectively. The angles at C and N in these groups are 122.4(0.4)° and 121.0(0.4)° respectively in 80.4, 124.1(0.3)° and 120.8(0.3)° respectively for 40.8 and for IBPBAC they are 122(1)° and 118(1)°

TABLE V(b)

Bond angles (°) with e.s.d.'s in parentheses.

H(C1)(1)—C(1)—H(C1)(2)	106.9(2.4)
H(C1)(1)—C(1)—H(C1)(3)	108.2(2.3)
H(C1)(2)—C(1)—H(C1)(3)	111.9(2.3)
H(C1)(1)—C(1)—C(2)	110.4(1.9)
H(C1)(2)—C(1)—C(2)	111.3(1.8)
H(C1)(3)—C(1)—C(2)	108.0(1.7)
H(C2)(1)—C(2)—C(1)	113.6(1.4)
H(C2)(2)—C(2)—C(1)	114.0(1.2)
H(C2)(1)—C(2)—H(C2)(2)	108.7(1.8)
C(1)—C(2)—C(3)	110.4(0.4)
H(C2)(1)—C(2)—C(3)	103.9(1.4)
H(C2)(2)—C(2)—C(3)	105.4(1.2)
H(C3)(1)—C(3)—C(2)	115.4(1.7)
H(C3)(2)—C(3)—C(2)	111.0(2.1)
H(C3)(1)—C(3)—H(C3)(2)	131.4(2.6)
C(2)—C(3)—C(4)	111.4(0.4)
H(C3)(1)—C(3)—C(4)	88.9(1.8)
H(C3)(2)—C(3)—C(4)	94.5(1.9)
H(C4)(1)—C(4)—C(3)	110.5(1.7)
H(C4)(2)—C(4)—C(3)	108.1(2.0)
H(C4)(1)—C(4)—H(C4)(2)	109.5(4.0)
C(3)—C(4)—C(5)	111.7(0.4)
H(C4)(1)—C(4)—C(5)	111.8(1.4)
H(C4)(2)—C(4)—C(5)	109.5(1.2)
H(C5)(1)—C(5)—C(4)	109.5(1.2)
H(C5)(2)—C(5)—C(4)	110.4(2.0)
H(C5)(1)—C(5)—H(C5)(2)	114.7(2.2)
C(4)—C(5)—C(6)	112.7(0.4)
H(C5)(1)—C(5)—C(6)	116.9(1.4)
H(C5)(2)—C(5)—C(6)	124.5(1.7)
H(C6)(1)—C(6)—C(5)	109.7(1.4)
H(C6)(2)—C(6)—C(5)	110.3(1.5)
H(C6)(1)—C(6)—H(C6)(2)	108.1(2.0)
C(5)—C(6)—C(7)	111.5(0.3)
H(C6)(1)—C(6)—C(7)	108.0(1.4)
H(C6)(2)—C(6)—C(7)	109.1(1.5)
H(C7)(1)—C(7)—C(6)	105.8(1.4)
H(C7)(2)—C(7)—C(6)	111.3(1.4)
H(C7)(1)—C(7)—H(C7)(2)	111.3(1.9)
C(6)—C(7)—C(8)	114.3(0.3)
H(C7)(1)—C(7)—C(8)	107.3(1.4)
H(C7)(2)—C(7)—C(8)	106.8(1.4)
H(C8)(1)—C(8)—C(7)	110.6(1.5)
H(C8)(2)—C(8)—C(7)	109.1(1.3)
H(C8)(1)—C(8)—H(C8)(2)	113.6(1.8)
C(7)—C(8)—O(1)	106.3(0.3)
H(C8)(1)—C(8)—O(1)	108.2(1.4)
H(C8)(2)—C(8)—O(1)	108.8(1.3)
C(8)—O(1)—C(9)	119.2(0.3)

TABLE V(b) (*Continued*)

O(1)—C(9)—C(10)	125.2 (0.4)
O(1)—C(9)—C(14)	115.3 (0.4)
C(10)—C(9)—C(14)	119.5 (0.4)
H(C10)—C(10)—C(9)	121.0 (1.5)
C(9)—C(10)—C(11)	118.9 (0.4)
H(C10)—C(10)—C(11)	119.9 (1.5)
H(C11)—C(11)—C(10)	121.3 (1.5)
C(10)—C(11)—C(12)	122.6 (0.4)
H(C11)—C(11)—C(12)	116.2 (1.5)
C(11)—C(12)—C(13)	117.7 (0.4)
C(11)—C(12)—C(15)	121.7 (0.4)
C(13)—C(12)—C(15)	120.6 (0.4)
H(C13)—C(13)—C(12)	112.5 (1.3)
C(12)—C(13)—C(14)	120.3 (0.4)
H(C13)—C(13)—C(14)	127.2 (1.3)
C(9)—C(14)—C(13)	121.0 (0.4)
H(C14)—C(14)—C(9)	116.9 (1.4)
H(C14)—C(14)—C(13)	122.0 (1.4)
H(C15)—C(15)—C(12)	87.3 (2.3)
C(12)—C(15)—N(1)	122.4 (0.4)
H(C15)—C(15)—N(1)	150.1 (2.3)
C(15)—N(1)—C(16)	121.0 (0.4)
N(1)—C(16)—C(17)	126.6 (0.4)
N(1)—C(16)—C(21)	116.3 (0.4)
C(17)—C(16)—C(21)	117.1 (0.4)
H(C17)—C(17)—C(16)	117.2 (1.3)
C(16)—C(17)—C(18)	121.4 (0.4)
H(C17)—C(17)—C(18)	121.3 (1.3)
H(C18)—C(18)—C(17)	122.3 (1.5)
C(17)—C(18)—C(19)	121.8 (0.4)
H(C18)—C(18)—C(19)	115.8 (1.5)
C(18)—C(19)—C(20)	117.5 (0.5)
C(18)—C(19)—C(22)	120.9 (0.5)
C(20)—C(19)—C(22)	121.7 (0.4)
H(C20)—C(20)—C(19)	117.5 (1.4)
C(19)—C(20)—C(21)	121.5 (0.4)
H(C20)—C(20)—C(21)	121.4 (1.4)
C(16)—C(21)—C(20)	120.7 (0.4)
H(C21)—C(21)—C(16)	114.3 (1.6)
H(C21)—C(21)—C(20)	124.9 (1.6)
H(C22)(1)—C(22)—C(19)	117.1 (1.4)
H(C22)(2)—C(22)—C(19)	107.6 (1.8)
H(C22)(1)—C(22)—H(C22)(2)	101.7 (2.2)
C(19)—C(22)—C(23)	113.8 (0.4)
H(C22)(1)—C(22)—C(23)	105.9 (1.4)
H(C22)(2)—C(22)—C(23)	110.1 (1.8)
H(C23)(1)—C(23)—C(22)	110.2 (1.4)
H(C23)(2)—C(23)—C(22)	109.8 (1.9)

TABLE V(b) (*Continued*)

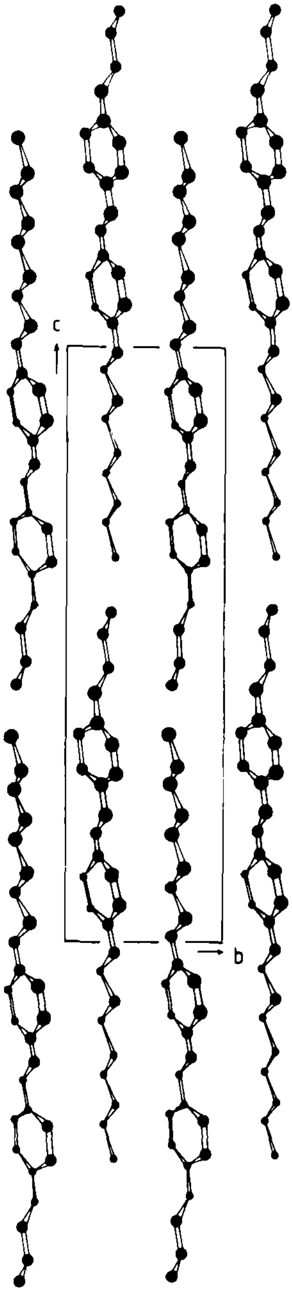
H(C23)(1)—C(23)—H(C23)(2)	99.0(2.2)
C(22)—C(23)—C(24)	113.9(0.4)
H(C23)(1)—C(23)—C(24)	110.5(1.4)
H(C23)(2)—C(23)—C(24)	112.5(1.8)
H(C24)(1)—C(24)—C(23)	107.8(1.6)
H(C24)(2)—C(24)—C(23)	106.8(1.7)
H(C24)(1)—C(24)—H(C24)(2)	108.8(2.2)
C(23)—C(24)—C(25)	112.8(0.4)
H(C24)(1)—C(24)—C(25)	107.0(1.7)
H(C24)(2)—C(24)—C(25)	113.5(1.8)
H(C25)(1)—C(25)—C(24)	112.2(1.8)
H(C25)(2)—C(25)—C(24)	105.4(1.8)
H(C25)(1)—C(25)—H(C25)(2)	108.1(2.3)
H(C25)(3)—C(25)—C(24)	114.7(1.7)
H(C25)(1)—C(25)—H(C25)(3)	108.9(2.2)
H(C25)(2)—C(25)—H(C25)(3)	107.3(2.3)

Molecular conformation

The conformational features of the molecule are described in terms of the least-squares planes calculated for various portions of the molecule (Figure 1). The equations and r.m.s. displacements for these planes are given in Table 6. The distances between these planes and the individual atoms in the molecule are given in Table 7. The dihedral angles of these planes are given in Table 8. Both the phenyl rings are planar within experimental error; the mean r.m.s. deviation is 0.006(3) Å in ring A and 0.004(2) Å in ring B, compared with, 0.002 Å and 0.003 Å respectively in molecule 1 and, 0.010 Å and 0.007 Å respectively in molecule 2 of 40.8.[3] The dihedral angle between the ring planes is 2.2°, significantly less than the values of 13.3° and 29.2° for molecules 1 and 2 respectively of 40.8. The CH═N group is nearly coplanar with both rings, the dihedral angle between the plane of ring A and the plane containing the C═N—and ring B is 2.0°. The twist at the CH═N link is thus considerably smaller than for 40.8 and IBPBAC. The dihedral angle between the octyloxy group and ring A is 1.5° compared with the larger values of 8.6° between the butyloxy group and ring A in molecule 1 and 18.3° in molecule 2 of 40.8. However, the dihedral angle between the butyl group and plane B is 63.6°, which is comparable with that of 61.4° between the octyl group and ring B in molecule 1 and 64.9° in molecule 2 of 40.8.

Molecular packing in 80.4 and 40.8 and its relation to smectic structures

The molecular packing in 80.4 is very simple and is clearly revealed by Figures 1–4 and Table 8. The extended octyloxy tail and the molecular core are coplanar within 3° and are essentially colinear; relative to this part of the mole-



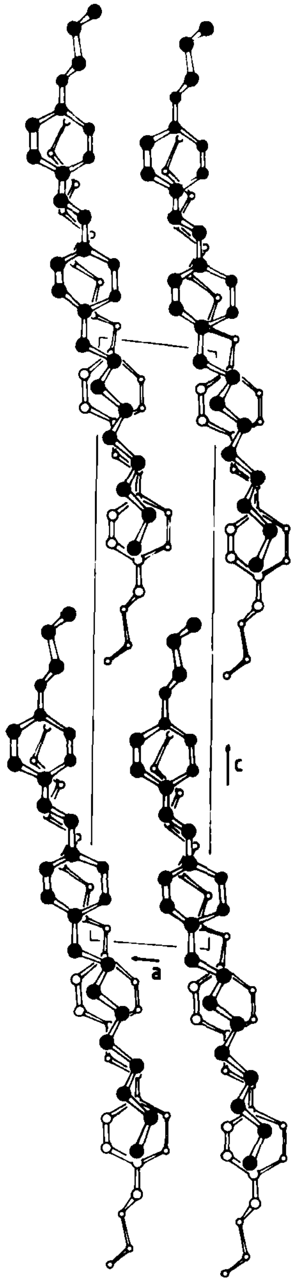


FIGURE 2 80.4 P$\bar{1}$ viewed along a axis. FIGURE 3 80.4 P$\bar{1}$ viewed along b axis.

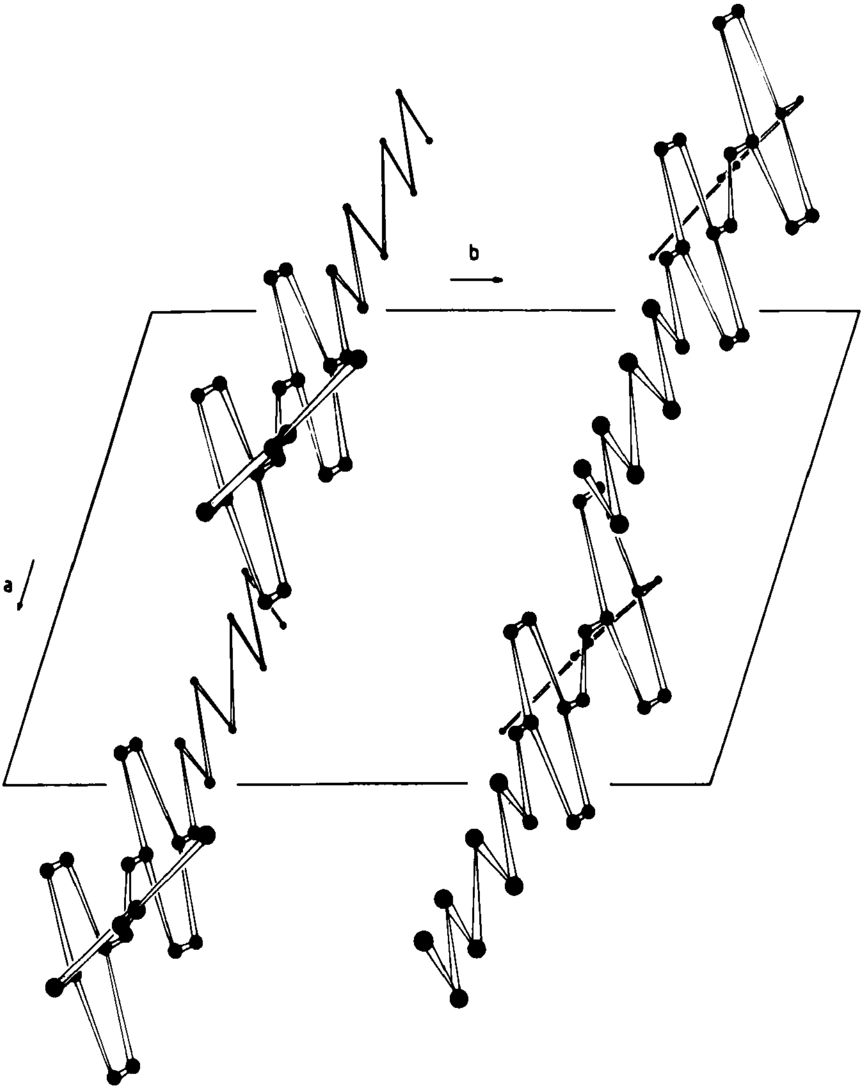


FIGURE 4 80.4 viewed along c axis.

cule the extended butyl tail is at an angle of about 37° and in a plane tilted by about 60°. The molecules are then arranged in sheets parallel to the ac plane, each sheet comprising molecules with the same long axis orientation. Adjacent sheets have opposite long axis orientations and are displaced parallel to c to give interdigitation of each of the linear parts of the molecules: the butyl groups in a distorted hexagonal close packing and the core plus octyloxy units packed so that each sub unit has two like and four unlike neighbors.

TABLE VI

Coefficients p, q, r, s, in the equation px + qy + rz = s of the least-squares plane in 80.4.

Plane Atoms	p	q	r	s	r.m.s. displacement (Å)
1. Phenyl ring A	−2.886	7.576	4.086	1.879	0.006
2. Phenyl ring B	−3.052	7.480	4.321	1.728	0.005
3. C(15) to C(21)	−2.980	7.489	4.737	1.891	0.037
4. C(1) to C(9)	−2.781	7.590	4.572	1.879	0.038
5. C(19), C(22) to C(25)	2.576	5.487	0.630	2.348	0.012
6. C(1) to C(25)	−1.128	7.881	1.780	2.025	0.408

TABLE VII

Deviations (Å) of individual atoms from the least-squares planes.

Atom	Plane 1	Plane 2	Plane 3	Plane 4	Plane 5	Plane 6
C(1)	0.150	0.252	−0.082	−0.056*	−1.839	0.240*
C(2)	0.136	0.273	−0.048	−0.056*	−2.430	−0.087*
C(3)	0.183	0.287	−0.003	0.030*	−1.515	0.263*
C(4)	0.196	0.336	0.061	0.058*	−2.108	−0.050*
C(5)	0.079	0.185	−0.058	−0.016*	−1.203	0.170*
C(6)	0.043	0.182	−0.047	−0.038*	−1.759	−0.159*
C(7)	0.049	0.155	−0.044	0.009*	−0.836	0.164*
C(8)	0.033	0.169	−0.015	0.009*	−1.326	−0.125*
O(1)	0.020	0.118	−0.038	0.033*	−0.346	0.218*
C(9)	−0.009*	0.106	−0.030	0.027*	−0.541	0.043*
C(10)	0.006*	0.174	0.032	0.031	−1.623	−0.422*
C(11)	0.002*	0.181	0.060	0.051	−1.674	−0.522*
C(12)	−0.008*	0.131	0.038	0.077	−0.678	−0.166*
C(13)	0.006*	0.093	0.005	0.103	0.420	0.329*
C(14)	0.002*	0.077	−0.032	0.074	0.478	0.424*
C(15)	−0.010	0.142	0.071*	0.102	−0.751	−0.278*
N(1)	−0.127	−0.009	−0.056*	0.018	0.080	−0.065*
C(16)	−0.128	0.004*	−0.021*	0.042	−0.021	−0.184*
C(17)	−0.180	0.002*	−0.026*	−0.018	−1.074	−0.693*
C(18)	−0.197	−0.006*	−0.012*	−0.009	−1.070	−0.779*
C(19)	−0.146	0.004*	0.024*	0.078	−0.004*	−0.345*
C(20)	−0.097	0.003*	0.026*	0.135	1.042	0.157*
C(21)	−0.096	−0.007*	−0.006*	0.109	1.046	0.236*
C(22)	−0.142	0.018	0.063	0.111	−0.010*	−0.428*
C(23)	1.090	1.278	1.324	1.342	0.018*	0.457*
C(24)	1.096	1.295	1.365	1.377	0.010*	0.373*
C(25)	2.312	2.540	2.612	2.590	−0.014*	1.227*

*atoms defining the plane.

TABLE VIII

Angles between normals to the planes of various portions of 80.4.

Plane	Plane	Dihedral angles (°)
1	2	2.2
1	3	2.0
1	4	1.5
1	5	61.4
1	6	21.3
2	3	1.2
2	4	3.4
2	5	63.6
2	6	23.5
3	4	2.6
3	5	62.9
3	6	23.0
4	5	60.3
4	6	20.4
5	6	40.4

The packing in 40.8 is remarkably similar to that in 80.4. Although emphasis was given in the original paper to the coplanar arrangement of all the dipoles, associated with O and CN groups, comparison of the two structures now shows this to be only of secondary importance. Again the molecules consist of two roughly linear parts: the octyl tails and the core plus butyloxy units. They are arranged in sheets alternately containing molecules with long axis directions either all up or down. Most importantly, however, the molecules in alternate sheets are displaced so that all the octyl tails are interdigitated in a roughly close packed manner as are the core plus butyloxy units. The most important factor determining the structures in both cases therefore appears to be the most efficient packing of molecules containing a linear alkyl group which is bent through roughly 37° relative to the approximately linear remainder of the molecule. This packing is best achieved by an arrangement of sheets so as to give interdigitation of identical parts of the molecules. The different alkyl tail lengths result in somewhat different conformations and crystallographic unit cells but the essential features of the packing are closely similar.

The structural parameters of the S_G phase of 80.4 have also been determined and are given in Table 9. The S_G structure is C-centred monoclinic with pseudo hexagonal packing of the molecules in the plane normal to *c* (the average "long axis" direction) and the parameters are similar to those for the other S_G phases of nO.m compounds.

The molecular length determined from the crystal structure, with an assumed Van der Waals radius of 2.0 Å for the terminal methyl groups is 28.4 Å which is the same as that measured on a CPK atomic model. Within experi-

TABLE IX

Structural parameters of the S_G phase of 80.4.

$a = 9.5$ Å
$b = 5.0$ Å
$c = 28.3$ Å
$\beta = 113.5$ Å
$V = 1232.8$ Å^3
Molecular length $l = 28.4$ Å

mental error the c-axis length in S_G is identical to the molecular length as for other nO.m compounds.[5]

The transition from crystal to S_G may be envisaged as taking place via relative translation of ac sheets and the onset of rotation about the long axis—almost certainly coupled with intramolecular rotations of various kinds. It seems clear that as for the crystal-S_B transition in 40.8 some longitudinal molecular displacements are required. However, we have found no simple relationship between crystal and smectic structures nor any structural arguments which would enable the type of smectic phase formed from the crystal to be predicted. This is not surprising when one considers that the crystal-smectic transition is a very strong one: the entropy and volume changes are as follows:

	ΔS/J K^{-1}mol^{-1}	$\Delta V/V_{Cryst}$
40.8 Crystal-S_B	140	0.136
80.4 Crystal-S_G	110	0.096

These are about an order of magnitude or more larger than the other transitions involved in reaching the isotropic liquid and indicate the considerable amount of disorder in even the crystalline[15] S_G and S_B phases. This is confirmed by neutron scattering studies on the S_G and S_B phases of 50.7 which show molecular rotation plus longitudinal displacements of $\lesssim 1.5$ Å occurring on a time scale of $\sim 10^{-11}$s in both phases. In conclusion therefore it seems than in general simple static structural correlations between crystal and smectic phases should not be expected. The disorder in the smectic phase (even those which are essentially crystals[15]) is of dominant importance and it is certainly not true that the crystal structures of smectic precursors are simple layer structures.

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