

CHAPTER 4

**Crystal and molecular structure of 4(3ⁿ - Pentenyl) - 4' (Ethoxy) 1,1'
bicyclohexane**

4.1 INTRODUCTION :

Since liquid crystals may possess long range one-dimensional or quasilong range two-dimensional translational symmetry, one expects that the molecular arrangement in the crystalline state will predetermine the molecular arrangement in the mesomorphic state¹⁻⁴. In this context, the crystal and molecular structure of one polar alkenyl compound PCBCH was reported by us⁵ and described in chapter 3. In this chapter, I describe the crystal and molecular structure of one non-polar alkenyl compound 4(3"-pentenyl) -4'-(ethoxy)-1,1'-bicyclohexane [PEBCH in short] and discuss the change in the molecular packing which accompanies the solid to nematic phase transition.

4.2 EXPERIMENTAL DETAILS :

4.2.1 Crystal data

The compound was obtained from Hoffmann-La Roche and Co., Basel, Switzerland. Single crystal, suitable for x-ray analysis, was obtained from an acetone solution by slow evaporation. Lattice parameters and space group were determined by oscillation and weissenberg photographs which were not of sufficiently good quality to be reproduced here. The crystal belongs to the orthorhombic system. From the systematic absences of $h00$ with h odd, $0k0$ with k odd and $00l$ with l odd, the space group was uniquely determined to be $P 2_1 2_1 2_1$. Accurate cell parameters was determined by a least squares fit of $\sin^2 \theta$ values of 23 reflections having θ values $39 < \theta < 43$, measured on an Enraf Nonius CAD-4 diffractometer using CuK_α radiation and a graphite monochromator. A total of 2136 reflections were measured on $\omega - 2\theta$ scan mode, of which 1855 were treated as observed with $I > 2.5\sigma(I)$. The data were collected at -45°C and corrected for Lorentz and Polarization factors but no absorption correction was made. Important crystallographic data are listed in table 4.1.

Table - 4.1
Summary of crystallographic data

Molecular formula	$C_{19}H_{34}O$
Molecular weight/g*mol ⁻¹	278.426
Crystal system	Orthorhombic
Lattice type	Non-centrosymmetric
Space group	$P 2_1 2_1 2_1$
a/Å	4.7095 (10)
b/Å	17.8195 (2)
c/Å	21.1616 (19)
$\alpha, \beta, \gamma / ^\circ$	90
$V/\text{Å}^3$	1775.901
$D_c / \text{g*cm}^{-3}$	1.042
Z	4
$\lambda (\text{CuK}_\alpha) / \text{Å}$	1.5418
No. of independent reflection	2136
No. of observed reflection	1855

4.3 STRUCTURE DETERMINATION AND REFINEMENT.

Since the structure is non-centrosymmetric, phases were estimated using generalised tangent procedures using the programme GENTAN of XTAL systems⁹. Multiple phase sets were initialized using magic integer procedure. Phase extension was performed by cascade technique. Hall-Irwin statistical weighting scheme was used for tangent formula. E-map was calculated from the phase set 1 having CFOM 0.85 and AMOS 98%. 300 strong reflections were phased through the application of tangent formula using triplet and quartet structure invariant relationship. E-map is shown in figure 4.1. From the E-map we could locate eighteen non-hydrogen atoms. With the help of Fourier and difference Fourier map the other two atoms could be located. The structure thus obtained was refined and initially five cycles of full matrix least squares with individual isotropic temperature factor brought the R-value to 0.20. Introduction of individual anisotropic temperature factors reduced the R-value to 0.15. At this point it was observed that the bond lengths and angles involving the double bond of the alkenyl chain have large values, the thermal vibrations were also found to be very large. A difference Fourier map was computed and the atoms were relocated. But subsequent refinement did not show any improvement in the structure. Attempts were also made to refine the structure by varying the occupancy of those atoms but no better result was obtained. The positions of hydrogen atoms were then calculated from the known geometry around the carbon atoms and these positions were subsequently confirmed on a difference Fourier map. The hydrogen atoms were given isotropic temperature factors of the parent carbon atoms. Then the structure was refined through several cycles by full matrix, first keeping hydrogen atoms fixed, allowing non-hydrogen atoms to vibrate anisotropically and then with hydrogen atoms vibrating isotropically and non-hydrogen atoms fixed. This resulted in an R-value of 0.119. From structure factor tables three

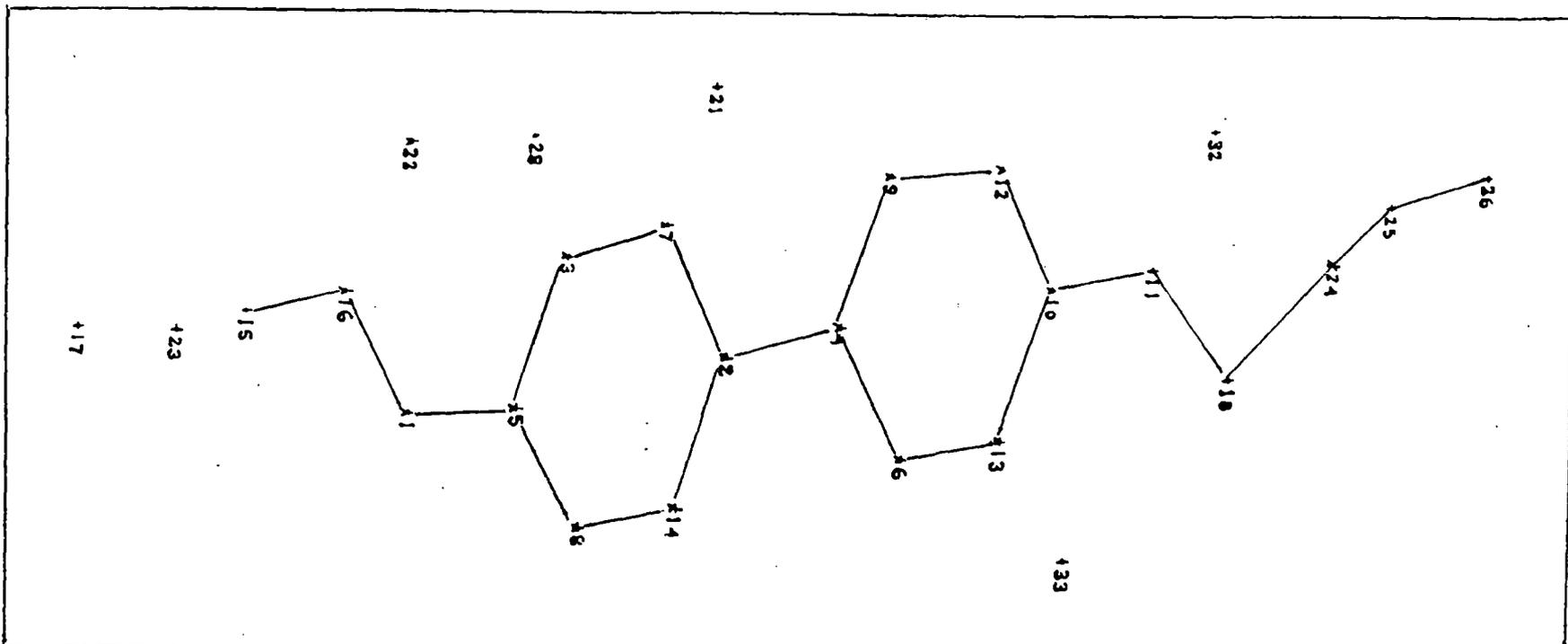


Figure 4.1 : E-map of 4(3''-pentenyl)-4'-(ethoxy)-1,1'-bicyclohexane.

reflections 021, 200 and 101 were found to have secondary extinction effects. These reflections were excluded. Finally six cycles of refinement was carried out keeping all the hydrogen atoms fixed and non-hydrogen atoms to vibrate anisotropically. The final R-value was 0.077 and $R_w = 0.077$. A difference Fourier map at this stage showed no electron density greater than $0.42 \text{ e}/\text{A}^3$. Therefore, the large bond lengths and angles in the alkenyl chain may be due to disordering in that part of the molecule.

All the calculations were done using PC version of the NRCVAX package utilities¹⁰.

4.4 RESULTS AND DISCUSSIONS

4.4.1 Molecular Structure

Final positional and thermal parameters of the non-hydrogen and hydrogen atoms are given in tables 4.2 - 4.4. The molecular structure of PEBCH is presented in figure 4.2 indicating the atom numbering scheme. It also shows that both the cyclohexyl rings are in chair conformation. The length of the molecule in the crystalline state (C1- C19) is 17.28 \AA whereas the model length is found to be 17.4 \AA . Thus the molecules are in most extended form with all trans - conformation of both the pentenyl and ethoxy groups as is also observed in figure 4.2. Bond lengths and bond angles involving non-hydrogen atoms are given in table 4.5. The average C - C bond lengths in the two cyclohexyl rings A and B (figure 4.2) is 1.529 \AA and 1.534 \AA respectively. The value of the C - O bond distance is 1.393 \AA . The maximum and minimum bond angles are respectively 112.4° and 108.7° in ring A, 112.9° and 108.9° in ring B. All these distances and angles are normal and comparable with PCBCH⁵ and other reported values⁸⁻¹⁰. However the length of the double bond C17-C18 is 1.077 \AA and the angle C17-C18-C19 is 145.7° which differ from normal values to a large extent. Atoms C17 and C18 in the chain have large temperature factors. There may be some conformational disorder

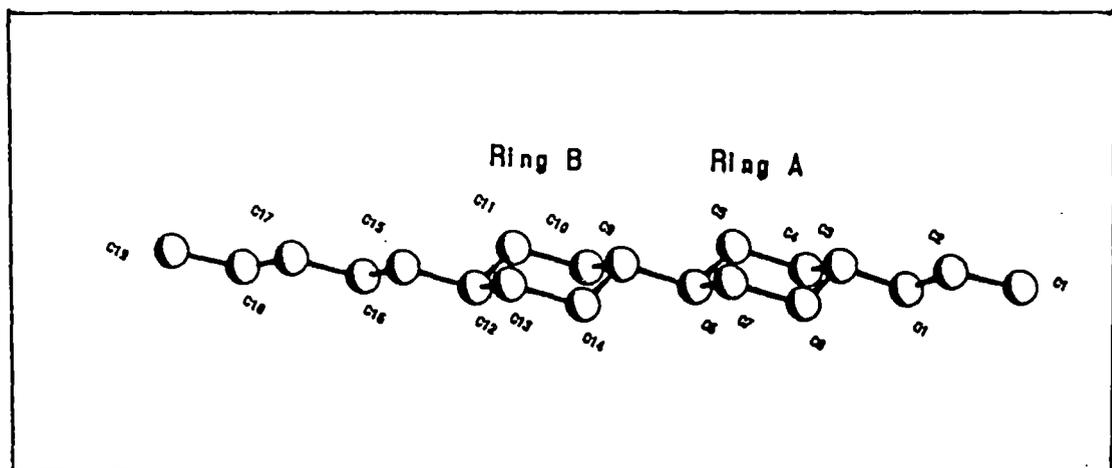


Figure 4.2 : The perspective view of the PEBCH molecule depicting the chair conformation of the cyclohexyl rings and the atom numbering scheme.

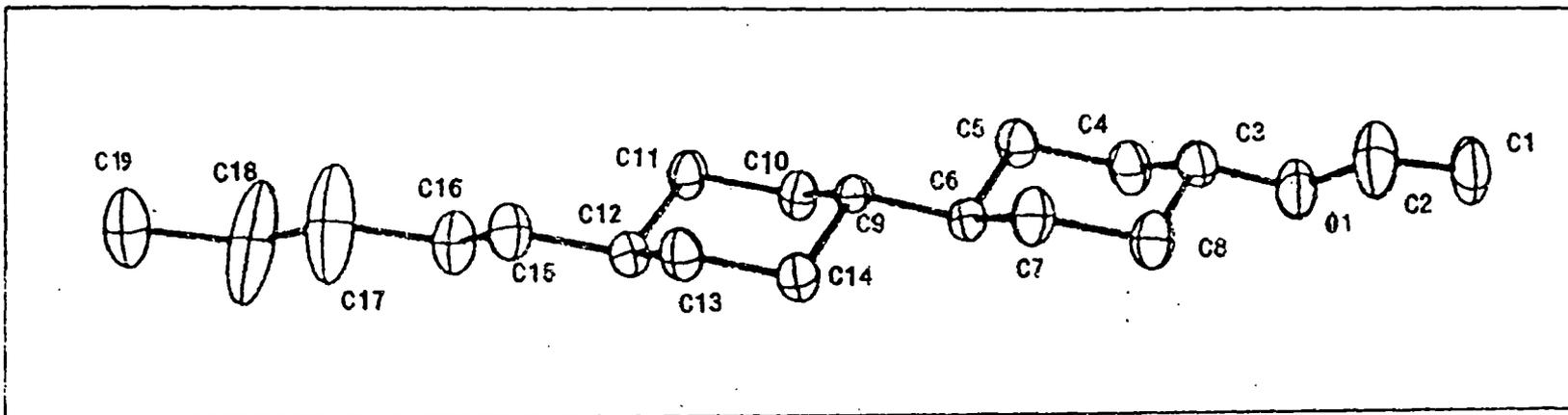


Figure 4.3 : ORTEP drawing of the PEBCH molecule showing the thermal ellipsoids of the non-hydrogen atoms.

in the molecular structure around the double bond. It was difficult to obtain appropriate geometries for these disordered atoms. In liquid crystals such conformational disorder has been reported earlier^{9,11,12}.

ORTEP drawing showing the thermal ellipsoids of the non-hydrogen atoms is given in figure 4.3. Two disordered atoms in the chain have large thermal displacements in the direction perpendicular to the long molecular axis thereby resulting in an abnormal value of the C17 - C18 double bond.

4.4.2 Molecular Packing

In order to describe the molecular packing we have given the a, b and c-axis projection of the structure in figures 4.4 - 4.6. In describing the packing we have to keep in mind that the compound crystallized in non-centrosymmetric orthorhombic cell with four molecules in the unit cell. The figures clearly depicts that the molecules are packed parallel to the crystallographic c-axis with a tilt angle of about 5° . The symmetrically related molecules are also parallel to each other in head-tail or head-head manner. These parallel molecules are packed in an imbricated mode. This type of packing is normally observed where transition occurs from crystalline to nematic phase where the molecules possess no positional correlation but have only orientational ordering about a director. Also we note from figure 4.4 that the bulky cyclohexane groups overlap with either less bulky alkenyl or ethoxy group.

We calculated the interatomic distances between the neighbouring molecules and no such distance was found which is less than the sum of the van der Waals' radii of the atoms involved. So in PEBCH no molecular "association", as a result of van der Waals' type of interaction, occurs in the crystalline state. On transition to nematic phase the picture does not alter as is evident from the fact that the average length of the molecules, obtained from x-ray

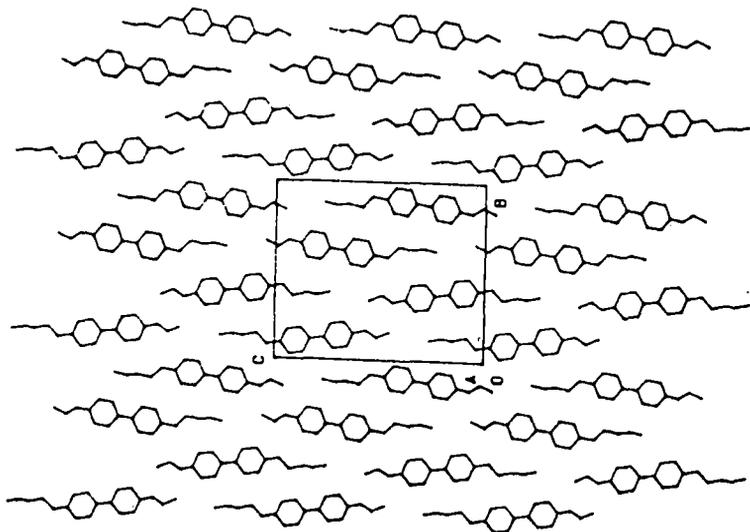


Figure 4.4 : Molecular packing projected along [100].

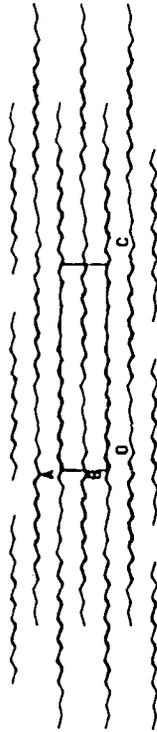


Figure 4.5 : Molecular packing projected along [010].

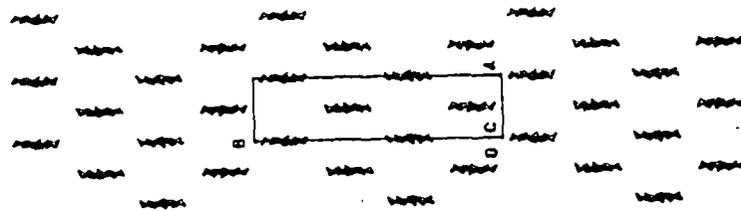


Figure 4.6 : Molecular packing projected along [001].

diffraction study¹³, in the nematic phase is 17.0 Å, almost equals to the length of a single molecule.

It would be of interest to compare at this point the phase sequences and molecular packing of two related compounds^{5,8,13,14} CCH5 and PCBCH with the present compound PEBCH. Relevant data are given in table 4.6.

The only structural difference between CCH5 and PCBCH is that in PCBCH a double bond has been introduced at a specific position of the alkyl chain whereas the structural difference between PCBCH and PEBCH is that, in PEBCH a non-polar ethoxy group has been introduced at the position of the polar cyano group. Introduction of the double bond in CCH5 causes suppression of smectic phase and increase of both the C-N and N-I transition temperatures but the nematic range does not increase. On other hand introduction of the ethoxy group in PCBCH considerably reduces the C-N transition temperature as well as widens the nematic range.

If we look into the crystal structures of the compounds, we observe that various types of molecular overlapping is present in the compounds. In CCH5 bulky central cyclohexyl rings of neighbouring molecules overlap in head to tail manner⁸. While in PCBCH and PEBCH no overlapping of the core cyclohexyl rings is observed. In both smectic and nematic phases of CCH5 and PCBCH "bimolecular association" is observed but in the crystalline state of CCH5 evidence of such association is not found whereas in PCBCH a very weak association is observed. On the other hand, PEBCH shows no evidence of molecular association both in nematic and crystalline states.

Moreover, in crystalline state, both CCH5 and PCBCH have layered structure and within the layers the molecules are tilted with respect to the normal to the layer. These type of packing may be precursor to the tilted smectic phase but not to the observed orthogonal SmB or SmA phases wherein the molecules are parallel to

the smectic layer normals. The parallel imbricated type of packing of PEBCH, however, corresponds to the observed nematic phase. Qualitatively it can also be inferred that the lateral interaction between the molecules is strong in all cases. But in CCH5 the terminal interaction is sufficient to maintain the layer structure so that it melts to smectic phase, in PCBCH it is not sufficient to maintain the layer structure on melting (it shows SmA monotropically, that too within a very small temperature range) and in PEBCH this terminal interaction is negligible so that from imbricated packing it melts to nematic phase. However, we can not give any quantitative explanation only from crystal structure analysis.

Tables - 4.2

Atomic Parameters x,y,z and Biso. E.S.Ds. refer to the last digit printed. Biso is the Mean of the Principal Axes of the Thermal Ellipsoid.

Atom	x	y	z	Biso
C1	.4800(16)	.1608 (3)	.45152(19)	4.8 (3)
C2	.5739(15)	.1285 (3)	.51364(21)	5.0 (3)
O1	.4403(8)	.16667(18)	.56278(12)	3.75(14)
C3	.5525(10)	.15078(23)	.62387(17)	2.79(16)
C4	.4568(12)	.21378(22)	.66654(18)	3.19(18)
C5	.5585(12)	.20269(20)	.73501(17)	2.71(16)
C6	.4560(10)	.12660(19)	.76197(16)	2.05(14)
C7	.5560(12)	.06388(21)	.71804(17)	2.83(17)
C8	.4571(11)	.07555(22)	.64982(17)	3.03(17)
C9	.5588(9)	.11564(19)	.83087(16)	1.91(13)
C10	.4637(11)	.17999(19)	.87428(16)	2.51(16)
C11	.5518(11)	.16835(20)	.94315(16)	2.52(15)
C12	.4471(10)	.09390(19)	.97018(16)	2.10(14)
C13	.5436(11)	.02927(19)	.92736(17)	2.60(16)
C14	.4521(11)	.04045(18)	.85873(16)	2.35(15)
C15	.5408(11)	.08059(21)	1.03844(17)	2.75(16)
C16	.4246(12)	.13959(23)	1.08544(18)	3.42(20)
C17	.5114(21)	.1234 (3)	1.15212(21)	7.5 (4)
C18	.4534(20)	.1318 (4)	1.20081(22)	7.9 (4)
C19	.5283(16)	.11659(25)	1.26745(19)	4.3 (3)

Tables - 4.3

Anisotropic thermal parameters $u(1,j)$ values *100.

E.S.Ds. refer to the last digit printed.

	u11	u22	u33	u12	u13	u23
C1	9.5 (5)	6.0 (3)	2.84(21)	-1.4 (4)	.2 (3)	.28(20)
C2	7.9 (4)	7.9 (3)	3.37(22)	2.4 (4)	.3 (3)	-.78(23)
O1	4.69(19)	6.74(20)	2.83(14)	1.61(20)	.05(16)	.29(14)
C3	3.20(22)	4.77(22)	2.64(18)	.15(23)	.13(20)	.62(16)
C4	5.5 (3)	3.55(20)	3.05(19)	.1 (3)	.21(24)	.84(16)
C5	4.6 (3)	2.64(18)	3.01(18)	-.34(22)	.05(22)	.51(15)
C6	2.72(20)	2.48(17)	2.58(17)	.31(19)	-.07(18)	.10(13)
C7	4.9 (3)	3.16(19)	2.73(18)	1.06(23)	-.03(22)	-.28(15)
C8	4.8 (3)	3.76(20)	2.90(19)	.70(25)	.08(22)	-.51(16)
C9	2.18(19)	2.52(17)	2.55(16)	-.03(17)	-.12(18)	.29(13)
C10	4.5 (3)	2.36(16)	2.72(18)	-.10(21)	-.24(21)	.13(14)
C11	4.24(24)	2.83(18)	2.52(17)	-.15(21)	-.09(20)	-.22(14)
C12	2.98(21)	2.55(17)	2.44(16)	.35(18)	.17(18)	.07(13)
C13	4.38(25)	2.41(16)	3.09(18)	-.02(21)	.05(21)	.25(14)
C14	4.11(24)	2.02(16)	2.79(17)	-.26(20)	.10(20)	-.06(13)
C15	4.3 (3)	3.43(19)	2.77(17)	.87(22)	.08(21)	.19(15)
C16	6.0 (3)	4.20(23)	2.82(19)	.8 (3)	-.13(24)	-.13(17)
C17	17.1 (9)	8.5 (4)	2.88(22)	7.1 (6)	-.2 (4)	-.19(24)
C18	16.6 (9)	10.3 (5)	3.20(23)	9.9 (6)	-1.7 (4)	-1.0 (3)
C19	9.0 (5)	4.40(24)	2.91(20)	1.0 (3)	.0 (3)	.19(17)

Table - 4.4

Atomic Parameters x,y,z and Biso of the hydrogen atoms
 Biso is the mean of principle axis of the thermal ellipsoid

Atom	x	y	z	Biso
H1A	.584	.129	.414	3.3
H1B	.250	.150	.447	5.7
H1C	.524	.218	.448	5.7
H2A	.802	.137	.518	5.6
H2B	.529	.070	.517	5.6
H3	.779	.151	.621	3.3
H4A	.548	.266	.649	3.9
H4B	.231	.217	.666	3.9
H5A	.787	.206	.737	3.6
H5B	.470	.248	.764	3.6
H6	.228	.127	.761	2.8
H7A	.469	.011	.734	3.7
H7B	.784	.061	.719	3.7
H8A	.552	.032	.621	3.7
H8B	.232	.072	.648	3.7
H9	.785	.114	.830	2.6
H10A	.240	.187	.872	3.1
H10B	.569	.231	.858	3.1
H11A	.776	.171	.947	3.3
H11B	.453	.213	.971	3.3
H12	.220	.094	.969	2.7
H13A	.448	-.022	.944	3.2
H13B	.770	.024	.929	3.2
H14A	.545	-.005	.831	3.0
H14B	.226	.038	.856	3.0
H15A	.768	.080	1.041	3.3
H15B	.459	.026	1.053	3.3
H16A	.198	.140	1.083	4.2
H16B	.507	.194	1.072	4.2
H17	.711	.093	1.151	7.3
H18	.269	.169	1.202	8.5
H19A	.379	.145	1.299	3.3
H19B	.522	.058	1.276	4.8
H19C	.741	.138	1.278	4.8

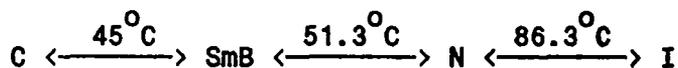
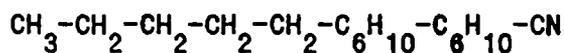
Tables - 4.5

Bond distances (Å) and angles ($^{\circ}$) with e.s.d's in parenthesis.

C(1)-C(2)	1.502(7)	C(9)-C(14)	1.548(5)
C(2)-O(1)	1.393(6)	C(10)-C(11)	1.529(5)
O(1)-C(3)	1.425(5)	C(11)-C(12)	1.527(5)
C(3)-C(4)	1.510(6)	C(12)-C(13)	1.534(5)
C(3)-C(8)	1.517(6)	C(12)-C(15)	1.529(5)
C(4)-C(5)	1.539(6)	C(13)-C(14)	1.528(5)
C(5)-C(6)	1.548(5)	C(15)-C(16)	1.547(6)
C(6)-C(7)	1.528(5)	C(16)-C(17)	1.497(6)
C(6)-C(9)	1.548(5)	C(17)-C(18)	1.077(7)
C(7)-C(8)	1.531(5)	C(18)-C(19)	1.479(6)
C(9)-C(10)	1.536(5)		
C(1)-C(2)-O(1)	109.5(5)	C(6)-C(9)-C(14)	111.5(3)
C(2)-O(1)-C(3)	114.4(4)	C(10)-C(9)-C(14)	108.9(3)
O(1)-C(3)-C(4)	106.5(3)	C(9)-C(10)-C(11)	112.9(3)
O(1)-C(3)-C(8)	113.2(4)	C(10)-C(11)-C(12)	112.8(3)
C(4)-C(3)-C(8)	110.6(3)	C(11)-C(12)-C(13)	109.6(3)
C(3)-C(4)-C(5)	112.0(4)	C(11)-C(12)-C(15)	113.3(3)
C(4)-C(5)-C(6)	111.2(3)	C(13)-C(12)-C(15)	110.8(3)
C(5)-C(6)-C(7)	108.7(3)	C(12)-C(13)-C(14)	112.3(3)
C(5)-C(6)-C(9)	111.1(3)	C(9)-C(14)-C(13)	112.6(3)
C(7)-C(6)-C(9)	112.6(3)	C(12)-C(15)-C(16)	113.6(3)
C(6)-C(7)-C(8)	112.4(3)	C(15)-C(16)-C(17)	112.2(4)
C(3)-C(8)-C(7)	111.8(4)	C(16)-C(17)-C(18)	143.7(8)
C(6)-C(9)-C(10)	112.2(3)	C(17)-C(18)-C(19)	145.7(8)

Table - 4.6

CCH5

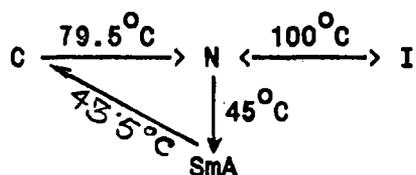
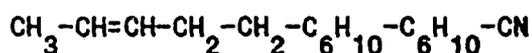


Single molecule model length = 16.5 Å

Smectic layer spacing = 31.2 Å

Molecular length in nematic phase = 27.2 Å

PCBCH

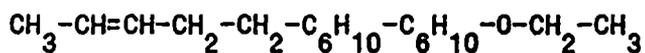


Single molecule model length = 16.3 Å

Smectic layer spacing = 24.0 Å

Molecular length in nematic phase = 30.0 Å

PEBCH



Single molecule model length = 17.4 Å

Molecular length in nematic phase = 17.0 Å

References :

- [1] R. F. Bryan, Proceedings of the Pre-Congress Symposium on Organic Crystal Chemistry, Poznan, Poland, 105, (1979).
- [2] W. Haase, H. Paulus and H. T. Muller, Mol. Cryst. Liq. Cryst., 97, 131 (1983).
- [3] P. Mandal and S. Paul, Mol. Cryst. Liq. Cryst., 131, 223 (1985).
- [4] W. Thyen, F. Heinemann and P. Zugenmaier, Liq. Crystals, 16, 993 (1994).
- [5] S. Gupta, A. Nath, S. Paul, H. Schenk and K. Goubitz, Mol. Cryst. Liq. Cryst. (1994). (In Press).
- [6] S. R. Hall, J. M. Stewart and R. J. Munn, Acta. Cryst., A36, 979 (1980)
- [7] P. S. White, PC version of NRCVAX (1988) , University of New Brunswick, Canada.
- [8] W. Haase and H. Paulus, Mol. Cryst. Liq. Cryst., 100, 111, (1983).
- [9] S. Bhattacharjee and G. A. Jeffrey, Mol. Cryst. Liq. Cryst., 101, 247 (1983).
- [10] S. Gupta, P. Mandal, S. Paul, M. Wit, K. Goubitz and H. Schenk, Mol. Cryst. Liq. Cryst., 195, 149 (1991).
- [11] P. Mandal, S. Paul, C. H. Stam and H. Schenk, Mol. Cryst. Liq. Cryst., 180B, 369 (1990).
- [12] P. Zugenmaier and A. Heiske, Liquid Crystals, 15, 6, 835 - 849, (1993).
- [13] A. Nath, B. Chaudhury and S. Paul, Mol. Cryst. Liq. Cryst., 265, 699 (1994).
- [14] G. J. Brownsey and A. J. Leadbetter, J. Physique-letters, 42, 135 (1981).