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Structural analysis by X-ray diffraction of a non-polar alkenyl liquid crystalline compound

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Structural analysis by X-ray diffraction of a non-polar alkenyl liquid crystalline compound

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The crystal and molecular structure of a non-polar alkenyl nematogen 4-(3″-pentenyl)-4′-(ethoxy)-1,1′-bicyclo-hexane (PEBCH) have been determined from single crystal X-ray diffraction analysis. The compound crystallizes in the form of a non-centrosymmetric orthorhombic cell with dimensions 4·7095(10), 17·8195(2), 21·1616(19) Å, space group $P2_12_12_1$ and 4 molecules in the unit cell. A parallel imbricated type of molecular arrangement is observed in the crystalline state as a precursor to the nematic phase. Molecular packing and phase sequences are compared with two related mesogenic compounds.

1. Introduction

As the complexity and diversity of liquid crystal display technology increases, demands for tailoring new liquid crystal materials with wide range of material properties also increases. New types of polar and non-polar bicyclohexane liquid crystals containing alkenyl side chains were reported in this context [1–3]. The compounds have low optical anisotropy, low viscosity but high elastic constants, and thus can be used in display devices as materials with short response times. The properties of these compounds change markedly with respect to the position of the double bond in the alkenyl chain. Since liquid crystals may possess long range one-dimensional or quasi-long range two-dimensional translational symmetry, one expects that the molecular arrangement in the crystalline state will predetermine the molecular arrangement in the mesomorphic state [4–7]. The crystal and molecular structure of one polar alkenyl compound, PCBCH, was first reported by us [8] in this context. Here we report the X-ray structural analysis of a non-polar alkenyl compound, 4-(3″-pentenyl)-4′-(ethoxy)-1,1′-bicyclohexane [PEBCH in short], and try to explain molecular organization in the mesomorphic phase in relation to the packing in the crystalline state.

2. Experimental

2.1. *Crystal data*

The compound was obtained from Hoffmann–La Roche and Co., Basel Switzerland. A single crystal, suitable for X-ray analysis, was obtained from an acetone solution by slow evaporation. 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 is uniquely determined to be $P2_12_12_1$. Accurate cell parameters are determined by a least squares fit of $\sin\theta$ 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 $I > 2{\cdot}5\sigma(I)$. 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 1.

2.2. *Structure determination and refinement*

Since the structure is non-centrosymmetric, phases were estimated with generalized tangent procedures using the program GENTAN of XTAL systems, a crystallographic program [9]. From the E-map we could locate eighteen non-hydrogen atoms. With the help of Fourier and difference Fourier maps the other two atoms could be located. The structure thus obtained was refined by full matrix least squares with an individual isotropic temperature factor to an R-value of 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

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Table 1. Summary of crystallographic data.

Parameter	
Molecular formula	$C_{19}H_{34}O$
Molecular weight/g mol^{-1}	278·426
Crystal system	Orthorhombic
Lattice type	Non-centrosymmetric
Space group	$P2_12_12_1$
a/Å	4·7095(10)
b/Å	17·8195 (2)
c/Å	21·1616(19)
α, β, γ/°	90
V/Å^3	1775·901
D_c/g cm^{-3}	1·042
Z	4
λ (CuK_α)/Å	1·5418
No. of independent reflections	2136
No. of observed reflections	1855

of the alkenyl chain show high values; the thermal vibrations were also found to be large. Relocation of the atoms from difference Fourier synthesis and then refinement leads to the same structure. Attempts were also made to refine the structure by varying the occupancy of these atoms but no improvement was achieved. The positions of the hydrogen atoms were then calculated from the known geometry around the carbon atoms. Full matrix least squares refinement, first keeping the hydrogen atoms fixed and allowing non-hydrogen atoms to vibrate anisotropically and then hydrogen atoms vibrating isotropically and non-hydrogen atoms fixed, resulted in an R-value of 0·119. From structure factor tables three reflections 0 2 1, 2 0 0 and 1 0 1, were found to have secondary extinction effects. These reflections were excluded. From final refinement the R-value was 0·077 and $R_w = 0{\cdot}077$. A difference Fourier map at this stage showed no electron density greater than 0·42 e Å^{-3}. The high R-value may be caused by disorder in the alkenyl chain.

All the calculations were done using the PC version (MSDOS) of the NRCVAX package utilities [10].

3. Results and discussion

3.1. *Molecular structure*

Final positional and thermal parameters of the non-hydrogen atoms are given in tables 2 and 3, respectively. The molecular structure of PEBCH is presented in figure 1 indicating the atom numbering scheme. The cyclohexyl rings are in a chair conformation. The length of the molecule in the crystalline state (C1–C19) is 17·28 Å whereas the stereo-model length with all-*trans*-tails is found to be 17·4 Å. Thus the molecules are in the most extended form with the all *trans*—conformation of both the pentenyl and ethoxy groups as is also evident from figure 1. Bond lengths and bond angles involving non-hydrogen atoms are given in table 4. The average C–C bond lengths in the two cyclohexyl rings A and B (see figure 1) are 1·529 Å and 1·534 Å, respectively. The value of the C–O bond distance is 1·393 Å. The maximum and minimum bond angles are, respectively, 112·4° and 108·7° in ring A, and 112·9° and 108·9° in ring B. All these distances and angles are normal and comparable with PCBCH [8] and other reported values [11–13]. However the length of the double bond C17–C18 is 1·077 Å and the angle C17–C18–C19 is 145·7° which differ from normal values to a large extent. As noted earlier, thermal parameters of atoms C17 and C18 were also very large compared to other atoms. There may be, therefore, some conformational disorder in the molecular structure around the double bond. The large bond lengths and angles in the alkenyl chain may be due to disorder in that part of the molecule. In liquid crystals such conformational disorder has been reported earlier [12, 14, 15].

3.2. *Molecular packing*

In order to describe the molecular packing we have given the a, b and c axes projection of the structure in figures 2–4 and a three-dimensional stereo view in figure 5. In describing the packing we have to keep in mind that the compound crystallized in a non-centrosymmetric orthorhombic cell with four molecules in the unit cell. The figures clearly depict that the molecules are packed parallel to the crystallographic c axis with a tilt angle of about 5°. The symmetrically

Table 2. Atomic parameters x, y, z and B_{iso}. ESDs refer to the last digit printed. B_{iso} is the mean of the principal axes of the thermal ellipsoid.

Atom	x	y	z	B_{iso}
C1	0·4800(16)	0·1608(3)	0·45152(19)	4·8(3)
C2	0·5739(15)	0·1285(3)	0·51364(21)	5·0(3)
O1	0·4403(8)	0·16667(18)	0·56278(12)	3·75(14)
C3	0·5525(10)	0·15078(23)	0·62387(17)	2·79(16)
C4	0·4568(12)	0·21378(22)	0·66654(18)	3·19(18)
C5	0·5585(12)	0·20269(20)	0·73501(17)	2·71(16)
C6	0·4560(10)	0·12660(19)	0·76197(16)	2·05(14)
C7	0·5560(12)	0·06388(21)	0·71804(17)	2·83(17)
C8	0·4571(11)	0·07555(22)	0·64982(17)	3·03(17)
C9	0·5588(9)	0·11564(19)	0·83087(16)	1·91(13)
C10	0·4637(11)	0·17999(19)	0·87428(16)	2·51(16)
C11	0·5518(11)	0·16835(20)	0·94315(16)	2·52(15)
C12	0·4471(10)	0·09390(19)	0·97018(16)	2·10(14)
C13	0·5436(11)	0·02927(19)	0·92736(17)	2·60(16)
C14	0·4521(11)	0·04045(18)	0·85873(16)	2·35(15)
C15	0·5408(11)	0·08059(21)	1·03844(17)	2·75(16)
C16	0·4246(12)	0·13959(23)	1·08544(18)	3·42(20)
C17	0·5114(21)	0·1234(3)	1·15212(21)	7·5(4)
C18	0·4534(20)	0·1318(4)	1·20081(22)	7·9(4)
C19	0·5283(16)	0·11659(25)	1·26745(19)	4·3(3)

Table 3. Anisotropic thermal parameters *u*(*i*, *j*) values × 100. ESDs refer to the last digit printed.

Atom	*u*11	*u*22	*u*33	*u*12	*u*13	*u*23
C1	9·5(5)	6·0(3)	2·84(21)	−1·4(4)	0·2(3)	0·28(20)
C2	7·9(4)	7·9(3)	3·37(22)	2·4(4)	0·3(3)	−0·78(23)
O1	4·69(19)	6·74(20)	2·83(14)	1·61(20)	0·05(16)	0·29(14)
C3	3·20(22)	4·77(22)	2·64(18)	0·15(23)	0·13(20)	0·62(16)
C4	5·5(3)	3·55(20)	3·05(19)	0·1(3)	0·21(24)	0·84(16)
C5	4·6(3)	2·64(18)	3·01(18)	−0·34(22)	0·05(22)	0·51(15)
C6	2·72(20)	2·48(17)	2·58(17)	0·31(19)	−0·07(18)	−0·10(13)
C7	4·9(3)	3·16(19)	2·73(18)	1·06(23)	−0·03(22)	−0·28(15)
C8	4·8(3)	3·76(20)	2·90(19)	−0·70(25)	0·08(22)	0·51(16)
C9	2·18(19)	2·52(17)	2·55(16)	−0·03(17)	0·12(18)	0·29(13)
C10	4·5(3)	2·36(16)	2·72(18)	−0·10(21)	−0·24(21)	0·13(14)
C11	4·24(24)	2·83(18)	2·52(17)	−0·15(21)	−0·09(20)	0·22(14)
C12	2·98(21)	2·55(17)	2·44(16)	−0·35(18)	0·17(18)	0·07(13)
C13	4·38(25)	2·41(16)	3·09(18)	−0·02(21)	0·05(21)	0·25(14)
C14	4·11(24)	2·02(16)	2·79(17)	−0·26(20)	0·10(20)	0·06(13)
C15	4·3(3)	3·43(19)	2·77(17)	0·87(22)	0·08(21)	0·19(5)
C16	6·0(3)	4·20(23)	2·82(19)	0·8(3)	−0·13(24)	0·13(17)
C17	17·1(9)	8·5(4)	2·88(22)	7·1(6)	0·02(4)	0·19(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)	0·0(3)	0·19(17)

Table 4. Bond distance (Å) and angles (°) with ESDs 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)	122·2(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)

related molecules are also parallel to each other in a head–tail or a head–head manner. These parallel molecules are packed in an imbricated mode. This type of packing is normally observed where transition occurs from the crystalline to the nematic phase in which the molecules possess no positional correlation but have orientational ordering about a director [4, 5, 7, 16]. Also we note from figure 2 that the bulky cyclohexane groups overlap with either the less bulky alkenyl or ethoxy group.

We calculated the interatomic distances between the neighbouring molecules and no such distance was found which was less than the sum of the van der Waals' radii of the atoms involved. So in PEBCH no molecular 'association', as a result of a van der Waals' type of interaction, occurs in the crystalline state. On transition

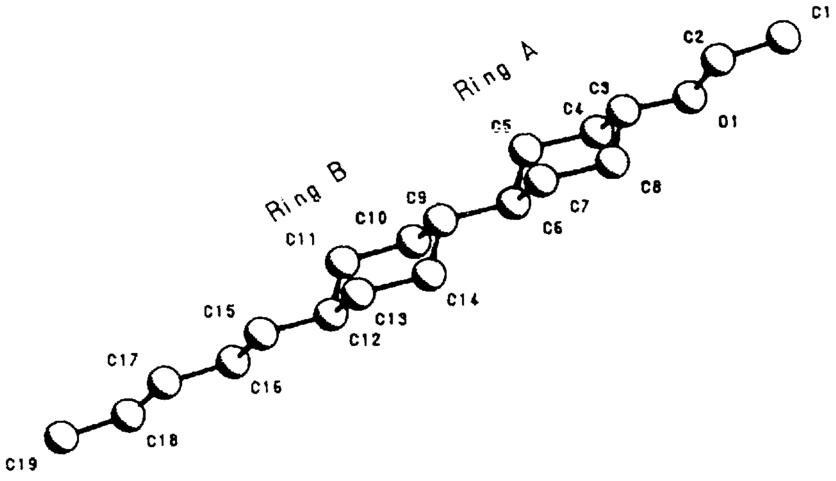

Figure 1. The perspective view of the PEBCH molecule depicting the chair conformation of the cyclohexyl rings and the atom numbering scheme.

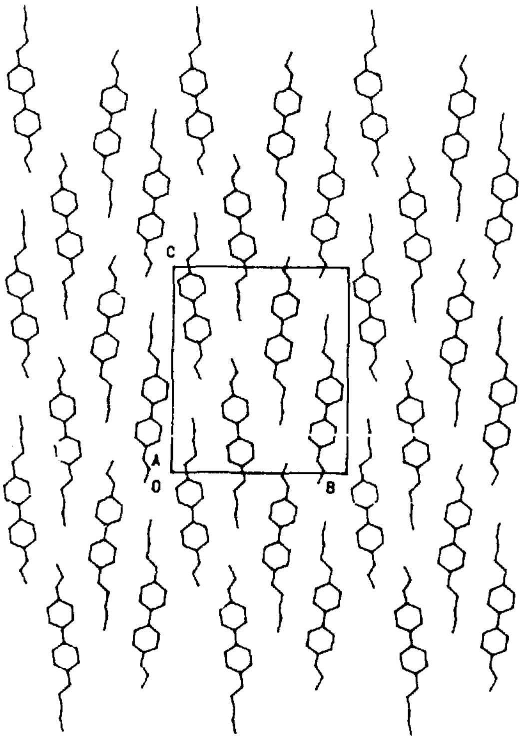

Figure 2. Molecular packing projected along [1 0 0].

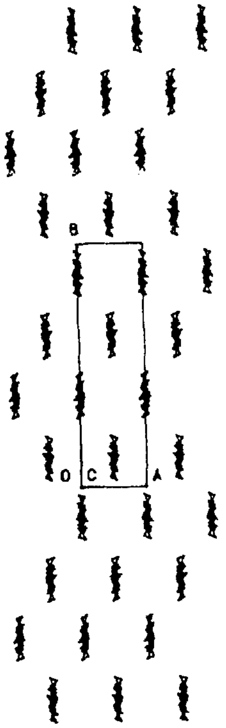

Figure 4. Molecular packing projected along [0 0 1].

Figure 5. Stereographic view of the three-dimensional molecular packing.

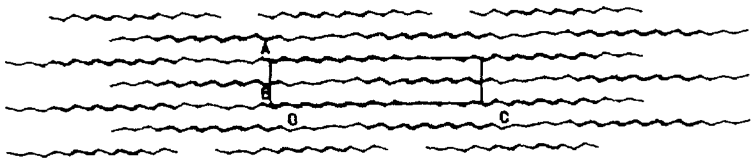

Figure 3. Molecular packing projected along [0 1 0].

to the nematic phase the picture does not alter. This is evident from the fact that the average length of the molecules in the nematic phase is 17·0 Å, as obtained from an X-ray diffraction study [17]. This is almost equal 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 CCH5 and PCBCH [8, 11, 17, 18] with the present compound PEBCH. Relevant data are given in table 5.

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 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 the smectic phase and an increase of both the Cr–N and N–I transition temperatures, but the nematic range does not increase. On the other hand, introduction of the ethoxy group in PCBCH considerably reduces the Cr–N transition temperature as well as widening the nematic range.

If we look at the crystal structures of the compounds, we observe that various types of molecular overlapping are present in the compounds. In CCH5 bulky central cyclohexyl rings, neighbouring molecules overlap in a head-to-tail manner [11], while in PCBCH and PEBCH no overlapping of the core cyclohexyl rings is observed. In both the smectic and nematic phases of CCH5 [11, 18] and PCBCH [17] dimerization through polar interactions is observed, as reported for other polar mesogenic compounds [6, 19, 20]. However, in the crystalline state of CCH5 evidence of molecular association is not found whereas in PCBCH a very weak association is observed. On the other hand, PEBCH shows no evidence of molecular association in both the nematic and crystalline states.

Though not true in general, from the reported crystal structures of the mesogenic materials it is observed that in most of the cases the ‘smectic precursors’ form layered structures, while the ‘nematic precursors’ possess imbricated structures [7]. The crystalline states of both CCH5 and PCBCH have layered structures and within the layers the molecules are tilted with respect to the layer normal. These types of layered structures may give rise to a smectic phase. Since the molecules are tilted within the layers it was expected to lead to a tilted smectic phase rather than the observed orthogonal S_B or S_A phases [11, 17]. Although the molecules are slightly tilted, the parallel imbricated type of packing found in PEBCH may be the precursor of the observed nematic phase.

The observed phases may be explained in terms of inter-molecular interactions. 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 a smectic phase; in PCBCH it is not sufficient to maintain the layer structure on melting (it shows the S_A phase monotropically to within a very small temperature range) and in PEBCH this terminal interaction is negligible so that

Table 5.

CCH5

CH_3–CH_2–CH_2–CH_2–CH_2–C_6H_{10}–C_6H_{10}–CN

$$\mathrm{Cr} \xleftrightarrow{45^{\circ}\mathrm{C}} S_B \xleftrightarrow{51{\cdot}3^{\circ}\mathrm{C}} \mathrm{N} \xleftrightarrow{86{\cdot}6^{\circ}\mathrm{C}} \mathrm{I}$$

Single molecule model length = 16·5 Å
Smectic layer spacing = 31·2 Å
Molecular length in nematic phase = 27·2 Å

PCBCH

CH_3–CH = CH–CH_2–CH_2–C_6H_{10}–C_6H_{10}–CN

$$\begin{tikzcd}
\mathrm{Cr} \arrow[r, "79{\cdot}5^{\circ}\mathrm{C}"] & \mathrm{N} \arrow[r, leftrightarrow, "100^{\circ}\mathrm{C}"] \arrow[d, "45^{\circ}\mathrm{C}"] & \mathrm{I} \\
 & S_A \arrow[ul, "43{\cdot}5^{\circ}\mathrm{C}"] &
\end{tikzcd}$$

Single molecule model length = 16·3 Å
Smectic layer spacing = 24·0 Å
Molecular length in nematic phase = 30·0 Å

PEBCH

CH_3–CH = CH–CH_2–CH_2–C_6H_{10}–C_6H_{10}–O– CH_2–CH_3

$$\mathrm{Cr} \xleftrightarrow{44^{\circ}\mathrm{C}} \mathrm{N} \xleftrightarrow{76{\cdot}5^{\circ}\mathrm{C}} \mathrm{I}$$

Single molecule model length = 17·4 Å
Molecular length in nematic phase = 17·0 Å

from the imbricated packing it melts to the nematic phase.

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