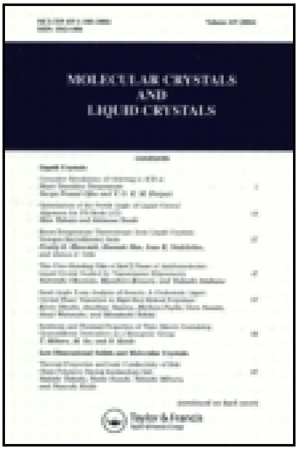

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Structures and Properties of an Alkenyl Liquid Crystalline Compound

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Structures and Properties of an Alkenyl Liquid Crystalline Compound

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The crystal and molecular structure of the mesomorphic compound 4(3″-Pentenyl)4′(cyano)1,1′-bicyclohexane having the molecular formula C_5H_9–C_6H_{10}–C_6H_{10}–CN has been determined by direct methods. The crystal belongs to the monoclinic system with space group $P2_1/n$, $a = 5.609$, $b = 31.390$, $c = 9.562$ Å, $\beta = 98.89°$ and $Z = 4$. Least squares refinement leads to $R = 0.065$ ($R_w = 0.081$) for 2326 observed reflections. The packing in the solid crystalline state of the compound is discussed and is compared with that derived from X-ray diffraction data in the liquid crystalline state.

Keywords: Structure property relation, crystal structure of a mesogen.

1. INTRODUCTION

We have undertaken X-ray diffraction study of 4(3″-Pentenyl)4′(cyano)1,1′-bicyclohexane both in the crystalline and mesomorphic state. Compounds with alkenyl end chains belong to different structural classes.[1] Their common features are low viscosities as well as low optical anisotropies. The alkenyl compounds differ from each other in many of their properties with respect to the systematic changes made in the position of the alkenyl double bond. The molecular arrangement in the crystalline state is one of the factors which sometimes predetermines the properties in the liquid crystalline state. The structure of the compound CCH_5 (trans, trans-4′-pentyl bicyclohexyl-4 carbonitrile) has already been determined by Haase *et al.*[2] In this paper, we report the crystal structure of the pentenyl compound and try to explain the mesomorphic organization in relation to its solid state packing and molecular interactions.

2. EXPERIMENTAL

Under a crossed polarizing microscope (150X) a marbled texture of nematic phase has been observed both during heating and cooling. The transition is found to be

TABLE I

Summary of Crystallographic Data

Molecular formula	$C_{18}H_{29}N$
Molecular weight	259.422 gm/mol.
Crystal system	Monoclinic
Space group	$P2_1/n$
Form/habit	Plate shaped
$a = 5.609(1)$ Å	
$b = 31.390(2)$ Å	
$c = 9.562(1)$ Å	
$\beta = 98.89(9)^\circ$	
$V_c = 1663.43$ Å^3	
$D_c = 1.084$ gm/cm^{-3}	
$Z = 4$	
$\lambda(\mathrm{CuK}\alpha) = 1.542$ Å	
Number of independent reflections	3381
Number of observed reflections	2326

monotropic. A fan-shaped texture of Smectic A phase was observed over a very short range of temperature during cooling. X-ray diffraction photographs were taken in the whole of the mesomorphic range.

The transition temperatures of different phases as determined by X-ray diffraction and texture studies are given below:

$$\begin{tikzcd}
\mathrm{C} \arrow[r, "79.5^\circ\mathrm{C}"] & \mathrm{N} \arrow[r, shift left, "\sim 100^\circ\mathrm{C}"] \arrow[d, "45^\circ\mathrm{C}"] & \mathrm{I} \arrow[l, shift left] \\
& \mathrm{SmA} \arrow[ul, "43.5"] &
\end{tikzcd}$$

2.1. Crystal Data

Transparent plate shaped crystals were obtained by means of slow evaporation from a solution of acetone. The crystal belongs to centrosymmetric monoclinic system. From the systematic absences *h*0*l* with *h* + *l* odd 0*k*0 with *k* odd, the space group was determined to be $P2_1/n$. Accurate cell parameters was determined by a least squares fit of $\sin\theta$ values of 23 reflections having θ values $40^\circ < \theta < 42^\circ$, measured on an Enraf Nonius CAD-4 diffractometer using CuKα radiation and a graphite monochromator. A total of 3381 reflections were measured on $\omega - 2\theta$ scan mode, of which 2326 were treated as observed with $I > 2.5\,\sigma(I)$. The data were corrected for Lorentz and Polarization factors and no absorption correction was neccessary. The crystal data are given in Table I.

3. STRUCTURE DETERMINATION AND REFINEMENT

The structure was determined by means of direct method program SIMPEL-83 of Kiers and Schenk.[3] The strongest 300 reflections were phased using 4 symbols. Phase set with best CFOM revealed the structure. From *E* map all the non-hydrogen atoms could be located. Five cycles of least squares with individual isotropic temperature factors brought the *R* value to 0.19. Introduction of individual anisotropic temperature factors reduced the *R* value to 0.13. From the difference Fourier we could not determine the positions of the large number of hydrogen atoms present in the molecule. They were located from energy optimisation using the program Sybyl[4] at the work station Iris. The structure was refined by block diagonal least squares method to a final $R = 0.065$ ($Rw = 0.081$), the hydrogen atoms being allowed to vibrate isotropically and non-hydrogen to vibrate anisotropically. The scattering factors were taken from Cromer and Mann.[5] All the calculations were done using XTAL[6] and PC version of the NRCVAX[7] package utilities.

4. RESULTS AND DISCUSSIONS

4.1. Molecular Conformation

The perspective view of the molecule is shown in Figure 1. Final positions and thermal parameters of the atoms are listed in Tables II–IV using the atomic numbering scheme shown in Figure 1. Bond lengths and bond angles are given in Table V. It has been seen that alkenyl chain is in the trans conformation. The average CC bond length in the cyclohexane ring is 1.535(8) Å. These values are consistent with our previous observations and have expected values. Carbon–Carbon distances both for single and double bonds are found to be as expected. The C_{18}–N_1 distance and bond angle C_{15}–C_{18}–N_1 compare well with other results.[8,9]

TABLE II

Fractional Co-Ordinates and Equivalent Isotropic Thermal Parameters of the Non-Hydrogen Atoms with e.s.d.'s in Parentheses. $U_{eq} = 1/3(U_{11}a^2a^{*2} + U_{22}b^2b^{*2} + U_{33}c^2c^{*2} + U_{13}aa^*cc^*\mathrm{Cos}\beta)$.

Atom	$x(\sigma)$	$y(\sigma)$	$z(\sigma)$	U_{eq}
C1	1.2349(1)	0.3423(2)	0.1708(9)	0.0886(3)
C2	1.0351(1)	0.3726(2)	0.1932(8)	0.0830(2)
C3	1.0574(1)	0.4106(2)	0.2382(8)	0.0761(2)
C4	0.8573(1)	0.4411(2)	0.2633(8)	0.0753(2)
C5	0.8723(1)	0.4833(2)	0.1883(7)	0.0675(2)
C6	0.6790(1)	0.5158(2)	0.2138(7)	0.0583(2)
C7	0.6787(1)	0.5539(2)	0.1162(7)	0.0686(2)
C8	0.4883(1)	0.5872(2)	0.1371(6)	0.0692(2)
C9	0.5116(1)	0.6029(2)	0.2917(6)	0.0534(2)
C10	0.5165(1)	0.5643(2)	0.3908(7)	0.0674(2)
C11	0.7101(1)	0.5313(2)	0.3683(7)	0.0701(2)
C12	0.3108(1)	0.6348(2)	0.3134(6)	0.0565(2)
C13	0.2919(1)	0.6719(2)	0.2085(7)	0.0809(2)
C14	0.0881(1)	0.7025(2)	0.2277(7)	0.1202(2)
C15	0.1221(1)	0.7196(2)	0.3812(7)	0.0704(2)
C16	0.1436(1)	0.6835(2)	0.4881(7)	0.0753(2)
C17	0.3445(1)	0.6530(2)	0.4650(7)	0.0722(2)
C18	−0.0859(1)	0.7476(2)	0.3967(8)	0.0772(2)
N1	−0.2504(1)	0.7684(2)	0.4037(8)	0.1051(2)

TABLE III

Fractional Co-Ordinates and Isotropic Thermal Parameters of the Hydrogen Atoms with e.s.d.'s in Parentheses. Atoms are Numbered According to the Heavy Atoms to which they are Attached.

Atom	$x(\sigma)$	$y(\sigma)$	$z(\sigma)$	U
H11	1.1747(1)	0.3195(1)	0.1280(1)	0.2572(4)
H12	1.3165(1)	0.3360(1)	0.2454(1)	0.2856(4)
H13	1.3151(2)	0.3495(1)	0.1171(1)	0.2954(4)
H21	0.8674(2)	0.3617(2)	0.1861(1)	0.1592(5)
H31	1.2420(2)	0.4239(2)	0.2594(1)	0.1393(3)
H41	0.7026(2)	0.4270(1)	0.2276(1)	0.1103(5)
H42	0.8660(1)	0.4472(1)	0.3726(1)	0.0986(5)
H51	1.0451(1)	0.4978(1)	0.2263(1)	0.0975(5)
H52	0.8561(2)	0.4773(1)	0.0825(1)	0.0960(5)
H61	0.5061(2)	0.5005(1)	0.1869(1)	0.0753(6)
H71	0.6518(1)	0.5424(1)	0.0108(1)	0.0944(5)
H72	0.8451(1)	0.5662(1)	0.1397(1)	0.0852(6)
H81	0.5008(2)	0.6146(1)	0.0758(1)	0.0883(7)
H82	0.3187(1)	0.5723(1)	0.1131(1)	0.0943(4)
H91	0.6424(1)	0.6202(1)	0.3113(1)	0.0828(6)
H101	0.3446(1)	0.5508(1)	0.3680(1)	0.0942(5)
H102	0.5342(1)	0.5748(1)	0.4957(1)	0.0884(5)
H111	0.8899(1)	0.5464(1)	0.3959(1)	0.0988(5)
H112	0.7004(0)	0.5052(1)	0.4380(1)	0.0868(4)
H121	0.1540(1)	0.6162(1)	0.2913(1)	0.0815(4)
H131	0.2702(1)	0.6590(1)	0.0170(1)	0.0923(6)
H132	0.4586(1)	0.6858(1)	0.2261(1)	0.1131(7)
H141	0.0780(1)	0.7299(1)	0.1549(1)	0.1127(8)
H142	−0.0838(1)	0.6844(1)	0.2020(1)	0.1136(7)
H151	0.2877(1)	0.7374(1)	0.4158(1)	0.1235(7)
H161	−0.0121(1)	0.6696(1)	0.4755(1)	0.1029(7)
H162	0.7121(1)	0.6970(1)	0.5940(1)	0.1084(5)
H171	0.5061(1)	0.6697(1)	0.4825(1)	0.0877(6)
H172	0.3414(1)	0.6284(1)	0.5363(1)	0.0808(6)

TABLE IV

Anisotropic Thermal Parameters of the Non-Hydrogen Atoms with the e.s.d.'s in Parentheses. The Temperature Factor is of the Form Exp[$-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^* + 2U_{13}hla^*c^*+2U_{23}\,klb^*c^*$].

Atom	$U_{11}(\alpha)$	$U_{22}(\alpha)$	$U_{33}(\alpha)$	$U_{12}(\alpha)$	$U_{13}(\alpha)$	$U_{23}(\alpha)$
C1	0.0833(5)	0.0813(5)	0.0942(6)	0.0146(4)	0.0152(5)	−0.0102(5)
C2	0.0818(6)	0.0856(5)	0.0795(5)	−0.0018(4)	0.0220(4)	−0.0016(4)
C3	0.0786(5)	0.0797(5)	0.0764(5)	0.0004(4)	0.0187(4)	−0.0010(4)
C4	0.0815(5)	0.0752(5)	0.0742(5)	0.0054(4)	0.0253(4)	−0.0018(4)
C5	0.0636(4)	0.0687(4)	0.0669(4)	−0.0017(3)	0.0201(3)	−0.0061(3)
C6	0.0554(4)	0.0649(4)	0.0586(4)	−0.0055(3)	0.0172(3)	−0.0084(3)
C7	0.0795(5)	0.0806(5)	0.0523(4)	0.0044(4)	0.0239(3)	−0.0029(3)
C8	0.0848(5)	0.0768(5)	0.0480(3)	0.0114(4)	0.0196(3)	−0.0031(3)
C9	0.0559(4)	0.0644(4)	0.0488(3)	−0.0057(3)	0.0149(3)	−0.0056(3)
C10	0.0820(5)	0.0713(4)	0.0529(4)	0.0041(4)	0.0231(3)	0.0009(3)
C11	0.0815(5)	0.0750(5)	0.0555(4)	0.0090(4)	0.0199(3)	0.0004(3)
C12	0.0584(4)	0.0634(4)	0.0489(3)	−0.0034(3)	0.0163(3)	−0.0040(3)
C13	0.0968(6)	0.0889(5)	0.0595(4)	0.0214(5)	0.0303(4)	0.0112(4)
C14	0.1011(5)	0.0927(5)	0.0611(5)	0.0293(4)	0.0282(4)	0.0048(4)
C15	0.0692(5)	0.0649(4)	0.0797(5)	−0.0011(3)	0.0254(4)	−0.0069(3)
C16	0.0918(5)	0.0769(5)	0.0554(4)	0.0055(4)	0.0251(4)	−0.0052(3)
C17	0.0877(5)	0.0738(5)	0.0531(4)	0.0079(4)	0.0160(3)	−0.0088(3)
C18	0.0908(5)	0.0750(5)	0.0756(5)	−0.0073(4)	0.0267(4)	−0.0130(4)
N1	0.1006(5)	0.1038(5)	0.1091(5)	0.0218(4)	0.0341(4)	−0.0136(4)

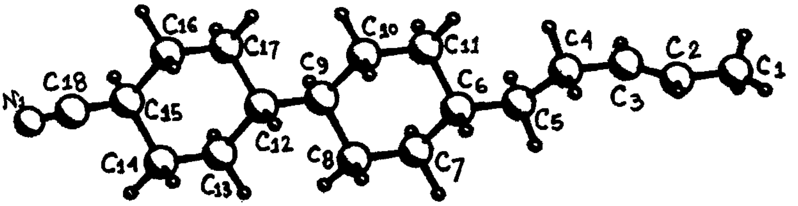

FIGURE 1 The perspective view of the molecule showing the atomic numbering scheme.

TABLE V

Bond Distance (Å) of the Non-Hydrogen Atoms with Standard Deviations in Parentheses.

C1–C2	1.51(8)	C10–C11	1.54(8)
C2–C3	1.27(8)	C12–C13	1.53(8)
C3–C4	1.52(8)	C12–C17	1.54(8)
C4–C5	1.51(8)	C13–C14	1.53(8)
C5–C6	1.54(8)	C14–C15	1.55(8)
C6–C7	1.52(8)	C15–C16	1.52(8)
C6–C11	1.54(8)	C15–C18	1.49(8)
C7–C8	1.53(8)	C16–C17	1.52(8)
C8–C9	1.54(8)	C18–N1	1.14(8)
C9–C10	1.54(8)		
C9–C12	1.54(8)		

Bond angles (°) of the Non-Hydrogen Atoms with Standard Deviatons in Parentheses.

C1–C2–C3	127(5)	C10–C9–C12	111(4)
C2–C3–C4	127(5)	C9–C10–C11	112(4)
C3–C4–C5	112(5)	C6–C11–C10	111(4)
C4–C5–C6	114(5)	C9–C12–C13	112(4)
C5–C6–C7	111(4)	C9–C12–C17	112(4)
C5–C6–C11	112(4)	C13–C12–C17	108(4)
C7–C6–C11	109(4)	C12–C13–C14	112(4)
C6–C7–C8	113(5)	C13–C14–C15	110(4)
C7–C8–C9	112(4)	C14–C15–C16	111(4)
C8–C9–C10	109(4)	C14–C15–C18	108(4)
C8–C9–C12	112(4)	C16–C15–C18	110(5)
		C15–C16–C17	110(4)
		C12–C17–C16	112(4)
		C15–C18–N1	177(6)

The molecule as a whole is not planar. The cyclohexane rings are in chair conformation, the angle between them is 34°. The angle between chain part and cyclohexane ring is found to be 27°. Because the molecules are flexible, during the process of crystallisation they twist themselves for favourable packing.

4.2. Molecular Packing and Liquid Crystal Phase

Figure 2 is a projection along the short crystallographic *a*-axis. The molecules related by inversion centre of symmetry lie collinear to each other. They are arranged in layers

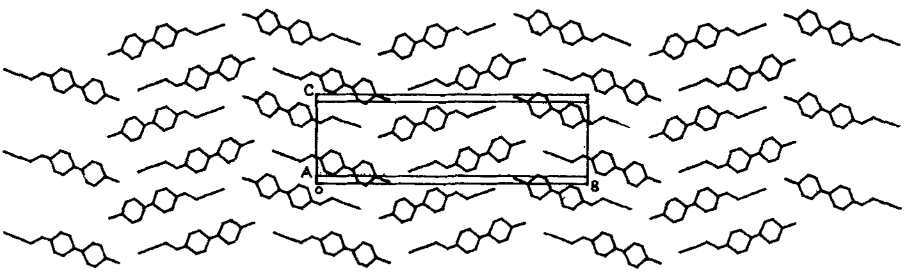

FIGURE 2 Crystal structure of the compound along [100].

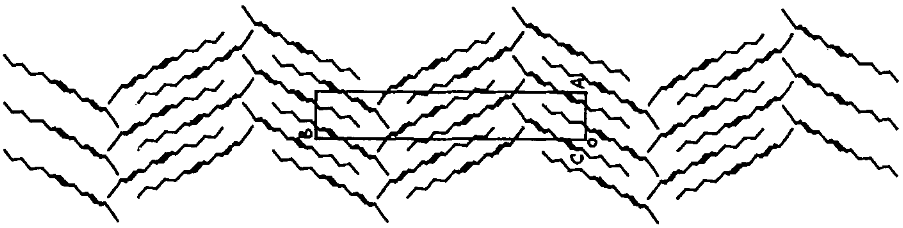

FIGURE 3 Crystal structure of the compound along [001].

parallel to *bc* plane and layers are stacked along *a*-axis. The direction cosines of the molecular long axis, defined as best fitted line through C_5 to N_1 are .5598, −.8055 and −.1945 which shows that the molecule makes an angle of 36° with *b*-axis. In Figure 3 the projection along *c*-axis is presented. The long axis of the molecules makes an angle 74° with one another, thus resulting in a herringbone—like pattern. This type of packing is mostly observed in crystals which gives rise to smectic phase on melting. In the present case the long chains from adjacent layers are deeply interdigitated. The terminal dipole–dipole interaction between CN groups of the neighbouring molecules in the adjacent layers hinders the formation of layer like structure of smectic.

The length of the molecule in the crystalline state is 16.1 Å whereas the theoretical length is at a maximum 16.3 Å, indicating that the molecule is in its most extended conformation. The intermolecular distances smaller than 4 Å are given in Table VI. Most of these distances occur between the molecules related through a centre of symmetry. Pairs of molecules related through the centre of symmetry are bound together by dipole induced dipole interaction between the chain part and polar cyano groups. The length of this pair is 18.7 Å. X-ray diffraction study in the nematic phase shows the presence of this dimerizaion, the length of which is found to be 30 Å. At C—N transition temperature these molecules gain sufficient energy to move within the layers and undergo rotations about axes other than the long molecular axis.

On cooling the compound exhibits a monotropic SmA phase with two incommensurate collinear periodicities, one approximately equal to the molecular length 1, 14.94 Å and the other having a periodicity between *1* and 2*1*, 24.01 Å (Figure 4). This phase change in the supercooling region was also observed in our experimental

TABLE VI

Intermolecular Contact Distances less than 4 Å (Involving Non-Hydrogen Atoms)

C2–C5[a]	3.589	C10–C13	3.918
C2–C16[b]	3.787	C10–C17	3.066
C3–C6[a]	3.911	C11–C12	3.934
C4–C7	3.885	C12–C7	3.932
C4–C11	3.158	C12–C11	3.934
C5–C2	3.589	C13–C18	3.815
C5–C8	3.898	C16–C2[c]	3.787
C5–C10	3.924	C18–C17	3.819
C6–C9	3.022	N1–C2[d]	3.696
C7–C12	3.932	N1–C13[a]	3.443
C8–C17	3.941	N1–C14[a]	3.481
C9–C14	3.918	N1–C15[e]	3.813
C9–C16	3.922	N1–C16	3.477

None x, y, z

[a] $(1/2+x)-1, (1/2-y)+1, 1/2+z$

[b] $1/2-x, 1/2+y, (1/2-z)+1$

[c] $1-x, 1-y, 1-z$

[d] $1/2-x, 1/2+y, 1/2-z$

[e] $x-1, y, z$

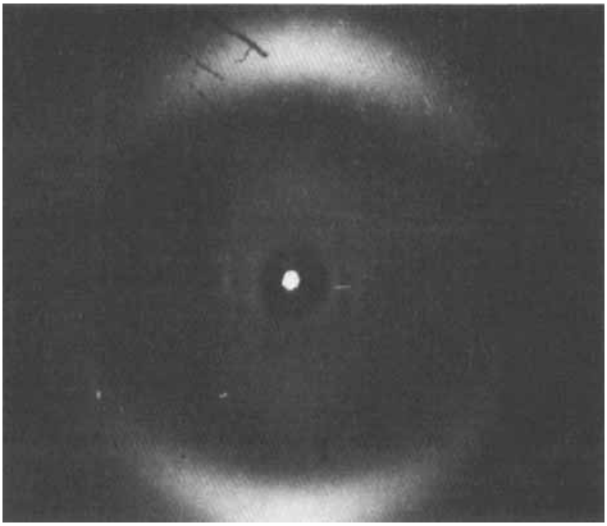

FIGURE 4 X-ray diffraction photograph of an aligned sample in the supercooled smectic phase at 45°.

determination of density. This type of SmA phase has never been observed so far for pure compounds. This smectic phase extends over a very narrow temperature range. We can not explain the existence of this smectic phase from the structural studies in the solid phase. Different kinds of intermolecular interactions are responsible for this phase formation. Further studies are needed for a complete understanding of this phase.

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