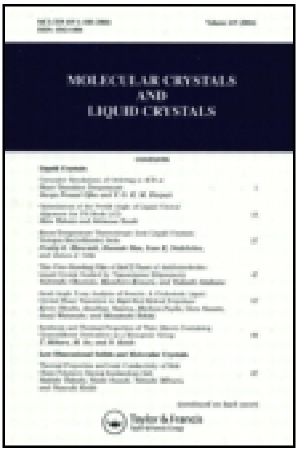

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STUDY OF MESOMORPHIC PROPERTIES OF THREE ALKENYL LIQUID CRYSTALLINE COMPOUNDS.

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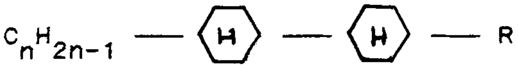
Abstract We have undertaken the study of the physical properties e.g. density, optical birefringence and x-ray diffration of three liquid crystalline compounds having bicyclohexane rigid core and isolated C=C double bond in the chain. The physical properties of these liquid crystals are strongly affected by the positional changes of the double bond. We have measured the refrative indices (n_o,n_e) for three diffarent wavelengths and calculated the polarizability values (α_o,α_e) at different temperatures. It is found that for all the compounds optical birefringence is very low ($\Delta n < 0.1$). We have also calculated the intermolecular distance, pseudo layer spacing, correlation length and the orientational order parameter values at different temperatures from low angle x-ray diffraction photographs of aligned samples. Orientational order parameters at different temperatures were calculated both from birefrigence and x-ray study.

INTRODUCTION

It is well known that structures of the rigid core of liquid crystal molecules strongly affect the physical properties of mesogens. It has been found that the introduction of a double bond at specific side chain positions also markedly affects the material properties of liquid crystals[1]. Common features of these type of compounds are low viscosities as well as low optical anisotropies. Since the end chains in nematics are usually quite short, double bonds are close to the core and steric interactions between the core and the double bonds are certainly important. In view of these we have undertaken the study of some alkenyl liquid crystalline compounds which have nematic phase over a wide range.

In this paper we report the experimental result of x-ray diffration and optical studies on three compounds which have the following structures :



(I) n=3, R=CN, 4(1''-propenyl)4'(cyano)1,1' bicyclohexane (in short P_rCBCH). (1d(1)CC)

(II) n=5, R=CN, 4(3''-pentenyl)4'(cyano)1,1' bicyclohexane (in short P_tCBCH) (1d(3)CC)

(III) n=5, R=OC_2H_5, 4(3''-pentenyl)4'(ethoxy)1,1' bicyclohexane. (in short PEBCH) (1d(3)CCO2)

The molecular and the crystal structure of mesogenic compounds may provide clues for the formation and stability of liquid crystalline phases. It has been confirmed by a number of studies that the molecular packing in the solid phase predetermines the assembly of molecules in the mesophase. So we undertook the structural analysis of mesogens using single crystals. The structure for compound P_tCBCH has already been solved and reported[2], the analysis of the crystal structure of other two compounds have not been solved yet.

EXPERIMENTAL DETAILS

Texture Study

The phase transition of the three compounds were studied by observing textures under crossed polarizers with a polarising microscope of magnification 150x. The transition temperatures agree well with the litarature values[1], except that we get supercooling in all three compounds and for P_tCBCH we get SmecticA phase for a very short range of temperature during cooling. The compounds P_rCBCH and PEBCH both during heating and cooling showed marbled textures, often found in the nematic phase. The compound P_tCBCH showed a fan shaped texture of SmecticA phase and a nematic marbled texture. The existence of these phases were also confirmed from x-ray studies.

X-ray diffraction study

A detailed description of the experimental method for x-ray diffration study is given elsewhere[3]. The alkenyl bicyclohexanes under investigation have very small magnetic anisotropy, virtually zero[4] and these could not be aligned by usual magnetic field. By heating the sample slowly to the isotropic state and then cooling it down to the desired tempereture we succeeded to obtain well aligned sample. The diffration photogrphs of aligned compound were taken at regular intervals during cooling from isotropic phase.

In order to determine the various parameters, the photographs were scanned, both linearly and circularly, by an optical micro densitometer (VEB Carl Zeiss Jena, Model MD 100) equiped with an automatic recording facility. The measured optical densities were converted to x-ray intensity values with the help of a calibration curve.

Optical study

Birefringence measurements were made using the technique of thin prism and the experimental procedures were the same as adopted by Zeminder et al[5,6]. A precision spectrometer and a nicol prism were used to measure the refractive indices (n_o,n_e) within ± 0.001 for three different wavelengths.

The densities of the sample were determined by a dilatometer of capillary type. Temperature during the experiment was controlled to about ± 0.5°C by a temperature controller. The experimental uncertainty of density measurement is 1%.

RESULTS AND DISCUSSIONS

From texture and x-ray diffraction studies the three compounds are found to have the following mesophase behaviour,

(I) P_rCBCH

$$\begin{tikzcd} C \arrow[r, shift left, "65.5^\circ C"] & N \arrow[l, shift left, "47.5^\circ C"] \arrow[r, leftrightarrow, "100.5^\circ C"] & I \end{tikzcd}$$

(II) P_tCBCH

$$\begin{tikzcd} C \arrow[r, "79.5^\circ C"] & N \arrow[r, leftrightarrow, "100.5^\circ C"] \arrow[d, "45^\circ C"] & I \\ & SmA \arrow[ul, "43.5^\circ C"] & \end{tikzcd}$$

(III) PEBCH

$$\begin{tikzcd} C \arrow[r, shift left, "44^\circ C"] & N \arrow[l, shift left, "29.5^\circ C"] \arrow[r, leftrightarrow, "76.5^\circ C"] & I \end{tikzcd}$$

Refractive index measurements

Variations of density measurements with temperatures for the samples are given in fig.1. The density graph for the compound P_tCBCH shows a first order phase transition at 45°C in the super cooled state. The phase was identified

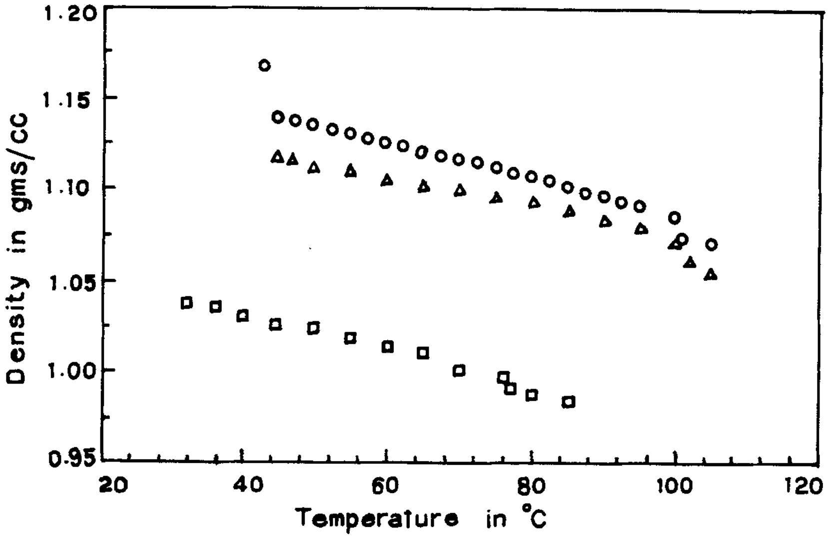


FIGURE 1 Variation of Density with Temperature.

O - P_tCBCH, Δ - P_rCBCH, □ - PEBCH.

to be SmA by our x-ray and texture studies.

It is found that the value of birefringence(Δn) is very low for these compounds. This low anisotropy may be due to the influence of the Π-electron of -C=C- double bond in the alkenyl side chain which for all the three compounds are in even position making angles with the long axis of the molecule. Over and above this, the cyclohexane cores are less polarizable compared to the biphenyl cores. It will be interesting to study the optical anisotropy of compounds having double bonds in the odd positions.

From the values of refractive indices the molecular polarizabilities (α_o,α_e) were calculated using Vuks isotropic (1966) and Neugebaur's(1954) anisotropic internal field models. From these polarizabily anisotropy values at different temperatures we calculated the orientational order parameter $<P_2>$ for all the three compounds. It was found that the order parameter values $\langle P_2 \rangle$ calculated from birefringence data is much larger than the theoretical Maier-Saupe values. The relation[7] (de Gennes, 1971) we used to calculate the orientational order parameter $\langle P_2 \rangle$ is as follows

$$\langle P_2 \rangle = (\alpha_o - \alpha_e)/(\alpha_{\parallel} - \alpha_{\perp})$$

where $\alpha_{\parallel}$ and $\alpha_{\perp}$ are molecular polarizabilities parallel and perpendicular to the long molecular axis. due to lack of refractive index data in the crystalline state the values of $\alpha_{\parallel}$ and $\alpha_{\perp}$ were not calculated directly. In order to obtain $(\alpha_{\parallel} - \alpha_{\perp})$ we took help of Haller's extrapolation procedure.

Estimation of the polarizabilities of the molecules was carried out using the additive rule of bond polarizability proposed by Le Fevre[8] (1965). This molar polarizability is approximated as a sum of bond polarizabilities

$$a = \sum a_k$$

the summation extending over all covalent bonds k in the molecule. Assuming rotational symmetry around the bonds, a_k is specified by its longitudinal component $(\alpha_{\parallel})$ its transverse component $(\alpha_{\perp})$ and the orientations of the bond[9]. The bond polarizability values were taken from Le Fevre.

Table-1 shows the experimental and calculated values of mean polarizability α and molecular polarizability anisotropy $\Delta\alpha$. Since α_o and α_e values at different wavelengths are quite close we have given values for λ=5780 Å. From the table it is clear that the calculated of mean polarizability for all the three compounds differ from the experimental value. But the experimental $\Delta\alpha$ values are almost same to that of the calculated values. For the compound P_tCBCH α and $\Delta\alpha$ were calculated considering the molecular geometry from the crystal structure data. These values are found to be the same.

TABLE - 1

Comparison of experimental and calculated polarizability values.

Compounds	α		$\Delta\alpha$		
	Calculated	Expt.	Calculated	Experimental	
				Vuks	Neug.
P_rCBCH	27.96	22.14	8.31	6.89	5.81
P_tCBCH	31.54	24.53	10.52	9.92	8.49
PEBCH	33.57	27.32	8.04	9.97	8.76

α and $\Delta\alpha$ are in 10^{-24} cm^3 unit.

Parameters from x-ray diffraction study

Extensive investigation have already been reported[10] of the structure of nematic and smectic phases of a variety of compouns having bicyclohexane as their rigid core. Here we discuss the results of x-ray diffraction studies of three compounds having double bond in side chain as well as bicyclohexane as the core.

From the x-ray diffraction photograph, fluctuation wavelengths parallel and perpendicular to the director and correlaton lengths for all the compounds have been calculated. X-ray intensity data from linear scanning of outer halo were fitted to a gaussian form with a background varying linearly with the scattering vector q as follows,

$$I(q) = a + \exp\{-b\,(q-c)^2\} + d + eq$$

The best fitted values of q_o, the peak position, give the value of inter-molecular distance D using the relation $D = 2\pi(1.117/q_o)$. The D values are found to be temperature independent for all the compounds. From the best fitted value of Δq we calculated the correlation length and it has been found that the local director is random beyond five molecular diameters.

Fluctuation wavelength l parallel to the director are obtained from scattering about the meridional direction using Bragg's formula. For P_tCBCH this pseudo layer spacings in the nematic phase is about 1.7 times the molecular length (16 Å). Antiparallel molecules have dipole-dipole interaction forming dimers. The compound P_rCBCH have molecular length 13.8 Å. We could not determine the pseudo layer spacing because of the weakness of the intensity in the meridional direction. Compound PEBCH is weakly polar and the layer spacing is found to be almost same as the molecular length (16.5 Å). Van der Walls type of interations are involved in mesophase stability in this compound.

The compound P_tCBCH exhibits a monortopic SmA phase with two collinear but incommensurate density modulation of periodicity 14.94 Å which is almost the same as the molecular length and the other periodicity is 24.01 Å, which is between 1 and 2l. This type of SmA phase is never been observed so far for pure compounds. We could not explain the existence of this smectic phase from the structural studies in the solid phase. Different kind of intermolecular interaction are responsible for this phase formation.

Orientational order parameters

The x-ray intensity $I(\theta)$ around the diffuse equatorial arc is related to the distribution function $f_d(\beta)$ as follows[12]

$$I(\theta) = C \int f_d(\beta) \sec^2\theta \, [\tan^2\beta - \tan^2\theta]^{-1/2} \, d(\cos\beta)$$

where $f_d(\beta)$ describes the distribution function of the directors of a local cluster of molecules which are assumed to be perfectly aligned within the cluster. However, $f_d(\beta)$ can be expected to be almost the same as the singlet distribution function $f(\beta)$. The detailed procedures for the calculation of $\langle P_2 \rangle$ and $\langle P_4 \rangle$ has been discussed earlier[12]. Orientational order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ calculated for these compounds at different temperatures are shown in Fig.2a, Fig.2b and Fig.2c. The experimental uncertainties in both $\langle P_2 \rangle$ and $\langle P_4 \rangle$ are estimated to be ± 0.02. As seen from the graph the order parameter determined from x-ray data agree reasonably well with the MS theoretical curve

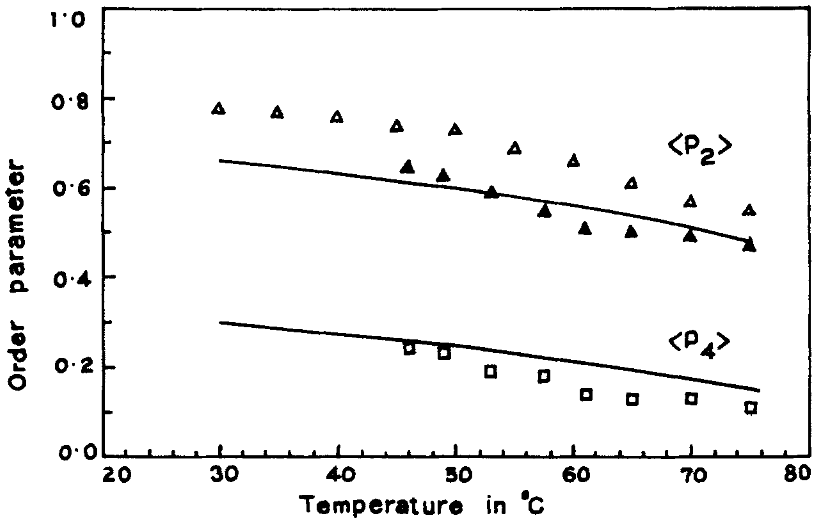


FIGURE 2a Variation of Order Parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ with Temperature for the compound P_rCBCH

△ - Optical data, ▲ - X-ray $\langle P_2 \rangle$ data, □ - X-ray $\langle P_4 \rangle$ data

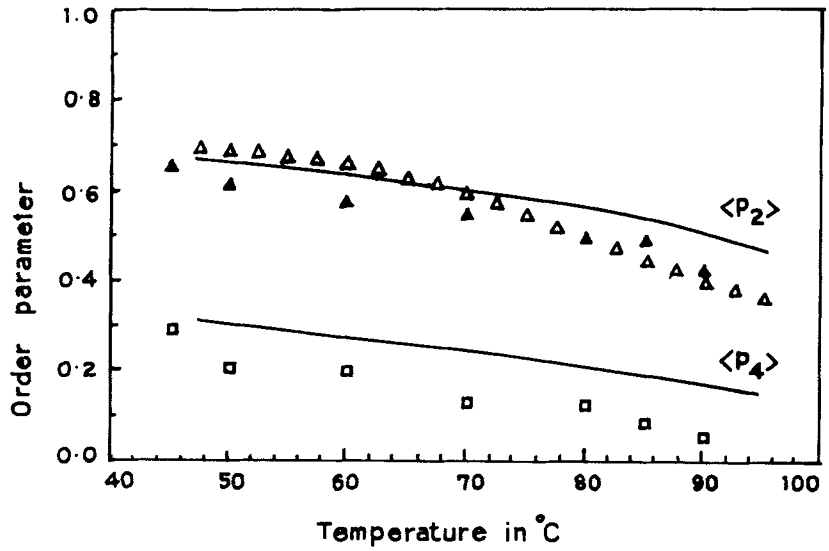


FIGURE 2b Variation of Order Parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ with Temperature for the compound P_rCBCH
Δ - Optical data, ▲ - X-ray $\langle P_2 \rangle$ data, □ - X-ray $\langle P_4 \rangle$ data

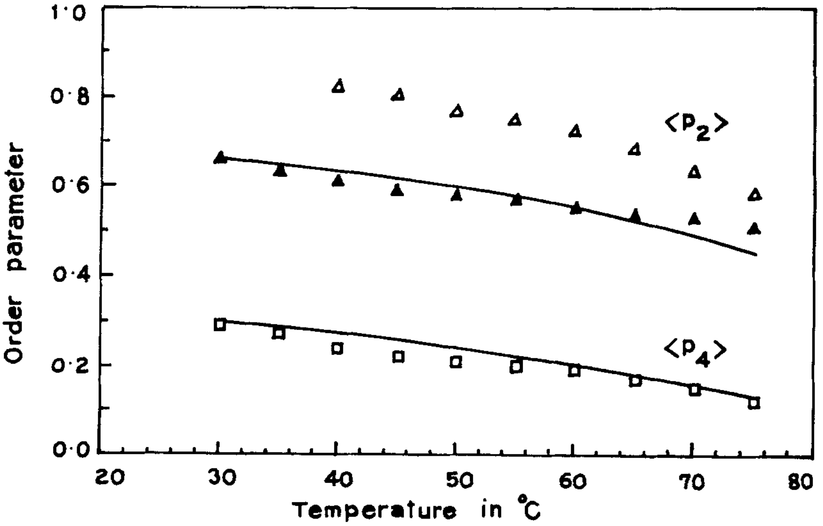


FIGURE 2c Variation of Order Parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ with Temperature for the compound P_rCBCH
Δ - Optical data, ▲ - X-ray $\langle P_2 \rangle$ data, □ - X-ray $\langle P_4 \rangle$ data

for P_rCBCH and PEBCH. Even the order parameter $\langle P_4 \rangle$ is found to be in good agreement. For the compound P_tCBCH the $\langle P_2 \rangle$ values are in agreement with the theoretical values within experimental errors. $\langle P_2 \rangle$ values determined from birefringence measurement for the compound are in good agreement with theories apart from the fluctuations at high temp[13]. For the other two compounds P_rCBCH and PEBCH the order parameters from optical studies are much higher than MS theoretical values. It may appear that these high values of order parameter may be due to unjustifiable Haller's extrapolation procedure besides the additive rule of bond polarizibility is not free from limitations. The properties of the alkenyl compound depends on the position of double bond, the distance of the double bond from the core, the molecular structure and the specific steric conformation of the side chains.

Surface treatment produced highly ordered oriented molecules for samples P_rCBCH and PEBCH resulting in high value of order parameters determined by optical studies. More studies on the physical properties of this type of alkenyl compounds are needed to give a quantitative explanation of the large discrepancy between M.S. between theoretical values and the experimental values.

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REFERENCES

1. M. Schadt, R. Buchecker and K. Muller. Liquid Crystals, 5, No.1. ,293 (1989).
2. S. Gupta, A. Nath, S. Paul, H. Schenk and K. Goubitz. Mol. Cryst. Liq. Cryst. (1994). (In Press)
3. B. Jha and R. Paul, Proc. Nucl. Solid. State. Phys. Symp (India), 19C, 491 (1976).
4. M. Schadt, R. Buchecker, F. Leenhouts, A. Boller, A. Villiger and M. Pertzilka. Mol. Cryst. Liq. Cryst., 139, 1 (1986).
5. A. K. Zeminder, S. Paul and R. Paul. Mol. Cryst. Liq. Cryst., 61, 191 (1981).
6. M. Mitra, S. Gupta., R. Paul and S. Paul. Mol. Cryst. Liq.Cryst., 199., 257 (1991).
7. P. D. De Gennes, Physics of liquid crystals, (1971).
8. R. J. W. Le Fevre, Advances in physical organic chemistry Edited by V. Gold, 3, (1965).
9. S.De Jong, F. Groeneweg and F. Van Voorst Vader. J. Applied Cryst , 24, 171, (1991).
10. G. J. Brownsey and A. J. Leadbetter. J. Physique Letters, 42 (1981).
11. K. Usha Deniz, G. Pepy, G. Paratte and P. Keller. Physica B, 174, 147 (1991).
12. B. Bhattarcharjee, S. Paul and R. Paul. Mol.Phys., 44, 1391 (1981).
13 S. Gupta, B.Majumdar, P. Mandal, R. Paul and S. Paul, Phase Transitions, 41, 73 (1992).