

Investigations on Low birefringent Liquid Crystalline Materials for High Information Content Displays

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Abstract:

The physical properties in the nematic phase of six non-polar alkenyl liquid crystalline compounds having same bicyclohexane core differing in the terminal chains has been investigated from optical birefringence and dielectric permittivity measurements. Low optical birefringence is reported in these compounds. The structure property correlation in the light of optical as well as dielectric anisotropy has been elucidated. The birefringence data has been determined from high resolution optical transmission (OT) method and thin prism method and the two sets of values are found to be in good agreement with a small deviation of about 2–3%. Orientational order parameter in the nematic phase has been determined directly from OT and also using Vuks Internal field model. It has been found that temperature dependent behavior of these two sets of order parameters agree quite well up to 10°C below the nematic-isotropic transition and deviates on the average around 2% far from the clearing temperature. Possible cause for this discrepancy has been discussed. These low birefringent materials find important application in commercial mixtures applicable for high information content display devices.

Keywords: Liquid crystals, Bicyclohexane compounds, Birefringence, Optical transmission, Orientational Order parameter.

I. Introduction

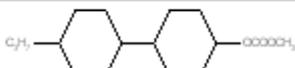
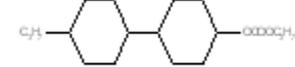
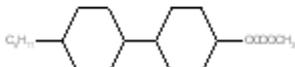
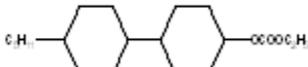
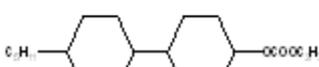
Liquid crystal material research has contributed significantly both to the development of liquid crystal display (LCD) technology [1-2] as well as to a deeper understanding of soft condensed matter systems. Quantitative knowledge of orientational ordering is necessary so that improved materials may be devised for applications. Study of pure compounds is also an important prerequisite in the preparation of mixtures, better tuned to meet the specific demands of the electro-optical display devices. The compounds studied in this work are of extraordinary interest since they contain bicyclohexane core, uncommon to most liquid crystalline compounds. They belong to a separate class of liquid crystals, expected to show low optical anisotropy ($\Delta n < 0.1$), low rotational viscosity, low magnetic and dielectric anisotropy ($\Delta\chi \approx 0$, $\Delta\epsilon \approx 0$) [3] and low visco-elastic ratios leading to faster response times in field effect liquid crystal displays. The results of refractive indices (n_o and n_e) and dielectric permittivity ($\epsilon_{||}$ and ϵ_{\perp}) measurements on six alkenyl bicyclohexane compounds of which four compounds show only nematic phase while other two compounds possess a smectic B phase which is the precursor of nematic phase, has been presented. Optical transmission (OT) method [4] has also been employed to obtain a high resolution (accuracy $\sim 10^{-6}$) measurement of the temperature dependences of the optical birefringence, $\Delta n (= n_o - n_e)$, which provides a macroscopic measure of the anisotropy of the liquid crystalline phase, and can also, be considered as a measure of the orientational ordering $\langle P_2 \rangle$ of the compounds. The optical birefringence data obtained from optical transmission method also have been compared with those determined from thin prism technique [5]. Additionally, the splay elastic constant K_{11} and rotational bulk viscosity (η) throughout the nematic range of the six pure liquid crystalline compounds also has been determined. The structure property correlations in the light of the experimental findings have been elucidated.

II. Experimental

2.1 Materials

The compounds were procured from AWAT Co. Ltd., Warsaw, Poland and were used without further purification. The chemical structure and transition temperatures of the compounds are shown in Table 1.

Table 1. Chemical structure and transition temperatures of compounds **a-f**.

Compound No.	Structure	T_m ($^{\circ}\text{C}$)	$T_{\text{SmB-N}}$ ($^{\circ}\text{C}$)	T_{NI} ($^{\circ}\text{C}$)
a		79.8	---	87.6
b		59.7	---	70.8
c		44.2	---	62.4
d		70.2	52	95
e		35	41	85.1
f		63.2	---	80.5

Sofar, there are only a few liquid crystal classes described in the literature which exhibit a low birefringence and whose rigid core consists of two cyclohexane rings. All of these compounds possess saturated side chains. Due to their simultaneously very small dielectric and diamagnetic anisotropy ($\Delta\epsilon \sim 0$; $\Delta\chi \sim 0$), the pure, non-polar bicyclohexanes can be aligned neither in usual magnetic nor in electric fields and surface alignment techniques are usually employed to align them. The transition temperatures and textures [6] were observed using polarizing microscope (Motic BA300) equipped with Mettler Toledo FP900 Hot Stage. The temperature dependence of the principal refractive indices n_o and n_e , were measured at a wavelength of $\lambda = 632.8$ nm for the six compounds were measured by thin prism technique where a hollow glass prism (refracting angle $< 2^\circ$) was constructed by placing the rubbed surfaces inside, with the rubbing direction parallel to the refracting edge of the prism. The temperature of the sample filled prism was controlled by a temperature controller (Eurotherm 2404) with an accuracy of $\pm 0.1\text{K}$. High resolution optical birefringence measurements were done by measuring the intensity of a laser beam ($\lambda = 632.8\text{nm}$) transmitted through a planar aligned cell of thickness $5.0\mu\text{m}$ filled with liquid crystalline (LC) sample and hence probing the related phase retardation. The densities of liquid crystals were measured with the help of a dilatometer of the capillary type. A weighed sample of the liquid crystal was introduced inside the capillary tube of the dilatometer, placed in an insulated glass chamber, the temperature of which was controlled by a temperature controller (Eurotherm PID 2404). The dielectric permittivities along and perpendicular to the molecular long axis respectively were determined, by measuring the capacitance of suitably aligned liquid crystal filled cells using Agilent E4980A digital LCR-bridge was used to measure the dielectric permittivity with a relative accuracy of 0.05%.

III. Results and Discussions:

3.1 Texture Studies

Typical thread-like textures characteristic of the nematic phase was observed upon heating for all the compounds. Upon cooling, compounds **d** and **e** exhibited Smectic B phase with mosaic texture, while compounds **a-c** and **f** showed only nematic phase. All the compounds showed large super cooling.

3.2 Refractive index measurements

The results for compound **a** and compound **e** are shown in Figures 1.1(a)-1.1(b). Similar behaviour has been observed for compounds **b**, **c**, **e** and **f**. For all the compounds, the values of the extraordinary refractive index decrease with increase in temperature, while the values of the ordinary refractive index remain almost constant in the lower temperature region but increases with increase in temperature near the N–I phase transition. The birefringence values of all the compounds are very low and are less than 0.1 even in the smectic B phase [7]. This is not surprising because all the bicyclohexane compounds have low polarizability anisotropy due to their nonlinear structure and absence of conjugated π -bond in the molecules. Incidentally such low birefringent materials are an important component in the preparation of commercial mixtures for application in high information content display devices.

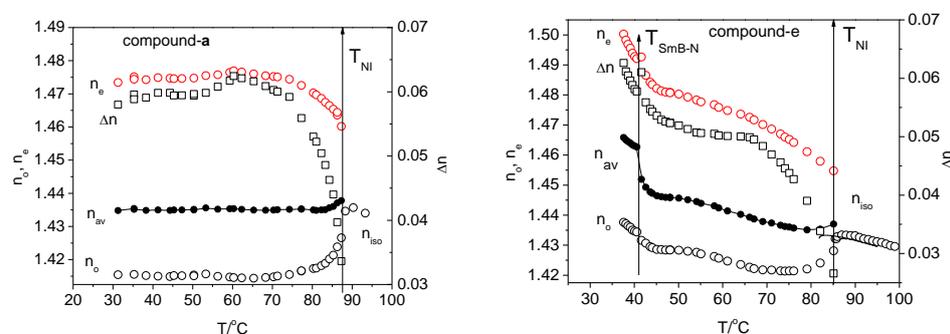


Figure 1(a) and 1(b). Experimental values of refractive indices $n_o, n_e, n_{av}, n_{iso}$ and Δn as a function of temperature for (a) compound **a** and (b) compound **e**. T_{NI} = nematic - isotropic phase transition temperature. Key to symbols : \circ n_e , \circ n_o , \square Δn and \bullet n_{av} .

3.3 High resolution optical birefringence measurement

The optical birefringence (Δn) of the compounds have also been measured for wavelength $\lambda = 632.8$ nm using high resolution temperature scanning technique. These values have been compared with those obtained from thin prism technique and is shown in Figure.2 (a – b) for compounds **a** and **b**. It is observed that the Δn values obtained from thin prism technique are slightly lower than the values obtained from optical transmission (OT) method [5]. The possible reason for this discrepancy in the two sets of measurements is due to the fact that in case of thin prism, the sample thickness is much higher (40–80 times) than the 5.0 mm cell which is used in the optical transmission method. Also shown in figure 2a is the temperature dependence of the density determined using capillary method. The birefringence of these materials in order of decreasing values is as follows: Δn : $b > e > c > f > a > d$. It is observed that increase in the alkyl chain length decreases the birefringence due reduction in the polarizability anisotropy accompanied with enhanced chain length.

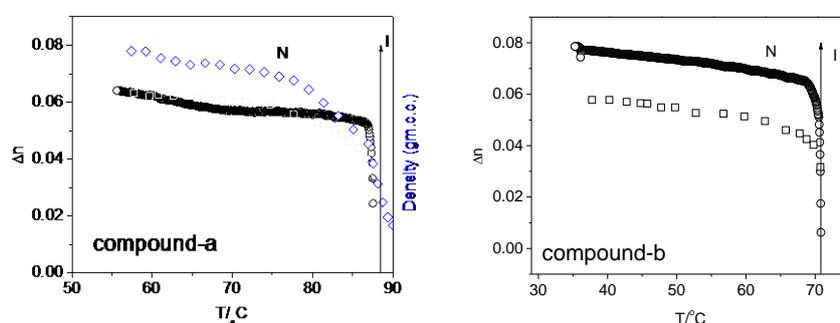


Figure 2a and 2b. Birefringence (Δn) as a function of temperature for (a) compound **a** and (b) compound **b**. Key to symbols : \circ - represent the birefringence data from O.T. method and \square - represent the birefringence data from thin prism method.

3.4. Determination of order parameter from the high-resolution birefringence measurement

According to de Gennes [8], the anisotropy of any physical quantity can be a measure of the order parameter. Moreover, de Jeu have showed that birefringence (Δn) can be used for this purpose. Kuczynski *et al.* [9] have also proposed a simple method to obtain the order parameter from birefringence (Δn) data which can be

applied to nematogens as well as some smectogens. The temperature dependent birefringence is related to the order parameter as:

$$\langle P_2 \rangle = \frac{\Delta n}{\Delta n_0} \quad (1)$$

where Δn_0 is the birefringence obtained in the most ordered state. The order parameters determined in this way for compounds **a** and **b** are shown in Figure 3(a) and 3(b) respectively. The temperature dependence of orientational order parameter $\langle P_2 \rangle$ obtained from the above-mentioned method for compounds **a** and **b** are shown in Figure 3(a) and 3(b) respectively. From the figures it is observed that the temperature variation of the orientational order parameter determined from Vuks method and direct extrapolation method are close to each other. The two sets of experimental data from two different methods differ by about 2%.

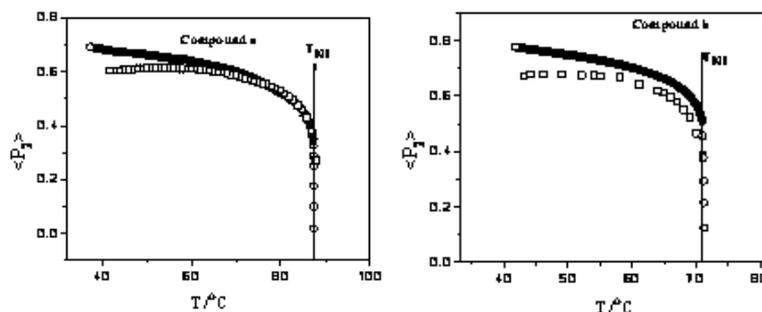


Figure 3a and 3b. Temperature variation of $\langle P_2 \rangle$ for (a) Compound **a** and (b) Compound **b**. Solid arrow indicates nematic–isotropic phase transition temperature (T_{NI}). Key to symbols: \circ - from the birefringence data and \square - from Vuks method.

3.5 Dielectric permittivity measurements:

The static permittivities [10] ϵ_{\parallel} and ϵ_{\perp} along and perpendicular to the molecular long axis and the mean value

$$\bar{\epsilon} = \frac{\epsilon_{\parallel} + 2\epsilon_{\perp}}{3},$$

are shown in Figure 4(a)-4(c). The differences observed in their measured dielectric parameters are due to the difference in terminal alkyl chains. A tiny difference in the anisotropy value for different molecules is possible as dielectric permittivities are influenced by the molecular rotation, and again molecular rotation changes due to the dissimilarity in flexibility of the side chains.

All the compounds exhibit a low positive dielectric anisotropy ($\Delta\epsilon > 0$) due to the presence of non planar cyclohexane ring.

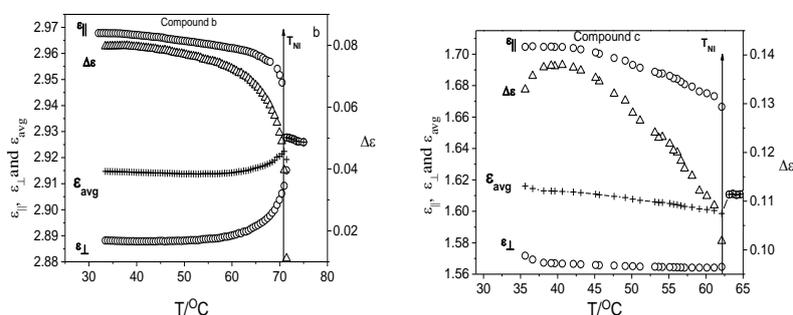


Figure 4a-4b. Variation of dielectric permittivities (ϵ_{\parallel} and ϵ_{\perp}), dielectric anisotropy ($\Delta\epsilon$) and average value of dielectric permittivity (ϵ_{avg}) with temperature for (a) compounds **b** and (b) compound **c**. Key to symbols: \circ ϵ_{\parallel} , \square ϵ_{\perp} , Δ $\Delta\epsilon$ and $+$ ϵ_{avg} .

It is observed that by increasing the length of the terminal hydrocarbon from CH_3 to C_2H_5 , both the permittivity values along and perpendicular to the molecular long axes ϵ_{\parallel} and ϵ_{\perp} and the dielectric anisotropy values $\Delta\epsilon$ decrease as follows: ϵ_{\parallel} : **b** > **a** > **d** > **e** > **f** > **c**, ϵ_{\perp} : **b** > **a** > **d** > **e** > **f** > **c**, $\Delta\epsilon$: **a** > **d** > **c** > **b** > **e** > **f**. Such observation corroborates the fact that increased chain length leads to enhanced vibrations of these flexible thereby affecting a drop in the dielectric anisotropy of the molecule.

IV. Conclusions:

The physical properties of six non polar bicyclohexane liquid crystalline pure compounds have been investigated in the nematic phase from optical and dielectric measurements. Interesting structure property correlations could be observed in terms of reduced anisotropy whether optical or dielectric, prevalent in compounds having larger terminal chain length. Thermal fluctuations contribute towards increased vibrations of these flexible molecules thereby affecting an overall reduction in the anisotropy of the molecules. However, these compounds are an important component in mixtures where reduction in birefringence is an important prerequisite. The agreement between the birefringence measurements from two different probing methods *viz.* thin prism and optical transmission are within 2-3 %. Moreover, $\langle P_2 \rangle$ values determined directly from OT data and this prism method agree quite well up to 10°C below the nematic-isotropic transition and deviates on the average around 2% far from the clearing temperature. Such discrepancy in the optical properties probably arises due the approximations involved in determining the local field surrounding the molecule well inside the nematic phase.

References:

- [1]. The electro-optic properties of a vertically aligned fast response liquid crystal display with three-electrode driving, C. Y. Xiang, X. W. Sun and X. J. Yin, *J. Appl. Phys.*, 37, 994 (2004).
- [2]. Mesomorphic and structural properties of some liquid crystals possessing a bicyclohexane core, D.S. Seo, *Liq. Cryst.*, 27(9), 1147 (2000). R. Yamaguchi and S. Sato, *Mol. Cryst. Liq. Cryst.*, 301, 67 (1997).
- [3]. Nematic liquid crystals with positive dielectric and negative diamagnetic anisotropy L. Pohl, R. Eidenschink, J. Krause and G. Weber, *Physics Letters A.*, 65(2), 169 (1978).
- [4]. A high resolution temperature scanning technique for optical studies of liquid crystal phase transitions, A. Saipa and F. Gisselmann, *Liq. Cryst.*, 29, 347 (2002).
- [5]. Optical birefringence studies of a binary mixture with the nematic–smectic Ad-re-entrant nematic phase sequence, A. Prasad and M.K. Das, *J. Phys.: Condens. Matter* 22, 195106 (2010).
- [6]. Anomalous heat capacity of nematic liquid crystals, M.A. Anisimov, S.R. Garber, V.S. Esipov, V.M. Mamnitskii, G.I. Ovodov, L.A. Smolenko and E.L. Sorkin, *Sov. Phys. JETP*, 45, 1042 (1977).
- [7]. Determination of K33/K11 ratio of a polar-nonpolar mixture showing injected smectic phase, B. Adhikari and R. Paul, *Mol. Cryst. Liq. Cryst.*, 301, 419 (1997).
- [8]. Short range order effects in the isotropic phase of nematics and cholesterics, P.G.de Gennes, *Liq. Cryst.*, 12, 193 (1971).
- [9]. Determination of Orientational Order Parameter in Various Liquid-Crystalline Phases, W. Kuczyński, B. Żywucki & J. Małecki, *Mol. Cryst. Liq. Cryst.*, 381, 1-19 (2010).
- [10]. Dielectric and visco-elastic properties of laterally fluorinated liquid crystal single compounds and their mixture, P. Dasgupta, M. K. Das and B. Das, *Liq. Cryst.*, 1297-1304 (2012).

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