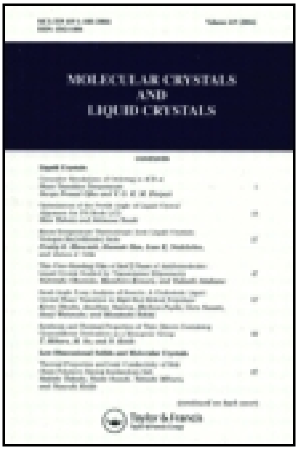

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Study of Optical Properties of Two Mesogenic Mixtures as a Function of Temperature

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Optical studies as a function of temperature have been conducted on two liquid crystalline mixtures:

Mixture 1: containing phenyl cyclohexane, biphenyl cyclohexane and cyclohexane carboxylate (Code Name: ZLI 1701);

Mixture 2: containing phenyl cyclohexane, cyano cyclohexane and cyclohexane carboxylate. (Code Name: ZLI 1800-000).

Each of the mixtures exhibits only the nematic phase and has similar temperature ranges for the same. Both the mixtures contain phenyl cyclohexane and cyclohexane carboxylate groups. However, mixture 1 contains biphenyl cyclohexane whereas mixture 2 contains cyano cyclohexane. Untill now no systematic study on the optical properties of the two mixtures have been reported. Our interest is to compare the macroscopic properties of the two mesogenic mixtures and to study the effect of replacing the biphenyl cyclohexane group in mixture 1 by cyano cyclohexane group in mixture 2. With this aim in view the variation of the refractive indices with temperature has been determined for both samples. We have also determined the thermal dependence of the orientational order parameter of the two mixtures from the optical studies.

Keywords: birefringence; mesogen; orientational order parameter

INTRODUCTION

In recent years mesogenic mixtures are being prepared and synthesized with a view to tailor and optimize material characteristics for

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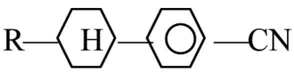
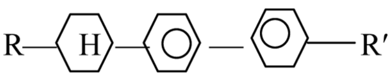
use in electro-optical devices. This is because nematic and cholesteric liquid crystals are extremely sensitive to external fields, especially electric and magnetic fields. The main advantage of liquid crystal devices over other types of equipments is that they work under low voltage and consume low power. Since mesogenic properties of thermotropic liquid crystals are temperature dependent, study of the thermal variation of their properties is of great interest and significance. Each of the mixtures is in the liquid crystalline state at very low temperature and is expected to prove beneficial in the manufacture of low temperature LC devices.

Mixture 1 (Code Name: ZLI 1701) contains:



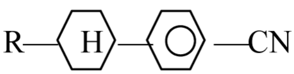
(phenyl cyclohexane or PCH)



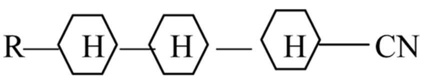
(biphenyl cyclohexane)

(cyclohexane carboxylate)

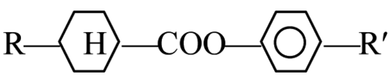
Mixture 2 (Code Name: ZLI 1800-000) contains:



(phenyl cyclohexane or PCH)



(cyano cyclohexane or CCH)



(cyclohexane carboxylate)

where $R = C_nH_{2n+1}$.

The transition temperatures of the two mixtures as supplied (by the manufacturer, Merck Ltd.) are

Mixture 1:

$$\text{Solid} \xrightarrow{-15^\circ\text{C}} \text{Nematic} \xrightarrow{61^\circ\text{C}} \text{Isotropic}$$

Mixture 2:

$$\text{Solid} \xrightarrow{-9^\circ\text{C}} \text{Nematic} \xrightarrow{60^\circ\text{C}} \text{Isotropic}$$

A distribution model has been proposed to determine the pretilt angle for nematic liquid crystals and they show that the mixture 2 (ZLI 1800-000) having strongly polar cyano group has high pretilt angle [1]. We have reported elsewhere [2] the dielectric properties of the two mixtures as a function of temperature and also calculated angle of inclination β of the molecular dipole moment with the director direction. However, no systematic study has been made on the optical properties of the two mixtures till date. In this article we present some experimental findings of the optical properties of two liquid crystalline mixtures. We have determined the thermal variation of the polarizabilities (extraordinary and ordinary) and thereby the orientational order parameter, which is a fundamental characteristic of liquid crystalline material, and compared it with theoretical

Maier-Saupe [3] values. We are interested to study the effect of replacing the biphenyl cyclohexane group in mixture 1 by the cyano cyclohexane group to yield mixture 2.

EXPERIMENTAL METHODS

Texture Studies

Prior to undertaking the optical studies, routine texture studies were carried out to confirm the nature of the phases and the phase transition temperatures for both the samples. The transition temperatures were noted using a polarizing microscope (Leitz) in conjunction with a hot stage (Mettler FP 82 HT). Observations were made under crossed polarizers with a magnification of 150X. Heating and cooling were done at the rate of 1°C/min. Both the samples were heated to temperatures well above the isotropic transition temperatures and then allowed to cool. Texture photographs were taken of the sample in the nematic phase.

Optical Studies

Birefringence studies were conducted on the samples in the presence of an ordering magnetic field. The refractive indices n_e and n_o of the extraordinary and the ordinary rays were measured at different temperatures from which the polarizabilities α_e and α_o could be calculated from density measurement data. The experimental details are given below.

Prisms with angles of the order of 1°–2° were constructed using glass slides whose inner faces were treated with polyvinyl alcohol and rubbed in a direction parallel to the prism edge for better alignment of the sample. The liquid crystal sample was then introduced by melting the sample at the top of the open edge and allowing the melted sample to flow in. The open edge of the prism was then sealed and the prism encapsulated in a sample holder whose temperature may be regulated upto $\pm 1^{\circ}$C with the help of a temperature controller. The sample holder (built in-house) with the prism was then placed within the pole pieces of an electromagnet in a manner such that the direction of rubbing (along the prism edge) is along the magnetic field. Magnetic field strength of ~ 8 kGauss was used. The combination of rubbing and magnetic field along the same direction produces a homogeneous monodomain specimen, the optic axis being parallel to the edge of the prism. Light from a He–Ne laser ($\lambda = 633$ nm) was directed normally on the sample through a hole drilled in the sample holder. The angular deflections of the refracted beams were measured by observing the light spots on a screen held ~ 6 meters away. From the changes in the patterns observed on the screen the transition temperatures may be verified. They were found to be in conformity with the temperatures found from texture studies. The samples were heated at the rate of 1°C/min to temperatures beyond the isotropic temperatures and allowed to cool at the same average rate. From angular deflection measurements the refractive indices n_e and n_o of the extraordinary and ordinary rays were determined using the knowledge of the prism angle. The prism angle was determined by measuring the difference in angular deviations of the laser beams reflected from the front and back surfaces of the prism, prior to the introduction of the sample. The spot has a finite dimension and measurements are taken of both the top and bottom ends of each of the circular spots and mean of these used for calculation. The large sample to screen distance introduces a much larger angular separation of the extraordinary and ordinary rays than is normally obtained without any appreciable loss in intensity; thereby increasing the resolution and accuracy of the measurements. The details of the experimental arrangement have been discussed in [4].

To determine the polarizabilities α_e and α_o, to be able to calculate the orientational order parameter, Vuk's formula [5] viz.

$$\frac{n_\gamma^2 - 1}{n^2 + 2} = \frac{4\pi}{3} N \alpha_\gamma$$

was used (γ is e or o, $N = N_A d/M$, where N is the number of molecules per cc, N_A is the Avogadro number, d the density of the sample and M the molecular weight). The density 'd' at various temperatures was obtained by introducing the weighed sample in the molten form in a dilatometer, which was then placed in a heat bath. The length of the sample column in the dilatometer tube was measured with a traveling microscope at intervals of 2°C and the density of the sample material calculated. Since the ratio of the different moieties in each sample mixture is not known, the molecular weight could not be ascertained and only α_γ/M could be determined using the density values and optical data. However this did not pose any problem in the determination of the orientational order parameter $\langle P_2\rangle$ since it is the ratio of the differences of the polarizabilities (ordinary and extraordinary) at the concerned temperature and at $T = 0$. Thus instead of plotting $\ln(\alpha_e - \alpha_o)$ vs. $\ln(T_c - T)$ in Haller's extrapolation procedure [6], $\ln(\alpha_e/M - \alpha_o/M)$ vs. $\ln(T_c - T)$ were plotted and the straight line extrapolated to $T = 0$ i.e., to $\ln T_c$ to obtain $(\alpha_{||} - \alpha_\perp)/M$. $\langle P_2\rangle$ is then obtained from the expression $\frac{(\alpha_e-\alpha_o)/M}{(\alpha_{II}-\alpha_\perp)/M}$.

RESULTS AND DISCUSSION

Texture Studies

The transition temperatures as observed from text studies are as follows
Mixture 1:

$$\text{Solid} \longrightarrow \text{Nematic} \underset{57.5^\circ\text{C}}{\overset{60.4^\circ\text{C}}{\rightleftarrows}} \text{Isotropic}$$

Mixture 2:

$$\text{Solid} \longrightarrow \text{Nematic} \underset{60.3^\circ\text{C}}{\overset{59.5^\circ\text{C}}{\rightleftarrows}} \text{Isotropic}$$

The phase transition temperatures from nematic to isotropic for both the mixtures are in excellent agreement with the quoted values supplied by Merck Ltd. Since there is no arrangement to cool the sample below room temperature no observations could be made below 30°C and no photographs taken in this temperature region. Representative texture photographs of the nematic phase of the two mixtures are shown in Figs. 1 and 2, respectively.

Optical Studies

The nature of variation of n_e and n_o with temperature are depicted in Figs. 3 and 4 for mixtures 1 and 2, respectively. n_{ave} is almost constant throughout the nematic region and continuous with n_{iso} at nematic-isotropic transition for mixture 1, a behavior, identical to that shown by the dielectric curve [2] and exhibited by nonpolar molecules such as di-alkyl azobenzene [7]. For mixture 2, however, n_{ave} is discontinuous with n_{iso} at nematic–isotropic temperature; this discontinuity is a feature which persists in the dielectric curves [2] and is attributed to

FIGURE 1 Nematic phase of mixture 1 at 55°C during cooling.

nematics with sharply polar end groups and believed to be the consequence of antiparallel local ordering [8]. In case of mixture 1, $\Delta n = 0.1$ over a major part of the nematic region, a value which is in very good agreement with the supplied value of 0.1 by Merck. For mixture 2, Δn has a value of 0.08 (identical with the supplied value by Merck), i.e., a value slightly less than that of mixture 1. The estimated error in determination of refractive index for both the mixtures is 1%. Variations of α/M with temperature for both the samples are plotted in Fig. 5.

The order parameter variations for the two mixtures are illustrated in Figs. 6 and 7. In case of mixture 1, the orientational order

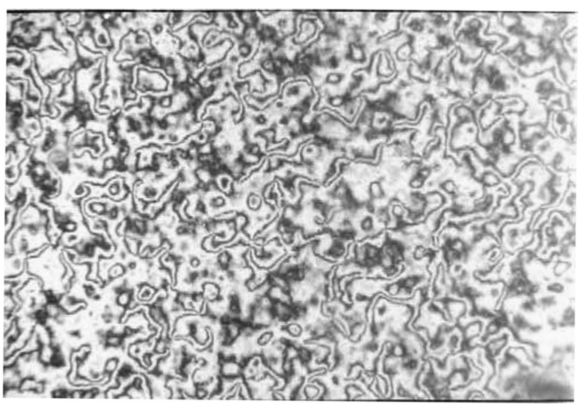


FIGURE 2 Nematic phase of mixture 2 at 55°C during cooling.

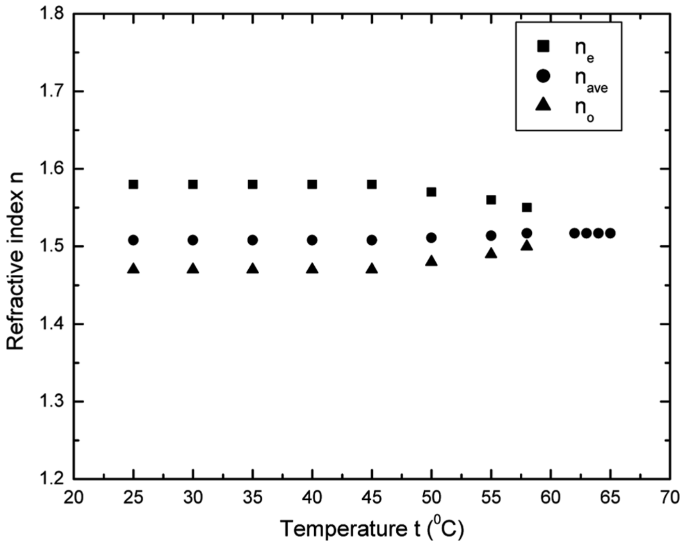


FIGURE 3 Variation of refractive indices with temperature of mixture 1.

parameter values remain almost constant throughout the nematic range and falls only near the nematic–isotropic transition. For mixture 2, on the other hand, $\langle P_2 \rangle_{expt}$ decreases very gradually always

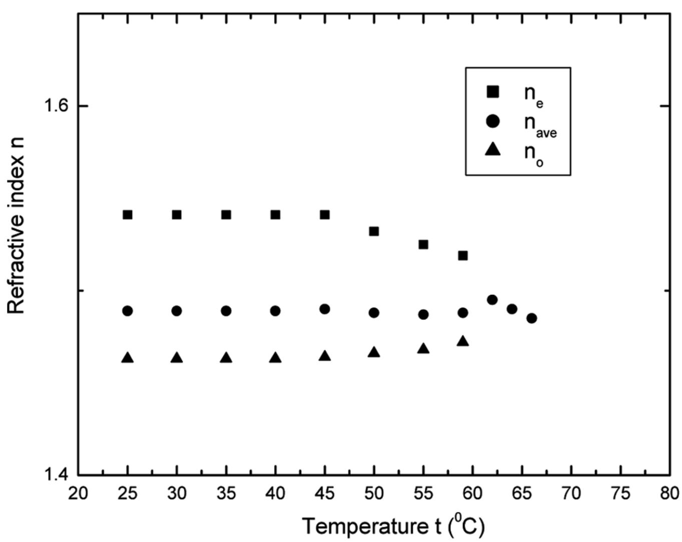


FIGURE 4 Variation of refractive indices with temperature of mixture 2.

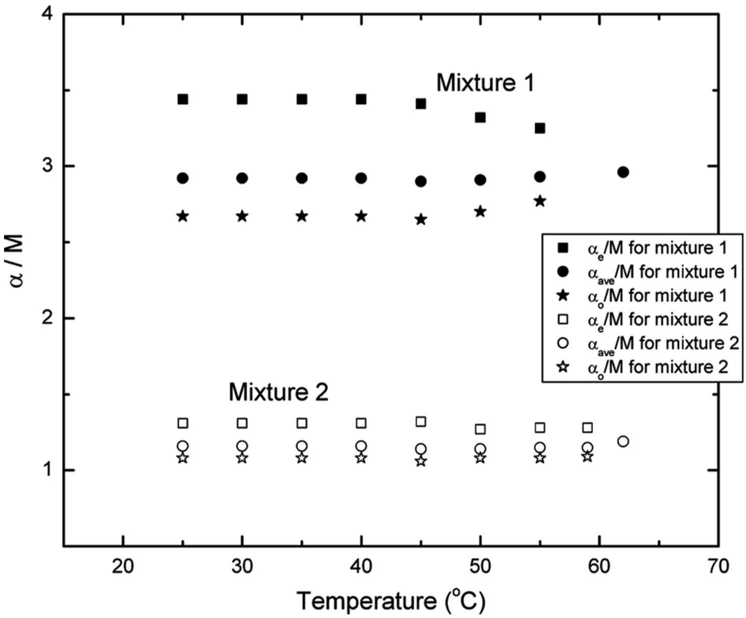


FIGURE 5 Variation of α/M with temperature of mixture 1 & 2.

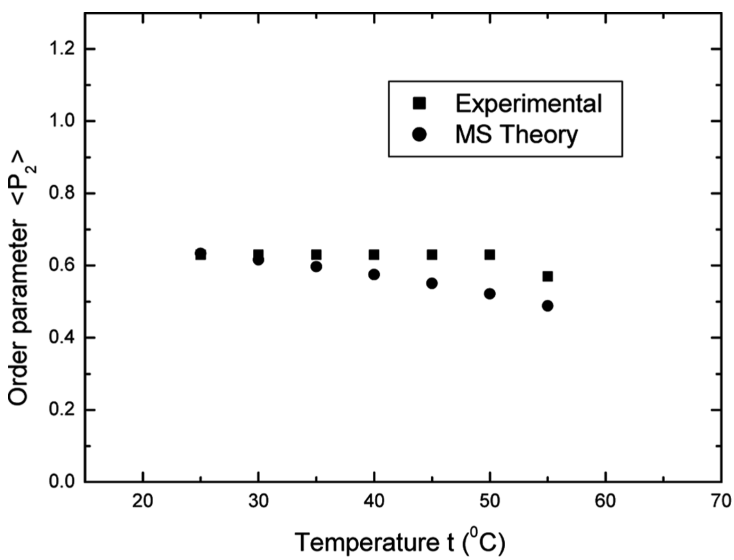


FIGURE 6 Variation of order parameter with temperature of mixture 1.

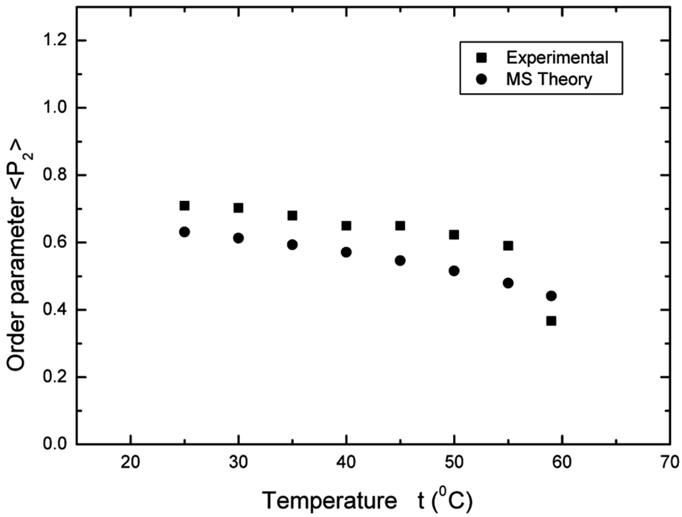


FIGURE 7 Variation of order parameter with temperature of mixture 2.

remaining higher than $\langle P_2 \rangle_{MS}$ and falls significantly only near nematic–isotropic transition.

Results of our optical studies (polarizability and order parameter values) have been used in calculating the angle of inclination of the molecular dipole moment with the director direction [2].

CONCLUSION

In conclusion, it may be said that the replacement of the biphenyl cyclohexane group in mixture 1 by cyano cyclohexane in mixture 2 produces discontinuities in the optical and dielectric behavior at the transition temperature suggesting a significant change in the nature of polarization and local ordering of the molecules. Though mixture 2 has a higher order parameter value as compared to mixture 1, the almost constant value of $\langle P_2 \rangle$ for mixture 1 in contrast to the gradually decreasing values of mixture 2 suggests a greater stability of performance of 1 as far as its use in liquid crystal devices is concerned. The crystalline to nematic transition temperature of each of the constituent moieties is much higher (above 0°C) than that of the resulting mixtures (−9°C and −15°C). It is thus expected that the mixtures may prove to be useful in low temperature LC devices.

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