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Optical and Dielectric Studies of a Mesogenic Mixture: Determination of Orientational Order Parameter and Angle of Inclination

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Optical and dielectric studies have been conducted on a liquid crystalline mixture (code name: ZLI 1275) containing phenyl cyclohexane, cyclohexyl phenyl carboxylate, and cyclohexyl benzoate. From optical studies, the orientational order parameter has been determined as a function of temperature and compared with theoretical Maier–Saupe values. The thermal variation of dielectric permittivity has been determined for different operating frequencies and the thermal dependence of the angle of inclination of the effective molecular dipole moment with the director direction has been investigated. Comparison of the optical and dielectric properties of ZLI 1275 has been made with two similar mixtures (ZLI 1701) and (ZLI 1800-000) exhibiting similar nematic temperature ranges and each containing three moieties of which one (phenyl cyclohexane) is common with ZLI 1275.

Keywords: birefringence; dielectric; mesogen; order parameter; polarizabilities

INTRODUCTION

The study of liquid crystalline mixtures especially with respect to their optical and dielectric properties has grown in importance over the years because of their use in the manufacture of electro-optic devices. Their stability of performance over the mesogenic temperature range is thus of great interest and significance. The present sample of study is: mixture ZLI 1275 containing the following moieties

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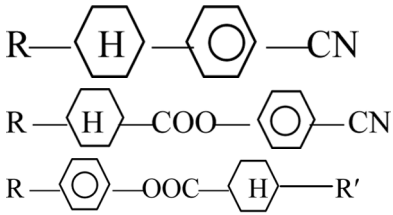

($R = C_nH_{2n+1}$, $R' = C_mH_{2m+1}$)

and exhibits the following phase transitions.

$$\text{Solid} \xrightarrow{0^\circ C} \text{Nematic} \xrightarrow{80^\circ C} \text{Isotropic}.$$

Two other mixtures, ZLI 1701 and ZLI 1800-000, both containing phenyl cyclohexane and exhibiting only nematic behavior:

ZLI 1701

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

containing phenyl cyclohexane, biphenyl cyclohexane, and cyclohexane carboxylate, and

ZLI 1800 – 000

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

containing phenyl cyclohexane, cyano cyclohexane, and cyclohexane carboxylate have been investigated [1,2]. The pretilt angle for mixture ZLI 1800-000 has been determined from a proposed distribution model [3]. No systematic study of either optical or dielectric properties have been performed on the present sample. In the present article we report the results of birefringence and dielectric studies conducted over the nematic range commencing from room temperature of about 30°C. From birefringence studies, the thermal variation of the polarizabilities (extraordinary and ordinary) and thereby the orientational order parameter have been determined. The values have been compared with theoretical Maier–Saupe [4] values. The angle of inclination β of the molecular dipole moment with the director as a function of temperature has also been determined. We are interested to see how the properties compare with those of ZLI 1701 and ZLI 1800-000 which have phenyl cyclohexane as the common moiety. Henceforth we shall refer to the present sample (ZLI 1275) as mixture 1, ZLI 1701 as mixture 2 and ZLI 1800-000 as mixture 3.

EXPERIMENTAL METHODS

Texture Studies

Preliminary routine texture studies were carried out on the sample before undertaking dielectric and optical work with a view to confirming the phase transition temperatures. Observations were made under crossed polarizers using a polarizing microscope (Leitz) with a magnification of 150X with a heating and cooling rate of 1°C/min. using a hot stage and temperature controller (Mettler FP 82 HT). 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 using the Chatelain Wedge principle in which the sample was introduced into a glass prism of angle between 1–2° formed with glass slides whose inner surfaces were treated with polyvinyl alcohol for planar surface alignment. 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 end of the prism was then sealed and the prism encapsulated in a sample holder whose temperature may be regulated upto ± 1°C with the help of a temperature controller. The sample holder was placed in an aligning field of ~ 8 KGauss. A He-Ne laser beam ($\lambda = 633$ nm) was directed onto the sample, through a hole in the sample holder, and the refracted beams (ordinary and extraordinary) emerging from the sample prism were projected on a screen placed 5.0 m away. From measurements on the screen, the angular deviation and consequently the refractive indices n_e and n_o of the extraordinary and ordinary rays may be determined with the knowledge of the prism angle. The prism angle was determined using the same method, prior to the introduction of the sample. In this method the refracted extraordinary and ordinary beams are projected on a screen several meters away without any appreciable loss of intensity (laser beam) thereby increasing the angular separation and resolution of the refracted beams and providing an accurate method of refractive index determination. The spot has a finite dimension and measurements were taken of both the top and bottom ends of each of the circular spots and the mean of these was used for calculation. Details of the experimental arrangement are given in [5]. All readings were taken at intervals of 5°C.

To determine the polarizabilities α_e and α_o, to be able to calculate the orientational order parameter, Vuk's formula [6] 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 travelling microscope at intervals of 2°C, and the density of the sample material was 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 $<P_2>$ 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 $\ln(\alpha_e - \alpha_o)$ *versus* $\ln(T_C - T)$ as in Haller's extrapolation procedure [7], $\ln(\alpha_e/M - \alpha_o/M)$ *versus* $\ln(T_C - T)$ were plotted and the straight line extrapolated to $T = 0$, *i.e.*, to $\ln T_c$ to obtain $(\alpha_\parallel - \alpha_\perp)/M$). $<P_2>$ is then obtained from the expression $\frac{(\alpha_e - \alpha_o)/M}{(\alpha_{II} - \alpha_\perp)/M}$.

Dielectric Studies

Sample cells (capacitor) were formed with a pair of indium tin oxide (ITO) coated conducting glass plates separated by thin cover slips on three sides. The effective sample cell size is 4.0 cm by 2.5 cm by 0.05 cm, and its capacitance (air) is 21 pF (approx.). Calibration of the cell was done using standard liquids: benzene and p-xylene with the help of a inductance-capacitance-resistance (LCR) meter (6471 Forbes Tinsley). The sample was introduced into the cell in the isotropic liquid phase, and the open end then sealed. The sample cell was encapsulated within a sample holder whose temperature may be controlled (±1°C). The sample was taken through a number of temperature cycles in the presence of the magnetic field of approximately 8 kGauss to get an aligned monodomain sample. Readings for the parallel and perpendicular components of the capacitance were taken at intervals of 5°C during cooling at frequencies of 1, 10, and 100 kHz. The values of the parallel and perpendicular components of the

dielectric permittivity $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ were obtained from the capacitance values by standard procedure. The bridge voltage across the sample was maintained sufficiently low ($\sim$0.3 V) so as not to produce any electric field induced instabilities.

RESULTS AND DISCUSSION

Texture Studies

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

$$\text{Solid} \longrightarrow \text{Nematic} \underset{76^{\circ}\text{C}}{\overset{78^{\circ}\text{C}}{\rightleftarrows}} \text{Isotropic}.$$

The phase transition temperatures from nematic to isotropic is in close 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. A representative texture of the nematic phase of the mixture is depicted in Fig. 1.

Optical Studies

The nature of variation of n_e and n_o with temperature is depicted in Fig. 2. For mixture 1 it is evident that n_{ave} is almost constant throughout the nematic region and continuous with n_{iso} at nematic–isotropic transition, a behavior exhibited by nonpolar molecules such as di-alkyl

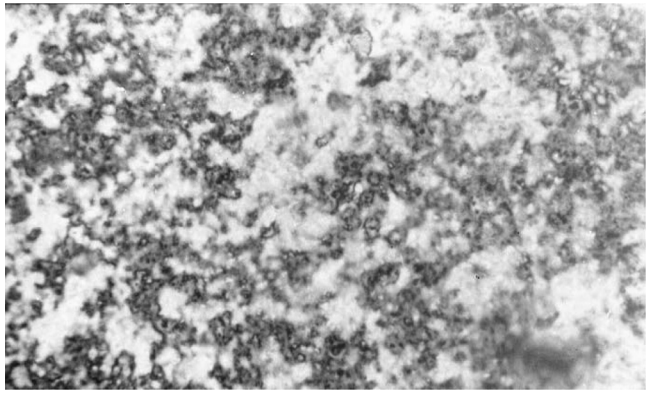

FIGURE 1 Nematic phase of mixture 1 at 50°C during cooling.

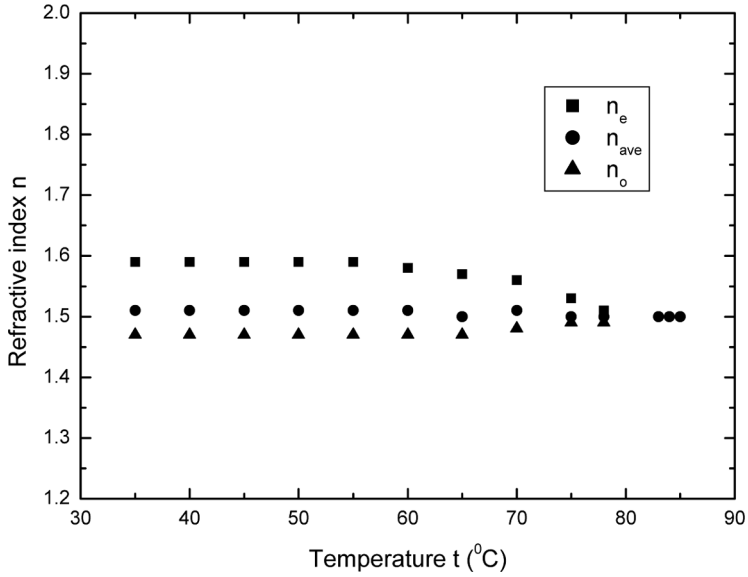

FIGURE 2 Variation of refractive indices with temperature of mixture 1.

azobenzene [8]. This is also true for mixture 2 [2]. For both these mixtures $\Delta n = 0.1$ over the major part of the nematic region, a value which is in very good agreement with the value of 0.1 supplied by Merck. In case of mixture 3, n_{ave} is discontinuous with n_{iso} at nematic isotropic temperature [2]; the discontinuity is a feature which persists in the dielectric curves and is discussed in the following section. For mixture 3, Δn has a value of 0.08 (identical with the value supplied by Merck), *i.e.*, a value slightly less than that of mixtures 1 and 2. The estimated error in determination of refractive index is about 1%. Variation of polarizability in terms of molecular weight (α/M) is plotted in Fig. 3.

The order parameter variation for the present case has been illustrated in Fig. 4(a). Figures 4(b) and (c) taken from our previous work [2] and superposed here for easy comparison, show the variations for mixtures 2 and 3. There is a gradual decrease of $<P_2>_{expt}$ from 0.68 (at 40°C) to 0.33 (at 79°C) for mixture 1, the nature of the fall being very similar to the theoretical $<P_2>_{MS}$ values except in the region very close to the clearing temperature. Mixture 2, on the other hand, shows a very different trend so far as $<P_2>_{expt}$ is concerned. $<P_2>_{expt}$ values remain almost constant throughout the nematic region for mixture 2 and falls only near the nematic–isotropic transition. In case of mixture 3, the behavior of $<P_2>_{expt}$ is intermediate between that

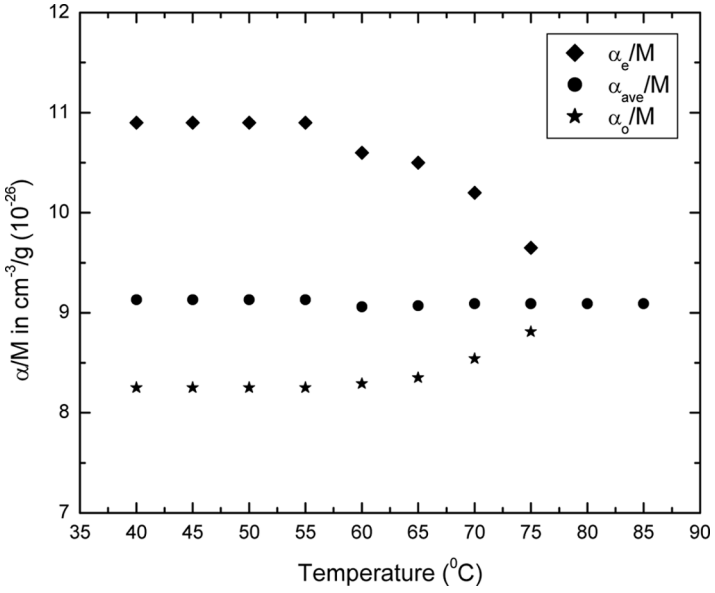

FIGURE 3 Variation of α/M with temperature of mixture 1.

of mixtures 1 and 2, it decreases but very gradually always remaining higher than $<P_2>_{MS}$ and falls significantly only near nematic–isotropic transition.

Dielectric Studies

The nature of variation of $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ with temperature for mixture 1 at frequencies of 1, 10, and 100 kHz are depicted in Figs. 5–7. Dielectric permittivity decreases with increasing frequencies for the present mixture as well as for mixtures 2 and 3 [1]. The average values of the dielectric permittivity for the present sample are 3.63, 3.42, and 3.22 at frequencies of 1, 10, and 100 kHz (60°C), *i.e.*, with an increase in operating frequency from 1 to 10 and 1 to 100 kHz, dielectric permittivity decreases by 5.79% and 11.29%, respectively, at 60°C. The corresponding values for mixture 2 are 5.28, 5.05, and 4.92 at 45°C and 7.04, 5.83, and 5.60 (at 45°C) for mixture 3 [1]. We thus observe that of the three mixtures, the present mixture (mixture 1) has the lowest ε_{ave} value. The ε_{ave} for mixture 1 is continuous with ε_{iso} at T_{NI} (as in the birefringence curves, Fig. 5). In case of mixture 3, ε_{ave} is discontinuous with ε_{iso} at T_{NI}, a feature which is observed in nematics with strongly polar end groups. This has been interpreted

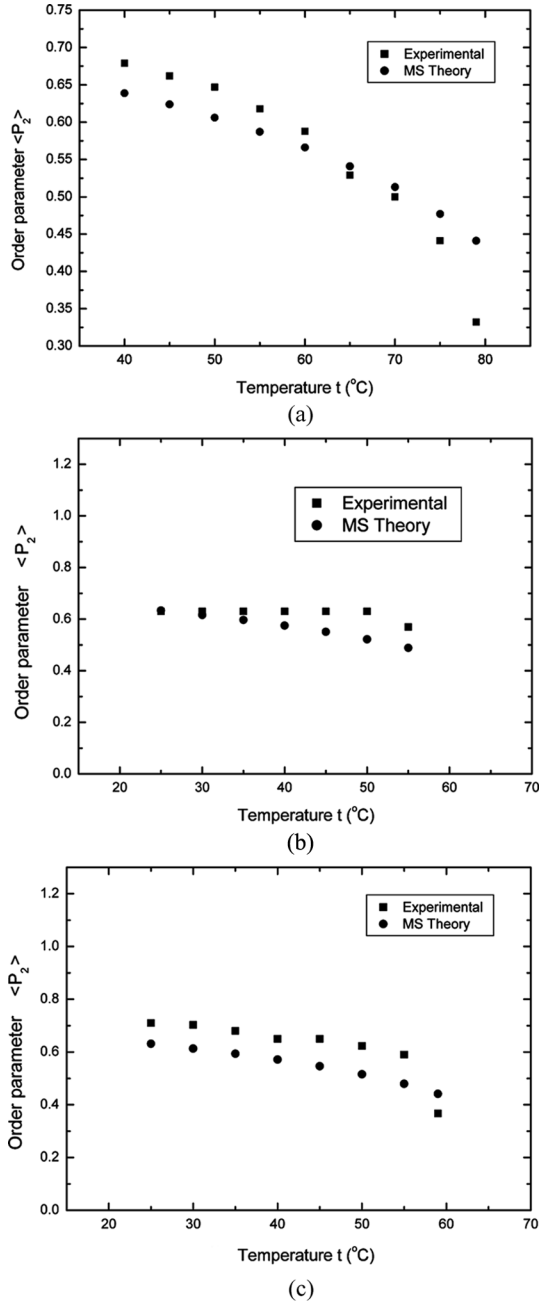

FIGURE 4 (a) Variation of order parameter with temperature of mixture 1; (b) Variation of order parameter with temperature of mixture 2; (c) Variation of order parameter with temperature of mixture 3.

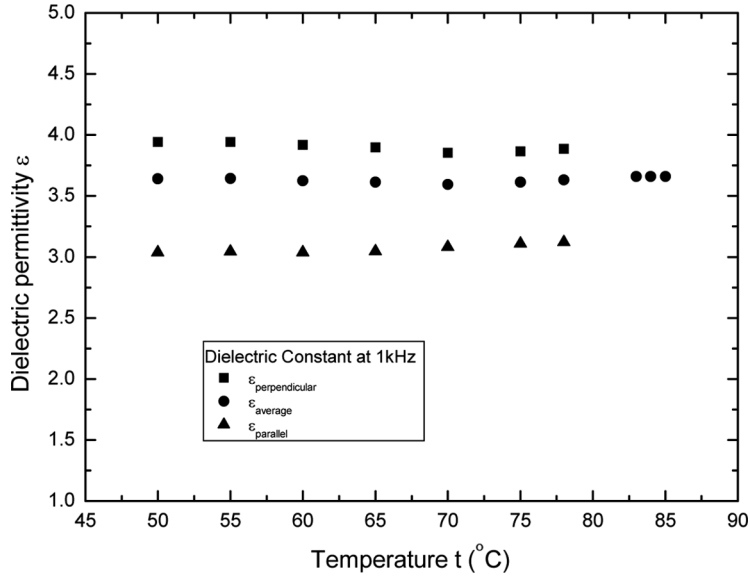

FIGURE 5 Variation of dielectric permittivity with temperature at 1 kHz of mixture 1.

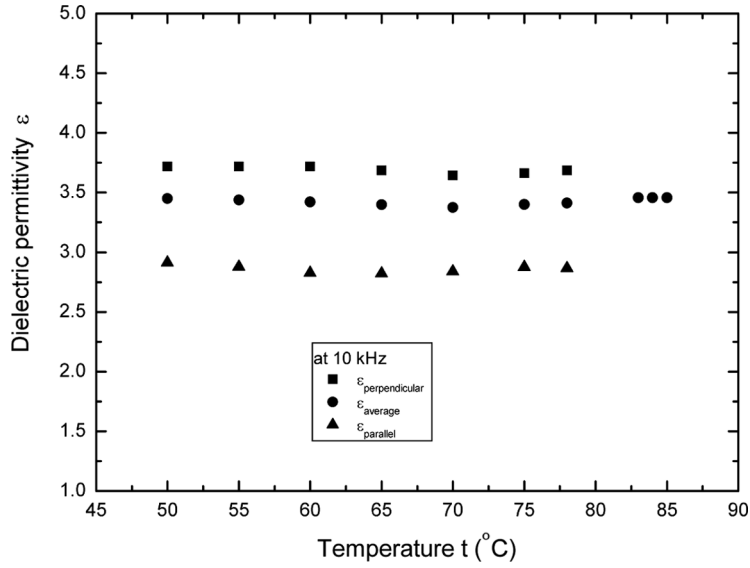

FIGURE 6 Variation of dielectric permittivity with temperature at 10 kHz of mixture 1.

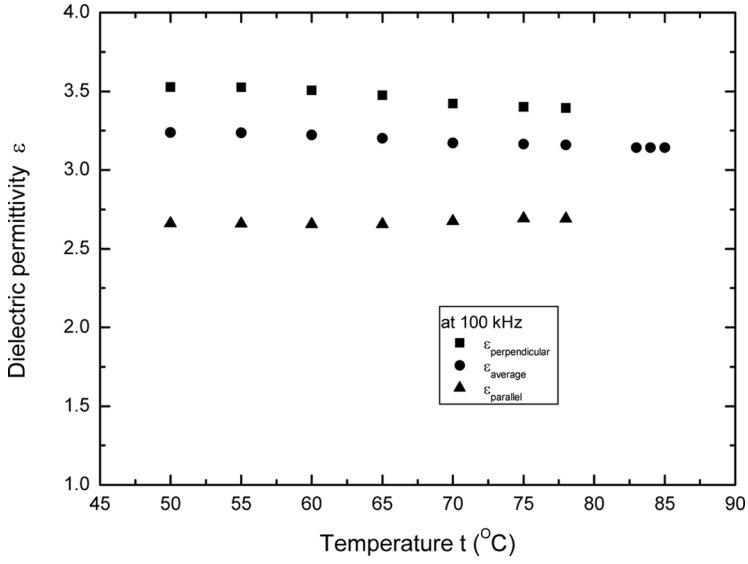

FIGURE 7 Variation of dielectric permittivity with temperature at 100 kHz of mixture 1.

as a consequence of antiparallel local ordering, which produces the discontinuity [9]. Such pretransitional effects in dielectric permittivity in nematics with cyano end groups have been reported [10,11]. The reduced contribution of molecular dipole moment μ to dielectric permittivity has been attributed to the apparent reduction in μ values due to formation of dimers in antiparallel local ordering [12]. The pretransitional effect on ε_{iso} showing a maximum near T_{NI} is explained as being due to an appreciable concentration of dimers in a dynamic dimer-monomer equilibrium.

Calculation of the Angle of Inclination β

Values of polarizability anisotropy $\Delta\alpha$, average polarizability α_{ave}, and order parameter $<P_2>$ from our optical studies were used to calculate the angle of inclination β between the molecular dipole moment and the molecular axis by applying the following expression [13]:

$$\varepsilon_{ave} = 1 + 4\pi NhF(\alpha_{ave} + F\mu^2/3KT)$$

and

$$\Delta\varepsilon = 4\pi NhF\{\Delta\alpha - F\mu^2(1 - 3\cos^2\beta)/2kT\} < P_2 >,$$

where

$$\varepsilon_{ave} = (\varepsilon_{\parallel} + 2\varepsilon_{\perp})/3,\ \alpha_{ave} = (\alpha_e + 2\alpha_o)/3,\ f = 4\pi N(2\varepsilon_{ave} - 2)/3(2\varepsilon_{ave} + 1)$$

$$h = 3\varepsilon_{ave}/(2\varepsilon_{ave} + 1),\ F = 1/(1 - \alpha_{ave} f).$$

N is the number of molecules per cc ($N = N_A d/M$, d is the density measured at different temperatures, N_A is Avogadro number, and M is the molecular weight). However, in this case, since the proportion (in weight) of the constituents in the mixture are unknown, the molecular weight could not be determined, and N could be obtained only in terms of M (as discussed in the previous section). The value of the effective dipole moment could therefore not be determined. However, with the help of simple algebra, the problem was circumvented to calculate β (worked out in the Ph.D. thesis of Saswati Chakraborty). The nature of variation of β with temperature is shown in Fig. 8, and β is seen to decrease with an increase in frequency from 1 to 10 to 100 kHz. This is also observed for mixture 3 [1] as opposed to the trend in mixture 2. In the case of the present sample, β remains fairly constant around 45°, whereas for mixtures 2 and 3, there is a discontinuity of β between 40 and 45°. On average, β values lie around 45° for mixture

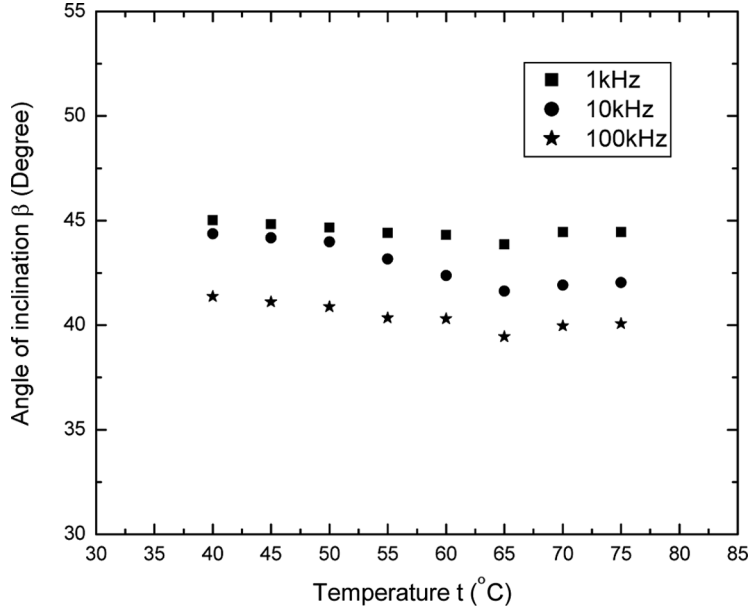

FIGURE 8 Variation of angle of inclination with temperature of mixture 1.

1, whereas for mixtures 2 and 3, β values are much higher $\sim$75–80°. The cause of the discontinuity in β for mixtures 2 and 3 has not been explained. The estimated error in the determination of β is approximately 4%.

CONCLUSION

To conclude, the present mixture exhibits the characteristics of non-polar molecules like di-alkylazobenzene despite the presence of phenyl cyclohexane. The replacement of cyclohexyl phenyl carboxylate and cyclohexyl benzoate by biphenyl cyclohexane and cyclohexane carboxylate (to form mixture 2) do not effectively change the nature of polarization as is evident from the birefringence and dielectric permittivity curves at T_{NI}. However, the introduction of another cyano group viz cyano cyclohexane in mixture 3 produces discontinuity 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. The almost constant value of $<P_2>$ for mixture 2 as compared to the decrease of $<P_2>$ with temperature for mixture 1 suggests a greater stability of performance of mixture 2 as far as its use in liquid crystal devices is concerned. A point to be noted is that the crystalline to nematic transition temperature of each of the moieties constituting the mixtures are higher (above 0°C), than the resulting mixture (0°C), and it is expected that the mixtures may prove to be useful in low temperature LC devices.

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REFERENCES

[1] Chakraborty, S. & Mukhopadhyay, A. (2006). *Mol. Cryst. Liq. Cryst., 460*, 117.
[2] Chakraborty, S., Mukhopadhyay, A., & Roy, S. K. (2008). *Mol. Cryst. Liq. Cryst.*, *487*, 13.
[3] Myrvold, B. O. & Kondo, K. (1994). *Liq. Crys.*, *17*(3), 437.
[4] Maier, W. & Saupe, A. (1959). *Z. Naturforsch*, *14a*, 822.
[5] Bhowmick, K., Mukhopadhyay, A., & Mukherjee, C. D. (2003). *Phase Transitions*, *76*(7), 671–682.
[6] Vuks, M. F. (1971). *Optics and Spectroscopy*, *20*, 193.
[7] Haller, J., Huggins, H. A., Linienthal, H. R., & McGure, T. R. (1973). *J. Phys. Chem.*, *77*, 950.

[8] de Jue, W. H. & Lathouwers, Th. W. (1974). *Z. Naturforsch*, *29a*, 905.
[9] Madhusudana, N. V. & Chandrasekhar, S. (1973). *Proc. Int. Conf. Liq. Cryst.*, *Bangalore*, *427*.
[10] Brandshaw, M. J. & Raynes, E. P. (1981). *Mol. Cryst. Liq. Cryst.*, *72*, 73.
[11] Theon, J. & Menu, G. (1983). *Mol. Cryst. Liq. Cryst.*, *97*, 163.
[12] Longa, L. & de Jue, W. H. (1982). *Phys. Rev. A*, *26*, 1632.
[13] Maier, W. & Meier, G. (1961). *Z. Naturforsch*, *16a*, 1200.