Optical parameter measurements of a nO.m liquid crystalline compound

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Differential scanning calorimetry (DSC) and density studies for a Schiff's base liquid crystalline nO.m compound N (4 - n - hexyloxybenzylidine) 4´- m - hexylaniline (6O.6) have been carried out. Using the previously reported refractive index data and present density data, the molecular polarizability values for the sample have been obtained. Vuks' method and Neugebauer's method have been used to calculate the parallel and perpendicular components of molecular polarizabilities. The calculation of order parameters have been previously done using direct extrapolation method and modified Vuks' method from the measured refractive indices. The order parameters of the sample have been calculated using the refractive indices and density values following Vuks' method and Neugebauer's method. The results obtained have been compared and analysed in detail.

Keywords: Differential scanning calorimetry, nO.m, Molecular polarizability, Order parameter

1 Introduction

The liquid crystals formed by the N-(4–n-alkyoxy benzylidene)-4′-m-alkylanilines popularly known as nO.m liquid crystals serve as an interesting and important class of liquid crystals[1]. The n and m denote the length of the terminal alkyl chains in the compound and these compounds are often referred[1-4] to as nO.m. Many physical studies have been done on this group of liquid crystals[1-5]. The liquid crystalline compounds of this group contain two benzene rings connected by a Schiff's base forming the core part and the other part consists of the long alkyl chains attached to both sides of the core. The liquid crystalline materials belonging to the class of nO.m compounds exhibit fascinating mesomorphic behaviour associated with a distinct molecular ordering and also exhibit quite complex smectic polymorphism. Therefore, the study of different physical properties of these compounds is important as well as interesting.

Order parameter is one of the most important parameters of a liquid crystal which governs almost all its physical properties[6-10]. Most of the physical properties of the liquid crystals emerge from the order that exist in the compounds[11]. The order parameter for

a liquid crystal can be determined by using different techniques such as nuclear magnetic resonance, dielectric permittivity, diamagnetic susceptibility, refractive indices, X-ray scattering, UV and IR dichroism, elastic constants and various other methods[6-10,12,13]. Also, the order parameter of a particular liquid crystal determined from different experimental methods or by using different theoretical models may differ significantly[12,14,15].

In this paper, the molecular polarizability values of a liquid crystalline compound N (4 - n - hexyloxybenzylidine) 4´- m - hexylaniline (6O.6) are reported. The calculation of order parameters using Vuks' method[16] and Neugebauer's method[17] have also been done for the sample. The refractive index data required for the calculation of molecular polarizability and order parameters values have been taken from data previously reported by the present authors[18].

2 Experimental Details

The phase transition temperatures and different textures observed for the phases are studied using a polarizing microscope (Leica DMLP; Leica Microsystems, Wetzlar, Germany) equipped with a Linkam hot stage LTSE-350 (Linkam, UK) and TMS 94 temperature programmer. The molecular structure, transition temperature and textures of the liquid

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crystalline compound 6O.6 have been previously reported[18].

The thermal behaviour of the samples was studied using a differential scanning calorimeter (DSC) Pyris-1 spectrometer (Perkin Elmer international, Switzerland). The heating or cooling rate was maintained 5 °C/min.

The densities of the compound as a function of temperature were measured using a dilatometer of the capillary type. The weighed samples were introduced inside the dilatometer which was placed in a water bath. The water bath was heated and its temperature was controlled. The length of the sample column was measured at different temperatures with the help of a high precision travelling microscope. Measurements were done while cooling the sample from its isotropic phase.

3 Results and Discussion
3.1 DSC studies

The DSC curve for the compound is shown in Fig. 1. The enthalpy of transitions from one phase to another phase was also calculated from the DSC data. The chemical name, phase transition temperatures and transition enthalpies of 6O.6 obtained from polarizing microscopy study and DSC study are shown in Table 1.

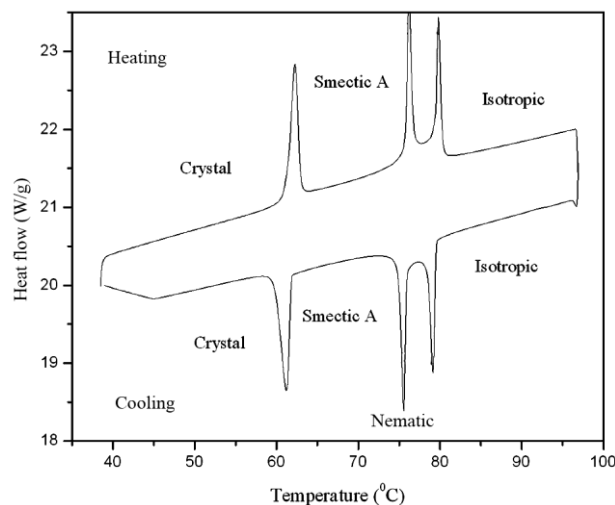The enthalpies associated with crystal to smectic A transition was 1.77 kJ/mol. Smectic A to nematic transition enthalpy was 1.05 kJ/mol and enthalpy of nematic to isotropic phase was 0.83 which was comparatively small.

3.2 Density studies

Measurements of density of the liquid crystal sample have been done at different temperatures. The temperature variation of density for the compound 6O.6 is shown in Fig. 2. The density values are found to increase as the temperature is decreased. However the increase in the density values in the crystalline and isotropic state of the liquid crystal is not that prominent. In the nematic and smectic A phase of the liquid crystal, the density values are observed to increase sharply as the temperature is decreased. The isotropic-nematic, nematic- smectic A and smectic A - crystal transitions in the liquid crystal are shown by the small jumps seen in the graph. The small jumps at the transition temperatures indicate that all the transitions are weakly first order kind.

3.3 Calculation of molecular polarizabilities

Measured refractive indices and density values have been used to calculate the molecular polarizabilities for the parallel and perpendicular components. The commonly used models viz., Vuks' and Neugebauer's models have been used to find the molecular polarizabilities of the sample.

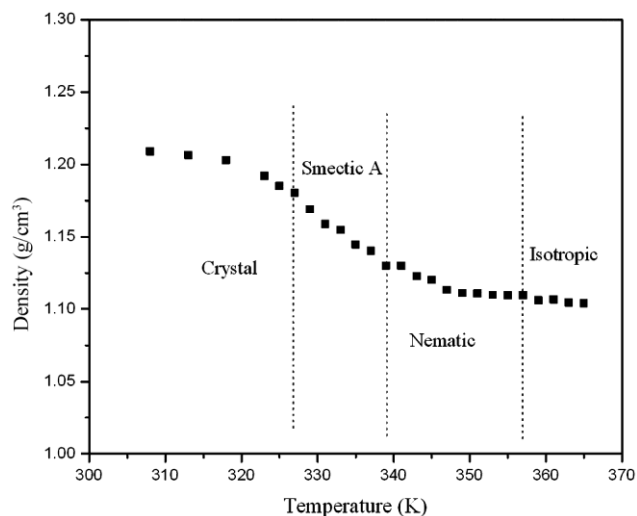Fig. 1 – DSC curve for the sample 6O.6

Fig. 2 – Temperature variations of density for the compound 6O.6

Table 1 – Chemical name, phase transition temperatures and transition enthalpies of 6O.6

N (4-n-hexyloxy benzylidine) 4´-m-hexylaniline (6O.6)

$Cr \xrightarrow{59.9^0C} Sm\ A \underset{65.5^0C}{\overset{69.5^0C}{\rightleftharpoons}} N \underset{83^0C}{\overset{83.9^0C}{\rightleftharpoons}} Iso$ $Cr \xrightarrow{60.4^0C} SmA \underset{65.5^0C}{\overset{72.7^0C}{\rightleftharpoons}} N \underset{77.5^0C}{\overset{78.9^0C}{\rightleftharpoons}} Iso$ 1.77   1.05   0.83

3.3.1 Vuks' method

The principal molecular polarizabilities for extraordinary and ordinary rays were obtained using the following equations given by Vuks:

$$\frac{\left(n_e^2 - 1\right)}{\left(\langle n^2 \rangle + 2\right)} = \frac{4\pi N \alpha_e}{3} \quad \text{... (1)}$$

$$\frac{\left(n_o^2 - 1\right)}{\left(\langle n^2 \rangle + 2\right)} = \frac{4\pi N \alpha_o}{3} \quad \text{... (2)}$$

$N = N_A \rho / M$ is the number of molecules per c.c., N_A is the Avogadro number, ρ is the density of the liquid crystal molecules, M is the mass of the liquid crystal sample taken. $\langle n^2 \rangle$ is the mean value of square of refractive indices and given by:

$$\langle n^2 \rangle = \frac{\left(2n_o^2 + n_e^2\right)}{3} \quad \text{... (3)}$$

3.3.2 Neugebauer method

In this model, the anisotropic internal field is given by:

$$n_e^2 - 1 = \frac{4\pi N \alpha_e}{1 - N \alpha_e \gamma_e} \quad \text{... (4)}$$

$$n_o^2 - 1 = \frac{4\pi N \alpha_o}{1 - N \alpha_o \gamma_o} \quad \text{... (5)}$$

where γ_e, γ_o are the internal field constants and have the relation

$$\gamma_e + 2\gamma_o = 4\pi \quad \text{... (6)}$$

Since order parameter of a liquid crystal is dependent on temperature the factors γ_e and γ_o are also temperature dependent. Using the condition given by Eq. (6), the relevant equations for finding the molecular polarizabilities α_e and α_o are obtained using the following equations:

$$\frac{1}{\alpha_e} + \frac{2}{\alpha_o} = \frac{4\pi N}{3} \left(\frac{n_e^2 + 2}{n_e^2 - 1} + \frac{2\left(n_o^2 + 2\right)}{n_o^2 - 1} \right) \quad \text{... (7)}$$

$$\alpha_e + 2\alpha_o = 3\langle \alpha \rangle = \frac{9}{4\pi N} \left(\frac{\langle n \rangle^2 - 1}{\langle n \rangle^2 + 2} \right) \quad \text{... (8)}$$

From the measured refractive index and density data, the molecular polarizabilities α_e, α_o can be easily determined. $\langle \alpha \rangle$ is the mean polarizability of the liquid crystal molecules and is defined by:

$$\langle \alpha \rangle = \frac{2\alpha_o + \alpha_e}{3} \quad \text{... (9)}$$

Figure 3 shows the temperature dependence of α_o, α_e and $\langle \alpha \rangle$ of the sample 6O.6. From the figure, it can be observed that the values of average polarizabilities of the sample obtained by using Vuks' and Neugebauer's method are same. This suggests that the experimental conditions required by the sample are same for the two methods.

The values $\alpha_e - \alpha_o$ obtained from Vuks' and Neugebauer's method are plotted against temperature in Fig. 4. As seen from Figure, the $\alpha_e - \alpha_o$ values increase as temperature is decreased. This increase in the values indicates that the
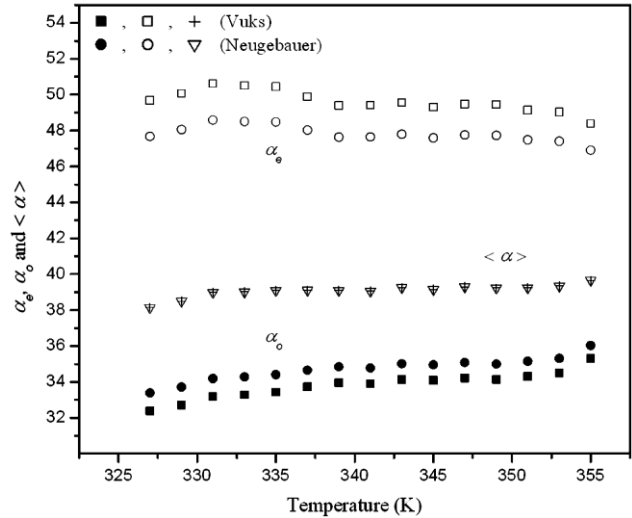

Fig. 3 – Temperature variations of α_o, α_e and $\langle \alpha \rangle$ for the compound 6O.6
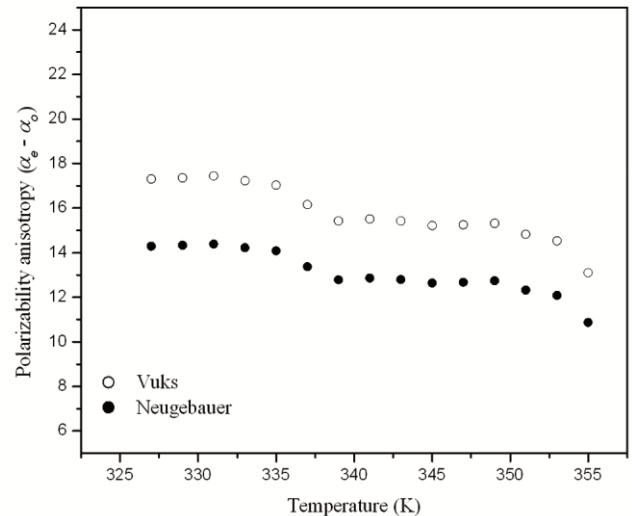

Fig. 4 – Temperature variations of $\alpha_e - \alpha_o$ for the compound 6O.6

molecular distribution becomes more anisotropic as the liquid crystal molecules were cooled down from its isotropic state. A slight variation in the values obtained from the two approaches is seen from the graph. However, the trends remain exactly the same.

Further, the Lorentz field factors for extraordinary L_e and ordinary rays L_o were calculated from the following relations[17,19]:

$$L_e = \frac{1}{4\pi N\alpha_e}\left[1 - \frac{4\pi N\alpha_e}{n_e^2 - 1}\right] \qquad \dots (10)$$

$$L_o = \frac{1}{4\pi N\alpha_o}\left[1 - \frac{4\pi N\alpha_o}{n_o^2 - 1}\right] \qquad \dots (11)$$

The Lorentz factors L_e and L_o are plotted against temperature in Fig. 5. L_e values are found to decrease as temperature was decreased while L_o values increase with the decrease of temperature.

The anisotropy of Lorentz factors ($\Delta L = L_e - L_o$) shows same trend as that of optical birefringence as seen from Fig. 6. It is observed from Fig. 6 that the anisotropy of molecular distribution of the compound decreases with the increase of temperature and almost drops to zero at the nematic-isotropic transition temperature.

Also, Lorentz field factors for the sample satisfy the condition:
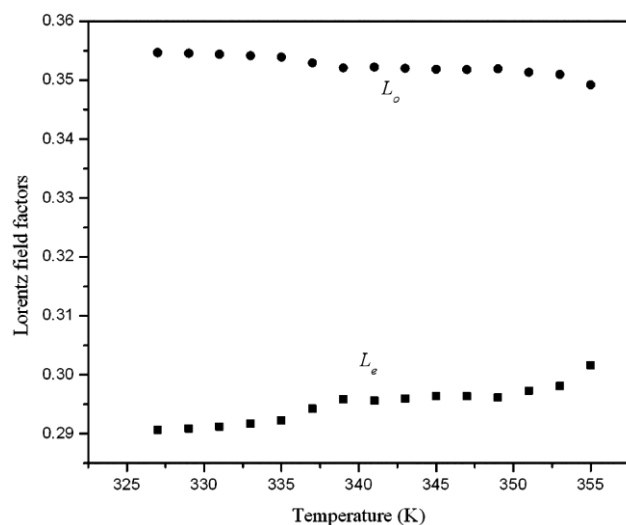
$$L_e + 2L_o = 1 \qquad \dots (12)$$

Fig. 5 – Temperature dependence of L_e and L_o for the compound 6O.6

3.4 Calculation of order parameters

The order parameter of a liquid crystal is a key parameter in the identification of the universality class to which the particular liquid crystal phase belongs. Its behaviour at the phase transition can be used to establish the kind of order (first or second order) of the phase transition[20]. The applicability of the liquid crystal material in technological applications is also determined by this parameter[5].

The molecular polarizabilities α_e and α_o obtained from Vuks' and Neugebauer's method have been used to obtain the order parameters of the liquid crystal. The order parameters of the sample have also been calculated using direct extrapolation using the birefringence data and modified Vuks' method.

3.4.1 Vuks' and Neugebauer's method

The order parameters of liquid crystals can be calculated using both Vuks' method and Neugebauer's method from the relation given below:

$$S = \frac{\alpha_e - \alpha_o}{\alpha_\parallel - \alpha_\perp} = \frac{\alpha_e - \alpha_o}{\Delta\alpha} \qquad \dots (13)$$

In case of the calculation of order parameter by Vuks' method, α_e and α_o values are obtained from Eqs (1) and (2), whereas in the case of Neugebauer's method, α_e and α_o values are obtained from Eqs (7) and (8).

In order to find the value of $\Delta\alpha$ in Eq (13), the well-known Haller's extrapolation[21] method is used in both the approaches. The graph drawn between the values of $(\alpha_e - \alpha_o)$ and $\ln(1 - T/T_c)$ is extrapolated at $T = 0$ K and the intercept at $T = 0$ K gives the required value of $\Delta\alpha$. The scaling factors obtained by Haller's
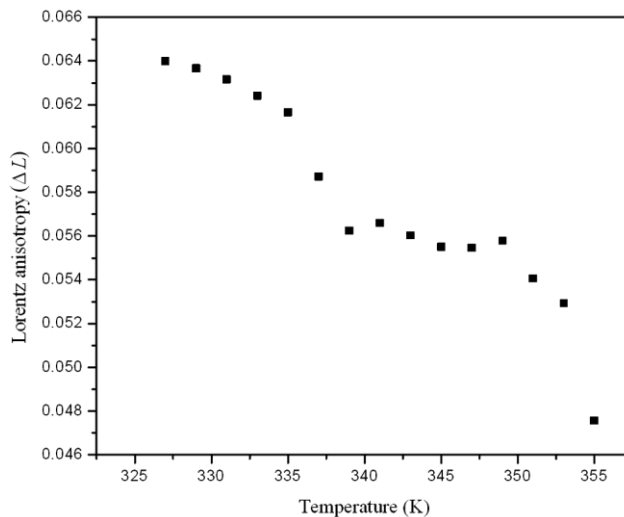

Fig. 6 – Temperature dependence of ΔL for the compound 6O.6

Table 2 – Values of scaling factors used for the evaluation of order parameter using different methods

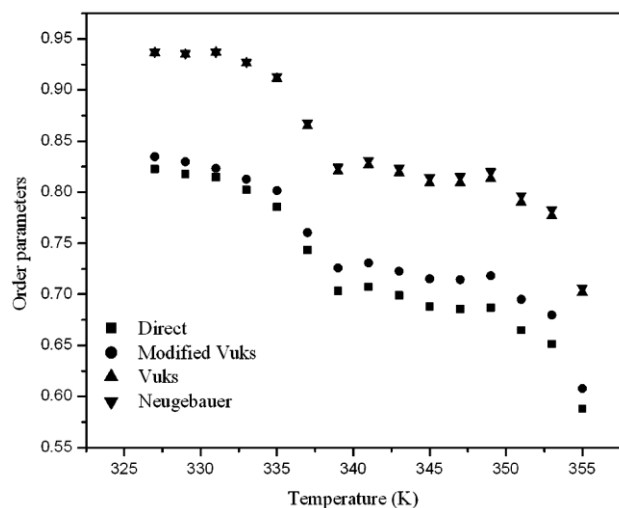| Sample	Direct extrapolation (Δn_o)	Modified Vuks ($\Delta\alpha/\langle\alpha\rangle$)	Vuks ($\alpha_{\mathrm{II}}-\alpha_{\perp}$)$\times10^{-24}$	Neugebauer ($\alpha_{\mathrm{II}}-\alpha_{\perp}$) $\times 10^{-24}$
6O.6	0.2383	0.5434	18.68	15.41

Fig. 7 – Temperature variations of order parameters for the compound 6O.6

extrapolation for the different methods are given in Table 2.

The values of order parameters of the sample obtained from the different methods are shown in Fig. 7. The order parameter values calculated from birefringence measurements[12,22] and modified Vuks method[22] are also plotted in the same figure. Figure 7, in order to obtain a comparison of the different approaches the results from birefringence measurements[12,22] and modified Vuks method were calculated and reported by us in an earlier paper[18].

Order parameter values of the sample 6O.6 are observed to be reasonably high. This makes the sample suitable for various applications. The similar results of order parameter from Vuks' and Neugebauer's method is due to the fact that the anisotropy of the molecular polarizabilities ($\alpha_e - \alpha_o$) increases in the same proportion whether one uses Vuks' or Neugebauer's approach. The values of order parameter obtained from Vuks' and Neugebauer's method are found to be slightly higher than the values obtained from the direct method and modified Vuks' method. In Neugebauer's method, the internal field constants are considered different along and perpendicular to the molecular axis[13]. This is the reason that among the various methods adopted for the calculation of order parameters, Neugebauer's method proved to be theoretically sound and is preferred.

4 Conclusions

Particular sample that has been selected for present study was found to be sticky in nature and difficult to work for various studies. It was found quite difficult to carry out the density studies for this sample specially while filling the sample inside the dilatometer tube. This may be the reason why very few works have been found in literature for this kind of liquid crystalline compounds. The values of order parameters obtained for the compound 6O.6 are found to be fairly high which makes the sample suitable for better applications in display devices. The nature of graph shown by $\alpha_e-\alpha_o$, ΔL and order parameters with temperature are found to be similar in nature. It can be concluded from this similarity that these parameters are interrelated and interdependent to each other. Also, comparing the results obtained with those available in literature[5], it is obvious that small changes of *n* and *m* of the *n*O.*m* series can bring about major changes in the values refractive of indices, Δn and also the order parameter.

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