Birefringence and temperature-gradient refractive index study of a laterally Fluorinated Terphenyl LC compound.

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Abstract. The temperature behaviour of the refractive indices in the nematic range of a laterally fluorinated terphenyl LC compound, viz, 2,3-difluoro-1,4 bis(4',4"-dipropyl phenyl) benzene was determined using the thin prism experiment. Birefringence of this LC compound was calculated from the measured refractive indices. Using the four parameter model, the temperature variation of the refractive indices and birefringence were theoretically fitted. The compound is found to have high value of birefringence. The temperature gradients of refractive indices i.e, $\frac{dn_e}{dT}$ and $\frac{dn_o}{dT}$ were determined, as a result, a cross over temperature was also found. The values of order parameter were obtained in two ways one by direct calculation using the effective geometry parameter α_{eg} .and the other by using the modified Vuks' method. Both show the same trend. It has been observed also α_{eg} changes almost linearly with the birefringence.

1. The Introduction

Liquid crystals (LCs) are a class of materials whose thermodynamic phase lies between that of a conventional liquid and a crystalline solid [1]. As a result of this, they share some of the properties of liquids and some of crystalline solids. One such case is the anisotropy in the optical properties. The refractive indices of LCs and their temperature dependence play a crucial role from the application point of view [2, 3]. An aligned LC behaves like uniaxial crystal and therefore it has two refractive indices viz., ordinary (n_o) and extraordinary (n_e) refractive index. The difference of the two values i.e., $\Delta n = n_e - n_o$ defines the birefringence of the LC. High birefringence nematic LCs are of great interest in display and communication devices because they help in reducing the cell gap which is required for achieving a fast response time [4, 5, 6]. Refractive indices and hence birefringence of LC depends on the wavelength of the incident light, molecular structure and temperature. The temperature gradients of refractive indices ($\frac{dn_e}{dT}$ and $\frac{dn_o}{dT}$) and the crossover temperature, defined as the temperature at which $\frac{dn_o}{dT}$ changes sign from negative to positive, play an important role in the characterization of LC materials in display technology and non-linear optical effects [7,8]. The effective geometry parameter,

defined by $\alpha_{eg} = \frac{n_o}{n_e}$, is also very useful in understanding of light propagation in LC and it can be used to determine the order parameter [9-11].

In this paper, we present the study of the variation of the refractive indices with temperature in the nematic range of an LC compound, viz, 2,3-difluoro-1,4 bis(4',4"-dipropyl phenyl) benzene, or in short as C3PP(23F)PC3. Birefringence of this LC compound was calculated from the measured refractive indices. The experimental results were fitted theoretically using the Four Parameter Model [12]. The temperature gradients of refractive indices were determined using the formulae derived by Wu [7] and a crossover temperature was also calculated. The values of order parameter were obtained by two different methods. One is by direct calculation using the effective geometry parameter as reported in literature [10, 13]; and the other is by using modified Vuks' method [17, 18].

2. The Theoretical Framework

The expression for the average refractive index is given as

$$< n >= \frac{n_e + 2n_o}{3} \tag{1}$$

Using the experimental data of n_e and n_o, the average refractive index $<n>$ decreases linearly as the temperature increases and can be expressed as

$$< n >= A - BT \tag{2}$$

The values of A and B are obtained by plotting the temperature (K) and $<n>$ by linear regression. And the results validated by solving system of linear equations given by (2).

The birefringence is also given as [14]

$$\Delta n = \Delta n_0 \left(1 - \frac{T}{T_c}\right)^{\beta} \tag{3}$$

where, Δn_o is the birefringence in the crystalline state (S=1)–obtained by extrapolating the birefringence at T = 0K. T_c is the clearing temperature of LC under investigation, and β is a material constant which is obtained by fitting the Δn data. The four-parameter model [12] describes the temperature variation of the LC refractive indices which eventually gives the theoretical value of n_o and n_e as

$$n_e(T) \approx A - BT + \frac{2\Delta n_0}{3}\left(1 - \frac{T}{T_c}\right)^{\beta} \tag{4a}$$

$$n_o(T) \approx A - BT - \frac{\Delta n_0}{3}\left(1 - \frac{T}{T_c}\right)^{\beta} \tag{4b}$$

The temperature gradients of refractive indices are obtained from (4a) and (4b) respectively as:

$$\frac{dn_e}{dT} = -B - \frac{2\beta\Delta n_0}{3T_c}\left(1 - \frac{T}{T_c}\right)^{\beta-1} \tag{5a}$$

$$\frac{dn_o}{dT} = -B + \frac{\beta\Delta n_0}{3T_c}\left(1 - \frac{T}{T_c}\right)^{\beta-1} \tag{5b}$$

The value of T in equation (5b) at which $\frac{dn_o}{dT} = 0$ gives the crossover temperature as

$$T_{CO} = T_c\left[1 - \left\{\frac{3BT_c}{\beta\Delta n_0}\right\}^{\frac{1}{\beta-1}}\right] \tag{6}$$

The order parameter S in terms of effective geometry parameter α_{eg} is given as [13]

$$S = \frac{3 < n > \left(1 - \alpha_{eg}\right)}{\left(2\alpha_{eg} + 1\right)\Delta n_0} \tag{7}$$

In the modified Vuks' method, the order parameter S is calculated using Vuks' hypothesis [19]:

$$S\left(\frac{\Delta\alpha}{\langle\alpha\rangle}\right) = \frac{n_e^2 - n_o^2}{\langle n^2\rangle - 1} \tag{8}$$

where $\frac{\Delta\alpha}{\langle\alpha\rangle}$ is a scaling factor which can be determined by plotting the term $\frac{n_e^2 - n_o^2}{\langle n^2\rangle - 1}$ as a function of $\ln\left(1 - T/T_c\right)$. The graph is a straight line and can be extrapolated to T = 0K at which S=1. Thus, the intercept at T = 0 K gives the value of the scaling factor. Then the required order parameter S was obtained by substituting this value of scaling factor in the equation (8).

3. Experimental

The LC compound (Fig.1.) used in this work was obtained from Military University of Technology, Poland. To determine the refractive indices, the thin prism method (Fig.2) was used [15].

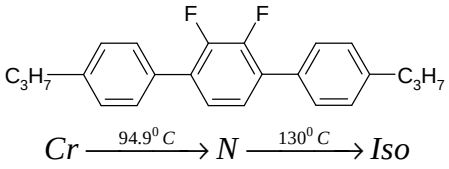

Fig.1. Molecular structure of 2,3-difluoro-1,4 bis(4',4"-dipropyl phenyl) benzene

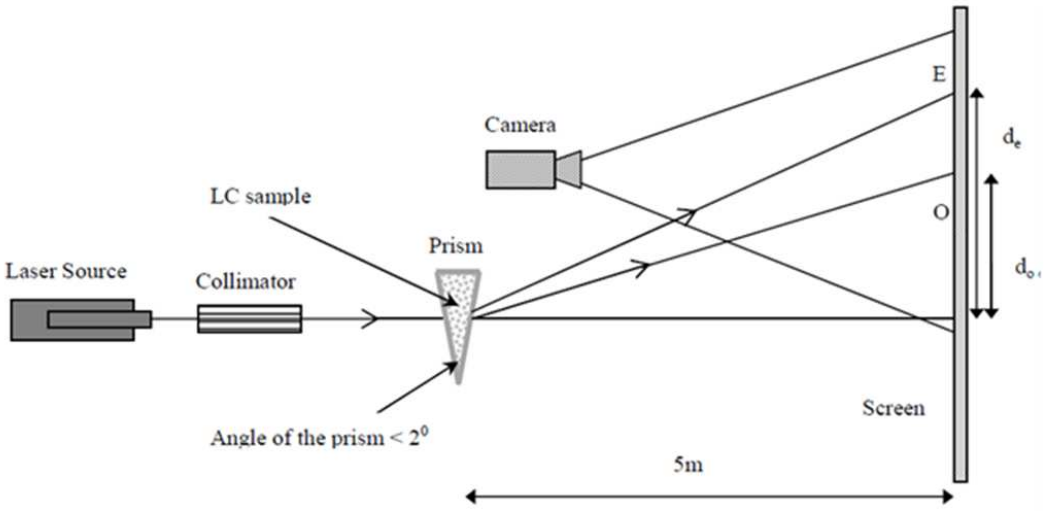

Fig.2. Experimental Setup

The sample was introduced in a thin prism (refracting angle less than 2°). The prism was made of glass slides whose inner surfaces were coated with a 1% polyvinyl alcohol (PVA) solution and

unidirectional rubbing was done for a homogeneous alignment of sample. The prism was enclosed inside an electrically heated hot stage with a circular aperture, whose temperature is controlled manually to ±0.5°C. He−Ne laser (λ= 632.8 nm) beam was focused onto the prism through a collimator. Two refracted spots from the LC−filled prism corresponding to e-ray and o-ray were obtained on a screen placed at a distance of about 5 meters from the prism. The images of the spots were photographed using a high resolution digital camera and those photos were analysed, and the data obtained were used to calculate the required refractive indices.

The ordinary (n_o) and extraordinary (n_e) refractive indices were calculated using the formula [16]:

$$n_e = \frac{1+2d_e}{d} \quad (8a)$$

$$n_o = \frac{1+2d_o}{d} \quad (8b)$$

where 'd_e' and 'd_o' are respectively the distance of extraordinary spot and that of ordinary spot from the direct spot on the screen. The direct spot was obtained on the screen by passing the laser beam through the empty prism without the sample. 'd' is the distance between the position of the direct spot and the spots formed by reflected beams from the two reflecting surfaces of the empty prism when the prism was placed symmetrically with its apex facing the direct beam.

4. Results and Discussions

The measurements of n_e and n_o were done during cooling of the sample from its isotropic phase. The variation of refractive indices with temperature is shown in Figure 3.

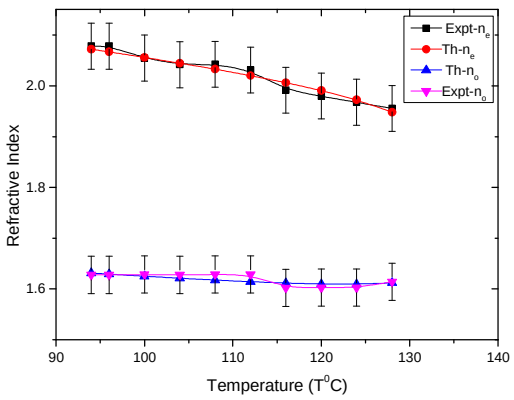

Fig.3. Temperature variation of refractive indices. In the Figures, (Th-stands for theoretical and Expt-stands for experimental.

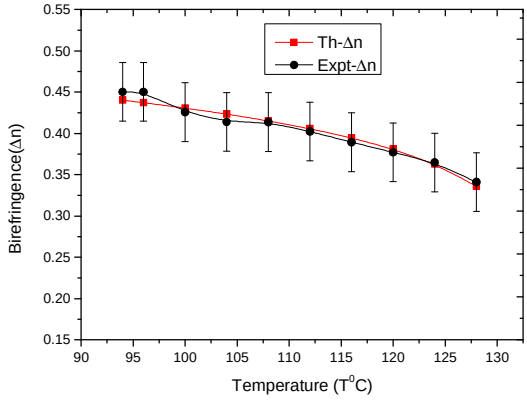

Fig. 4. Temperature variation of birefringence. (Th-stands for theoretical and Expt-stands for experimental)

From this experiment, The nematic–isotropic transition temperatures and the crystal–nematic transition is observed at 133^o C and 94^o C respectively, which are very close to those observed under DSC recorded by the manufacturer of the compound. As seen in Fig.3, it was found that n_e and n_o follow the general behaviour of temperature dependent refractive indices of NLCs except that n_o does not increase much.

The values of Δn are found to be high and decrease with temperature as shown in Fig.4. The theoretical values fit well with the experimental values in both the cases

The values of ⟨n⟩ as expected also decrease with temperature as shown in Fig.5. The value of A and B are given in the following table:-

Table. Fitting parameters

A	B [K^{-1}]	Δn_o	β
2.36557	0.0016	0.599206	0.13158

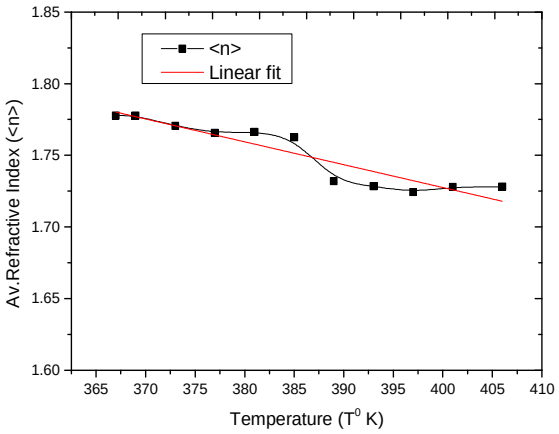

Fig.5. Temperature variation of average refractive index

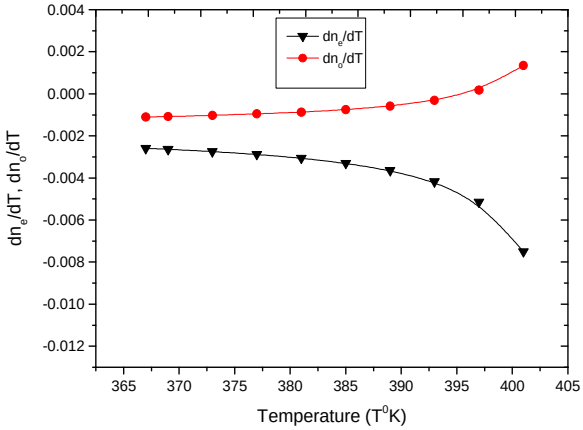

Fig.6. Temperature variation of temperature gradients of n_e and n_o

From Fig. 6, we can see that dn_e/dt remains negative throughout the nematic range. However, there is crossover behaviour of n_o as dn_o/dt changes its sign from negative to positive at a particular temperature known as crossover temperature, T_{CO}. Using Eq (6) it was found that T_{CO} is equal to 395.896^o K and from the graph of Fig. 6. , it is found to be 395.908^o K. This implies that below $T_{CO,}$ n_o decreases with temperature but above T_{CO}, it increases as temperature increases.

It is observed that α_{eg} decreases linearly with the birefringence as shown in Fig.7. This shows that with increase in the molecular order of the LC compound, α_{eg} decreases. LCs having higher value of the α_{eg} parameter is known to exhibit a lower deflection of light [11]. The order parameter S was determined in two ways one by using Eq (7) and by Eq (8), its temperature dependent is shown in Fig.8.

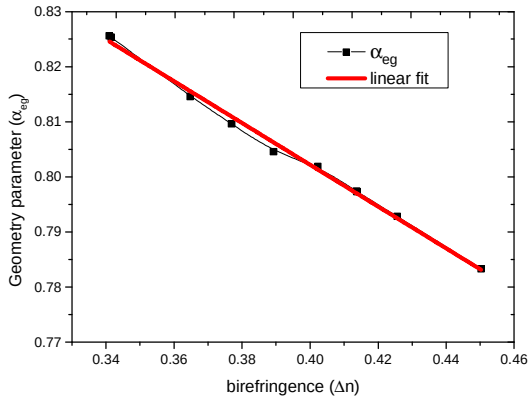

Fig.7. Effective geometry parameter α_{eg} vs birefringence Δn

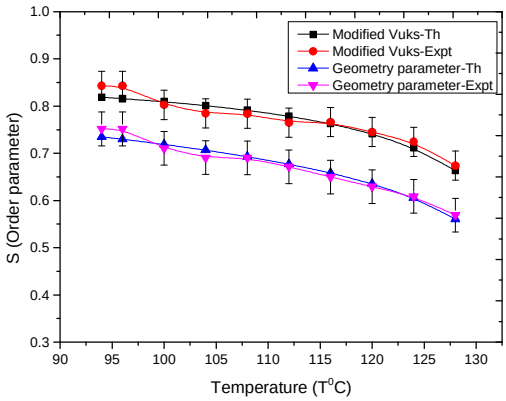

Fig.8. Order parameter S vs Temperature.

The theoretical values fit well with the experimental values in both the cases and the values of S determined from both the methods follow the same trend and they differ from each other by 0.1 approximately.

5. Conclusion

By using the thin prism technique, refractive indices and birefringence of an LC compound: 2,3-difluoro-1,4 bis(4',4"-dipropyl phenyl) benzene were determined and their variation with temperature was found to follow a normal trend. Birefringence of this LC compound was found to be high with values between 0.34~0.45. We have used a Four-parameter model for describing the temperature effect on the refractive indices and birefringence of this LC compound. Excellent agreement between the experimental data and fitted value is obtained. The temperature gradients of refractive indices i.e, dn_e/dt and dn_o/dt shows behaviour which are similar to the ones reported for other compounds [7, 8, 10]. Finally, we had determined the order parameter values without any density study but using only the values of the effective geometry parameter α_{eg} and the modified Vuks' method.

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