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Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

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To cite this article: G. K. Narasimhamurthy, C. M. Subhan, Seema Agarwal, S. Rangappa, C. V. Yalamaggadd & K. Fakruddin (2016) Orientational order parameter of some CBOnO.m liquid crystalline compounds—an optical study, Molecular Crystals and Liquid Crystals, 641:1, 25-36, DOI: 10.1080/15421406.2016.1241126

To link to this article: http://dx.doi.org/10.1080/15421406.2016.1241126

MOLECULAR CRYSTALS AND LIQUID CRYSTALS
2016, VOL. 641, 25–36
http://dx.doi.org/10.1080/15421406.2016.1241126

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Orientational order parameter of some CBOnO.m liquid crystalline compounds—an optical study

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ABSTRACT

Orientational order parameter is one of the important parameter of the liquid crystalline mesogens. This parameter governs nearly all physical properties of mesogens. Many methods are known for the estimation of orientational order parameter in liquid crystalline phase. In the present investigation the birefringence and dilatometric techniques have been exploited on some liquid crystalline CBOnO.m compounds with spacer $n = 7$, 10, 8, 5, and terminal group $m = 10$. Using density and birefringence data, the molecular polarizability and the orientational order parameter by Vuks and Neugebauer methods were evaluated and discussed the results with available data on number of liquid crystalline compounds.

KEYWORDS

Liquid crystalline mesogens; birefringence; polarizability; orientational order parameter

Introduction

Liquid crystals (LCs) describes the state of aggregation that exhibits molecular order in a size range similar to that of a crystal but acts more or less as a viscous liquid. The LC materials exhibit anisotropy in their mechanical, electrical, and optical properties. Several researchers have developed and reported number of LC devices and their applications [1–7]. The attempts are continuously being made to study the material properties of compounds for better insight into the basic understanding of liquid crystalline behavior. The orientational order parameter is considered to be one of the most important material parameter of the nematic phase, which determines all of its anisotropic properties and the relations between macroscopic and microscopic properties [8, 9].

CBOnO.m compounds are new and novel LC compounds with different spacer length. In this work, the homologous series of the compounds with spacer length $n = 7$, 10, 8, 5, and terminal group $m = 10$ are taken for birefringence and dilatometric studies [10, 11] at various temperatures. By using the refractive indices and density data, molecular polarizability and order parameter were estimated for the compounds. The compounds are synthesized at

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Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/gmcl.

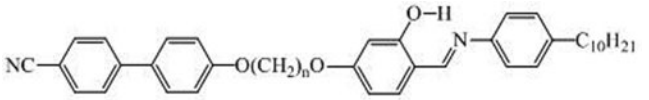
Table 1. Transition temperatures (°C)[a] and enthalpies (J/g) of compounds C1-C4. I = Isotropic phase; N = Nematic phase; SmA_b = Biaxial A phase; SmA = Uniaxial smectic A phase; Cr = Crystalline phase.

Compound	Phase tranition temperature (°C)
C1 ($n = 7$)	**I** 140.1 (0.9) **N** 91.3 (0.9) **SmA** 88.2[b] **SmA_b** 66.1 (46.1) Cr
C2 ($n = 10$)	**I** 157.2 (8.9) **N** 124.6[b] **SmA** 84.8 (63.3) **Cr**
C3 ($n = 8$)	**I** 164.6 (8.0) **N** 75.7 (63.3) Cr
C4 ($n = 5$)	**I** 140.8 **(1.1) N** 127.1[b] **SmA** 95.6[b] **SmA_b** 82.5 (64.3) Cr

[a] Peak temperatures in the DSC profiles obtained during the first heating and cooling cycles at a rate of 5 °C/min.
[b] The transition to this phase was observed under the POM and too weak to get recognized in DSC thermogram.

Centre for Nano and Soft Matter Sciences, Jalahalli, Bangalore, India, and donated us to carry out the present studies.

The molecular structure of the studied compounds is shown below and their transition temperatures are represented in Table 1.



C1: n = 7; **C2** : n = 10; **C3**: n = 8 and **C4**: n = 5

$\boldsymbol{n} = 7, 10, 8, 5$ and $\boldsymbol{m} = 10$

Experimental

Refractive index measurements

Refractive indices measurements were done with wedge-shaped glass cell similar to the one used to obtain birefringence by Haller et al. [12, 13] and modified spectrometer. A wedge-shaped glass cell was prepared with two optically flat rectangular glass plates (50 mm × 25 mm) sandwiched with glass slide of 0.05-mm thick, which acts as a wedge spacer. The liquid crystal compound is filled in the cell. The compound in the cell acts as a uniaxial crystal with its optic axis parallel to the edge of the spacer glass plate. The accuracy in the measured refractive indices was ±0.0005.

Density measurements

The U-shaped bi-capillary pyknometer in conjunction with cathetometer was used for the density measurements at various temperatures. The absolute error of the measurement of the density is $\pm 10^{-4}$ g/cm^3. The designed pyknometer used in the present investigation is shown in Fig. 1

Estimation of molecular polarizability

To estimate molecular polarizabilities of CBOnO.m compounds, the authors have considered Vuks and Neugebauer models. These methods were used by several researchers [14–18] to estimate the molecular polarizabilities in liquid crystalline state and the relevant equations in these methods are represented later.

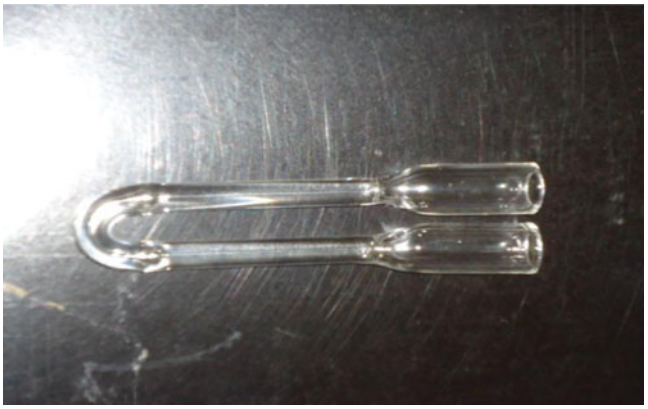


Figure 1. Pyknometer.

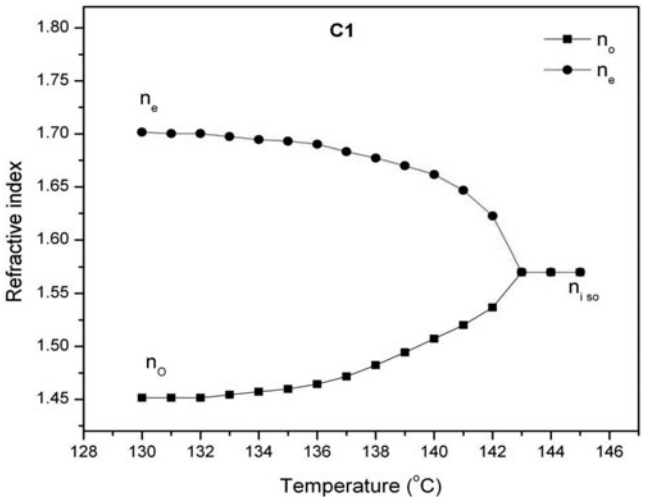


Figure 2. Temperature variation of refractive index in C1.

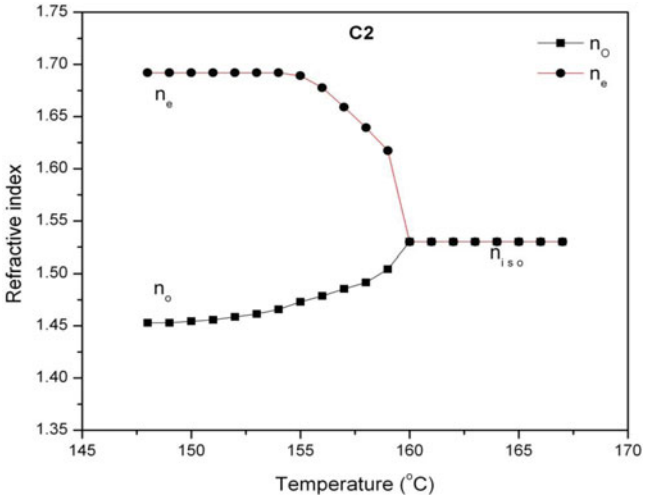


Figure 3. Temperature variation of refractive index in C2.

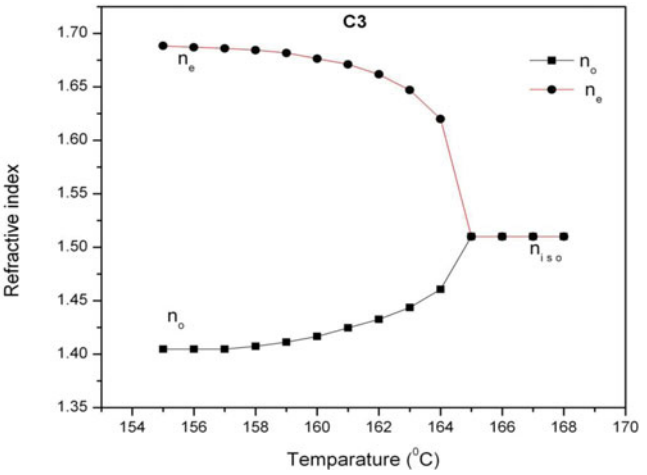


Figure 4. Temperature variation of refractive index in C3.

Vuks method

According to this method the ordinary and extraordinary polarizabilities are

$$\alpha_e = \left[\frac{3}{4\pi N}\right] \frac{{n_e}^2 - 1}{\bar{n}^2 - 1} \tag{1}$$

$$\alpha_o = \left[\frac{3}{4\pi N}\right] \frac{{n_o}^2 - 1}{\bar{n}^2 - 1} \tag{2}$$

where N is the number of molecules per unit volume, n_e and n_o are the extraordinary and ordinary refractive indices of the LC molecule.

$\bar{n}^2 = [\frac{n_e^2+2n_o^2}{3}]$ and $N = N_A\rho/M$, where N_A is the Avogadro number, ρ is the density, and M is the molecular weight.

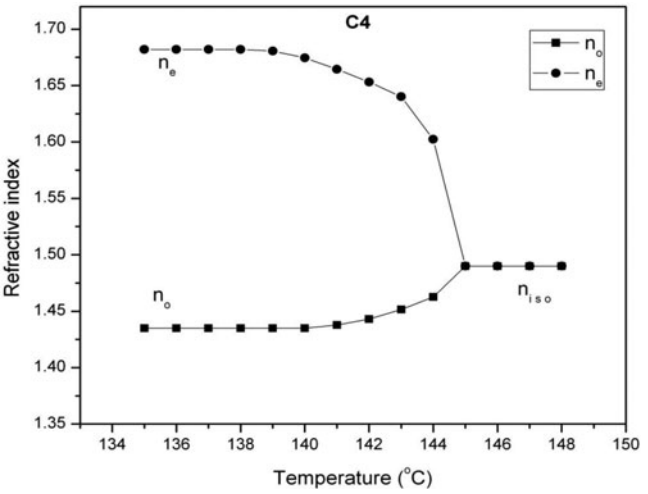


Figure 5. Temperature variation of refractive index in C4.

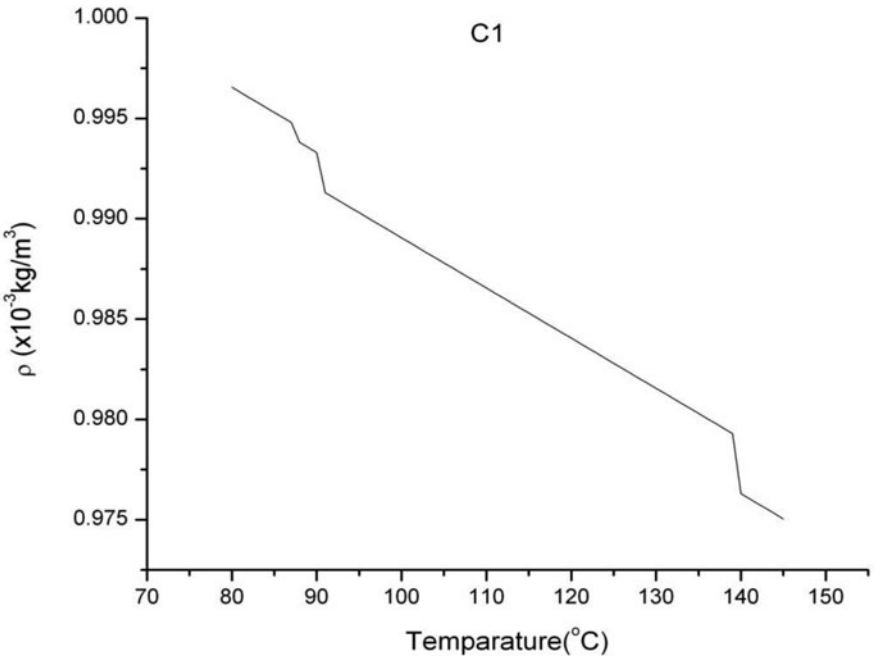


Figure 6. Temperature variation of density in C1.

Neugebauer method

According to this method the molecular polarizabilities are

$$\alpha_e = (AB - 3 \pm \sqrt{(AB-3)^2 - 4AB})/2A \tag{3}$$

$$\alpha_o = (AB + 3 \pm \sqrt{(AB+3)^2 - 16AB})/4A \tag{4}$$

where $A = [\frac{4\pi N}{3}]\,[\frac{{n_e}^2+2}{n_e^2-1}] + [\frac{2({n_o}^2+2)}{n_o^2-1}]$ and $B = [\frac{9(\tilde{n}^2-1)}{[(4\pi N_i)(\tilde{n}^2+2)]}]$, N_i is the number of molecules per unit volume in the isotropic phase.

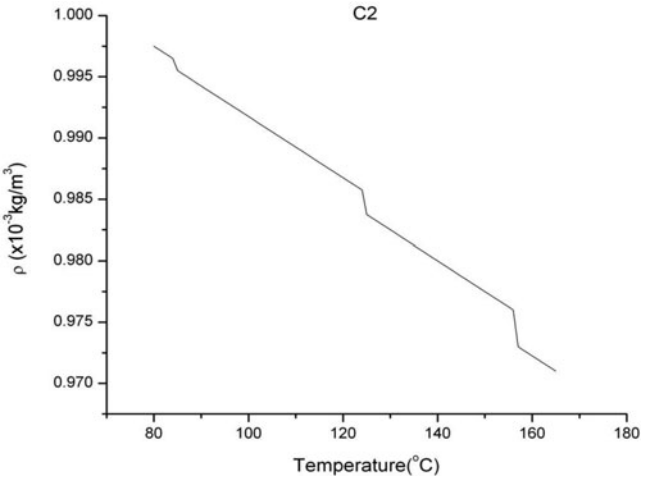


Figure 7. Temperature variation of density in C2.

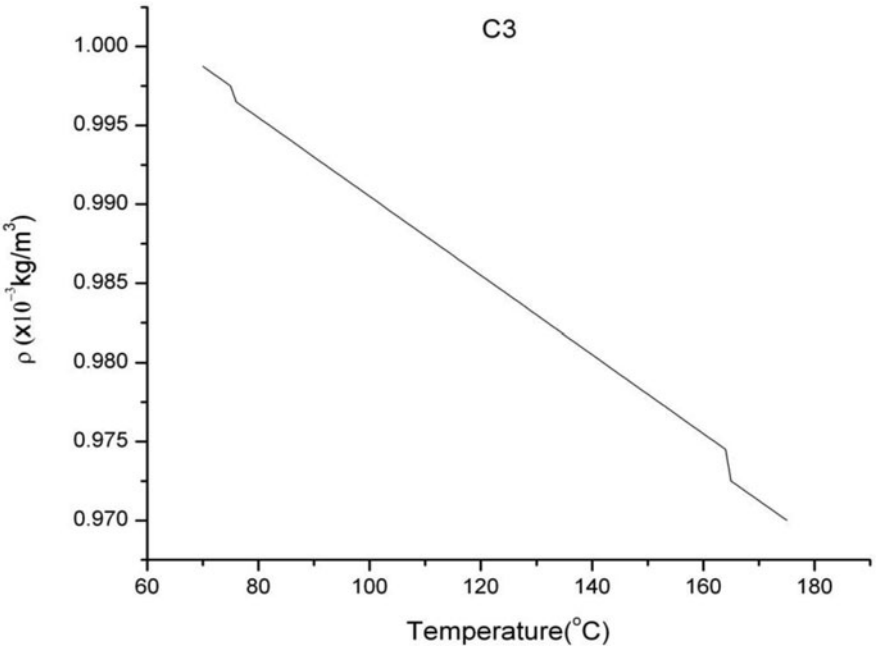


Figure 8. Temperature variation of density in C3.

Estimation of molecular polarizability from modified Lippincott δ-function method

The modified Lippincott δ-function model [19, 20] was used for different types of liquid crystals. In this method, the mean polarizability is estimated in terms of parallel bond component ($\sum \alpha \|_p$), the perpendicular bond component ($\sum 2\alpha_\perp$), and the non-bond region electron contribution ($\sum \alpha \|_n$). The expression for the mean polarizability is given as

$$\alpha_{\mathrm{M}} = \frac{1}{3}\left(\sum \alpha \|_p + \sum \alpha \|_n + \sum 2\alpha_\perp\right), \tag{5}$$

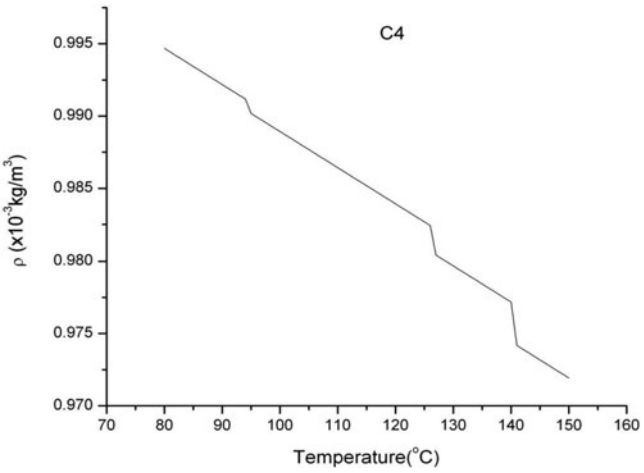


Figure 9. Temperature variation of density in C4.

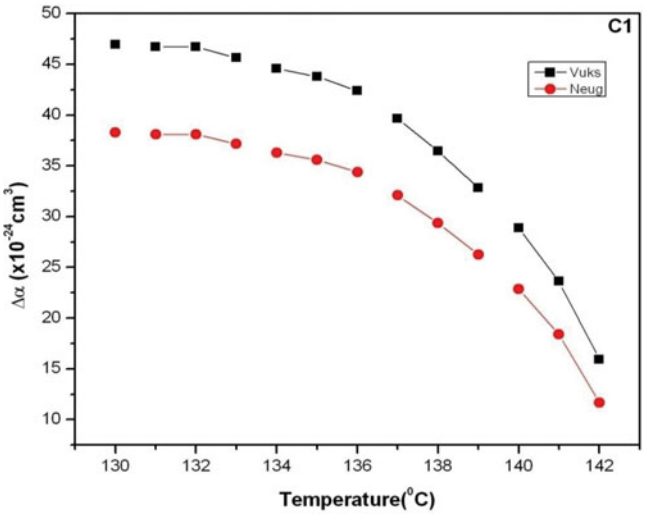


Figure 10. Polarizability anisotropy with temperature in C1.

where the parallel bond component is given as

$$\sum \alpha \parallel_p = \frac{4nA}{a_0} \exp\left[\frac{T - T_C}{T_C}\right]\left[\frac{R^2}{4} + \frac{1}{2C_R^2}\right] \exp\left[-\frac{(x_A - x_B)^2}{4}\right] \tag{6}$$

here n is the bond order, A is the δ-function strength, R is the bond length, X_A and X_B are the Pauling's electro negativities of atoms A and B in the bond AB, a_o is the radius of the first Bohr orbit of the hydrogen atom, and C_R is the geometric mean molecular δ -function strength. For

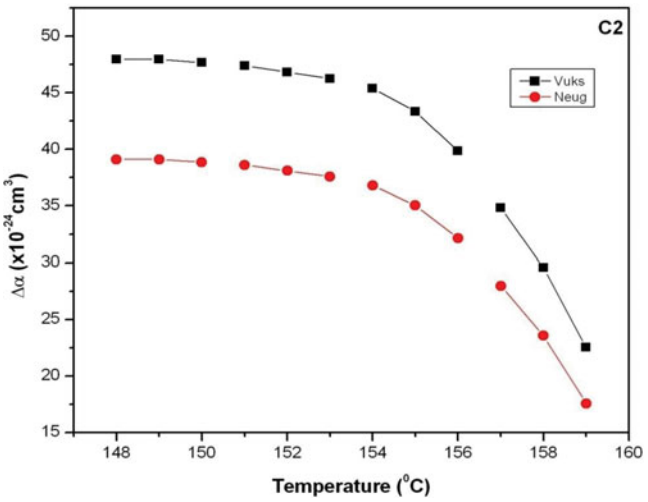


Figure 11. Polarizability anisotropy with temperature in C2.

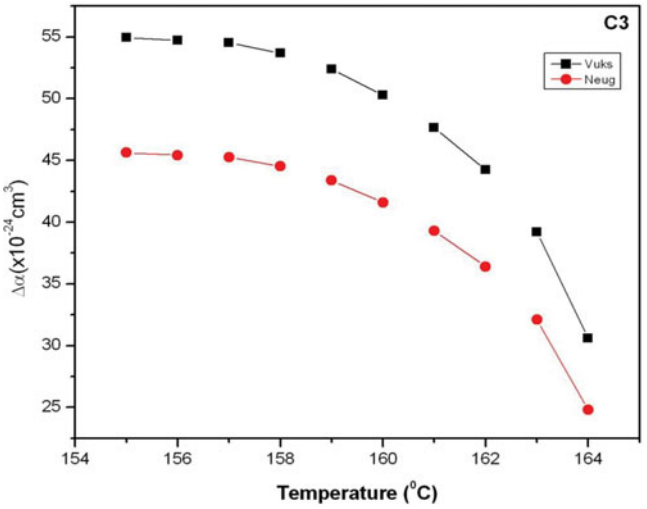


Figure 12. Polarizability anisotropy with temperature in C3.

the second term on the right-hand side of the equation (5), we have

$$\sum \alpha \parallel_n = \sum_j f_j \alpha_j \,, \tag{7}$$

here f_j is the fraction of the nonbonded electrons of the jth atom and α_j is its atomic polarizability.

For the third term in equation (5),

$$\sum 2\,\alpha_\perp = n_{\mathrm{df}} \frac{\sum \boldsymbol{x}^2{}_j \boldsymbol{\alpha}_j}{\sum \boldsymbol{x}^2{}_j} \tag{8}$$

here n_{df} is the number of degrees of freedom given by the equation $n_{\mathrm{df}} = (3N - 2n_{\mathrm{b}})$, where N is the number of atoms and n_{b} is the number of bonds in the molecule.

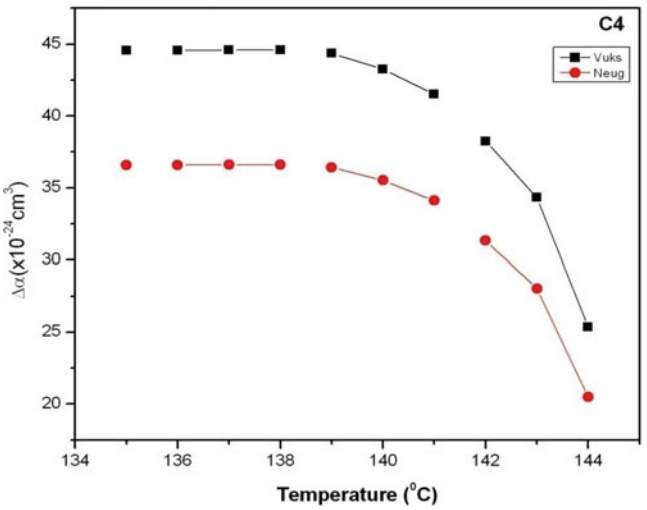


Figure 13. Polarizability anisotropy with temperature in C4.

Table 2. Mean molecular polarizabilities obtained in the liquid crystalline compounds by different methods [10^{-24} cm^3].

Compound	Lippincott δ-function model				Vuks model	Neugebauer model
	$\alpha_{\parallel p}$	$\alpha_{\parallel n}$	$2\alpha_{\perp}$	α_M	α_M	α_M
C1	169.88	1.779	74.13	81.93	83.41	82.82
C2	183.20	1.779	81.30	88.76	87.28	87.77
C3	167.74	1.779	76.37	82.08	80.00	79.87
C4	164.69	1.779	62.61	76.36	74.97	75.90

Estimation of orientational order parameter in the nematic phase

In the nematic phase, the Vuks method [21] is employed to estimate the order parameter. The equations used in this method are

$$S = \left(\frac{\alpha}{\alpha_{\parallel} - \alpha_{\perp}}\right) \frac{n_e^2 - n_o^2}{\bar{n}^2 - 1} \tag{9}$$

Where

$$\bar{n}^2 = \left[\frac{n_e^2 + 2n_o^2}{3}\right]$$

The order parameter in case of Neugebauer method [22] is

$$S = \left[\frac{\alpha}{\alpha_{\parallel} - \alpha_{\perp}}\right] f(B) \tag{10}$$

Where

$$f(B) = \left(\frac{9}{4AB}\right)\left[\left(B^2 - \left(\frac{10}{3}\right)B + 1\right)^{1/2} + \frac{B}{3} - 1\right]$$

and

$$B = \frac{n^2 - 1}{n^2 + 1}\left(\frac{n_e^2 + 2}{n_e^2 - 1} + \frac{2(n_o^2 + 2)}{n_o^2 - 1}\right)$$

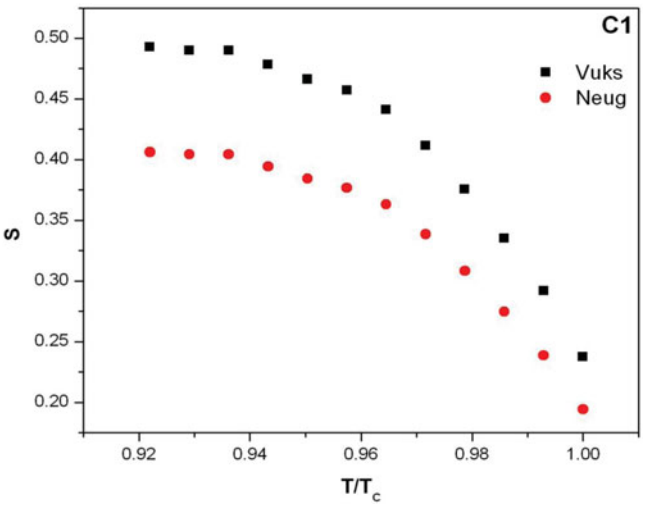


Figure 14. Variation of S with Reduced temperature in C1.

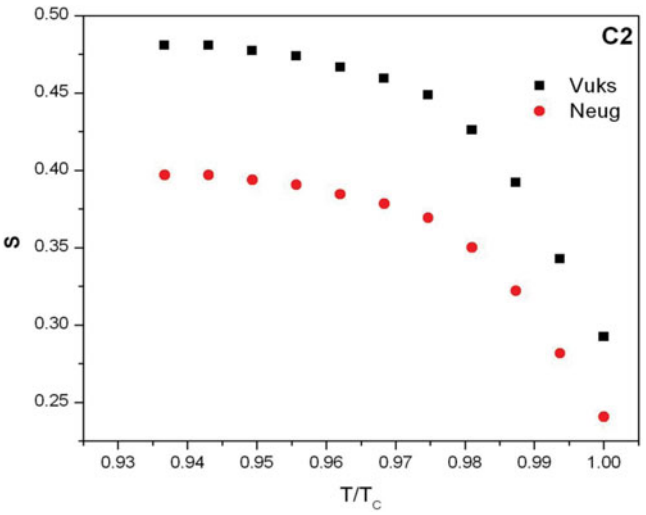


Figure 15. Variation of S with Reduced temperature in C2.

Results and discussion

In this investigation, the refractive indices of the CBOnO.m liquid crystalline compounds are measured at different temperatures using modified spectrometer with small-angled prism which houses the liquid crystalline compound and a monochromatic sodium source of wavelength 589.3 nm is used. During isotropic nematic-phase transformation the incident light splits into two lines with one higher and the other lower than the isotropic values. These are called extraordinary n_e and ordinary n_o refractive indices. In the nematic region, the value of n_e increases, whereas the value of n_o decreases with decrease in temperature and both attains saturation deep in nematic region. The variation of refractive indices with temperature in isotropic and nematic region is illustrated in Figs. 2–5.

The temperature variation of density is measured using dilatometer attached with U-shaped bi-capillary pyknometer and represented in Figs. 6–9. It is found that with rise in

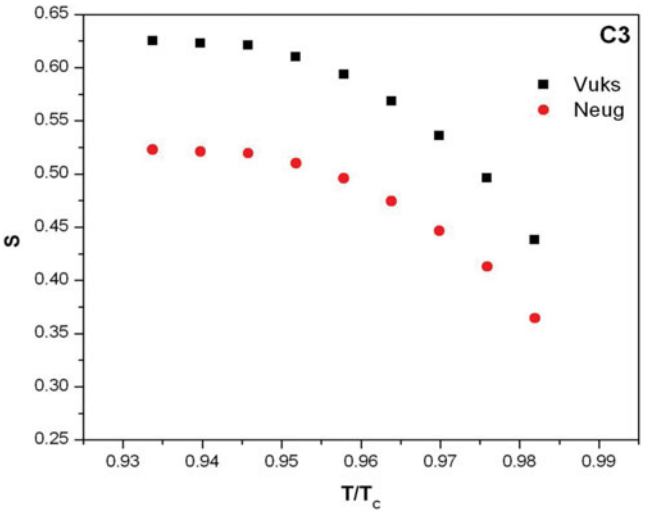


Figure 16. Variation of S with Reduced temperature in C3.

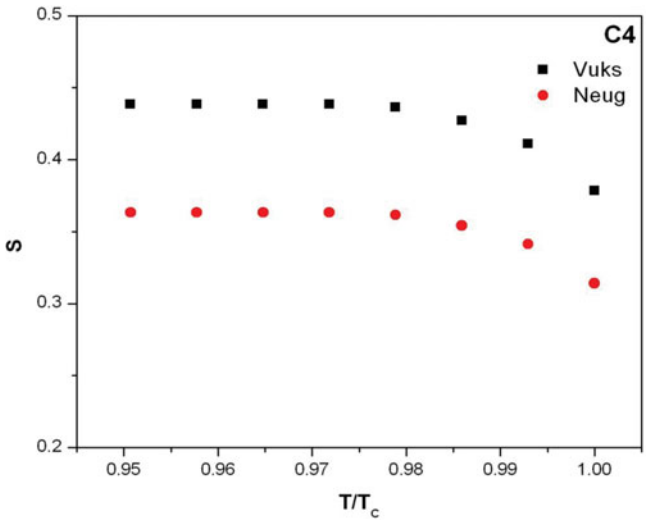


Figure 17. Variation of S with Reduced temperature in C4.

temperature density decreases and at phase transformations, the molecules align in a particular direction hence volume decreases and density increases. The same is noticed in the form of density jumps.

The polarizability anisotropy obtained during liquid crystalline phase at different temperatures is presented in Figs. 10–13. Using refractive indices data, the molecular polarizabilities were estimated by Vuks and Neugebauer internal field models at different temperatures. Further, the mean molecular polarizability is evaluated by modified Lippincott δ-function model. These values are compared with Vuks and Neugebauer models and the results are shown in Table 2. The polarizability values obtained by Lippincott δ-function model and by refractivity method are found to be nearly same and hence confirm the applicability of Lippincott δ-function model for liquid crystals. The order parameter with reduced temperature is evaluated for the above compounds by Vuks and Neugebauer methods and shown in Figs. 14–17.

4. Conclusions

- The ordinary and extraordinary refractive indices attain saturation deep in the nematic phase.
- The molecular polarizability values evaluated by Vuks and Neugebauer models are nearly same with that of the polarizability values calculated by modified Lippincott δ-function model.
- The orientational order parameter evaluated using both the models shows decrease with increase of temperature.
- The orientational order parameter estimated by Vuks and Neugebauer method is in between 0.3 to 0.7 which is in accordance with literature data available.
- The orientational order parameter value evaluated using Neugebauer method is always low when compared to other methods. The same results are obtained in our investigations.

Acknowledgments

Authors express their thanks to the Department of Physics, Ghousia College of Engineering, Ramanagaram for providing laboratory facilities. The authors are thankful to Dr. C.M. Yellamagad and Dr. D.S. Shankar Rao for providing liquid crystalline compounds to carry out the present studies. The financial support rendered by the VTU Belgaum under VTU research grant scheme for the research project (No. VTU/Aca/2011-12/A-9/750) is gratefully acknowledged.

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