



REFRACTIVE INDICES, ORDER PARAMETER AND DENSITY STUDY OF BKS/B07 NEMATIC LIQUID CRYSTAL

V.S. Chandel *, R. Manohar ** and J.P. Shukla **

abstract: The paper discusses the results of refractive indices, densities, order parameter and molecular polarizabilities of BKS/B07 nematic liquid crystal at different temperatures. The orientational order parameter has been determined from the calculated polarizability values obtained from the measured refractive indices. Density measurement indicates that the nematic-isotropic transition is of the first order. The order parameter as stated above was determined using direct extrapolation method, Neugebauer's method, Saupe and Maier's method, Vuks' and modified Vuks' method. The observed values differ slightly in crystal state but are in good agreement in the nematic phase.

key words: order parameter; refractive indices; polarizability; nematic liquid crystal.

received: July 11, 2011

accepted: September 15, 2011

1. Introduction

Liquid crystals have great importance in display devices and in many other scientific uses nowadays. The most important property of a liquid crystal which governs almost all its physical properties is its orientational order [1-4]. The orientational order S is expressed in terms of microscopic order parameter. The value of S lies between 1 (for complete order) and 0 (for complete disorder in isotropic liquid). The microscopic order parameter S differs from the macroscopic order parameter Q , which can be determined by nuclear magnetic resonance, dielectric permittivity, diamagnetic susceptibility, refractive indices, X-ray scattering, UV and IR dichroism, elastic constants, *etc.* In this paper order parameter of the liquid crystal has been reported from the measurement of refractive indices and densities at different temperatures in nematic and isotropic phase. The optical anisotropy is an important property and is very useful in display devices, which also governs the thickness of the liquid crystal layer to be used in such devices. Study of optical behavior of liquid crystals is thus important. For practical applications the liquid crystal should have a low birefringence and high order parameter. The order parameter has been calculated using direct extrapolation method, Neugebauer's Method, Saupe and Maier's Method, Vuks' and modified Vuks' method. Order parameter of nematic liquid crystals has been reported using optical anisotropy data by many workers [5-9].

* Department of Physics, Integral University, Lucknow-226026, India.
corresponding author e-mail: chandel.integral@gmail.com

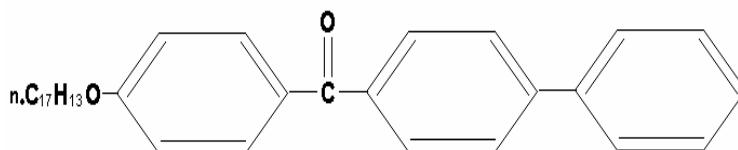
** Department of Physics, Lucknow University, Lucknow-226007, India.

2. Material and Methods

The liquid crystal used for the present investigation, namely BKS/B07 was procured from Prof. B. K. Sadashiva of Raman Research Institute, Bangalore and was used directly without further purification. The phase transitions are as follows:



The structure of nematic liquid crystal is as given below.



3. Experimental

3.1. Refractive index measurement

The refractive indices n_e and n_o for the extraordinary ray and ordinary ray in the nematic phase and refractive index n in the isotropic phase at different temperatures were measured by means of an Abbe's refractometer [10]. The temperature of the refractometer was maintained constant within $\pm 0.1^{\circ}\text{C}$ by means of a micro processor based temperature controller (Julabo, model no. F-25 HD).

3.2 Density measurement

The densities of the liquid crystal in the nematic and isotropic phases were determined by introducing the weighted sample of liquid crystal inside a glass capillary tube in a thermostat. The length of the column in the capillary was measured at different temperatures with a traveling microscope. The density was calculated after correcting for the expansion of the glass tube [10-13].

3.3 Theory (order Parameter)

Direct extrapolation method

In homogeneous alignment a nematic liquid crystal behaves like a uniaxial crystal. The relation between macroscopic order parameter and refractive indices in parallel and perpendicular direction of the long molecular axis were obtained by modifying the equation for uniaxial crystal as [13]:

$$n_{\parallel} = \bar{n} + \frac{2}{3} Q \Delta n \quad (1)$$

$$n_{\perp} = \bar{n} - \frac{1}{3} Q \Delta n \quad (2)$$

where \bar{n} is the average refractive index and Δn is the birefringence corresponding to complete alignment and for uniaxial alignment and for uniaxial crystal $n_{\parallel} = n_e$, $n_{\perp} = n_o$ and $\delta n = n_e - n_o$ [14,15]. From both the equations 1 and 2, we get

$$Q = \frac{n_{\parallel} - n_{\perp}}{\Delta n} = \frac{n_e - n_o}{\Delta n} = \frac{\delta n}{\Delta n} \quad (3)$$

The value of macroscopic order parameter Q becomes 1 at absolute temperature that is at 0K $\delta n = \Delta n$. This can be determined by extrapolating δn for $T = 0K$. This extrapolation is done on the linear portion of the graph drawn between birefringence (δn) versus $\ln\left(1 - \frac{T}{T_c}\right)$ as done by other workers [13, 16].

Modified Vuks' method

In order to find out the microscopic order parameter (S), the refractive indices n_e and n_o have been analyzed following the method of Haller [17] and Horn [18]. This method uses Vuks' relation [19]

$$S\left(\frac{\delta\alpha}{\alpha}\right) = \frac{3(n_e^2 - n_o^2)}{(n_e^2 + 2n_o^2 - 3)} \quad (4)$$

where $\delta\alpha$ is the polarizability anisotropy and α is the molecular polarizability. The principal polarizabilities are determined as described by Sarna *et al.* [20].

For the determination of effective polarizabilities α_e and α_o following three methods are used.

Neugebauer's method

In this model the anisotropic internal field is given as

$$n_e^2 - 1 = 4\pi N \alpha_e (1 - N \alpha_e \gamma_e)^{-1} \quad (5)$$

$$n_o^2 - 1 = 4\pi N \alpha_o (1 - N \alpha_o \gamma_o)^{-1} \quad (6)$$

Where N is the number of molecules per c.c., n_o and n_e are refractive indices for ordinary and extra-ordinary rays, and γ_e and γ_o are the internal field constants. The expression for calculating the effective polarizabilities α_e and α_o obtained from equation 5 and 6 and using the condition $\gamma_e + 2\gamma_o = 4\pi$, produces

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

In isotropic phase

$$\gamma_e = 2\gamma_o = \frac{4\pi}{3}$$

$$\alpha_e = \alpha_o = \bar{\alpha}$$

$$\alpha_e + 2\alpha_o = 3\bar{\alpha} = \frac{9}{4\pi N} \left[\frac{n^2 - 1}{n^2 + 2} \right] \quad (8)$$

Vuk's method

This model of isotropic field was modified from Lorentz-Lorenz equation as follows

$$\frac{n_e^2 - 1}{\bar{n}^2 + 2} = \frac{4\pi N\alpha_e}{3} \quad (9)$$

$$\frac{n_o^2 - 1}{\bar{n}^2 + 2} = \frac{4\pi N\alpha_o}{3} \quad (10)$$

where

$$\bar{n}^2 = \frac{1}{3}(n_e^2 + 2n_o^2) \quad (11)$$

Saupe and Maier's method

This model of anisotropic internal field where internal field is assumed as having single internal field constant can be given as:

$$\frac{n_e^2 - 1}{n_e^2 + 2 + a(n_o^2 - 1)} = \frac{4\pi N\alpha_e}{3} \quad (12)$$

$$\frac{n_o^2 - 1}{n_o^2 + 2 + a(n_o^2 - 1)} = \frac{4\pi N\alpha_o}{3} \quad (13)$$

Here the internal field constant 'a' can be calculated using the relation:

$$\frac{n^2 - 1}{n^2 + 2} V_{\text{iso}} = \frac{1}{3} \left[\frac{n_e^2 - 1}{n_e^2 + 2 - 2a(n_e^2 - 1)} + \frac{2(n_o^2 - 1)}{n_o^2 + 2 + a(n_o^2 - 1)} \right] V_{\text{Nem}} \quad (14)$$

The effective polarizabilities α_e and α_o have been obtained by solving the equations (7), (8) and (9), (10) and (12), (13) shown above for three different models.

The order parameter is given by $S = (\alpha_e - \alpha_o) - (\alpha_{\parallel} - \alpha_{\perp})$. Since we have only α_e and α_o values and not the principal polarizabilities α_{\parallel} and α_{\perp} , the parallel and perpendicular components respectively to the long axis of the molecule, we use the extrapolation method for calculating the values of α_{\parallel} and α_{\perp} . The extrapolation is done for the values of $(\alpha_e - \alpha_o)$ on the plot of $(\alpha_e - \alpha_o)$ against $\ln\left(1 - \frac{T}{T_c}\right)$ for $T = 0$ K.

4. Results and discussion

From Fig. 1 it is observed that the slope of the extraordinary refractive index n_e changes at the temperature 126°C indicating the phase transition. Similar type of the behavior can be seen from the data of ordinary refractive index n_o which changes slightly at 126°C , indicating the crystal–nematic phase transition. The ordinary refractive index n_o increases slowly, on the other hand extraordinary refractive index n_e decreases faster with increase in temperature. At 130°C the refractive index changes sharply, which exhibits the nematic – isotropic phase transition. After the transition from nematic to isotropic phase, the value of the refractive index remains almost constant, showing the isotropic phase of the material. This type of behavior has also been reported for different nematic mixtures by several other workers [21-29].

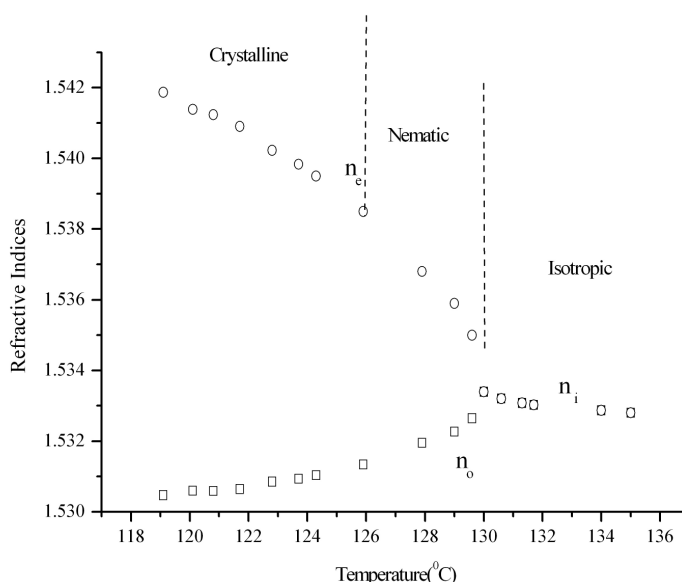


Fig. 1 Variation of n_o and n_e with temperature for the nematic sample BKS/B07.

It is observed from Fig. 2 that birefringence of the sample BKS/B07 decreases slowly with increases in temperature and the curve changes its slope at 126°C indicating crystalline to nematic transition. Also it can be observed that in isotropic phase the liquid crystal behaves like a normal organic liquid, [29,30] giving only one refractive index resulting almost into zero birefringence in the value δn . The zero birefringence value at 130°C indicates the isotropic phase of the material.

Fig. 3 shows the variation of density of nematic sample BKS/B07 with temperature, which remains almost constant with increase in temperature. After the temperature of the sample increases further, a sudden discontinuity in density curve of the sample at 126°C appears. This indicates the crystalline to nematic phase transition of the first order [31-35]. In the nematic phase the density of the sample decreases with increases in temperature and again the curve changes its nature at 130°C indicating the nematic to isotropic transition. The slight broadening of the transition temperature is probably due to the presence of some small impurity components in the sample. In isotropic phase the density decreases with

increase in temperature [20, 35]. Demus *et al.* [31] and Singh *et al.* [13] have also observed similar type of behavior. Also Chang and Mayer [36] have reported pre-transition temperature of 11 K in a mesogens. Further it may be noted that the phase transitions of the nematic material obtained by different methods that is refractive indices measurement technique and density measurement technique are almost same.

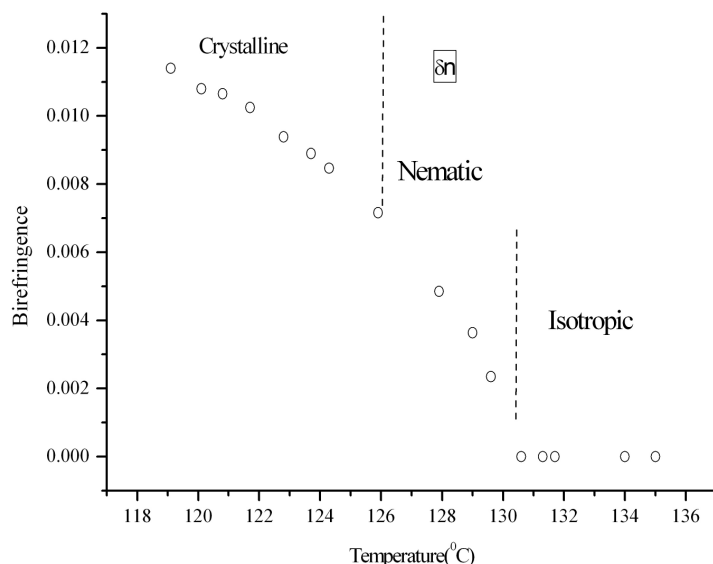


Fig. 2 Variation of birefringence with temperature for the nematic sample BKS/B07.

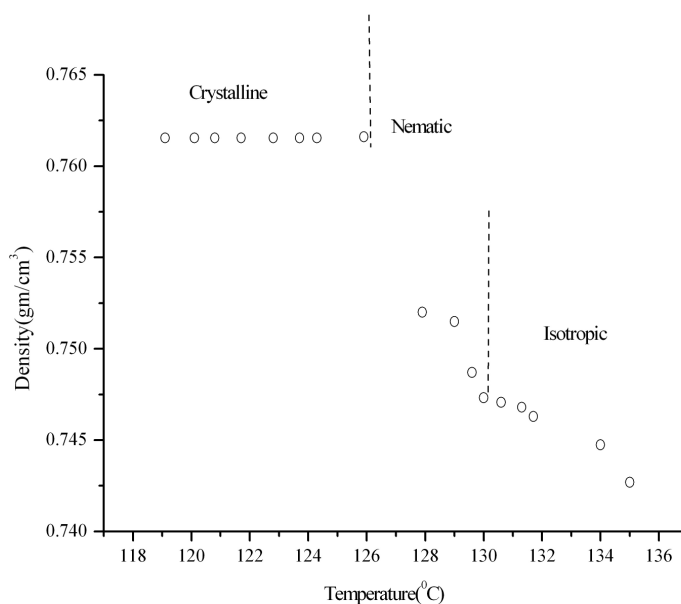


Fig. 3 Variation of density with temperature for the nematic sample BKS/B07.

In Fig. 4, the microscopic order parameter (S) as calculated using dielectric data matched very well with macroscopic order parameter (Q) determined using refractive indices data for the nematic sample BKS/B07 in all phases.

The microscopic order parameter (S) and macroscopic order parameter (Q) both decrease as the temperature of the sample increases and shows a slight change in its value at temperature 126°C showing crystal to nematic phase transition and at 130°C order parameter shows an abrupt change and become zero indicating the isotropic phase. The order parameters (S and Q) decrease from 0.4048 at 126°C to 0.2081 at 129°C and then become zero in the isotropic phase. The nature of the order parameter curve is almost similar to that observed for other nematic samples [11,16,37-39]. It can be seen from figure 4 that the microscopic order parameter (S) calculated from Vuks', Neugebauer's and Saupe and Maier's methods are in good agreement with the macroscopic order parameter (Q). The macroscopic order parameter (Q) may not essentially be same to that of microscopic order parameter (S). However, W. Kuczynski *et al.* [39] has suggested that one can expect similar values within a given local field as has been found in the present study.

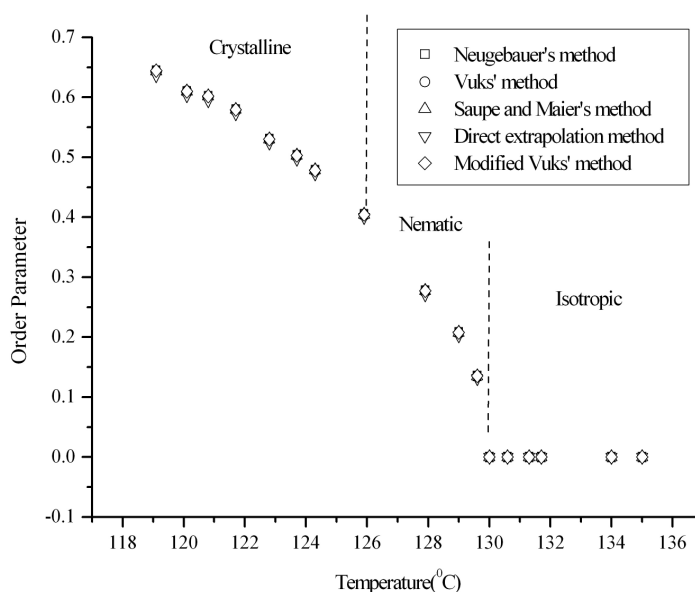


Fig. 4 Variation of order parameter with temperature for the nematic sample BKS/B07.

The variation of ratio of principal polarizability with temperature decreases with increase in temperature as shown in Fig. 5 and at the crystal to nematic transition that is at 126°C its value decreases more rapidly than that in crystalline phase. At nematic to isotropic transition its ratio becomes 1 showing the isotropic phase. The change in the value of $\frac{\alpha_e}{\alpha_0}$ is mainly due to the change in the order parameter. It shows that orientation of long molecular axis with director, changes and the value of θ increases with increase in temperature which in turn implies that the sample is more disordered.

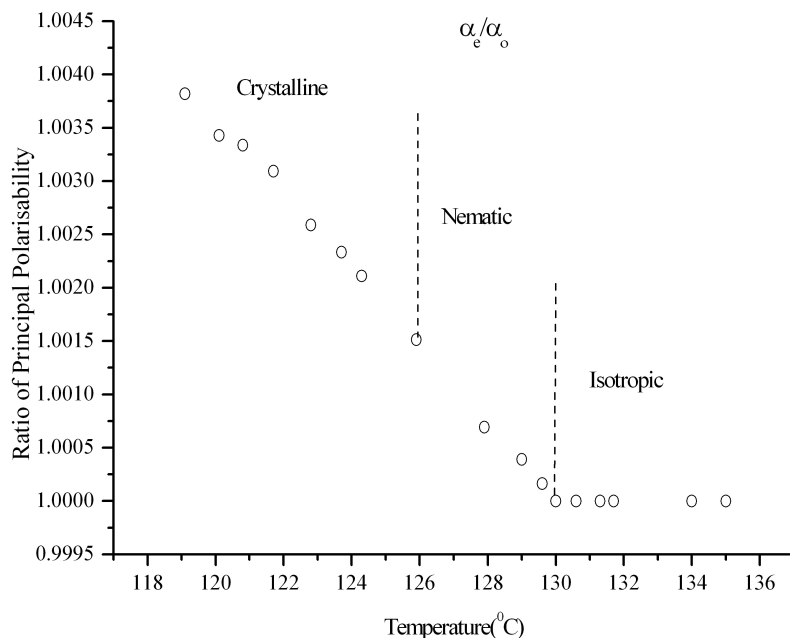


Fig. 5 Variation of ratio of principal polarizability with temperature for the nematic sample BKS/B07.

Conclusion

It may be concluded that the phase transition temperature obtained by different methods are in good agreement for the nematic material BKS/B07. But a slight broad width of phase transition for density may be due to the presence of some components in the sample which are acting as an impurity. The order parameters obtained by different methods are almost same in both the nematic and the isotropic phase.

Acknowledgement. Authors are thankful to Prof. B. K. Sadashiva of Raman Research Institute, Bangalore, India for providing the nematic sample.

REFERENCES

1. Bhowmick, K., Mkhopadhyay, A. and Mukherjee, C. D. (2003) *Phase Transitions*, **76**, 671-682.
2. Dhar, R., Srivastava, A. K. and Agarwal, V. K. (2003) *Phase Transitions*, **76**, 959-974.
3. Pandey, M. B., Dhar, R., Agarwal, V. K., Dabrowski, R. and Tykarska, M. (2004) *Liq. Cryst.*, **31**, 973-987.
4. Sasaki, A., Inodo, M. and Ishibashi, T. (1981) *Mol. Cryst. Liq. Cryst.*, **65**, 39-49.
5. E. G., Hanson, and Shen, Y. R. (1976) *Mol. Cryst. Liq. Cryst.*, **132**, 193-207.
6. de Gennes, P. G. (1974) **The Physics of Liquid crystals**, Oxford University press, London.
7. Chandrasekhar, S. (1977) **Liquid Crystals**, Cambridge university press, Cambridge.
8. M. J., Stephen, and Straley, J. P. (1974) *Rev. Mod. Phys.* **46**, 617-704.
9. Jun, L., Gauzia, S. and Wu, S. T. (2004) *Optics Express*, **12**(9), 2002-2010.

10. Garg, A. K., Agarwal, V. K. and Bahadur, B. (1985) *Mol. Cryst. Liq. Cryst.*, **130**, 11-24.
11. Sarna, R. K. and V. G. Bhide, (1982) *Mol. Cryst. Liq. Cryst.*, **88**, 65-79.
12. Bahadur, B., Sarna, R. K. and Bhide, V. G. (1982) *Mol. Cryst. Liq. Cryst.*, **72**(lett.), 139-145.
13. Singh, R., Agrawal, V. K., Anand, P. P. and Arora, V. P. (1990) *Nat. Acad. Sci. Lett. India*, **13**, 129-131.
14. Musevic, I., Drevensek, I., Blinc, R., Kumar, S. and Doane, J. W. (1989) *Mol. Cryst. Liq. Cryst.*, **172**, 217-222.
15. Jeu, W. H. De, (1980) **Physical Properties of Liquid Crystalline Materials**, Gordon and Breach Scientific Publisher, New York.
16. Arora, V. P., Prakash, S., Agarwal, V. K. and Bahadur, B. (1992) *Ind. J. of Pure and Appl. Phys.*, **30**, 406-408.
17. Haller, I. (1975) *Prog. Solid State Chem.*, **10**, 103-112.
18. Horn, R. G. (1978) *J. Phys (France)*, **39**, 105-109.
19. Vuks, M. F. (1966) *Opt. Spektrosk (USA)*, **20**, 361-364.
20. Sarna, R. K., Bahadur, B. and Bhide, V. G. (1979) *Mol. Cryst. Liq. Cryst.*, **51**, 117-135.
21. Subramaniam, N. C., Abdoh, M. M. M., Srinivasha and Prasad, J. S. (1982) *Mol. Cryst. Liq. Cryst.*, **80**, 179-193.
22. Phaovibul, O., Chantanasmrit, K. and Tang, I. M. (1981) *Mol. Cryst. Liq. Cryst.*, **71**, 233-247.
23. Denprayoonwang, S., Limcharoem, P., Phaovibul, O. and Tang, I. M. (1981) *Mol. Cryst. Liq. Cryst.*, **69**, 313-326.
24. Prasad, J. S. and Subramaniam, H. S. (1976) *Mol. Cryst. Liq. Cryst.*, **33**, 77.
25. Gunyakov, V. A., Shestakov, N. P. and Shibli, S. M. (2003) *Liq. Cryst.*, **30**(7), 871-875.
26. Sungsitayakorn, P., Limcharoen, P., Tang, I. M. and Phaovibul, O. (1981) *Mol. Cryst. Liq. Cryst.*, **71**, 293-301.
27. Li, J. and Wu, S. T. (2004) *J. Appl. Phys.*, **95**(3), 896-901.
28. Bogi, A., Faetti, S. (2001) *Liq. Cryst.*, **28**(5) 729-739.
29. Jun, L., Gauzia, S. and Wu, S. T. (2004) *J. Applied Phys.*, **96**(1), 19-24.
30. Smyth, C. P., (1975), Dielectric behaviour and Structure, McGraw-Hill. Handbook of Physics and Chemistry (CRC) 57th edition, 77 (1976):
31. Demus D., Hahn, H. G. and Kuschel, F. (1978) *Mol. Cryst. Liq. Cryst.*, **44**, 61.
32. Harstone, N. H. and A. Stuart, (1970) **Crystals and Polarising Microscope**, Edwards Arnold Publishing Ltd., London.
33. Zaminder, A. K., Paul, S. and Paul, R. (1980) *Mol. Cryst. Liq. Cryst.*, **61**, 191-206.
34. Ratna, B. R., Nagbhushana, C., Raza, V. N., Shashidhar, R., Chandrashekhar, S. and Heppke, G. (1986) *Mol. Cryst. Liq. Cryst.*, **138**, 245-257.
35. Bhowmick, K., Mukhopadhyay, A. and Mukherjee, C. D. (2001) *Mol. Cryst. Liq. Cryst.*, **366**, 229-238.
36. Cheng, J. and Meyer, R. B. (1974) *Phys. Rev.*, **A 9**, 2744-2760
37. Mitra, M. Paul, S. and Paul, R. (1987) *Pramana -J. Phys.*, **29**(4), 409-417.
38. Sen, S., Brahma, P., Roy, S. K., Mukherjee, D. K. and Roy, S. B. (1983) *Mol. Cryst. Liq. Cryst.*, **100**, 327-340.
39. Kuczynski, W., Zywuicki, B. and Malecki, J. (2002) *Mol. Cryst. Liq. Cryst.*, **381**, 1-19.