

ANALYSIS OF THERMO-OPTICAL & PHASE TRANSITION STUDIES OF LIQUID CRYSTALS MIXTURES

Deepa Sharma

KNGD Modi Engineering College
Modinagar

Jitendra Kumar Kushwaha

IIMT Engineering College
Mawana Road Ganga Nagar Meerut

V. P. Arora

Vardhman (PG) College
Bijnor

ABSTRACT: We have thermo-optical studies as a function of temperature in liquid crystal mixtures. The main contribution to optical phenomena in liquid crystals arises from Thermo-Optical & Phase Transition processes. While the thermal effect is similar to that observed in other materials, the phase transition effect is characteristic only in liquid crystalline phases. The nonlinearity due to the reorientation effect in nematic phase leads to numerous effects not observed in another types of nonlinearity. The reorientation nonlinearity induces extremely large nonlinear changes of refractive index that can be obtained for relatively low light power. This nonlinearity depends on boundary conditions and geometry of the system and it can be easily modified by external electric or magnetic fields. The nonlinearity depends on light polarization but within a wide range is independent on light wavelengths. The main drawback is slow response time, but by special optimization of the system, this response could be fairly fast.

KEYWORDS: thermal-optical, liquid crystal mixture

INTRODUCTION:

The order in the liquid crystal is affected by various microscopic properties, e.g., dielectric constant, magnetic susceptibility, refractive index, viscosity etc. Optical isotropy is observed, if light passes parallel to the director, where as optical birefringence is observed if the light passes in the direction perpendicular to the director. Polarized rays parallel to the director have a different index of refraction from those polarized perpendicular to the director. Many experiments demonstrate that the anisotropy of nematics arise because of the tendency of the rod like molecules in the fluid to align their long axis parallel to the director. This is shown schematically in **Fig.1.1(a)** The director is denoted by the symbol \hat{n} ; the rod-like molecules are represented by the short lines[1-2].

In **Fig. 1.1(b)**, let the director lie along the z-axis of a fixed rectangular co-ordinate system.

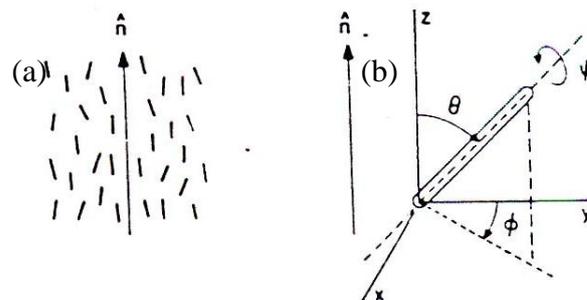


Fig.1.1: Schematic representation of the structure of (a) nematic liquid crystal (b) The Euler angles required to describe the orientation of a molecule in nematic liquid crystal.

When all the molecules are fully aligned with \hat{n} , all $\cos^2 \theta = 1$ and $\langle \cos^2 \theta \rangle = 1$. On the other hand, if the molecules are randomly distributed in direction, all values of $\cos^2 \theta$ are equally likely and $\langle \cos^2 \theta \rangle = 1/3$.

By tradition, the order parameter in any order-disorder problem is always taken such that it is unity in the perfectly ordered phase and vanishes for the completely disordered phase. Examination of the average values described above shows that the proper order parameter for the nematic liquid crystal is

$$\langle P_2 \rangle = \frac{1}{2} (3 \langle \cos^2 \theta \rangle - 1) \quad \dots(1.1)$$

Clearly, $\langle P_2 \rangle = 1$ for the completely ordered nematic phase and $\langle P_2 \rangle = 0$ for the disorder isotropic phase. The symbol $\langle P_2 \rangle$ is used for the order parameter because we recognize the particular combination in above equation to be the second-order Legendre polynomial, $P_2(\cos \theta) = (3 \cos^2 \theta - 1)/2$. In the original theory as well as in much of the literature, the symbol S is used to represent $\langle P_2 \rangle$. Values of $\langle P_2 \rangle$ between 0 and 1 describe degrees of ordering intermediate between completely isotropic and completely ordered. It is the task of order-disorder theory to determine the temperature dependence of $\langle P_2 \rangle$ and shown in **Fig.1.2**, In typical nematic phases, $\langle P_2 \rangle$ lies in the region of 0.4 to 0.8 indicating that the molecules are rather disorder [3-17].

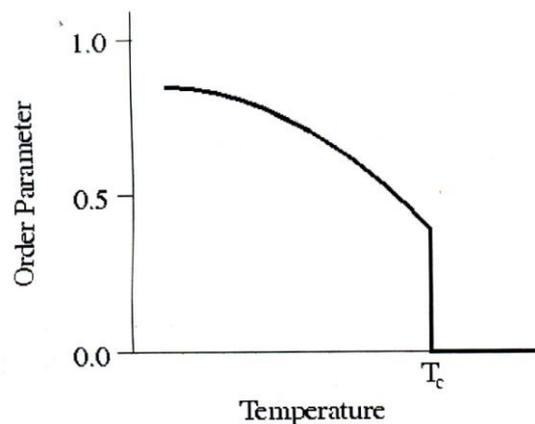
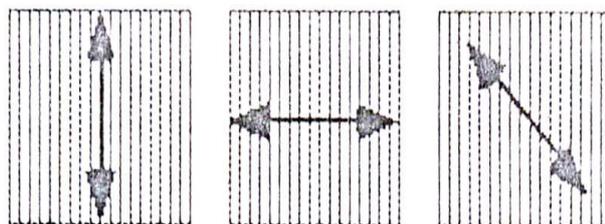


Fig. 1.2: Typical order parameter vs. temperature in a nematic liquid crystal material.

1.2 BIREFRINGENCE IN LIQUID CRYSTALS

Liquid crystals are found to be birefringent, due to their anisotropic nature. That is, they demonstrate double refraction (having two indices of refraction). Light polarized parallel to the director has a different index of refraction (that is to say it travels at a different velocity) than light polarized perpendicular to the director.

Thus, when light enters a birefringent material, such as a nematic liquid crystal sample, the light being broken up into the fast (called the ordinary ray) and slow (called the extraordinary ray) components. Because the two components travel at different velocities, the waves get out of phase. When the rays are recombined as they exit the birefringent material, the polarization state has changed because of this phase difference.



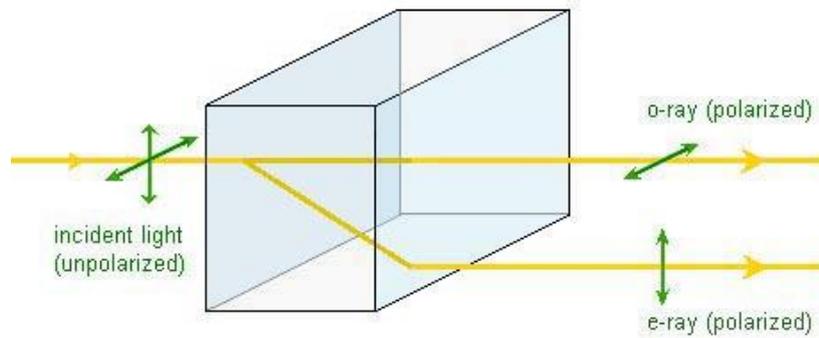


Fig. 1.3: Light traveling through a birefringence medium will take one of two paths depending on its polarization.

The birefringence of a material is characterized by the difference, Δn , in the indices of refraction for the ordinary and extraordinary rays. To be a little more quantitative, since the index of refraction of a material is defined as the ratio of the speed of light in a vacuum to that in the material, we have for this case, $n_e = c/V_{||}$ and $n_o = c/V_{\perp}$ for the velocities of a wave travelling perpendicular to the director and polarized parallel and perpendicular to the director, so that the maximum value for the birefringence, $\Delta n = n_e - n_o$. We won't deal here with the general case of a wave travelling in an arbitrary direction relative to the director in a liquid crystal sample, except to note that Δn varies from zero to the maximum value, depending on the direction of travel. The condition $n_e > n_o$ describes a positive uniaxial material, so that nematic liquid crystals are in this category. For typical nematic liquid crystals, n_o is approximately 1.5 and the maximum difference, Δn , may range between 0.05 and 0.5

The birefringence of liquid crystal mixture plays an important role in TN mode. This parameter is specially sensitive in multiplexed displays where it should be matched to the thickness of liquid crystal layer (i.e. cell spacing, d) by the relation of $d \cdot \Delta n = 2\lambda$ where λ is the wavelength of the visible light (0.4-0.7 μm), $d \cdot \Delta n < 2\lambda$ leads to colour while $\Delta n > 2\lambda$ leads to the narrow viewing angle especially in multiplexed displays. Attempts have been also made to use low birefringence material and apply the

relation $d \cdot \Delta n = \sqrt{\frac{3}{4}} \lambda$ for high level multiplexed displays. Generally for direct drive display, matching is not very critically assured and $d \cdot \Delta n$ is kept $\geq 2\lambda$.

Low birefringence materials with high positive dielectric anisotropy and order parameter are needed for dye phase change type displays [18].

1.3 WAVELENGTH DEPENDENT OF REFRACTIVE INDEX

Refractive indices of liquid crystal material change dramatically with the wave-length of light due to dispersion. The variation of the index of refraction of a medium with wavelength constitutes the phenomenon of dispersion. Mathematically it is represented by $dn/d\lambda$. An adequate theory of dispersion based on the electromagnetic theory of light was given by H.A. Lorentz and earlier attempts were made by Cauchy and Sellmeier.

In normal dispersion case, "The index of refraction increases as the wavelength decreases". The rate of increases $dn/d\lambda$ i.e the slope of the curve is greater at shorter wavelengths. In other words, dispersion increases as the wavelength decreases. Thus, the violet end of the prismatic spectrum is spread out on a larger scale than the red end [21-24].

1.4 MEASUREMENT OF REFRACTIVE INDEX

In this paper, we are reporting the results of the measurements taken of extraordinary refractive index (n_e), ordinary refractive index (n_o) in (n_i) in isotropic phase of a liquid crystal sample E48 as a function of temperature, using Abbe refract meter with a monochromatic light source. From the

experimental data we have calculated different useful parameters e.g. birefringence (Δn), normalized polarizabilities (α_e/α , α_o/α) and order parameter S [25-28].

1.5 RESULTS AND DISCUSSION

Vuks made a bold assumption that the internal field in a liquid crystal is the same in all directions and gave a semi-empirical equation correlating the refractive indices with the molecular polarizabilities for anisotropic materials.

$$\frac{n_{e,o}^2 - 1}{\langle n^2 \rangle + 2} = \frac{4\pi}{3} N\alpha_{e,o} \tag{1.2}$$

Where n_e and n_o are the refractive indices for the extra ordinary and ordinary ray respectively $\alpha_{e,o}$ are the corresponding molecular polarizabilities and N is the number of molecules per unit volume, and $\langle n^2 \rangle$ is given by

$$\langle n^2 \rangle = \frac{n_e^2 + 2n_o^2}{3} \tag{1.3}$$

In eq. 2, n_e and n_o are coupled together so that the relationship between the refractive indices and the corresponding molecular polarizabilities is not clear. To reveal this relationship, we should decouple n_e from n_o by solving Eq.1.2. Substituting Eq.1.3 to Eq. 1.2 and separating n_e and n_o , we obtain

$$n_e = \left(1 + \frac{4\pi N \alpha_e}{1 - \frac{4\pi}{3} N \langle \alpha \rangle} \right)^{1/2} \tag{1.4}$$

$$n_o = \left(1 + \frac{4\pi N \alpha_o}{1 - \frac{4\pi}{3} N \langle \alpha \rangle} \right)^{1/2} \tag{1.5}$$

Where $\langle \alpha \rangle$ is average polarisability of the liquid crystal molecules and given by (Li et al., 2004)

$$\langle \alpha \rangle = \frac{\alpha_e + 2\alpha_o}{3}$$

And birefringence of the LC sample is given by $\Delta n = n_e - n_o$. Now on using above equation's we have

$$\Delta n \approx \frac{\sqrt{2\pi NS}(y_e - y_o)}{1 - \frac{4}{3}\pi N \langle \alpha \rangle} \tag{1.6}$$

However the average refractive index $\langle n \rangle$ of liquid crystal is defined as

$$\langle n \rangle = \frac{n_e + 2n_o}{3} \tag{1.7}$$

on putting the values of the n_e & n_o in above equation, we drive

$$\langle n \rangle = \frac{3\sqrt{2}}{4} + \frac{\sqrt{2\pi N} \langle \alpha \rangle}{1 - \frac{4}{3}\pi N \langle \alpha \rangle} \tag{1.8}$$

On substituting Eq. 1.6 and 1.7 back to eq. 1.4 & 1.5 the refractive indices have the following simple expression.

$$n_e = \langle n \rangle + \frac{2}{3} \Delta n \tag{1.9}$$

$$n_o = \langle n \rangle - \frac{1}{3} \Delta n \tag{1.10}$$

1.6 ORDER PARAMETER (DIRECT EXTRAPOLATION METHOD)

Calculation of microscopic order parameter in the liquid crystal sample by optical birefringence's is based on Vuks direct extrapolation method. The refractive indices n_e and n_o have been analyzed by the method of Haller and Horn, this method uses Vuks relation.

$$S\left(\frac{\delta\alpha}{\alpha}\right) = \frac{3(n_e^2 - n_o^2)}{(n_e^2 + 2n_o^2 - 3)} \tag{1.11}$$

Here $\delta\alpha (= \alpha_o - \alpha_i)$ is the anisotropy of polarizability and α is mean molecular polarizability.

The logarithmic of the R.H.S. of above equation was plotted against $\log(T/T_c)$ and the straight line so obtained is extrapolated to $T = 0^0K$. The intercept at $T = 0^0K$ where $S = 1$ led to the scaling factor $\delta\alpha / \alpha$ in equation (1.11), we can obtain the value of order parameter at various temperatures.

Figures 1.4 and 1.5 respectively after clearing point the birefringence becomes zero. The ordinary refractive indices (n_o) increases slightly while the extra ordinary refractive index decreases sharply with increase in temperature the SmA to isotropic point i.e. at 104^0C refractive index values changes and becomes almost constant. It is in accordance with the results obtained by others on different samples. The reason for this kind of behavior is due to birefringent nature of liquid crystal phase. As we increase the temperature, the molecular ordering decreases and this birefringent nature becomes less significant and after the isotropic temperature, the Δn vanished and the sample behave like any ordinary organic liquid.

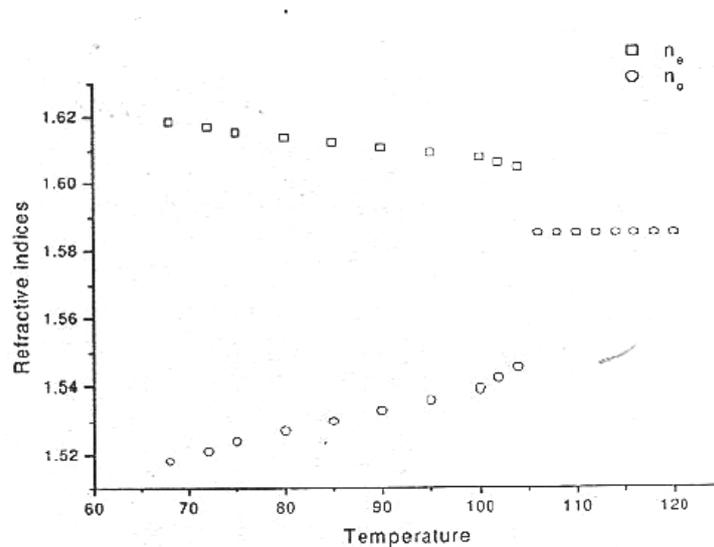


Fig. 1.4 : Variation of Refractive indices with temperature

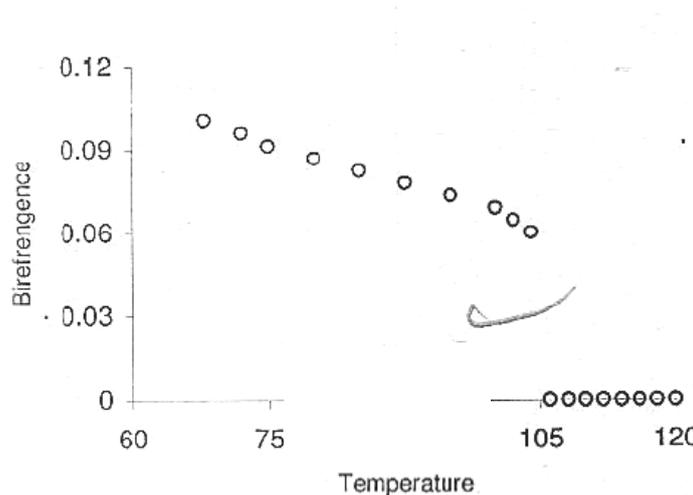


Fig. 1.5: Variation of Birefringence with temperature

To calculate the order parameter we have used birefringence values of the sample and Vuks approach. The variation of microscopic order parameter with temperature is shown in Figure 1.6, It is maximum in crystalline phase and as we increase the temperature the order parameter (S) decreases and becomes zero after the SmA to isotropic phase transition temperature i.e. the molecular order in the sample gets extinguished.

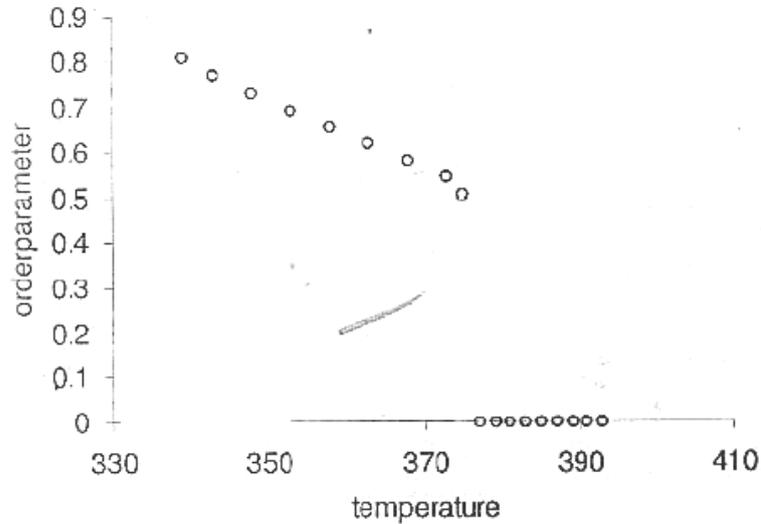


Fig. 1.6: Variation of order parameter with temperature

Figure 1.7 shows variation of percentage optical transmittance with reduced temperature ($T_c - T$). The value of optical transmittance increases first slowly with increase in temperature and then it increases near the SmA to isotropic phase transition temperature and as soon as the sample goes into isotropic phase the optical transmittance achieves its maximum value i.e. nearly 92% and after that it becomes constant with respect to increment in temperature.

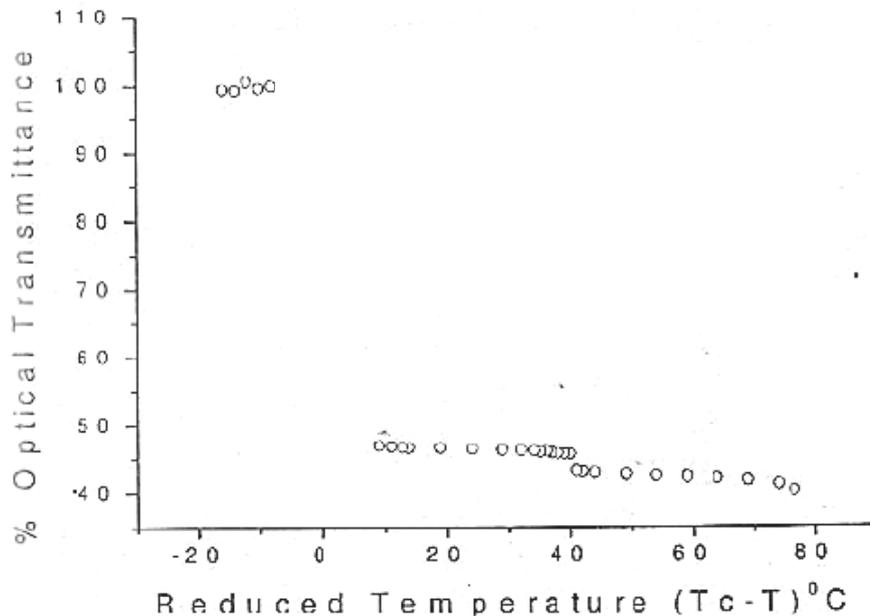


Fig. 1.7: Variation of % optical transmittance with reduced temperature

CONCLUSION

The order parameter decreases as we move from crystalline to isotropic phase by increasing temperature. The variation of order parameter is 0.8 to 0.45 in smectic phase while its value is zero in isotropic phase.

However, some liquid crystal phases are relatively recent discoveries and are more rarely encountered. Although such novel liquid crystal phases can usually be identified by optical microscopy accordingly, just as the field of liquid crystals draws on the expertise of scientists from many disciplines, the identification of mesophases requires a wide range of techniques to identify and classify fully the different structure of the various mesophases. As the identification techniques become more sophisticated, more novel mesophases will be discovered, possibly paving the way for the development of more technological applications.

REFERENCES

1. J.E. Goldmahr and J.A. Castellano. "Electro-optical compositions and devices, Patent 3540, 796, filed Marc. **31** (1967), issued Nov. **17**, (1970).
2. RCA announces breakthrough in liquid crystal field ; demonstrates thin screen displays of print, pictures, moving images, presented at the RCA Press Conf., New York, May **28**, (1968).
3. George Heilmeyer. The liquid crystal display Wall Street J. May **24**, (1993).
4. B. Bahadur Mol. Cryst. Liq. Cryst. 109 I (1984).
5. B. Kieser, D. Pauluth & G. Gauglitz, *Analyt. Chem. Acta.*, **434** 231 (2001).
6. S. Sato. *Optical Rev.* **6**, 471(1999).
7. M. Sutkowski, M. Kujawiska. *Optics and Lasers in Engineering*, **33**, 191(2000).
8. C.R. Smith, D.R. Sabatina & J.J. Baisner. *Experiments in Fluids*, **30**, 190 (2001).
9. H.J. Eichler, R. Elschner & G. Heppke et al. *Appl. Phys. B. Laser and Optics*, **61**, 59(1995).
10. Li F. Mukohzaka & N. Yoshida et al. *Optical Rev.* **5**, 174(1998).
11. R.K. Sarna, B. Bahadur & V.G. Bhide, *Mol. Cryst. Liq. Cryst.* **51**, 117(1979).
12. Maier and A. Saupe, *Z. Naturforschg.*, **Vol. 14a**, p. 882(1959) and **Vol. 159**, 287(1960).
13. P.J. Wajtowicz. "Generalized Mean Field theory of Nematic Liquid Cryst."
14. R. William. "Optical Rotatry Power and Linear Elctron-optoic effect in nematic liquid crystals of p-azoxyanisole. " *J. Chem. Phys.*, **Vol. 50**, p. 1324.
15. S. Chandrasekhar and N.V. Madhusudana. "Molecular stactical theory of nematic liquid crystal, " *Acta Cryst.*, **Vol. A27**, 303 (1971).
16. L.D. Landau and e.M. Lifshitz, *Statistical Physics*, 344, Pergamon Press Ltd., London (1958).
17. F.V. Allan, *Information Display*, **10**, 14(1983).
18. H.S. Cole Jr. and S.A. Fri. *Chem. Phys.*, **68**, 896(1978).
19. J. Billard, *Cr. Acad. Sci., Paris, B.* **274**, 333(1972).
20. Billard, *J. Bull. Soc. fr. Miner, Cristallogr.* **95**, 206(1972).
21. G.W.Gray, *Molecular structure and the properties of liquid crystals*, Academic Press, London (1962) ; the review of Browns, G.H. and Show, G.H. *Chem. Rev.*, **57**, 1049 (1957) and the list of mesomorphs established by Kast, W. Landolt-Bornstein, 6th edn., **Vol. II** part 2a, 2566, Springr, Berlin (1960).
22. Schroder, *J. Phys. Chem. Chem. II*, 449(1893) ; Van Laar, *J.J.Z. Phys. Chem.* **63**, 216(1908) ; **64**, 257(1908).
23. J. Billard, and Domon M. to be published
24. Jignesh Gandhi and James E. Anderson. Experimental measurement of Cauchy values for χ_n of Nematic Liquid Crystals. *SID* **02** 582 Digest (2002).
25. V.P. Arora and V.K. Agarwal. *J. Physics Soc. Japan*, **45**, 1360(1978).
26. S. Sen, P. Brahma, S.K. Roy, D.K. Mukherjee and S.B. Roy, *Mol. Cryst. Liq. Cryst.* 100, 327(1983).
27. Technical Information sheet from E-Merk and BDH (1992).
28. N.V. Madhusudana. *Mol. Cryst. Liq. Cryst.* **59** 117(1980).