Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Comparative Study of the Optical Properties of two Mesogenic Mixtures Containing Identical Moieties

Dutta Gupta [a], Anuradha Mukhopadhyay [a] & S. K. Roy [b]

[a] Department of Physics, Jadavpur University, Kolkata, India

[b] Department of Spectroscopy, Indian Association for the Cultivation of Science, Kolkata, India

Version of record first published: 03 Aug 2009

To cite this article: Dutta Gupta, Anuradha Mukhopadhyay & S. K. Roy (2009): Comparative Study of the Optical Properties of two Mesogenic Mixtures Containing Identical Moieties, Molecular Crystals and Liquid Crystals, 506:1, 77-86

To link to this article: http://dx.doi.org/10.1080/15421400902987446

Mol. Cryst. Liq. Cryst., Vol. 506, pp. 77–86, 2009

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400902987446

Comparative Study of the Optical Properties of two Mesogenic Mixtures Containing Identical Moieties

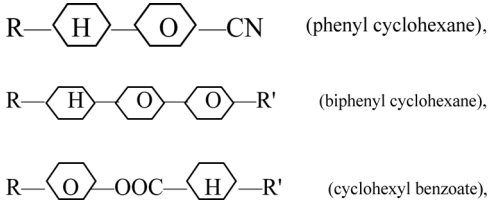
Dutta Gupta[1], Anuradha Mukhopadhyay[1], and S. K. Roy[2]
[1]Department of Physics, Jadavpur University, Kolkata, India
[2]Department of Spectroscopy, Indian Association for the Cultivation of Science, Kolkata, India

Optical properties of two mesogenic mixtures, code names ZLI 1221and ZLI 1291, possessing same constituents but exhibiting distinct nematic behavior, have been studied. Since both the mixtures possess identical moieties: phenyl cyclohexane, biphenyl cyclohexane and cyclohexyl benzoate, but in different proportions, and exhibit different mesogenic ranges, comparative study of their properties is of great interest. In this work we present a study of the thermal variation of their optical behavior. The variation of polarizability in terms of molecular weight has been obtained for both the mixtures and the thermal dependence of their orientational order parameters have been determined and compared.

Keywords: birefringence; mesogenic mixture; order parameter; polarisability

INTRODUCTION

The mesogenic mixtures ZLI 1221 and ZLI 1291 (code names) are known (Merck Ltd.) to contain the following moieties and exhibit the following phase transition temperatures:



Address correspondence to Anuradha Mukhopadhyay, Department of Physics, Jadavpur University, Kolkata 700032, India. E-mail: anuradha_mukhopadhyay@yahoo.com

where $R = C_nH_{2n+1}$, $R' = C_mH_{2m+1}$,

ZLI 1221 : Mixture1

$$\text{Solid} \xrightarrow{-11^\circ C} \text{Nematic} \xrightarrow{90^\circ C} \text{Isotropic}$$

ZLI 1291 : Mixture2

$$\text{Solid} \xrightarrow{-10^\circ C} \text{Nematic} \xrightarrow{107^\circ C} \text{Isotropic.}$$

The difference in the width of the nematic range and the enhancement of the nematic–isotropic phase transition suggests that the moieties though identical are present in different proportions in the two mixtures and affords a very good instance of the extent of tuning or tailoring of mesogenic behavior by varying proportional composition alone. We are, therefore, interested to explore the nature and degree of differences in mesogenic behavior of these two mixtures. The present work is concerned with the optical behavior of these two mixtures and their comparison. The orientational order parameters and their thermal variations have also been determined. Mesogenic mixtures containing two of the three moieties (phenylcyclohexane, biphenyl cyclohexane, and cyclohexyl benzoate) present in the above mixtures have been investigated [1–3]; these mixtures have the following codes: ZLI 1275, ZLI 1701, and ZLI 1800-000. Comparison has also been made with their properties and those of the present mixtures. No systematic study of the optical or dielectric properties of the present mixtures have been made to date.

EXPERIMENTAL METHODS

Optical Microscopy

In order to confirm the nature of the phase and the phase transition temperatures, optical microscopy of both the samples, mixtures 1 and 2, was undertaken prior to optical studies. Liquid crystal samples were taken on a clear glass surface, and a cover slip was used. The sample was then introduced into a hot stage (Mettler FP 82 HT) whose temperature was raised at the rate of 1°C/min during heating. A polarizing microscope (Leitz) fitted with crossed polarizer and having a magnification 150X was used for viewing the sample from room temperature to isotropic temperature range. Texture photographs of the sample were taken in the nematic phase.

Optical Studies

Optical studies were conducted using a He-Ne source (wavelength $\lambda = 633\,\text{nm}$) on the basis of the Chatelain–Wedge principle. Each sample was introduced into a glass prism of angle between 1°–2°. The prisms were formed with glass slides whose inner surfaces were treated with polyvinyl alcohol for planar surface alignment. The liquid sample was introduced into the prism in the liquid state at room temperature through the open edge of the prism, which was then sealed. The prism encapsulated in a sample holder whose temperature was regulated up to ±1°C with the help of a temperature controller was placed in an aligning magnetic field of 8 kGauss such that the direction of rubbing (along the prism edge) is along the magnetic field. The laser beam from the source was made incident on the sample through a hole in the sample holder, and the emerging beams (ordinary and extra ordinary) projected on a screen held several metres (5.0 m) away. The sample was taken through a number of temperature cycles in the presence of the magnetic field to ensure an aligned monodomain sample. Each sample was heated at the rate of 1°C/min to a temperature beyond its isotropic temperature and allowed to cool at the same average rate. From the changes in the patterns observed on the screen, the transition temperatures could be confirmed. They were found to be in agreement with the findings from the optical microscope study. From angular deflection measurements on the screen, the refractive indices n_e and n_o of the extraordinary and ordinary rays could be determined with knowledge of the prism angle. The prism angle was determined prior to the introduction of the sample by measuring the angular deviation of the laser beam reflected from the front and back surfaces of the prism. Measurements were taken of both the top and bottom ends of each of the circular spots (of ~0.6 cm in diameter) and mean of these used for calculation. Details of the experimental arrangement are given in [4].

To be able to determine the orientational order parameter, the polarizabilities α_e and α_o have to be determined for which the densities need to be measured. The density 'd' at various temperatures were obtained by introducing the weighed sample in a dilatometer, which was then placed in a heat bath. Measurements were made of the length of the sample column at intervals of 2°C, and the density of the material calculated. Using Vuks formula [5] viz

$$\frac{n_\gamma^2 - 1}{n^2 + 2} = \frac{4\pi}{3} N\alpha_\gamma$$

(γ is e or o, $n = n_{ave} = [n_e{}^2 + 2n_o{}^2]/3$ and N is the number of molecules per cc is given by $N = N_A d/M$, N_A is the Avogadro number, d the

density of the sample and M the molecular weight), α_γ could be determined only in terms of M, i.e., α_γ/M, since molecular weights are not known (percentage composition of the constituent moieties not given). However the orientational order parameter $\langle P_2 \rangle$ could still be ascertained using de Gennes expression [6] in the form

$$< P_2 >= \frac{(\alpha_e - \alpha_o)/M}{(\alpha_{\mathrm{II}} - \alpha_\perp)/M}$$

($\alpha_\parallel$ -$\alpha_\perp$)/M was determined by taking a modified approach to Haller's extrapolation [7] procedure and plotting ln $(\frac{\alpha_e}{M} - \frac{\alpha_o}{M})$ vs. In(T_C-T) and extrapolating the straight line thus obtained to T = 0, i.e., to ln T_c to obtain ($\alpha_\parallel$ -$\alpha_\perp$)/M from the intercept.

RESULTS AND DISCUSSIONS

Optical Microscopy

The transition temperatures observed from optical microscopy are as follows:

Mixture1 (ZLI 1221)

$$\text{Solid} - - - - > \text{Nematic} \underset{<-------}{\overset{89.2^\circ\text{C}}{---}} > \text{Isotropic},$$
$$88.5^\circ\text{C}$$

Mixture2 (ZLI 1291)

$$\text{Solid} - - - - > \text{Nematic} \underset{<-------}{\overset{106.5^\circ\text{C}}{---}} > \text{Isotropic}.$$
$$106.1^\circ\text{C}$$

The transition temperatures from nematic to isotropic phase are in close agreement with the quoted values (Merck Ltd.). Since there is no arrangement to cool the sample below room temperature, the crystalline to nematic transition temperatures could not be verified. Representive photographs of the nematic phase are presented in Figs. 1 and 2.

Optical Studies

The variation of the refractive indices n_e, n_o of mixtures 1 and 2 are given in Figs. 3 and 4, respectively. There is no distinctive difference between the n_e, n_o variation of the two mixtures. $n_{ave} = (n_e^2 + 2n_o^2)/3$ is almost constant throughout the nematic range and continuous with the respective n_{iso} values at T_{NI} for both the mesogens. This behavior

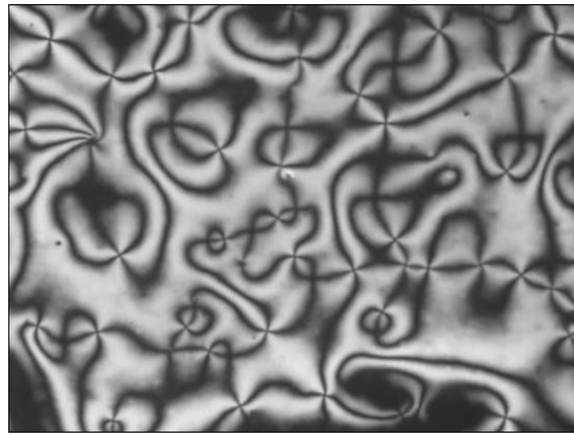


FIGURE 1 Schlieren texture of the nematic phase of mixture 1 showing four brushes centred at several points at 82°C during cooling.

is generally attributed to nonpolar compounds such as di-alkyl azobenzene [8], and it is only natural to expect that two mesogens having the same constituents, will not differ on this aspect. However a lowering of the optical anisotropy is observed on comparing the Δn values of mixture 2 with that of mixture 1, the experimental Δn values being 0.127 (30°C) and 0.147 (30°C), for mixtures 1 & 2 respectively. The quoted values (supplied by Merck Ltd.): 0.13 and 0.15, respectively

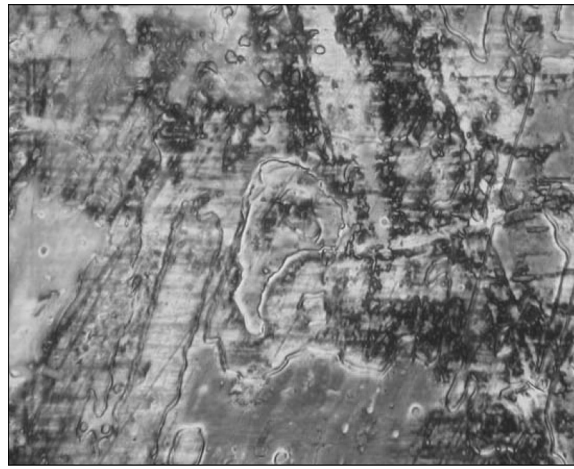


FIGURE 2 Nematic phase of mixture 2 at 48.5°C during cooling.

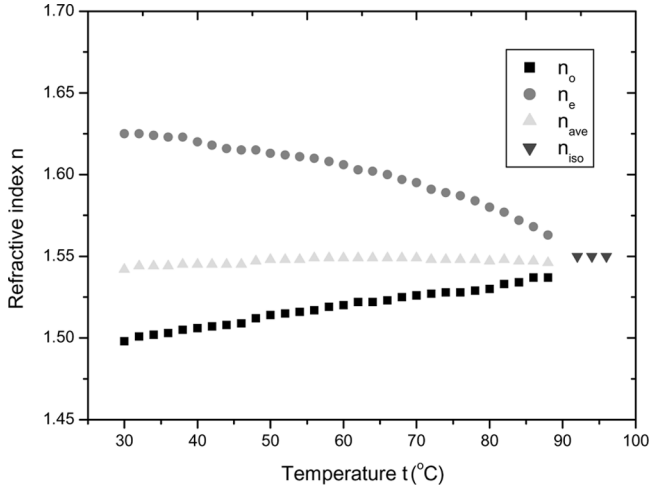


FIGURE 3 Thermal variation of refractive indices of mixture 1.

(temperatures not specified) compare very well with our experimental findings. n_{ave} values are also close; being slightly greater for mixture 2 ($\sim$1.56) than mixture 1 ($\sim$1.55). The behavior of n_{ave} is similar for mixtures ZLI 1275 (phenyl cyclohexane, cyclohexyl phenyl carboxylate, and cyclohexyl benzoate) and ZLI 1701 (phenyl cyclohexane, biphenyl cyclohexane, and cyclohexane carboxylate) which contain two of the

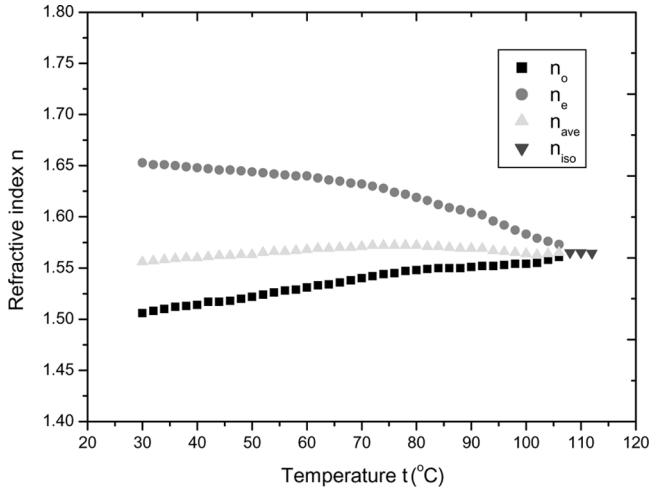


FIGURE 4 Thermal variation of refractive indices of mixture 2.

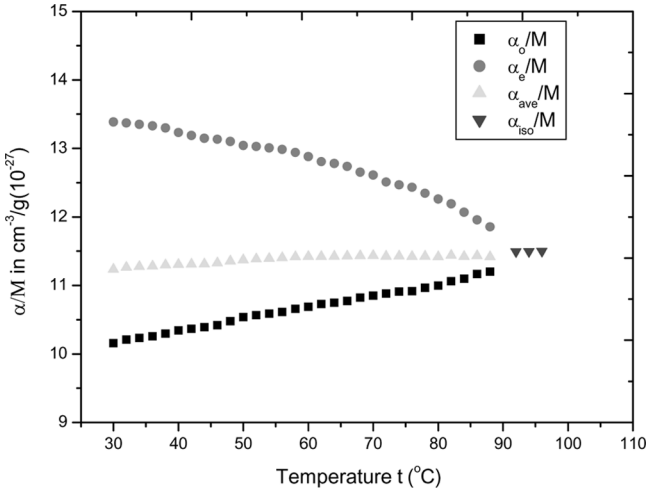


FIGURE 5 Thermal variation of α/M of mixture 1.

three moieties in the present compounds; both the mixtures show no discontinuity of n_{ave} with n_{iso} at T_{NI} and remain fairly constant throughout the nematic range. For the mixture ZLI 1800-000 containing phenyl cyclohexane, cyano cyclohexane, and cyclohexane carboxylate, n_{ave} is discontinous with n_{iso} at T_{NI} [1] as is expected for molecules with polar cyano groups [9]. The estimated error in determination of refractive index is about 1%.

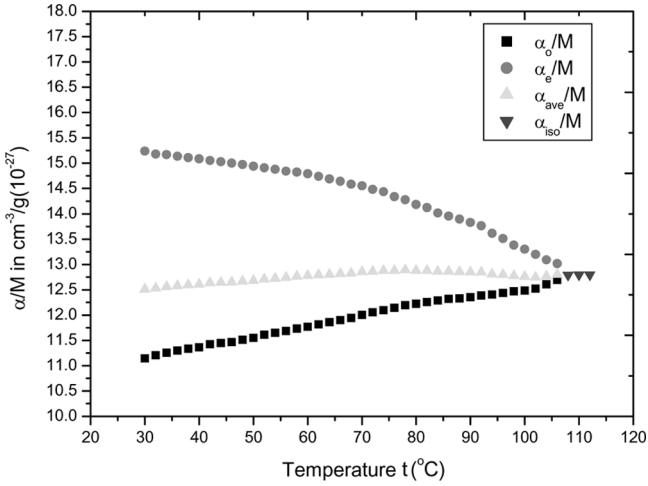


FIGURE 6 Thermal variation of α/M of mixture 2.

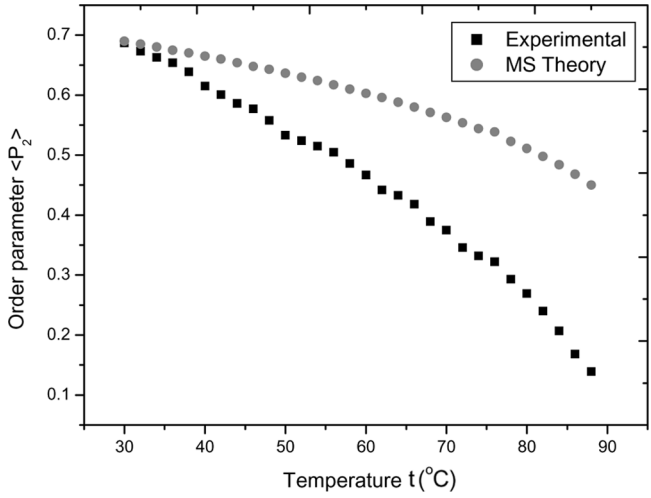


FIGURE 7 Thermal variation of order parameter of mixture 1.

The variation of polarizability in terms of molecular weight, i.e., α_γ/M for the two compounds, are shown in Figs. 5 and 6, respectively. α_{ave}/M is greater for mixture 2 ($\sim 12.5 \times 10^{-27} cm^{-3}/g$ (30°C)) than for mixture 1 ($\sim 11.2 \times 10^{-27} cm^{-3}/g$ (30°C)). Figures 7 and 8 depict the variation of the orientational order parameter $\langle P_2 \rangle$ with temperature for the two mixtures. Though $\langle P_2 \rangle_{mixture2}$ is slightly greater than

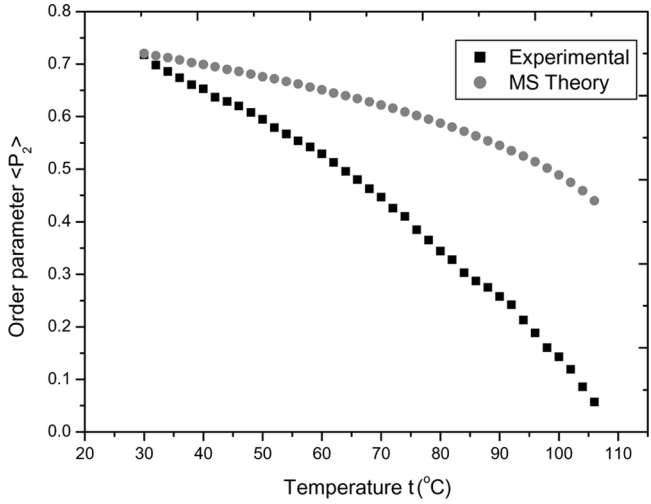


FIGURE 8 Thermal variation of order parameter of mixture 2.

$\langle P_2 \rangle_{\text{mixture1}}$, the variations show more or less similar trends, falling steeply as the isotropic temperature is approached; the decline in $\langle P_2 \rangle_{\text{mixture1}}$ being less steep as compared to mixture 2. In both cases, Maier–Saupe [10] theoretical values ($\langle P_2 \rangle_{\text{M.S}}$) have been plotted. The experimental $\langle P_2 \rangle$values show a trend very different from $\langle P_2 \rangle_{\text{M.S.}}$ in both cases suggesting that the basic assumption of cylindrical symmetry of the constituent molecules in an average field is not a valid assumption in this case of mesogenic mixtures. In case of ZLI 1275, $\langle P_2 \rangle_{\text{exp}}$ variation had been found to be very close to theoretical $\langle P_2 \rangle_{\text{M.S.}}$ values [2]. For mixtures ZLI 1701, $\langle P_2 \rangle_{\text{exp}}$ remained almost constant through the nematic range and close to Maier–Saupe values except near the transition, whereas for ZLI 1800-000 $< P_2 >_{\text{exp}}$ decreased, but very gradually always remaining higher than $\langle P_2 \rangle_{\text{M.S.}}$[1]. Figures 9(a),(b), and (c), showing the variation of $\langle P_2 \rangle_{\text{exp}}$ and corresponding $\langle P_2 \rangle_{\text{M.S.}}$, for the above three mesogenic mixtures,

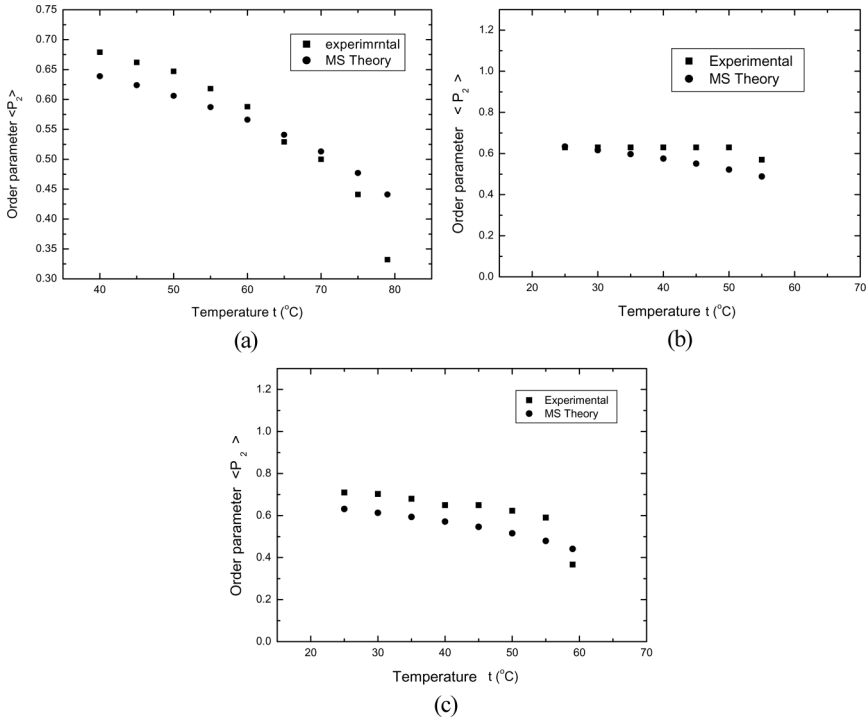


FIGURE 9 (a) Thermal variation of order parameter of mixture ZLI 1275; (b) Thermal variation of order parameter of mixture ZLI 1701; (c) Thermal variation of order parameter of mixture ZLI 1800-000.

have been included here from our previous work [1,2] for easy comparison. The estimated error in determination of order parameter is about 3%.

CONCLUSION

The above study deals with an instance of how property tuning may be achieved by variation of proportional composition alone. In the present case, though the mesogenic range of mixture 2 has been enhanced in comparison to mixture 1 indicating greater thermal stability ,it cannot be said that there is significant difference in the nature of variation of the orientational order parameter with temperature. However, at any particular temperature within the common nematic range, mixture 2 has a higher order parameter than mixture 1 indicating greater functional performance. Optical anisotropy is also reduced for mixture 1 in comparison to mixture 2. Both the mixtures exhibit nematic phase below 0°C (which is lower than the crystalline to nematic transition of the constituent moieties) suggesting that the mixtures may be used to advantage in devices in the low temperature region.

REFERENCES

[1] Chakraborty, S., Mukhopadhyay, A., & Roy, S. K. (2008). *Mol. Cryst. Liq. Cryst.*, *487*, 13.
[2] Chakraborty, S., Mukhopadhyay, A., & Roy, S. K. (2008). *Mol. Cryst. Liq. Cryst.*, *493*, 31.
[3] Chakravorty, S., Mukhopadhyay, A., & Roy, S. K. (2006). *Mol. Cryst. Liq. Cryst.*, *460*, 117.
[4] Bhowmick, K., Mukhopadhyay, A., & Mukherjee, C. D. (2003). *Phase Transition*, *76*(7), 671.
[5] Vuks, M. F. (1971). *Optics and Spectroscopy*, *20*, 193.
[6] deGennes, P. G. (1971). *Mol. Cryst. Liq. Cryst.*, *12*, 193.
[7] Haller, J., Huggins, H. A., Linianthal, H. R., & McGure, T. R. (1973). *J. Phys. Chem.*, *77*, 950.
[8] de Jue, W. H. & Lathouwers, T. W. (1974). *Z. Natureforsch, 29a*, 905.
[9] Madhusudana, N. V. & Chandrasekhar, S. (1973). *Proc. Int. Conf. Liq. Cryst., Bangalore*, 427.
[10] Maier, W. & Saupe, A. (1959). *Z. Naturforsch*, *14a*, 822.