Effect of pressure on liquid crystal dimers

K. L. Sandhya[a]; D. S. Shankar Rao[a]; S. Krishna Prasad Corresponding author[a]; Uma S. Hiremath[a]; C. V. Yelamaggad[a]

[a] Centre for Liquid Crystal Research, Jalahalli, Bangalore 560 013, India

Online publication date: 19 May 2010

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis
Taylor & Francis Group

Effect of pressure on liquid crystal dimers†

K. L. SANDHYA, D. S. SHANKAR RAO, S. KRISHNA PRASAD*,
UMA S. HIREMATH and C. V. YELAMAGGAD

Centre for Liquid Crystal Research, Jalahalli, Bangalore 560013, India

We report high pressure investigations on a homologous series of liquid crystalline dimeric molecules in which the terminal chain length is kept constant but the length of the methylene spacer connecting the two mesogenic units is varied. We find that unlike the nematic–isotropic transition temperature and associated entropy change, there is no alternation in the slope of the nematic–isotropic phase boundary in the pressure–temperature plane as a function of the length of the spacer group in the molecule. By applying the Clausius–Clapeyron equation we conclude that the volume change at the transition should exhibit a strong odd–even effect. Measurements on the shortest homologue of the series, which is non-mesomorphic, show the expected result that the application of pressure induces mesomorphism in non-mesomorphic compounds.

1. Introduction

A liquid crystalline dimer molecule consists of two conventional mesogenic groups linked via a flexible spacer, which is generally an alkyl chain [1]. Although first prepared in the 1920s, only recently have they attracted much attention, due to their quite different properties when compared with conventional low molar mass liquid crystals, and their ability to act as model compounds for semi-flexible main chain liquid crystal polymers. Indeed, they are the simplest oligomers containing only two repeating blocks connected through a flexible linkage. Liquid crystalline dimers are classified into two broad categories: symmetric dimers in which the two mesogenic units are identical, and non-symmetric dimers containing two different mesogenic units. The liquid crystalline properties and the structure of different mesophases of these types of dimer are found to be dependent on the number of carbon atoms in the spacer. The nematic – isotropic (N–I) transition temperature is found to exhibit a dramatic alternation as the parity of the spacer changes from odd to even. However, the alternation is attenuated as the spacer increases in length. In contrast, the alternation in the entropy change associated with the N–I transition is essentially unattenuated; at least for spacers containing up to twelve carbon atoms. Furthermore, the entropy

†Article based on a poster presentation at the International Conference on High Pressure Science and Technology, New Delhi, India Nov.26–30, 2001. The presentation was adjudged as the best poster at the conference.

*Author for correspondence; e-mail: skprasad1@yahoo.com

change at the N–I transition for dimers with odd spacers is comparable to that of monomers while for even spacers it is typically three times larger. This behaviour suggests that the orientational order for even spacer dimers should be significantly greater than that for odd spacer dimers.

It is known [2–5] that for both low molecular mass liquid crystals as well as for main chain polyesters, the slope of the phase boundary dT/dP, alternates with respect to the chain length in the same sense as the transition temperature (T_{NI}) itself. It is now of interest to carry out high pressure studies [6] on dimeric compounds belonging to a homologous series to see if similar behaviour is observed. In this paper we investigate the effect of pressure on the propyl to undecyl members of the homologous dimer series the materials α,ω-bis (4′-*n*-butylazobenzene-4-oxy)alkanes.

2. Experimental

The general molecular structure of the compounds studied is given in figure 1; we designate these compounds as **m4**, **m5**, **m6**, etc., where the numeral indicates the number of methylene units in the spacer. These compounds have been prepared using a procedure similar to that reported by Blatch and Luckhurst [7]. All the homologues **m4** to **m11** exhibit the nematic mesophase. In addition, a smectic A phase is seen for the **m4**, **m5**, **m6** and **m8** homologues; this is enantiotropic in nature for **m4** and **m6**, and monotropic for the other two. Figure 1 also shows a plot of the transition temperatures versus spacer length. As expected, there is a large alternation in the values for the odd and even

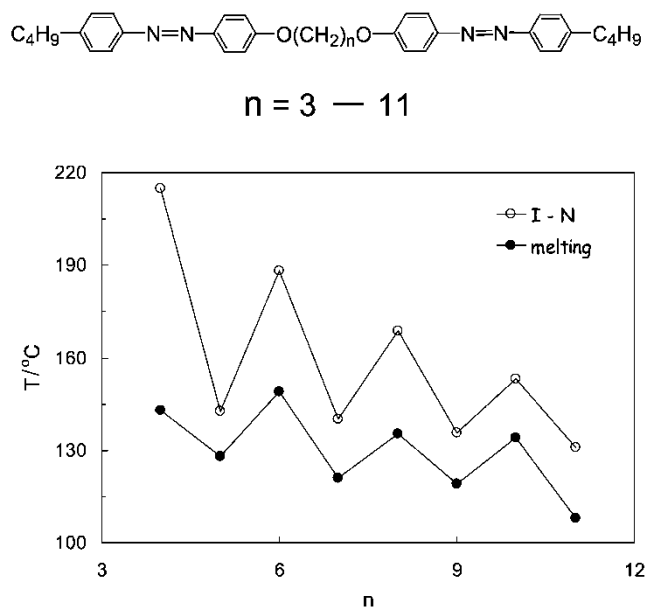C_4H_9—⟨⟩—N=N—⟨⟩—O(CH$_2$)$_n$O—⟨⟩—N=N—⟨⟩—C_4H_9

n = 3 — 11

Figure 1.   Dependence of the transition temperature on the number of methylene units, n, in the alkyl spacer of the series studied. Note the large odd–even effect observed for the nematic–isotropic transition temperatures: For the sake of clarity the smectic A–nematic transition temperatures are not shown.

members. This is true for both the melting and clearing point transitions, although the magnitude is large for the latter.

Pressure studies were carried out using an optical high pressure cell, details of which are described in an earlier paper [8]. Essentially it consists of a sample sandwiched between optically polished sapphire rods enclosed in an elastomeric tube. Low viscosity oil was used as the pressurizing medium. At different fixed pressures the intensity of a He-Ne laser beam transmitted through the sample was monitored as a function of temperature with the help of a photodiode with a built-in amplifier. The sample pressure was measured using a precision Heise gauge. The experiments were always conducted along isobars and in the heating mode, i.e. keeping the pressure constant at any desired value and increasing the sample temperature at a constant rate of $\sim 1°C\,min^{-1}$. A PC handled the data acquisition and control of the experiment. For optical microscopy applications a long focus stereo microscope (Leica MZ8) was employed.

3.   Results and discussion
3.1. *The N–I transition*
Figure 2 shows the raw trace of the temperature variation of the transmitted intensity obtained for the **m7** dimer at a pressure of $\sim 1.7\,kbar$. Similar traces
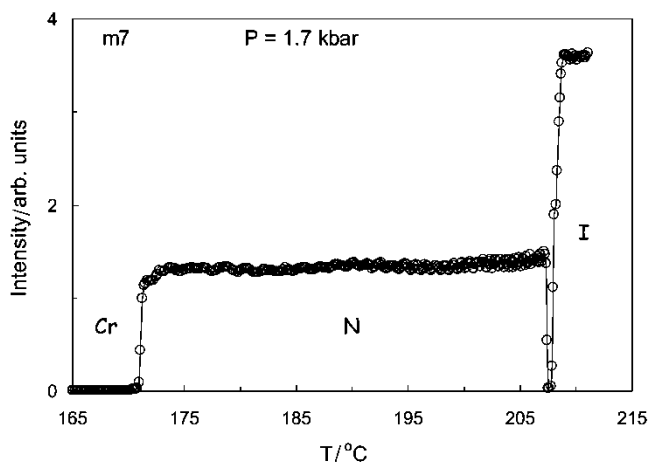

Figure 2.   Representative raw isobaric trace of the laser transmission as a function of temperature obtained for the dimer **m7** showing abrupt variations in the transmitted intensity at temperatures corresponding to the melting (Cr–N) and clearing (N–I) points. The line is meant as a guide to the eye.

were obtained at all pressures and for the different compounds studied here. The abrupt variations in the transmitted intensity in an otherwise smooth background mark the occurrence of phase transitions, viz. crystal to nematic and N–I transitions. The pressure–temperature (P–T) diagrams obtained for one odd (**m9**) and one even (**m10**) dimer, are shown in figures 3 and 4, respectively. Two salient features observed are: firstly, for both compounds the slope, dT/dP, is slightly larger for the N–I transition than for the melting transition.
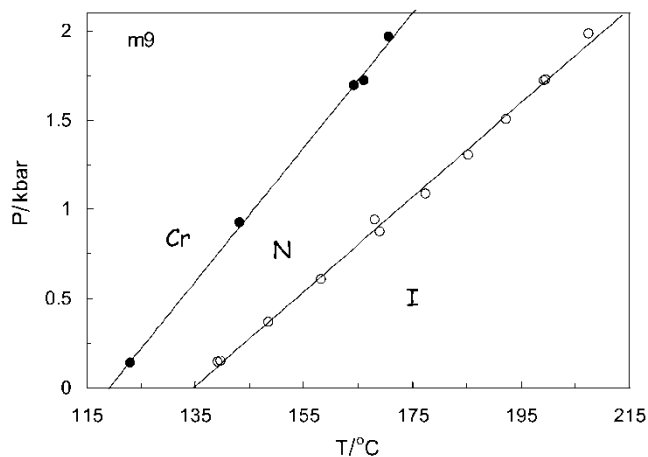

Figure 3.   Pressure–temperature phase diagram for the **m9** dimer having an odd number of methylene groups in the spacer unit. Note that the pressure dependence of the N–I transition is greater than that of the melting line. Consequently, the temperature range of the nematic phase increases with increasing pressure.
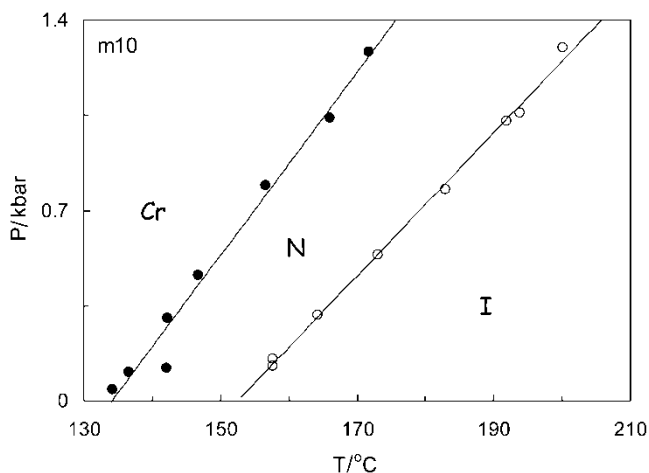
Figure 4. Pressure–temperature diagram for the **m10** dimer with an even number of methylene groups in the spacer unit. The pressure behaviour is similar to that observed for the **m9** dimer shown in figure 3.

In consequence, the temperature range of the nematic phase increases slightly with increasing pressure; this enhancement in the temperature range of the nematic phase is seen for all the dimers studied here. Secondly, and at least on a qualitative level, the slopes of the corresponding phase boundaries appear to be the same for both dimers. The N–I boundary obtained for all the dimers has been plotted in figure 5 and they appear nearly parallel to one another.

The slope dP/dT of the N–I boundary was determined at room pressure (1 bar) as a function of the
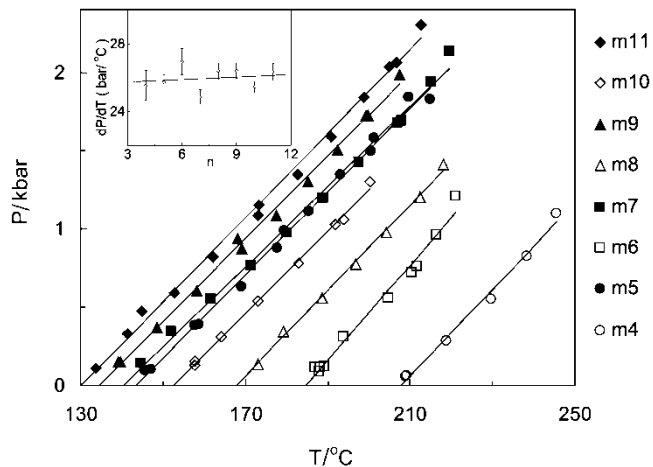

Figure 5. Plot showing the N–I boundaries of the all the (**m4** to **m11**) homologues studied here. Note, particularly, the similarity in the slopes for the odd and the even members. The inset shows the value of the slope dP/dT of the N–I phase boundary as a function of the spacer length. Within the error limits of the determination of the slopes, there is no systematic dependence on the spacer length.

spacer length of the dimer molecule by fitting the (P,T) data to a straight line. This data, shown in the inset of figure 5 clearly shows that the value of dP/dT is influenced by neither the parity nor the length of the spacer. This is surprising, particularly in the light of measurements made on a homologous series of polyesters [5]. In these main chain polymers, having regularly alternating 2,2′-dimethoxyazobenzene mesogenic moieties and alkanedicarboxylic acid spacers, a clear odd–even effect was observed in the dP/dT values of the N–I phase boundary, with the compounds having an odd number of spacers exhibiting a higher value than the even ones. It should also be recalled that such odd–even effects have also been reported for homologous series of monomeric compounds [2–4]. Thus the absence of an odd–even effect in the data for the dimers is puzzling.

As the N–I transition is first order in nature, its thermodynamic behaviour can be described by the Clausius–Clapeyron equation

$$dT/dP = (\Delta V/\Delta S) \qquad (1)$$

where ΔV and ΔS are the changes in volume and entropy at the transition, respectively. The ΔS values were calculated using the transition enthalpy ΔH data obtained from differential scanning calorimetry and are plotted in figure 6 as a function of the spacer length of the dimers. The absolute values of ΔS and the magnitude of the alternation obtained are comparable to those seen for the α,ω-bis (4′-n-cyanobiphenyl-4-yloxy)alkane series [1]. The alternation of ΔS and also of T_{NI} is generally attributed to the dependence of the molecular shape on the parity of the spacer considered in
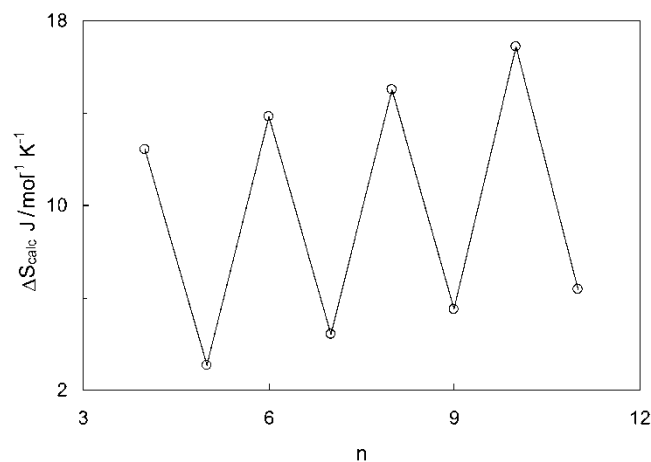

Figure 6. Dependence of the N–I transition entropy on the number of methylene units, n, in the alkyl spacer of the series studied. Unlike the behaviour seen for the transition temperature, the length of the spacer unit does not affect the magnitude of the alternation in the transition entropy.

the all-*trans* conformation. A simple molecular model depicting the molecules in the all-*trans* configuration shows that the dimer with an even number spacer will have an overall rod-like shape. In contrast, the odd membered dimer will have a significantly bent structure (see figure 7). As the rod-like structure is more conducive to the formation of the nematic phase or at least will enhance the orientational order of the system, it will result in a larger entropy change across the N–I transition.

Molecular models developed on the basis of these ideas have been quite successful in explaining the properties of dimeric molecules [1]. Using the experimentally determined values of dT/dP and ΔS, ΔV was calculated using equation (1) and is plotted as a function of the spacer length in figure 8. Again, a significant alternation is observed in the values as the parity of the spacer changes from odd to even. Furthermore, the values for the odd members are comparable to those for the homologues of the 4,4′-dialkoxyazoxybenzenes, a structurally very similar monomeric series, while the even members have values that are a factor of 3 to 4 higher. The measured data for the 4,4′-dialkoxyazoxybenzenes itself showed an alternation, although of a much smaller magnitude than calculated here [9]. Such a large difference between the odd and the even homologues of the dimer series could perhaps be due to the shape factor discussed already. The odd membered compounds having a bent structure should have a
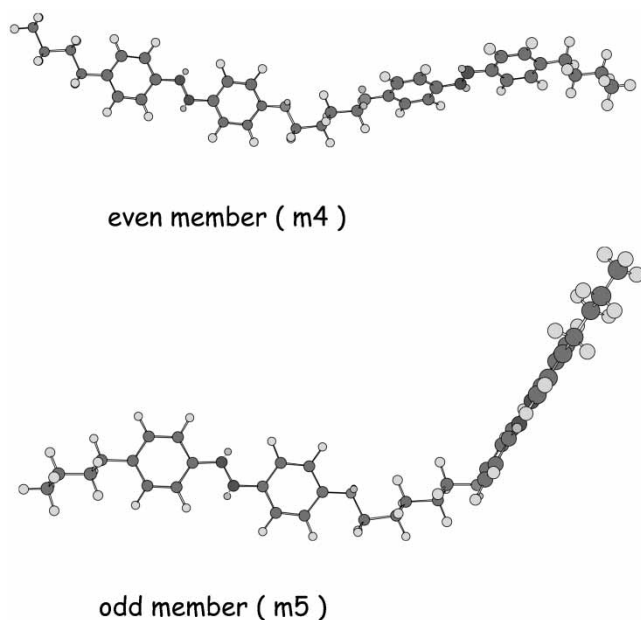

Figure 7. Energy minimum configurations for even (**m4**) and odd (**m5**) dimers highlighting the fact that the shape of the molecule significantly depends on the parity of the spacer unit.
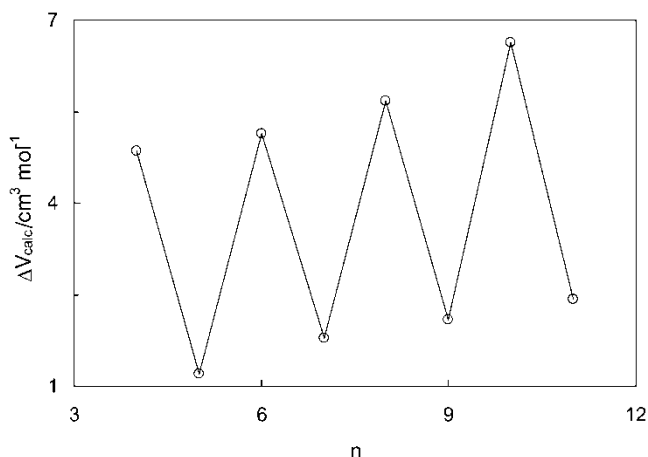

Figure 8. Dependence of the volume change at the N–I transition, calculated using the Clausius–Clapeyron equation, on the number of methylene units, n, in the alkyl spacer.

smaller volume change across the transition than the rod-like even membered compounds. Actual measurements of the volume change in the dimeric series will shed more light on this issue.

3.2. *Pressure-induced mesomorphism*

Perhaps the most significant of the early results on high pressure investigations in liquid crystals was the prediction and observation of pressure-induced mesomorphism, i.e. the induction of liquid crystalline behaviour at high pressure in materials which do not form liquid crystals at atmospheric pressure [10]. The first such phase diagram reported was for 4-methoxybenzoic acid, a compound that is non-mesomorphic at room pressure, but shows two pressure-induced mesophases at higher pressures [10]. In order to see whether dimeric materials also show similar pressure-induced mesomorphism, we performed high pressure investigations on **m3**. This compound, having three methylene units in the spacer is non-mesomorphic at atmospheric pressure. Figure 9 shows the raw traces of the temperature-dependent transmitted intensity at two different pressures. At a pressure of 0.9 kbar, the material directly transforms from the crystalline to the isotropic phase just as at room pressure. However, the run at 2.24 kbar shows the appearance of a new phase—a pressure-induced phase. To ascertain the nature of the induced phase we undertook optical microscopic observations. The schlieren texture seen close to the clearing point transition, and the director fluctuations observed, confirm that the pressure-induced phase is indeed the nematic phase. The P–T phase diagram obtained for this compound is shown in figure 10. It is seen that the
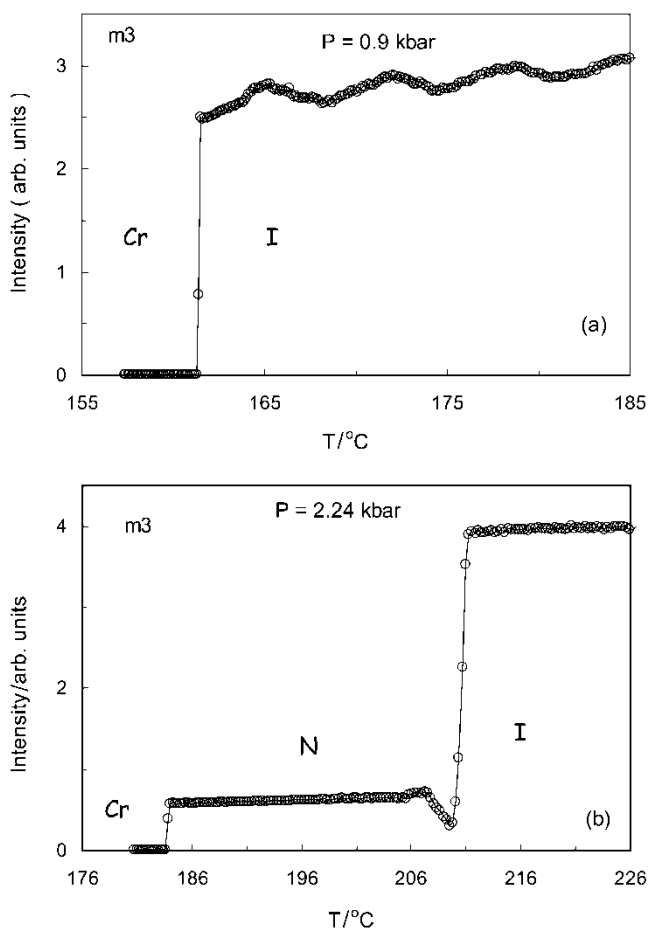
Figure 9. Raw traces of the laser trasmission as a function of temperature at two pressures for **m3**: (*a*) 0.9 kbar, (*b*) 2.24 kbar. The **m3** dimer is non-mesomorphic, having a direct transition from the crystal to the isotropic phase at lower pressures (*a*), but at higher pressures the nematic phase is induced (*b*).
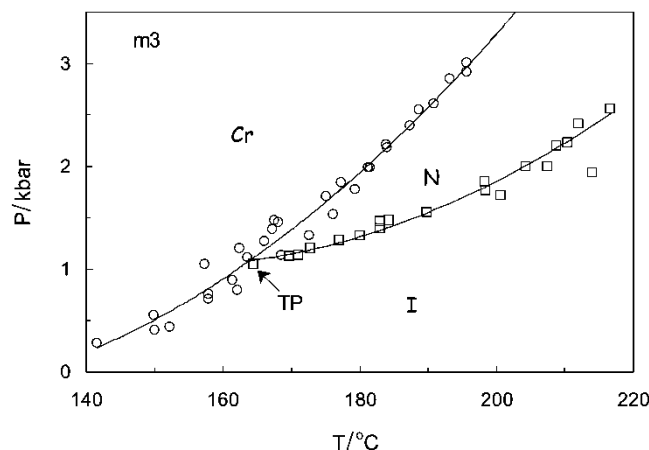

Figure 10. Pressure–temperature diagram for the **m3** dimer, showing the appearance of the nematic phase above a pressure of 1 kbar. Since all the three phase boundaries meeting at the point are first order in nature the point is a simple triple point (TP).

room pressure exhibits a pressure-induced nematic phase.

phase sequence is crystal–isotropic at pressures below 1.1 kbar, whereas above it the nematic phase intervenes between the two phases. This leads to a crystal–nematic–isotropic meeting at a pressure of 1.1 kbar. Since all the three transitions involved are first order in nature the meeting point is a triple point.

4. Summary

We have carried out high pressure investigations on a homologous series of symmetric dimeric compounds. The study shows that although the transition temperature and the entropy change associated with the N–I transition exhibit large odd–even effects characteristic of dimeric compounds, the slope of the N–I phase line in the pressure–temperature plane is not influenced either by the parity or by the length of the spacer. The shortest homologue of the series, which is non-mesomorphic at

References

[1] For a review article see, for example, IMRIE, C. T., and LUCKHURST, G. R., 1998, *Handbook of Liquid Crystals*, edited by D. Demus, J. W. Goodby, G.W. Gray, H. W. Spiess and V. Vill (Weinheim: Wiley-VCH), p. 801.

[2] IMRIE, C. T., and HENDERSON, P. A., 2002, *Curr. Opinion. Coll. Inter. Sc.*, **7**, 298.

[3] FEYZ, M., and KUSS, E., 1974, *Ber. Bunsenges. Phys. Chem.*, **78**, 834.

[4] SHASHIDHAR, R., and VENKATESH, G., 1979, *J. de Physique*, **40**, C-396.

[5] HERMANN, J., KLEINHANS, H. D., and SCHNEIDER, G. M., 1983, *J. chim. Phys.*, **80**, 111.

[6] RAJA, V. N., SHASHIDHAR, R., CHANDRASEKHAR, S., BLUMSTEIN, A., BLUMSTEIN, R. B., and KUMAR, S., 1988, *Mol. Cryst. liq. Cryst.*, **155**, 521.

[7] MAEDA, Y., FURUYA, H., and ABE, A., 1996, *Liq. Cryst.*, **21**, 365.

[8] BLATCH, A. E., and LUCKHURST, G. R., 2000, *Liq. Cryst.*, **6**, 775.

[9] SHANKAR RAO, D. S., GUPTA, V. K., KRISHNA PRASAD, S., MANICKAM, M., and KUMAR, S., 1998, *Mol. Cryst. Liq. Cryst.*, **319**, 193.

[10] TRANSFIELD, R. V., and COLLINGS, P. J., 1982, *Phys. Rev. A.*, **25**, 2744.

[11] CHANDRASEKHAR, S., RAMASESHAN, S., RESHAMWALA, A. S., SADASHIVA, B. K., SHASHIDHAR, R., and SURENDRANATH, 1975, *Pramana Suppl.* **1**, 117; Shashidhar, R., and Chandrasekhar, S., 1975, *J.de Physique. Coll.*, C1, **36**, 49.