

OPTICAL AND ELASTIC PROPERTIES OF LIQUID CRYSTALS

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By

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DECLARATION

I hereby declare that the thesis was composed by me independently and that it has not formed the basis for the award of any Degree, Diploma, Associateship, Fellowship or other similar title.

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I certify that this thesis has been composed by Sri Lakshminarayana Moodithaya, K.P. based on investigations carried out by him at the Liquid Crystals Laboratory, Raman Research Institute, under my supervision. The subject matter of this thesis has not previously formed the basis of the award of any degree, diploma, associateship, fellowship or other similar title.



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Correction added to the thesis after submission

We have recently come to know that the extrapolation procedure mentioned in page vii of the Preface and page 112 of the thesis was proposed some years ago by Haller (see I. Haller, Progress in Solid State Chemistry, 10, 103 [1975]). As such we no longer claim that the extrapolation procedure is 'new'.

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PREFACE

This thesis describes the results of some experimental investigations carried out by the author on nematic liquid crystals. The main emphasis is on the study of mesogens whose molecules have the strongly polar cyano group.

The work reported here can be broadly classified into three parts.

- 1 The discovery of re-entrant behaviour in some pure mesogens at atmospheric pressure and the study of some optical and elastic properties of the 'normal' and the 're-entrant' nematic phases of these compounds and some binary mixtures (Chapters II, III and IV).**
- 2 The study of the optical and elastic properties of binary mixtures some of which exhibit induced smectic mesomorphism (Chapters V and VI).**
- 3 Observations of some new electrohydrodynamic patterns and electro-optic effects (Chapters VII and VIII).**

In chapter I, we give a general introduction to the subject of liquid crystals with particular reference to the optical and elastic properties of nematic liquid crystals.

Generally, when a mesogen exhibiting both nematic and smectic A phases is cooled the following sequence of phase transitions is observed*

Isotropic — Nematic — Smectic A — Crystal.

It was discovered by Gladis in 1975 that some binary mixtures of mesogenic compounds show a different sequence of phase transitions, viz.,

Isotropic — Nematic — Smectic A — Nematic — Crystal.

The nematic phase obtained on cooling the smectic A phase is called the re-entrant nematic phase. Gladis et al (1977) later observed that some pure compounds like 8 OOB exhibit the re-entrant nematic phase at elevated pressures. In the beginning of 1979, we discovered the occurrence of the re-entrant nematic phase in three pure compounds at atmospheric pressure. These compounds are (1) trans-4-n-decyloxy- α -methyl-4'-cyanophenyl cinnamate (10 OMOPC), (2) 4-cyanophenyl-3-methyl-4-(4-n-undecylbenzoyloxy)benzoate (11 CPMBB), and (3) 4-cyanophenyl-3-methyl-4-(4-n-dodecylbenzoyloxy)benzoate (12 CPMBB). The occurrence of the re-entrant phase was confirmed by microscopic observations, differential scanning calorimetry and miscibility studies. These are reported in chapter II.

We have also studied the phase diagrams of binary mixtures of these compounds with other mesogens. The phase diagrams are compared with the results of some recent thermodynamic theories (Heppke et al 1980, Billard 1980).

All the compounds exhibiting the re-entrant nematic phase consist of molecules having the cyano group almost along their long axes. In such compounds the neighbouring molecules have strong antiparallel correlations (Madhusudana and Chandrasekhar 1973). This, in turn, leads to a bilayer structure (Leadbetter et al 1975). It is presumed that subtle changes taking place in the bilayers are responsible for the occurrence of the re-entrant nematic phase (Chandrasekhar et al 1980).

The discovery of the re-entrant phenomenon in pure compounds at atmospheric pressure has opened up the possibility of many new experimental investigations. In an attempt to understand the re-entrant behaviour in liquid crystals, we have conducted a few experiments to determine the orientational order parameter s and the elastic constants.

In chapter III, we give the details of the measurement of s . It is very difficult to get good homogeneously aligned samples in the smectic A phase and in the nematic phase close to the smectic A-nematic (AN) transition points of the compounds under study. Hence s had to be determined by methods which make use of homeotropically aligned samples. One such method is the infrared dichroism method wherein an unpolarised radiation could be used (Kelker et al 1973, Fernandes and Venugopalan 1976). s was determined by this

method by measuring the dichroic ratio corresponding to the localised -CN stretching mode. However, this method has only limited accuracy due to certain inherent experimental limitations. Hence α was also determined by measuring birefringence. Since we could use only homeotropically aligned samples, a new method was adopted for the purpose. A light beam was incident at an oblique angle on the sample and the phase retardation produced by it was measured by using a quarter wave plate and a polariser. The order parameter was found to vary in a fairly smooth manner across both AN and AN_r (smectic A - re-entrant nematic) transition points.

Chapter IV deals with the Freedericksz transition technique of measuring the splay and bend elastic constants of nematic liquid crystals. The results of measurement of k_{33} of the normal nematic and re-entrant nematic phases of some compounds and mixtures are presented in this chapter. It was observed that in both the nematic phases k_{33} shows pretransitional increases as the transition to the smectic phase is approached.

The pretransitional increase in k_{22} could not be studied by the Freedericksz transition technique as this needs a homogeneously aligned sample. A light scattering experiment was conducted for the purpose. In an appropriate geometry, the intensity of the depolarised component of the light scattered from a homeotropically aligned sample is

proportional to $(\Delta n)^2/k_{22}$ where Δn is the birefringence. Experimentally, it was observed that as the sample was cooled, the intensity drops down to almost zero at the AN transition point, remains at the minimum value all along the smectic phase and rises rapidly at the AN_r transition point. This indicates the presence of pretransitional increases in k_{22} in both the normal and the re-entrant nematic phases. All these observations confirm that the phase obtained on cooling the smectic A phase is nematic and that St is similar in its properties to the normal nematic phase.

Commonly, when two nematogens are mixed together, the mixtures exhibit only the nematic mesophase. But when one of the components of the mixture consists of molecules having strong polar end groups along their long axes, the mixtures show 'induced smectic A' phase in some composition ranges (Park et al 1975; Oh 1977). We have studied the phase diagrams of three binary mixtures exhibiting induced smectic mesomorphism. These are (1) mixtures of 4-n-heptyl-4'-cyanobiphenyl (7 CB) and (2-hydroxy)-4-ethoxybenzylidene-4'-butylaniline (OH-EBBA); (2) mixtures of 4-cyanophenyl-trans-4'-n-heptylcyclohexane (POX-7) and OH-EBBA; and (3) mixtures of 7CB and 4,4'-diheptyloxyazobenzene (HOAB). The components of the first two mixtures show only the nematic mesophase, but the mixtures show induced smectic A (A_I) phase

in some range of compositions. In both the cases, the A_I N transition curves exhibit a peak. For higher concentrations of the cyano compound, the A_I and nematic phases coexist over fairly wide ranges of temperature. The third mixture, 7CB/HOAB also exhibits induced smectic mesomorphism. For some compositions of this mixture, the A_I phase goes over directly to the isotropic phase.

Engelen et al (1979) measured the layer spacing of a binary mixture exhibiting the A_I phase, as a function of composition. They found that the layer spacings of the mixtures roughly correspond to an appropriate average length of the molecules up to a certain concentration of the strongly polar component of the mixture. This composition roughly corresponds to the peak in the A_I N transition curve. With further increase in the concentration of the strongly polar component, the layer spacing increases rapidly approaching the bilayer spacing of the polar component. We have proposed a possible mechanism of formation of the A_I phase on the basis of the experimental results mentioned above.

For low concentrations of the strongly polar component (say, 7CB) the individual molecules of 7CB may be expected to be surrounded by the molecules of the other component (say, OH-EBBA). The 7CB molecules will polarise the neighbouring OH-EBBA molecules and this interaction would favour a collection of OH-EBBA molecules around a 7CB molecule giving rise to the

formation of a layered arrangement. Beyond a certain concentration of 7CB, the layered arrangement takes on long-range characteristics leading to the formation of the A_I phase. As the concentration of 7CB is increased further, some of the neighbours of a given 7CB molecule will be 7CB molecules themselves and beyond a certain concentration ($\sim 35\%$ of 7CB for 7CB/OH-EBBA system) which roughly corresponds to the peak in the A_I -N transition curve, a part of 7CB will retain the bilayer structure and consequently the layer spacing starts to increase. For these concentrations, the medium will consist of mixtures of bilayer and monolayer species.

We have measured the refractive indices of 7CB, OH-EBBA and two of their mixtures exhibiting the A_I phase, to find the temperature variation of the order parameter s . Knowing the refractive indices, the relative temperature variation of s can be determined. However, to find the absolute values of s , one should know the value of $\bar{\alpha}/\Delta\alpha$ where $\bar{\alpha}$ is the average polarisability of a molecule and $\Delta\alpha$ is the anisotropy in the polarisability of a perfectly ordered medium (with $s = 1$). For OH-EBBA, this data is not available. We have obtained this value from the relative temperature variation of s , following a new extrapolation procedure. In this, we have made use of the fact that if the NI transition were of second order, s would have continuously decreased to zero at a temperature $T_{NI}^* > T_{NI}$. We have assumed a relation of the form

$s = \left(\frac{T_{NI}^* - T}{T_{NI}^*} \right)^x$ where x is a positive index. From the temperature variation of the relative order parameter, the value of T_{NI}^* which gives the best fit to this relation was obtained and hence the temperature variation of absolute value of s was determined. This method makes use of the values of refractive indices corresponding to the entire range of nematic phase unlike the other extrapolation procedures (Haller et al 1973, Subramanyam et al 1974) wherein the data in only a relatively small temperature range away from T_{NI} could be used.

We have also determined k_{11} and k_{33} for the systems mentioned above. It was observed that for 7CB, $(k_{33}/k_{11}) > 1$ at temperature well below T_{NI} and it decreases to one as T_{NI} is approached. In OH-EBBA, $(k_{33}/k_{11}) < 1$ and is almost temperature independent. For mixture I (which has 16% 7CB), $(k_{33}/k_{11}) < 1$ at temperatures close to T_{NI} and it decreases to fairly low values (0.6) as the temperature is lowered. For the other mixture (II) which has 62% 7CB, k_{33}/k_{11} is slightly less than one close to T_{NI} and it increases slowly as the temperature is lowered. Both the mixtures show pretransitional increase in k_{33} as the A_I transition point is approached.

Some of these results can be understood in terms of Priest's (1973) theory. According to this theory, $(k_{33}/k_{11}) < 1$

usually implies that the order parameter $\bar{P}_4$ is negative where $\bar{P}_4$ is the average fourth order Legendre polynomial. This is probably the case in OH-EBBA. The still lower value of k_{33}/k_{11} in mixture I is probably caused by the formation of monomolecular layers containing 7CB and OH-EBBA molecules. If the lateral correlation length $\xi_{\perp}$ is much larger than the longitudinal correlation length $\xi_{\parallel}$, k_{33}/k_{11} can become quite small (Leenhouts et al 1979, Karat and Madhusudana 1977). k_{33}/k_{11} for mixture II lies between those of 7CB and mixture I. This is a consequence of the fact that mixture II is indeed a mixture of monomolecular and bimolecular species as described earlier. These studies are the subject matter of chapter V.

In chapter VI, we report some studies made on 2-cyano-4-heptylphenyl-4'-pentyl-4-biphenyl carboxylate [7P(2CN)5BC] which has a cyano group making a large angle ($\sim 60^\circ$) with the molecular axis. The compound exhibits nematic phase over a wide range of temperatures and has a large negative dielectric anisotropy (~ -4). The ordinary refractive index n_o of this compound shows an unusual temperature variation. As the sample is cooled down from the NI transition point, n_o initially decreases as usual, but, on further cooling it shows an increasing trend after reaching a broad minimum. On the other hand n_e shows the normal temperature variation. The birefringence also shows the normal temperature variation since the change in n_e is considerably larger than the corresponding

change in n_o . X-ray investigations of a monodomain sample of the compound showed that in the nematic phase the compound has the skewed cybotactic (i.e., a smectic C) type of short range order.. Further it was found that the tilt angle of the skewed cybotactic groups decreases as the temperature is increased. We have made an attempt to correlate the variation of tilt angle with the peculiar temperature variation of n_o .

However, the calculation of the order parameter itself is not very sensitive to these small variations in the structure. The value of s calculated using the Vuks' formula shows the normal trend in temperature variation. Indeed, the temperature variation of s agrees quite well with that obtained by using the wideline NMR technique.

We have also studied the phase diagram of binary mixtures of 7CB and 7P(2CN)5BC and found that these mixtures do not exhibit induced smectic mesomorphism. Among the various interactions between a molecule of 7CB and one of 7P(2CN)5BC, the dipole-dipole interaction between the terminal cyano group of 7CB and the lateral cyano group of 7P(2CN)5BC is the strongest. This interaction does not favour the formation of layers which could give rise to the smectic A phase.

The order parameters and splay elastic constants of a few mixtures of 7CB and 7P(2CN)5BC were measured. The mixtures having high concentrations of 7P(2CN)5BC also show the unusual

temperature variation of n_o . k_{11} and s of 7P(2ON)5BC are greater than those of 7CB. As the concentration of 7CB in the mixture is increased, both k_{11} and s decrease, attain a broad minimum around a concentration of ~ 60 per cent of 7CB and thereafter increase slightly.

In chapter VII, we report some studies on electrohydrodynamic (EHD) flow patterns exhibited by nematics having positive dielectric anisotropy ($\Delta\epsilon$) and negative conductivity anisotropy ($\Delta\sigma$). In some mixtures of 7UB and HOAB exhibiting induced smectic A phase, the nematic phase has these characteristics in a small temperature range above the AN transition point. It is a well known fact that nematics having negative $\Delta\epsilon$ and positive $\Delta\sigma$ exhibit EHD patterns in the form of Williams domains under the action of DC or low frequency AC electric fields above a threshold voltage. This is well understood in terms of the Carr-Helfrich theory. In principle, almost similar type of instabilities should occur in nematics having positive $\Delta\epsilon$ and negative $\Delta\sigma$. In the latter case, the instabilities arise due to the amplification of splay fluctuations (Durand, 1976) whereas in the former case they arise due to bend fluctuations. We have made observations on a homeotropically aligned sample taken in a sandwich geometry. The patterns observed grow with circular symmetry. At a given temperature, the threshold voltage of instabilities increases monotonically with frequency. At a given frequency, as the

temperature is increased from the AN transition point, the threshold voltage decreases in the beginning, reaches a broad minimum and increases thereafter. Above a certain temperature no instabilities are observed even at voltages as high as 250 V. We have explained these observations in terms of the Carr-Helfrich mechanism.

In the last chapter we describe an interesting electro-optic phenomenon observed in cells having asymmetrically treated electrodes and containing nematic liquid crystals of high positive dielectric anisotropy. The cell usually consisted of one electrode coated with silicon monoxide (SiO) at an oblique angle of $\sim 60^\circ$ with respect to the normal and another electrode rubbed unidirectionally. When the cell is subjected to an electric field, it is observed that the sample undergoes vigorous EHD motion when the SiO coated electrode is positive. On the other hand, the EHD motion is very much less vigorous when the SiO coated electrode is at a negative potential. This polarity dependent electro-optic effect is found under low frequency AC electric fields also.

Sussmann (1978) found a rectification action in nematic liquid crystals contained between SiO coated and rubbed electrodes. He explained this by assuming that negative ions present in the sample are electrosorbed more readily at the positive electrodes than the positive ions at the negative electrode. The same mechanism explains the electrooptic effect mentioned

above.

In the absence of EHD motion, under the action of an electric field larger than the Fredericksz threshold, the molecules will align in a direction normal to the glass plates since $\Delta\epsilon$ is positive. Then the system comprising of the cell placed between crossed polarisers will not transmit any light. The presence of ionic impurities gives rise to EHD motion in the sample. This motion disturbs the alignment of molecules resulting in the transmission of considerable amount of light through the system. In the present case where the sample has high positive $\Delta\epsilon$ and small positive $\Delta\sigma$, the EHD motion arises most probably due to injection of charges at the boundary (Pelici 1369) or electro-convective processes (Barnik et al 1976). When the SiO coated electrode is at a positive potential, the EHD motion is more vigorous compared to that in the reverse case. Consequently, more light passes through the system in the former case compared to that in the latter. Some experimental evidences confirming this mechanism have also been discussed.

Some of the results discussed in this thesis were reported in the following publications.

- 1 The electro-optic characteristics of a nematic liquid crystal cell with asymmetrically treated electrodes. 1979 (N.V.Madhusudana and K.P.L.Moodithaya) - Molecular Crystals and Liquid Crystals 51, 137.

- 2 **Re-entrant nematic phase in pure compounds at atmospheric pressure (N.V.Madhusudana, B.K.Sadashiva and K.P.L. Moodithaya) 1979 Current Science 48, 613.**
- 3 **Re-entrant nematic phase in some pure compounds and their mixtures at atmospheric pressure (K.P.L.Moodithaya and N V.Madhusudana) 1980 Proceedings of the International Liquid Crystals Conference, Bangalore, December 1979 Ed. S. Chandrasekhar, Heyden, London, p. 121.**
- 4 **Induced smectic mesomorphism in some binary mixtures: A new type of electrohydrodynamic pattern in the nematic phase of the mixtures (K.P.L.Moodithaya and N. V.Madhusudana) - 1980 Proceedings of the International Liquid Crystals Conference, Bangalore, December 1979, Ed. S. Chandrasekhar, Heyden, London, p. 297.**
- 5 **Studies on some binary mixtures exhibiting the induced smectic A phase (N.V.Madhusudana and K.P.L.Moodithaya) - Molecular Crystals and Liquid Crystals (submitted).**

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