

INVESTIGATIONS ON LIQUID CRYSTALLINE MIXTURES

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for the Degree of
Doctor of Philosophy

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MAY 1988

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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C E R T I F I C A T E

I certify that this thesis has been composed by Ms. R. Pratibha based on investigations carried out by her at the Liquid Crystal Laboratory, Raman Research Institute, Bangalore, 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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P R E F A C E

This thesis describes some experimental studies on thermotropic liquid crystalline mixtures. The main emphasis is on investigating some unusual phenomena exhibited by the liquid crystalline phases of these mixtures.

Chapter I gives a general introduction and the background information on the various phenomena discussed in the later chapters of the thesis. Specifically, molecular theories of the nematic phase, phase diagrams involving nematic and smectic A phases, the continuum theory including the hydrodynamics of nematic liquid crystals, defects and textures occurring in nematics are reviewed. Our discussions pertain to only thermotropic liquid crystals. Thermotropic liquid crystals made up of rod-like molecules have been known for a long time but only recently it was found that compounds composed of disc-shaped (or plate-like) molecules also show thermotropic phases (Chandrasekhar et al., 1977).

Chapter II deals with the study of phase diagrams of compounds composed of rod-like and plate-like molecules. When two nematogens, one made up of rod-like molecules and the other of disc-shaped molecules are mixed together, purely for geometrical reasons the plate-like molecules can be expected to align with their short axes perpendicular to the long axes of the rod-like molecules. This can result in a biaxial phase if the rods and plates are themselves orientationally ordered in mutually orthogonal directions. There have been many theoretical studies that lead to the occurrence of a biaxial nematic phase

in such mixtures (Alben 1973, Caflisch et al 1984, Chen and Deutch 1984, Rabin et al. 1982). A biaxial nematic phase was first discovered in a lyotropic system by Yu and Saupe (1980). Since thermotropic nematics made of disc-like molecules have become available in recent years, we have experimentally studied the phase diagram of two systems consisting of mixtures of rod-like and disc-like molecules. Instead of the biaxial phase predicted by the above theories we found the coexistence of two nematic phases, N_R rich in the rod-like compound and N_D rich in the disc-like compound. This is in agreement with a theoretical model put forth recently (Palffy-Muhoray et al. 1984A, 1985A, 1985B). According to their theory in which the chemical potentials have been properly calculated, the free energy density of the system in the two coexisting uniaxial phases can be lower than that of the biaxial phase. In Chapter II we have discussed our experimental studies on the phase diagrams of these mixtures (Fig.1).

In mixtures exhibiting the coexistence of the two nematics, the N_R phase appears as droplets and the N_D phase spreads around the N_R droplets (see for e.g., Fig. 2). The director (\vec{n}) which defines the average direction of orientation of the molecules is continuous across the interface of the N_R and N_D phases. System I consists of the rod-like nematic 4-trans-4-n-propyl-cyclohexylphenyl-4-n-propyl benzoate (3CHP3B) and the disc-like nematic hexa-n-heptyloxybenzoate of triphenylene (C_7 OHBT). The N_R droplets of this system have a point defect of strength +1 at the centre. When mixtures exhibiting the coexistence in this system are taken between plates coated with SiO, only the N_D phase aligns parallel to the glass plates and N_R droplets

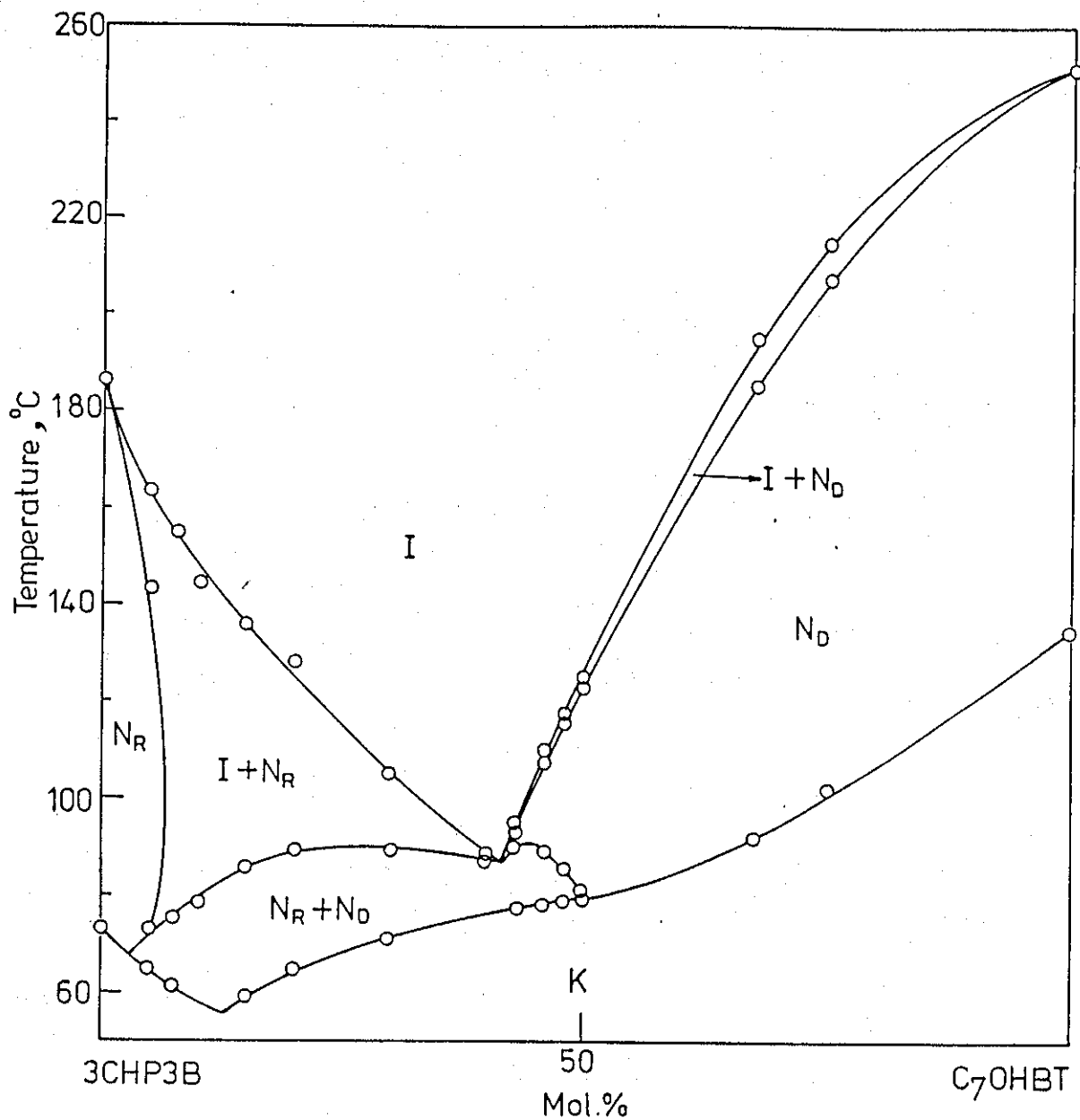


Figure 1

Phase diagram of binary mixtures of C₇OHBT and 3CHP3B (transition temperatures determined on cooling) [System I].

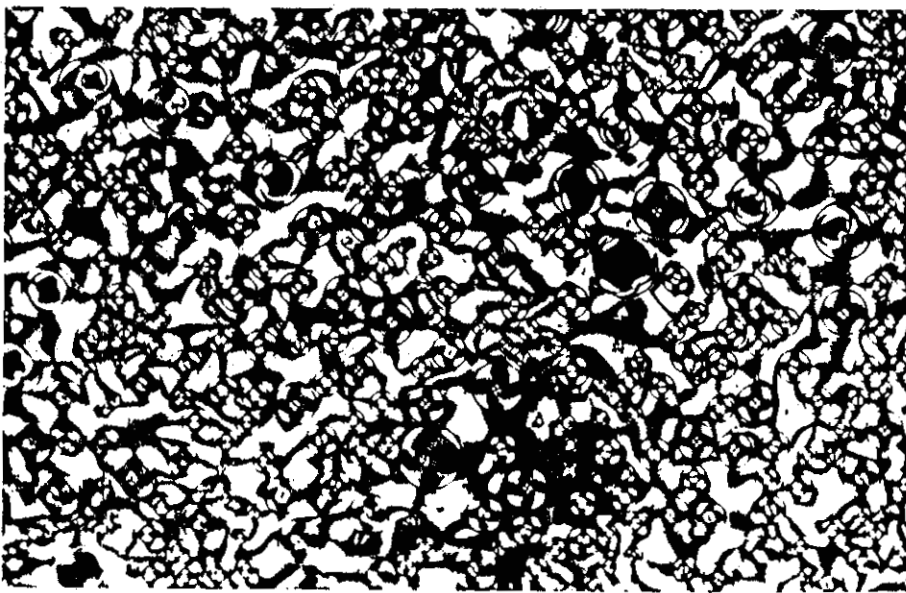


Figure 2

Coexistence of N_R and N_D phases in a mixture with 30 mol % of C_7OHBT at $88^\circ C$. Crossed linear polarizers. Note the continuity of dark brushes between the two types of nematics (x 450).

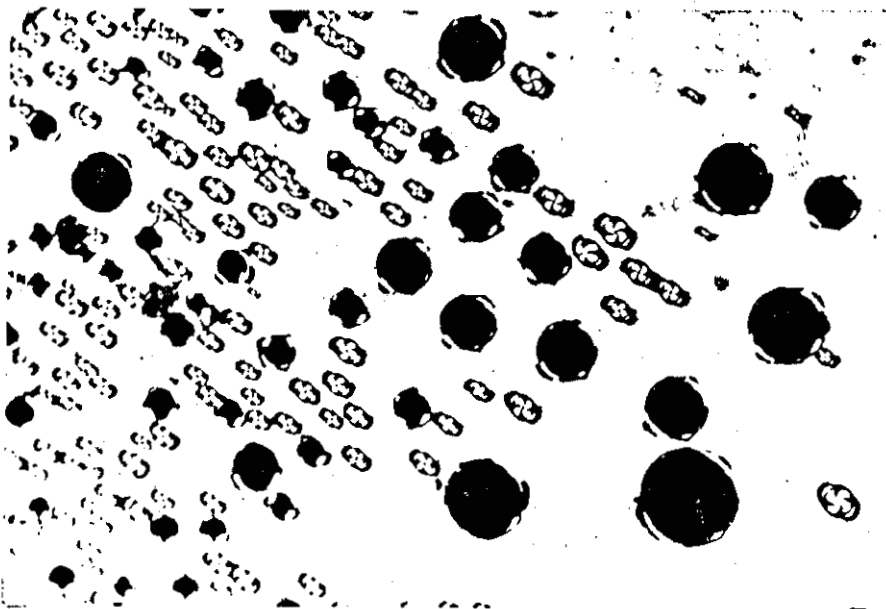


Figure 3

Coexistence of N_R and N_D phases in a mixture with 30 mol % of C_7OHBT at $88^\circ C$. Sample taken between SiO coated plates, Crossed linear polarisers (x 450).

continue to have the point defect at the centre (Fig. 3). In agreement with topological arguments, the director distortion due to the point defect of strength +1 at the centre of N_R droplet is found to be annulled by that of a singular ring defect of strength -1/2 lying in a suitable vertical plane at the periphery of the N_R droplet. This aspect is also discussed in Chapter II.

In Chapter III we give results of our experimental studies of the orientational order parameter in binary mixtures. The uniaxial nematic phase with cylindrically symmetric molecules is characterized by an orientational order, the order parameter being defined by $S = \langle 3\cos^2\theta - 1 \rangle / 2$, where θ is the angle that the long axis of the molecule makes with the director and $\langle \rangle$ denotes a statistical average. A convenient method of measuring the orientational order parameter experimentally is by Infrared dichroism measurements. Isolated and pronounced bands available in the Infrared spectra of the compounds can be used for this purpose, if the orientation of the related transition moment with respect to the molecular geometry is known. In binary mixtures, it has been theoretically shown (Palffy-Muhoray et al, 1984B) that in general the order parameter of the two components are different.

The measurements of the order parameters of two cyano biphenyls 4'-n-octyloxy-4-cyanobiphenyl (8OCB) and 4'-n-heptyl-4-cyanobiphenyl (7CB) in several mixtures belonging to two binary systems as a function of temperature have been given in Chapter III. In system 'I, the cyanobiphenyl 8OCB exhibits a smectic A phase, but the mixtures for

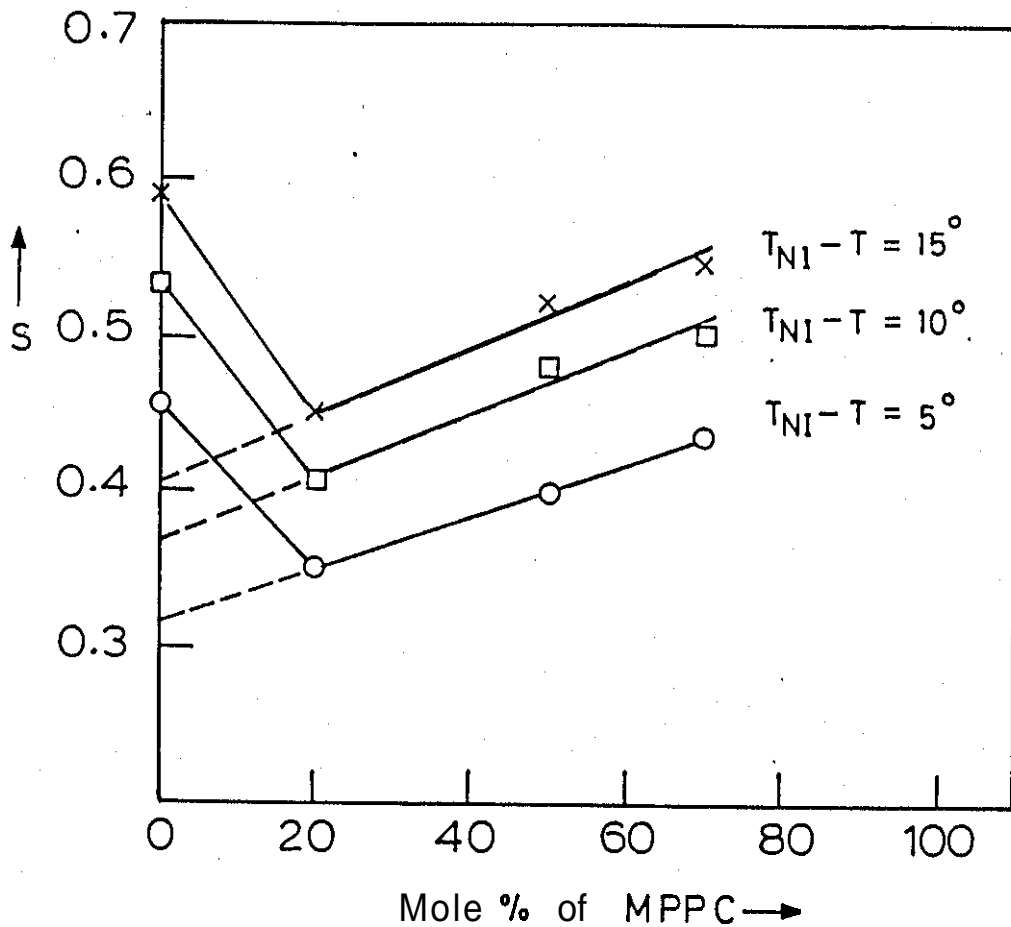


Figure 4

Variation of the order parameter s as a function of the concentration of MPPC, at three relative temperatures. (MPPC is the non-cyano compound in System I).

which we have measured the order parameters exhibit only the nematic phase down to room temperature. Though both components of system II exhibit only nematic phases, some of the mixtures exhibit an induced smectic A phase. The experimentally measured values of S in the nematic phase of pure 80CB in System I^{and} in the nematic phase of System II are seen to be influenced by the smectic-like short range order. A clear enhancement in the value of the orientational order parameter is observed as the temperature is lowered and the smectic phase is approached (Fig. 4).

In Chapter IV we discuss an unusual transport phenomenon observed in cholesteric liquid crystals. The cholesteric liquid crystal is a chiral system consisting of orientationally ordered optically active anisotropic molecules, with the director twisting about an axis orthogonal to the director. In parity conserving systems the Curie principle requires that the symmetry of physical effects must be contained in the causes which give rise to them. In chiral systems which lack mirror symmetry the principle predicts novel types of coupling between fluxes and forces. In cholesterics this principle leads to a coupling between thermal and mechanical effects. This type of thermomechanical effect was observed by Lehmann long ago (1900). He found that in small cholesteric drops taken between two glass surfaces, a thermal gradient along the helical axis gives rise to a continuous rotation of the structure about that axis. Leslie (1968) and others have worked out a detailed hydrodynamic theory of cholesterics and obtained solutions corresponding to the Lehmann effect. de Gennes (1974) has pointed

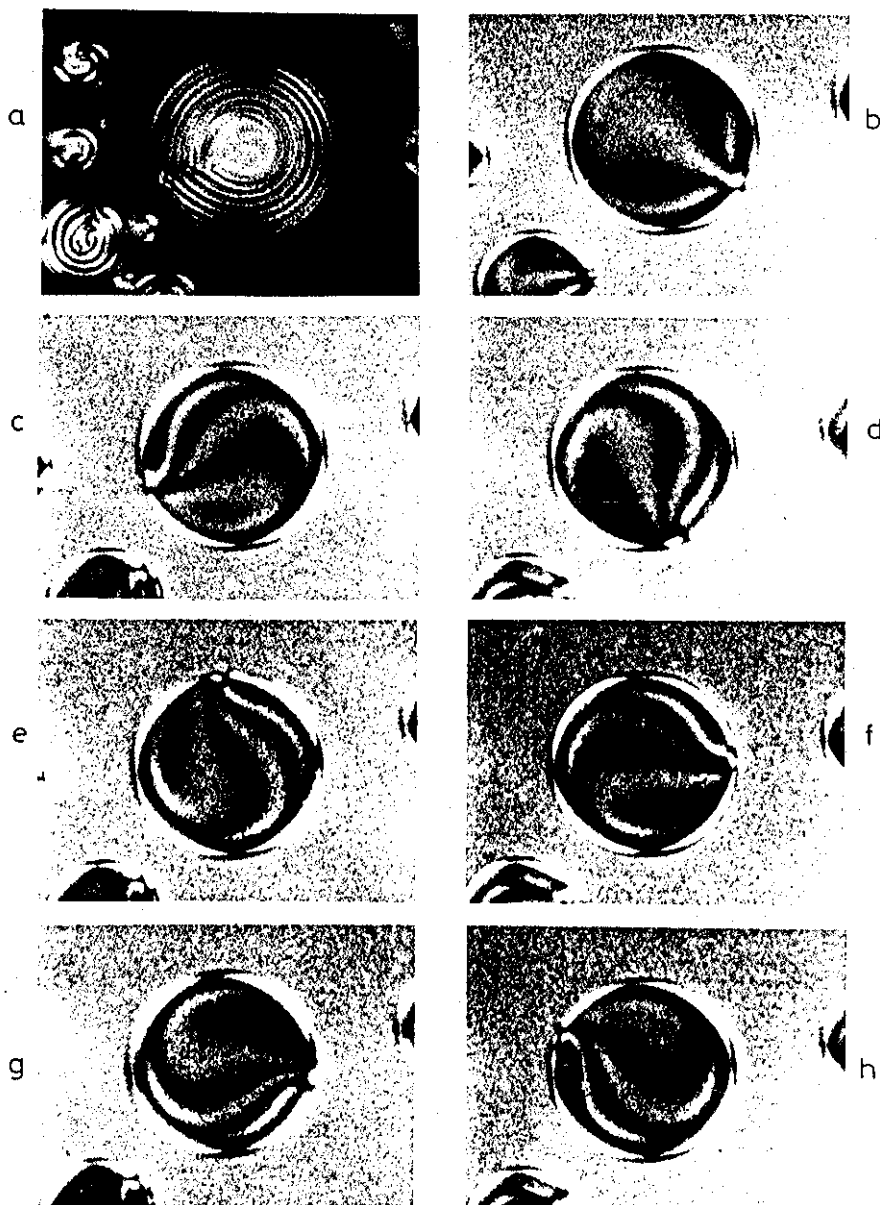


Figure 5

Photographs of cholesteric droplets, demonstrating the electromechanical effect (Lehmann rotation).

out that any transport current should in principle give rise to a similar effect. However the Lehmann experiment has never been reproduced. For a free rotation of the structure to be possible it is essential to have weak anchoring at the surface of the cholesteric drop. This condition was probably not fulfilled in attempts to reproduce the "Lehmann" rotation. We have for the first time obtained an analogous effect - the electromechanical coupling in a cholesteric, under the action of a DC electric field.

In Chapter IV the experimental observation of such an effect is given. A suitable system in which flat cholesteric drops, whose structure can rotate freely under the action of an electric field, was first obtained. The "Lehmann" rotation phenomenon could therefore be reproduced under the action of an external DC electric field (Fig. 5). We have also determined the sign and magnitude of the electromechanical coupling coefficient.

Chapter V deals with the measurement of a particular elastic constant of nematic liquid crystals, the determination of which has so far proved to be extremely difficult. The deformations of the director field in a liquid crystal are described by the continuum theory. These deformations cost elastic energy. The elastic free energy is usually written as

$$F_d = \frac{1}{2} [K_{11} (\text{div } \vec{n})^2 + K_{22} (\vec{n} \cdot \text{curl } \vec{n})^2 + K_{33} (\vec{n} \times \text{curl } \vec{n})^2],$$

where K_{11} , K_{22} and K_{33} denote the splay, twist and bend elastic constants respectively (Oseen 1933, Frank 1958). Nehring and Saupe (1971)

argued that another term which is a second derivative of the curvature components, associated with the elastic constant K_{13} is also of similar order and should be considered. This term is of the form $\text{div} (\vec{n} \text{ div } \vec{n})$. Now terms of the form $\text{div } \vec{u}$, where $\vec{u}(\mathbf{r})$ is an arbitrary vector field may be transformed to surface integrals using the Gauss theorem. These terms do not contribute to the equilibrium condition (Euler-Lagrange equation) when strong-anchoring prevails at the boundaries. However when the anchoring is weak these terms do make a contribution and cannot be neglected. Therefore in order to measure the elastic constant K_{13} it is necessary to have a weakly anchored surface. This is very difficult to achieve in practice.

We have developed a technique to obtain an estimate of K_{13} which we describe in Chapter V. A hybrid aligned cell in which one surface was treated for planar alignment with a strong anchoring and the other surface was treated for homeotropic alignment with a weak anchoring was used in this experiment. Though the thesis mainly deals with liquid crystalline mixtures these preliminary experiments on K_{13} have been conducted on a pure nematogen. We have succeeded in obtaining weak anchoring of the nematic liquid crystal p-cyano-p'-heptyl phenyl cyclohexane by a suitable surface treatment. A magnetic field was applied perpendicular to the glass plates to vary the director profile. Optical phase difference measurements were made to obtain the value of the tilt angle θ_0 at the surface with weak homeotropic anchoring. This value could then be used in the surface torque balance equation to obtain K_{13} . Our measurements made on a few independent samples

indicate that K_{13} has the same order of magnitude as that of the other elastic constants and has a positive sign. A molecular model (Nehring and Saupe 1972) which takes into account only the attractive interaction between molecules but ignores the shape anisotropy of the molecules and short range order predicts K_{13} to be negative. The positive sign that we get for K_{13} clearly indicates the important influence of the latter.

Chapter VI deals with the observation of some special defects occurring in nematic mixtures. If one of the components in a binary mixture is non-mesomorphic, the nematic isotropic transition temperature of the nematogen is depressed. Further the nematic and isotropic phases coexist over a considerable range of temperatures (Martire 1979). During the course of our study of such systems we discovered some unusual defects, viz., high strength defects. This is the first observation of such "high strength defects" in thermotropic liquid crystalline systems.

The actual configuration around the defects can be obtained by minimising the free energy density. If a planar structure is assumed with the director \vec{n} lying in the x-y plane, the components of \vec{n} are $\cos \psi$, $\sin \psi$ and 0, where ψ is the angle between \vec{n} and the X-axis. The solutions corresponding to the defects obtained by minimisation of the free energy is $\psi = s\alpha + c$, where $\alpha = \tan^{-1} y/x$ and c is a constant. The strength of the disclination line, $s = 1/2 m$, where $m = \pm 1, \pm 2, \dots$. If the deformation energy per unit length of an isolated defect is calculated the energy is found to be proportional to



Figure 6

A relatively isolated $+3/2$ defect, crossed linear polarisers (x 1920).

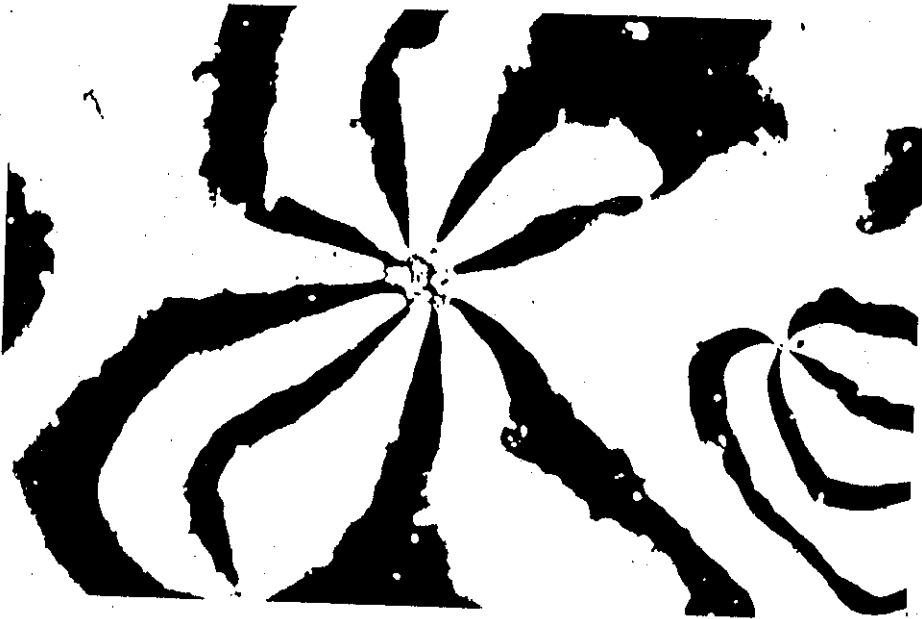


Figure 7

A relatively isolated $+2$ defect, crossed polarisers (x 1920).



Figure 8

A $+3/2$ and $-3/2$ pair of defects, crossed linear polarisers
(x 3700).

s^2 . This leads to the result that only defects of strength $s = \pm 1/2$ should be stable. However defects of strength ± 1 are frequently seen in nematics. This was accounted for by Meyer (1973) and Cladis and Kleman (1972) who considered the possibility of a collapse of the director in the third dimension. This lowers the energy and the defects with $s = \pm 1$ can be stable. Until recently experimental observations of only defects of strength $s = \pm 1$ or $s = \pm 1/2$ had been reported. In Chapter VI we describe our experimental observations of defects with strength $s = \pm 3/2$ and ± 2 (Figs. 6 and 7). Pairs of such defects have also been observed (Fig. 8). The concentration gradient of the impurity appears to stabilise such high strength defects.

The author has also reanalysed the elastic constant data on several cyanobiphenyls previously measured in our laboratory. A paper published on the subject is reproduced in Appendix I.

Some of the results discussed in this thesis are reported in the following publications:

- 1 Elasticity and orientational order in some cyanobiphenyls: Part IV. Reanalysis of the data, (N.V.Madhusudana and R.Pratibha) - Molecular Crystals and Liquid Crystals, 89, 249 (1982)
- 2 High strength defects in nematic liquid crystals (N.V.Madhusudana and R.Pratibha) - Current Science, 51(8), 877 (1982)
- 3 Studies on high strength defects in nematic liquid crystals. (N.V.Madhusudana and R.Pratibha) - Molecular Crystals and Liquid Crystals, 103, 31 (1983)

- 4 Evidence for two coexisting nematic phases in mixtures of rod-like and disc-like nematogens. (R.Pratibha and N.V.Madhusudana) - Molecular Crystals and Liquid Crystals Lett., 1(3-4), 111 (1985)

- 5 Electromechanical coupling in cholesteric liquid crystals. (N.V. Madhusudana and R. Pratibha) - Molecular Crystals and Liquid Crystals Letters, 5(2), 43 (1997).

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