DIELECTRIC PROPERTIES AND SHORT RANGE ORDER
IN
LIQUID CRYSTALS

A Thesis Submitted to the University
of Mysore for the Degree of
Doctor of Philosophy

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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CERTIFICATE

I certify that this thesis has been composed by Mrs. B.R.Ratna based on investigations carried out by her 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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CONTENTS

CHAPTER I

INTRODUCTION

The discovery of liquid crystals in 1888 by Reinitzer,[1] an Austrian botanist, opened up new vistas for the investigation of these fundamental new states of matter. In his letter to hmann who coined the name 'Liquid Crystals' in 1900,[2] Reinitzer describes his epoch making observations: "…. the substance shows such striking and beautiful phenomena that 3 can hopefully expect that they will also interest you to a high degree …. the substance has two melting points …. At 145.5°C it melts to a cloudy, but fully liquid

which at 178.5°C suddenly becomes completely clear …. the cloudiness is caused not by crystals but by a liquid which forms oily streaks in the melt."[3] These observations were on cholesteryl benzoate, the first liquid crystal to be discovered. Thousands of organic compounds are now known to exhibit liquid crystallinity or mesomorphism.[4]

Liquid crystals are termed thermotropic or lyotropic depending on whether the mesophase is obtained by change of temperature or by addition of solvents. The characteristic feature of these mesomorphic materials is that they are composed of highly anisotropic rod-like or lath-like molecules. Very recently thermotropic mesomorphism has been discovered in disc-like molecules also.[5] In this thesis we are concerned only with thermotropic liquid crystals composed of rod-like molecules.

Friedel[6] classified thermotropic liquid crystals broadly into three types: nematic, smectic and cholesteric.

<u>Nematic liquid crystals</u> possess long range orientational order but no long range positional order (figure 1.1a). The molecules are spontaneously oriented about a mean direction $\underline{n}$ which is referred

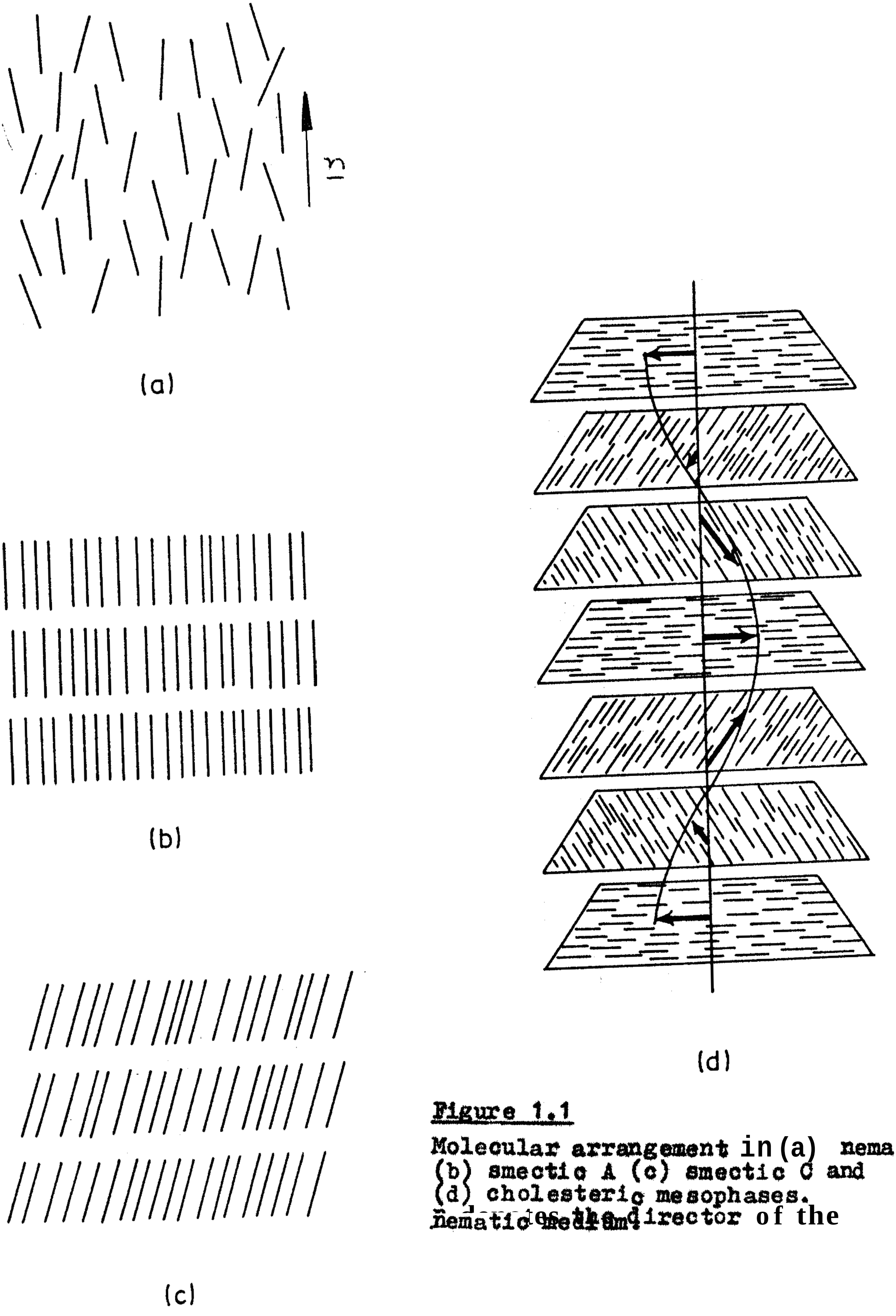


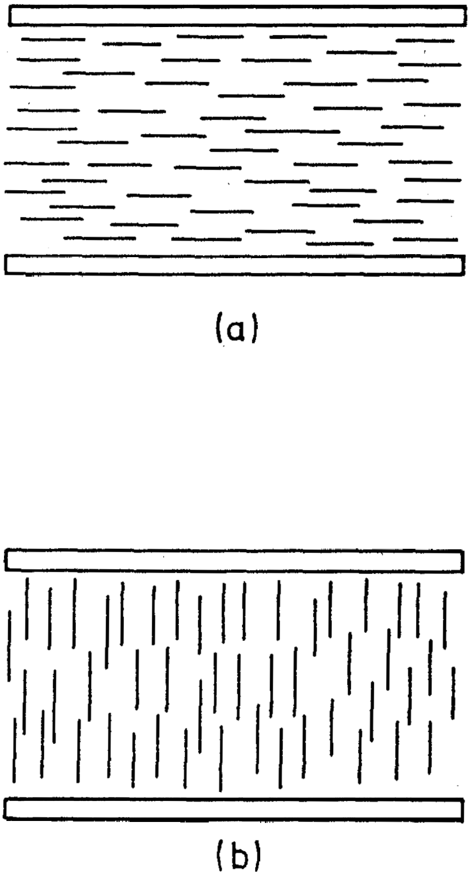
Figure 1.1

Molecular arrangement in (a) nematic (b) smectic A (c) smectic C and (d) cholesteric mesophases. $\underline{n}$ denotes the director of the nematic medium.

1.1c) is similar to smectic A except that the molecules are now tilted with respect to the layer. Several other types of smectics have been identified on the basis of the optical textures exhibited by them. But on a molecular level not much is understood about them.

Cholesteric liquid crystal is essentially of the nematic type with the difference that its structure has a screw axis normal to the director (figure 1.1d). This helicity in the structure imparts certain extraordinary properties to the cholesteric, like the exceptionally high optical rotatory power, selective reflection, etc. The pitch of a cholesteric, particularly near a smectic A-cholesteric transition, is highly sensitive to temperature.

Experiments have shown that the nematic phase is apolar, i.e., n and -n are equivalent. The direction of <u>n</u> in an unaligned sample varies from point to point, but a monodomain sample is uniaxial. Any measurement of the anisotropic properties of a nematic requires a monodomain sample with either a 'homogeneous' or 'homeotropic' alignment. A homogeneous sample is one in which the molecules are parallel to the enclosing surfaces (see figure 1.2a) whereas in a homeotropic sample (figure 1.2b) they are normal to the surfaces. Homogeneous alignment can be achieved by unidirectional rubbing[7] of the glass plates or by the application of a strong magnetic field parallel to the plates. Good homogeneous samples can also be obtained by oblique deposition of materials[8] like silicon monoxide or gold on substrates. Homeotropic alignment, which can also be obtained by a magnetic field applied normal to the plates, is more often obtained by by treating the surface of the glass plates with surfactants.[9]



(a)

(b)

Figure 1.2

Schematic representation of (a) homogeneous and (b) homeotropic structures.

The order parameter, being a measure of the anisotropy of a nematic liquid crystal, manifests itself in diamagnetic anisotropy, birefringence, dielectric anisotropy, etc. These anisotropic properties and their temperature dependence are fairly well explained by the molecular field approximation developed by Maier and Saupe.[10] We shall now discuss in some detail the origin of the dielectric anisotropy which forms a substantial part of the work presented in this thesis.

Dielectric Properties

(i) Static Dielectric Constants

The nematic liquid crystal being uniaxial has two dielectric constants, $\epsilon_{\parallel}$ in the direction of the optic axis and $\epsilon_{\perp}$ in any perpendicular direction. The dielectric anisotropy $\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp}$ has contributions both from the permanent dipoles and molecular polarizabilities. Due to the elongated shape of the molecule the polarisability along the long molecular axis is always greater than that in a perpendicular direction. Therefore in the absence of a permanent dipole moment the dielectric anisotropy is always relatively small and positive.

The presence of a strong dipole moment μ directed along the long molecular axis increases the dielectric constant to a high positive value. Large negative dielectric anisotropy can be obtained by introducing a strong dipole perpendicular to the long molecular axis. Thus nematics with any desired sign and value of $\Delta\varepsilon$ can be obtained depending on the strength of the dipole moment and the angle it makes with the long molecular axis. These widely varying dielectric properties of nematics were explained qualitatively by Maier and Meier[11] (see chapter II) using the molecular field approximation.

The drawback with the molecular field theory is that it completely neglects short range order. As a result it is unable to explain the pretransition anomalies in the isotropic phase. Madhusudana and Chandrasekhar[12] extended the Maier-Saupe theory by taking into account near neighbour correlations using the Bethe approximation.[13] In particular, for polar compounds they suggested that there should be antiparallel correlation between neighbouring molecules and showed theoretically that as a consequence the mean dielectric constant in the nematic phase ($\bar{\epsilon} = \frac{\epsilon_{\parallel} + 2\epsilon_{\perp}}{3}$) should be less than the value in the isotropic phase owing to a discontinuous decrease in the antiparallel short range order at the transition. Such a difference ($\sim 3\%$) had in fact been clearly noticed earlier by Schadt[14] in his measurements of the dielectric constants of a few strongly polar p-substituted benzylidene cyanoanilines, though he did not attempt to explain the reason for it.

It was felt worthwhile to confirm this result in other cases and therefore tha present writer undertook systematic measurements of the dielectric constants as functions of temperature for a number of polar compounds.

The strongly polar compounds studied by the author belong to two homologous series, vis., 4'-n-alkyl 4-cyanobiphenyls (nCB) and trans-p-n-alkoxy α-methyl p'-cyanophenyl cinnamates (n OMCPC). The dielectric properties of these two series presented in chapters III and IV are very similar. The dielectric anisotropy is quite large due to the presence of $C\equiv N$ end group with a dipole moment of 4.05 D[15] acting along the long molecular axis. A marked decrease (~ 3-4%) in the mean dielectric constant was observed on going over to the nematic phase from the isotropic phase. (A similar decrease has been observed subsequently by other workers for 7CB[16,17] and 8CB.[18]) Further, $\bar{\varepsilon}$ decreases with decrease of temperature, the effect being greater in compounds in which the nematic phase is preceded by a smectic A phase. This is evidently due to the increase in the antiparallel ordering at lower temperatures which may be expected to be more pronounced when there is a pretransitional smectic-like ordering in the nematic. Another interesting fact observed is that although the nematic-isotropic transition temperature (T_{NI}) and the order parameter[19] within a homologous series show an alternation with increasing end chain length, the dielectric anisotropy shows only a continuous decrease. This may be partly due to the fact that an increase in the order parameter increases the effect of antiparallel correlation which results in a diminution of the dielectric anisotropy.

These results are in contrast to the behaviour of low positive biphenyl-4-p-n-alkoxy benzoates (B NOB) discussed in chapter V. In this new homologous series $\triangle\varepsilon$ for the successive homologues, when plotted at a common relative temperature, shows an alternation similar to that exhibited by T_{NI}. Further, the difference between the isotropic and mean dielectric constants is very small ($\sim 0.5\%$).

In non-polar compounds ($\mu = 0$) one would not expect any antiparallel correlation and thus theoretically ε_{is} should be equal to $\bar{\varepsilon}$ at transition. This has indeed been found to be the case in a number of non-polar compounds like 4,4'-di-n-alkyl azobenzenes.[20]

(ii) Dielectric Dispersion and Activation Energy

The dipole moment μ of a molecule making an angle β to the long molecular axis can be resolved into a longitudinal component $\mu_l = \mu\cos\beta$ and a transverse component $\mu_t = \mu \sin\beta$. Owing to the presence of the molecular order in the nematic phase the reorientation of μ_l is hindered, resulting in a low-frequency dispersion of $\varepsilon_{\parallel}$ in the radio-frequency region. On the other hand, the reorientation of μ_t about the long molecular axis is relatively easy and $\varepsilon_{\perp}$ exhibits a dispersion in the microwave region. Because of imperfect order μ_t also contributes to $\varepsilon_{\parallel}$ leading to a second dispersion of $\varepsilon_{\parallel}$ in the microwave region. In the isotropic phase the dielectric constant exhibits the usual Debye relaxation.

Martin et al.[21] explained the dielectric behaviour of nematic liquid crystals by extending the Debye theory[22] of dielectric relaxation. Due to the presence of the long range orientational order in the nematic phase, the relaxation time (τ_R) corresponding to the reorientation of μ_l is orders of magnitude higher than the normal Debye relaxation time (τ_0) in the isotropic phase. The ratio τ_R/τ_0 is called the retardation factor 'g' which is evidently a function of the nematic potential q. Meier and

Saupe[23] derived a relation between g and q using the same distribution function as in the molecular field theory (see chapter II).

In the isotropic phase the resistance to the reorientation of the dipole moment is mainly due to the viscosity of the medium, the temperature dependence of which can be expressed as a rate equation involving an activation energy q_η. In the nematic phase, in addition to q_η the molecule has to overcome the nematic potential q. Therefore a measurement of the low-frequency relaxation of $\varepsilon_{\parallel}$ at different temperatures yields $W = q + q_\eta$.

In chapters III and IV we have discussed our dispersion measurements on nCB and nOMCPC. The relaxation frequency $f_R (= \frac{1}{2}\pi\tau_R)$ was measured at different temperatures. The results obtained are very similar for the two homologues. The value of W is ~ 0.56 eV for nCB and ~ 0.91 eV for nOMCPC.

The higher value of W for n OMCPC is due to the greater length of the molecule and the expected higher viscosity.[24] An interesting new result that emerged from our dispersion measurement is that f_R far successive homologues, when plotted at a common relative temperature, shows an alternation similar to that of T_{NI} and s. This is the first observation of 'odd-even' effect in f_R.

Both nCB and n OMCPC exhibit a change in the sign of dielectric anisotropy in the MHz region. The frequency at which the dielectric anisotropy becomes zero, i.e., the frequency of dielectric isotropy f_0 was determined at different temperatures. We observe that f_0 gives the same value of W as that determined from f_R. Also it shows an alternation with respect to the end chain length similar to f_R.

The reversal in the sign of $\Delta\varepsilon$ in nCB referred to above has also been observed recently by

Druon and Wacrenier in the case of the octyl derivative.[18] The authors found that $\Delta\varepsilon$ in fact exhibits two reversals, one around 10 MHz and the other at about 300 MHz when $\Delta\varepsilon$ again becomes positive (see figure 3.19). The reason fur this has not been understood so far.

In chapter V we discuss our results on the dielectric dispersion of Bn OB. Even in this homologous series bath f_R and f_0 show an alternation similar to T_{NI}. Also tho value of W determined from f_R and f_0 is the same. The differences in the dielectric properties of this homologous series on the one hand and strong positive nCB and n OMCPC on the other are discussed.

Pretransitional Effects

(i) Electric and Magnetic Birefringence in the Isotropic Phase.

Even though the long range order goes to zero at T_{NI}, nematic-like short range order persists in the isotropic phase. As a result, a number of physical properties of the isotropic phase like the electric and magnetic birefringence exhibit anomalous behaviour in the vicinity of T_{NI}. Tho first measurement of the pretransitional anomaly was in 1930 when Zadoc-Kahn[25] measured tho magnetic birefringence (Δn_M) of p-azoxyanisole (PAA) and observed that in the vicinity of T_{NI} it is hundred times greater than in ordinary organic liquids.

The molecular field theory such as that of Maier and Saupe is inadequate to explain the short range order effects since it completely ignores the near-neighbour correlations. It was shown by de Gennes[26] that the pretransitional effects are best described by a phenomenological model based on the Landau theory of phase transitions.[27] According to this model the magnetic birefringence should vary essentially as $(T - T^*)^{-1}$, where T^* is the hypothetical second order transition point slightly below T_{NI}. This inverse dependence of A& on temperature has been experimentally verified for PAA and p'-n-methoxy benzylidene p'-butylaniline[28] (MBBA) with $T_{NI} - T^* \simeq$ 1 K.

However when Tsvetkov and Ryumtsev[29] measured the electric birefringence (Δn_E) in the isotropic phase of PAA, they observed a very unusual behaviour. The Kerr constant showed a reversal of sign at about $T_{NI} + 5$ K. Madhusudana and Chandrasekhar[30] showed that this reversal can be explained when proper allowance is made for the contributions of the polarizabilities and the permanent dipole moment (μ) to the free energy. The polarizability anisotropy ($\Delta\alpha$) always makes a positive contribution to Δn_E. The contribution from the permanent dipole moment can be positive or negative depending on the strength of the dipole moment and the angle (β) it makes with the long molecular axis. It has been shown from the theory of dielectric anisotropy[11] that the dipolar contribution is negative for $\beta > 55°$ and that this contribution decreases with increase of temperature. Thus in PAA for which $\beta \simeq 62.5°$ there, can, in principle, be a reversal in the sign of Δn_E from negative to positive at a certain temperature. However, when β is either zero or very small as in strongly polar compounds, the dipolar contribution is always positive and we therefore expect Δn_E and Δn_M to behave similarly.

We undertook for the first time measurements of both Δn_M and Δn_E for strongly polar compounds, viz., 4'-n-hexyl 4-cyanobiphenyl (6CB) and trans-p-n-octyloxy α-methyl p'-cyanophenyl cinnamate (8 OMCPC) to verify the above predictions (chapter VI). The birefringences were measured over a wide range of temperature. They showed a $(T - T^*)^{-1}$ type of behaviour throughout the temperature range measured. Both Δn_M and Δn_E gave identical values of T^*, $T_{NI} - T^*$ being 1°C for 6CB and 1.4°C far 8 OMCPC.

(ii) Effect of Pressure on Cholesteric Pitch

Another manifestation of short range order, namely, the effect of smectic-like short range order on the pitch (P) of a cholesteric, is discussed in chapter VII. It has been observed experimentally that twist (k_{22}) and bend (k_{33}) elastic constants[31,32] increase anomalously as the smectic A-nematic (or cholesteric) transition is approached. This is obviously due to the build up of short range smectic order which makes the twist and bend distortions energetically unfavourable. de Gennes[33,34] has proposed a Landau type of phenomenological model to describe these pretransition anomalies near the smectic A-nematic transition, according to which these elastic constants diverge as $(T - T_c)^{-\nu}$, where

T_c is the apparent smectic A-nematic transition temperature and ν is the critical exponent. The pitch of a cholesteric, being related to k_{22},[35] should also exhibit a similar temperature dependence.

Recently Pollmann and co-workers[36-39] have measured the pitch as a function of pressure for a number of cholesterics having a smectic A phase at lower temperatures. They found that the pitch increases rapidly with pressure and becomes infinite at a critical pressure p_c. This was first interpreted as due to an increase in the viscosity[36] with pressure and subsequently explained as the result of the formation of smectic-clusters in the cholesteric phase. In chapter VII we present a simple calculation which reveals that the rapid increase is indeed due to the increase of short range smectic order as the smectic A-cholesteric transition is approached.

Some of the results discussed in this thesis have been published in the following papers:

1 Experimental Studies of Short Range Order in Nematogens of Strong Positive Dielectric Anisotropy (in collaboration with M.S. Vijaya, R. Shashidhar and B.K. Sadashiva).

Proc. Int. Liquid Crystal Conf., Bangalore 1973; Pramana Suppl. 1, 69.

2 Dielectric Properties of 4'-n-alkyl-4-cyano biphenyls in their Nematic Phases (in collaboration with R. Shashidhar), Pramana, 6, 278 (1476).

3 Pressure Dependence of the Pitch of Cholesteryl Oleyl Carbonate (in collaboration with S. Chandrasekhar), Mol. Cryst. Liquid Cryst. 35, 109 (1976).

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5 Dielectric Dispersion in 4'-n-alkyl-4-cyanobiphenyls (in collaboration with R. Shashidhar), Mol. Cryst. Liquid Cryst. 42, 185 (1977).

6 Dielectric Properties of Some Nematics of Positive Dielectric Anisotropy (in collaboration with R. Shashidhar), Mol. Cryst. Liquid Cryst. 45, 103 (1978).

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