CHAPTER I

INTRODUCTION

A large number of organic compounds are known to exhibit liquid crystallinity or mesomorphism.[1] The degree of order in liquid crystals is intermediate between that of a three dimensionally ordered crystal and a completely disordered isotropic liquid. Liquid crystallinity can be brought about either by varying the temperature or by adding a solvent. In the case of the former, the materials are referred to as thermotropic while in the case of latter, they are lyotropic. For a long time it was believed that a characteristic feature of the materials exhibiting mesomorphism should be the rod-like shape of the molecules. However recently thermotropic mesomorphism has been discovered even in disc-like molecules.[2] In this thesis, we shall be concerned only with thermotropic liquid crystals composed of rod-like molecules.

1.1 CLASSIFICATION OF THERMOTROPIC LIQUID CRYSTALS

Following the classification of Friedel,[3] the thermotropic liquid crystals composed of rod-like molecules can be broadly categorised into nematic, cholesteric and smectic.

The nematic phase is the simplest of the mesophases — it has only long range orientational order but no long range positional order.

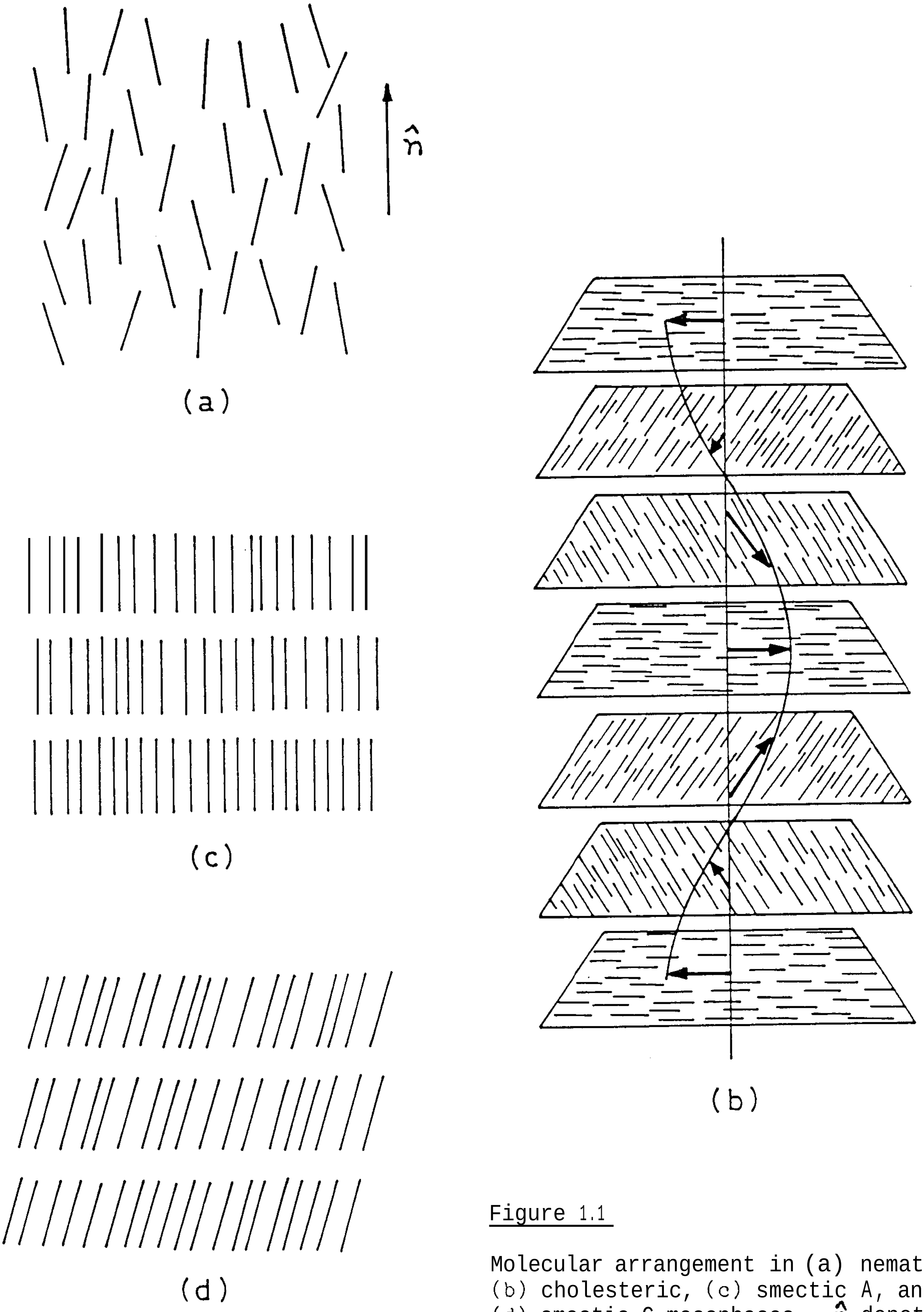
The molecules in this phase(Fig.1. 1a)are on the average oriented about a mean direction referred to as the "director" denoted by a unit vector $\hat{n}$. The degree of orientation is defined in terms of the order parameter

$$S = \frac{1}{2} < 3\cos^2 \theta - 1 >$$

where 8 is the angle made by the long molecular axis with $\hat{n}$. For a perfectly parallel alignment (crystal) s = 1 while for a totally random orientation (isotropic liquid) s = 0. In the nematic phase S has a value intermediate between 0 and I and is strongly temperature dependent.

The cholesteric liquid crystal is essentially of the nematic type with the difference that its structure has a screw axis normal to the director (Fig. 1.1b). 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.

Smectic liquid crystals are characterised by a layered structure, several types of molecular arrangements being possible within a layer. In smectic A, the molecules are perpendicular to the layer plane while in smectic C they are tilted(Fig.1.1c&d). In both these cases the centres of the molecules within each layer are arranged in a liquid-like manner. Some of the smectic modifications have ordering within a layer also, e.g., smectic B, smectic H, etc. Here we



(a)

(c)

(d)

(b)

Figure 1.1

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

shall mainly deal with the nematic, smectic A and smectic B phases.

The above picture of the smectic A phase is somewhat simplistic. A more realistic description of the A phase is to look upon it as a one-dimensionally ordered fluid with a mass density[4] wave along the director (Fig.1.2). The periodicity of this density wave is given by the smectic layer spacing. If the molecule is symmetric the layer thickness (d) is found to be approximately equal to the molecular length ℓ. However when the molecule is highly asymmetric, and has a strong polar group at one end, (as, for example, 8CB, whose molecular structure is given in Fig. 1.3), the situation is quite different. It was proposed by Madhusudana and Chandrasekhar[5,6] that in such cases, there should be antiparallel near-neighbour correlations. They showed theoretically that as a consequence the mean dielectric constant in the nematic phase should be less than the value in the isotropic phase owing to a discontinuous decrease in the antiparallel short range order at the transition. A consequence of this antiparallel ordering is that the smectic A can have a "bilayer" structure, so that the layer thickness can be greater than ℓ. Primarily due to experiments conducted by the Bordeaux group,[7,8] it is now recognised that materials with a strongly polar cyano (CN) or nitro (NO_2) end group exhibit different kinds of smectic A phases. A number of Xray studies have been conducted to classify the different kinds of A phases and to understand the structural differences between them. To-date

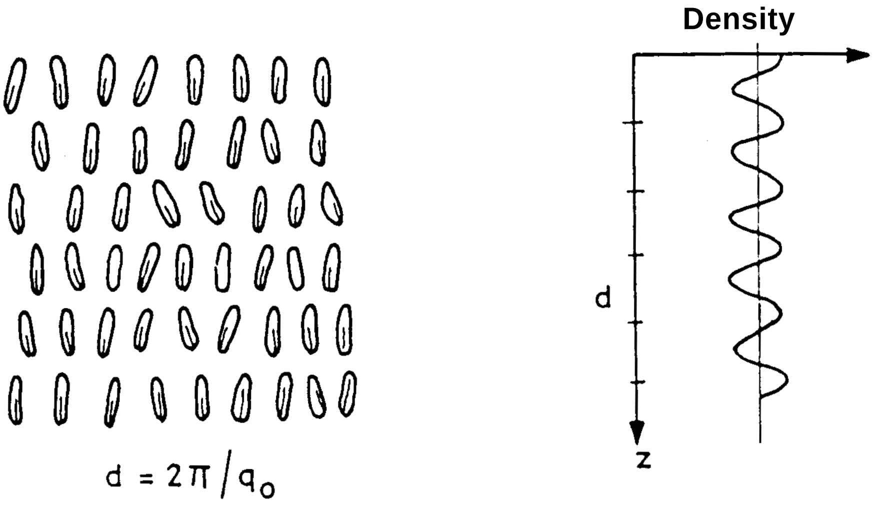
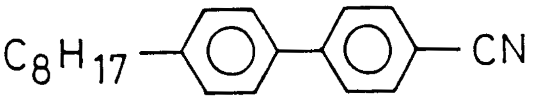


Figure 1.2

Schematic diagram. of smectic A phase with its one-dimensional density wave along the average direction of the molecular axis (Ref. 4).



4'-n-octyl-4-cyanobiphenyl

(8CB)

Figure 1.3

Structural formula of 8CB.

the different types of A phases which are known are the monolayer (A_1), partially bilayer (A_d, bilayer (A_2) and the incommensurate (A_{ic}) phases. The structures of these phases will be discussed in detail in Chapter V. Since it is known[9] that antiparallel correlations manifest themselves in the dielectric properties, it is of interest to apply this technique to study the different kinds of nematic-smectic A (N-A) transitions, as well as the transitions between the different polymorphic forms of the A phase. This thesis describes the results of a variety of dielectric studies taken up with this in view.

1.2 EXPERIMENTAL SET UP

The experimental set up used for the investigations discussed in this thesis is described in chapter II. The alignment of the sample (homeotropic for $\varepsilon_{\parallel}$ measurement and homogeneous for $\varepsilon_{\perp}$ measurement) was achieved by a 2.4 T magnetic field. Most of the work described here was carried out by collecting the data manually using an impedance analyser. However in some studies wherein a large amount of data had to be collected near a phase transition, e.g., the A_d-A_2 transition, the impedance analyser was interfaced to a computer (HP86B). The data acquisition as well as analysis in such cases was performed by this computer. A temperature regulating system permitted the sample to be heated or cooled at any desired rate. Typically, the data on the static dielectric constants were collected by varying the temperature at a rate of about 3-4°C/hr, this rate being even slower close to the phase transition. For the dispersion measurements, the temperature was held constant to +25 mK.

1.3 NEMATIC-SMECTIC A (N-A) TRANSITION

The dielectric behaviour of the liquid crystals is determined by the permanent dipoles and molecular polarizability. Because of the uniaxial symmetry of the nematic and smectic A liquid crystals, the dielectric permittivity differs in value along and perpendicular to the director. As mentioned earlier, the substances with terminally strongly polar end groups exhibit a variety of smectic A phases. A dielectric study of the different kinds of N-A transitions, viz., $N\text{-}A_1$, $N\text{-}A_d$ and $N\text{-}A_2$ has been taken up. (In fact the $N\text{-}A_1$ transition has been investigated in two types of systems, viz., those with a strongly polar end group as well as those with a terminally non-polar group.) The results of these studies have been described in chapter III. The results on strongly polar materials exhibiting the A_1 phase show that the dipole-dipole correlations in the longitudinal direction increase at the $N\text{-}A_1$ transition leading to the sharp drop in $\varepsilon_{\parallel}$. With increase in the chain length, the strength of this drop decreases and for largest n (n representing the number of carbon atoms in the alkyl chain), the change is hardly perceptible. These results are correlated with the different kinds of the cybotactic order in the nematic phases of these materials. In the case of the $N\text{-}A_d$ transition, there appears to be a very small decrease of $\varepsilon_{\parallel}$ at N-A transition, there being a saturation of $\varepsilon_{\parallel}$ in the A_d phase. The most dramatic behaviour of the static permittivity is seen at the N-A_2 transition. A very strong decrease of $\varepsilon_{\parallel}$ is observed close to the transition which can be attributed to the decrease in the effective longitudinal dipole moment due to the head-to-head arrangement of the dipoles accompanying the formation of the A_2 phase. The dispersion studies show that the activation energy in the nematic phase (W_N) is greater than that in the A_d phase (W_{A_d}) — a trend that is generally seen for most of the materials exhibiting A_d phase.[10-14] In the case of the terminally non-polar materials exhibiting the N-A, transition also essentially a similar behaviour is seen except that the W values in the case of the non-polar materials is much higher than that in the polar counterparts.[15,16] In the case of N-A_2 transition, it was again found that $W_N > W_{A_2}$. However, an unusual result was found that the frequency of relaxation f_R shows a jump at N-A_2 transition, the frequency in the A_2 phase being higher indicating a decrease in the hindrance to the molecular reorientation about the short axis due to the formation of the molecular pairs.

1.4 STUDIES ON REENTRANT NEMATIC BEHAVIOUR

For a long time it was presumed that the general sequence of phase transitions occurring in a polymesomorphic material (on cooling) should be

Isotropic → Nematic → Smectic → Solid.

But Cladis[17] discovered that in some systems there can be a nematic phase at higher as well as lower temperatures relative to the smectic A phase. She designated the lower temperature nematic phase as the reentrant nematic (N_{re}) phase in analogy with similar phenomena found in condensed matter physics.[18,19] The reentrant nematic phase was initially observed in either a binary mixture at atmospheric pressure or in a single component system at high pressures.[20] However, subsequently, single component systems exhibiting the reentrant nematic behaviour at atmospheric pressure were found[21-23] and this led to a variety of experimental studies to understand this interesting behaviour. It is now generally known that the N_{re} phase is exhibited by the materials whose molecules possess a strongly polar CN or NO_2 end groups. (Some rare exceptions[24,25] to this rule have been found. These will be discussed later.) For instance the material 4-n-octyloxy-benzyloxy-4'-cyano stilbene (T_8)[21] shows the sequence on cooling :-

$$I - N - A_d - N_{re} - A_1 . \qquad \text{(I - isotropic phase)}$$

Perhaps the richest variety of phases is exhibited by 4-nonyloxyphenyl-4'-nitrobenzoyloxy benzoate ($DB9ONO_2$)[26,27]:

$$I - N - A_d - N_{re} - A_{d(re)} - N_{(re)} - A_1 - \tilde{C} - A_2 - C_2$$

As seen above, the material T_8 exhibits two nematic and two smectic phases while $DB9ONO_2$ exhibits three nematic and four smectic A phases. Thus substances are known wherein the nematic phase reenters once or even twice. The dielectric studies conducted on materials exhibiting different types of reentrant polymorphism are described in chapter IV. These studies show that generally the dielectric anisotropy $\Delta\varepsilon$ increases smoothly with decreasing temperature on going from $N-A_d-N_{re}$. This behaviour is seen regardless of the number of times the nematic phase reenters. $\Delta\varepsilon$ is therefore seen to be indifferent to the various $N-A_d$ transitions. These results indicate that the dipolar changes accompanying the A_d-N or A_d-N_{re} transitions should be very subtle. As regards the activation energy, $W_{N_{re}}$ is always found to be greater than W_N while $W_{A_d} < W_N$. Also the W value appears to be definable only when the temperature range of the phase is small.

As mentioned earlier, the reentrant nematic behaviour is generally exhibited only when the constituent molecules possess strongly polar CN or NO_2 end group. However some exceptions to this rule have been found by the Halle group[24,25] who observed that certain binary mixtures, whose constituent compounds do not have a strongly polar end group, exhibit the N_{re} phase. Although such phase diagrams were reported, no detailed study of the physical properties of such systems had been undertaken. In Part II of Chapter IV, the results of .the dielectric studies on reentrant systems consisting of terminally non-polar materials[28-30] are described. These studies show that the dielectric properties of the non-polar reentrant mesogens appear to be somewhat different from those of strongly polar reentrant materials. This chapter also gives the dielectric results on a terminally non-polar material[29] which exhibits partially bilayer smectic A – the only such case to be observed so far. Also, the interesting new result is found that $\Delta\varepsilon$ shows a reversal of sign well inside the A phase. This appears to be the first instance of such a behaviour in a pure smectogenic material. This result also shows the existence of pronounced dipole-dipole correlations in the A_d phase.

1.5 A-A TRANSITIONS

As mentioned earlier, the following types of A phases have been clearly shown to exist: the monolayer (A_1), the bilayer (A_2), the partially bilayer (A_d) and incommensurate (AIC) phases.[31] Two other phases, viz., antiphase ($\tilde{A}$) and crenelated (A_{cre}) phases are also known.[32-34] However, these are biaxial phases and therefore cannot be considered as A phases. The different types of A phases have been characterised on the basis of the Xray diffraction patterns obtained by monodomain samples. The situation concerning the transitions between the different polymorphic forms of A phases has been discussed on the basis of a phenomenological model introduced by Prost[35-38] and developed later by Barois et al.[39] Since A_d and A_2 phases have the same symmetry, a second order transition cannot exist between them. The theory of Barois et al. predicts that under certain conditions, the first order A_d-A_2 transition can terminate at a critical point (CP) of the gas-liquid type. Such a critical point has indeed been observed experimentally.[40] Essentially the same arguments can be applied to the A_d-A_I transition also. The dislocation-loop theory of Prost and Toner[41] has shown that the A_d-A_1 transition can also terminate at a critical point of gas-liquid type but in the presence of fluctuations, the theory predicts a nematic island existing at the terminus of the A_d-A_I transition boundary. Cladis and Brand[42] had in fact previously found the existence of such a nematic island. In the case of the A_1-A_2 transition, it can be first order or even second order[43] because of the exact doubling of the lattice periodicity.[44] We have undertaken dielectric studies on materials exhibiting all these types of transitions, viz., A_d-A_2, A_1-A_2 and A_d-A_1. The results of these investigations are given in Chapter V. These studies show that the transition to the A_2 phase is always accompanied by a sharp reduction of $\varepsilon_{\parallel}$ caused by the head-to-head formation of dipolar pairs. Although a slight decrease of $\varepsilon_{\parallel}$ is also seen near the A_d-A_1 transition, a comparison of this effect with that seen near the A_d-A_2 transition shows that the dipolar heads are more disordered in the A_1 phase compared to the A_2 phase. This supports the generally assumed notion that the dipoles in the polar A_1 phase are, statistically speaking, somewhat randomly oriented. Dispersion results show that W in the A_d phase is always less than that in the lower temperature A phase, i.e., A_1 or A_2. Also, these results do not support the theoretical prediction[45] concerning the existence of two relaxation mechanisms in the bilayer A_2 phase.

1.6 A-B_{cryst} AND A-B_{hex} PHASE TRANSITIONS

Two types of smectic B phases are known, viz., crystalline B (B_{cryst}) and hexatic B (B_{hex}) phases. In the B_{cryst} phase, there are long-range positional correlations which are three-dimensional, the extent of in-planar ordering being greater than 14000 Å (resolution limited).[46] The B_{hex} phase has short-range in-plane positional correlations but long-range, three-dimensional six-fold bond-orientational order.[47] Since the discovery of the B_{hex} phase, a number of of studies[48-52] have been conducted to understand the nature of the A-B_{hex} transition. Experimentally, it is found that the A-B_{hex} transition is second order while A-B_{cryst} is first order. Dielectric studies conducted on substances exhibiting these two different types of A-B transitions are described in chapter VI.

It is found that although the static permittivity shows essentially the same behaviour near the A-B_{cryst} and A-B_{hex} transitions, there are some significant differences with regard to the dispersion results. The activation energy in the B_{cryst} phase is found to be less than in the A phase while the opposite is found to be the case for A and B_{hex} phases. It is also shown that accurate dispersion studies support the Xray results[46,52] concerning the order of the transitions, viz., A-B_{cryst} transition is first order and A-B_{hex} transition is second order.

1.7 SWALLOW-TAILED MATERIALS

As mentioned before, thermotropic liquid crystals generally consist of molecules which are rod-like, i.e., which have an elongated shape. Although initial studies seem to indicate that only systems with relatively short lateral substituents showed liquid crystallinity, the recent work by Weissflog et al.[53] shows the existence of liquid crystallinity in compounds which have two lateral chains at one end of the molecule. These materials are referred to as "swallow-tailed" compounds. Preliminary Xray studies showed that the smectic A phases formed by these compounds are of the monolayer type and it was suggested that the molecules are perhaps arranged in an antiparallel configuration. Dielectric studies conducted on two such swallow-tailed compounds are described in chapter VII. These studies show clearly the existence of pronounced antiparallel correlations in the nematic as well as in the isotropic phases of the swallow-tailed compounds. It is interesting that such correlations should be present even when the A phase formed by these molecules is of the monolayer type. These antiparallel correlations have been found to be so strong that even an addition of 30% of a material consisting of rod-like molecules is unable to reduce the antiparallel correlation.

Most of the results described in this thesis have been published in the following papers:

1 Dielectric studies of monolayer smectic A phases of strongly polar liquid crystals. (in collaboration with B.R.Ratna, R.Shashidhar and G. Heppke) - Mol. Cryst. Liq. Cryst., 139, 209 (1986).

2 Experimental studies on a triply reentrant mesogen. (in collaboration with R. Shashidhar, B.R.Ratna, V.Surendranath, V.N.Raja and S.Krishna Prasad) - J. de Physique Lett., **46,** L-445 (1985)

3 Density, dielectric and Xray studies of smectic A-smectic A transitions. (in collaboration with B.R.Ratna, V.N.Raja, R.Shashidhar, S.Chandrasekhar and G.Heppke) - Mol. Cryst. Liq. Cryst., 138, 245 (1986).

4 Dipole-dipole interactions in swallow-tailed liquid crystalline mixtures. (in collaboration with H. Kresse, W. Weissflog and R. Shashidhar) - Phys. Stat. Sol. (a) 101, K77 (1987).

5 Dielectric studies of the hexatic B-smectic A and crystal B-smectic A transitions. (in collaboration with Geetha G. Nair, B.R.Ratna, R.Shashidhar and J.W.Goodby) - Liquid Crystals (in press).

6 Antiparallel ordering of molecules in liquid crystals of swallow-tailed compounds. (in collaboration with B.R.Ratna, R.Shashidhar,

S. Chandrasekhar, H. Kresse and W. Weissflog) - Mol. Cryst. Liq. Cryst. Lett. (in press).

7 Experimental studies on a terminally non-polar reentrant nematic mixture. (in collaboration with B.R.Ratna, R.Shashidhar, V.N.Raja, S.Chandrasekhar, A. Pelzl, S. Diele, I.Latif and D.Demus) - Liquid Crystals (submitted).

8 Partially bilayer smectic A phase in a terminally non-polar compound. (in collaboration with B.R.Ratna, R.Shashidhr, V.N. Raja, S.Chandrasekhar, A. Pelzl, S.Diele, I.Latif and D.Demus) - Mol. Cryst. Liq. Cryst. Lett. (to be submitted).

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