

## CHAPTER I

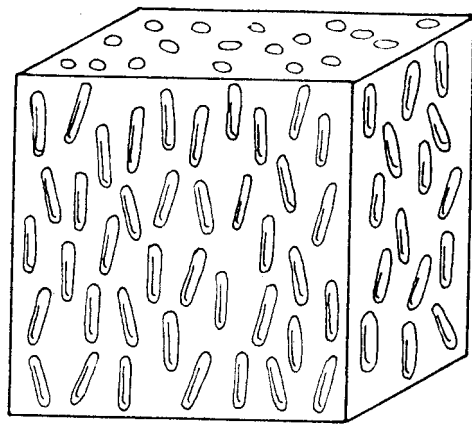
### **INTRODUCTION**

Liquid Crystals<sup>1</sup> (also known as mesophases) are states of matter in which the degree of ordering is between the three dimensionally ordered solid and the isotropic liquid. Similar to crystals they exhibit anisotropy in their optical, magnetic and electrical properties. At the same time they possess some of the mechanical properties of a fluid, e.g., inability to support shear. Compounds exhibiting mesophases can be generally classified into (i) thermotropic liquid crystals and (ii) lyotropic liquid crystals. In thermotropic liquid crystals the transitions are brought about by the effect of temperature, while in the case of lyotropic liquid crystals the mesomorphism is by the influence of solvents. Here we shall give a brief description of liquid crystals and their broad structural characteristics. A detailed account of their structure and physical properties may be found in several reviews and monographs available in the literature.<sup>2,3</sup>

#### 1.1 Classification of Thermotropic **Liquid** Crystals

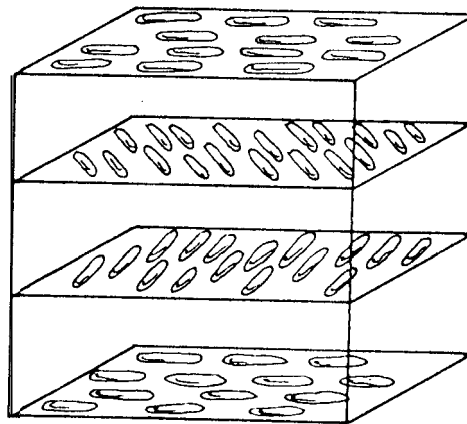
Friedel<sup>4</sup> classified thermotropic liquid crystals of rod like molecules broadly into three types: nematic, cholesteric and smectic.

The nematic phase: A simplified picture of the arrangement of the molecules in the nematic phase is shown in fig. 1.1a. This phase is characterised by



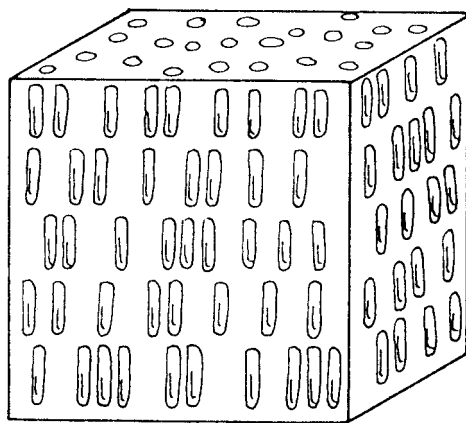
Nematic

(a)



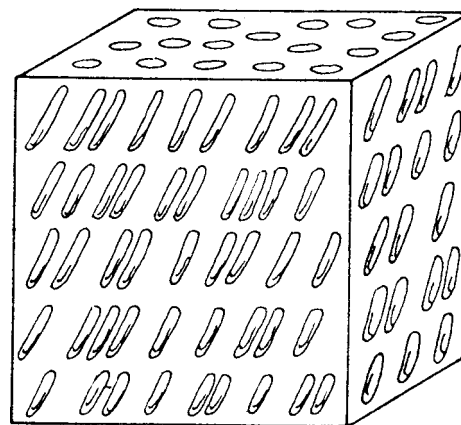
Cholesteric

(b)



Smectic A

(c)



Smectic C

(d)

Figure 1.1. Schematic representation of the molecular arrangement in (a) nematic, (b) cholesteric, (c) smectic A and (d) smectic C phases

a long range orientational order of the molecules without any long range positional order. The molecules are spontaneously oriented with their long axes parallel to some preferred direction referred to as the "director" denoted by a unit vector  $\mathbf{n}$ . The preferred direction usually varies from point to point in the medium but a homogeneously aligned sample is optically uniaxial, positive and strongly birefringent (Recently, biaxial nematics have been discovered in lyotropic systems.<sup>5</sup>) The director  $\mathbf{n}$  is apolar, i.e.,  $\mathbf{n}$  and  $-\mathbf{n}$  are indistinguishable and thus the mesophase is non-ferroelectric.

The cholesteric phase : This phase exhibited by materials composed of optically active molecules, is essentially a nematic phase except that its structure has a screw axis superimposed normal to the director (fig. 1.1b). The spiral structure imparts certain unique optical properties to the phase like selective reflection of circularly polarized light, very high optical rotatory power etc.

• Unlike the nematic, the cholesteric phase in certain compounds goes to the isotropic phase through another mesophase called the "Blue Phase". In recent years this mesophase has attracted the attention of both theoreticians and experimentalists for some of its unique properties.

The smectic phase : This phase is characterised by a layered structure in addition to the orientational order of the nematic phase. Depending on the order within a layer and the inter-layer correlations, the smectics have been classified into several types. We shall mention here, in brief, the structure of two smectic phases, viz., smectic A and smectic C, as we will be mainly interested in these smectics in this thesis. For a recent review on the stru-

ctural properties of smectics, refer to the article by Chandrasekhar and Madhusudana<sup>6</sup> and for the physical properties see Prost.<sup>7</sup>

In smectic A the average orientation of the molecules is normal to the layers with their centres irregularly spaced in a liquid like fashion (see fig. 1.1c). This arrangement has been described by a one-dimensional mass density wave<sup>8-10</sup> parallel to the director. The inter-layer correlation exhibits a quasi long range order. The Landau-Peierls instability<sup>11</sup>, arising in such a system having one-dimensional order in a three-dimensional space should manifest itself in a non-Bragg Xray line profile.<sup>12</sup> Recently, Als-Nielsen et al<sup>13</sup> have shown that this is indeed the case as the Xray scattering intensity goes as  $(q-q_0)^{-2+\eta}$  instead of the Bragg-like  $(q-q_0)^{-2}$  ( $q_0$  is the wave vector of the mass density wave). It should be mentioned here that although conceptually useful, the idealised picture of the nematic and the smectic A phases shown in figs. 1.1a and 1.1c are far from correct. A closer to reality molecular picture<sup>14</sup> of the two phases is depicted in fig. 1.2

Smectic C can be regarded as a tilted form of smectic A. In this phase, the molecules in each layer are tilted with respect to the layer normal (fig. 1.1d). While the smectic A phase is optically uniaxial, smectic C is optically biaxial.

Until recently it was believed that for mesomorphism to occur, the molecules must be rod like. But recently, Chandrasekhar et al<sup>15</sup> have established for the first time that ordering of the symmetry axes of the disc shaped mole-

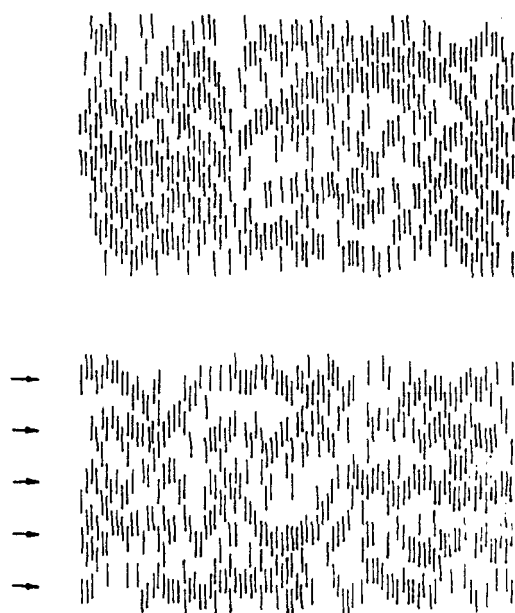
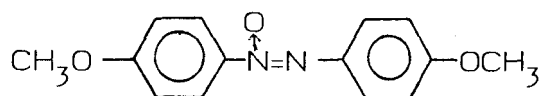


Figure 1.2 A realistic distribution of the molecules in the nematic (top) and the smectic A (bottom) phases. The arrows in the lower figure denote the crests of the density wave. (From ref. 14)

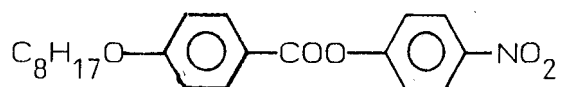
cules can also give rise to the occurrence of stable mesophases. It is now known that these mesophases exhibit a rich polymorphism, comparable to that observed in liquid crystals of rod like molecules (for a recent review on liquid crystals of disc like molecules see Chandrasekhar<sup>16</sup>). We shall not be referring to discotic phases any further in this thesis.

## 1.2 Sequence of Phase Transitions

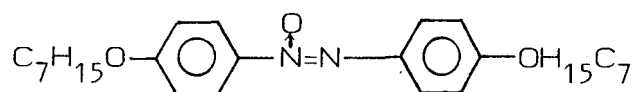
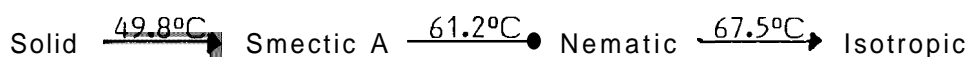
Some typical examples of mesogens, compounds exhibiting mesophases, along with the sequence of phase transitions exhibited by them are given below:



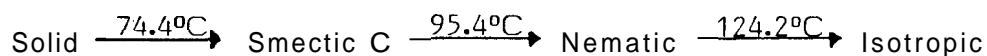
4,4'-Di-methoxyazoxybenzene or p-azoxyanisole (PAA)



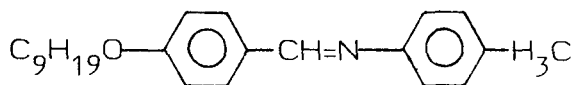
4-nitrophenyl-4'-n-octyloxybenzoate (NPOOB)



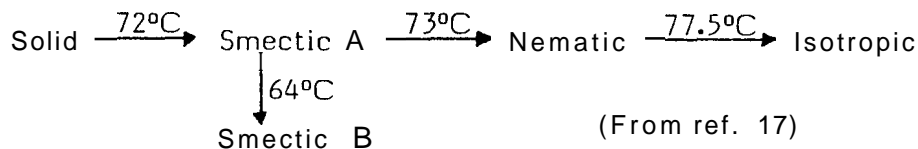
4,4'-Di-heptyloxyazoxybenzene (HOAB)



4.

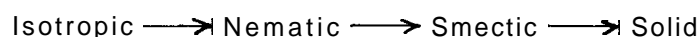


N-(4-n-nonyloxy benzylidene)-4'-n-methylamine (90.1)



If the transitions to the liquid crystalline phase occur both during heating and cooling cycles (with respect to the solid phase) then they are termed as "enantiotropic" whereas if they occur only in the cooling mode they are called "monotropic". An example of such a case is the smectic B phase of 90.1 shown in example (4) above.

Until recently, it was believed that on cooling from the isotropic phase, the sequence of phase transitions observed in a typical mesogen is as follows:



A departure from the above mentioned sequence was observed for the first time by Cladis.<sup>18</sup> She found that in a binary liquid crystalline system, the nematic-smectic A transition becomes multivalued i.e., the nematic phase occurs at higher as well as lower temperatures with respect to the smectic A phase. The lower temperature nematic phase has been designated as the reentrant nematic ( $N_{re}$ ) phase. Subsequently<sup>19,20</sup> reentrant behaviour was observed in single component systems at high pressure. Soon afterwards, compounds (single component systems) which exhibit reentrant nematic phase at atmospheric pressure were synthesised.<sup>21,22</sup> This led to not only the synthe-

sis of a large number of reentrant nematogenic compounds, but also to a variety of experiments conducted with a view to understanding the nature of the reentrant nematic phase.

Except for the recent observations of the Halle group<sup>23</sup> reentrant nematic behaviour has been so far seen only in compounds which possess a strongly polar group at one end of the molecule.

Another new and totally unexpected discovery was made<sup>24</sup> in 1979, interestingly, involving again strongly polar liquid crystals. It was observed by the Bordeaux group that mixtures of DB5 and TBBA exhibit a transition between two types of A-phases which are optically indistinguishable. This observation was soon followed by Xray diffraction studies<sup>25</sup> on the same binary system, which showed that the two A phases involved are a "monolayer" smectic A or  $A_1$  ( $d \approx l$ ) and a "bilayer" A or  $A_2$  ( $d \approx 2l$ ) [ $d$  is the smectic A layer spacing and  $l$  is the length of the molecule as measured in its most extended configuration using a molecular model]. So far four types of smectic A phases are known, viz.,  $A_1$ ,  $A_2$ ,  $A_d$  (partially bilayer i.e.,  $1 < d < 2l$ ) and a  $\tilde{A}$  (antiphase). Most of this thesis describes the results of experiments conducted on strongly polar liquid crystalline systems at high pressure.

### **Experimental Set Up**

A study of liquid crystals under pressure poses certain problems which are normally not encountered in the study of the solid state. In particular,



the chemical reactivity of liquid crystals with the materials of the container as well as with all known pressure transmitting media - liquid, solid or gas - create difficulties in the design of a suitable cell. Also considering the paucity of the availability of materials, most of which have been synthesised in our own laboratory, it became necessary to fabricate a cell which could work with a very small quantity (5 mg or less) of the sample. Taking into consideration all these factors, a high pressure optical cell was designed and fabricated using which the author has conducted light transmission experiments as well as microscopic observations upto a pressure of about 5 kbar.

A detailed description of this cell forms the subject matter of most of chapter II. Using this cell transition temperature at any pressure could be determined to a very high degree of accuracy. Special care and techniques were adapted in the measurement of pressure depending upon the experiment. For instance, in the high resolution experiments conducted with a view to study the topology of the phase diagram near the multicritical point, pressure had to be electronically monitored and maintained to within  $\pm 0.1$  bar. Since many of the results obtained at high pressure had to be substantiated by other experiments, for example, Xray diffraction, dielectric studies etc., the author has used other apparatus which have been specially constructed for such studies. In particular, the Xray diffraction set up and the dielectric set up used by the author are briefly described in chapter II.

### **Multicritical Points in Single Component Liquid Crystalline Systems**

The nematic-smectic A-smectic C multicritical point (NAC point) was

first theoretically predicted by Chen and Lubensky<sup>26</sup> and by Chu and McMillan.<sup>27</sup> Soon afterwards the NAC point was realised experimentally by Johnson et al<sup>28</sup> and independently by Sigaud et al<sup>29</sup> in binary liquid crystal mixtures. This was followed by high resolution Xray,<sup>30</sup> calorimetry<sup>31</sup> and light scattering<sup>31</sup> experiments which initiated explicit comparisons with the predictions of the theoretical models. Brisbin et al<sup>33</sup> recently obtained high resolution temperature - concentration (T-X) diagrams of four binary systems exhibiting the NAC point. On the basis of these diagrams they showed that although gross differences exist in the global features, the topology of the phase diagrams in the vicinity of the NAC point is universal. Since all these studies have been on binary systems, the need arises to observe the NAC point in a single component liquid crystalline system in the pressure - temperature (P-T) plane, in order to test whether both density and concentration fluctuations would produce the same topological distortions of the phase diagram.

There have been several high pressure studies<sup>34-36</sup> conducted with a view to locating the NAC point in a single component system. These studies did lead to a multicritical point but not a NAC point. Studies on DORBCA by Shashidhar et al<sup>36</sup> showed the existence of a new type of multicritical point, viz., reentrant nematic - smectic C - smectic A (RN-C-A) point. However, the precision in these measurements was not sufficient to make any definitive conclusions regarding the topology of the P-T diagram in the vicinity of the RN-C-A point. Chapter III gives the result of more accurate studies on the same compound (DOBBCA). These results show that the singularities are conspicuously absent near the RN-C-A point.

Studies on another strongly polar system, namely, 7 APCBB have finally led to the first observation of a NAC point in a single component system. As mentioned earlier, in order to obtain high resolution data very close to the NAC point, pressure was electronically monitored and controlled to a precision of  $\pm 0.1$  bar. The high resolution P-T diagram obtained with this precision clearly shows that the topology of the phase diagram near the multicritical point indeed exhibits universality. The exponents obtained for the different phase boundaries agree exactly with those obtained by Brisbin et al<sup>55</sup> from T-X diagrams of four binary systems. These results are presented in Chapter III. A qualitative comparison of experimental results with the predictions of the existing theories of the multicritical point (including the renormalisation group approach of Grinstein and Toner<sup>37</sup>) is also made in this chapter.

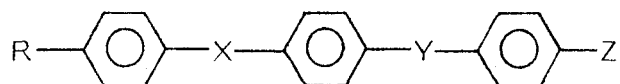
### **Studies on Strongly Polar Mesogens**

As mentioned earlier, the synthesis of single component systems exhibiting reentrant nematic phase at 1 bar<sup>21,22,38-44</sup> led to a considerable activity in this field and a variety of experiments<sup>45-49</sup> have been conducted to understand the nature of reentrant nematic phase. Kalkura et al<sup>50</sup> conducted detailed high pressure studies on many compounds exhibiting the reentrant nematic phase at atmospheric pressure. They showed that (i) the AN phase boundary in the P-T plane has the shape of an ellipse (ii) the maximum pressure of smectic stability ( $P_m$ ) which is nothing but the maximum pressure upto which the smectic A phase exists in the P-T plane, is related uniquely to the

range  $R$  of the nematic phase at 1 bar by the relation  $P_m = P_o \exp(-mR)$ . Here  $P_o$  and  $m$  are empirical constants which depend only on the number of phenyl rings that the constituent molecules possess (iii) compounds with two phenyl rings are less likely to show the reentrant behaviour than those with three phenyl rings.

The author has conducted high pressure studies on a number of strongly polar systems, three phenyl as well as two phenyl ring ones, possessing a cyano end group. These results which are described in chapter IV confirm the observations of Kalkura et al.

Presently, a large number of  $\pi$  benzene systems are known which exhibit the reentrant nematic behaviour. A typical chemical structure of a molecule of a reentrant nematogen would be



Here  $R$  is alkyl or alkoxy chain,  $X$  and  $Y$  are bridging dipoles and  $Z$  denotes the strongly polar end group.

For  $Z = CN$ , a reentrant nematic behaviour is seen when the longitudinal component of  $X$  is additive with respect to that of the cyano end group regardless of the disposition of  $Y$ . On the otherhand, when these directions are opposite, an A-A transition<sup>44,51</sup> is normally observed. In the case of  $Z = NO_2$ , the reentrant nematic behaviour as well as A-A transitions have been seen *only* when the longitudinal component of  $X$  opposes that of the nitro end group.<sup>44,51</sup>

Chapter V describes the results of high pressure, miscibility, Xray diffraction and dielectric studies on a terminally substituted nitro compound in which both X and Y are disposed additively with respect to the nitro group. These results clearly show that this compound has a latent reentrant nematic behaviour, showing thereby that the occurrence of the reentrant nematic behaviour at 1 bar in terminally nitro substituted compounds in which the longitudinal component of the bridging dipoles are additive with respect to the nitro end group is a distinct possibility.

As already mentioned, the transition between two polymorphic forms of smectic A has been seen in single component systems only when the longitudinal component of the bridging group dipoles oppose that of the polar end group regardless of whether the end group is cyano or nitro.<sup>52-56</sup> Miscibility, high pressure, Xray and dielectric studies on binary mixtures of 4-nitrophenyl-4'-(4"-n-hexyloxy benzoyloxy)benzoate (6 ONPBB) and p-nonyloxybenzoyloxy-p'-cyanoazobenzene (9 OBCAB) have been carried out and the results of these investigations are given in Chapter VI. 6 ONPBB is a terminally nitro substituted compound while 9 OBCAB is a terminally cyano substituted one, the bridging group dipoles being additive to the polar end group dipole in both the cases. However, contrary to the norm discussed above, mixtures of these exhibit over a range of concentrations two kinds of A-A transitions, namely,  $A_1-A_d$  and  $A_d-A_d$ , the latter being observed for the first time. Although the transition between the A phases are themselves unobservable optically in the P-T plane, they leave dramatic signatures on the A-N boundary. Accurate Xray determination of the layer spacing carried out as a function of

temperature for different concentrations clearly permit us to identify three kinds of A phases.

1. the  $A_1$  phase ( $d/l \approx l$ ) at low temperatures with a temperature independent layer spacing
2. the  $A_d$  phase with a temperature dependent layer spacing
3. another  $A_d$  phase at high temperatures which is characterised by a temperature invariant layer spacing.

The results of these studies discussed in this chapter clearly show that the differences between these A phases are very subtle.

### **Pressure Studies on Materials Exhibiting a Chiral Smectic C Phase**

Based on the thermal dependence of the tilt angle, smectic C phases have been classified into three categories:<sup>57-60</sup> (i) those which precede a smectic A phase showing a temperature dependent tilt angle that goes to zero at the transition. (ii) those which precede a nematic phase having a thermally invariant tilt angle which goes to zero at the transition. (iii) those in which the tilt angle is weakly temperature dependent and remains finite in the smectic A phase also.

Kalkura et al<sup>61</sup> have conducted pressure studies on compounds exhibiting the different types of C phases. They found that in all the cases pressure has the destabilizing effect on the C phases. It was of interest to see whether this is true even for the chiral smectic C phase. So far there has been only one detailed pressure study.<sup>62</sup> The author has therefore carried out high

pressure studies on three compounds, namely, OOBAMBC, DOBAMBC and HOBACPC. It may be mentioned that all the three compounds are well known ferroelectric liquid crystals.<sup>63</sup> All these compounds exhibit A, C\* and I\* phases. In two of these, viz., OOBAMBC and DOBAMBC, the C\* phase gets suppressed and the I\*-C\*-A triple point has been observed at 1.7 and 3.8 kbar respectively. In case of the third compound, HOBACPC, the rate of decrease in the range of the C\* phase with increasing pressure is quite small and hence a triple point is expected (by extrapolating the phase boundaries) to occur only at a pressure of about 8 kbar. The phase diagrams are discussed in relation to the temperature dependence of the tilt angle in the C\* phase.

### **Pressure Studies on Phospholipids**

Phosphatidylcholine is a major phospholipid of animal membranes. Studies of the phase transition in these systems are useful in understanding the structure and properties of natural biomembranes. Phase transitions in hydrated Dimyristoyl- and Dipalmitoyl phosphatidylcholine (DMPC and DPPC) have been investigated in detail by several authors.<sup>64-67</sup> DMPC exhibits, in the low hydration regime, four distinctly different transitions, the transition temperatures being strongly dependent on the water concentration. When the amount of water exceeds 30% by weight, there exist a main transition and a pre transition, the temperature of both of these being independent of composition. Similar transitions occur in DPPC in the high hydration regime. Detailed Xray diffraction studies<sup>66</sup> have shown that the main transition is between a liquid crystalline (LC) phase and a solid like gel phase (Gel I), while

the pre transition is between the Gel I phase and a second gel phase, Gel II. The LC phase has a lamellar structure in which the hydrocarbon chains have been conformationally disordered. The structure of the Gel I phase is one in which the lipid bilayer lamellae are distorted by the periodic ripple, the chains being tilted with respect to the bilayer normal and are packed in a hexagonal lattice. In the case of the Gel II phase, the ripple appears to have evened out the chains which are now packed in a somewhat distorted hexagonal lattice. A subtransition between Gel II and another gel (Gel III) has been known to occur in DPPC<sup>68</sup> when the sample is annealed at low temperatures for long periods of time. Such a subtransition has been observed only recently in the case of DMPC.<sup>69,70</sup> The structure of the Gel III phase is yet to be elucidated. Pressure studies on phase transitions in both hydrated DMPC and DPPC systems have been conducted by the author. Results of these investigations are given in **Appendix**. In the case of DMPC, the interesting features are:

1. Existence of Gel III - Gel II - Gel I triple point at 3.5 kbar and 41°C.
2. Gel III - Gel II transition which has been seen at atmospheric pressure only after protracted temperature annealing is seen to occur at high pressure after pressure-annealing of the samples for relatively shorter periods (for about 12 hours).

The P-T diagram of DPPC is even more interesting. A ~~new~~ but still unidentified pressure induced phase designated as X appears beyond a pressure' of 930 bar, the X-Gel I boundary forking out of the Gel II - Gel I phase line.



With further increase in pressure the range of the X phase grows at the expense of the Gel I phase resulting ultimately in the complete suppression of the Gel I phase at 2.87 kbar beyond which pressure the X phase directly transforms into the LC phase. Thus the P-T diagram of DPPC has two triple points, viz., (i) Gel II - X - Gel I and (ii) X - Gel I - LC. Although the nature of the X phase still remains in question, the X - Gel I phase transition could possibly be a ripple - ripple transition like the ones seen by Sackmann et al.<sup>71,72</sup> and Strenk et al.<sup>73</sup>

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

1. Nematic - smectic A - smectic C multicritical point in a single component system (in collaboration with R.Shashidhar and B.R.Ratna) Phys. Rev. Lett., 53, 2141 (1984).
2. The topology of the P-T diagram of DOBBCA in the vicinity of the reentrant nematic - smectic C - smectic A multicritical point (in collaboration with R.Shashidhar and S.Chandrasekhar) Presented at the IX Int. Liq. Cryst. Conf., Bangalore, December 1982; Mol. Cryst. Liq. Cryst., 103, 137 (1983).
3. High pressure studies on partially bilayer and monolayer smectics (in collaboration with R.Shashidhar, K.A.Suresh, A.N.Kalkura, G.Heppke and R.Hopf) Presented at the IX Int. Liq. Cryst. Conf., Bangalore, December 1982; Mol. Cryst. Liq. Cryst. 99, 185 (1983).
4. Effect of pressure on strongly polar liquid crystals (in collaboration with

- S.Pfeiffer, G.Heppke and R.Shashidhar) Z. Naturforsch. (in press).
5. Experimental studies on a terminally substituted nitro compound with a latent reentrant nematic phase (in collaboration with B.R.Ratna, R.Shashidhar, G.Heppke and S.Pfeiffer) Presented at the X Int. Liq. Cryst. Conf., York, July 1984; Mol. Cryst. Liq. Cryst. 124, 21 (1985).
  6. A new kind of A-A transition : studies on binary mixtures of terminally substituted cyano and nitro compounds (in collaboration with R.Shashidhar and B.R.Ratna) Mol. Cryst. Liq. Cryst. Lett., ~~102~~, 105 (1984).
  7.  $A_d-A_d$  transition in a binary liquid crystal system (in collaboration with R.Shashidhar and B.R.Ratna) Presented at the X Int. Liq. Cryst. Conf., York, July 1984; Mol. Cryst. Liq. Cryst. (in press).
  8. Pressure studies on ferroelectric liquid crystals (in collaboration with B.R.Ratna, R.Shashidhar and V.Surendranath) Ferroelectrics, Special Issue on Ferroelectric Liquid Crystals, 58, 101 (1984).
  9. High pressure study of phase transitions in DMPC - water system (in collaboration with R.Shashidhar, B.P.Gaber and S.Chandrasekhar) Presented at the Am. Chem. Soc. Meeting, St. Louis 1984; Mol. Cryst. Liq. Cryst., 110, 153 (1984).
  10. Pressure studies on two hydrated phospholipids - DMPC and DPPC (in collaboration with R.Shashidhar, B.P.Gaber and S.Chandrasekhar) Biochim. Bio Phys. Acta., (Submitted).

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