

## CHAPTER I

### INTRODUCTION

Liquid crystals possess a degree of molecular order which is intermediate between that of a three dimensionally ordered solid and that of a fully disordered isotropic liquid.<sup>1,2</sup> Liquid crystalline phases or mesophases can be obtained either by varying temperature or by the addition of a solvent.<sup>3</sup> The former are referred to as thermotropic liquid crystals and the latter as lyotropic liquid crystals. This thesis deals only with thermotropic liquid crystals.

#### 1.1 CLASSIFICATION OF THERMOTROPIC LIQUID CRYSTALS

Friedel<sup>4</sup> classified thermotropic liquid crystals composed of rod-like molecules into three categories - nematic, cholesteric and smectic. The schematic representation of the molecular arrangements in these mesophases is shown in Fig. 1.1.

##### **Nematic**

The molecules in the nematic phase have a spontaneous long range orientational order (Fig. 1.1a) i.e., the molecules are, on the average, oriented parallel to a mean direction referred to as the director (indicated by the unit vector  $\vec{n}$  in the figure). The preferred direction in the nematic usually changes from point to point in the medium but an oriented sample is optically uniaxial

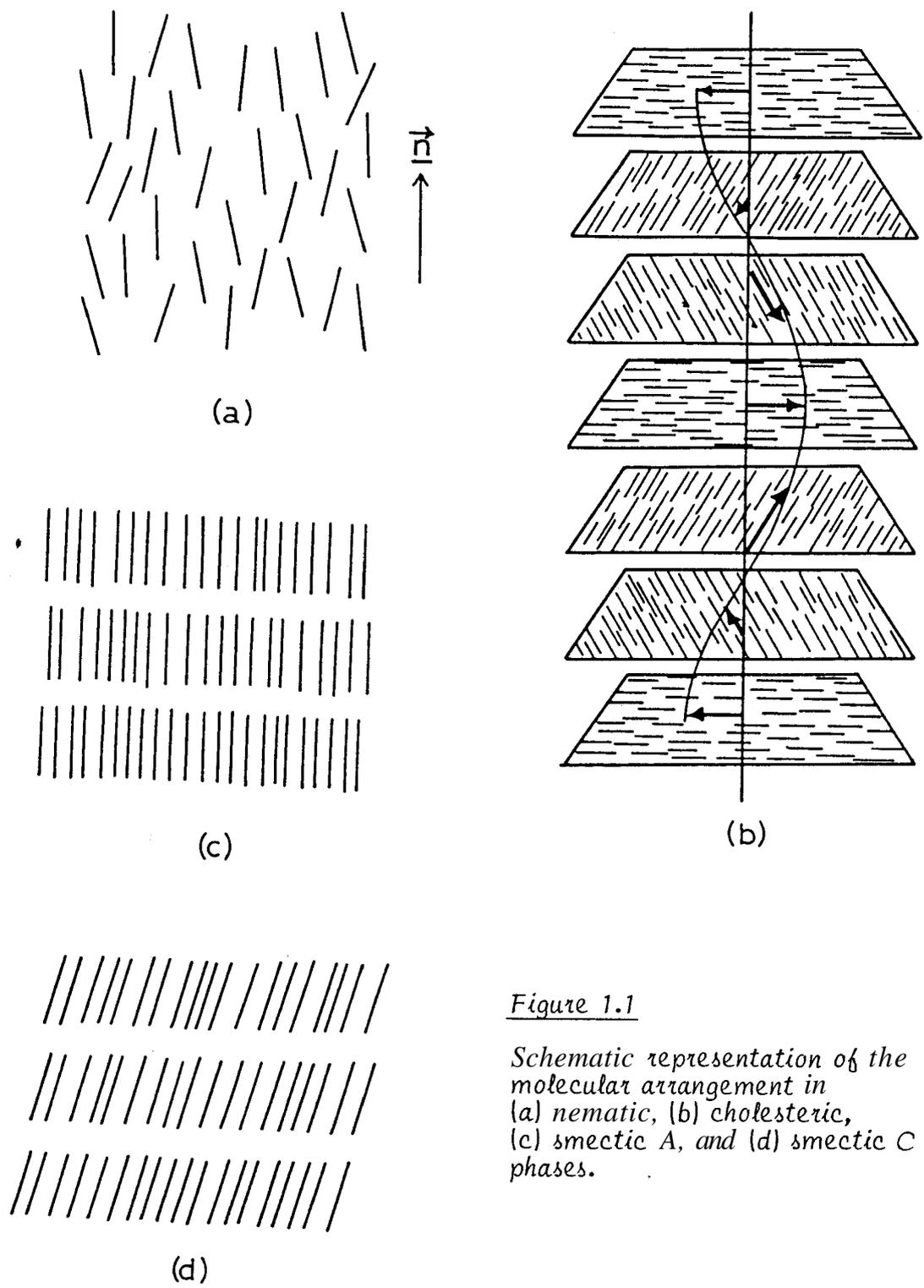


Figure 1.1

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

and strongly birefringent. The director  $\vec{n}$  is apolar, i.e.,  $\vec{n}$  and  $-\vec{n}$  are equivalent and therefore the mesophase is non-ferroelectric.

### **Cholesteric**

This mesophase, which is exhibited by materials composed of optically active molecules, is essentially of the nematic type except that the structure has a screw axis which is superimposed normal to the director (see Fig. 1.1b). Due to this helical structure the cholesteric phase exhibits some unique optical properties, e.g., selective reflection of circularly polarized light, very high optical rotatory power, etc. Whereas the nematic transforms directly into the isotropic phase, a cholesteric phase of sufficiently low pitch ( $\leq 5000 \text{ \AA}$ ) transforms into the isotropic phase via an intermediate phase called the "blue phase", which usually occurs over a very narrow region of temperature. At least three kinds of blue phases are known experimentally so far, but the detailed structural aspects are still not yet precisely known.<sup>5</sup>

### **Smectics**

Smectic liquid crystals are characterized by a layered structure, and thus they have both positional and orientational ordering. Different types of smectic liquid crystals are classified depending on the order within the layer and the interlayer correlation. In the smectic A phase the long axis of the molecule is, on the average, perpendicular to the layer plane while in the C phase it is tilted (see Fig. 1.1(c) & (d)). However, in both cases, the

arrangement of the molecules within a layer is liquid like. Several other types of smectic phases are also known (for a recent review on smectic liquid' crystals, see ref. 6). But since this thesis deals only with smectic A and smectic C, the other smectic modifications will not be discussed here.

The picture of the smectic A phase described above is somewhat simplistic. A more realistic description of the smectic A phase is to look upon it as a one-dimensionally ordered fluid with a mass density wave along the optic axis<sup>7-9</sup>:

$$\rho(r) = \rho_0 [1 + \text{Re}|\psi| \exp i (q_0 z + \phi)] ,$$

where  $q_0 = 2\pi/d$  is the wavevector at which the X-ray diffraction peak corresponding to the layer spacing ( $d$ ) occurs in reciprocal space,  $\phi$  is a phase factor which fixes the position of the layers,  $|\psi|$  is the amplitude of the density wave which is a measure of the strength of the smectic order and  $\rho_0$  is the average density. For a long time only one type of smectic A phase was known, viz., the monolayer A phase in which the layer thickness is approximately equal to the length of the molecule (as measured in its most extended configuration). However, due to the pioneering work carried out by the Bordeaux group<sup>10</sup> it is now known that when the constituent molecules have a strongly polar cyano or nitro end group at one end of the molecule, various types of smectic A phases can be observed. This will be discussed in greater detail later.

## 1.2 SEQUENCE OF TRANSITIONS

It has been known that the general sequence of transitions occurring in a poly mesomorphic substance cooling from the isotropic phase is :

Isotropic → Nematic → Smectic → Solid

However a departure from this sequence was observed by Cladis<sup>11</sup> when she found in the binary mixture of n-p-cyanobenzylidene-p'-octyloxyaniline (CBOOA) and p-[(p'-hexyloxybenzylidene)amino]benzotrile (HBAB) the sequence

Isotropic → Nematic → Smectic A → Nematic → Solid

The lower temperature nematic has been designated as the reentrant nematic phase. Since then a variety of materials have been synthesized which exhibit reentrant polymorphism. (For a recent review of materials exhibiting reentrant nematic phase see Ref. 12.)

## 1.3 DISC-LIKE MESOGENS

For a long time it was believed that one of the pre-requisites for the observation of liquid crystalline phases was that the constituent molecules should be "rod-like". However recently Chandrasekhar et al.<sup>13</sup> observed the occurrence of mesophases in compounds having disc-like molecules. The chemical structure of these compounds is shown in Fig. 1.2. Based on optical and X-ray studies Chandrasekhar et al.<sup>14</sup> proposed a structure which is schema-

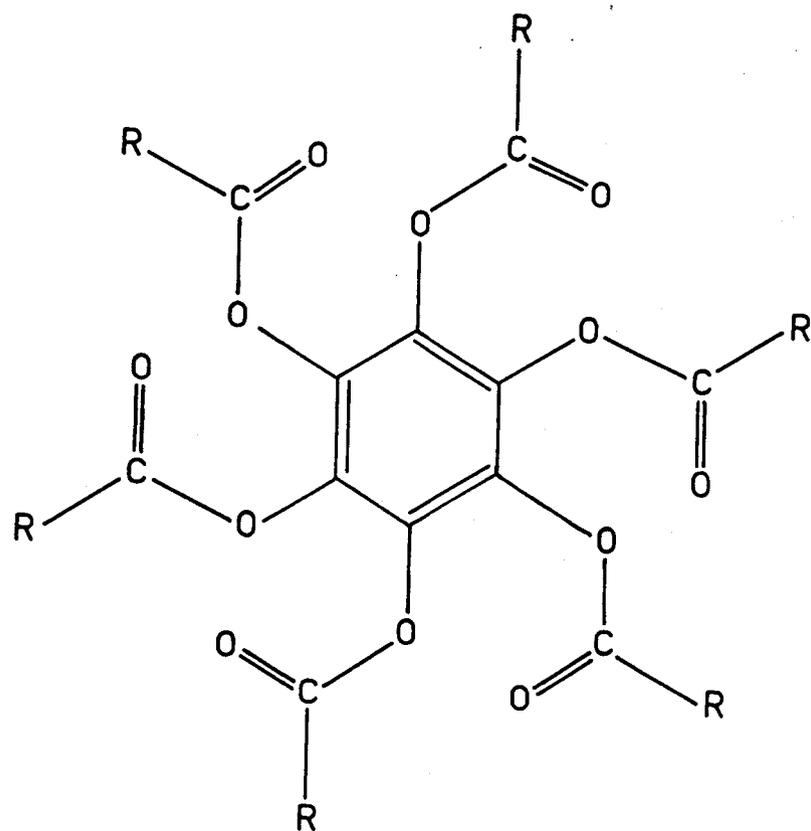


Fig. 1.2: The chemical structure of hexa-n-alkanoates of benzene.

tically shown in Fig. 1.3. It consists of discs arranged aperiodically along the columnar axis and stacked so as to form columns. This "columnar structure" has been subsequently confirmed by the X-ray studies of Levelut.<sup>15</sup> It is now known that discotic substances exhibit a rich degree of mesomorphism, comparable to that of rod-like systems. (For a recent review of discotic-mesogens see Ref. 16 and 17).

#### **1.4 POLYMERIC LIQUID CRYSTALS**

Liquid crystalline phases are also exhibited by thermotropic polymeric systems. There are two types of thermotropic polymeric liquid crystals, viz., main-chain and side-chain polyesters.<sup>18</sup> These are represented in Fig. 1.4. Main chain polyesters show generally the nematic phase while the side chain polyesters are now known to show not only nematic but also smectic A and smectic C phases.

#### **1.5 EXPERIMENTAL SET UP**

The results described in this thesis have been obtained using X-ray diffraction, high pressure and miscibility studies. The details of the X-ray and high pressure apparatus are given in Chapter II. The miscibility technique is described in detail in Chapter V.

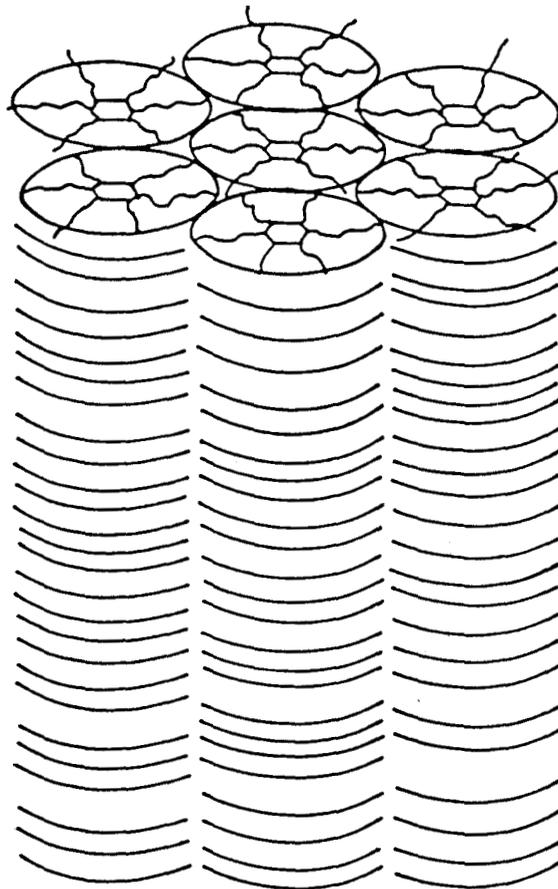


Figure 1.3

*Schematic representation of the columnar structure of the mesophase. The discs are spaced irregularly to form liquid-like columns. (From Ref. 14).*

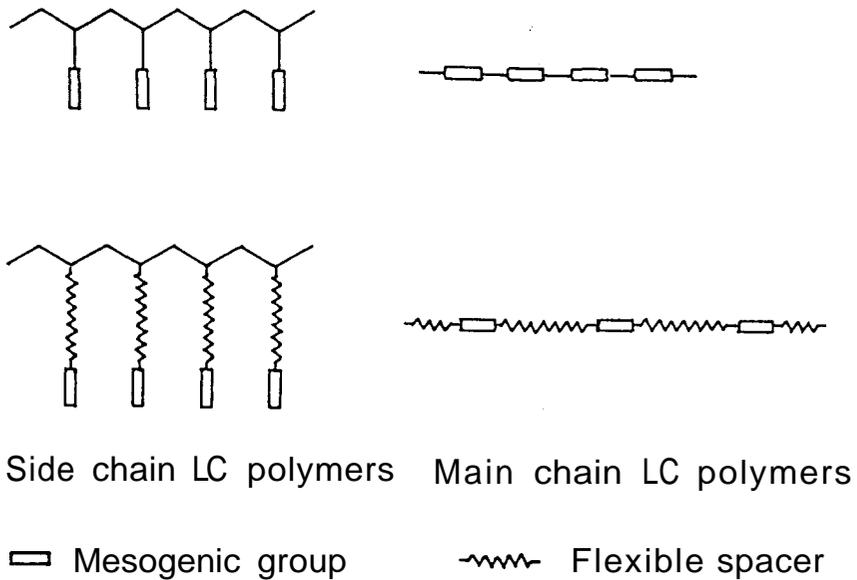


Figure 1.4

*Thermotropic polymers with either main-chain or side-chain mesogenic units.*

### X-ray diffraction

Most of the X-ray experiments described in this thesis (i.e., except those described in Chapters IV and V) were conducted using the photographic method. A bent quartz monochromator was used and  $K_{\alpha}$  radiation was focussed on to a photographic film which served as the detector. The liquid crystalline sample, taken in a Lindemann capillary, was aligned 'in situ' in a magnetic field. The set up gave very sharp X-ray diffraction spots. The constancy of temperature during any exposure was found to be  $\pm 100$  mK and the accuracy in the layer spacing measurement is reckoned to be  $\pm 0.1 \text{ \AA}$ .

The X-ray diffraction experiments described in Chapters IV and V were conducted using a computer-controlled Guinier diffractometer (Huber 644). By means of a bent quartz monochromator used in the Johansson geometry,  $\text{Cu}K_{\alpha 1}$  and  $K_{\alpha 2}$  lines were separated and only  $K_{\alpha 1}$  was used for the experiment. The liquid crystalline sample in a Lindemann capillary (0.5 mm diameter) was oriented by slow cooling from the nematic phase in the presence of a magnetic field (2.4T). The detector (NaI Scintillation Counter, Bicron) was mounted on a rotatable graduated base whose angular scans could be controlled by a stepper motor. A Hewlett-Packard computer (HP-86B) was used for controlling the angular movement of the detector, as well as for data acquisition and analysis. Temperatures were held constant to  $\pm 10$  mK or better during any measurement of the Bragg angle  $\theta$ . The precision in the determination of the wavevectors

was  $\pm 2 \times 10^{-4} \text{ \AA}^{-1}$ .

### High Pressure Studies

High pressure studies were conducted using an optical high pressure cell with sapphire windows. The transitions were detected by the light transmission technique and by varying the temperature slowly at any desired pressure. At the transition there was a sudden change in the intensity of the light transmitted by the sample. Pressure was measured to an accuracy of  $\pm 1.5$  bar while temperature was determined to  $\pm 25$  mK.

### Miscibility Studies

For the observation of high resolution temperature-concentration (T-X) diagram the major problem that was encountered was that the materials were available only in small quantities from which at least 25 - 30 mixtures of different compositions had to be prepared so as to map out the phase boundaries. However this problem was overcome by evolving a technique of careful weighing and sample preparation. Using this method a high resolution T-X phase diagram near an expected bicritical point could be obtained, as will be seen in Chapter V.

## 1.6 THE WEAKLY COUPLED INCOMMENSURATE SMECTIC A PHASE

As already mentioned, the smectic A phase can be considered to be an orientationally ordered fluid with a one-dimensional mass-

density wave along the optic-axis. When the constituent molecules consist of strongly polar cyano or nitro end groups then the adjacent molecules favour an antiparallel near neighbour arrangement.<sup>19</sup> This antiparallel correlation leads to a variety of A phases. The different types of A phases known so far are the monolayer phase  $A_1$ , the bilayer phase ( $A_2$ ) and the partially bilayer ( $A_d$ ) phase. These phases have been characterized on the basis of the X-ray diffraction patterns exhibited by monodomain samples. In the case of  $A_1$ , the diffraction spot is seen at a wavevector  $2q_0$  which corresponds to a layer spacing  $d \approx \ell$ . The  $A_2$  phase exhibits two diffraction spots, one at wavevector  $q_0$  and the other at  $2q_0$ , corresponding to the bilayer and monolayer periodicities respectively. On the other hand  $A_d$  gives a diffraction spot at a wavevector  $q_0 = 2\pi/\ell'$ , where  $\ell < \ell' < 2\ell$ .

Smectic A polymorphism has been explained by the phenomenological theory developed by Prost.<sup>20</sup> In this theory the free energy is expressed in terms of two order parameters - one associated with the mass density and the other with the dipolar order which accounts for the antiparallel associations of the molecules. This theory predicts that under certain conditions (viz., when the elastic term of the free-energy is greater than the lock-in term) there should exist an incommensurate A phase with two collinear periodicities which are incommensurate with respect to each other. Although this prediction was made some time ago, an incommensurate phase had never been observed experimentally. Studies conducted here

on the binary system 4-n-heptyloxyphenyl-4'-cyanobenzoyloxybenzoate, and 4-n-octyloxy-4'-cyanobiphenyl (DB70CN and 8OCB) showed the existence of such an incommensurate phase ( $A_{iC}$ ) for the first time. The signature of the incommensurate phase in the X-ray experiment was the existence of condensed reflections at  $q_0$ ,  $q'_0$  and  $2q_0$ , the relative intensities of the peaks at  $q_0$  and  $q'_0$  varying with temperature. This incommensurate phase which was found to intervene between  $A_d$  and  $A_2$  phases was seen over a narrow region of concentration in the temperature-concentration (T-X) plane of the binary system. Careful experiments performed on different concentrations exhibiting the  $A_{iC}$  phase show clearly that the behaviour of the layer spacing in the incommensurate phase is completely different from what is expected if it were to be a two phase region. Thus existence of the first fluid incommensurate phase has been established. These results are presented in Chapter III.

### 1.7 THE STRONGLY COUPLED INCOMMENSURATE PHASE

The phenomenological theory of Prost<sup>21</sup> referred to in the previous section in fact predicts the possibility of two types of incommensurate smectic A phases, viz., (i) the weakly coupled type in which the two collinear density waves exist almost independent of each other, and (ii) the strongly coupled type in which the phases of the two density waves are modulated in one-dimension (i.e., along the director). The latter type of incommensurate phase should therefore exhibit X-ray reflections corresponding to the

combination of the incommensurate wavevectors or solitons whose periodicity corresponds to the difference or ~~sum~~ of the incommensurate wavevectors. The absence of any such combination reflections in the incommensurate phase described in Section 1.6 indicates that this is probably of weakly coupled type. Fontes et al.<sup>22</sup> have observed incommensurate fluctuations corresponding to the soliton periodicity in the  $A_1$  phase, but the incommensurate phase itself was not observed by them. Experiments conducted here on 4-n-octyloxy-4'-cyanobenzoyloxybenzoate (DB80CN) and 4-octyloxybenzoyloxy-4"-cyanoazobenzene (80BCAB) have finally led to the 'observation of a strongly coupled incommensurate phase. For a range of concentrations, it was observed that on cooling the  $A_d$  phase goes over to a weakly coupled incommensurate phase with coexisting  $q_0$  and  $q'_0$  modulations which in turn crosses over to another type of weakly coupled incommensurate phase with the  $2q_0$  and  $q'_0$  modulations. On further cooling the strongly coupled incommensurate A phase ( $A_{iS}$ ) with the X-ray diffraction spots at  $q''_0$  ( $\neq q'_0$ ),  $2q_0$  and  $q_S = 2q_0 - q''_0$  is observed. The occurrence of the combination reflection  $q_S$  shows the existence of 'solitons' in one-dimension (i.e., along the optic axis of the medium) formed due to a coupling of the phases of the incommensurate density modulations ( $q''_0$  and  $2q_0$ ). Finally a lock-in transition to the  $A_2$  phase was observed wherein  $q''_0$  and  $q_S$  converge to a value  $q_0$ . These results are described in Chapter IV.

## 1.8 A NEW ALTERNATIVE FOR THE $A_1 - N_{re} - A_d$ BICRITICAL POINT

Transitions involving the different types of smectic A phases have been the subject of several experimental as well as theoretical investigations. From symmetry arguments<sup>23</sup> both  $A_d - A_1$  and  $A_d - A_2$  transitions can be only first order while  $A_1 - A_2$  can be either first or second order because of the doubling of the layer periodicity. The phenomenological theory discussed earlier has been extended by Barois, Prost and Lubensky<sup>23</sup> to calculate the different phase diagrams that are possible involving various forms of the A phase. The theory predicts the existence of different types of critical points: (1)  $A_1 - A_2$  and  $N - A_2$  tricritical points, (2)  $A_d - A_2$  critical point, and (3)  $A_1 - N_{re} - A_d$  bicritical point ( $N_{re}$  referring to thereentrant nematic phase).

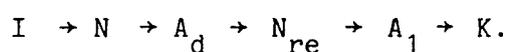
The  $A_1 - A_2$  tricritical point as well as  $A_d - A_2$  critical point have been experimentally observed,<sup>24,25</sup> while the  $N - A_2$  tricritical point has not been seen so far. The situation concerning the  $A_1 - N_{re} - A_d$  bicritical point is very interesting. Phase diagrams have been reported with such a  $A_1 - N_{re} - A_d$  point<sup>10,26</sup> and it has been pointed out<sup>27</sup> that the topology of the phase diagram resembles the typical topology of the magnetic bicritical point.<sup>28</sup> However high resolution studies of the phase diagram in the immediate vicinity of the  $A_1 - N_{re} - A_d$  point have not been conducted so far. Also there is a difficulty regarding the theoretical prediction. Although the mean field theory does predict the existence of a  $A_1 - N_{re} - A_d$  bicritical point,

the existence of such a bicritical point becomes questionable when the effect of fluctuations are considered. It has been argued<sup>23</sup> that since both  $A_1$  and  $A_d$  phases have the same symmetry, the  $N_{re} - A_1$  and  $N_{re} - A_d$  transitions should both belong to the same universality class namely, the inverted XY universality class.<sup>29</sup> Renormalization group calculations<sup>30</sup> show that under such a circumstance the resulting multicritical point cannot be a bicritical point but a tetra-critical point. An off-shoot of this is the prediction that an incommensurate phase should exist between  $A_d$  and  $A_1$  phases close to the expected  $A_1 - N_{re} - A_d$  point.

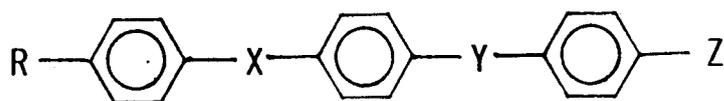
Detailed high resolution study of the phase diagram and DSC studies have been performed on the 4-n-octyloxyphenyl-4'-(4"-nitrobenzoyloxy)benzoate (DB8.O.NO<sub>2</sub>) and 4-n-decyloxyphenyl-4'-(4"-nitrobenzoyloxy)benzoate (DB10.O.NO<sub>2</sub>) binary system. These studies clearly show that the topology of the phase diagram in the immediate vicinity of the  $A_1 - N_{re} - A_d$  point does not resemble the typical topology of the magnetic bicritical point. Calorimetric studies prove that the heat associated with the  $A_1 - A_d$  transition does not go to zero at the  $A_1 - N_{re} - A_d$  point as it should if it was a bicritical point.<sup>21</sup> These studies suggest a new alternative for the  $A_1 - N_{re} - A_d$  point, viz., that the bicritical point has in fact split up into a critical end point (for the  $A_d - N_{re}$  boundary) and tricritical point (for  $A_1 - N_{re}$  boundary). Such a situation has not been envisaged by any of the existing theories so far. These investigations are presented in Chapter V.

### 1.9 PRESSURE INDUCED TRIPLY REENTRANT BEHAVIOUR IN A SINGLE COMPONENT SYSTEM

After the discovery by Cladis<sup>11</sup> of reentrant behaviour in a binary mixture at atmospheric pressure, Cladis et al.<sup>31</sup> reported the observation of the reentrant nematic phase in a single component system at high pressures. Soon single component systems with a reentrant nematic phase at atmospheric pressure were synthesized.<sup>32,33</sup> In fact, even the first few compounds in which reentrant behaviour was observed at atmospheric pressure, exhibited not only the reentrant nematic phase but also the reentrant smectic A phase. The sequence of transitions seen in these cases is

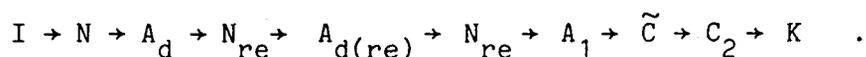


Since then a large variety of materials have been synthesized which exhibit reentrant polymorphism.<sup>12</sup> It can be generalized that the molecular structure favouring the  $N_{re}$  phase is as follows.



where R stands for the alkyl or alkoxy group, X and Y are the bridging dipoles and Z is the strongly polar end group, viz., cyano or nitro end group. It is observed that when  $Z = CN$  reentrant behaviour is seen when the longitudinal component of the dipole X is additive with respect to the cyano end group regardless of the

disposition of the dipolar group Y. On the other hand, when the terminal group is  $\text{NO}_2$ , reentrant behaviour is seen only when the longitudinal component of both X and Y oppose that of the  $\text{NO}_2$  group. Also the occurrence of  $\text{N}_{\text{re}}$  phase in terminally nitro compounds is less frequent than in terminally cyano compounds, and in addition, it is extremely sensitive to changes in molecular length. This is, in fact, most dramatically demonstrated in the 4-n-alkoxyphenyl-4'-(4"-nitrobenzoyloxy) benzoate ( $\text{DBn.O.NO}_2$ ) series. The  $n=7, 8$  and  $10$  compounds show only one type of smectic A-nematic transition ( $\text{A}_1 - \text{N}$  or  $\text{A}_d - \text{N}$ ) while  $n=9$  exhibits perhaps the richest variety of the liquid crystalline phases seen in a single component system so far. When initially synthesized,<sup>34</sup> the material was found to exhibit the following sequence of transitions:



X-ray as well as high pressure studies have been conducted on a purer form of  $\text{DB9.O.NO}_2$  synthesized in the laboratory. These studies have revealed the existence of an additional phase namely the  $\text{A}_2$  phase between  $\tilde{\text{C}}$  and  $\text{C}_2$  phases. Pressure-temperature diagram of  $\text{DB9.O.NO}_2$  is found to be extremely interesting with both  $\text{A}_d$  and  $\text{A}_{d(\text{re})}$  phases getting bounded by the nematic phase at high pressures. In contrast pressure does not show such effects in  $\text{DB8.O.NO}_2$  and  $\text{DB7.O.NO}_2$ . On the other hand pressure induces a variety of phases in  $\text{DB10.O.NO}_2$  - first the  $\text{A}_2$  and then the  $\text{A}_1$  phases. In addition a reentrant nematic phase is also induced. Perhaps the most dramatic

observation is that  $A_d - N_{re}$  boundary bends twice towards the pressure axis and thereby in the pressure range of 1.26 to 1.38 kbar, the sequence of transition on decreasing the temperature is found to be nothing but that observed in DB9·O·NO<sub>2</sub> at atmospheric pressure. This is the first observation of the pressure-induced triply reentrant behaviour. These results are described in Chapter VI.

#### 1.10 STUDIES ON TERMINALLY NON-POLAR MATERIALS

It has already been pointed out that reentrant nematic behaviour is generally exhibited by compounds possessing a strongly polar end group. However very recently, Pelzl et al.<sup>35</sup> have reported the observation of a reentrant nematic phase in a binary system whose constituent compounds do not possess a strongly polar end group. X-ray and high pressure studies have been taken up on one such binary system. It is observed that the  $d/\ell$  value is about 1.02 showing thereby that the A phase is probably of the partially bilayer type. The pressure-temperature diagram of the mixture is very similar to that observed for the strongly polar reentrant systems.<sup>36</sup> These results are presented in Chapter VII. Dowell<sup>37</sup> has shown on the basis of the molecular lattice theory that the partially bilayer smectic A phase as well as the reentrant nematic phase can be exhibited by terminally non-polar materials. X-ray studies conducted on 12EBAMC, a terminally non-polar smectogenic material, have shown that the A phase of this substance is of the partially bilayer ( $A_d$ ) type with the relatively large  $d/R$  value

of  $-1.13$ . Interestingly this value is very similar to that seen for strongly polar reentrant systems.<sup>38</sup> Also, this is the first observation of the partially bilayer phase in a terminally non-polar material. These results are described in the second part of Chapter VII.

#### 1.11 PRESSURE STUDIES ON COMPOUNDS POSSESSING DISC-LIKE MOLECULES

Early pressure experiments<sup>3</sup>, carried on benzene-hexa-*n*-alkanoates, the materials in which the discotic mesophase was discovered,<sup>14</sup> showed that the  $dT/dP$  for the mesophase-isotropic transition is extremely low compared to that seen for rod-like thermotropic materials. Pressure studies have been conducted on two other discotic materials hexa-*n*-octyloxytriphenylene (HOT) and hexa-*n*-decanoyloxy-triphenylene (HDOOT). It is found that the columnar-isotropic phase boundary is vertical in the  $P$ - $T$  plane right up to the highest pressure, namely 2 kbar studied, i.e.,  $dT/dP \approx 0$ , a very unusual result. Considering that the heat associated with the columnar-isotropic transition is large, the above result implies that the volume change associated with the phase transition should be extremely small. These results are discussed in Chapter VIII.

#### 1.12 PRESSURE STUDIES ON THERMOTROPIC MAIN CHAIN POLYESTERS

It has been recently shown<sup>40</sup> that the nematic-isotropic ( $N$ - $I$ ) transition temperature ( $T_{NI}$ ) as well as the transition enthalpy

associated with this transition ( $\Delta H_{N-I}$ ) in a homologous series of a thermotropic main chain polyesters shows a very pronounced alternation with  $n$ , where  $n$  is the number of methylene groups in the spacer. Since it is well known from the early studies<sup>41,42</sup> on rod-like liquid crystals that such an alternation in  $T_{N-I}$  and  $\Delta H_{N-I}$  are also reflected in the pressure behaviour of the N-I transition, high pressure studies have been conducted on thermotropic main chain polyesters based on alternating 2,2'-dimethylazoxy benzene mesogen and alkanedicarboxylic acid spacer. It is found that  $dT/dP$  for the N-I transition does indeed show an alternation similar to that of  $\Delta H_{N-I}$  and  $T_{N-I}$ . These results are described in Chapter IX.

### 1.13 BIAXIAL NEMATIC PHASE IN THERMOTROPIC LIQUID CRYSTALS

The occurrence of a biaxial nematic phase in an amphiphilic system was first observed by Yu and Saupe<sup>43</sup> in the ternary system of potassium laurate/1-decanol/D<sub>2</sub>O. Subsequently, evidence of biaxiality has been presented in certain nematic polymers.<sup>44,45</sup> The possibility of observing the nematic biaxial phase in a thermotropic liquid crystal was suggested a few years ago by Chandrasekhar<sup>46</sup> who pointed out that this could be achieved by bridging the gap between rod-like and disc-like molecules, i.e., by preparing a mesogen which combines the features of both. Such materials have been synthesized recently.<sup>47,48</sup> Careful conoscopic observations conducted here have revealed the occurrence of the biaxial nematic

phase in bis[1-(p-n-decylbiphenyl)3-(p-ethoxy phenyl)propane-1,3-dionato]copper(II). Addition of a very small quantity of a pure rod-like (uniaxial) nematogen results in a uniaxial nematic to biaxial nematic transition with decreasing temperature, the latter phase getting suppressed for slightly larger concentrations (~1%) of the uniaxial component. This also yields interesting phase diagrams. All these results are presented in Chapter X.

Most of the results presented in the thesis have been published in the following papers.

- 1 Smectic A phase with two collinear incommensurate density modulations. (in collaboration with B.R.Ratna and R.Shashidhar) - Physical Review Letters, 55, 1476 (1985); *ibid*, 56, 269 (1986).
- 2 An incommensurate smectic A phase. (in collaboration with B. R. Ratna and R. Shashidhar) - in "Incommensurate Crystals, Liquid Crystals and Quasi Crystals", Eds. J.F.Scott and N.A. Clark (Plenum, New York, 1987), p. 259.
- 3 A new alternative for the smectic  $A_1$ -reentrant nematic-smectic  $A_2$  bicritical point. (in collaboration with R.Shashidhar, B.R.Ratna, G.Heppke and Ch. Bahr) - Physical Review A (Rapid Communications), 37, 303 (1988)
- 4 Experimental studies on a triply reentrant mesogen. (in collaboration with R.Shashidhar, B.R.Ratna, V.Surendranath, S.Krishna Prasad and C.Nagabhushan) - Journal de Physique Lettres, 46, L-445 (1986)
- 5 Density, dielectric and X-ray studies of smectic A - smectic A transitions. (in collaboration with B. R. Ratna, C.Nagabhushan,

- R.Shashidhar, S.Chandrasekhar and G.Heppke) - *Molecular Crystals and Liquid Crystals*, 138, 245 (1986)
- 6 Pressure studies on two discotic liquid crystals. (in collaboration with R.Shashidhar, S.Chandrasekhar, R.E.Boehm and D.E.Martire) - *Pramana, J. Phys.*, 25, L-119 (1985)
  - 7 Phase transitions of nematic main-chain polyesters under high pressure. (in collaboration with R.Shashidhar, S.Chandrasekhar, A.Blumstein, R.B.Blumstein and S.Kumar) - presented at the International Conference on Liquid Crystal Polymers, Bordeaux, July 1987 - *Molecular Crystals and Liquid Crystals*, 155, 521 (1988)
  - 8 Experimental studies on a terminally non-polar reentrant nematogenic mixture. (in collaboration with B.R.Ratna, R.Shashidhar, C.Nagabhushan, S.Chandrasekhar, G.Pelzl, S.Diele, I.Latif and D.Demus) - *Molecular Crystals and Liquid Crystals* (submitted).
  - 9 Partially bilayer smectic A phase in a terminally non-polar compound. (in collaboration with B.R.Ratna, R.Shashidhar, C.Nagabhushan, S.Chandrasekhar, G.Pelzl, S.Diele, I.Latif and D.Demus) - *Molecular Crystals and Liquid Crystals Letters* (submitted)
  - 10 Pressure studies on phase transitions in 4-alkoxyphenyl-4'-nitrobenzoyloxy benzoate (DBn.O.NO<sub>2</sub>). (in collaboration with B.R.Ratna, R.Shashidhar, G.Heppke and Ch. Bahr) - to be presented at the Twelfth International Liquid Crystal Conference, to be held at Freiburg, August 1988.
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