

**EXPERIMENTAL STUDIES OF THE RE-ENTRANT PHENOMENON
IN
LIQUID CRYSTALS**

**THESIS SUBMITTED TO THE
BANGALORE UNIVERSITY
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY**

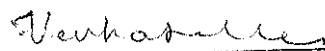
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MAY 1981

DECLARATION

I hereby declare that the entire work embodied in this thesis is the result of the investigations carried out by me independently in the Liquid Crystals Laboratory, Raman Research Institute, Bangalore, and that no part of it has been submitted for the award of any Degree, Diploma, Associateship, Fellowship or any other similar title.



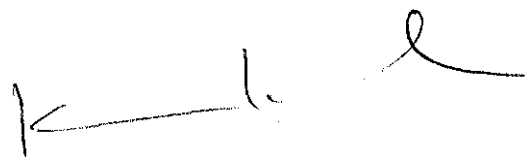
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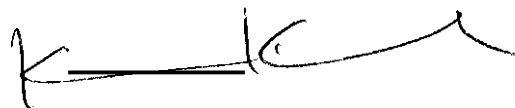
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CHAPTER I

INTRODUCTION

Many organic compounds are known to form intermediate phases between the cryetalline solid and the isotropic liquid phase by the aotion of heat. The intermediate phases (oalled mesophases) have some proper- ties of the arystal, like optical and dielectric anisotropy and also the mechanical properties of a liquid. They are hence called thermotropic liquid crystals.¹

Liquid crystalline phases are also formed in solutions of amphiphilic molecules in water or other polar solvents over a range of concentrations. These are called lyotropia liquid crystals.

The organic compounds which form mesophases have moleoulee which are geometrically anisotropic. The moleoulee may be either elongated or disc shaped. Liquid crystals composed of elongated or rod like molecules are

common. The thermotropic mesomorphism in disc like molecules was discovered only very recently by Chandrasekhar et al.² The structure suggested by them is columnar, the different columns forming a two-dimensional lattice-like array (figure 1.1).

In this thesis, we are concerned with thermotropic liquid crystals of rod like molecules.

Friedel³ classified mesophases into three types depending on the molecular arrangement. They are (i) nematic, (ii) cholesteric, and (iii) smectic.

Nematics.

There is no long range translational or positional order for the molecules in this phase. But there is an orientational order in that the molecules in this phase tend to align themselves parallel to some common axis called the director ($\hat{n}$) (see figure 1.2a). Hence an orientational order parameter S is defined, the value of which is characteristic of the material and is a

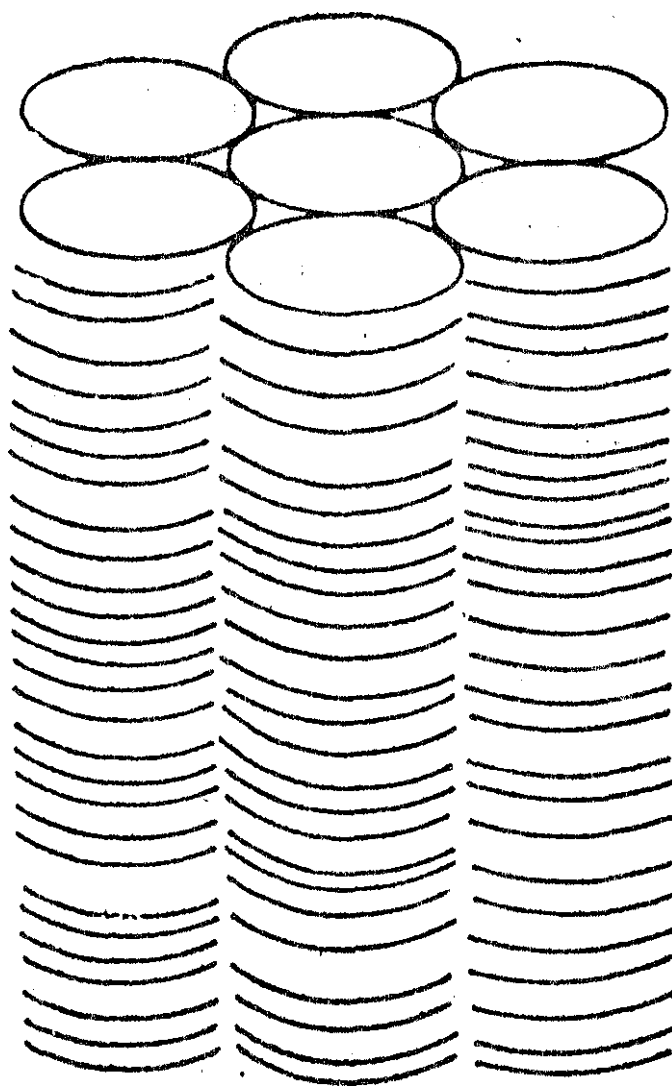


FIGURE 1.1

**Schematic representation of columnar
phases of disc-like molecules**

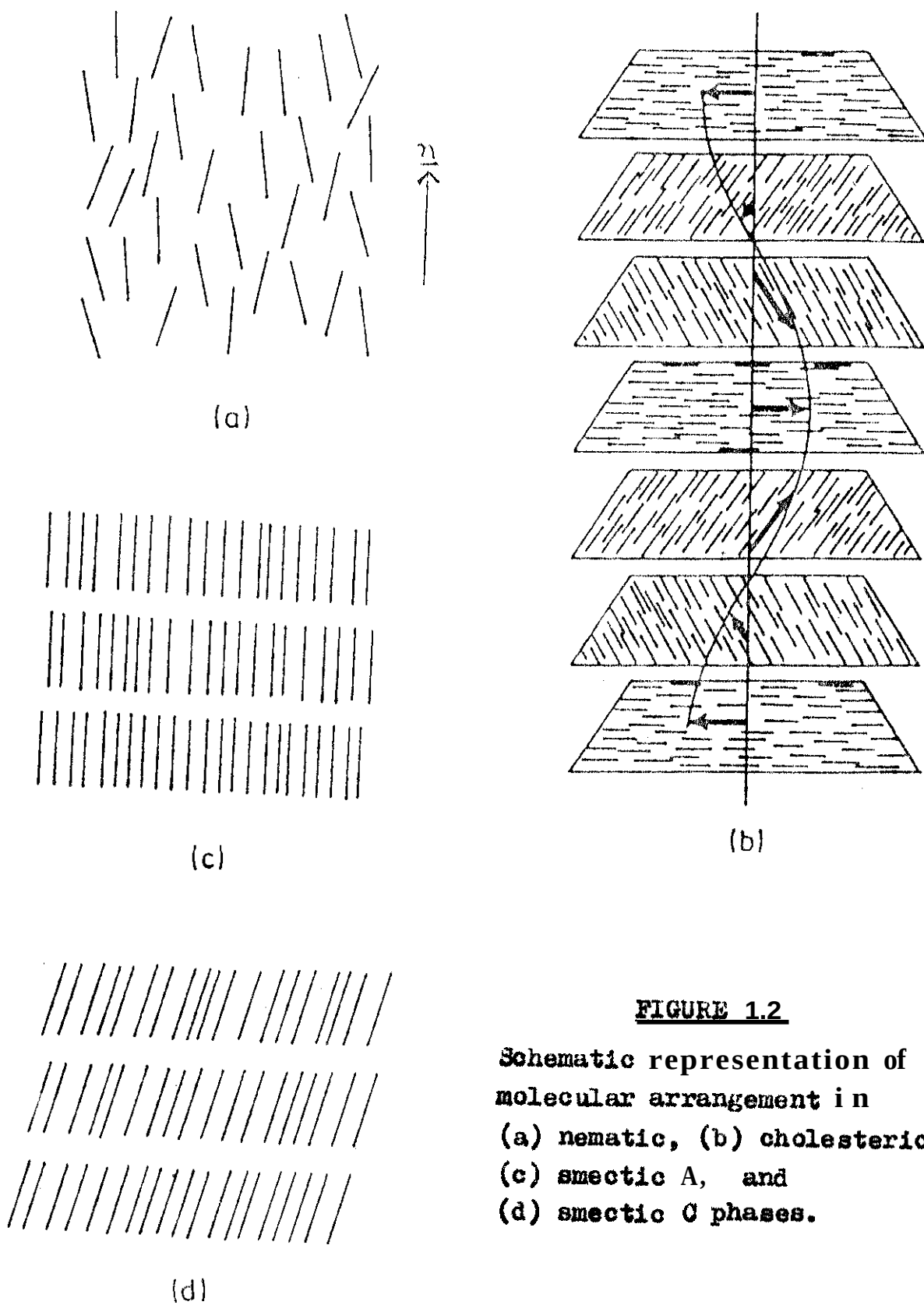
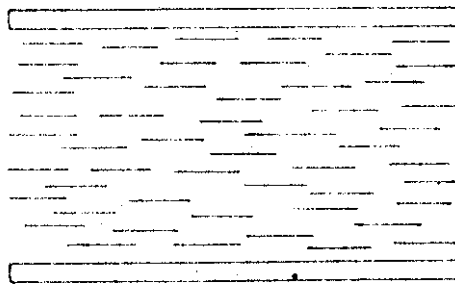


FIGURE 1.2

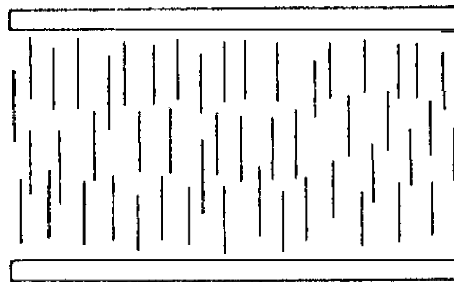
Schematic representation of molecular arrangement in (a) nematic, (b) cholesteric, (c) smectic A, and (d) smectic C phases.

function of temperature. If θ is the angle between the long molecular axis and the director, $s = \langle \frac{1}{2}(3\cos^2 \theta - 1) \rangle$ where the outer brackets denote the statistical average. The value of $s = 1$ for an ordered sample where the molecules are exactly parallel to one another and is zero for an isotropic liquid.

In a nematic, $\hat{n}$ and $-\hat{n}$ are indistinguishable, i.e., it is apolar. Even though the direction of $\hat{n}$ varies from point to point in a nematic, an alignment of the molecules where $\hat{n}$ has the same direction throughout is often required in experiments. If the molecules are aligned parallel to the surfaces of the container, the alignment is called homogeneous (figure 1.3a). It is obtained by unidirectional rubbing of the surfaces of the container, or by oblique coating of silicon monoxide or some other material on the glass surfaces, or by the application of a strong magnetic field in a direction parallel to the surfaces. An alignment of the molecules perpendicular to the walls of the container



(a)



(b)

FIGURE 1.3: Schematic representation of (a) homogeneous and (b) homeotropic alignments of liquid crystals.

is called homeotropic (figure 1.3b). This is achieved by the application of a strong magnetic field perpendicular to the surfaces or by treating the surfaces by surfactants.

The x-ray diffraction pattern of a randomly oriented nematic consists of one 'inner ring' (close to the centre of the diffraction pattern) and one 'outer ring'. The inner ring is faint and diffuse and the outer ring is also diffuse. The diffraction angle corresponding to the inner ring is of the order of a few degrees and that corresponding to the outer ring is of the order of 20'. Isotropic phases also have diffraction patterns similar to nematics but the inner ring is generally more diffuse. To distinguish the two phases by x-ray means, one can use aligned samples. Box an aligned nematic, the rings split up into crescents or spots whereas an isotropic medium cannot be aligned and will always show rings.

The diffraction maximum at smaller angles

(inner ring) is related to the length of the molecule. The way in which this ring splits up for an aligned nematic indicates the degree of short range order. The diffraction maxima at larger angles (outer ring) is due to the breadth of the molecule. The line joining the centres of the outer maxima is therefore normal to the direction of the molecules in an aligned sample.

By x-ray diffraction studies, de Vries⁴ has established that in many nematic phases there also exists a short range smectic like order. (We will discuss smectics in the next section.) Thus, for a group of molecules in the nematic phase, called the cybotactic group, a short range translational order exists. The molecules in the group are arranged in layers. If the angle between the long molecular axis and the layer is significantly different from 90° , the group is called skewed cybotactic. If the angle is 90° , it is called normal cybotactic.

For cybotactic nematics, the intensity of the

inner ring is far greater than that of the outer ring. Aligned samples of skewed cybotactic **nematics** give four discrete spots whereas **normal** cybotactia **nematics** give only two spots.

Cholesterics

The cholesteric phase is also of the nematic type except that the **molecules** in this phase are optically active which results in a helical arrangement of the director (figure 1.2b). **Thermodynamically**, this phase is usually **considered** to be identical to the nematic phase.

The x-ray **diffraction pattern** of a **cholesteric** phase is similar to that of a nematic phase. But for a **monodomain** sample of a **cholesteric** the pattern **obtained** are rings whereas an aligned nematic gives two outer **crescents** and two **inner** spots.

Smectics

Smectic liquid crystals are **stratified** structures,

the molecules being arranged in well defined parallel layers. Smectics are classified into several types depending on the order within a layer and on the inter-layer correlation. In the smectic A, the molecules are upright and are unequally spaced within the layer (figure 1.2c). There is thus a positional order in one dimension in addition to the orientational order. An oriented smectic A is optically uniaxial, the optic axis being normal to the plane of the layers.

The x-ray diffraction patterns of randomly oriented smectic A phases have an inner ring which is sharp and an outer ring which is quite diffuse. (There may be more than one inner ring also, but these correspond to the different orders of diffraction.) For an aligned sample the inner ring condenses into two spots and the outer ring into two crescents. The line that is drawn through the spots stands perpendicular to the preferred direction of the smectic planes. The line one can draw between the centres of the maxima in the outer ring stands perpendicular

to the preferred direction of the long axis of the molecules. From the x-ray pattern of an aligned smectic A, it can be seen that the molecules are more or less perpendicular to the smectic planes.

The diameter of the inner ring (or the distance between the spots) is used to calculate the layer spacing d of the smectic A phase. In many cases, this corresponds to the molecular length, $\%helength$ being calculated from the all trans configuration with extended chains. But in some cases, this is equal to approximately 1.4 times the molecular length. We will discuss this in some detail later.

The outer ring in the smectic A phase corresponds to the lateral distances between the molecules. The diffuse nature of the ring indicates the random distribution of the molecules in the layer, i.e., there is no order with respect to the centres of gravity of the molecules in the plane of the layers.

Smectic C is a tilted form of smectic A. The

molecules in this phase are inclined to the layer m—
(figure 1.—). The tilt angle θ in many cases is
dependent on temperature. Smectic C is biaxial.

For an unaligned sample, the x-ray diffraction
pattern of the smectic A and C are more or less similar.
But for a well aligned smectic A, the line through the
inner maxima (spots) and that through the outer maxima
(crescents) are perpendicular to each other whereas in
the pattern for aligned smectic C, they are at an angle.
From the x-ray diffraction patterns, the tilt angle can
be determined.

Several other types of smectics like smectic B, D,
E, F, etc. are known. From x-ray studies, their structures
are being established. The appearance of outer ring (or
rings) gives a clue towards the nature of molecular order
within the layer. Thus smectic B is known to have hexa-
gonal close packed order in the plane of the layer and
smectic D is reported to be cubic. We shall not discuss
the structural details of these smectics here.

1.1 Sequence of Phase Transitions

Some typical examples of mesophase transitions in thermotropic liquid crystals are given below. The transitions which occur during both the heating and cooling modes are referred to as enantiotropic while those which occur only in the cooling mode are called monotropic.

(i) 4'-n-Pentyl-4-cyanobiphenyl (5CB)



(ii) N-p-Cyanobenzylidene-p-octyloxyaniline (CBOOA)



(iii) Cholesteryl nonanoate



Cooling



it) **4-Biphenyl-4"-n-octyloxybenzoate**



Cooling



From the above examples, it can be seen that with increase in temperature., usually transitions take place from a well ordered phase (like the solid) to a less ordered phase (like the smectic or nematic). As the temperature is increased further, the transition is finally to the isotropic liquid phase of maximum disorder. This is what is expected generally from the principles of thermodynamics. Also, while cooling the sample from the isotropic phase, one expects transitions from the nematic to the smectic and thereafter to the well ordered solid phase. The reversal to the solid phase is usually accompanied by supercooling.

When a sample in the nematic phase is cooled, a

short range smectic like translational order may develop in the phase. The presence of such cybotactic groups, referred to earlier, can be directly verified by x-ray studies. If there is a nematic-smectic A transition, with the decrease in temperature in the nematic range, the inner ring in the x-ray diffraction pattern becomes sharper so the smectic A phase is approached. This is due to the smectic like short range ordering developed in the nematic phase and is a pretransitional effect. Many related properties of the system change as a consequence and we shall have occasion to refer to such effects observed in our studies in the next few chapters.

12 The Re-entrant Behaviour

Recently, Cladis⁵ made an interesting discovery while working with mixtures of p-[(p-hexyloxybenzylidene)-amino]benzonitrile (HBAB) and N-p-cyanobenzylidene-p-n-octyloxyaniline (CBOOA). She observed that the nematic-smectic A transition temperature of these mixtures becomes multivalued with increasing concentration of HBAB.

The sequence of transitions that she observed on cooling the sample is,

isotropic $\rightarrow$ nematic $\rightarrow$ smectic A $\rightarrow$ nematic $\rightarrow$ solid.

Thus the nematic phase occurs again, at a lower temperature than the smectic phase. This lower temperature nematic phase has been designated as 're-entrant nematic phase' in analogy to similar phases observed at the normal to superconducting phase boundary in materials containing magnetic impurities⁶ and in one of the He³ phase transitions.⁷ The bend elastic constant k_{33} in HBAB-CBOOA mixtures behaved similarly on both sides of the smectic phase - it exhibited sharp pretransitional increases as the smectic phase is approached from both sides. It was concluded that there is no macroscopic difference between the higher temperature (normal) nematic and the re-entrant nematic phases.

Subsequently, Gladis et al.⁸ found that re-entrant nematic transition could be induced under pressure. In a

pure compound like 4'-n-octyloxy-4-cyanobiphenyl (8 OCB) the re-entrant nematic phase was observed by Gladis et al. over a range of high pressures (about 1.6 to 1.8 kbars) in the cooling mode. They also observed the re-entrant nematic phases in CBOOA, mixtures of CBOOA with HBAB and in mixtures of N-p-cyanobenzylidene-p-nonylaniline (CBNA) with N-p-cyanobenzylidene-p-heptylaniline (CBHA) under high pressures.

In all these high pressure investigations where the re-entrant nematic phase is observed,⁹ there is an unusual departure in the behaviour of the nematic-smectic A phase boundary, in the cooling mode. In the P-T phase diagrams obtained, the nematic-smectic A boundary is found to be 're-entrant', i.e., it curves round towards the pressure axis resembling the arc of an ellipse.

Very recently, re-entrant nematic phases have been discovered in pure compounds at atmospheric pressure by Madhusudana et al.¹⁰ in our laboratory. Hardouin et al.¹¹ from France also reported the re-entrant behaviour in pure

compounds at atmospheric pressure at about the same time.

The pure compounds showing the re-entrant nematic phase, synthesised by Sadashiva¹² in our laboratory are: 4-cyanophenyl-3-methyl-4(4-n-undecylbenzoyloxy)benzoate (11 CPMBB) and 4-cyanophenyl-3-methyl-4(4-n-dodecylbenzoyloxy)benzoate (12 CPMBB). The transition temperatures of these nematogens are:

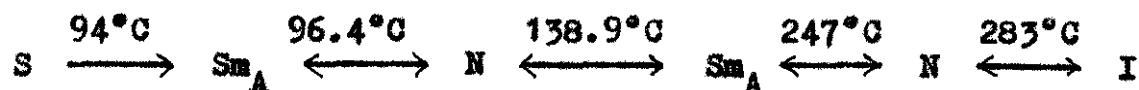
(1) 11 CPMBB (on cooling)



(11) 12 CPMBB (on cooling)



The nematogen reported by Hardouin et al. is 4-octyloxybenzoyloxy-4'-cyanostilbene (T8). The transition temperatures are:



[I - isotropic, N - nematic, Sm_A - smectic A, S - solid].

Following this, Nguyen Huu Tinh and Gasparoux¹³ have also reported the discovery of pure compounds showing the re-entrant behaviour at atmospheric pressure.

There have been some attempts to give a theoretical explanation for the experimental results obtained in the re-entrant phenomena and to understand the thermodynamics of the smectic A - re-entrant transition. Pershan and Prost¹⁴ have shown that the smectic A - re-entrant nematic phase transition follows from the Landau theory if one assumes the existence of an optimum density for smectic ordering. The shape of the smectic A-nematic phase boundary in the P-T plane for 8 OCB (in the cooling mode) appears to fit exactly with that evaluated from theory. A thermodynamical model which accounts for the elliptical shape of the phase boundaries and which facilitates determination of the various parameters determining the phase boundary is presented by Clark¹⁵. Klug and Whalley¹⁶ have shown that the smectic A-nematic phase boundaries that resemble arcs of ellipses can be analysed by quadratic expansion

in temperature and pressure of the Gibbs free energy.

Heppke and Schneider¹⁷ have given a thermodynamic theory of re-entrant nematic mixtures which describe the phase diagrams, i.e., the temperature versus concentration diagrams.

It is thus seen that the re-entrant phenomenon in liquid crystals, both at elevated pressures and at atmospheric pressures, is one of the rare examples where a phase transition takes place from an apparently more ordered smectic state at a higher temperature to an apparently less ordered lower temperature nematic. The interesting discoveries have therefore opened up an entirely new field of investigation.

To understand the phenomenon of the occurrence of re-entrant nematic phase on a molecular level, a study of the physical properties of the phases of the system exhibiting the re-entrant behaviour becomes necessary. With this in view, a variety of experiments have been taken up by the author. The studies include high pressure and

room pressure x-ray studies, dielectric studies and conductivity studies. The results of these investigations form the subject matter of this thesis.

The compounds which exhibit the re-entrant nematic phase have molecules with a cyano ($\text{C} \equiv \text{N}$) group at one end, along the long molecular axis. This terminal group has a large dipole moment $\mu = 4.05$ debye.¹⁸ The contribution from this cyano group to the dipole moment of the molecule makes it highly polar. Therefore, all the compounds with a cyano end group are strongly polar in nature.

Madhusudana and Chandrasekhar¹⁹ have theoretically shown that such polar molecules arrange themselves in an antiparallel configuration with their nearest neighbours. Gray and Lydon,²⁰ in their x-ray studies of 4'-n-octyl-4-cyanobiphenyl (8OB - a compound which has a cyano end group) noticed that the layer spacing in the smectic A phase is far in excess compared to the molecular length. Later, Lydon and Coakley²¹ and also Leadbetter et al.²²

found in their x-ray investigations of cyanobiphenyls that the measured layer spacing in the smectic A phase is equal to nearly 1.4 times the molecular length.

To explain these results, a bimolecular layer structure of the smectic A phase was proposed.²¹⁻²⁴ In this model, the polar aromatic cores with the cyano group overlap in the middle of the layers and the non-polar aliphatic chains extend outwards in both the directions to the layer boundaries (see figure 1.4). The essential feature of the structure is that the strong dipoles due to the cyano groups tend to be opposed and give efficient packing of the cores. In the Leadbetter model,²³ the aliphatic chains are held in the all trans conformation whereas in the model proposed by Gladis²⁴ the chains are in 'melted' configuration.

This interdigitation or head-to-tail arrangement of the molecules where the aromatic segments overlap is called the bilayer smectic A. The antiparallel correlation between neighbouring molecules in compounds with cyano end

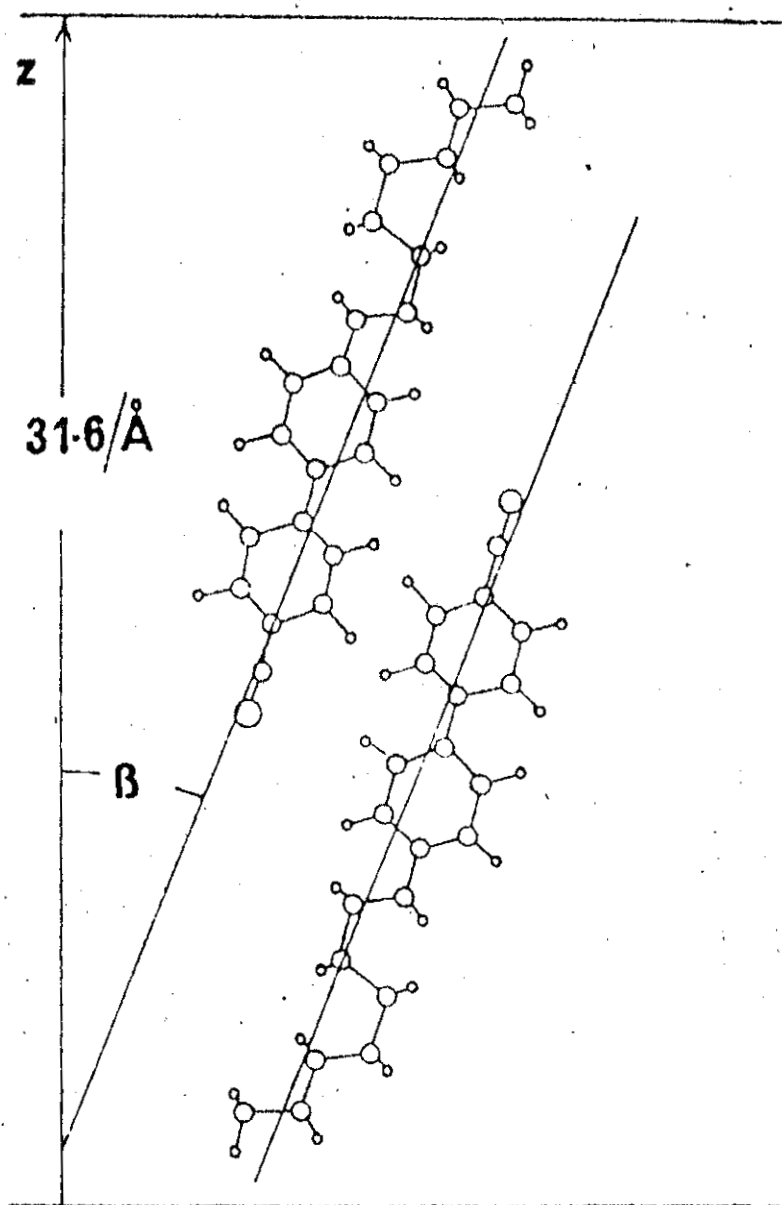


FIGURE 1.4

Schematic diagram of the bimolecular unit cell for SOB according to Leadbetter et al.²⁵ The molecules here are shown with kinked alkyl chain conformation. For the best experimental fit of the neutron scattering data, $\beta = 0$.

groups is now very well established by Leadbetter et al.²⁵ in neutron scattering studies. The bilayer structure is suggested as being essential for the re-entrant nematic behaviour.

According to Cladis et al.⁸ the short range attractive interactions of the non polar tails stabilise the smectic layers. Applying pressure results in the core region trying to pack even closer together and the onset of a strong repulsive force resisting this compression. Assuming that the polar-polar and non polar-non polar interactions must be maintained to ensure the stability of the bilayer smectic A under pressure, Cladis et al. proposed that the layer spacing probably expands with increasing pressure. This according to them accounts for the transition between the less dense smectic and more dense nematic phases which occur on the high pressure side of the re-entrant phase diagrams. The prediction could be tested only by a high pressure x-ray study of the compound showing the re-entrant behaviour.

1 3 A high pressure x-ray cell

High pressure studies of liquid crystals have yielded several interesting results in recent years.²⁶ The pressure induced mesomorphism in certain compounds which are normally non-mesomorphic, change of the nature of transition from monotropic to enantiotropic by the application of pressure, observation of bounded phase, triple, points and tricritical behaviour are but a few examples. The discovery of the re-entrant nematic behaviour at high pressures itself is one more, example of a new phenomenon observed in high pressure studies.

While a number of such high pressure experiments have been conducted on liquid crystals, no high pressure x-ray study, which is the only method of probing the changes at the molecular level, had ever been done at the time when the present writer undertook these investigations. A high pressure x-ray cell which is useful for liquid crystal studies was therefore developed for the first time.

After considering the applicability of several

possible cells, an opposed diamond anvil cell, with special features of relevance to x-ray study of liquid crystals at high pressures was designed and fabricated in our laboratory. It is essentially of the same type as that designed at the National Bureau of Standards by Piermarini and Block.²⁷ All the components of the cell, except the parts which seat the diamonds, were made of stainless steel 310. The translating plate and the piston hemisphere, to which the diamond anvils are cemented by epoxy, were made of high carbon high chromium (HC-HC) steel, heat treated to a hardness of about HRC 60-65 in order to take the load when the diamonds are pressed together. A spring loaded lever arm assembly generates a uniform and continuously variable force as a pressure bolt is rotated and this pressurises the sample in the gasket in between the two anvils.

The anvils were brilliant-cut gem quality diamonds whose culets were removed by grinding and the faces re-polished. Both the translating plate & the piston hemisphere which seat the diamonds facilitate the axial and

tilting alignments which are necessary for getting parallelism of the anvil surfaces normal to the common axis. This parallelism was ascertained optically.

The anvils were used in the gasketed configuration. Inconel and nickel, which were often used²⁷ as gasket materials were found to be unsuitable for containing the liquid crystalline sample at the relatively low pressures of a few hundred bars. After experimenting with several materials, it was found that aluminium is best suited for the purpose. The anvil faces were made slightly unequal in areas so that the flow of the gasket material around the conical surface of the smaller area anvil acts as a supporting belt to the gasket. Thus, two important functions have been achieved. (i) The liquid crystalline sample is maintained in hydrostatic conditions for long periods of time without any pressure leaks, and (ii) The cell, which is normally used for pressures beyond a few tens of kilobars only, is found suitable for pressures as low as a few hundred bars. Typically the gaskets were about 1 mm thick with a central hole of 1 mm diameter into

which the sample in the powdered form was packed avoiding air pockets.

For the determination of the pressure experienced by the sample in the cell, the conventional ruby fluorescence technique^{28,29} could not be employed. This is because the pressure shift of the ruby line is quite small and the accuracy of the method is ± 300 bars. Since we were interested in fine variations of pressure, an Indirect but still accurate method was adopted. In this, an accurate 'in situ' optical determination of the transition temperature of the sample was made @ follows. At any fixed pressure, the temperature was varied slowly and the intensity of a laser beam transmitted by the sample was monitored by a photocell. The intensity was fed to the Y axis and the temperature to the X axis of a high sensitivity XY recorder. At the phase transition, there was an abrupt change in intensity. The pressure experienced (by the sample) was then read out from an accurate P-T diagram of the sample. The transition temperatures at any

pressure could be reproduced to an accuracy of $\pm 0.2^\circ\text{C}$.

The pressure values were estimated to be accurate to ± 15 bars. These constructional and operational details of the cell are described in chapter II.

1.4 High Pressure ~~x-ray~~ Study

The $\sim$ e lvar-used for the x-ray investigation of the pressure variation of the layer spacing in the smectic A phase of 8 OCB, which, as mentioned earlier, shows a re-entrant nematic phase in the pressure range of 1.6 to 1.8 kbars. For measuring small variations in the layer spacing accurately, (i) the sample-to-film distance was kept large and (ii) Ni-filtered CuK_α radiation from a fine focus tube was used despite the fact that the intensity of the beam was attenuated to a large extent on passage through the diamonds. The time for each exposure was around 100 hours and the temperature was maintained constant to within $\pm 0.25^\circ\text{C}$. The transition temperatures of the sample under pressure were checked after each exposure. They were found to be the same as that before starting the

exposure, indicating that the pressure was constant during the exposure. Also, the transition temperatures of the sample used were checked after each exposure at atmospheric pressure to detect any decomposition of the compound. It was found that the temperatures did not change from their initial values measured earlier, proving thereby that the compound did not undergo any decomposition.

A new gasket packed with fresh sample was used for the experiment at each exposure. At every pressure, the photograph was taken 3°C below the normal nematic-smectic A transition point to minimise the effect of temperature on layer spacing. The diameters of the rings were measured accurately using a microdensitometer and a comparator.

It was found that as the pressure is increased, the spacing decreases more or less linearly at a rate of about 6.6 Å per kilobar till the pressure reaches a value of about 1.4 kbar. Beyond this pressure, the spacing increases.

To see whether there is a temperature contribution

to this variation, the layer spacing was determined at atmospheric pressure over the entire smectic range at different temperatures. There was no change in layer spacing with temperature within the limits of our experimental accuracy (± 0.1 Å). Hence we can conclude that the re-entrant behaviour of 8 OCB, observed at elevated pressures, is associated with an expansion of the smectic A layer spacing as anticipated by Gladis et al.⁸ The experimental details and the results are presented in chapter III.

1.5 Room Pressure X-ray Studies

Now that the variation of layer spacing with pressure for a pure compound exhibiting re-entrant phenomenon was established, it was felt that it would be interesting to carry out an accurate determination of the temperature variation of layer spacing in the smectic A phase in pure compounds exhibiting re-entrant nematic phase at atmospheric pressure. Chapter IV deals with these investigations conducted on two pure compounds

4-cyanophenyl-3-methyl-4(4-n-dodecylbenzoyloxy) benzoate (12 CPMBB) and 4-cyanophenyl-3-methyl-4(4-n-undecyl benzoyloxy)benzoate (11 CPMBB). Both the compounds have a wide smectic range.

As the changes in the layer spacing involved were expected to be very small, a *bent* quartz crystal monochromator was set up and a new x-ray cell was designed. Also, the sample-to-film distance was kept large. The sample was taken in a Lindemann capillary which was subsequently evacuated and sealed to prevent the decomposition of the compound.

The x-ray photographs were taken for aligned samples. The experimental set up and the procedure followed gave sharp x-ray reflections. Each exposure was around 20 hours and the temperature during the exposure could be maintained to $\pm 0.25^\circ\text{C}$. The transition temperatures of the sample in the capillary were checked after each exposure to detect any decomposition. The diameters of the rings were accurately measured using a microdensitometer and an accurate comparator. The relative accuracy

of the measurements is estimated to be better than $\pm 0.1 \text{ \AA}$.

The observed behaviour is similar in both the compounds studied. When the temperature is decreased from the normal nematic-smectic A transition point, the layer spacing decreases initially. On further cooling, the spacing increases from the middle region of the smectic range till the region near the smectic A - re-entrant nematic transition point. The variation is about 3% for 12 CPMBB over a temperature range of about 80°C and 1.4% for 11 CPMBB over a range of 50°C. The experiment thus clearly shows that some kind of structural change in the smectic bilayer takes place as a precursor to the formation of the re-entrant nematic phase.

1.6 Experiment to prove the antiparallel correlation

It has been mentioned earlier that in compounds with a terminal cyano group, the near neighbour correlations are antiparallel and the molecules form a bilayer in the smectic A phase. A direct confirmation of the antiparallel correlation was provided by the following

experiment. A pure compound with a cyano end group, 4'-n-pentyl 4-cyanobiphenyl (5CB) was chosen for the study. The dielectric constant and the refractive index of solutions of 5CB in a non polar solvent (benzene) were measured over a range of concentrations at a temperature 3°C above the nematic-isotropic transition point of pure 5CB. The effective dipole moment per molecule was calculated from these measurements.

It was found that for very dilute solutions the value of the dipole moment is 5.3 debye, which is the dipole moment of an isolated molecule of 5CB. The dipole moment was found to decrease with the increase in concentration, the effective dipole moment in the isotropic phase of pure 5CB being 3.33 debye. This conclusively proves that the near neighbour correlations are anti-parallel in such compounds. The results form the first part of chapter V.

1.7 Static Dielectric Constants

We recall an earlier observation that the contribution

of the $C \equiv N$ end group to the molecular dipole moment along the long molecular axis is 4.05 D. This affects the dielectric properties of the medium. The dielectric anisotropy $\Delta\epsilon = (\epsilon_{\parallel} - \epsilon_{\perp})$, where $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ are the principal dielectric constants measured parallel and perpendicular to the optic axis, becomes positive and has a large value. Hence strongly polar compounds are also characterised by a strongly positive dielectric anisotropy.

One of the important consequences of the antiparallel near neighbour correlation in the bilayer structure, as pointed out by Madhusudana and Chandrasekhar¹⁹ is that the average dielectric constant $\bar{\epsilon} = \frac{1}{3}(\epsilon_{\parallel} + 2\epsilon_{\perp})$ should be less than the extrapolated isotropic value (ϵ_{is}). This has been verified experimentally in a number of cyano compounds by Ratna and Shashidhar.³⁰ They showed that $\bar{\epsilon}$ as well as ϵ_{is} decrease with decrease of temperature, which may be attributed to the increase of antiparallel ordering at lower temperatures. Hence a study of the dielectric properties of the compounds² showing re-entrant behaviour is expected to reveal informations regarding the changes

that take place in the bilayer, prior to the formation of the re-entrant nematic phase.

The x-ray studies established that subtle changes in the bilayer structure were responsible for the formation of the re-entrant nematic phase. Since the dielectric studies are important in understanding the nature of molecular associations in different phases, a study of the static dielectric constants was taken up in the two pure compounds 11 CPMBB and 12 CPMBB and in a binary mixture 6 OCB/8 OCB, all of which show the re-entrant behaviour. The results are discussed in the latter part of chapter V. Both $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ were measured in the presence of a strong magnetic field (15 KGauss) which was used for obtaining good alignment as the sample was cooled from the isotropic phase. A Wayne Kerr bridge (B642) was used for the measurements. The temperature could be measured to within $\pm 0.025^{\circ}\text{C}$. The accuracy of the relative variation of the static dielectric constants is 0.1% and the absolute accuracy is reckoned to be 2%.

The study of the variation of the principal dielectric constants of the systems in their isotropic, normal nematic, smectic A and re-entrant nematic phases has given some interesting results.

- (i) With decreasing temperature, $\epsilon_{||}$ increases and $\epsilon_{\perp}$ decreases, thus showing the normal behaviour exhibited by polar compounds.
- (ii) The average dielectric constant $\bar{\epsilon}$, evaluated from the measured values of $\epsilon_{||}$ and $\epsilon_{\perp}$ [which is less than the extrapolated isotropic value (ϵ_{is}) due to the antiparallel ordering of the molecules] shows quite an unexpected variation. As the temperature is decreased, $\bar{\epsilon}$ decreases throughout the nematic range and over a part of the smectic range. On further cooling, $\bar{\epsilon}$ starts increasing. This is perhaps related in some way to the reversal in sign of the thermal expansion of the layer spacing discussed in chapter IV. The increasing trend in $\bar{\epsilon}$ continues right through up to almost the lowest temperature of the re-entrant nematic phase, where it practically merges with the extrapolated value of ϵ_{is} . This increase in $\bar{\epsilon}$ signifies a decrease in antiparallel ordering as the

re-entrant nematic phase is approached.

1.8 Dielectric Dispersion

The dielectric constants $\epsilon_{||}$ and $\epsilon_{\perp}$ of liquid crystals are frequency dependent. $\epsilon_{\perp}$ exhibits the normal Debye type relaxation which usually occurs in the GHz region whereas $\epsilon_{||}$ shows an additional dispersion in the low frequency region. This low frequency dispersion of $\epsilon_{||}$ has been extensively studied for a number of polar compounds notably by Ratna and Shashidhar.³¹ It was first shown by Meier and Saupe³² that the relaxation time is proportional to the exponential of $(q + q_{\eta})/kT$ where q is the nematic potential and q_{η} is the activation energy due to viscosity of the medium. The total activation energy $W=(q + q_{\eta})$ therefore can be determined by measuring the temperature variation of τ_R of $\epsilon_{||}$. Hence the low frequency relaxation of $\epsilon_{||}$ in the normal nematic, smectic A and the re-entrant nematic phases was studied in both the pure compounds 11 CPMBB, 12 CPMBB and in the mixture 6 OCB/8 OCB.

The dispersion of $\epsilon_{||}$ in the frequency region 1 KHz to 20 KHz was measured by a Wayne Kerr bridge (B642) using an external source and detector. Bar measurements in the frequency range 100 KHz to 10 MHz another Wayne Kerr bridge (B602) was used in conjunction with a Wayne Kerr (SR268L) source and detector. The maximum error in the determination of the frequency of relaxation (f_R) of $\epsilon_{||}$ is estimated to be 7%. The significant results which emerged out of these studies are discussed in chapter VI. Some of the interesting observations made are:

- 1 The activation energy for dielectric relaxation is high in the normal nematic phase than that in the smectic phase. Druon and Wacrenier³³ have also made similar observations on 8CB. This is contrary to what one would expect since the smectic phase is more ordered and has higher viscosity than the nematic phase. Perhaps the bilayer structure of the smectic phase somehow makes the reorientation of the molecules easier.

- ii Ia the smectic phase, the plot of the frequency of relaxation versus $1/T$ gives two distinct straight lines with different slopes (or different activation energies) indicating a kind of structural change in the system. A point to be noted is that the temperature at which the slope changes roughly corresponds to the temperature at which becomes a minimum.
- iii The re-entrant nematic phase has a much higher activation energy (the increase being more than 60%) than the normal nematic phase. This clearly shows that the hindrance to the reorientation of the molecules is more in the re-entrant nematic phase. This is the first experimental evidence to show that the molecular associations are different in the two nematic phases. It may be mentioned here that many of the previous theoretical discussions of re-entrant behaviour have assumed that the two nematic phases are identical.

1.9 Conductivity Studies

It is worthwhile to recall an earlier discussion regarding the temperature variation of $\bar{\epsilon}$ in the three re-entrant nematogens studied which is indicative of some structural change in the system. In the study of the dielectric dispersion, it was noticed that there are differences in the normal nematic and the re-entrant nematic phases. It is instructive and interesting to find out whether the changes are reflected in the transport properties. Hence a study of the temperature dependence of the principal electrical conductivities of the pure compound 12 CPMBB and of the binary mixture 6 OCB/8 OCB was taken up. The experimental set up used for measuring the static dielectric constants was used to measure the conductivities $\sigma_{||}$ and $\sigma_{\perp}$. The accuracy of the relative variation of $\sigma_{||}$ and $\sigma_{\perp}$ was $\pm 0.2\%$, and the absolute accuracy was estimated to be about 3 to 4%. The results form chapter VII.

The ratio of the conductivities $R = \sigma_{||}/\sigma_{\perp}$ shows an interesting variation with temperature in both the

systems studied. As the temperature is decreased from the nematic-isotropic transition point, R increases throughout the nematic range. It reaches a maximum value at a temperature close to the nematic-smectic A transition point. On further cooling, R decreases over part of the smectic range. Similar decrease of R in the smectic A phase have been observed for several bilayer smectics by Mircea-Roussel et al.³⁴ After this decrease, R increases with further decrease of temperature, the rate of increase becoming very fast in the vicinity of the re-entrant nematic-smectic A transition temperature. The increase continues even in the re-entrant nematic phase. This sharp increase of R on approaching the smectic A - re-entrant nematic transition region is significant. It indicates a nematic like behaviour manifested as a pretransitional effect even in the smectic phase.

Some of the results of these investigations have been published in the following publications of which the

present writer is a co-author.

- 1 The re-entrant phenomenon in 4'-n-octyloxy-4-cyanobiphenyl: A high pressure x-ray study of the smectic A layer spacing (in collaboration with S. Chandrasekhar and R. Shashidhar) - Paper presented at the Third Liquid Crystal Conference of Socialist Countries, Budapest, Hungary, August 1979 (to be published in the Proceedings of the Conference, Academic Press).
- 2 A high pressure x-ray cell for liquid crystals: Pressure dependence of the smectic A layer spacing of 8 OCB in relation to its re-entrant behaviour (in collaboration with R. Shashidhar) - Proceedings of the International Liquid Crystals Conference, Bangalore, 1979. Ed. S.Chandrasekhar, Heyden, London, p. 115.
- 3 Temperature dependence of the smectic A layer spacing in two re-entrant nematogens. (in collaboration with S. Chandrasekhar and K.A.Suresh) - Proceedings of the International Liquid Crystals Conference, Bangalore, 1979. Ed. S. Chandrasekhar, Heyden, London, p. 131.

- 4 Dielectric studies of some re-entrant nematogens.
(in collaboration with B.R.Ratna and R.Shashidhar).
Proceedings of the International Liquid Crystals
Conference, Bangalore, 1979. Ed. S. Chandrasekhar,
Heyden, London, p. 135.
- 5 Experimental studies on the electrical conductivity
of two re-entrant nematogens. (in collaboration
with B.R.Ratna and R. Shashidhar) - Presented at
the Eighth International Liquid Crystals Conference,
Kyoto, Japan, June-July 1980, to be published in
the Proceedings of the Conference, in Molecular
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