

CHAPTER I

I N T R O D U C T I O N

Liquid crystals, as the name itself suggests, are states of aggregation that are intermediate between the crystalline solid and isotropic liquid. A liquid crystal has fluidity, which in some cases may be comparable to that of an ordinary liquid, while some other properties like birefringence are reminiscent of those of an anisotropic crystalline phase. Many organic compounds composed of molecules having shape anisotropy are known to exhibit liquid crystalline phases (or mesophases). These in general are classified into (i) thermotropic liquid crystals and (ii) lyotropic liquid crystals. In thermotropic liquid crystals, the transition to the mesophase is obtained by the effect of heat. On the other hand, lyotropic mesomorphism is brought about by the influence of solvents. Some general references covering the subject are the monographs by Chandrasekhar (1977), de Gennes (1974) and Priestley et al (1974).¹

Though liquid crystals of rod like molecules have

been known for a long time (since the discovery of liquid crystals by Reinitzer in 1888), mesogenic compounds composed of disc like molecules were discovered only recently by Chandrasekhar et al.² In this thesis we are exclusively concerned with thermotropic liquid crystals of rod like molecules.

1.1 Classification of Liquid Crystals

Friedel³ classified thermotropic liquid crystals of rod like molecules into three types depending upon the molecular arrangement. They are (i) nematic, (ii) cholesteric, and (iii) smectic.

The nematic phase (also referred to as N phase) is characterized by a long range orientational order of the molecules, with no long range translational order. The molecular order in an N phase is shown schematically in fig. 1.1a. The molecules are spontaneously oriented with their long axes having a potential energy minimum for a direction parallel to a preferred direction called the director (\vec{n}). The director is apolar, i.e., \vec{n} and $-\vec{n}$ are indistinguishable. The properties of nematic liquid crystals indicate that the N phase is optically uniaxial (optic axis along \vec{n}), positive and strongly birefringent. (Recently, biaxial nematics have been discovered in lyotropic systems.⁴)

The cholesteric phase, composed of optically active molecules, is essentially an N phase with a screw axis normal to the director (fig.1.1b). This helicity imparts certain unique optical properties to the phase like very high optical rotatory power and selective reflection, both along the twist axis. Normally, the pitch of a cholesteric is highly sensitive to temperature. For all practical purposes, the cholesterics are thermodynamically identical to nematics. But in recent times, some cholesteric compounds have been found to go through an intermediate phase called the blue phase before melting into the isotropic phase. We shall not be interested in the cholesteric phase in this thesis.

Smectic liquid crystals are characterized by stacked parallel layers of molecules. Depending on the molecular arrangement within the layers, smectics have been classified into several types. Among these only the smectic A and smectic C will be of interest to us in the present thesis.

In the smectic A phase (also referred to as, A phase), the average orientation of the molecules is along the layer normal with a liquid like organization

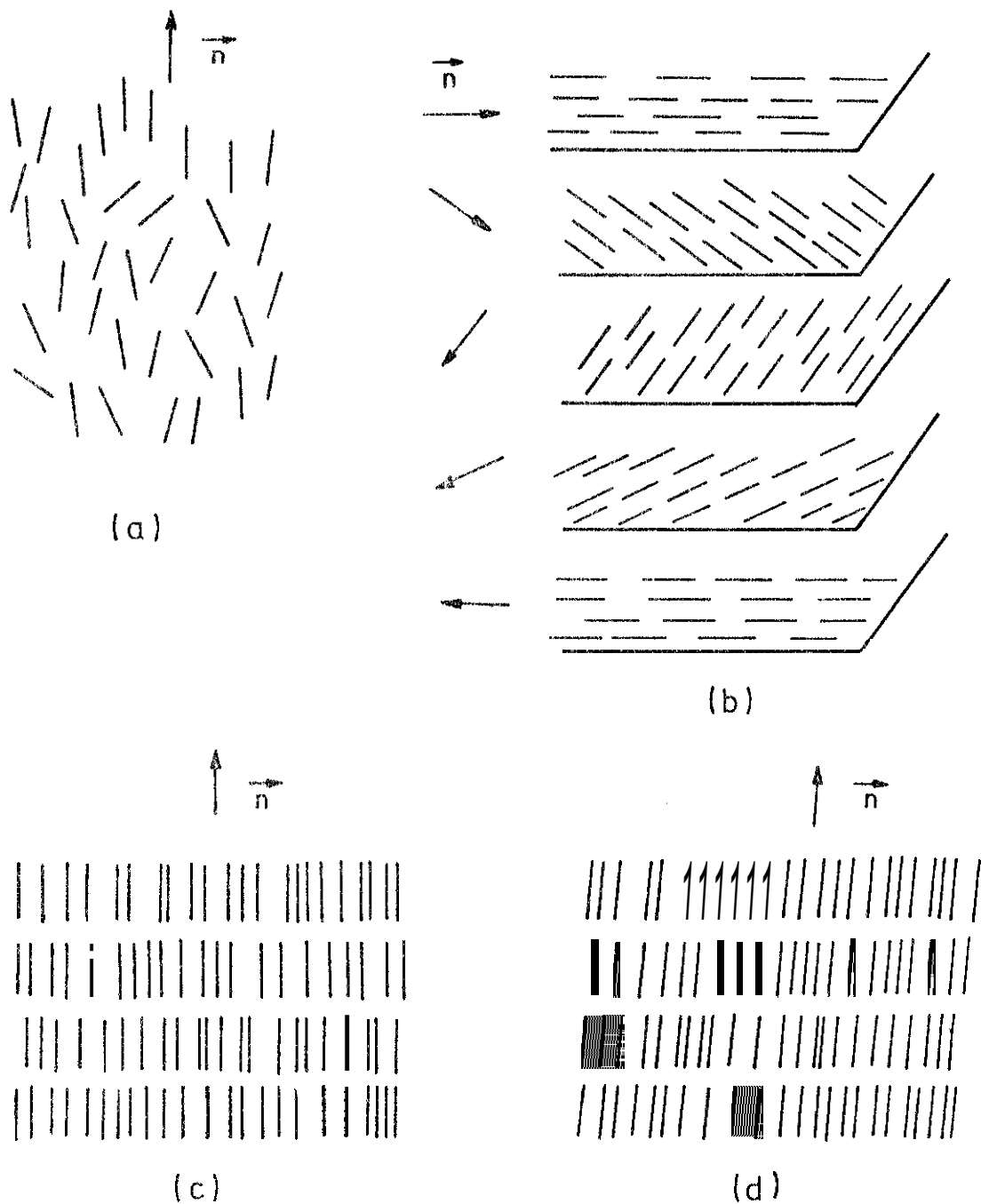


FIG.1.1: Schematic diagram showing the molecular arrangement in different types of liquid crystals, viz., (a) nematic, (b) cholesteric, (c) smectic A, and (d) amphoteric C. \vec{n} denotes the director.

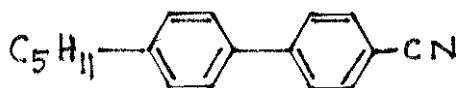
within the layers (fig.1.1c). Smectic A liquid crystals are optically uniaxial, the optic axis being normal to the plane of the layers.

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

Most mesogenic molecules have central aromatic cores which are quite rigid and relatively flexible alkyl chains at one or both ends (fig. 1.2).

We give below some typical examples of compounds exhibiting mesophases along with the sequence of phase transitions.

1)



4'-n-pentyl-4-cyanobiphenyl (5CB)⁵

crystal $\xrightarrow{22.5^{\circ}\text{C}}$ nematic $\xleftarrow{35^{\circ}\text{C}}$ isotropic .



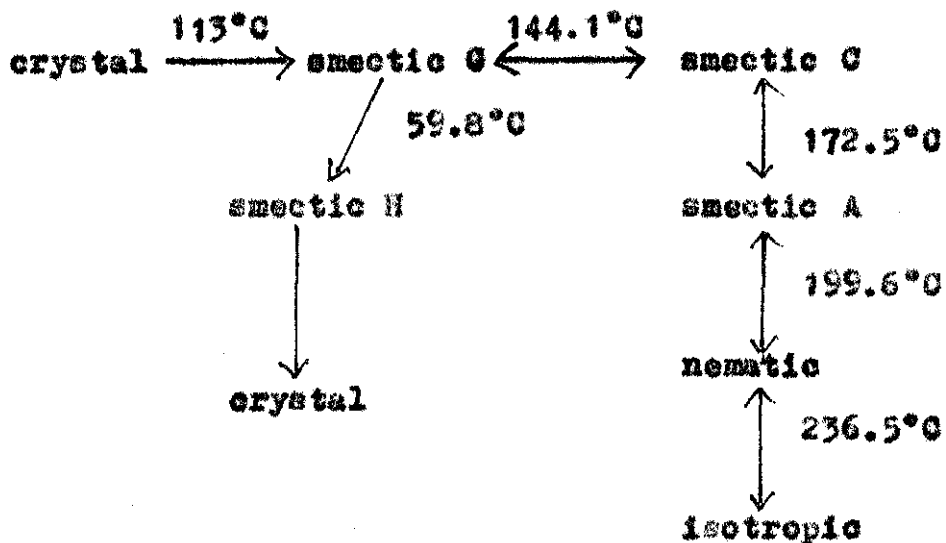
FIGURE 1.2

Chemical structure of a typical mesogenic
compound

(11)



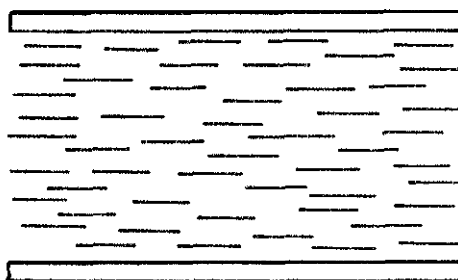
Terephthal-bis-n-butylaniline (TBBA)⁶



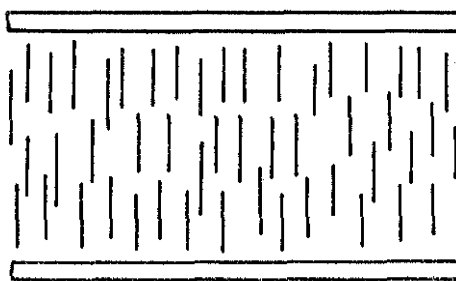
If the transitions to the liquid crystalline phase occur both during heating and cooling cycles, then they are said to be 'enantiotropic' whereas if they occur only in the cooling mode they are called 'monotropic'. For example, in TBBA, the smectic H phase occurs only during cooling and hence is monotropic in character.

1.2 Alignment of nematic and smectic A liquid crystals

In a monodomain sample of a nematic or smectic A liquid crystals \vec{n} is in the same direction throughout the sample. If, in a sample enclosed between two plane surfaces, the director is aligned along a direction parallel to the surfaces then it is referred to as homogeneous alignment (fig.1.3a). It can be obtained in the N phase by unidirectional rubbing of the surfaces⁷ or by coating the surfaces at an oblique angle with silicon monoxide,⁸ or if the, diamagnetic anisotropy $\Delta\chi > 0$, by applying a strong magnetic field in a direction parallel to the surfaces. Homogeneous alignment of the director in the A phase can be obtained by cooling slowly a homogeneously aligned sample from the N phase, especially if the smectic A - nematic transition is nearly second order in character. If the director is aligned perpendicular to the surfaces, the alignment is said to be homeotropic (fig.1.3b). This can be effected by treating that surfaces with surfactants like lecithin or cetyl trimethyl ammonium bromide, or if $\Delta\chi > 0$, by applying a strong magnetic field perpendicular to the surfaces. The smectic A liquid crystals can be relatively easily aligned in the homeotropic state, as the layers would prefer to be parallel to the bounding , lates.



(a)



(b)

FIGURE 1.3

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

1.3 Nematic Liquid Crystals

As mentioned earlier, nematic liquid crystals have long range orientational order with no long range correlation in the positions of the molecular centres of gravity. The degree of alignment of molecules in the uniaxial N phase is specified by an orientational order parameter S defined⁹ as $S = \frac{1}{2}(3\overline{\cos^2 \theta} - 1)$, where θ is the angle between the long axis of the molecule and the director \vec{n} , the bar indicating a statistical average. For perfect orientation, when all the molecules are aligned in a single direction $S = 1$, and for the completely disordered isotropic phase $S = 0$. In the N phase S has an intermediate value and decreases with increase of temperature. The rate of decrease of S is enhanced as the nematic-isotropic point (T_{NI}) is approached and in all cases drops discontinuously from a finite value to zero at T_{NI} indicating a first *order!* phase transition. The orientational order parameter can be determined experimentally by studying various physical properties like diamagnetic and optical anisotropies.

(1) Molecular Models

As Onsager¹⁰ (1949) originally showed, the shape anisotropy of the molecule itself is adequate to ensure

the stability of the orientationally ordered N phase when the number density of the molecules exceeds a certain value, even in the absence of intermolecular attractive interactions. Later Maier and Saupe¹¹ developed a simple statistical mechanical theory of the N phase based entirely on anisotropic attractive interactions and ignoring the shape anisotropy completely. In this theory, the dipole-dipole part of the anisotropic dispersion forces is supposed to determine the stability of the N phase. An analysis of the measured thermodynamic properties of various nematic liquid crystals shows that both anisotropic shape and attractive interactions play important roles in determining these properties. In the mean field approximation, the molecular distribution function can be written as

$$w(\theta_1, \rho, T) = \frac{\exp\left\{A(\rho) + \frac{B(\rho)}{T}\right\} \left(\frac{3\cos^2\theta_1 - 1}{2}\right)}{\int_0^\pi \exp\left\{A(\rho) + \frac{B(\rho)}{T}\right\} \left(\frac{3\cos^2\theta_1 - 1}{2}\right) d(\cos\theta_1)}$$

where $A(\rho)$ and $B(\rho)$ are density dependent terms arising from the hard rod and attractive parts of the intermolecular interactions respectively, and θ_1 the angle made by the long axis with the director. A statistical theory based on this distribution function leads to

results which are in broad agreement with the experimental results.

(ii) Curvature elasticity

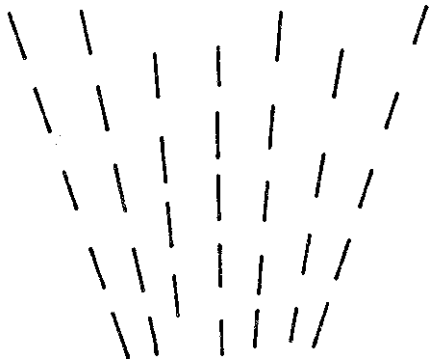
The state of uniform director orientation is the configuration with the lowest free energy for a nematic sample. As such, if there is a curvature of the director, restoring torques come into play trying to restore the medium to a state of uniform alignment. The curvature of the director can be analysed into three basic deformations, viz., splay, twist and bend which are schematically represented in fig. 1.4. The elastic free energy density of a non-uniformly oriented sample is given by

$$F = \frac{1}{2} [K_{11} (\text{div } \vec{n})^2 + K_{22} (\vec{n} \cdot \text{curl } \vec{n})^2 + K_{33} (\vec{n} \times \text{curl } \vec{n})^2]$$

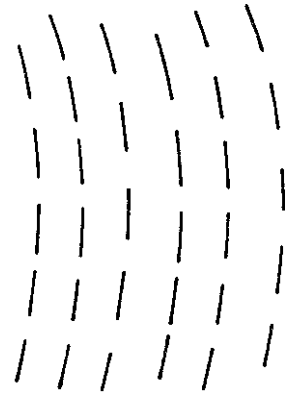
where K_{11} , K_{22} and K_{33} are the curvature elastic constants corresponding to splay, twist and bend respectively.

(iii) X-ray diffraction patterns

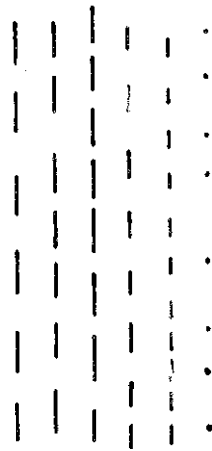
The X-ray diffraction pattern of a randomly oriented nematic has one inner ring (diffraction ring close to the centre of the diffraction pattern with the



(a)
SPLAY



(b)
BEND



(c)
TWIST

FIG.1.4 : The three types of basic distortions in a nematic liquid crystal

diffraction angle \sim few degrees) and an outer ring (diffraction angle $\sim 20^\circ$) and both are diffuse.

Isotropic phases have similar diffraction patterns, but the inner ring $2s$ generally more diffuse than that for the corresponding N phase. Aligned samples are generally used to distinguish between the two phases by X-ray techniques. In the case of a nematic aligned with its director normal to the incident beam, say with an external magnetic field, the rings split up into crescents whereas an isotropic medium cannot be aligned and continue to exhibit rings.

The outer ring is ascribed to the average spacing between the nearest neighbours in the direction perpendicular to the director. The way this ring splits up when the nematic is aligned gives information about the mean direction of the long axis of the molecules; the crescents are formed in a direction perpendicular to the director.

The diameter of the inner ring is related to the length of the molecule. The way in which this splits up for an aligned nematic gives information about the nature of short range order.

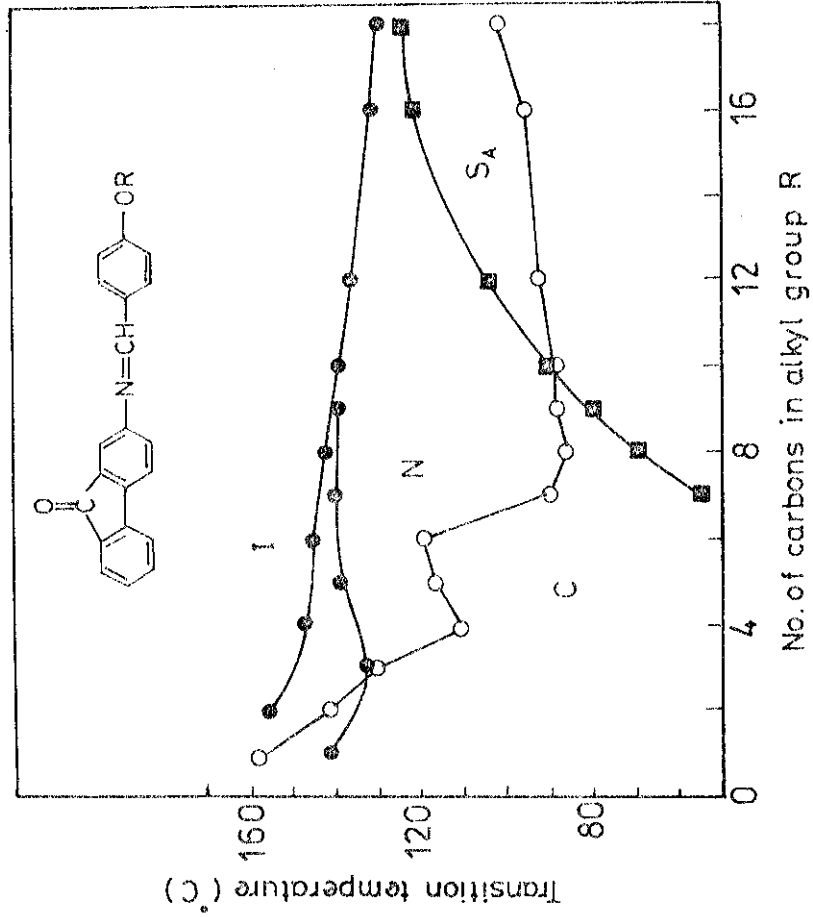
X-ray diffraction studies by Chistyakov and by de Vries¹⁵ have shown that some N phases possess smectic

like short range order. One can think of a group of molecules in the N phase (called a cybotactic group) in which the molecules are arranged in layers, i.e., in which a short range translational order exists.

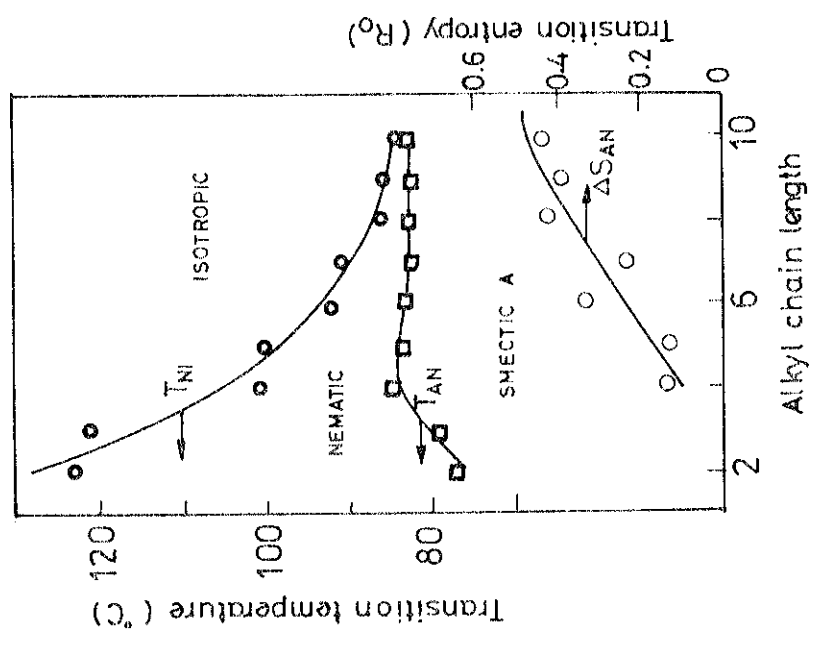
If the angle between the long molecular axis and the smectic like layer: is Different from 90° (smectic C like order) the group is known as skewed cybotactic. If the angle is 90° , then it is called normal cybotactic. The small angle diffraction patterns of aligned samples of skewed cybotactic nematics consist of four spots whereas normal cybotactics give only two spots.

1.4 Smectic A Liquid Crystals

Experimentally it is well known that the lower members of a homologous series (i.e., compounds with smaller alkyl chains) exhibit only the N phase. The A phase appears when the alkyl chain is made relatively long (fig.1.5). The first smectogen in the series shows a second order or a relatively weak first order smectic A - nematic (&-%) transition. As the chain length is increased, the nematic range decreases and the heat of the A-N transition increases (fig.1.5b), and finally beyond a certain length, the A phase goes over directly to the isotropic phase. These observations can be understood on the basis of the assumption that the strongest



(a) Transition temperature vs. alkyl chain length for the series of 2-(4'-n-alkoxybenzylidene)aminofluorenones. (Reproduced from ref.68).



(b) Transition temperature and entropy vs. alkyl chain length for 4-ethoxybenzal-4-amino-n-alkyl- α -methyl cinnamates. (Reproduced from ref.16).

intermolecular attractive interactions are confined to the aromatic cores of the molecules. This would obviously lead to the formation of a layered arrangement of molecules (characteristic of smectic phase) having relatively long alkyl chains at both the ends. This is the physical idea behind McMillan's¹⁶ molecular theory of the A phase. He extended the Maier-Saupe theory of the nematics to the A phase by assuming a density wave along the director and introducing a translational order parameter. Assuming that the translational and orientational orders are coupled, the one particle distribution function f_1 written as

$$f_1(z, \cos \theta) = \exp\left[\frac{V}{k_B T} \left\{ S + \alpha \cos\left(\frac{2\pi z}{d}\right) \right\} \left(\frac{3\cos^2 \theta - 1}{2}\right)\right]$$

where $\alpha = \langle \cos\left(\frac{2\pi z}{d}\right) \left(\frac{3\cos^2 \theta - 1}{2}\right) \rangle$ is the coupled order parameter, $a = 2 \exp[-(\pi r_0/d)^2]$ where r_0 is of the order of the length of the rigid part of the molecule, d the layer thickness and $S (= \frac{3\cos^2 \theta - 1}{2})$ the orientational order parameter and k_B the Boltzmann constant. The free energy can then be easily written and the solutions minimizing the free energy are of the form

$$\sigma \neq 0 \quad S \neq 0 \quad (\text{A phase})$$

$$\sigma = 0 \quad S \neq 0 \quad (\text{N phase})$$

and $\sigma = 0 \quad S = 0 \quad (\text{isotropic phase}).$

Detailed calculations based on this theory broadly reproduces the experimental trend as a function of chain length. In particular, the theory predicts that the A-N transition is of second order character if the ratio $(T_{AN}/T_{NI}) < 0.87$ and is of first order for higher ratios.

1.5 Analogy between superconductor-normal metal transition and the smectic A -nematic transition

As we have noted earlier, the A phase is characterized by a density wave along the director. The density along the Z axis (director \vec{n}) is well described by $\rho = \rho_0 [1 + \text{Re}\{|\psi| e^{i(q_0 z + \varphi)}\}]$, where $q_0 = 2\pi/d$, d being the layer spacing and φ a phase factor which defines the position of the layers and $|\psi|$ the amplitude of the density wave (degree of smectic order). The second and higher order maxima are hardly seen in the X-ray diffraction pattern from the A phase of most of the compounds¹⁷ thus confirming sinusoidal density modulation along the director. Fig. 1.6 depicts schematically the smectic A layering with its sinusoidal density wave.

Thus the A phase is characterized by a two component order parameter. The two components are the amplitude

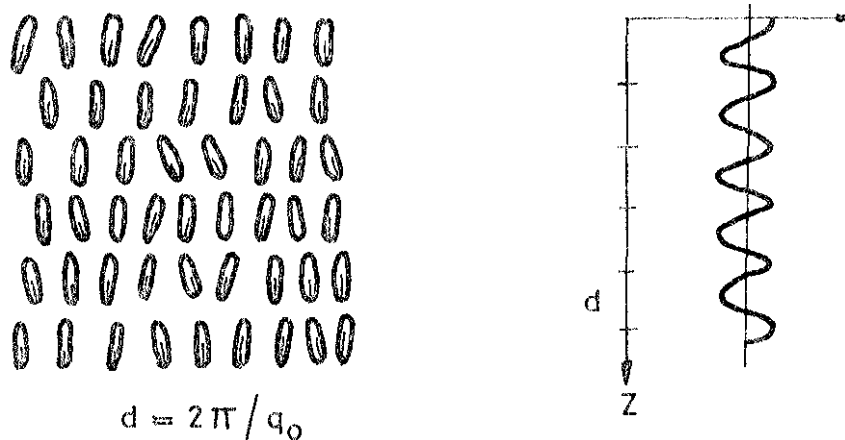


FIGURE 1.6

Schematic diagram of smectic A phase with its one dimensional density wave along the average direction of the molecular axis.

and the phase of the density wave. This is analogous to the order parameter of a superfluid.^{16,18}

In any layered arrangement, as for example in the A phase, twist and bend deformations change the layer spacings which requires very high energy. These deformations are therefore forbidden in an ideal A phase. This is analogous to the absence of a magnetic field ($\text{curl } \vec{a}$) in a superconductor. The close analogy between second order A-N transition under $\text{curl } \vec{n}$ distortion and superconductor-normal metal transition under a magnetic field was recognized by de Gennes.¹⁸ Based on this analogy he predicted (i) the divergence of twist and bend elastic constants as T_{AN} (smectic to-nematic transition point) is approached from the nematic side, and (ii) a reduction in T_{AN} of a nematic sample with a $\text{curl } \vec{n}$ type of deformation due to the expulsion of this type of curvature deformation from the A phase. This is again analogous to the reduction of the superconductor-normal metal transition point under the action of an external magnetic field. A large number of experimental investigations have been carried out as regards the divergence of twist and bend elastic constants.¹⁹ On the other hand, there has been no quantitative investigation of the second prediction.

We have made the first measurement of the phase diagram of T_{AN} as a function of $|\text{curl } \vec{n}|$ distortion. This forms the subject matter of chapter II.

1.6 X-ray diffraction from smectic A phase

The one dimensional translational order found in the A phase is reflected in X-ray diffraction patterns. Randomly oriented smectic A samples give sharp inner ring and a diffuse outer ring. In an aligned monodomain sample, the inner diffraction is concentrated in two 'Bragg spots' along the director and the outer ring in two crescents. The line joining the inner spots is normal to the line going through the centres of the outer maxima; indicating that the director is perpendicular to the smectic planes. The distance between the inner spots is related to the layer spacing (or layer thickness) while that between the outer diffuse maxima corresponds to the distance between the neighbouring molecules in the plane of the layers.

A one dimensional translational order in an infinite 3-dimensional system cannot have long range order due to the Landau-Peierls instability of such a system.²⁰ This is reflected in the X-ray diffraction from the smectic A layers. High resolution studies on

monodomain samples have shown that the diffraction intensity decays as $\sim 1/(q - q_0)^x$ in reciprocal space (where $x = x(T)$, and $q_0 = 2\pi/d$) rather than $(q - q_0)^{-2}$ variation of intensity of a Bragg diffraction arising from a system with a truly long range translational order.²¹ We will however not be interested in these finer details of X-ray diffraction from smectic A liquid crystals.

One can intuitively expect that the layer spacing of a smectic A liquid crystal is equal to the molecular length, as is indeed found for all weakly polar compounds including some studied by us (which will be reported in chapter III). However, this is not true for compounds with strongly polar end groups, as will be discussed in the next few paragraphs.

1.7 Nematic and smectic A phases exhibited by compounds with strongly polar end groups

The synthesis and studies on the mesomorphic properties of compounds with the strongly polar cyano and nitro end groups have been a rather fertile field of investigation over the past decade. The initial motivation for such studies came from the invention of the twisted nematic display device²²; the compounds with strongly polar end groups can have a large anisotropy

of dielectric constant $\Delta\epsilon$ ($= \epsilon_{\parallel} - \epsilon_{\perp}$, see later sections) and hence a relatively low voltage for operating the displays. The very first systematic study of the dielectric properties of such compounds by Schadt²³ led to the interesting observation of a positive jump in the mean dielectric constant $[\bar{\epsilon} = (\epsilon_{\parallel} + 2\epsilon_{\perp})/3]$ at the nematic-isotropic transition point (T_{NI}). This was interpreted by Madhusudana and Chandrasekhar²⁴ as arising from antiparallel dipolar correlations between neighbouring molecules. A discontinuous decrease in the antiparallel ordering at T_{NI} results in a positive jump in $\bar{\epsilon}$. It is worthwhile noting here that the very first statistical theory of the N phase was given by Born in 1916²⁵ by assuming that strong longitudinal dipoles associated with the rod like molecules would give rise to a ferroelectric order. However, as we have noted earlier, the director has been found to be apolar and the N-I transition is of first order character, which are contrary to the results of the Born's theory. The thermodynamic properties of the N phase has been well explained by Maier-Saupe type theories, as we outlined earlier. The N phase is a 3-dimensional liquid, and the antiparallel correlations between neighbouring strongly polar molecules have only a short range character. Later X-ray and neutron

scattering investigations in both the A and N phases,^{26,27} exhibited by compounds with cyano end groups revealed layer spacing ~ 1.4 times the molecular length which is a direct consequence of the antiparallel interactions between neighbouring molecules in these compounds. As we have noted earlier, the strongest intermolecular attractions are confined to the rigid molecular cores, and the additional polar interactions favouring an antiparallel orientation leads to the structure shown in fig. 1.7. This interdigitation of the molecules with an overlap of the aromatic cores is known as bilayer structure. Further, the antiparallel interactions can be expected to lead to the formation of 'antiparallel pairs', since a third molecule would feel 'frustrated' in its polar interactions with both the molecules of the pair. An interesting consequence of the formation of such antiparallel pairs is that they are much more symmetric than the individual molecules which are highly asymmetric because of the presence of the alkyl chain at one end and a polar group at the other. The pairs have alkyl chains at both the ends and the McMillan argument¹⁶ regarding the conditions of formation of the A phase is now valid for the pair and hence many such compounds with strongly polar cyano or nitro end groups show the A phase.²⁸ The A phase

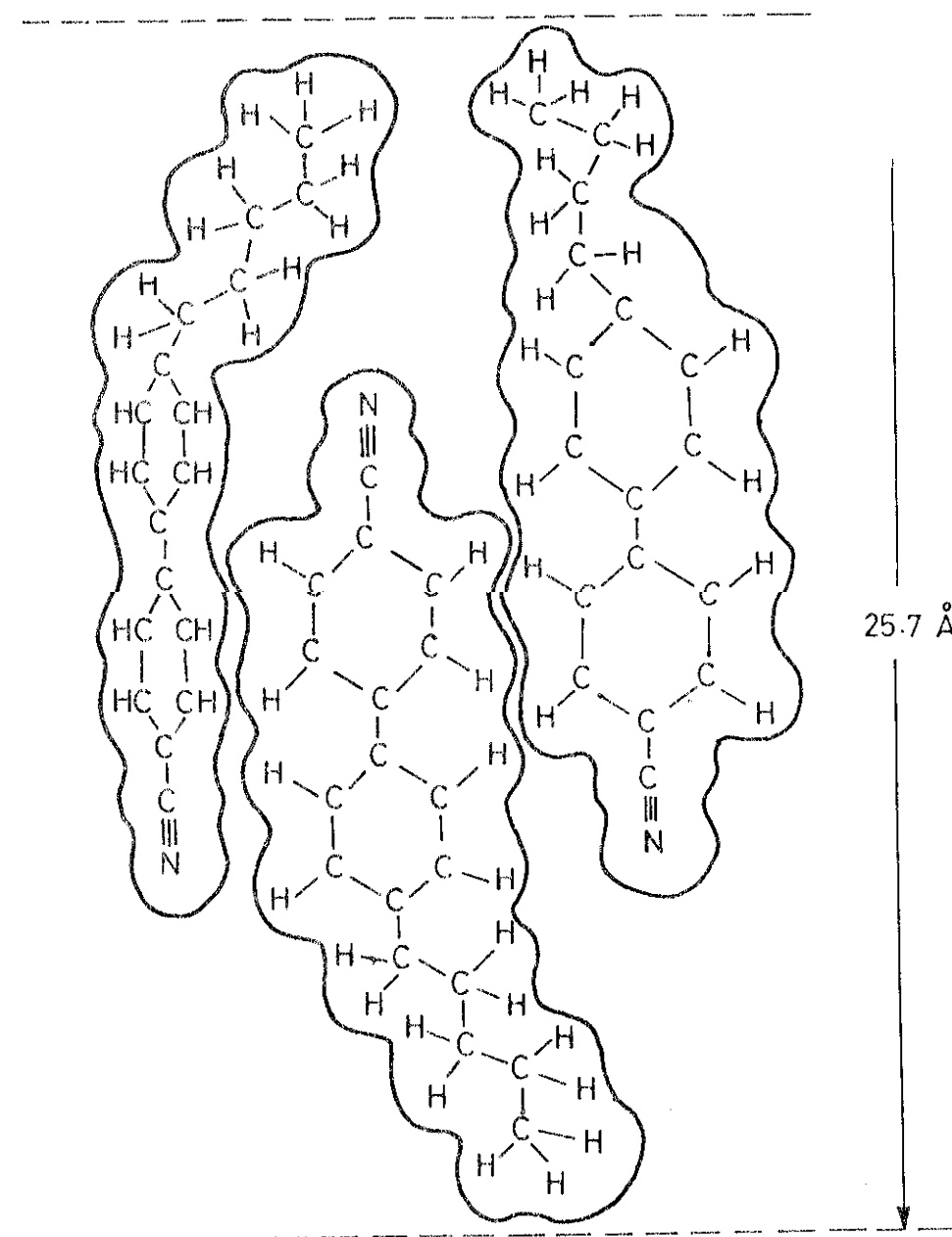


FIGURE 1.7

Schematic diagram of antiparallel local structure in pentyl-cyanobiphenyl. The repeat distance along the nematic axis is about 1.4 times the molecular length. (After Leadbetter et al.²⁶)

thus formed is referred to as a bilayer A phase. Even if these strongly polar compounds do not exhibit the A phase, smectic like short range order having bilayer characteristics have been observed in the N phase of such compounds.²⁶ The structure of the bilayer is an extra degree of freedom available to such systems and gives rise to several interesting phenomenon like reentrance²⁹⁻³⁵ and polymorphism of smectic A³⁶⁻³⁹ which have been discovered during the past few years.

(1) Reentrant phases

The usual sequence of transitions observed on cooling a mesogen showing both A and N phases is

Isotropic \rightarrow Nematic \rightarrow Smectic A \rightarrow Crystal.

However, Cladis²⁹ found that some binary mixtures of compounds with cyano end groups exhibit the following new sequence of phase transitions.

Isotropic \rightarrow Nematic \rightarrow Smectic A \rightarrow Nematic \rightarrow Crystal.

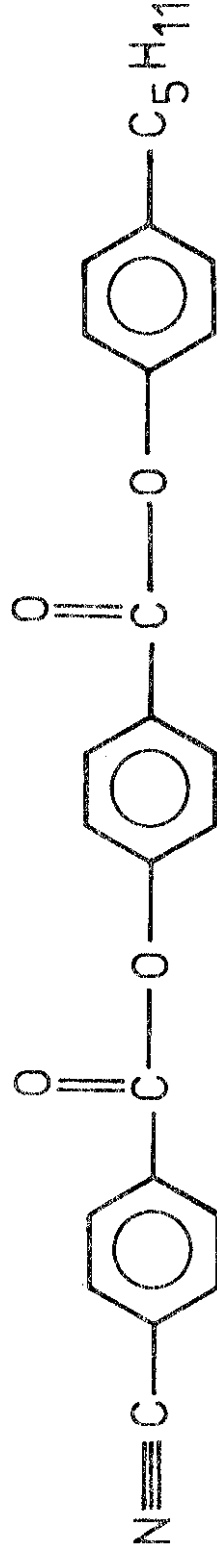
The N phase occurring at temperatures lower than the stability range of the smectic phase is called reentrant nematic phase, in analogy with similar reentrant phases observed in superconductor doped with magnetic impurities⁴⁰ and the solid-liquid He³ transition.⁴¹

Such an interesting phase sequence is found both in mixtures²⁹ and pure compounds at³²⁻³⁵ and above^{30,31} atmospheric pressure. Systems exhibiting a reentrant smectic phase below the temperature range of the reentrant nematic have also been observed.⁴² However, in this thesis we will not be directly interested in the more complex reentrant behaviour. Our investigations have more to do with another interesting phenomenon exhibited by some compounds with strongly polar end groups, viz., smectic A polymorphism.

(ii) Smectic A polymorphism

X-ray investigation have recently revealed various other interesting aspects of mesophases formed by strongly polar compounds. For example, in pentyl cyanoterphenyl, a nematogen, short range correlations corresponding to two different lengths, one somewhat less than the molecular length (λ)(0.93λ) and the other between λ and 2λ ($\sim 1.4\lambda$) are found.⁴³ In other words, two incommensurate wavelengths coexist.

DB5 [4-n-pentylphenyl-4'-(4'-cyanobenzoyloxy) benzoate] has two ester linkage groups in the aromatic core with their dipole moments opposing that of the terminal cyano group (fig.1.8). This compound has an



4 - n - pentyl phenyl - 4' - (4'' - cyanobenzoyloxy) benzoate
(DB5)

10-A transition point at 139°C and an N-I transition at 249°C. Consequently the ratio (T_{AN}/T_{NI}) \approx 0.78 and according to the McMillan's criterion¹⁶ it should exhibit only a second order 1-A transition. Actually, however, it has a moderately strong first order N-A transition. Mayer and Lubensky⁴⁴ developed a mean field theory of the A phase with a coupling between the first and the second translational order parameter to account for this anomaly. X-ray investigations³⁷ have revealed that DB5 and similar compounds possess bilayer spacings close to twice the molecular length (A_2 phase) and further, in many cases, a rich variety of smectic A polymorphism.

Calorimetric and diamagnetic susceptibility measurements by Sigaud et al³⁶ revealed a clear first order A-A transition line in the binary phase diagram of DB5 and terephthal-bis-butylaniline (TBBA). TBBA is a weakly polar compound exhibiting monolayer A phase with a layer spacing nearly equal to the molecular length (A_1 phase). Later X-ray investigations³⁷ showed that the A-A transition corresponds to that from a monolayer A_1 phase to a bilayer A_2 phase. The proposed molecular arrangements in the two phases are shown in fig.1.9. Recently, DB7 a higher homologue of DB5 has

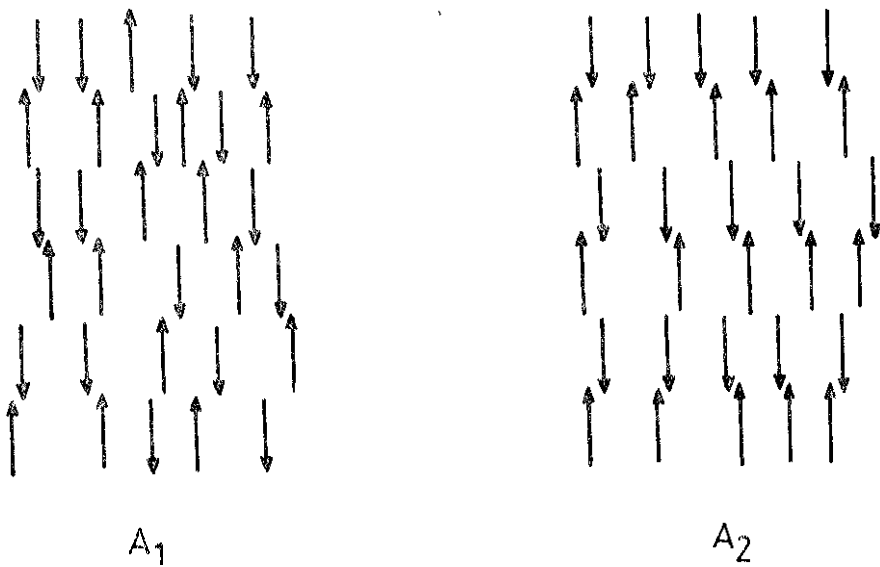


FIGURE 1.9

The molecular arrangement in (a) the A_1 phase,
and (b) the A_2 phase.

been found to exhibit a similar $S_A - S_A$ phase transition.³⁸ In the higher temperature A phase there is a coexistence of two incommensurate wavelengths with one spacing giving a Bragg's spot at $\sim 1.6l$ and the other a diffuse spot at $\sim l$. This phase with $l \lesssim d \lesssim 2l$ is called a partially bilayer A_d phase.⁴⁵ When the temperature is lowered, a phase transition takes place such that in the lower temperature phase there are two Bragg spots corresponding to l and $2l$ resulting in commensurate locking of the two wavelengths. The repeat unit has a spacing $\approx 2l$ in this case, i.e., it is an A_2 phase. Thus the phase transition is an $A_d - A_2$ transition.

More recently, yet another interesting type of smectic A (called smectic antipase \tilde{A}) has been discovered in some pure compounds³⁹ and mixtures.⁴⁶ This has a long range periodicity of $\sim 130 \text{ \AA}$ in the plane of the layers. The proposed structure is shown in fig. 1.10.

The different A phases have been accounted for by Prost et al⁴⁷ on the basis of a Landau theory, by assuming a competition between two order parameters, one of them corresponds to the usual mass density wave with a wavelength $\approx l$ and the other arises from the

$$\lambda = \frac{2\pi}{q_{1x}} > 130 \text{ \AA}$$

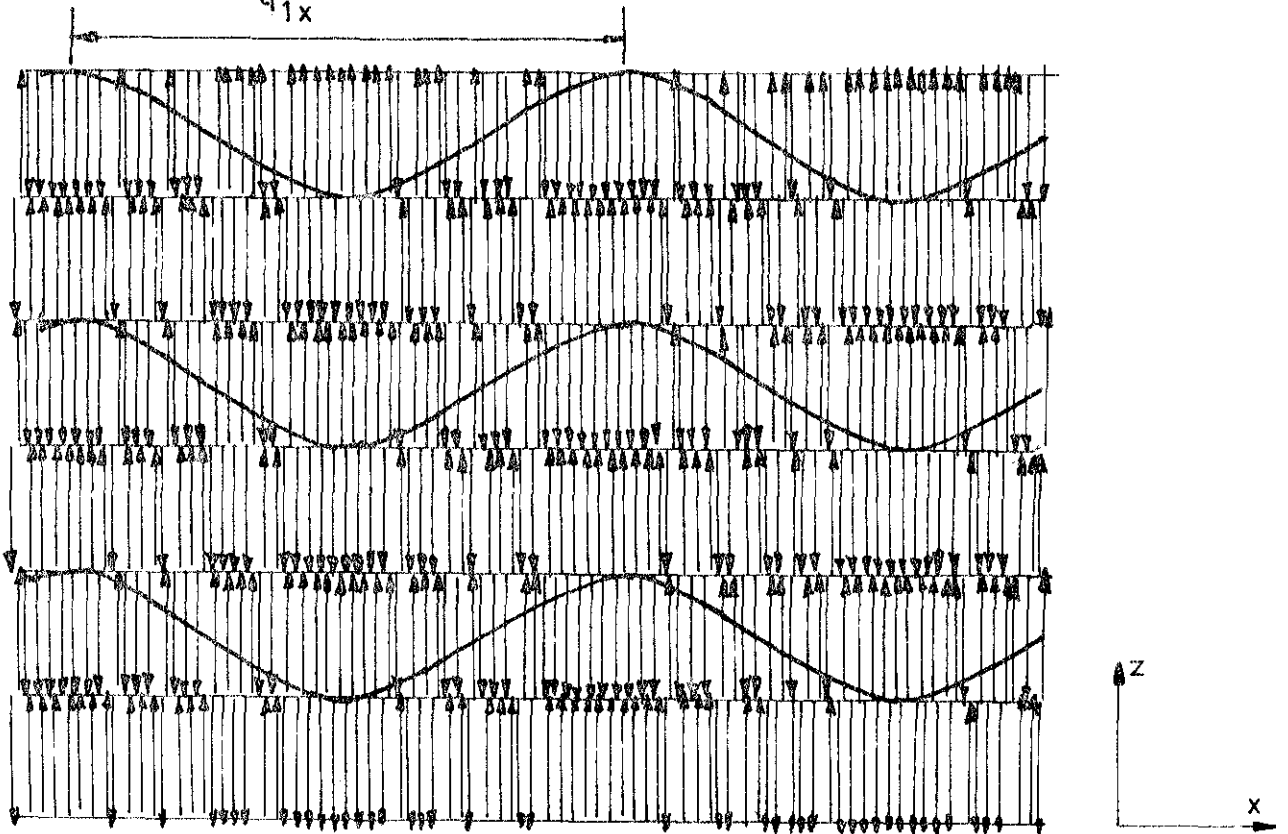
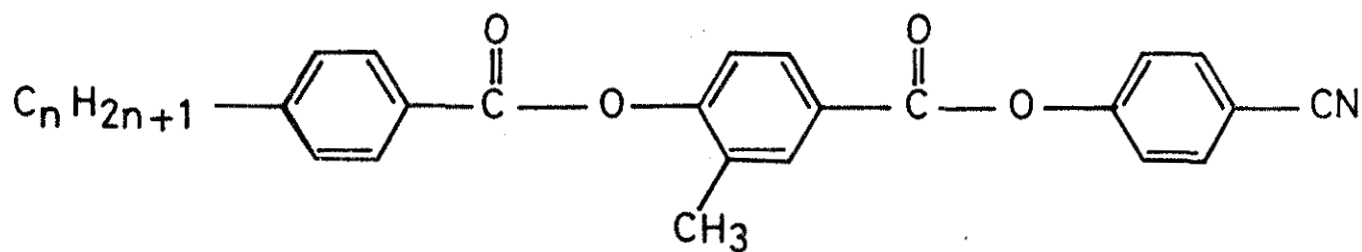


FIGURE 1.10

Schematic diagram of the arrangement of molecules in the smectic antiphase (\tilde{A})

antiparallel (or antiferroelectric) interactions between neighbouring molecules, which give rise to another density wave with a wavelength $> \lambda$. Thus the smectic phases exhibited by such highly polar compounds are described as 'frustrated' smectics, the 'frustration' arising out of the possibility of the simultaneous existence of two density waves in the medium.

We have undertaken X-ray studies on many compounds with a chemical structure similar to that of DB5, with the additional feature that a bulky methyl or methoxy lateral group is attached to the aromatic core. The original motivation for studying these compounds came from the fact that eleventh and twelfth members of 4-cyanophenyl-3'-methyl-4'-(4''-alkyl benzoyloxy)benzoate series (NCPMBB) (see fig. 1.11) which were earlier synthesised in our laboratory were amongst the first pure compounds which were found to exhibit the reentrant nematic phase at atmospheric pressure.³² The compounds studied in this thesis are got by interchanging the two end groups of NCPMBB molecules. We have also studied compounds in which the cyano group is replaced either by the nitro group or a bromine atom. The bulky methyl or methoxy lateral groups considerably reduce the intermolecular interaction energies compared to those in the



4-cyanophenyl - 3'-methyl - 4'-(4''-n-alkylbenzoyloxy) benzoates
(nCPMBB)

FIGURE 1.11

case of DB5. This in turn leads to certain interesting new features like a relatively easy break up of the bilayer structures in our compounds. The X-ray investigations on these compounds are the subject matter of chapter III.

1.8 Dielectric constants of nematic and smectic A liquid crystals

Nematic and smectic A liquid crystals being uniaxial have two dielectric constants: ϵ_{\parallel} along the director and ϵ_{\perp} in a perpendicular direction. The values of the anisotropic dielectric constants depend on various factors, viz., (i) molecular polarizability, (ii) magnitude and mutual disposition of the dipolar groups, (iii) internal field which is not easy to calculate for the anisotropic medium, and (iv) orientational order in the medium. A simple theory of the dielectric constants of the N phase taking into account all these factors was given by Maier and Meier.⁴⁸ As we have already mentioned, when the molecules have strong longitudinal dipole moments, the antiparallel correlations between neighbouring molecules have to be taken into account in understanding the dielectric properties of the medium.²⁴ In addition, some of the strongly polar compounds studied by us exhibit large bilayer spacings

which are extremely sensitive to temperature because of relatively weak intermolecular interactions. We can expect that this structural change has a noticeable influence on the dielectric properties of the medium. We have undertaken studies on the low frequency dielectric constants of several compounds whose layer spacings are reported in chapter III. Many of them exhibit a reversal of the sign of $\Delta\epsilon$ in the A phase. The results are discussed in chapter IV.

The nematic and smectic A liquid crystals also exhibit very interesting dielectric dispersion characteristics. Thus ϵ_{\parallel} is found to relax at a fairly low frequency of a few MHz or even 10s (tens) of KHz, in the case of compounds with an appreciable long axis component of dipole moment. Maier and Meier⁴⁹ interpreted this lowering of the relaxation frequency as arising from an additional hindering of the reorientational motion of the molecules about their short axes because of the nematic potential. The corresponding 'retardation factor' by which the relaxation frequency is lowered compared to that of the usual Debye relaxation was calculated by Meier and Saupe⁵⁰ on the basis of the Maier-Saupe nematic potential. One of the puzzling features noted in later studies is that the activation

energy for ϵ_0 relaxation is lower in the A phase than in the N phase in compounds exhibiting both the phases. We have studied the ϵ_0 relaxation in several compounds mentioned above and discuss the possible origin of the lowering of the activation energy in the A phase.

The ϵ_1 relaxation usually takes place in GHz region as in normal liquids. However, we have found that in one of the compounds which has a large bilayer spacing the ϵ_1 relaxation also occurs at relatively low frequencies, and over a rather broad range, due to various contributory factors. All these studied will be discussed in chapter IV.

1.9 Conductivity studies in nematic and smectic A liquid crystals

Pure liquid crystals are expected to be good insulators. However, unless special purification procedures are followed, the compounds have some conducting impurities which give rise to conductivities in the range of $10^{-9} - 10^{-11} \Omega^{-1} \text{cm}^{-1}$. Earlier studies have shown that in a pure nematic liquid crystal without any smectic like short range order the conductivity σ_{\parallel} , measured parallel to the director is always greater than

the conductivity σ_{\perp} , measured perpendicular to the director.⁵¹ The conductivity anisotropy $\Delta\sigma (= \sigma_{\parallel} - \sigma_{\perp})$ is strongly influenced by the short range order in the medium.⁵²⁻⁵⁶ The anisotropy ratio $\sigma_R (= \sigma_{\parallel}/\sigma_{\perp})$ is less than one in the A phase for the ions can flow more easily in the layers than in the perpendicular direction. Generally $\Delta\sigma$ changes sign close to T_{AN} , becoming negative at lower temperatures as the sample is cooled from the nematic. Further, it is known to depend on the structure of the A phase.⁵⁶ In addition the conductivity also depends on the frequency of measurement,⁵⁷ especially for σ_{\parallel} . This is caused by the relaxation of ϵ_{\parallel} . The absorption due to the low frequency tail of this relaxation causes an enhancement of the measured conductivity at any finite frequency. This contribution is of course zero for a DC measurement.

We have measured the principal conductivities in both in the N and A phases of several structurally related compounds on which X-ray and dielectric studies are reported in chapters III and IV respectively. The results are discussed in chapter V.

1.10 Induced smectic A phase

Another striking example of the effect of a

subtle type of molecular interaction in liquid crystals is the occurrence of the 'induced smectic' phases.

When two nematogens are mixed together, one would expect the mixtures also to exhibit only the N phase as indeed found in most mixtures.⁵⁸⁻⁵⁹ When T_{NI} of such mixtures are plotted against compositions, it is found to vary practically linearly with composition and only small deviations from linearity are observed.

However a different type of phase diagrams is observed⁶⁰⁻⁶⁴ when one of the components has the strongly polar cyano or nitro end group and the other component has no such group. Usually, an induced smectic A (or induced A phase) is observed in certain composition range of such mixtures even when both components are only nematogens (fig.1.12). The interactions between the permanent dipole of the polar component and the induced dipole of the weakly polar compound appear to be important for the occurrence of the induced phase. Further, there is an experimental evidence⁶⁵ that a charge transfer complex formation takes place between the molecules of the two kinds, the highly polar component

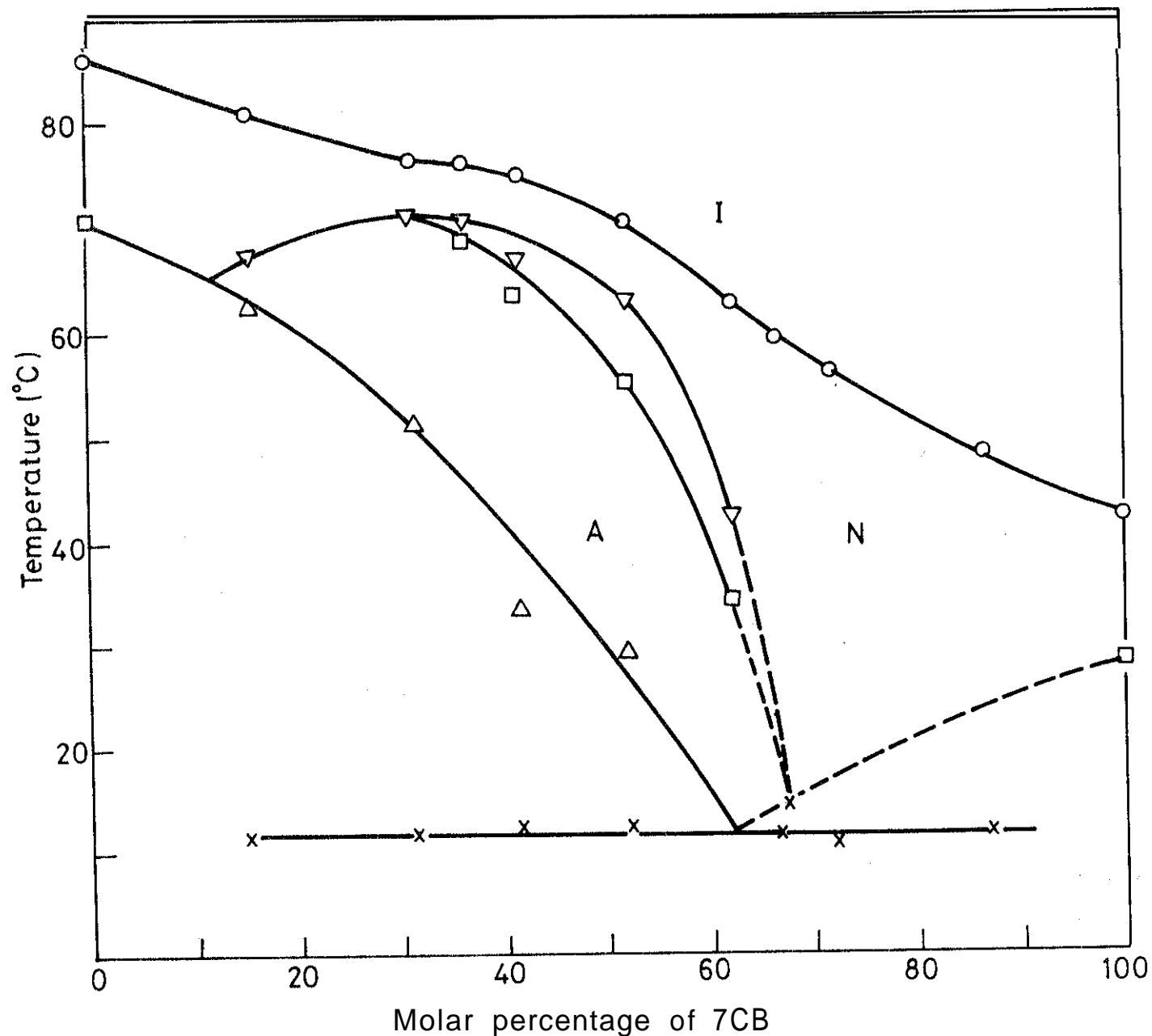


FIGURE 1,12

Phase diagram of mixtures of 4'-n-heptyl-4-cyanobiphenyl (7CB) with (2-hydmxy)-p-ethoxybenzylidene-p'-butylaniline (OH-EBBA). (Reproduced from ref. 64),

acting as the acceptor while the other component acts like a donor. This interaction appears to lead to the formation of a layered arrangement characteristic of smectic phases.

If the highly polar compound itself exhibits a A phase, it will have a bilayer structure which arises due to the antiparallel correlations between neighbouring molecules²⁴ as we have discussed earlier. In some cases, the bilayer A phase is immiscible with the induced A phase which is known to be a monolayer smectic (layer spacing \sim molecular length).⁶⁶ If the bilayer corresponds to nearly two molecular lengths (A_2 phase), A_1 - A_2 phase transitions is obtained as we have mentioned earlier.

We have studied the phase diagrams of two binary systems of a 'bilayer' smectogenic compound with a weakly polar nematogen. Both of them show a strong maximum in the A-N boundary indicative of an induced A phase, and further, a well defined minimum for a composition rich in the highly polar component. The interactions responsible for the formation of the induced A phase are much stronger in one system than in the other, as revealed by the phase diagrams. We have also made many

physical measurements like the temperature variations of the layer spacings in the A phase, the low frequency dielectric constants, the dispersion of ϵ_{11} and the principal conductivities for several compositions of both the systems. We find several interesting features which are discussed in terms of the interactions giving rise to the induced A phase. The results are presented in chapter VI.

1.11 Effect of skewed cybotactic structure on the dielectric constants and conductivities of a nematic liquid crystal

The presence of skewed cybotactic groups was noted by de Vries^{19a} in the N phase of bis-(4'-n-octyloxy-benzal)-2-chloro-1,4-phenylenediamine. More recently, Madhusudana et al.⁶⁷ have found a similar smectic C like short range order in the N phase of 2-cyano-4-heptyl-phenyl-4'-pentyl-4-biphenyl carboxylate (7P(2CN)5BC), a compound with a strongly polar cyano group making a large angle ($\sim 60^\circ$) with the long axis of the molecule. It is interesting to note that 7P(2CN)5BC does not exhibit smectic C phase at lower temperatures. This compound has a moderately strong negative dielectric anisotropy. The tilt angle of the skewed cybotactic

structure is temperature dependent and decreases from $\sim 43^\circ$ at 25°C to $\sim 40^\circ$ at 87°C . This had a noticeable influence on the temperature variation of the ordinary refractive index (n_o) of the compound⁶⁷; n_o decreases first, attains a broad minimum and then increases as the sample is cooled in the nematic phase (fig.1.13). In order to see the effect of the tilt angle variation on other physical properties like dielectric and conductivity anisotropies, detailed experimental investigations were undertaken on this compound and its mixtures with 4'-n-heptyl-4-cyanobiphenyl (7CB). Several interesting results have been obtained. For instance, a mixture of 85% of 7P(2CN)5BC with 15% of 7CB exhibits a reversal of dielectric anisotropy, unusually becoming negative at higher temperatures. These results are presented and discussed in chapter VII.

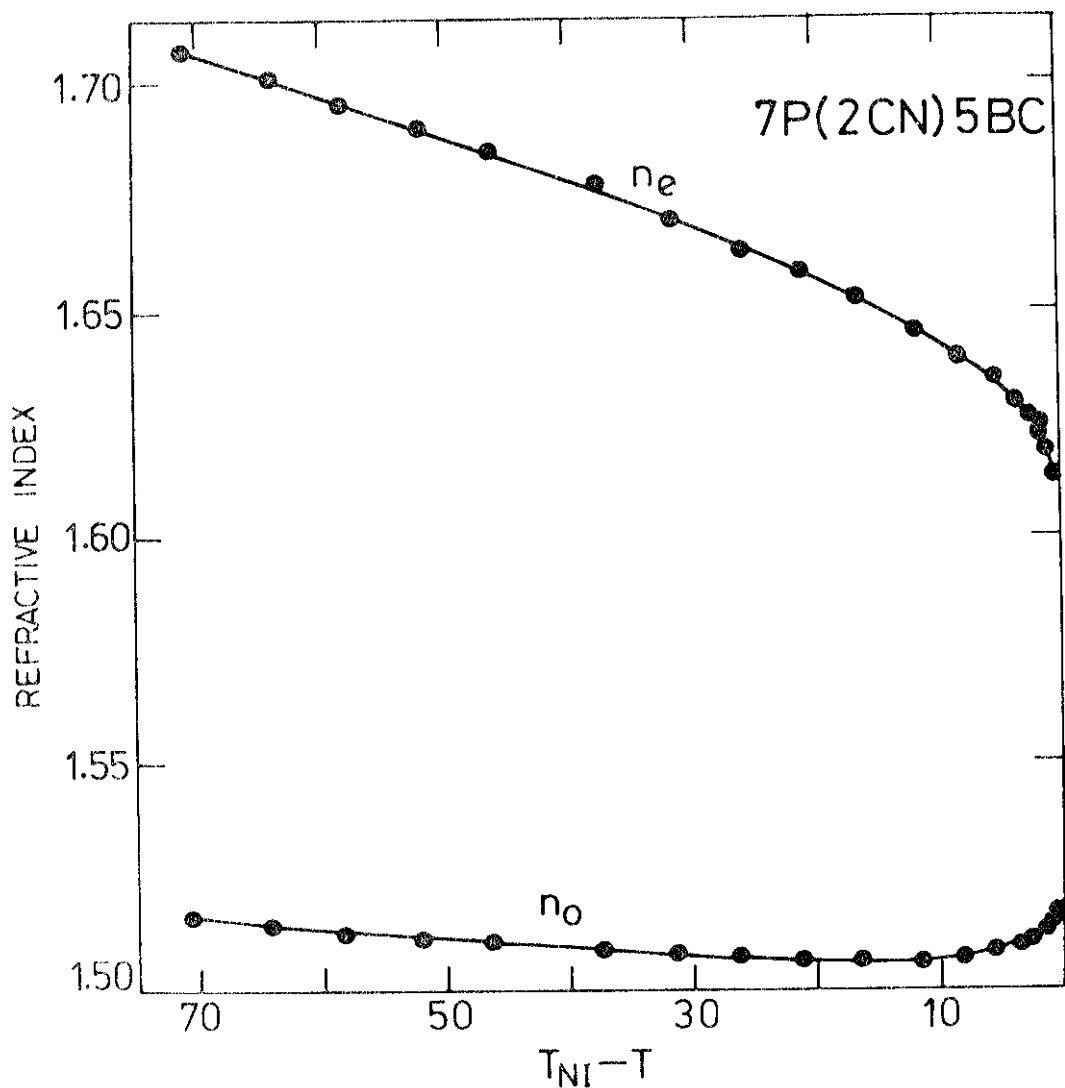


FIGURE 1.13

Refractive indices of 2-cyano-4-heptylphenyl-4'-pentyl-4-biphenyl carboxylate [7P(2CN)5BC] plotted against relative temperature ($T_{NI} - T$), T_{NI} being the nematic-isotropic transition temperature. (Reproduced from ref.67).

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