EXPERIMENTAL STUDY OF STRUCTURE AND PHASE TRANSITIONS IN SOME LIQUID CRYSTALS

BY

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I Mr. Bulbul Gogoi, hereby declare that the subject matter of this thesis is the record of work done by me, that the contents of this thesis did not form basis of the award of any previous degree to me or to the best of my knowledge to anybody else, and that the thesis has not been submitted by me for any research degree in any other University/Institute.

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CONTENTS

PREFACE

Liquid crystals, a state of condensed matter between that of three dimensional periodic crystalline solids and isotropic liquids, have experienced an explosive growth during the last couple of decades. They were ~~was~~ discovered by an Austrian botanist, Friedrich Reinitzer in 1888 and later, Lehman identified these liquid crystalline phases in cholesteryl compounds and named these as "intermediate phases" or mesophases. The most essential requirement for the occurrence of mesomorphism is that the molecule must be geometrically anisotropic in shape, like a rod or a disc. At the same time the molecule must also possess some rigidness of the long axis and strong dipoles. Liquid crystals possess the dual characteristics of solids and liquids, i.e., anisotropic properties of crystalline solids and flow properties of isotropic liquids. Not surprisingly, the intensive materials programme has quite frequently brought to light new materials with hitherto unknown liquid crystalline phases, particularly, the many exotic phases of smectic types and its successful applications in the electrooptical displays. This has stimulated phase transition and structural studies of these systems by Polarizing Thermal Microscopy, Calorimetric studies, X- ray diffraction, Nuclear Magnetic Resonance, Electron Spin Resonance, Neutron Scattering, Raman and FT-IR spectroscopy, Dielectric and Dilatomertic studies etc. The research area is interdisciplinary among chemists, physicists and technologists with a common goal for developing its useful applications.

In the present work discussed in this thesis, Laser Raman spectroscopy and dilatometric measurement techniques were employed to study the structure and phase transition of five liquid crystal compounds. Also, Differential Scanning Calorimetry and dilatometric techniques have been applied to explore tricritical point in Sm A – Sm C phase transition in the binary mixtures of Terepthalylidene-bis-p-n-alkylanine (TBAA) homologues series.

In Laser Raman spectroscopy, variation of some physical quantities are found to affect the polarizability tensor that results in changes in measurable parameters of bands from certain vibrational modes in the Raman spectrum of the system. Laser Raman spectroscopy has been found to be very effective in the study of phase transitions in liquid crystals. In the past couple of decades Raman spectroscopy has been extensively used in the study of liquid crystals to extract structural information, more specifically on the molecular structure and intra/inter-molecular interactions in the liquid crystalline phases. Also, the density measurement studies by either vibration densitometer or classical dilatometer is an important experimental technique for the study of phase transitions and related thermodynamical parameters. The density of the liquid crystalline compound varies with the variation of temperature in liquid crystals. A first order transition is associated with a discontinuity in the density values at the transition whereas the second order transition is accompanied by a continuous change in the density values.

The liquid crystal materials chosen for this thesis work are the liquid crystal dimers, α,ω-bis(4-n-alkylanilinebenzylidene-4′-oxy)alkane, popularly known as m.OnO.m homologues series of compounds for its rich smectic mesomorphism and their ability to act as model compounds for semi-flexible main chain liquid crystal polymers and also for their quite fascinating and unusual properties. The transitional properties of these dimers depend on the length and parity of the flexible spacer as well as the nature of linking group of the mesogenic units. In particular, the nematic-isotropic transition temperatures are found to exhibit a dramatic alternation on the number of carbon atoms as the alkyl spacer changes from odd to even. However, though a large number of schiff base liquid crystal dimers have been synthesized and characterized in the recent past, the detailed study of various rare and new phase transitions exhibited by the dimers and the detailed structural evaluations have not yet been carried out. Therefore, we have taken up the study of molecular dynamics and phase transitions of few symmetric liquid crystal dimers using Laser Raman spectroscopy and density measurement techniques.

We have also studied another well-known schiff base liquid crystalline compounds, Terepthalylidene-bis-p-n-alkylanine (TBAA) homologues series.This series is popularly known as TBAA homologues series and is interesting for its rich variety of polymorphism with wide thermal ranges. One of the TBAA series compound, TBBA exhibits six mesophases which offers the possibility to study the liquid crystalline modifications of different types and different phase transitions in a single compound. The other interesting aspects of these homologues series are the specific identification of Sm G and Sm H in a single compound, identification of Sm F and Sm I phases, identification of two or three second order phase transitions (Sm A-Sm C, Sm I - Sm F, Sm F-Sm G) in addition to the first order transitions (I - Sm A, Sm C - Sm I, Sm G - K) in a single compound. However, the TBDA, one of the higher homologue of the TBAA series exhibits a weakly first order Sm A - Sm C phase transition whereas the TBBA, the lower homologue exhibits a second order Sm A - Sm C phase transition. This implies that there exists a tricritical point (where the first order transition becomes second order) at the Sm A – Sm C phase transition in the binary mixtures of TBBA and TBDA. In order to explore tricritical point at the Sm A – Sm C phase transition, we have employed Differential Scanning Calorimetry and the density measurement techniques with varying temperature in the binary mixtures of TBBA and TBDA of different weight percent. The only other study of the Sm A – Sm C tricritical point in TBAA homologues series was reported using x-ray diffraction studies on binary mixtures of TBDA and TBOA where TBOA exhibits a second order Sm A – Sm C transition. However, density studies reported earlier confirm this to be a weakly first order transition in TBOA which prompted us to study the Sm A – Sm C tricritical point of the binary mixtures of TBBA and TBDA, where TBBA has been well established to exhibit a second order Sm A – Sm C phase transition

The thesis is presented in six chapters:

Chapter – 1 sets out a brief introduction to liquid crystals and their classifications. An overview of the structural description of different liquid crystalline phases has also been presented. The importance of schiff base liquid crystal dimers and TBAA homologues series are described briefly. A general focus on phase transitions in liquid crystals and types of experimental techniques used are also discussed. The prime experimental techniques, Laser Raman spectroscopy and density measurement by bicapillary pyknometer have been briefly discussed.

Chapter – 2 gives the description of the experimental techniques used in the present study. The methods of preparation of liquid crystal dimer and TBAA compounds are discussed. A brief discussion on DSC is given in the light of phase transition and transition enthalpy data. The thermal polarizing microscope and its accessory like heating block, for varying the temperature are described briefly. In order to carry out the temperature dependant Raman studies, a device having temperature variation facility is designed and fabricated, a brief description of this is also given. A brief description of different components used in Laser Raman Spectroscopy and Density measurement is also presented.

Chapter – 3 describes the phase transition studies of five liquid crystal dimers viz. 7.O4O.7, 7.O5O.7, 10.O4O.10, 10.O10O.10 and 10O.12O.10 by DSC and density measurements. Compounds 7.O4O.7, 7.O5O.7 and 10.O10O.10 exhibit Sm A and Sm F phases and Compound 10.O4O.10 exhibits Sm C and Sm F phases while the compound 10.O12O.10 exhibits only G phase. The synthesis and identification of the phases exhibited by these compounds are described in chapter 2, while the entropy studies are described in this chapter. DSC studies revealed that the entropy values of different phase transitions of the dimers are larger than that of other monomeric compounds (twice that of monomeric compounds). Further, the entropy value of even spacer dimer (7.O4O.7) at the Isotropic – Sm A transition is nearly double compared to the odd spacer dimer (7.O5O.7). These very large entropy values suggest that, both the orientational and translational ordering in the smectic A phase are high for even spacers and also reflect the alternation of entropies in varying the flexible spacer for any given length of terminal chain. The phase transitions Sm A – Sm F and I – G phase are rare kind of transitions. Only two compounds (10.O12O.10 being the second compound) are known to exhibit the I – G transition so far. The other compound is 18.O14; in which the I – G transition has been studied by density measurements. The nature of phase transitions is discussed from the changes in the density across the phase transitions and the calculated thermal expansion coefficients in the liquid crystalline phases of all the dimers studied. A comparison of the estimated pressure dependence of transition temperatures using Clausius – Clapeyron equation with those reported in literature ~~are~~ is also presented. All the transitions are found to be first order in nature but smaller jump were observed than expected in the density across certain transitions.

Chapter – 4 describes our results of the study of molecular dynamics using Laser Raman spectroscopy on 7.O4O.7 and 7.O5O.7. Laser Raman studies on two compounds of the series, α,ω-bis(4-alkylaniline benzylidene -4′-oxy)alkane, which were carried out in the spectral regions of 1140 – 1220 cm^{-1} and 1550 – 1650 cm^{-1} as a function of temperature, are presented. Compounds, 7.O4O.7 and 7.O5O.7, exhibit Sm A and Sm F phases. The Raman spectra of these liquid crystal dimers have been analyzed. This Raman spectra at the room temperature remarkably highlight the odd – even effect. We have explained the results on the basis of the bending dynamics of these compounds, and its manifestation in the odd – even effect at the molecular level by assuming a semi-rigid core region of the dimeric molecule. We find that the odd spacer dimer (7.O5O.7) satisfied the molecular model, whereas the even spacer dimer (7.O4O.7) is established to behave like monomeric compounds such as nO.ms. In both the cases, the dynamics about the C = N bond have a profound effect on the molecular shape in different phases and phase behaviour which have been discussed.

Chapter – 5 describes the tricritical behaviour of the Sm A – Sm C phase transition where a first order transition becomes second order transition in the TBAA homologues series. The only other study of the Sm A – Sm C tricritical point in TBAA homologues series was reported using x-ray diffraction studies on binary mixtures of TBDA and TBOA, where TBOA was found to undergo a second order Sm A – Sm C transition. However, density studies reported confirm this to be a weakly first order transition in TBOA. On the other hand, the TBNA and TBDA, higher homologues of the TBAA series, exhibit a weakly first order Sm A – Sm C phase transition, whereas the TBBA, the lower homologue exhibits a clearly second order Sm A – Sm C phase transition within the series. For this reason, we have chosen to study binary mixtures of TBBA and TBDA, where TBBA has been well established to exhibit a second order Sm A – Sm C phase transition. These imply the existence of a tricritical point. In order to investigate the tricritical point (TCP) of the Sm A – Sm C phase transition, binary mixtures of TBBA and TBDA (of different weight percent) of few compositions have been studied as tricritical point is approached using DSC and density measurements as a function of temperature. The results of these studies clearly suggest the decisive role played by the Sm A thermal range in determining the nature of the Sm A – Sm C transition and governing the TCP, since the transition becomes weakly first order as the thermal range of Sm A decreases. The TCP for TBOA was reported in the thermal range of 9.4°C, which is much lower than that of our TBDA+TBBA mixture (present study) where the Sm A thermal range is about 17°C.

Chapter – 6 deals with the summary and the major conclusions drawn from each chapter in this thesis. The major conclusions from the present thesis can be mentioned as follows.

1. Synthesized the liquid crystal dimers (7.O4O.7, 7.O5O.7, 10.O4O.10, 10.O10O.10 and 1OO.12O.1) and TBAA compounds (TBBA and TBDA) and characterized the phases and phase transition temperatures using the Polarizing Thermal Microscopy and Differential Scanning Calorimetry.
2. Characterized the two very rare phase transitions, Sm A – Sm F and I – G in addition to I –Sm A, Sm C – Sm F phase transitions using density measurements. The density jump and a peak in the thermal expansion coefficient in all the transitions confirm the first order nature of the transition but smaller jumps were observed (than expected) in the density across certain transitions.
3. Study of molecular dynamics using laser Raman spectroscopy on two liquid crystals dimers (7.O4O.7 and 7.O5O.7). The Raman spectra of these compounds at room temperature remarkably highlight the odd – even effect. Odd spacer dimer (7.O5O.7) satisfies the semi – rigid core of the molecular model, whereas the even spacer dimer (7.O4O.7) is established to behave like monomeric compounds such as nO.ms. In both the cases, the dynamics about the C = N bond

have a profound effect on the molecular shape in different phases and phase behaviour.

4. The results of the TCP studies on TBBA and TBDA mixtures clearly indicate the decisive role played by Sm A thermal range in determining the nature of the Sm A – Sm C transition. The transition becomes weakly first order as the thermal range of Sm A decreases. The earlier report on TCP for TBOA was found in the thermal range of 9.4°C, which is much lower than that of our TBDA+TBBA mixture where the Sm A thermal range is about 17°C.

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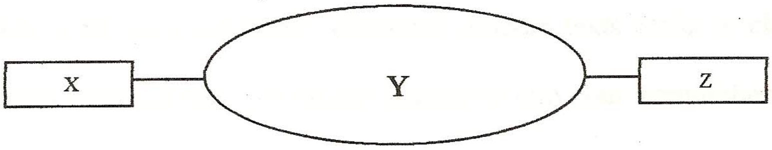
CHAPTER - 1

1. GENERAL INTRODUCTION

"Liquid Crystal" *may be defined as a thermodynamically stable phase characterized by anisotropy of properties without the existence of a three dimensional crystal lattice.* For many organic materials, the transition from the solid to the liquid phase does not occur in a single step but takes place in a cascade of transitions [1]. The molecular ordering in these intermediate phases, known as '***mesophases,***' lies between that of a solid and an isotropic liquid. These ordered fluid mesophases are commonly called liquid crystals and are most often composed of elongated molecules. In these mesophases, the molecules show some degree of rotational order (and in a few cases partial translational order as well) even though the crystal lattice does not exist. Lack of a lattice requires that these mesophases be fluid; they are, however, *'ordered fluid phases'*. It is this simultaneous possession of liquid-like (fluidity) and solid-like (molecular order) character in a single phase that makes liquid crystals unique and gives rise to so many interesting properties as well as technological applications. A most fascinating aspect of liquid crystals is that their study, which began as basic research with purely academic interests, has led to the development of a host of devices with very versatile applications. The research area of liquid crystals is interdisciplinary and is of equal interest to physicists, chemists, mathematicians and technologists for the development of high quality electro-optic devices.

Liquid crystals were discovered by an Austrian botanist, F. Reinitzer [2] in the year 1888. Later, Lehman [3] identified liquid crystalline phases in some cholesteryl compounds and termed them as intermediate phases. Liquid crystalline phases are generally characteristic of materials composed of molecules which are highly anisotropic in shape (i.e., anisometric) [4] and are commonly exhibited by rod or disc shaped molecules. This anisometry is essential since the molecules exhibiting liquid crystalline character should not only possess some rigidity but should also be able to rotate around the long molecular axis, sweeping a cylindrical volume, thereby undermining the importance of rotational order/disorder.

A liquid crystal generally comprises of anisometric organic molecules possessing some rigidity in the structure. The general structure of a liquid crystalline compound is shown below [5].



In this figure, X and Z represent the zigzag tails of the liquid crystal, which may be R (R= alkyl chains), RO, CN, NO_2, Cl, etc. Y is the central rigid part called core. Y is generally composed of phenyl rings, substituted phenyl rings (Aromatic), Aro-CH=N-Aro, Aro-N=N(O)-Aro Aro-CH=N-Aro=N-Aro, Aro-COO-Aro, etc. The properties regarding the liquid crystalline nature exhibited by the two molecules possessing the same molecular formula but different atomic arrangement are subtle. For example, the compounds (1) and (2),

(1) $CH_3CH_2CH_2CH_2CH_2O$AroCN

(2) $CH_3CH_2OCH_2CH_2CH_2$AroCN

possess the same formula with identical chain lengths and rod like shapes, but differ only in the location of oxygen. The compound (1) exhibits a mesomorphic phase between 53 °C and 65 °C while compound (2) does not show any liquid crystalline properties.

1.1 CLASSIFICATION OF LIQUID CRYSTALS.

Depending on the process by which transition of intermediate phases occur, the liquid crystals can be broadly classified into two categories viz. Thermotropic and Lyotropic liquid crystals. The term 'thermotropic' implies that the transition to the mesophases are brought about by thermal process i.e. thermotropic liquid crystals are formed due to variation of temperature (cooling or heating) while the lyotropic liquid crystals show mesomorphic behaviour due to influence of solvent on a solid or liquid and are biologically very important. However, modern texts prefer to classify liquid crystals on the basis of their molecular structures into four comprehensive groups which are:

a) Calamitic Liquid Crystals [6-10].

b) Discotic Liquid Crystals [11-15].

c) Lyotropic Liquid Crystals [16-20].

d) Defect Phases [21-25].

Based on structure and symmetry these liquid crystalline groups are further classified into different mesophases. Since the present thesis deals with the study of phase transitions as well as molecular dynamics in thermotropic mesophases, a brief description of various order parameters used to classify the liquid crystals is given in the next section.

1.1.1 ORDER PARAMETERS

When a system undergoes a phase transition, one cannot describe the two different phases by a single analytical function. Hence an extra parameter is required for describing the system in a low symmetry phase. This parameter which is used to quantify the positional or orientational order of the liquid crystalline molecules is thus appropriately termed as order parameter. A very important feature of order parameter is that, while describing the order of the molecules in the liquid crystalline materials, it also allows orientational deviation of the individual molecules from the director [26]. Typically the value of order parameter in liquid crystalline materials lie within a range of 0.3 to 0.9 depending on the temperature, with a value of unity for perfect order and a value of zero for the isotropic phase. The order parameters commonly considered in the study of liquid crystals are discussed here briefly, which will help us in the discussion on classification of liquid crystals.

1.1.1.1 Orientational order:

The orientational order can be described as a measure of the tendency of the molecules to align along the director on a long range basis. In a nematic liquid crystal, for example, with a preferred direction $\hat{n}$ for the long molecular axis (called the director) an average orientational distribution function f(θ) exists, where θ is the angle between the long axis of the molecule and the director. This distribution function can be expanded in a series of Legendre polynomials as,

$$f(\theta) = S_0 P_0(\cos\theta) + S_2 P_2(\cos\theta) + S_4 P_4(\cos\theta) + S_6 P_6(\cos\theta) + ... + \qquad (1.1)$$

The Legendre polynomials are denoted by $P_n(\cos\theta)$ and S_n are the coefficients describing the orientational distribution function. Only even powers of the Legendre polynomials are retained since the director can be defined in either of two opposite directions, $\hat{n}$ or $-\hat{n}$. The dominant parameter is S_2 and when properly normalised, i.e.,

$$S_2 = \frac{1}{2}\langle 3\cos^2\theta - 1\rangle, \qquad (1.2)$$

then S_2 can be used as the orientational order parameter.

1.1.1.2 Bond Orientational order:

This is an order parameter which describes a line joining the centres of nearest neighbour molecules without requiring a regular spacing along that line. Thus, a relatively long range order with respect to the line of centres becomes possible by only short range positional order along that line. This order parameter plays a very important role in the phase transitions of the hexatic phases. Thus a bond orientational order with six-fold symmetry in the plane of the layer actually is an expression for the arrangement of the hexagonal net i.e. the net is arranged in the same way from layer to layer, but there is no real positional correlations of the molecules between the layers. To represent mathematically, the bond angle variation can be expressed as,

$$\psi_6 = I_6 e^{6i\phi} \tag{1.3}$$

Where ϕ is the azimuthal angle and I_6 is the complex order parameter.

1.1.1.3 Translational order:

Positional order is used to describe the extent to which the position of an average molecule or group of molecules shows translational symmetry. For example, the layering tendency of the molecules can be described by an average density of the centres of mass $\rho(z)$, which sinusoidally varies along the normal to the layers. The amplitude of the sinusoidal part, ψ, describes the amount of positional order and can be used as an order parameter:

$$\rho(z) = \rho_0\left[1+\psi\cos\left(\frac{2\pi z}{d}\right)\right] \tag{1.4}$$

where ρ_0 is the average density, and d is the distance between the layers.

On the basis of these order parameters and other properties, the liquid crystals are broadly classified into the following categories.

1.1.2 Calamitic Liquid Crystals:

These are the most common type of thermotropic liquid crystals and are composed of rod-like molecules with one molecular axis much longer than the other two. Depending on the structure and symmetry, calamitic liquid crystals are further divided into three main classes, viz., the nematic liquid crystals, the cholesteric liquid crystals and the smectic liquid crystals.

i) **Nematic liquid crystals**:

Liquid crystalline compound possessing only nematic phase is called nematic liquid crystal. If we consider liquid crystalline compounds in terms of the translational and orientational ordering of their individual molecules, then in nematic liquid crystals, there is only orientational ordering, but no translational ordering between the molecules. To be more specific, in the nematic phase the molecular centre of mass positions are disordered as in a liquid but have a statistically parallel orientation of the molecular long axes of each molecule along the director ($\hat{n}$). Therefore, the molecular ordering in nematics is long range orientational order and there is no regular arrangement of the ends of the molecules. In the state of thermal equilibrium, the nematic phase has a symmetry ∞/mm and is therefore uniaxial. The direction of the director ($\hat{n}$) is arbitrary. The molecular arrangement of nematic liquid crystals is shown in Fig. 1.1a.

In some nematics, there exists a short-range smectic-like order in addition to the characteristic long-range orientational order. These nematics are termed as cybotactic nematics, skewed cybotactic nematics (N_{SC}) or normal cybotactic nematics

(N_{nc}). In the first case, the smectic like order involves not only the layered arrangement of the molecules but also significant tilt of the molecules whereas in the second case, the molecules are parallel to the layer normal of the smectic like groups. The nematic phase exhibits schlieren, threaded, marbled, pseudo-isotropic and homogeneous textures when viewed through crossed polarizer.

ii) **Cholesteric or spontaneously twisted nematic liquid crystals:**

The cholesteric mesophase is similar to the nematic mesophase except that it is composed of optically active molecules. In this phase, the different layers orient at a slight angle relative to each other (rather than parallel as in nematic). So the directors in each layer are twisted with respect to those of the preceding layers to form a continuous helix about the layer normal. Cholesteric phase is also known as "spontaneously twisted nematic phase". The term cholesteric has been borrowed from the word cholesterol since this phase was first reported in the derivatives of cholesterol. The cholesteric liquid crystals are uniaxial (positive or negative) and exhibit focal conic with Grandjean steps, homogeneous and isotropic textures. Apart from optical activity, this phase also exhibits circular dichroism. (Fig. 1.1b).

iii) **Smectic liquid crystals:**

Smectic liquid crystal phases are characterized by a one dimensional density wave along the average director giving rise to a layered structure. These liquid crystals have stratified structures but a variety of molecular arrangements are possible within each stratification [27-30]. There exists a number of smectic phases, but two of the most important cases occur when the director is parallel to the layer normal giving rise to orthogonal phases, and when the director is making an angle to the layer normal giving rise to the tilted phases. The smectic mesophase forms a one-dimensional periodic lattice in which the molecular arrangement within the individual layers are two-dimensional (liquids like). The interlayer attractions are weak as compared with the lateral forces between molecules and, as a consequence, the layers are able to slide over one another relatively easily. There are various modifications of the smectic phases, each with different combination of in-plane order and tilt angle. These have been named as the smectic A, B, C, D, E, F, G, H, I, J and K phases designated as, Sm A, Sm B, Sm C, Sm D, Sm E, Sm F, Sm G, Sm H, Sm I, Sm J and Sm K or S_A, S_B, S_C, S_D, S_E, S_F, S_G, S_H, S_I, S_J, and S_K, with the letters denoting the chronological order of discovery of these phases. The sequence of their appearance is S_A, S_D, S_C, S_B, S_E, S_I, S_F, S_G, S_G' (S_J), S_H and S_H' (S_K) with decreasing temperature. S_B, S_G, S_J, S_E, S_H and S_K are found to be more crystalline than liquid crystalline phases. Therefore, at present, these phases are treated as soft crystalline phases and designated as the B phase, G phase, J phase, E phase, H phase and K phase. If a compound exhibits both nematic as well as smectic phases, the nematic phase always appears on the higher temperature side. No single compound is found to exhibit all the smectic phases (modifications) so far. However, the maximum number of phases that a single compound can exhibit are found to be six so far, by terepthalylidene-bis-p-n-butyl aniline (TBDA) as well as N (p-n-pentoxy benzylidene) p-n-hexylaniline (5O.6). The structural identification of each smectic phase is briefly discussed below and their molecular arrangements are shown in the Fig. 1.1c.

SMECTIC A:

The molecular arrangement in this phase involves a parallel arrangement of the rod-like molecules with their ends in line to form layers in which the long axes of the molecules tend to be orthogonal to the layer planes. Rotational motion of the molecules is fairly free, but there is no long range packing of the centres of gravity of the molecules in the planes of the smectic layers. The layers are therefore liquid like in nature. The movement of the molecules from one layer to another, i.e., diffusion of molecules, occurs quite freely and the layers are free to slide on one another. The S_A phase is uniaxially positive. This phase usually exhibits pseudo-isotropic or homeotropic texture in which the smectic layers are parallel to the supporting surface and the optic axis is perpendicular to it. The characteristic textures observed are battonnets, focal conic fan and polygonal. If a liquid crystalline compound has S_A phase in addition to other smectic phases, the S_A phase is always found to be at the higher end of the temperature range.

<u>SMECTIC B:</u>

The smectic B phase generally exists along with S_A phase and occurs upon cooling the S_A phase. The molecules tend to be orthogonal to the layer planes and lamellar spacing is approximately equal to the molecular length. The layers in S_B phase are highly structured unlike in the case of S_A phase. The molecular centres lie on a hexagonal network and the molecules are free to rotate about their long axes. The dimensions of the hexagonal network are, however, small in relation to the size of the molecules, so that the molecular rotation can hardly be regarded as free, but is probably cooperative [31]. Three types of molecular stackings in smectic B phase are reported to be possible [32], namely AAA... (monolayer), ABA...(bilayer), which is also the most common one, and ABCA...(trilayer). The correlation between these layers was also reported in some compounds. Experimental studies [33] established a hexatic B phase which is different from the crystal S_B phase in a few compounds. The hexatic B exists at a higher temperature than the crystalline S_B phase and has short-range in-plane positional ordering and long range bond orientational ordering, both within and between the layers. Some compounds exhibit both types of smectic B phases [34]. If S_B follows the S_A phase upon cooling, S_B phase adopts all the textures exhibited by S_A phase with some modifications. This phenomenon is known as paramorphosis. However, the natural texture of S_B phase is mosaic, while the S_A -S_B transition is accompanied by the appearance of transient transition bars across the fans or focal conics while cooling from S_A phase. Hexatic B to crystal S_B phase transition also exhibits paramorphotic texture with difference in fans.

SMECTIC C:

This phase is the tilted analogue of the S_A phase i.e., the smectic layers have a liquid like, unsaturated arrangement of molecules where the molecular long axes or the directors ($\hat{n}$) are tilted with respect to the layer normal at an angle (θ) that varies from compound to compound. Three different tilt angles viz., one associated with the central atomic core region and the other two with the end alkyl chain regions of the smectic layers, are differentiated [35,36]. The tilt angle is temperature dependent [37] in some compounds and is temperature independent in some other compounds. The S_C phase either exhibits broken focal conic fan or schileren textures.

SMECTIC D:

Only a very few compounds [38,39] are known to exhibit this phase and the common variants observed are I- S_D- S_C or I- S_A -S_D- S_C. Diele et al [39] proposed a structural model for this phase with a cubic close packing of spherical units with each unit consisting of several molecules. No characteristic texture was observed because this phase is found to be optically isotropic. However, in the compound 4-hexyloxy-3-nitrobiphenyl-4-carboxylic acid, which exhibits S_D phase between S_A and S_C phases, a mosaic texture is observed initially which later transforms into an isotropic texture spontaneously.

SMECTIC E:

This phase is commonly observed [40] in the sequence N- S_A – S_B – S_E with decreasing temperature. The X-ray diffraction studies indicate (i) a high degree of order in smectic layers with a distinctly non-hexagonal lattice, (ii) orthogonal arrangement of molecules with respect to the layers, and (iii) a three dimensional lattice. In some of the S_E modifications optically biaxial properties are observed [41]. Goodby [42] has reported it to be optically uniaxial. Some compounds exhibiting S_E phase are found to possess an orthorhombic cell in the S_E layers. This phase exhibits mosaic and the paramorphotic fan textures with concentric curves across the fans.

SMECTIC F:

This phase is observed in the homologues of pyridene derivatives [43], higher homologues of terepthalydene bis-p-n-alkylaniline (TB$\overline{A}$ A) series [43], Schiff base liquid crystal dimers [44] and a few N (p-n-alkoxy benzylidene) p-n-alkylaniline (nO.m) compounds [45] and in α-ω-bis(alkyaniline benzylidene-4′-oxy)alkane (m.OnO.m) homologues series [69]. The S_F phase has long range order of tilt direction (similar to S_C phase) and has a quasi-two-dimensional structure, with essentially no correlation of molecular positions between layers. The molecules are packed in hexagonal layers with their long axes tilted with respect to the layer planes. It has a C-centred monoclinic lattice with long range three-dimensional order of the lattice direction but does not have long range positional ordering. Shift distortions of the hexagonal net occur between layers, indicating poor correlation between the layers. However, since mono-domains can be obtained with a uniform tilt direction, the hexagonal symmetry is apparently preserved through the bulk of the sample, and it may be concluded that the layers are free to slide over, but not free to rotate relative to one another, i.e., the phase has extensive three dimensional bond orientational ordering. The S_F phase exhibits stripped or chequered fan and schlieren textures under polarizing thermal microscope.

SMECTIC G:

The smectic G phase is more crystalline in nature and found almost all the nO.m and some of m.OnO.m compounds at low temperature. It has a pseudo-hexagonal structure with a local herringbone order. This phase, of course, has a three-dimensional structure but with a considerable disorder, i.e., the layer distribution is not sharp as in the case of crystals. Presumably this is associated with orientational disorder of the molecules about their long axes. As the layer thickness does not change discontinuously at the S_F -S_G transition, no change in tilt is expected and hence the tilt in S_G phase is of the same magnitude as in the S_F phase. The S_G phase exhibits paramorphotic focal conic fan or characteristic mosaic texture.

SMECTIC H:

Sakagami et al [46] had first differentiated S_G and S_H phases in the well known terepthalylidene bis-p-n-butylaniline (TBBA) and its higher homologues which are rich in S_G and S_H phases. In the S_H phase, the layers are highly structured and it is analogous to S_E phase with a tilt of the molecules. The arrangement of the molecules in the layers can be described as monoclinic when compared with the orthorhombic orthogonal arrangement of molecules in the S_E phase. The characteristic textures of S_H are mosaic which are different in the areas of the mosaic of S_G and the paramorphotic focal conic fan.

SMECTIC I:

Higher homologues of the TB$\overline{A}$A series (alkyl = nonyl, decyl, dodecyl) [47] exhibit the S_I phase. Esters like 4-(2′methylbutyl)phenyl 4′-n-octyloxybiphenyl-4′-carboxylate (8OSI) and amines, like N,N'-bis- (4′-n-heptyloxy benzylidene)-1, 4-phenylenediamine (7OBPD) also exhibit the S_I phase. The molecules are tilted in the layers and the tilt angle in this phase is equal to the tilt angle in the lower temperature S_G and S_F phases. It has more or less similar structure to that of the S_F phase. The only difference is that S_F phase has an in-plane short-range positional ordering whereas the S_I phase has a typical long range positional ordering. However, the S_F and S_I phases also differ in the direction of molecular tilt relative to the hexagonal packing of the molecular long axes. For the S_F phase the hexagon is tilted towards an edge, while for S_I phase, the tilt is towards an apex of the hexagon. The S_I phase exhibits broken fan, mosaic and schlieren textures.

SMECTIC J AND SMECTIC K:

Gane et al [48] first observed these phases in bis-(4′-heptyloxybenzylidene)-1,4′-phenylenediamine (HEPTOBPD) and confirmed that these are not new liquid crystalline phases, but two disordered crystal phases which are analogous to S_G and S_H phases except for the direction of tilt. Both the phases have monoclinic symmetry (with b>a) and pseudo-hexagonal packing of the molecules that are tilted towards the apex of the hexagon. The distortion from the hexagonal packing is greater in the lower temperature phases. Leadbetter et al [49] confirmed the existence of S_J phase in 4-n-hexylphenyl 4-n pentyl phenyl 4-n-decyloxybenzothiolate.

Some of the smectic phases exhibit ferroelectricity when they are composed of chiral molecules. The potential applications of these ferroelectric liquid crystals are so immense that it is studied as a new branch of material science and technology. It is separately discussed in forthcoming sections later.

1.1.3 Discotic liquid crystals:

Discotic phases are formed on heating compounds that are composed of relatively flat, disc-shaped molecules. These have been recognized as a distinct class of liquid crystalline compounds where the short axis of the molecules maintains a preferred orientation. Evidence for the formation of the mesomorphic phases by disc-like molecules dates back to 1960 [50-52]; however, identification of the discotic phase was made by Chandrasekhar et al [11,13] in 1977 with benzene-hexa-n-alkanoate compounds. Investigations have revealed that not only does the extended columnar discotic system exists, discotic analogues of the nematics are also well recognized now a days. Polymorphism of the columnar discotic systems is also possible depending upon the nature of the lateral packing of the columns and the tilt angle of the column with respect to the normal to molecular planes. Some discotic liquid crystals, analogous to smectic liquid crystals, possess no positional order parallel to the director, making them behave like one-dimensional liquids. In the columnar phase the molecules are more likely to be found in columns rather than between the columns. This phase possesses the orientational order of the nematic phase and also positional order in directions perpendicular to the director. The structures of a few discotic liquid crystals are shown in the Fig. 1.2.

1.1.4 Lyotropic liquid crystals:

Lyotropic liquid crystals are made up of two or more components. Generally, one of the components is an amphiphillic (containing a polar head group attached to one or more long hydrocarbon chains) and the other is water. A familiar example of such a system is soap (sodium dodecylsulphate) in water. As the water content is increased several mesophases are obtained. These phases differ from other liquid crystalline phases because these are multi-component systems and the concentration of the various components of the system is an important parameter in exhibiting the liquid crystalline properties by these systems [19,20,53].

A few modifications of lyotropic liquid crystals have been identified. In the lamellar, or the neat phase, water is sandwiched between the polar heads of adjacent layers, while the hydrocarbon tails, which are disordered or are in a liquid-like configuration, are in a non-polar environment. In the cubic, or the viscous isotropic phase, the layers are bent to form spherical units with a body-centred cubic arrangement. In the hexagonal or middle phase, the layers are rolled up into cylindrical units of indefinite length arranged parallel to one another in a hexagonal array. A nematic type ordering has also been observed in some soap systems. In hydrophobic dominated compositions, such as aerosol OT-water system, inverted middle and inverted viscous isotropic phases can occur in which the tails point outward towards the hydrophobic medium while water is trapped inside. Cholesteric liquid crystals are formed by the solutions of synthetic polypeptides, e.g., poly-γ-benzyl-L-glutamate, in organic liquids when the concentration exceeds a certain critical value. Lyotropic liquid crystals occur abundantly in nature, being ubiquitous in living systems. (Fig. 1.3.)

1.1.5 Defect phases:

One of the most important recent developments in the science of liquid crystals is the appreciation of liquid crystal phases which are possible only through the incorporation of periodic and non-periodic defects [54,55]. Defects in a liquid crystalline phase are points, lines or surfaces at which the orientational or positional ordering is not defined. These defects, thought to be energetically unfavourable, are a part of the structure of the new phases. These phases can be thought of as super structures in which individual regions exhibit liquid crystallinity and the regions are separated by defects. These defects may have the order of an isotropic liquid in analogy with a 'melted lattice.' Two of the important defect phases are the smectic twist grain boundary (TGB) phase and the blue phases formed by some highly chiral molecules. In the TGB phase, the tendency of the molecules to form a twisted phase is frustrated by an additional tendency to form layers. The result is a smectic A structure periodically interrupted by the grain boundaries where the smectic A structure twists by a small angle. In blue phases, regions with liquid crystalline order slightly different from the chiral nematic phase are separated by a lattice of line defects. A few of the defect phases are shown in Fig. 1.4.

1.2 FERROELECTRIC LIQUID CRYSTALS

The ferroelectric effect was first observed in 1921 by Valasek [56] during experiments on crystals of Rochelle salt (potassium sodium tartarate). A ferroelectric material is characterized by an electric dipole moment even in the absence of an external electric field. In these materials the centre of positive charge does not coincide with the centre of negative charge, resulting in the development of spontaneous polarization [57]. This spontaneous polarization, which is the most characteristic property of a ferroelectric material, usually vanishes above a certain temperature called the Curie temperature. There is an intimate relationship between the ferroelectric properties and the atomic arrangement of the ferroelectric materials. Two viewpoints contribute to the understanding of occurrence of ferroelectricity. One is the idea of polarization catastrophe where the local field caused by polarization increase faster than the elastic restoring force on an ion in the crystal, thereby leading to an asymmetrical shift in ionic positions. The other idea is that the static dielectric constant increases when the transverse optical phonon frequency decreases. Both of these ideas have been used to describe the origin of ferroelectricity in different types of materials [58].

In 1975, the American physicist Meyer using symmetry arguments suggested that the tilted smectic phases made up of chiral molecules should also exhibit ferroelectricity. [59,60] Ferroelectricity in the tilted smectic phases requires the molecules to be chiral. The concept of chirality and how it influences the tilted smectic phase, is discussed in the following section. We have confined our discussion to the chiral smectic S_C* phase since materials exhibiting this phase are used for device applications. However, the same arguments apply equally to other tilted chiral smectic phases like S_F*, S_I* and also the crystal smectic phases H*, J*, K* and G*.

The ferroelectric liquid crystals, the first group of compounds with fluid properties, can be thought of as the most recent members of the already rich family of ferroelectric materials,. They are very similar to the ferroelectric solids in some respects, like, they exhibit spontaneous polarization, have a Curie point and their macroscopic polarization vanishes as the system approaches this temperature. The electro-optic properties of the ferroelectric liquid crystals are widely different from those of the other kinds of liquid crystals. Ferroelectric liquid crystals switch at a very fast rate (~ 1μs) with a large change in the refractive index ($\Delta n \sim 0.1$). With such a fast response, ferroelectric liquid crystals have opened new avenues in the field of display technology. Today commercial applications of the ferroelectric liquid crystals include flat panel displays, miniature xerographic devices and high-resolution printheads, etc., to name a few. The molecular alignment and structure of ferroelectric liquid crystals are shown in Fig 1.5.

1.3. Importance of Schiff base Liquid Crystal

The first room temperature liquid crystal compound that exhibits only the nematic phase was N(p-n-methyloxybenzylidene)p-n-butylaniline [68], popularly known as MBBA. It was reported in 1969 and has paved the way for a new era in liquid crystals research and applications. In this present thesis we have chosen some schiff base liquid crystal dimers and TB*A*A compounds to study molecular structures and phase transitions.

1.3.1 Liquid Crystal Dimers

The liquid crystal dimers are different from conventional low molar mass mesogens in that they are composed of molecules, in which two anisotropic mesogenic groups are linked by a flexible spacer. They have been attracting a great deal of interest in recent years not only from their ability to act as model compounds for semi-flexible main chain liquid crystal polymers but also because they exhibit quite fascinating and unusual properties [69,70,71]. The transitional properties of the dimers depend on the length and parity of the spacer as well as the nature of linking group of the mesogenic units. In particular, the nematic-isotropic transition temperatures are found to exhibit a dramatic alternation on the number of carbon atoms as the alkyl spacer changes from odd to even. However, the odd-even effect thought to be a characteristic of dimer does not always occur and can also vanish when rod-like molecules are replaced by disc-like groups. Both theories and experiments, of varying degree of sophistication have been developed to understand the phase transition behaviour of the dimers. The liquid crystal dimers are classified into two categories: symmetric and non-symmetric. In the former class of dimers, the mesogenic groups are identical and in the latter, the mesogenic groups are not identical. However, though a large number of schiff base liquid crystal dimers have been synthesized and characterized in the recent past, the detailed study of various rare and new phase transitions exhibited by the dimers and the detailed structural evaluations have not yet been carried out. Therefore, in the present thesis density measurement studies as a function of temperature of few symmetric liquid crystal dimers as well as study of molecular dynamics using Laser Raman spectroscopy was taken up. The general molecular structure of symmetric liquid crystal dimer is shown in Fig 1.6a.

1.3.2. TBAA Compounds

Terepthalydene-bis-p-n-alkylanine, popularly known as TBAA homologues series is one of the well known and interesting series of schiff base liquid crystalline compounds for its rich variety of polymorphism with wide thermal ranges [72,73]. One of the TB*A*A series compound, TBBA exhibits six mesophases which offers the possibility to study the liquid crystalline modifications of different types and different phase transitions in a single compound. The other interesting aspects of these homologues series are the specific identification of S_G and S_H in a single compound [74,75], identification of S_F and S_I phases [76,77], identification of two or three second order phase transitions (S_A-S_C, S_I-S_F, S_F-S_G) in addition to the first order transitions (I-S_A, S_C-S_I, S_G-K) in a single compound. However, the TBDA, one of the higher homologue of the TBAA series exhibits a weakly first order S_A-S_C phase transition whereas the TBBA, the lower homologue exhibits a second order S_A- S_C phase transition. These imply the existence of a tricritical point, where the first order transition becomes second order. In order to explore tricritical point the binary mixtures of TBBA and TBDA of different weight percent have been chosen to study the variation of density as tricritical point is approached. Few compositions of these binary mixtures were chosen to study DSC and density measurements as a function of temperature. The general molecular structure of the TB*A*A series is shown in Fig 1.6b.

1.4. Phase Transition studies in Liquid Crystals

The liquid crystal phases are described by their positional as well as orientational ordering. The nematic liquid crystals possess long range orientational ordering whereas the smectic phases possess either three or two or one-dimensional periodic ordering (positional) of the molecules in addition to the orientational ordering. At any temperature, the state of the system can be described by an equilibrium value of the molecular parameters and fluctuations about that value. When the system transforms from one phase into other phase, it can be indicated by either a continuous or discontinuous change in the equilibrium value of the molecular property. A continuous change in the molecular property defines a second order transition while a discontinuous change defines first order transition. However, due to weakly first order nature of most mesophase transitions, large pretransitional effects, reminiscent of second order behaviour are usually observed in the region of transition point. In general, an nth-order phase transition is one in which it is the nth derivative of the chemical potential μ, with respect to temperature T and pressure P, which first becomes discontinuous at the point of transition. For an a-b equilibrium phase transition, $\mu^a(T,P) = \mu^b(T,P)$; the zeroth derivative is thus continuous. The $\mu(T,P)$

surfaces of the a and b phases intersect (first order) or "make contact" (second order) over a range of T and P. For a first order phase transition ($\partial\mu/\partial T$ and $\partial\mu/\partial P$ discontinuous), enthalpy ΔH (or entropy ΔS) and volume ΔV changes are observed. The projection of the line of intersection of the μ surfaces onto the P-T plane provides a consistency relation between dT/dP and $T\Delta V/\Delta H$ through the Clausius-Clapeyron equation. For a second order transition, both ΔH and ΔV are zero, but $\partial^2\mu/\partial T^2$, $\partial^2\mu/\partial T\partial P$ and $\partial^2\mu/\partial P^2$ lead to a change in the constant pressure heat capacity ΔC_p, expansion coefficient $\Delta\alpha$ and isothermal compressibility $\Delta\chi$, respectively.

With liquid crystals, change in the order parameters (s) must also be considered. At the first order nematic – isotropic transition, the orientational order parameter ηchanges discontinuously. The smectic A phase may be characterized by an additional order parameter σ. According to Mc Millan theory, η and σ may change discontinuously or continuously, depending on whether the smectic A – nematic transition is first order or second order transition respectively.

1.5. Experimental studies on liquid crystals.

Studies on liquid crystals have been conducted using a number of experimental techniques such as X-ray diffraction [78,79], Dilatometric analysis [80,81], Nuclear Magnetic Resonance (NMR) [82,83], Electron spin resonance (ESR) [84,85], Fourier Transform Infrared Spectroscopy (FTIR) [86,87] and Raman Spectroscopy [88,89]. These techniques have divulged an enormous volume of experimental data, which has been interpreted to understand the phase transitions in liquid crystalline systems and the associated changes in the various physical and chemical properties, including the electro-optic properties. In this regard, both Laser

Raman and FTIR spectroscopies have proved to be very important techniques as they are able to provide information both at the microscopic (molecular) as well as the macroscopic levels. In Laser Raman spectroscopy, variation of some physical quantities are found to affect the polarizability tensor that results in changes in measurable parameters of certain vibrational modes of the Raman spectrum of the system. Laser Raman spectroscopy has been found to be very effective in the study of phase transitions in liquid crystals. Therefore, in this thesis, Raman studies have been employed in the study of phase transitions and molecular dynamics of two symmetric liquid crystal dimers.

The density measurement studies by either vibration densitometer or classical dilatometer is an important experimental technique for the study of phase transitions. The density of the liquid crystalline compound varies with the variation of temperature. A first order transition is associated with a discontinuity in the density values at the transition whereas the second order transition is related to a continuous change in the density values.

1.5.1. Laser Raman spectroscopy and Density studies on liquid crystals.

Raman spectroscopy is one of the most important techniques used in the study of vibrational dynamics of the liquid crystals. Apart from being bond specific, the variation of physical quantities of the liquid crystalline phases affect the polarizability tensor which are reflected as changes in measurable parameters in the Raman spectra. In the past couple of decades, Raman spectroscopy has been extensively used in the study of liquid crystals to extract spectral information [90-104], more specifically on the molecular structure [90-98] and intra/inter-molecular interactions [105-107] in the liquid crystalline phases. During recent past, most of the studies using Raman techniques have concentrated on the ferroelectric [108,109] and polymer liquid crystals [110]. However, many basic aspects of the orientational and conformational changes during the process of phase transitions in non-ferroelectric liquid crystals are yet to be explored.

Density measurement as a function of temperature is an important experimental technique to study the phase transitions. A specially designed bicapillary Pyknometer was used for the density studies. The capillaries with a diameter of about 0.35 mm and about 40 cm long are arranged at the top of a bulb in a "U" shape. The capacity of the pyknometer is about 2 to 3 CC. The bulb contains 98% of the total volume of the sample. The accuracy in density is ±0.1 kg m^{-3}. The pyknometer was calibrated by measuring the molar volume of water at different temperatures. The mass of the liquid crystal sample was determined using a microbalance with an accuracy of ±0.001mg. For filling the sample in the pyknometer, the pyknometer was kept inside the heating chamber at a higher temperature of 10 to15°C above the mesophase-isotropic transition temperature of the liquid crystal sample and cooled down slowly until the sample level reaches the mark in the capillaries at isotropic phase. Special precautions were taken for removing excess sample and bubbles in the pyknometer. The sample level in the capillaries of the pyknometer was observed with the help of a cathetometer in the cooling cycle with a cooling rate of 2°C hr^{-1}.

The interest concerning the nature of smectic C – smectic A phase transition has grown steadily since de Gennes suggestion that the smectic C- smectic A transition may be continuous by symmetry reasons and proposed an analogy with superfluid helium [111]. The development of displays containing chiral smectic C liquid crystals has further reinforced and stimulated research efforts on the chiral smectic C- smectic A as well as chiral smectic C- cholesteric transitions. Most of the studies regarding the density studies stress on the order of phase transition. There are some examples of phase transitions, I – N, I - S_A, I – S_G, S_A - S_F S_C - S_I, S_G – K which show first order nature of transition whereas the transitions of N - S_A, S_A – S_C, S_I – S_F, S_F - S_G shows second order nature of the transition as confirmed by density studies. In addition, tricritical nature of some of the transitions viz., S_A – N, S_F – S_I and S_A – S_C was also reported.

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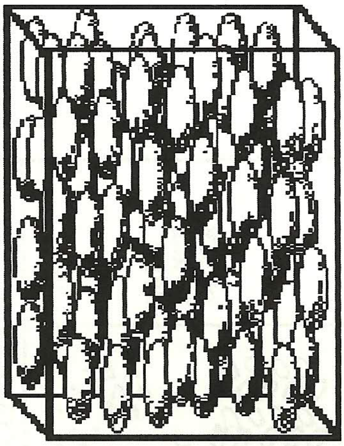


Fig. 1.1a Nematic liquid crystals

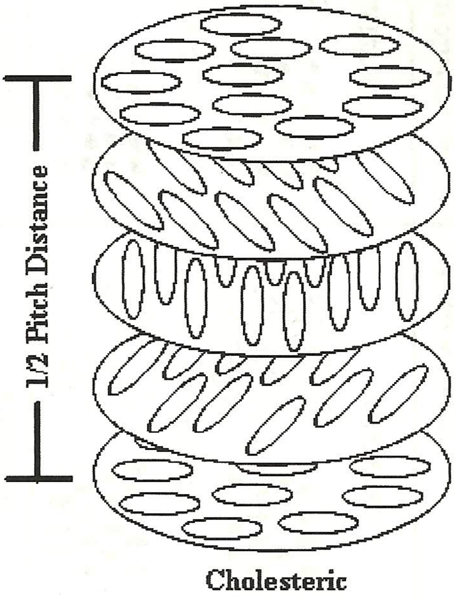
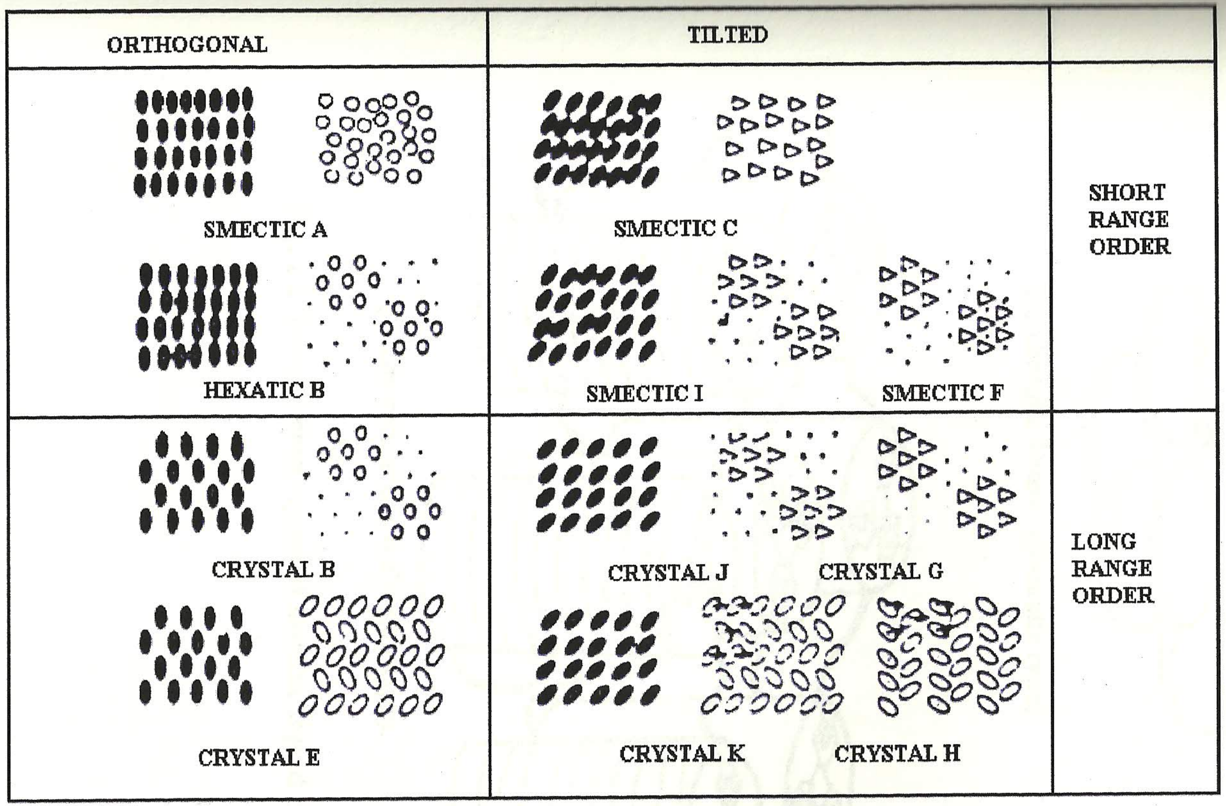
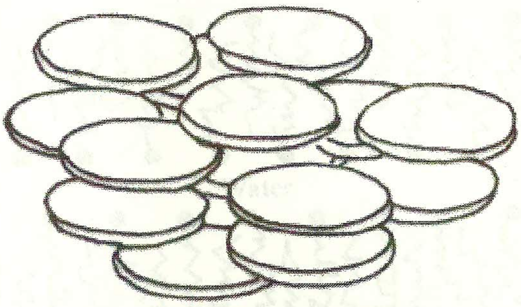


Fig 1.1b Cholesteric liquid crystals

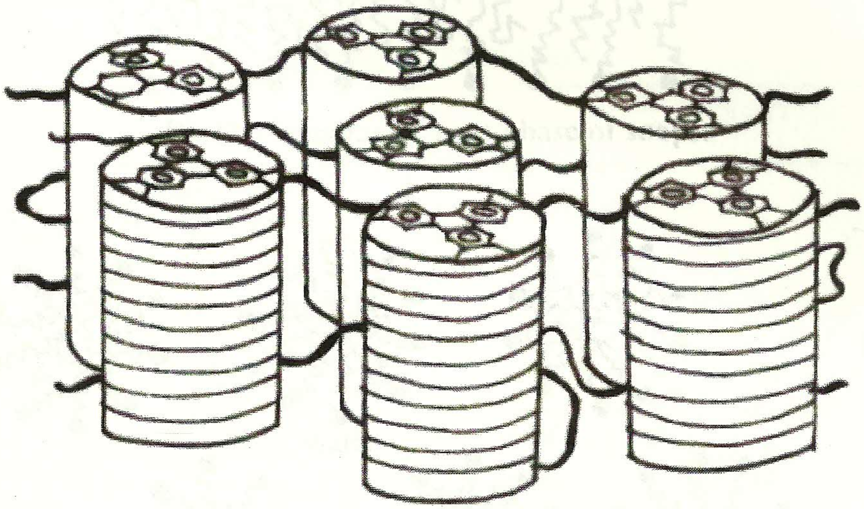


The structures of lamellar smectic mesophases. The side of the lath-like molecules are shown by black ellipses.

Fig 1.1c Various types of Smectic liquid crystals

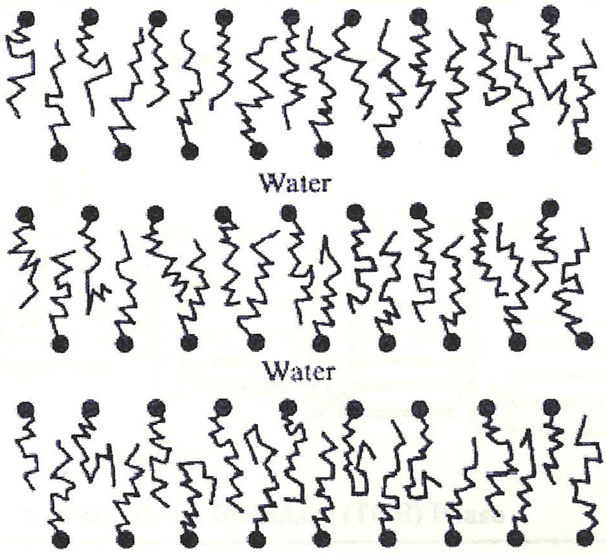


(a) Discotic Phase. (Nematic type)

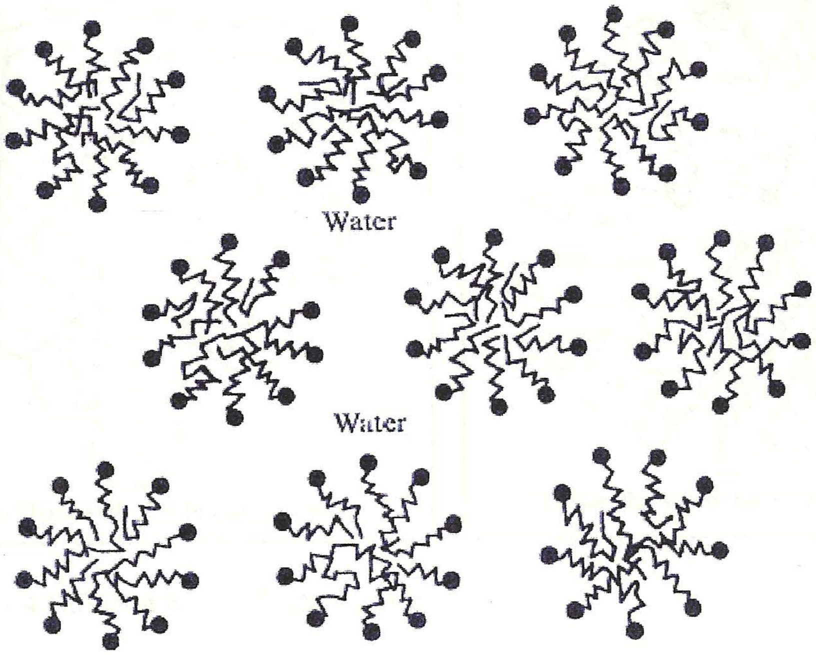


(b) Discotic phase (columnar type).

Fig. 1.2 Two different types of discotic liquid crystals

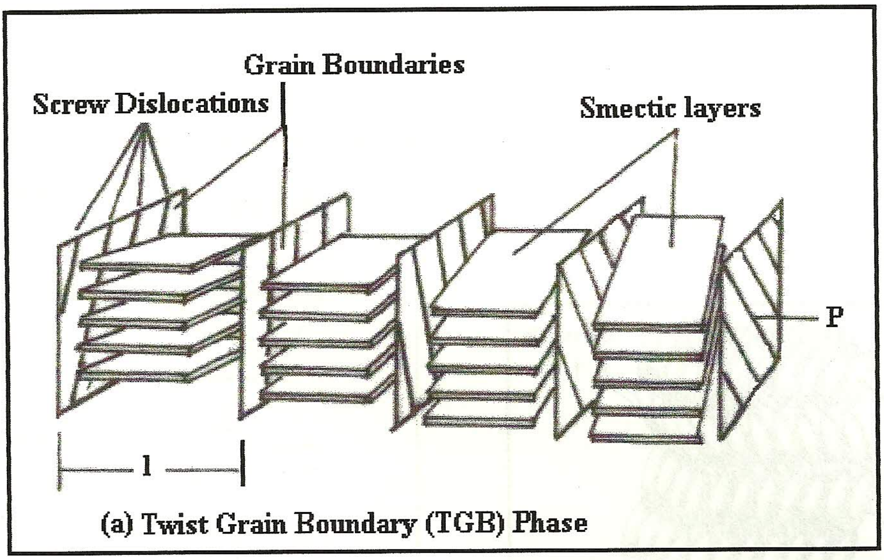


(a) The lamellar or neat phase of soaps.

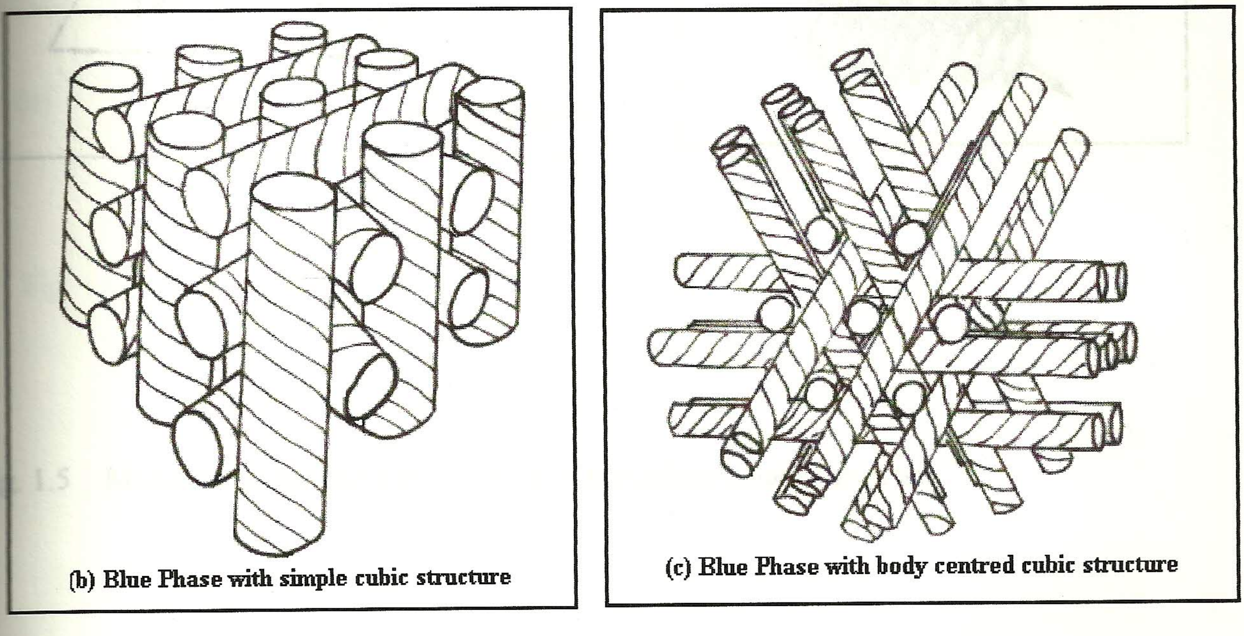


(b) The hexagonal or middle phase of soaps.

Fig 1.3 Different types of Lyotropic liquid crystals.



(a) Twist Grain Boundary (TGB) Phase



(b) Blue Phase with simple cubic structure

(c) Blue Phase with body centred cubic structure

Fig 1.4 Different types of defect phases

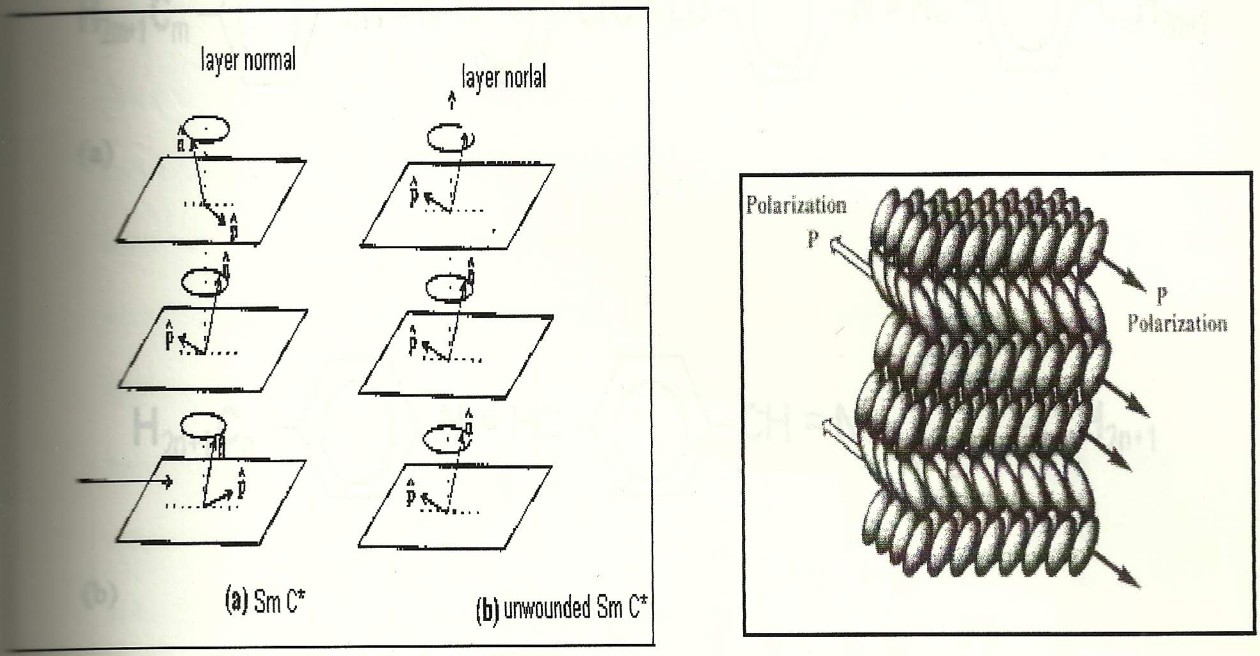


Fig. 1.5 Molecular alignment and structure of ferroelectric liquid crystals.

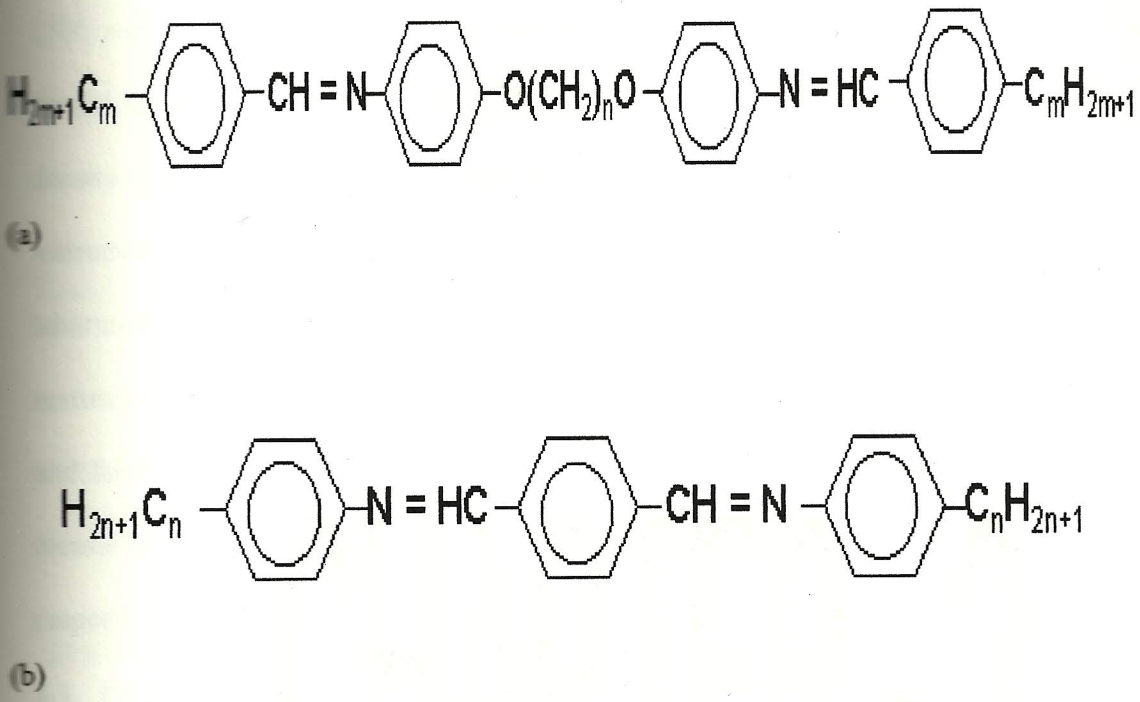


Fig. 1.6 (a) Molecular structure of symmetric liquid crystals

(b) Molecular structure of Terepthalylidene-bis-p-n-alkylaniline