

CHAPTER 1

INTRODUCTION

The words delicate, fantastic, stunning, mysterious, dynamic are not adequate to describe the rich class of liquid crystals. The first observations of liquid crystals were made by biologists in the 1850s; very soon physicists and chemists joined the fray. The German physicist Otto Lehmann and Austrian botanist Friedrich Reinitzer justified them to be called the grandfather of liquid crystal science due to their remarkable work around 1888 on cholesterol derivatives specifically cholesteryl benzoate [1-5]. But research on liquid crystals exploded during 1970s, with the discovery of cyanobiphenyl based liquid crystals. A detailed lucid history of early research on liquid crystals has been described in the book “Crystals That Flow” [6]. Liquid crystal (LC) materials are unique in their properties and uses. As research into this field continues and new applications are developed, liquid crystals are playing an important role in modern technology. The advancement of liquid crystal science and technology has been a truly interdisciplinary effort which combines basic principles of physics, chemistry and engineering. The field of liquid crystals covers a wide area of chemical structures, physical properties and technical applications. Many books and monographs are now available in this fascinating field of research [Appendix A]

Technologically, liquid crystals have become a part of our daily life, first showing up in wrist watches, measuring instruments and pocket calculators, but now being used for displays in all sorts of instrumentation, including laptops, TVs, telecommunication and office automation. In addition liquid crystals are used in optical devices, in thermography, as solvent in spectroscopy, chemical reaction and gas chromatography; in non destructive testing such as in electromagnetic radiation detectors, sound wave and pressure detectors etc. Liquid crystals are also used in medical applications like diagnosis of vascular diseases, cancer diagnosis and pharmaceutical tests. Ferroelectric LCs are the basis of a variety of potential devices ranging from large-area flat panel displays [7], ultra fast electro-optic modulators [8, 9] and special light modulators [10]. They are also being considered for novel nonlinear optical applications [11-13].

1.1 LIQUID CRYSTALS

It is well known that matter can exist in the three states: solid, liquid and gaseous. Solids may be crystalline or amorphous. Most of the solids melt directly into liquids where optical, electrical and magnetic properties do not depend upon direction - their properties are isotropic whereas crystalline solids possess anisotropic properties. However there exists another type of material which possesses two distinct melting points. While going from solid to isotropic liquid via an intermediate phase they flow like fluids yet possess some anisotropic physical properties characteristic of crystals. Such materials have thermodynamically stable phase between isotropic liquid and crystalline solid. Fascinatingly these phases are more ordered than the liquids but less than that of crystals. These thermodynamically stable phases grouped together are called 'liquid crystals', since they share properties of both liquids and crystals and since their nature of molecular ordering is intermediate between liquids and crystals. They have a lower symmetry than isotropic fluids but a higher symmetry than periodic crystalline solids. The terms liquid crystals, mesophases and mesomorphic states are used synonymously to describe such a state of aggregation and a substance that forms mesophase is called a mesogen. Molecular arrangements in crystalline solid, liquid crystal and isotropic liquid are shown in **Figure 1.1**.

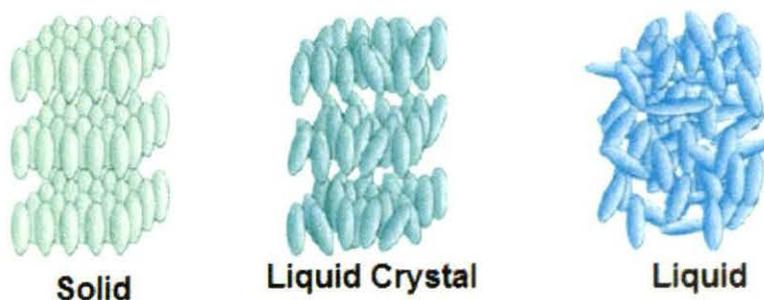


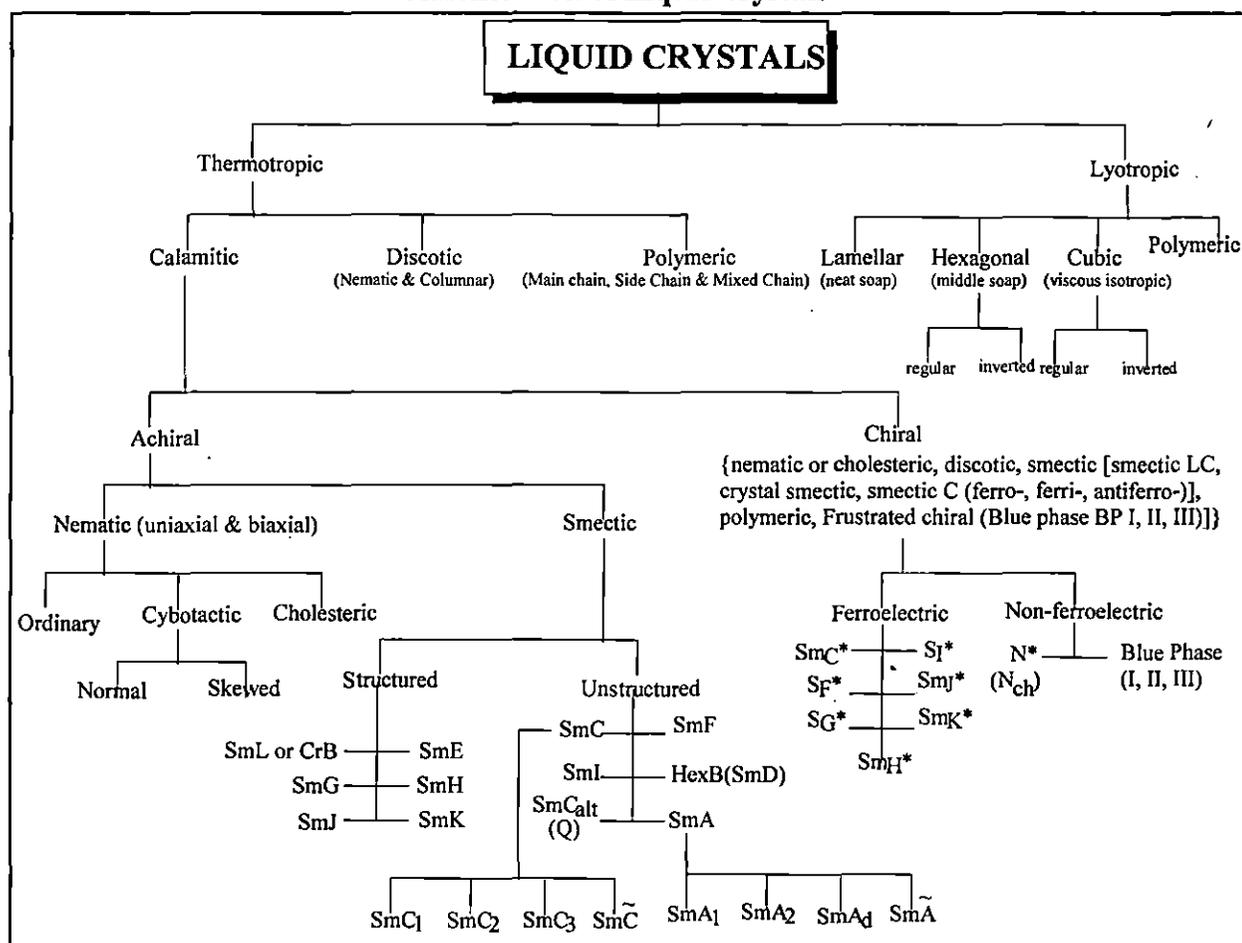
Figure 1.1. Molecular arrangements in crystalline solid, liquid crystal and liquid phases.

1.2 CLASSIFICATION OF LIQUID CRYSTALS

A large variety of phases are exhibited by liquid crystalline materials which differ from one to another by their structure and physical properties. Molecular shape [14-18] is an important controlling factor for the formation of a mesophase. A number of different types of geometrically anisotropic molecules such as rod like, lath like, disc like, banana shaped, Y-, T or star shaped, dendrites etc. form liquid crystal phases. The 'classical' liquid crystals

are derived from rod like molecules called ‘calamitic’ (derived from the Greek word *colomos* meaning rod). This class of liquid crystalline compounds have been investigated thoroughly and are most important with respect to practical applications. Liquid crystals derived from disc like molecules were discovered independently by Chandrashekar *et al.* [19] and Billard *et al.* [20]. These were called ‘discotic’ liquid crystals. Lath like molecules are intermediate between the rod like and the disc like molecules. Molecules of various other shapes are also found to exhibit mesomorphism [14, 21-23].

Table 1.1
Classification of Liquid crystals



Liquid crystals may be classified broadly into two main categories: ‘Thermotropic liquid crystals and Lyotropic liquid crystals’. A thermotropic liquid crystal exhibits thermally stable mesomorphic phases in a certain temperature range and shows phase transitions by changing temperature. A lyotropic liquid crystal, in contrary, show mesomorphic behavior in a certain range of concentration of the solute in a suitable solvent. These are often found in biological systems and are exploited in numerous biological applications. Many books and

review articles are available on this topic [24-28]. Since no work has been done on lyotropic liquid crystalline systems we will not discuss it further. A precise summary of different liquid crystalline phases, exhibited by various types of molecular systems; is shown in **Table 1.1**. Some of these phases that are relevant to the present work will be discussed in the following sections.

1.2.1 THERMOTROPIC LIQUID CRYSTALS

These are usually organic substances with variety of molecular structure. The most common type is a prolonged rod-shaped molecule i.e. one molecular axis is much more longer than the other two as shown in **Figure 1.2**. Axial ratios of 4-8 and molecular weights of 200-500 g/mol are typical for thermotropic liquid crystal mesogens. The basic structural requirements of the calamitic thermotropic liquid crystal can be shown by a general template (**Figure 1.3**). Here **B**

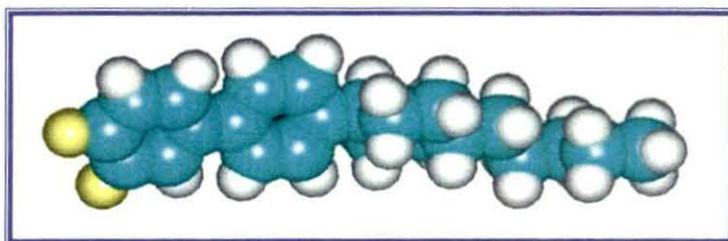


Figure 1.2. Space filling model of a typical rod-shaped liquid crystal molecule.

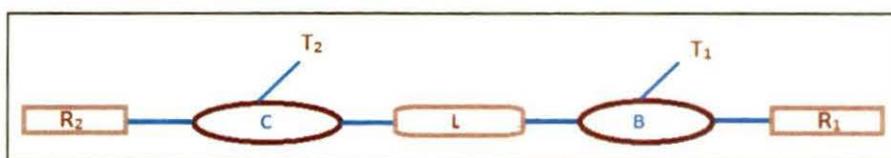


Figure 1.3. Basic structural features of thermotropic liquid crystal molecule

and **C** are rigid core units often aromatic or alicyclic either linked directly or by a linking group **L** (e.g., $-\text{COO}-$, $-\text{C}\equiv\text{C}-$, $-\text{CH}_2\text{CH}_2-$ etc.). **R₁** and **R₂** are terminal chains often alkyl or alkoxy chains or polar substituent group (e.g., CN , F , NCS , NO_2 etc.); **T₁** and **T₂** are lateral substituents may be polar or alkyl group. Molecular structure of 4-Cyanobiphenyl-4'-heptylbiphenyl carboxylate as a typical example of liquid crystal material is shown in **Figure 1.4**. Such a molecule can be represented in the first, approximation, as a solid rod or spherocylinder or ellipsoid of revolution (**Figure 1.5**). These compounds show many different phases. Disc-like molecules, namely molecules with one molecular axis much shorter than the

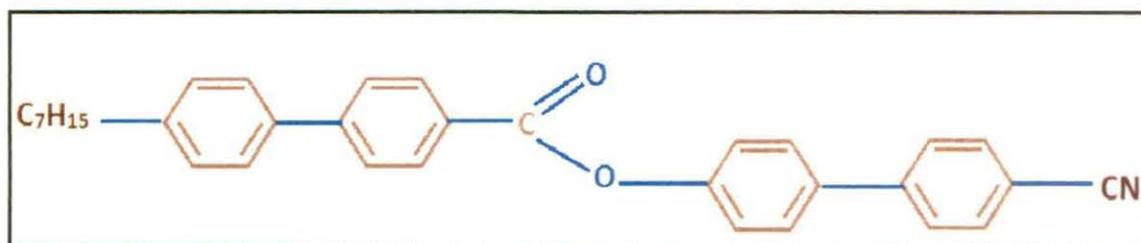


Figure 1.4. Molecular structure of 4-Cyanobiphenyl-4'-heptylbiphenyl Carboxylate (7CBB)

[Phase sequence: Cr 123 SmA₁ 136 N 350 I]

other two, also form liquid crystal phase (columnar phase), thereby calling them discotic liquid crystals, one such typical molecule and idealized stacking is shown in **Figure 1.6**. Another type of liquid crystals also observed i.e. polymer liquid crystals. Polymers are substances whose molecules are built up of a large number of chemically bonded repeating



Figure 1.5. Model for an ideal liquid crystal molecule as a rigid rod, spherocylinder or ellipsoid.

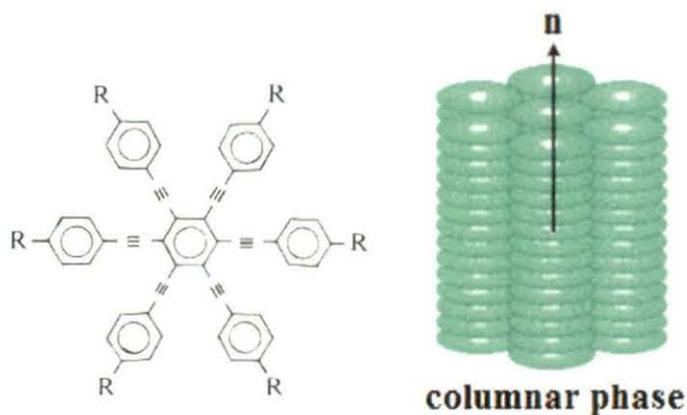


Figure 1.6. Typical molecular structure of discotic liquid crystalline Hexakis [(4-octylphenyl) ethynyl] benzene and its idealised stacking (columnar phase), \mathbf{n} is the director.

structural units. With a suitable mesogenic building units (monomers) the substance exhibits liquid crystalline properties. These mesogenic units, (usually calamitic but many discotic types exist) should be attached with appropriate functional end groups in order to obtain a polymer. There are two types of polymer liquid crystals viz., main chain and side chain displayed in **Figure 1.7**. Since no work is done in the present dissertation on such systems we will not discuss them any further.

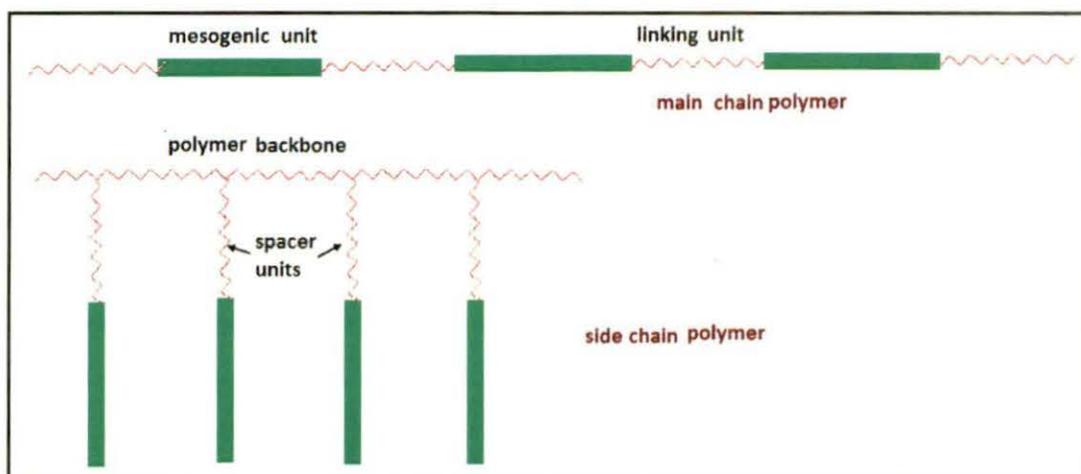


Figure 1.7. Liquid crystal Polymer (main and side chain).

1.2.1.1 ACHIRAL CALAMITIC PHASES

The symmetry of a molecule determines whether it is achiral or chiral. A molecule is *achiral* if it is superimposable on its mirror image, otherwise it is called a chiral molecule.

Thermotropic liquid crystals are principally classified, on symmetry consideration, into two main categories viz. nematic and smectic. The early names of the different liquid crystalline phases based on optical observations and confirmed by X-ray investigations, viz., nematic, cholesteric and smectics, are due to G. Friedel [29] and are used until now. Nematic is from the Greek word $\nu\eta\mu\alpha$ (Nematos) for thread-like, the defect seen under crossed polariser. Smectics are from $\sigma\mu\eta\gamma\mu\alpha$ (Smectos) for soap-like from which many layered mesophases are made. In macroscopic approach, the structure of liquid crystalline phases is usually characterized by the so-called director \mathbf{n} , a unit vector which shows an average orientation of the long molecular axes in some macroscopic bulk.

NEMATIC LIQUID CRYSTALS

Nematic phase is the simplest liquid crystalline phase shown in **Figure 1.8(a)** and its typical textures is also shown in **Figure 18(b)**. Remarkable features of this phase are:

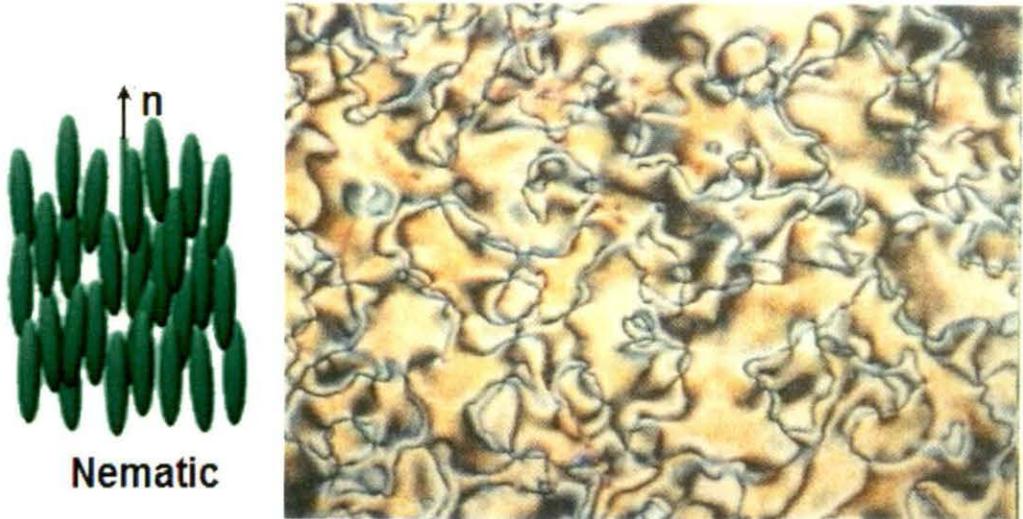


Figure 1.8(a). Molecular arrangements in Nematic phase, \mathbf{n} is the director and (b) Schlieren texture of nematic phase

1. Nematic liquid crystals have no positional long-range order in the arrangement of the centre of mass of the molecules as in isotropic liquid. Its point symmetry is $D_{\infty h}$
2. They have long-range orientational order with respect to the director \mathbf{n} .
3. The direction of \mathbf{n} of the bulk sample may be determined by surface force or externally applied field.
4. The preferred orientations \mathbf{n} and $-\mathbf{n}$ are not distinguishable.
5. They exhibit schlieren; threaded marbled; pseudo-isotropic; homogeneous textures.
6. Most nematics are optically uniaxial medium of positive birefringence, biaxial modification has also been observed in some materials [30].
7. The molecular properties of nematic is such that the left- and right-handed forms are indistinguishable (achirality). In the opposite case, the system must be a racemic (1:1) mixture of right- and left-handed molecules.
8. Antiparallel dipolar association is found between nearest neighbour molecules possessing permanent dipole moment.
9. Nematics are sensitive to external electric and magnetic fields and many different electro - (magneto-) optical effects occur in them.

When a compound exhibits both nematic and smectic phases, then, as a rule, nematic occurs at a higher temperature. Exceptions to the rule were discovered by Cladis [31] in certain strongly polar materials. The first observations were on binary mixtures of two cyano compounds: over a range of composition the sequence of transitions *on cooling* was as follows:

$$\text{Iso} \rightarrow \text{N} \rightarrow \text{S}_A \rightarrow \text{N}_R \rightarrow \text{Crystal},$$

where N stands for the usual nematic and N_R for a second nematic, called the *re-entrant* nematic, which appears at a lower temperature. The S_A phase occurring between two nematics was identified to be the partially bilayer A_d . Later, a similar effect was reported by Cladis *et al.* [32] in a pure compound at elevated pressures.

SMECTIC LIQUID CRYSTALS

Smectic liquid crystals have stratified structures but a variety of molecular arrangements and hence various phases are possible within each stratification. For smectics, the director has a slightly different definition than for nematics. In the former case, \mathbf{n} is a unit vector which shows the average orientation of the long molecular axes in each layer. Here the distinguishable features are:

1. Mesophase has a layered structure. It exhibit one-dimensional positional order, so that the structure is formed by parallel molecular monolayers or bilayers or partially bilayers.
2. Molecules are mobile in two directions within each layer and can rotate about one axis in some cases.
3. The interlayer attractions are weak as compared with the lateral forces between molecules and in consequence the layers are able to slide over one another easily.
4. Molecules may be normal to the plane of the layers or inclined to it.
5. This phase is more viscous than nematic.
6. For a given material usually it occurs at temperatures below the nematic domain.

Polymorphism is much more obvious in smectic phases. The lamellar smectic state is readily divided into four subgroups by considering first, the extent of the in-plane positional ordering of the constituent molecules and second, the tilt orientational ordering of the long axis of the molecules relative to the layer planes. These two groups are distinguished from each other by the extent of the positional ordering of the constituent molecules. Thus smectic A, C, C_{alt}, B_{Hex}, I and F are essentially smectic liquid crystals, whereas B, E, G, H, J and K are smectic-like crystal phases, which are distinguished from normal crystals in that their constituent molecules are reorienting rapidly about their long axes. So a large number of different smectic phases have been identified [2,3,14, 33-35]: In a hypothetical liquid crystal having all phases, the phase sequence on cooling, according to Goodby [36] will be as follows:

Isotropic liquid → N → SmA → SmD → SmC → SmC_{alt} → [SmB_{hex}, SmI] → B(cryst.)
 → SmF → J → G → E → K → H → Crystal.

The alphabetical order in smectic modifications merely indicates the chronological order of discovery. In the literature there is some ambiguity in naming higher order smectic phases – for example smectic E phase has been termed both as smectic E and Crystal E phase. Some of these phases (e.g., S_B, S_E, S_G, S_H, S_J and S_K) have three-dimensional long-range positional order as in a crystal, though with weak interlayer forces, while some others, referred to as hexatic phases, have three-dimensional long range bond-orientational order, but without any long-range positional order [37]. SmA, Hexagonal B, Crystal B, Crystal E phases are orthogonal whereas SmC, I, F, Crystal J, G, H, K are tilted in nature. The smectic D phase has a cubic structure [38-40] and would appear to be an exemption to the rule that smectics have layered structures. The cubic phases of thermotropic liquid crystals display an independent class of liquid crystalline phases besides the smectic and columnar ones [41]. The great variety of chemical structure leads to different cubic phases which can be expected to be constituted of molecular aggregates of different characters.

Structures of SmA and SmC phases are described below since these phases are relevant in the present dissertation.

SMECTIC A (SmA)

Molecular arrangement in this phase is shown in **Figure 1.9(a)**. Under polarizing microscope various textures are observed in this phase like fan-shaped, stepped drops, homogeneous, pseudoisotropic etc., a typical fan-shaped texture is shown in **Figure 1.9(b)**. Characteristic features of this phase are as follows:



Figure 1.9(a). Molecular arrangements in smectic A phase and (b) Typical fan-shaped texture of a SmA phase.

1. The director \mathbf{n} is perpendicular to the plane of the layer or parallel to the layer normal \mathbf{z} .
2. No positional order within the layers i.e., inside each layer nematic ordering exists. Its point symmetry is \mathbf{D}_{∞} .
3. Within each layer molecules have only orientational ordering.
4. The centres of mass of the molecules possess quasi long-range translational periodicity along the layer normal.
5. Phase is optically uniaxial in character.
6. The rotation around the short molecular axes is more or less hindered depending on the degree of order

A number of polymorphic types of SmA phase [16, 33, 42, 43] have been discovered, viz. SmA₁ (monolayer phase), SmA₂ (bilayer phase), SmA_d (partially bilayer phase), Sm $\tilde{\text{A}}$ (antiphase) and SmA_{ic} (phase intermediate between SmA_d and SmA₂) [44-46]. The smectic A liquid crystals, constituting of biaxial rod-like molecules, can have biaxial symmetry and the medium is then characterized by three directors. Recently a polymorphic system has been found to exhibit the biaxial SmA (Sm A_b) phase [47, 48].

SMECTIC C (SmC)

Molecular arrangement in SmC phase is shown in **Figure 1.10(a)**. Under polarizing microscope various textures are observed in this phase like broken focal conic, schlieren, homogeneous textures etc.; a typical texture is shown in **Figure 1.10(b)**. Characteristic features of this phase are given below:

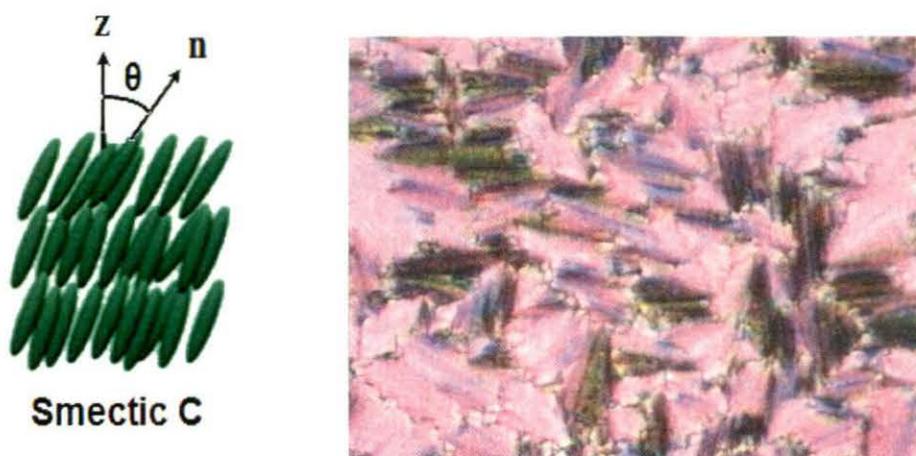


Figure 1.10(a). Molecular arrangements in SmC phase and (b) Typical broken fan-shaped texture of a SmC phase

1. Smectic C is a tilted form of smectic A, i.e., the director \mathbf{n} is tilted with respect to the layer normal. Each layer is a two dimensional liquid. Its point symmetry is C_{2h} .
2. Tilt angle may be constant or temperature dependent.
3. Due to the presence of pronounced tilt angles the phase is optically biaxial.
4. The rotation around the molecular long axes is not strongly hindered. The rotation around the short molecular axes is more or less hindered depending on the degree of order.

The sub-phases of the smectic C phase were discovered by Levelut et al [33,36]. It shows polymorphism into three subgroups, viz., C_1 , C_2 and C_3 depending on the nature of tilt angles [3, 14, 49]. However for system of molecules possessing terminal polar groups other sub-phases of Smectic C phase have also been observed. These phases are levelled as smectic C_1 , C_2 , C_d and C_{anti} phases which are direct analogues of smectic A_1 , A_2 , A_d and $Sm\tilde{A}$ phases [50]. Molecular arrangements and ordering in different liquid crystalline phases are summarised in **Table 1.2**.

Table 1.2
Molecular arrangements and ordering in liquid crystalline phases.

Phase type	Molecular orientation	Molecular packing	Molecular orientational ordering	Bond orientational ordering	Positional ordering	
					Normal to the layer	Within the layer
Isotropic	random	random	SRO	SRO	SRO	SRO
N	Parallelism of long molecular axis	random	LRO	SRO	SRO	SRO
SmA	orthogonal	random	LRO	SRO	QLRO	SRO
SmC	tilted	random	LRO	SRO	QLRO	SRO
SmB _{hex}	orthogonal	hexagonal	LRO	LRO	QLRO	SRO
SmI	Tilt to apex of hexagon	pseudo hexagonal	LRO	LRO	QLRO	SRO
SmF	tilt to side of hexagon	pseudo hexagonal	LRO	LRO	QLRO	SRO
B(cryst.)	orthogonal	hexagonal	LRO	LRO	LRO	LRO
J	Tilt to apex of hexagon	pseudo hexagonal	LRO	LRO	LRO	LRO
G	tilt to side of hexagon	pseudo hexagonal	LRO	LRO	LRO	LRO
E	orthogonal	Orthorhombic	LRO	LRO	LRO	LRO
K	tilted to longer side of cell	monoclinic	LRO	LRO	LRO	LRO
H	tilted to shorter side of cell	monoclinic	LRO	LRO	LRO	LRO

SRO → short range order, LRO → long range order, QLRO → quasi-long range order

1.2.1.2 CHIRAL CALAMITIC PHASES

A chiral molecule (from the Greek word for 'hand') is a molecule that cannot be superimposed on its mirror image. Human hands are perhaps the most universally recognized example of chirality. Chiral molecules are optically active in the sense that they rotate the plane of polarized light [2, 3]. Chiral compounds are able to form mesophases with structures related to those of non-chiral substances, however, with different properties.

CHOLESTERIC LIQUID CRYSTALS AND BLUE PHASES

When the constituent molecules of the nematic phase are chiral or a nematic liquid crystal when mixed with chiral (optically active) molecules, the structure undergoes a helical distortion about an axis normal to the preferred molecular direction \mathbf{n} , as shown in **Figure 1.11(a)**. Such a phase is called cholesteric or chiral nematic phase. The pitch length is usually several hundred times larger than the dimensions of the molecule. Under polarizing

microscope various textures are observed in this phase. Here cholesteric polygonal texture is shown in **Figure 1.11(b)**. The twist may be right or left handed depending on the molecular conformation. Locally a cholesteric phase is similar to a nematic phase and the molecular centre of mass have no long range order. Racemic mixture of optically active cholesterics

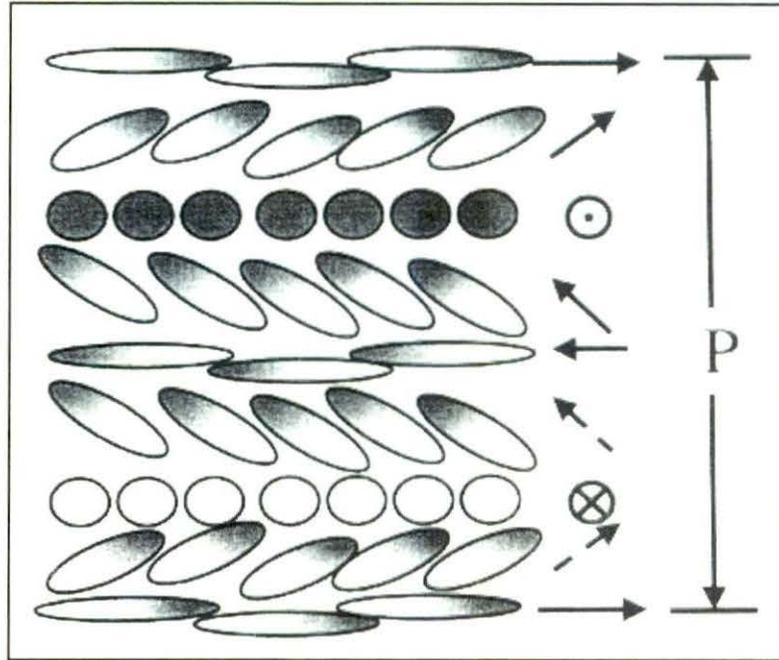


Figure 1.11(a). Schematic illustration of the helical superstructure of the cholesteric phase.

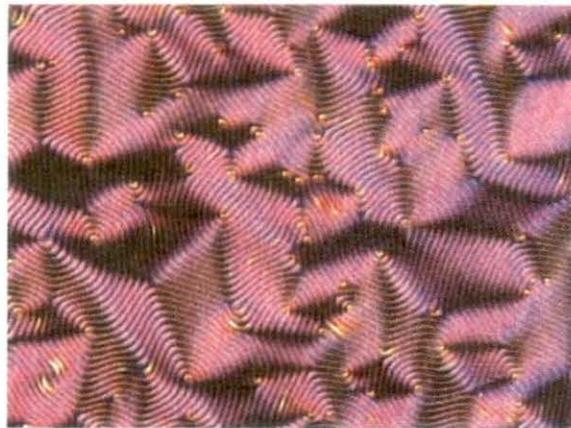


Figure 1.11(b). The texture of cholesteric phase (Cholesteric polygonal texture)

results in nematic phase. Therefore the nematic phase is a cholesteric of infinite pitch of the helix. The energy of twist form a small part (10^{-5}) of the total energy associated with the parallel alignment of the molecules so that even when small amount of cholesteric substance or a non-mesogenic optically active substance is added to nematic the mixture adopts helical conformation. The pitch of the spiral is temperature dependent and comparable to an optical wavelength. The cholesteric-nematic transition is found to be absent [51] when the

temperature of the cholesteric is changed and also when a strong magnetic field is applied normal to the helical axis [52, 53].

Cholesterics with pitch less than 5000\AA , exhibit what are known as blue phases. The blue phases exist over a small temperature range ($\sim 1^\circ\text{C}$) between the mesophase and isotropic liquid transition [54-56]. Three distinct blue phases (BPI^* , BPII^* , and BPIII^*) have been identified and occur in that order with increasing temperature. The BPIII^* phase, in the literature, is also referred to as the "fog phase" or the "blue fog". In contrast to BPI^* and BPII^* , which are cubic phases, BPIII^* is an amorphous phase which nevertheless reflects circularly polarized light, thus indicating some kind of helical superstructure.

FERROELECTRIC LIQUID CRYSTALS

Ferroelectrics are materials that possess a spontaneous polarisation (P_s) in the absence of an external field and on the application of an electric field, its orientation can be reversed. Ferroelectricity is usually observed in certain types of crystalline materials of a reduced symmetry space group and not fluid phases [57, 58]. However, R.B. Meyer and co-workers [59, 60] in 1975 discovered ferroelectricity in liquid crystals. This discovery was theoretically predicted by Meyer himself using symmetry arguments [61]. They synthesized the chiral SmC liquid crystalline material DOBAMBC in which ferroelectricity was first demonstrated and this initiated ferroelectric liquid crystal (FLC) research. The symmetry argument of Meyer goes as follows: the smectic C phase has monoclinic symmetry, the point group for which contains (i) only a two-fold rotation axis parallel to the layers and normal to the long molecular axis; (ii) a mirror plane normal to the two fold axis and the 'layer' and (iii) a centre of symmetry (C_{2h}). The reflection plane normal to the two-fold axis and the centre of inversion are eliminated when the constituent molecules are chiral, reducing the symmetry to C_2 . The remaining single two-fold axis allows the existence of a permanent dipole moment parallel to this axis. If all the molecules are identical then a net polarization of at most a few Debye per molecule will be produced. With these considerations in mind, a new chiral material DOBAMBC was synthesized; and hence Meyer was able to demonstrate ferroelectricity in liquid crystals.

In fact, reduced symmetry caused by molecular chirality is the case for all tilted smectic and disordered crystal phases like SmI^* and SmF^* and crystal smectic phases J^* , G^* , K^* and H^* . Excellent books, monographs and review or important articles on FLCs are available such as in [16, 17, 61-69]. A fairly recent review by M. Hird 'introduces the phenomena of ferroelectric liquid crystals and charts the development of the technology to commercially viable devices' [70].

A SmC^* material may have a positive or a negative sign of P_S in the natural state depending upon the nature of chirality of the constituent molecules. When an electric field is applied the molecules will switch around an imaginary cone through an angle 2θ , if θ is the tilt angle, so that the sign of the P_S would be reversed (**Figure 1.12**). P_S would remain in the same orientation until an electric field of opposite direction was applied and then the sign of the P_S would again be reversed. Hence, the SmC^* phase exhibits ferroelectricity.

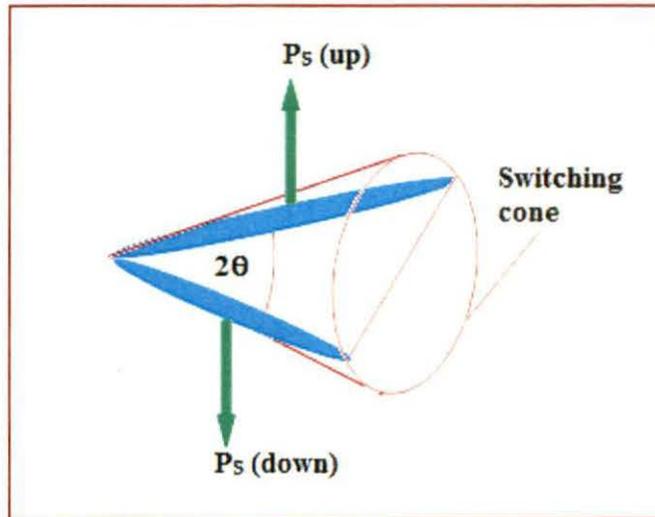


Figure 1.12. The two molecular orientations in the SmC^* phase [70].

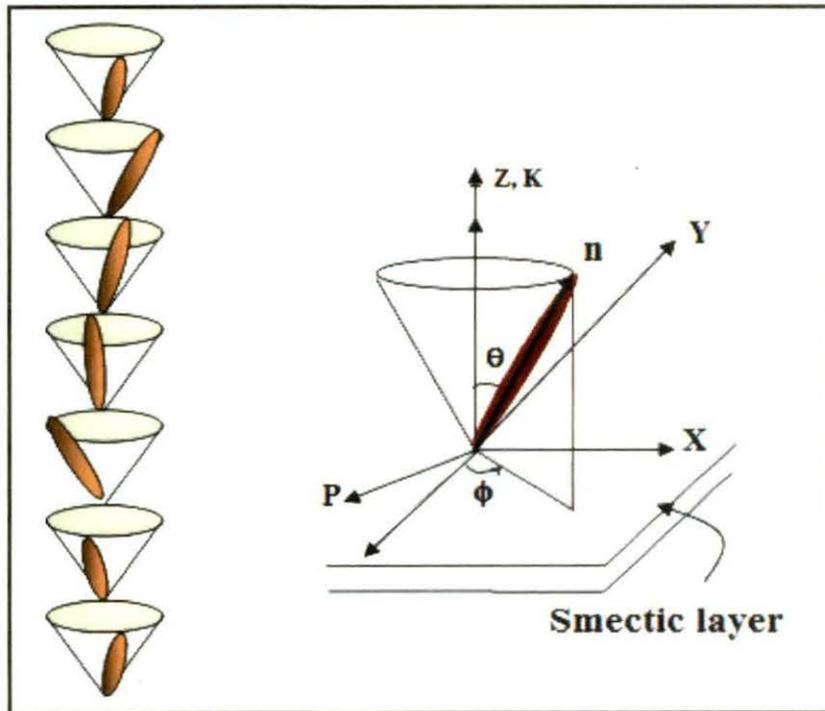


Figure 1.13. Spiralling of the director in SmC^* phase and basic geometry of the SmC^* phase showing layer normal Z , tilt angle θ , molecular director \mathbf{n} , polarization \mathbf{P} and azimuthal angle Φ .

Moreover, as a result of chirality, successive tilted smectic layers show a gradual change in the direction of tilt, such that the director precesses about the layer normal from layer to layer, always lying on the surface of a hypothetical cone of angle 2θ . The angle around the circle of precession is known as the azimuthal angle Φ . This creates a helical structure in the tilted chiral smectic mesophases with the pitch being the distance along the layer normal needed to reach the same molecular orientation. **Figure 1.13** shows the spiralling polarization direction in Sm C^* phase and the basic geometry of the Sm C^* phase.

Antiferroelectric and ferroelectric behaviour in liquid crystals were also discovered subsequently. The antiferroelectric order in liquid crystals was first observed in MHPOBC in 1989 [67], although the first antiferroelectric liquid crystalline material was synthesized already in 1983 [68]. Here, the director always lies in the layer plane and the polarization vector perpendicular to it. In subsequent layers the director is pointed in opposite directions and so is the polarization vectors. Thus because of an equal number of polarization vectors pointing up and down, the spontaneous polarization averages out to zero even for the unwound (nonhelical) state. This structure is evidenced by the fact that when a strong electric field is applied to this phase, the layer ordering is perturbed and the phase returns to a normal

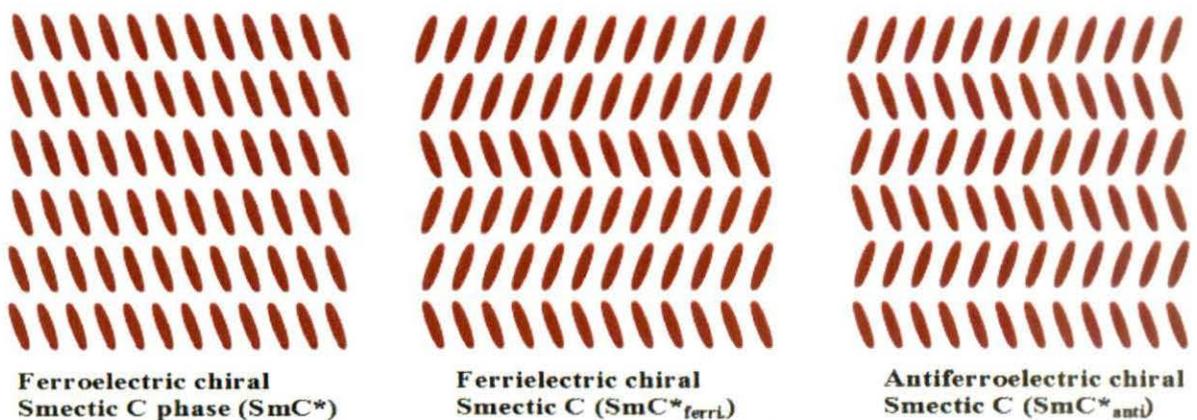
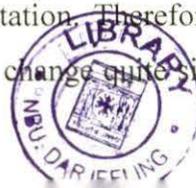


Figure 1.14. The structures of chiral smectic phases, SmC^* , $\text{SmC}^*_{\text{ferri}}$ and $\text{SmC}^*_{\text{anti}}$ (Helical form).

ferroelectric phase. In the switching of antiferroelectric phases three states are produced: one antiferroelectric and two ferroelectric [69]. This tristable switching occurs at a defined electric field and thus the presence of a sharp switching threshold may be useful in display applications, which require multiplexing with grey scales. The structure of ferroelectric SmC^* phase is repeated every 360° rotation of the helix, whereas the helical structure of the antiferroelectric phase repeats every 180° rotation. Therefore, the phase appears to have a relatively short pitch and the pitch appears to change quite significantly as the temperature is changed.



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In the ferroelectric smectic phase, the layers are stacked in such a way that there is a net overall spontaneous polarization. The number of layers of opposite polarization is not equal. It has also been suggested that the stacking of the layers has two interpenetrating sublattices. There are alternating layer structures, i.e., two layers tilted to the right and one to the left, with this arrangement repeating itself throughout the bulk of the phase. Thus, the ferroelectric phase has a measurable polarization. **Figure 1.14** shows the difference between ferro, antiferro, and ferroelectric chiral Sm C phases.

SURFACE STABILISED FERROELECTRIC LIQUID CRYSTAL DISPLAY DEVICES

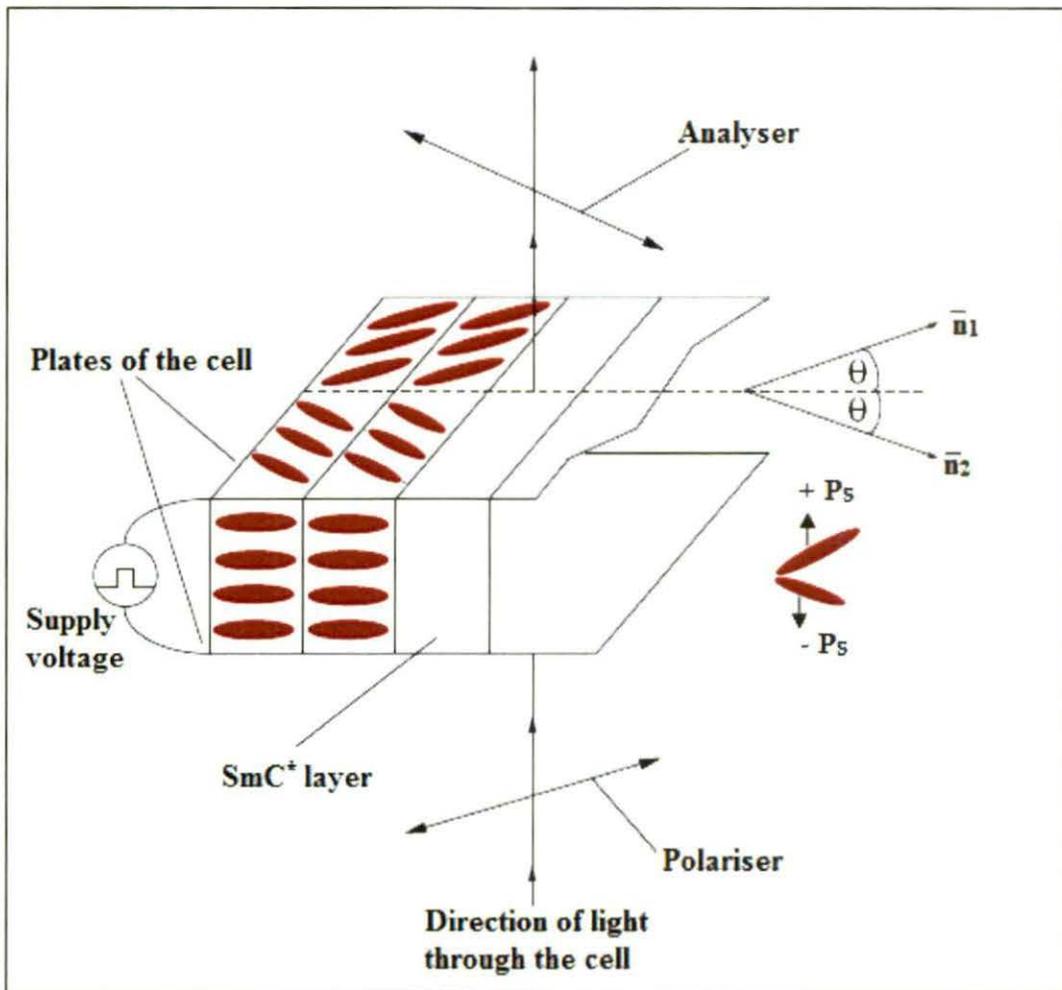


Figure 1.15. The basic construction of the SSFLC device [after ref. 70]

The phase structure of the SmC* phase is helical in nature, where the direction of the tilt changes very gradually from layer to layer throughout the natural phase structure. Hence, the direction of the P_S also changes gradually in the same way and so the P_S cancels to zero in the bulk phase (**Figure 1.13**). Accordingly, the bulk SmC* phase is more correctly termed

helielectric rather than ferroelectric. However, if the helix could be unwound, then the bulk phase would become ferroelectric. For any ferroelectric application of the SmC^* phase, the material is to be taken in a cell and the constituent molecules are to be aligned parallel to the cell surface. The surface forces generated in the constraints geometry of the cell effectively unwinds the helix. It was this type of unwinding of the helix on which the first ferroelectric display device concept was reported by Clark and Lagerwall as the surface stabilised ferroelectric liquid crystal (SSFLC) display device [66].

The device, as clearly described in the article by Hird [70], consists of a SmC^* liquid crystal contained between two ITO coated glass plates, pre-treated with aligning materials (polyimide or silicon dioxide) so that the molecules are aligned in a unidirectional manner called bookshelf geometry (**Figure 1.15**). The cell is placed between polariser and analyser at the crossed position. The bottom polariser is oriented in line with the molecular alignment direction, \bar{n}_1 , (the optic axis). Hence, the polarised light entering the cell is unaffected by the liquid crystal, and so is blocked by the top polariser (analyser) and the cell appears dark in this off state (back of **Figure 1.15** and left of **Figure 1.16**). The application of an electric field will cause molecular switching through 2θ as described above (**Figure 1.12**). Now assuming that $2\theta = 45^\circ$ then the molecular alignment direction, \bar{n}_2 , is mid-way between the polarizer directions, and hence the liquid crystal is able to act as a half-wave phase retardation plate to allow light through and appear bright in the on state (front of **Figure 1.15** and right of **Figure 1.16**).

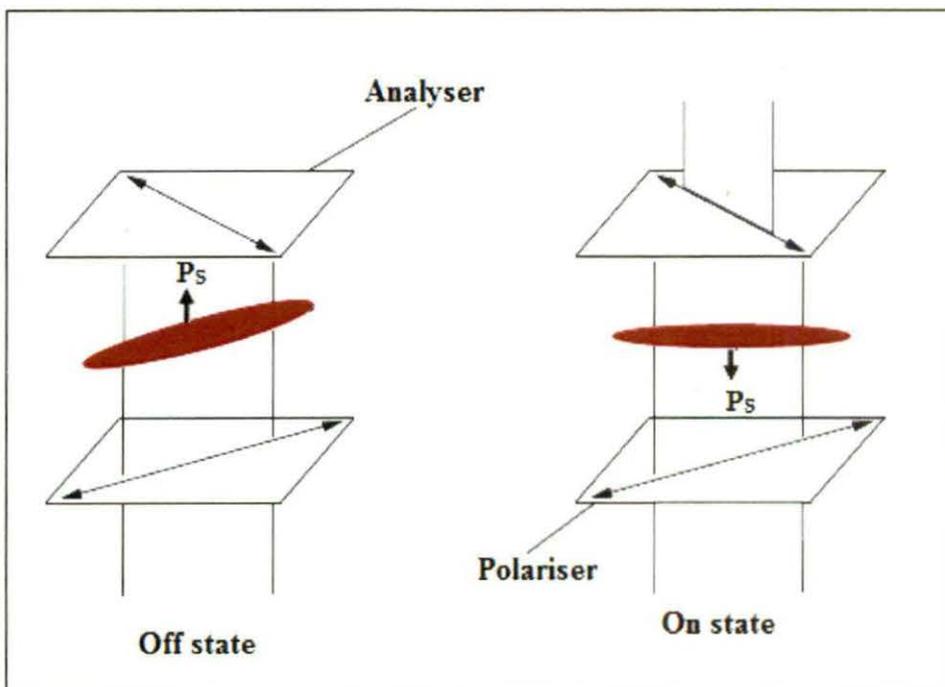


Figure 1.16. Off and On states in a SSFLC display device [after ref 70]

1.3 LIQUID CRYSTAL COMPOUNDS INVESTIGATED IN THE PRESENT DISSERTATION

Achiral fluorobenzene derivative compounds have wide-range nematic phase, high chemical stability, large dielectric anisotropy, low optical anisotropy and very good voltage holding ratio. Mixtures of these compounds are found to exhibit mesomorphism at ambient temperatures and have high bulk resistivity and low current consumption. All these features are important for liquid crystal displays (LCDs) with large information contents as in portable colour TVs and computer terminals. These materials are, therefore, expected to be useful in active matrix displays (AMDs) such as in TFT (thin-film-transistor) and MIM (metal-insulator-metal) systems. A number of achiral fluorobenzene derivatives were therefore selected for investigation in the present dissertation.

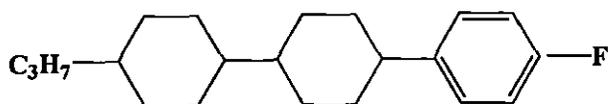
Members of the 4-(*trans*-4-alkylcyclohexyl) isothiocyanatobenzene (nCHBT) series are low melting polar nematic materials characterised by low viscosity and high chemical stability and are found to form eutectic systems with various mesogenic compounds, hence they seem to be interesting components for display applications. Similarly, members of 4-cyanobiphenyl-4'-*n* alkylbiphenyl carboxylate forms monolayer and partially bilayer smectic A phases, also in some cases re-entrant nematic phases. Hence two members of the above two series were also selected for investigation for finding their structure property relationships.

As mentioned before, ferroelectric liquid crystal (FLCs) have been the subject of intense investigation not only for their exciting properties for fundamental condensed matter research, but also for their application in fast switching flat panel displays, optical light modulators, optical signal processing and computing. These compounds combine the ferroelectric, electrooptic, piezoelectric and pyroelectric properties of solid polar dielectric materials with the physical flow characteristics of liquids. However FLC compounds for optoelectronic applications must have the following spectrum of physical properties customized to the specific application: broad temperature range from or below ambient temperature, rise time, birefringence, clarity, polarization, tilt angle, length of pitch, and thermal and UV stability. In general, no single FLC compound can satisfy all the above requirements. Multicomponent mixtures are, therefore, formulated to optimize all the required properties for practical applications. For this one has to select (i) proper achiral host materials, which controls the temperature range and tilt angle; (ii) proper chiral dopants to control the switching speed and helical pitch and (iii) proper birefringence dopants to adjust the birefringence to the desired level. Keeping these in view, various properties of a pure FLC compound have mainly been investigated using dielectric, electrooptic and x-ray diffraction

techniques. Several multicomponent FLC mixtures, taking both chiral and achiral type of dopants, have also been formulated and characterized.

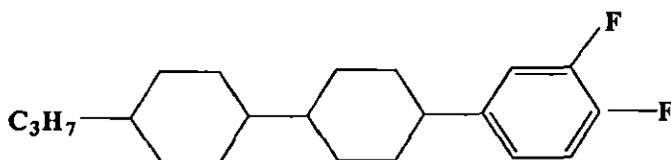
Names and structural formulae of the liquid crystalline compounds studied are given below:

1. 4-propyl-4'-(4-fluorophenyl) bicyclohexane (3ccp-f)



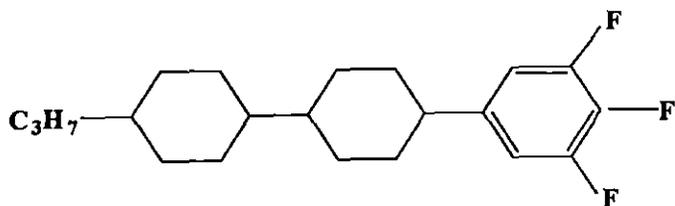
Cr 90.0 (71.0) N 158.0 I

2. 4-propyl-4'-(3,4-difluorophenyl) bicyclohexane (3ccp-ff)



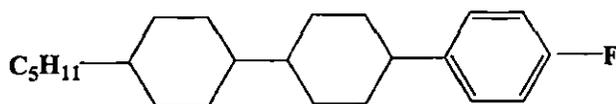
Cr 46.0 (38.5) N 123.8 I

3. 4-propyl-4'-(3,4,5-trifluorophenyl) bicyclohexane (3ccp-fff)



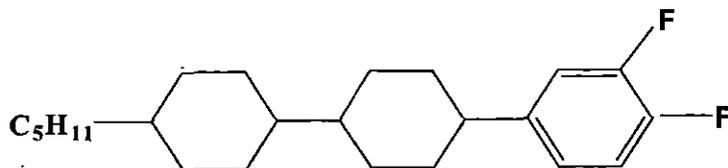
Cr 66.0 (49.0) N 94.1 I

4. 4-pentyl-4'-(4-fluorophenyl) bicyclohexane (5ccp-f)



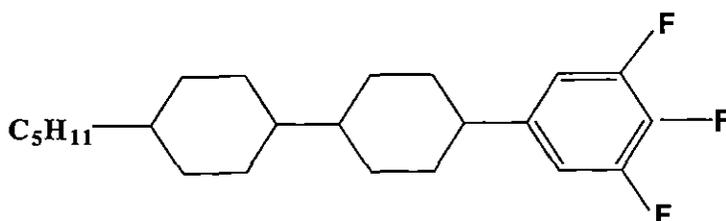
Cr 68.0 (44.0) S_B 75.5 N 157.0 I

5. 4-pentyl-4'-(3,4-difluorophenyl) bicyclohexane (5ccp-ff)



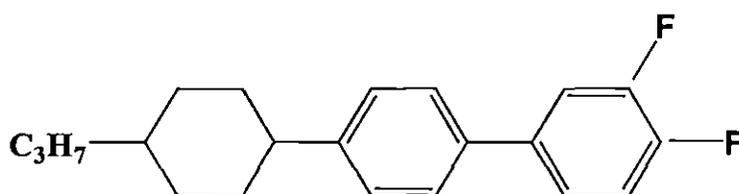
Cr 47.0 (26.8) N 125.2 I

6. 4-pentyl-4'-(3,4,5-trifluorophenyl) bicyclohexane (5ccp-fff)



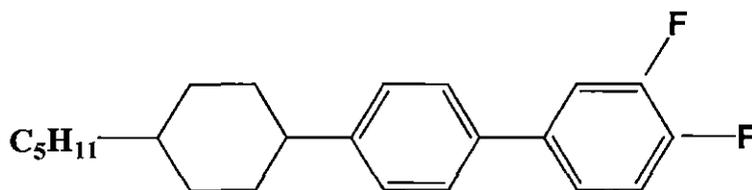
Cr 88.0 (57.0) N 102.4 I

7. 3,4-difluoro-4'-(4-propylcyclohexyl)-biphenyl (3cpp-ff)



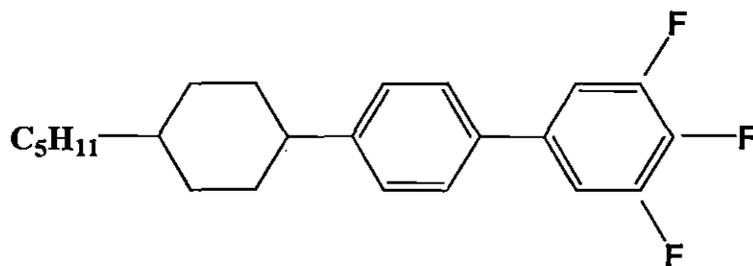
Cr 68.5 (46.4) N 97.9 I

8. 3,4-difluoro-4'-(4-pentylcyclohexyl)-biphenyl (5cpp-ff)

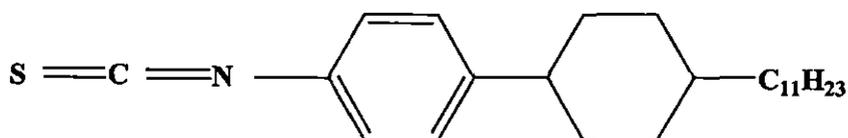


Cr 56.0 (38.7) N 105.8 I

9. 3,4,5-trifluoro-4'-(4-pentylcyclohexyl)-biphenyl (5cpp-fff)

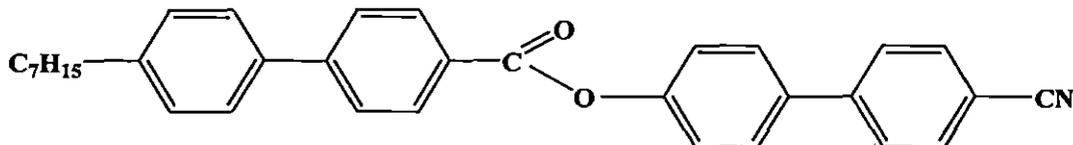
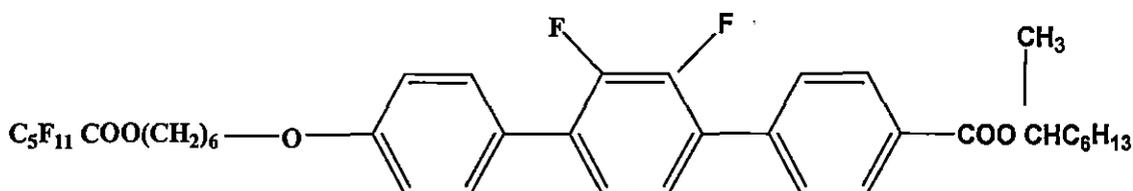


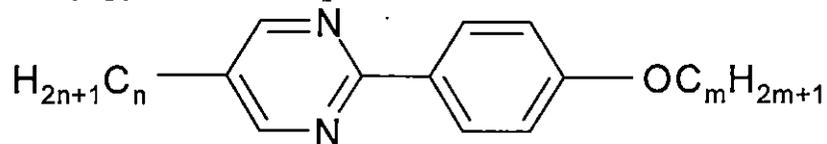
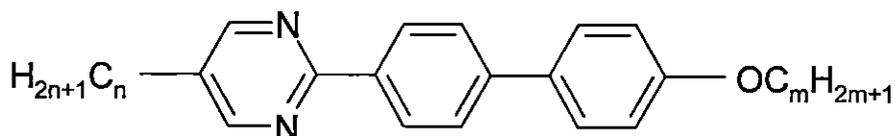
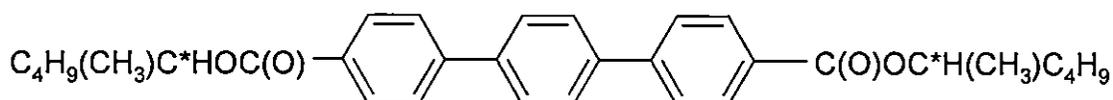
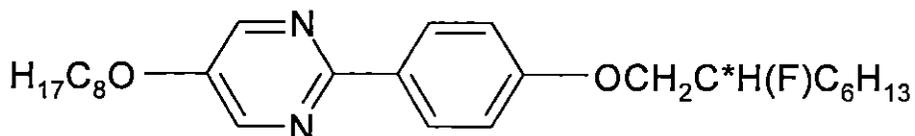
Cr 33.0 (27.0) N 54.8 I

10. 4-(*trans*-4-undecylcyclohexyl) isothiocyanatobenzene (11CHBT)

Cr 48.0 N 54.0 I

11. 4-Cyanobiphenyl-4'-heptylbiphenyl Carboxylate (7CBB)

Cr 123 SmA₁ 136 N 350 I12. (*S*)-4''-(6-perfluoropentanoiloxyhexyl-1-oxy)-2',3'-difluoro-4-(1-methylheptyloxycarbonyl)-[1,1':4',1'']terphenyl{5F6T(2',3'F)}Cr 41.1 SmC_A^{*} 50.2 SmC^{*} 71.5 SmA^{*} 91.9 Iso

13. Phenyl pyrimidine compounds**14. Biphenyl pyrimidine compound****15. Non-mesogenic chiral terphenyl compound with chiral centers at opposite ends****16. Singly fluorinated chiral phenyl pyrimidine compound with chiral center at one end****17. Singly fluorinated chiral phenyl pyrimidine compound with chiral centers at opposite ends**