CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

Liquid Crystal is a beautiful and fascinating state of matter. There is a little bit of liquid crystals in everybody's life since it is used almost in all our everyday gadgets like desktop computers, TV screens, laptops, mobile phones, calculators, digital watches, etc and it has become a multi-billion dollar industry. The liquid crystal technology is one of the important inventions of twentieth century that has found many applications as a visualization tool today. Liquid crystals change their color on application of external stimulus, for example temperature and shear stress distributions and thus act as a measure of their change. Liquid crystal technology has a major effect in many areas of science and engineering. Applications for this special kind of material are still being discovered and continue to provide effective solutions to many different problems.

Materials in nature can be divided into three main phases – solid, liquid and gas, depending on the mobility and amounts of ordering of the individual atoms or molecules. In a solid, particles are strongly bound to each other, and are not able to move about freely so shape and volume do not change. In a liquid, particles have more energy than in the solid state so they are able to move over each other and can flow to take up the shape of the container they are in, but the volume is fixed. In a gas, particles have enough energy to escape the attractive forces between them, so they are free to move in all directions at high speed. Particles will move around and fill whatever container they are in.

Although the three categories seem very well defined, the borders between the different states are not always clear. Apart from these three familiar states, there exist a large number of other intermediate phases. Liquid crystals are one of the intermediate phases in which the fluid nature of a liquid coexists with a partially ordered crystalline structure. 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 and thus has drawn considerable attention from all branches of science and technology [1].

1.2 HISTORY OF LIQUID CRYSTALS

Liquid crystals have been used by mankind since ancient times, when soap was first discovered without knowing about their nature. The story of liquid crystals starts with a few European investigators who observed some new and interesting phenomena but whom never fully realized exactly what was happening in their experiments. These early scientists are not given the credit for discovering liquid crystals. In 1853 one European biologist Rudolf Virchow observed the characteristic of the liquid-crystalline state in nerve myelin and in 1857 Mettenheimer had deduced that nerve myelin was both fluid and optically birefringent [2], but were not formally recognized for another three decades. In 1887, the German physicist Otto Lehmann [3] was investigating phase transitions in cholesteryl esters, when he noted that during heating one particular substance would change from a clear liquid to a cloudy liquid before crystallizing when viewed under a polarizing microscope, but dismissed this as simply an imperfect phase transition. The next year, Friedrich Reinitzer [4], Austrian botanist, observed that cholesteryl benzoate had two distinct melting points. In his experiments, Reinitzer increased the temperature of a solid sample and observed at 145.5°C it became a hazy liquid which on further heating changed into a clear, transparent liquid at 178.5°C. Because of this early work, Reinitzer is often credited with discovering the new phase of matter i.e. Liquid Crystal.

From the earliest days, there was controversy over the nomenclature of these materials, and even the very name ‘liquid crystal’ was opposed by a number of prominent scientists. The field was dominated until the early 1920s by the German school, joined after about 1910 by the French school. Lehmann himself continued to publish extensively in the field until his death in 1922. In that year, G. Friedel published his famous two-hundred page overview in the *Annales de Physique,* where he set out most of the basic classification of liquid crystals, although he himself preferred the term ‘mesomorphic state’, into nematic, smectic, and cholesteric types [5]. Thus from the very beginnings, liquid crystal research was an international and multidisciplinary field. The total number of registered synthesized liquid crystal compounds, till year 2000, was 80080, out of which 59000 were benzene derivatives, 9000 mesogenic derivatives of cyclohexanes [6]. The beauty of this field of research is that a large number of physicists, chemists, biologists, engineers and medical doctors from almost all of the industrialized countries of the world are involved in liquid crystal research. The details of historical evidences and perspectives in liquid crystal research are available in the references [2,7-14].

1.3 MOLECULAR ORDERING IN LIQUID CRYSTALS

In a crystalline solid the molecules have fixed orientation and the centre of mass of the molecules are distributed on a 3-dimensional periodic lattice. The crystal, therefore, possess long range ordering in both position and orientation of the molecules. But in case of an isotropic liquid the molecules do not have positional or orientational order. Their positions and the directions they point are randomly distributed. In liquid crystalline phase molecular arrangement is intermediate between the above two phases and they possess some typical properties of a liquid (e. g. fluidity, inability to support shear, formation and coalescence of droplets) as well as some properties of the crystalline state (anisotropy in optical, electrical, and magnetic properties, etc).

1.4 CLASSIFICATION OF LIQUID CRYSTALS

The various liquid-crystal phases can be characterized on the basis of geometrical structures of the molecules and type of ordering. Depending on the molecular structures, the system can pass through one or more mesomorphic states before it is transformed into an isotropic liquid. Transitions to these intermediate states may be induced by purely thermal process or by the influence of the solvents. Molecular systems that show mesomorphic behavior in a definite temperature range are called thermotropic liquid crystals. Lyotropic liquid crystalline phases, on the other hand, show mesomorphsm in solution. The temperature range in which these lyotropic liquid crystals exist is mainly determined by the amount of solvent.

The molecules of liquid crystals are mostly rigid non-spherical and rod like or disc like in shape. The liquid crystals which are derived from rod like molecules are called “Calamatic” (Greek word *colomos* = rod) and which are derived from disc like molecules are called “Discotic”. The discotic liquid crystals were discovered independently by Chandrashekar *et al.* [15] and Billard *et al.* [16].

Besides the above two molecular types, the molecules may be lath like which are intermediate between the rod like and the disc like molecules. However, the constituent molecules may be even banana-, bowl-, sofa-, Y-, H-, T-, crooked-shaped etc [14].

The molecular structure of a typical rod-like liquid crystal molecule is shown in the Figure 1.1. It consists of two or more ring systems connected by a central linkage group, with a terminal group at one end and a flexible chain on the other end or chains at both ends.

Figure 1.1: Typical structure of a rod-like liquid crystal molecule

The presence of the rings in the above provides the short range molecular forces needed to form the liquid crystalline phases, but also affects the optical, electrical and elastic properties. The chemical stability of a liquid crystalline compound depends strongly on the central linkage group. Compounds with a single bond at the center are among the most stable ones. The length of the side chain has a significant impact on the flexibility and phase transition temperatures of the liquid crystalline compounds and affects the elastic constant. It is also commonly found that introduction of a side chain (group) decreases the melting point. The aromatic rings that form the core of the basic liquid crystal molecular structure can be saturated cyclohexane, unsaturated phenyl rings, or a combination of both. The ring structures of a liquid crystal molecule have an intrinsic effect on the dielectric anisotropy, birefringence, elastic constant, viscosity, and absorption. Polar group substitution at a terminal position results in enhanced dipole moment along the long axis of the molecule and lateral polar group substitution can cause the dipole moment along the short axis to become larger than that along the long axis, thereby affecting the dielectric properties of the materials [17,18].

On the other hand lyotropic molecule contains a hydrophilic polar head group and one or more long hydrophobic alkyl chains. Solutions of soap and water and various phospholipids are typical examples of lyotropic liquid crystals. Like thermotropic liquid crystals, they are also fluid phases possessing considerable molecular order. Lyotropic liquid crystals are mainly of interest in biological applications and exhibit a considerable number of different phases. The biological aspects of lyotropic liquid crystals have been reviewed by J. W. Goodby [19].

1.4.1 THERMOTROPIC LIQUID CRYSTALS

Thermotropic liquid crystals are basically organic compounds and they exhibit a variety of phases as temperature is varied. Along with low molecular mass molecules some polymers also show thermotropic mesomorphic behavior, known as polymeric liquid crystals. In the low molecular mass category the constituent molecules may be achiral or chiral. If a molecule is asymmetric to mirror reflections i.e; cannot be superimposed on its mirror image, it is called a *chiral* molecule. On the other hand a molecule is *achiral* if it is super imposable on its mirror image. The achiral thermotropic liquid crystals are broadly classified into two main categories viz. nematic and smectic.

1.4.2 ACHIRAL CALAMATIC LIQUID CRYSTALS

Nematic Liquid Crystals

In nematic phase the centre of mass of the molecules are randomly distributed but the molecules possess long range orientational order. The molecules tend to align parallel to each other with their long axes all pointing roughly in the same direction. The average direction along which the molecules point is called the director and is usually denoted by a unit vector **n** (Figure 1.2).

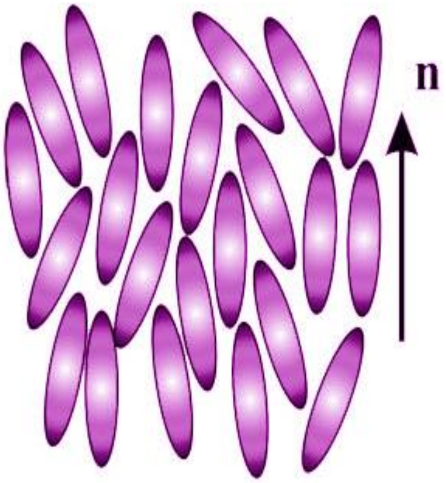


Figure 1.2: Molecular arrangement in nematic phase

The following characteristics of nematic phase are worth noting:

1. In the state of thermal equilibrium the nematic phase has symmetry $D_{\infty h}$ and is therefore uniaxial [20]. However some nematics are biaxial [21], meaning that in addition to orienting along their long axis, they also orient along a secondary axis.
2. There is long range orientational order i.e., the molecules tend to align parallel to each other.
3. There exists some preferential orientation of the molecules which is characterized by the axis of nematic order denoted by the unit vector **n**.
4. The direction of **n** is arbitrary in space and the preferred orientations **n** and – **n** are indistinguishable.
5. When viewed under crossed polarized light microscope thread like structures appear from which nematics take their name (Greek “νημα” means thread). They also show schlieren; pseudo-isotropic; homogeneous textures.
6. Nematic phase are very sensitive to external fields, electric or magnetic and mechanical stress, which may be translated into visible optical effect, for which they find wide application in display devices.

From X-ray diffraction study [22,23], it is observed that some nematics posses a lamellar type of short-range order, i.e., they consist of clusters of molecules, called cybotactic groups, the molecular centres in each cluster are arranged in layers and the molecules may either be arranged normal or tilted to the plane. The resulting phases are respectively called normal or skewed cybotactic nematic. Cladis [24] first observed that in a binary mixtures of two cyano compounds less ordered nematic phase reappears on cooling after more ordered smectic phase, such phases are called the re-entrant nematic. Re-entrant phenomena have been observed later in many pure systems.

Smectic Liquid Crystals

The smectic phases, which are found at lower temperatures than the nematic phase, form well-defined layers that can slide over one another in a manner similar to that of soap. The word "smectic" originates from the Latin word "smecticus", meaning cleaning, or having soap like properties. In general they are much more viscous than the nematics. The main characteristics of smectic phase are:

1. The elongated molecules exhibit orientational order as in the nematic phase but also align themselves in layers.
2. Molecules in this phase may show additional degrees of translational order within the layers.
3. Arrangement of the molecules may be normal to the plane of the layers or inclined to it.
4. The interlayer attractions are weaker than the lateral forces between molecules and hence the layers can easily slide over one another.

There are different types of packing of molecules in the layers, each of these types corresponds to different kinds of smectic phases [7,10,14,25-34]. The in plane positional ordering of the constituent molecules and the orientation of the molecules relative to the layer planes give rise to four sub-groups of smectic mesophases. The first two groups can be defined where the molecules have their long axes on an average normal to the layers with or without in plane ordering. The other two sub groups have their constituent molecules tilted relative to the layer planes. The smectic mesophases are Smectic **A**, Smectic **D**, Smectic **C**, Smectic **B**, Smectic **E**, Smectic **F**, Smectic **G**, Smectic **H**, Smectic **I**, Smectic **J**, Smectic **K**, Smectic **L**, Smectic **M**, Smectic **O** and Smectic **Q**. The alphabetic order merely indicates the chronological order of discovery.

Smectic A Phase

Smectic A (SmA) is a phase in which the molecules are more or less parallel to one another and are arranged in layers with the long axes perpendicular to the layer plane. Within the layers, liquid-like structure remains (Figure 1.3). Thus, the structure may be defined as an orientationally ordered fluid on which a one dimensional density wave is superimposed. The molecules are free to rotate about their long axes [35,36]. SmA has infinite fold rotational symmetry (D_∞) about an axis parallel to the director, for which this phase is uniaxial [37]. This gives rise to characteristic textures like focal conic (fan-shaped or polygonal), stepped drops, pseudoisotropic, etc.

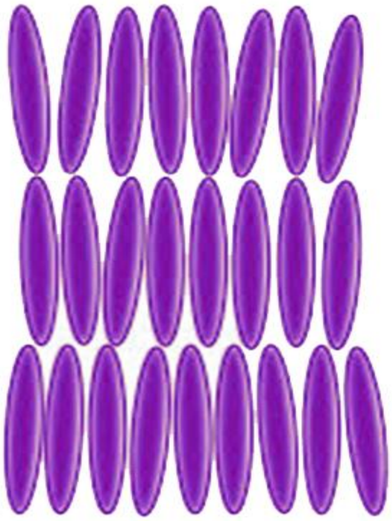


Figure 1.3: Molecular arrangement in SmA phase

Smectic A phase can further be divided into the following subphases. SmA_1 which is a conventional monolayer smectic A phase, where the molecules have random head to tail orientations, SmA_2 is a bilayer phase with antiferroelectric type ordering of the constituent molecules [38], SmA_d is a semi bilayer phase with partial molecular overlapping due to associations [39,40] and SmÃ is called anti-phase [41-43] and SmA_{ic} is an incommensurate phase intermediate between SmA_d and SmA_2 [44].

Smectic C Phase

On decreasing temperature, the SmA phase may transform into a phase with the director **n** is tilted with respect to the layer normal called smectic C (SmC) phase as shown in Figure 1.4. Tilting of the molecules, results in lower symmetry (2/m symmetry). Due to the presence of pronounced tilt angles the phase is optically biaxial. The tilt angle provides a natural order parameter to distinguish it from smectic A phase. It shows broken focal-conic, schlieren and homogeneous textures.

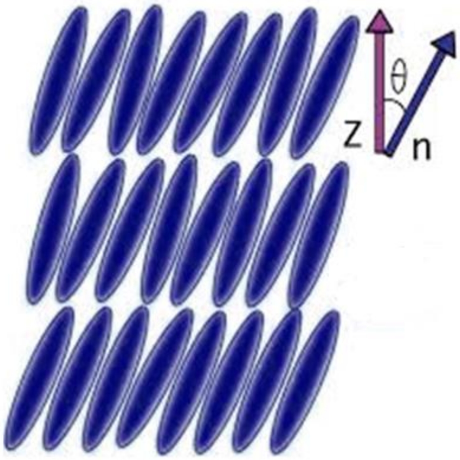


Figure 1.4: Molecular arrangement in SmC phase, z is layer normal

In SmC phase, when the constituent molecules are strongly axially polar, four sub phases are observed [45,46]; viz, SmC_1, SmC_2, SmC_d and SmC_{anti} are the analogues to A_1, A_2, A_d and Ã phases respectively.

Smectic B Phase

In SmB phase, in addition to the layered structure ordering of the constituent molecules within the layers is also observed. Within a layer molecular long axes are perpendicular to the plane of the layer and the centres of mass of the molecules are arranged in hexagonal symmetry (6/mm symmetry) [27,28,47-49]. Two different types of SmB phase have been observed – one is Crystal B (CrB) and another one is Hexatic B. Hexatic B phases have short range positional ordering as well as bond orientational ordering whereas Crystal B phases are smectic like soft crystal modifications [50,51] with the constituent molecules having long range positional ordering in 3-dimension. Thus the SmB phase is the most ordered of the three major smectic phase A, B and C. Under a microscope the SmB phase usually shows a mosaic texture.

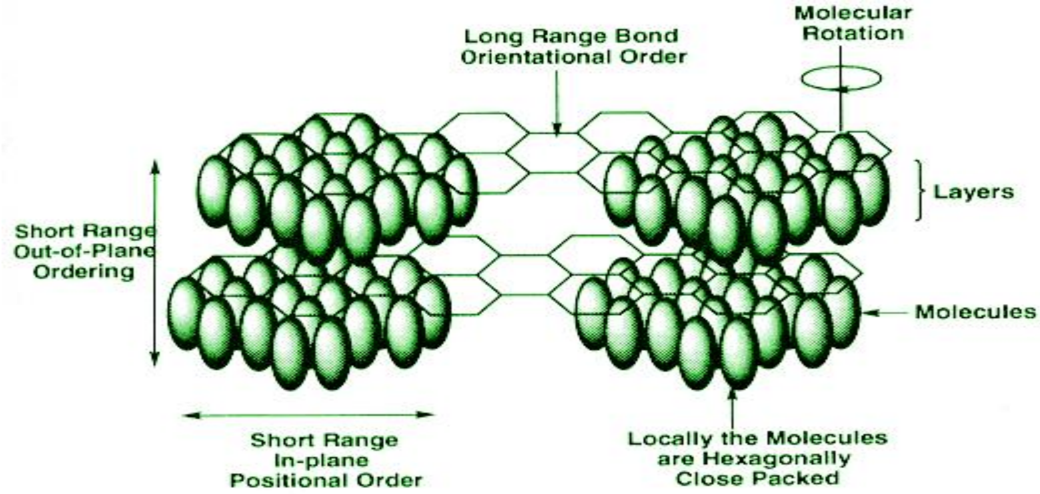


Figure 1.5: Molecular arrangement in smectic B phase [after reference 37]

Smectic I and Smectic F Phases

Smectic I (SmI) and Smectic F (SmF) phases are tilted analogues of hexatic SmB phase [52,53]. The tilt in the molecular long axis in SmI phase is directed towards an apex of the hexagonal packing net, whereas in SmF phase tilt is towards the edge of the hexagon (Figure 1.6 and Figure 1.7). SmF phase have slightly longer correlation length than SmI phase [54].

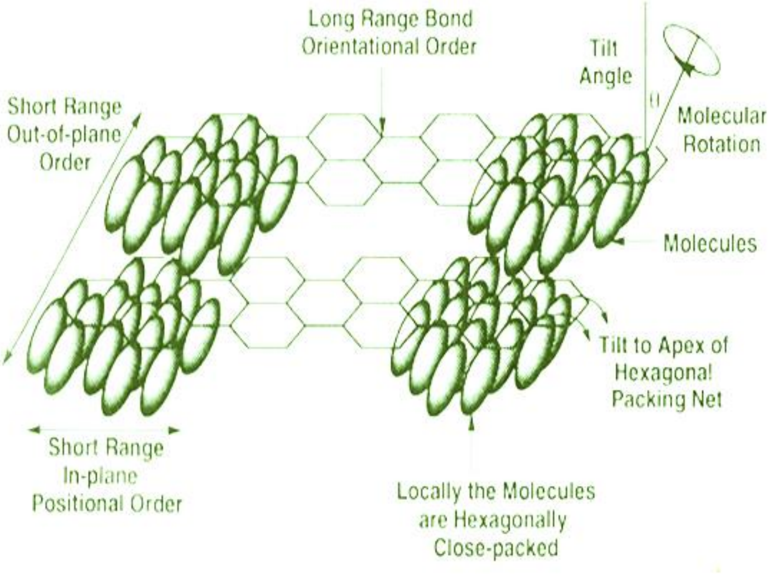


Figure 1.6: Molecular arrangement of smectic I phase [after reference 37]

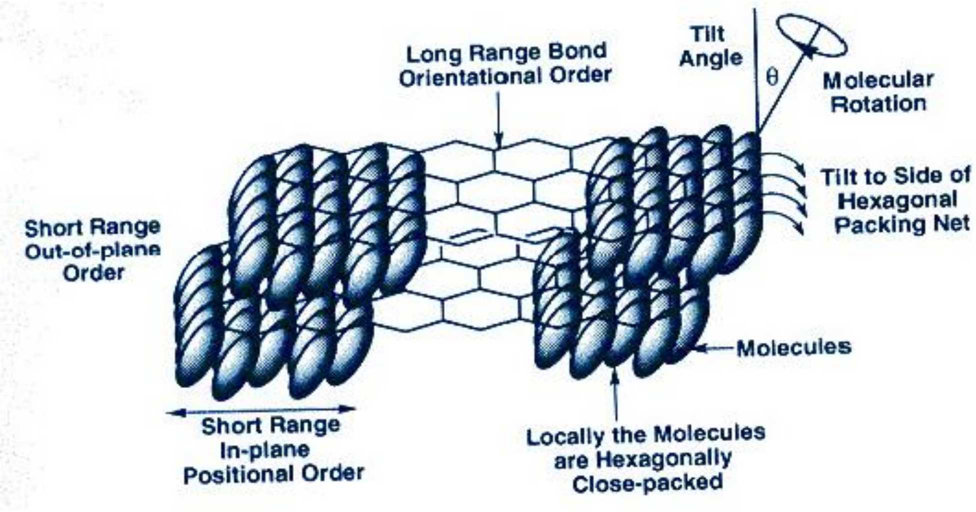


Figure 1.7: Molecular arrangement of smectic F phase [after reference 37]

Crystal J and G phases

The crystal J and G phases [55] are the crystalline analogues to smectic I and smectic F phases [27]. In crystal J phase the molecules are arranged in layer with their molecular long axes tilted relative to the layer planes. There is long range positional ordering within the layers and also between the layers [56]. The molecules in crystal J and G phases are packed in a pseudo-hexagonal structure when viewed down the tilt direction. The only difference between the two phases is the tilt direction. In the crystal G phase the tilt of the molecules is directed towards the edge of the hexagonal packing array whereas in J phase the tilt is towards the apex of the hexagonal net (Figure 1.8). The molecules undergo rapid re-orientational motion about their long axes [27,57].

(a) (b)

Figure 1.8: Molecular arrangement in (a) crystal J and (b) crystal G phase

1.4.3 CHIRAL CALAMATIC LIQUID CRYSTALS

Chiral calamitic compounds may form non-ferrolectric and ferroelectric phases which are discussed below.

Non Ferroelectric Phases

Cholesteric Liquid Crystals

A nematic liquid crystal when composed of chiral molecules or when mixed with chiral (optically active) molecules, the structure undergoes a helical distortion about an axis normal to the preferred molecular direction **n** [58-62] as shown in Figure 1.9, giving rise to cholesteric or chiral nematic phase (Ch or N^*). The helix may be right handed or left handed depending on the molecular conformation. The pitch of the helix is usually of the order of several hundred nanometers, corresponds to the wave length of visible range of electromagnetic spectrum.

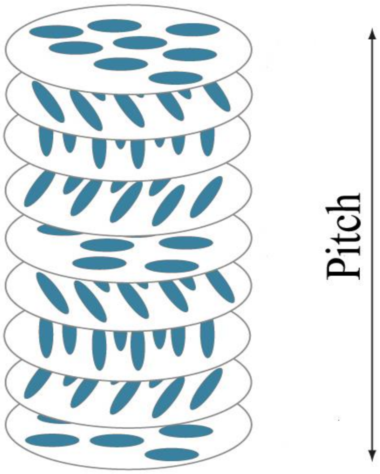


Figure 1.9: Molecular arrangement of cholesteric liquid crystal

In other words, a cholesteric liquid crystal with infinite pitch is nothing but a nematic liquid crystal. Pitch is highly sensitive to temperature, flow, chemical composition, and applied magnetic or electric field. The energy of twist form a small part (10^{-5}) of the total energy associated with the parallel alignment of the molecules [63] 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. In X-Ray diffraction pattern both nematic and cholesteric phases show long range positional order. The absence of Ch-N phase transition by variation of temperature [64] and by application of strong magnetic field normal to the helical axis [65,66] confirm that the cholesetric phase may be regarded as a twisted nematic phase.

Blue Phases

Blue phases are liquid crystal phases that appear in the temperature range between a chiral nematic phase and an isotropic liquid phase and was first reported by Lehmann in 1906 [67]. The temperature region in which these blue phases are stable is often quite small, some tenths of a degree. Recently the stabilization of blue phases over a temperature range of more than 60 K including room temperature (260–326 K) has been demonstrated [68,69]. Blue phases have a regular three-dimensional cubic structure of defects with lattice periods of several hundred nanometers, and thus they exhibit selective Bragg reflections in the wavelength range of visible light. This phase possesses a relatively short pitch length (< 5000 Å). Three distinct blue phases (BPI, BPII and BPIII) have been identified and occur in that order with increasing temperature [70]. Although BPI and BPII, are cubic phases, BPIII is an amorphous phase which nevertheless reflects circularly polarized light. Under a microscope a texture of uniformly colored platelets is found in this phase. Blue phases are of interest for fast light modulators or tunable photonic crystals, blue phases stabilized at room temperature allow electro-optical switching with response times of the order of 10^{-4} s [71]. In 2008, the first Blue Phase Mode LCD panel had been developed by ‘Samsung Electronics’.

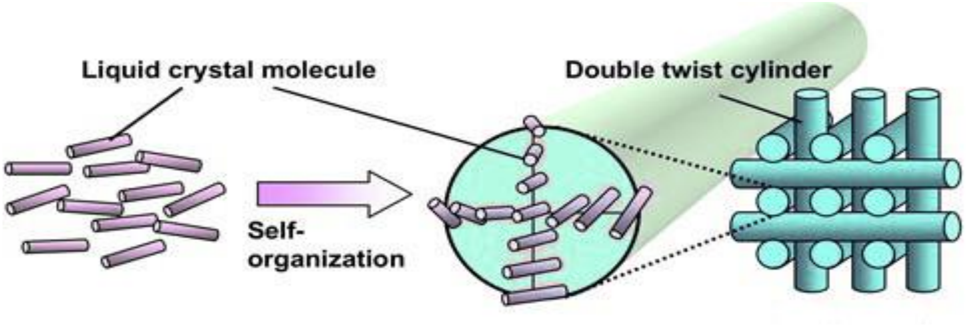


Figure 1.10: Molecular arrangement of liquid crystal possessing blue phase

Ferroelectric Liquid Crystals

All chiral smectic phases with tilted structure may exhibit ferroelectric properties if the molecules contain a transverse permanent dipole moment. The basic structure of a ferroelectric liquid crystal is shown in Figure 1.11. There are several types of smectic liquid crystal phases SmC*, SmI* and SmF* and crystal smectic phases SmJ*, SmG*, SmK* and SmH* in which the constituent molecules are chiral and their long axes are tilted with respect to the layer planes. Due to their low symmetry they are able to exhibit spontaneous polarization (P_s) when molecules have permanent dipole moment and are known as ferroelectric liquid crystals [72]. The chiral smectic mesophases take the form of a helix, which is different from the helix in chiral nematic phase.

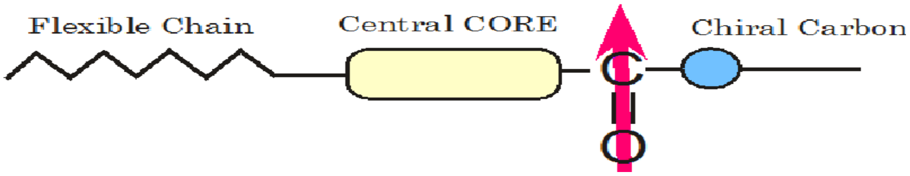


Figure 1.11: Basic structure of ferroelectric liquid crystal

The most commonly exhibited tilted chiral smectic phase is the SmC* phase. In the SmC* phase, where the molecules tilt with respect to the layer normal, the axis of the helix is along the layer normal. The director slowly rotates around the smectic cone progressively from layer to layer, preserving a constant azimuthal angle Φ within a single layer. This creates a helical structure with pitch being the distance along the layer normal needed to reach the same molecular orientation [73], as shown in Figure 1.12.

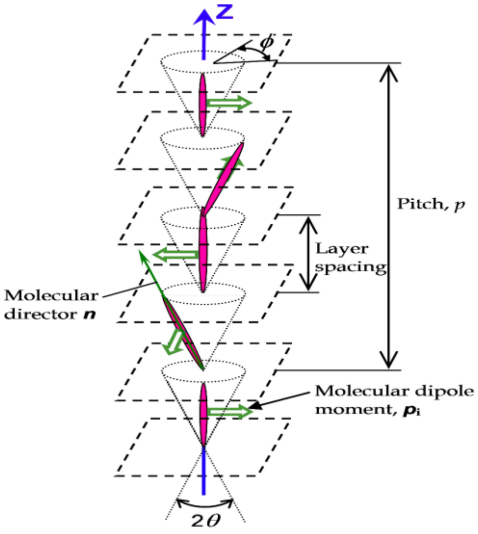


Figure 1.12: Spiralling of the director in SmC* phase showing layer normal **Z**, tilt angle θ, azimuthal angle **Φ**, molecular director **n** and dipole moment $\mathbf{p_i}$ [after reference 74]

In addition to producing this helical structure, chirality results in a spontaneous molecular polarization. Since in every SmC* layer the vector of spontaneous polarization is in the plane of the layer and perpendicular to the plane which goes through the normal to the layers and the director **n**, all possible directions of Ps are tangent to the basis of the smectic cone. When there is no field applied across a SmC* sample, where the helical superstructure has developed, the spontaneous polarization will average to zero over one pitch, resulting in no macroscopic polarization of the system [74] thus ferroelectric liquid crystals are regarded as helielectric. Application of an external electric field (perpendicular to the helix axis) will couple the polarization vector to the field direction and unwind the helix which suggests that Ps can be reoriented according to the direction of applied field. By virtue of their symmetry, ferroelectric liquid crystals are piezoelectric too, because polarisation in these materials can be induced by mechanical stress. Ferro electricity in liquid crystals was first discovered in 1975 by R.B. Meyer and his co-workers [72,75] and the first developed liquid crystalline material was DOBAMBC. According to Meyer the symmetry argument is as follows: the smectic C phase has monoclinic symmetry (C_{2h}), 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. When the constituent molecules are chiral, the reflection plane normal to the two-fold axis and the centre of inversion are eliminated which reduces the symmetry to C_2. The remaining single two-fold axis allows the existence of a permanent dipole moment parallel to this axis and if all the molecules are identical then a net polarization (a few Debye per molecule) will be produced. With these considerations Meyer was able to demonstrate ferroelectricity in the liquid crystalline material DOBAMBC.

There are other chiral smectic phases viz., antiferroelectric chiral smectic C* (SmC*$_A$) phase, the ferrielectric chiral smectic C* (SmC*$_{A.}$) phase as shown in Figure 1.13. The constituent molecules of the antiferroelectric chiral smectic C* (SmC*$_A$) phase have the tilted lamellar structure as that of the ferroelectric SmC* phase but the tilt direction alternates between the + θ and – θ positions from layer to layer to give a zig-zag structure resulting the spontaneous polarization of the phase to be zero (real materials may exhibit very small spontaneous polarization) [76]. 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 ferroelectric phase. 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. The first antiferroelectric liquid crystal (MHPOBC) was found by a Japanese group in 1989 [77,78]. The ferrielectric chiral smectic C (SmC*$_{\mathrm{ferri}}$) also has alternating tilted structure except that the alteration is not symmetrical and more layers are tilted in one direction than the other. This phase generates spontaneous polarization, the magnitude of which depends on the degree of alternation of tilt direction.

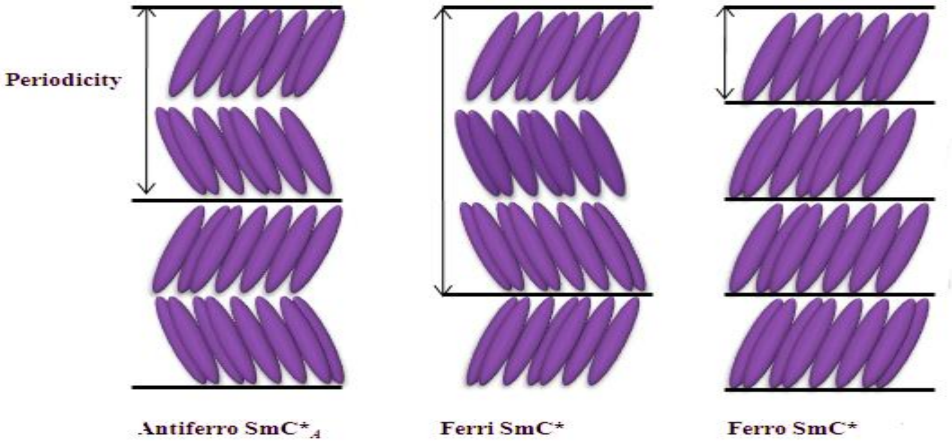


Figure 1.13: Molecular arrangement of antiferroelectric, ferrielectric and ferroelectric SmC* liquid crystal

In some recent investigations three subphases of SmC* phase, viz, SmC$^*_\alpha$, SmC$^*_\beta$ and SmC$^*_\gamma$ - have also been found in many antiferroelectric liquid crystals [79]. The study of ferroelectric liquid crystals has become important for their variety of applications such as in large area, high information content colour display devices. The various applications of FLCs have been explored in references [80-83].

Surface Stabilized Ferroelectric Liquid Crystal Display Devices

In ferroelectric SmC* phase the molecules in different layers create a helical structure. By suppressing the helix in FLCs, one can develop Surface Stabilized Ferroelectric liquid crystal (SSFLC). The way to suppress the helix was first proposed by Clark and Lagerwall [82], which resulted in the discovery of fast electrooptic switching. Although in solid ferroelectrics the macroscopic polarization is energetically stable in the absence of an external field, whereas due to helical structure bulk ferroelectric liquid crystals do not have any macroscopic polarization. In SmC* phase there is no crystal lattice and its stable configuration is characterized by the helicoidal structure and the P_S changes gradually in the same way and so the P_S cancels to zero in the bulk phase. However, if the helix could be unwound, then the bulk phase would become ferroelectric.

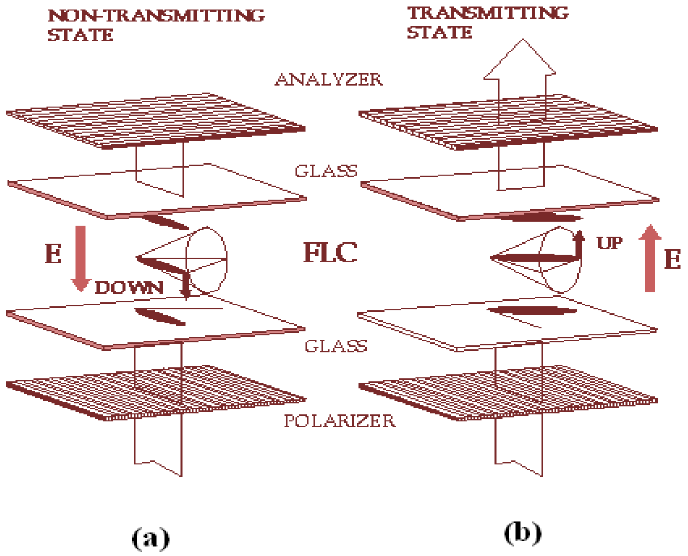


Figure 1.14: The basic construction of the SSFLC display device showing (a) off state and (b) on state [after reference 84]

In the surface-stabilized ferroelectric SmC* phase the helix is inherently absent. For unwinding the helix, the FLC material is to be taken in a cell where 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. In a SSFLC display device, the FLC material is taken in between two ITO coated glass plates which were pre-treated with aligning materials (polyimide or silicon dioxide). The molecules are aligned in a unidirectional manner called bookshelf geometry. When the planar layers of FLC material are arranged perpendicular to the glass plates of the display, the directions of the permanent electric dipoles are perpendicular to the long axis of the molecule (the director **n**). The cell is then placed in between polarizer and analyzer at the crossed position. The bottom polarizer is oriented in line with the molecular alignment direction. When a positive electric field is applied across the plates, the dipole wants to align toward one of the glass plates which make the director point to a particular direction. As soon as the field is reversed, the molecules will switch around an imaginary cone through an angle 2θ (θ is the tilt angle), as a result the dipole will rotate 180^o to point the other direction. Now, since the entering light is polarized along the director in one of these states, no light will be able to penetrate a crossed polarizer on the other side and the cell appears dark which is called OFF state. The application of the electric field will cause molecular rotation through $2\theta = 45^o$ since θ is around 22.5^o. Then the molecular alignment direction will be mid-way between the polarizer directions and hence the liquid crystal will be able to act as a half-wave retardation plate to allow light through. Thus the cell appears bright and it is called ON state. The device operation is clearly described in the article by Hird [84].

The main features of SSFLC display are that, it exhibits a fast response (~ μs order), wide viewing angle, high contrast ratio and bistable memory capability. Variety of novel FLC devices, including matrix-addressed arrays for displays and optical computing, linear arrays for printer applications, and single element switches for shuttering and light beam control are the targets in this research field.

1.4.4 DISCOTIC LIQUID CRYSTALS

Apart from the rod-like molecules, more advanced-shaped liquid crystals are possible such as disk-like liquid crystals which can give rise to another type of ordering. A discotic phase is one in which flat molecules typically with threefold or four fold symmetry that have a rigid core and several floppy side chains stacked with their planes lying roughly parallel to one another giving rise the director to be oriented roughly perpendicular to the plane of the molecule. There are two basic types of discotic mesophases that have been recognized viz., columnar and nematic. If the disks pack into stacks, the phase is called discotic columnar. On the other hand the nematic phase N_D exhibited by discotic materials shows similar optical textures as that of calamatic nematic phase N and has orientationally ordered arrangement of the disc without any long range positional order. Discotic mesophases have been reviewed by A. N. Cammidge, R J Bushby [85] and S. Kumar [86].

Figure 1.15: Molecular arrangement of discotic columnar liquid crystal

1.5 APPLICATIONS OF LIQUID CRYSTALS

From application point of view liquid crystal technology has a major effect in many areas of science and engineering, especially in device technology. Since liquid crystals are very sensitive to even weak external perturbations they are used in measurement of temperature, pressure and chemical contamination. Their dual nature and easy response to electric, magnetic and surface forces have generated innumerable applications in high-resolution TV displays, projection systems, optical computing, etc which are the tool for fundamental and basic research in physics, chemistry, space, engineering, mathematics, biology and medical sciences. Originally, nematic liquid crystals were used in calculators or digital watches and had only a few black-and-white pixels. But nowadays, LCD's are widespread in all kinds of applications such as flat panel displays for desktop applications or notebooks, laptops, tablets, mobile phones, projectors. Relatively low power consumption, low operating voltage and light weight etc. are the main advantages of liquid crystal displays (LCD’s) over other types of displays. Twisted nematic displays are still dominating the LCD field, as most of the displays produced today are either twisted nematic [87] or super-twisted [88] nematic displays. Recently, as a biomedical application, a simple, rapid and low-cost method has been reported for detecting Escherichia coli using a nematic liquid crystal (LC), 4-cyano-4’- pentylbiphenyl (5CB) [89].

Ferroelectric liquid crystal (FLC) technology [90,91] is enhanced broadly due to its fast switching and high resolution. These advantages and the possibility for dynamic gray scale and full color of SSFLC give it great potential for use in demanding applications such as high definition television (HDTV). The bistability offered by SSFLC devices makes them ideal where low energy consumption is concern. Polymer dispersed liquid crystals (PDLC) are also used in many types of displays [92].

Cholesteric liquid crystals are very useful for various applications. They are used in temperature sensitive devices, medical applications, thermometers, thermographs, visualization of RF (radio frequency) waves, tumor testing, battery testers, liquid crystal paints, mood rings, decoration and advertising. With the help of cholesteric liquid crystal technology skin infections and malignant skin tumours may be detected and located. It is possible due to the fact that the portion of the infected skin or tumor has higher temperature than the surrounding uninfected area. Liquid crystals are also used as anisotropic solvents for nuclear magnetic resonance (NMR) measurements, as solvents for the studies of infra red (IR) and ultra violet (UV) spectra of solute molecules in the form of liquid crystal films [92,93]. Lyotropic Liquid Crystals are important because of their role in biological applications [19]. Liquid crystals are used to detect electrically generated hot spots for failure analysis in the semiconductor industry. Liquid crystals are also used for lasing action. So a crucial contribution to this progress will be the design and synthesis of new liquid crystals having suitable applications.

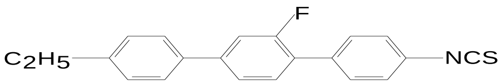
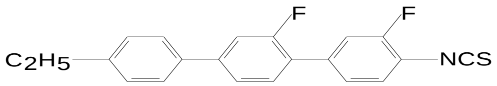
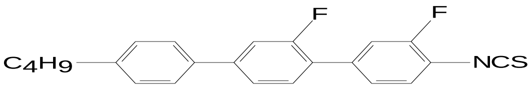
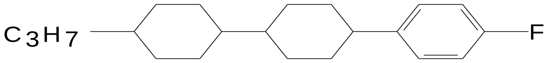
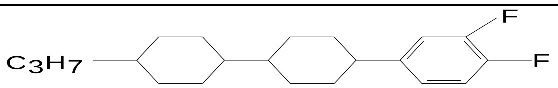
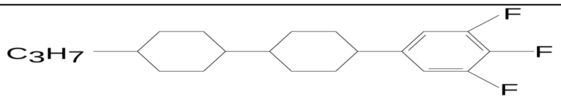
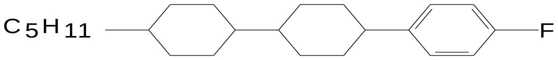
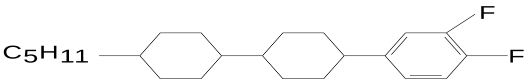
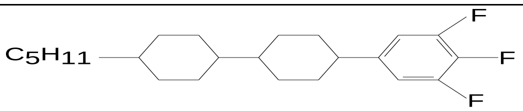
1.6 LIQUID CRYSTAL COMPOUNDS INVESTIGATED IN THE PRESENT DISSERTATION

In a liquid crystal the existence of different mesophases depend on the intermolecular association of the molecules constituting the liquid crystal. The existence as well as the thermal range of different mesophases can be modified by changing the degree of association between the molecules. One way of overcoming the strength of the pre-existing molecular association is by decreasing the melting temperature of the system so that different mesophases may arise before the isotropic phase is reached. Another way of modifying the molecular association is to introduce some substituents. The substituents are very limited and can be divided into two categories viz., multi-atomic (CH_3, OH, CN, NH_2, etc) and mono-atomic (F, Cl, B, I, etc). The substituents may increase or decrease the molecular association by increasing dipolar attraction or by increasing the separation of the molecules.

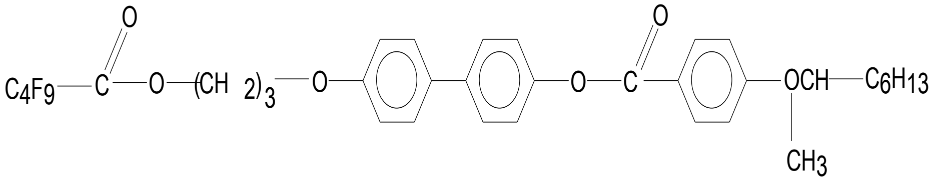
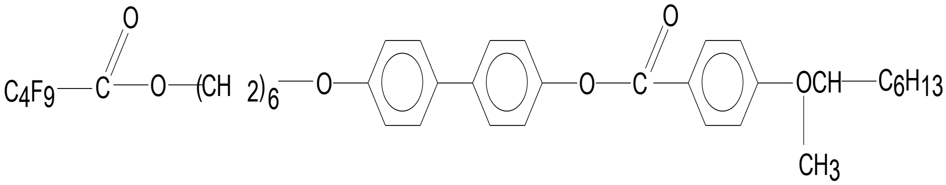
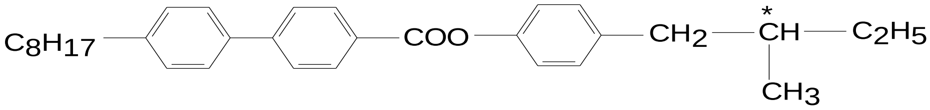
An effective mono-atomic substituent is fluorine (F). Fluorine is the most electronegative of all elements and its polarity is very high which produces a strong dipole moment thus affects the molecular association. For aliphatic or alicyclic compounds fluorine substitution causes a strong dipole moment which is introduced by the C(δ+)-F(δ-) bond and the inductive effect arising from the high electro negativity of fluorine. The fluorine substitution can be introduced in different positions within a molecular structure to modify the properties of the parent system. Fluoro substitution at the terminal position enhances the dielectric anisotropy and elastic constants because of the introduction of high polarity C-F bond. Compounds having terminal fluoro substitution posses a high resistivity, high photo-chemical stability and low viscosity which is suitable for active matrix (thin-film transistor, TFT) displays. Another way of introducing fluorine is at the lateral position. Lateral fluoro substitution reduces the melting points of the compounds and also reduces the smectic phase stability. Additionally, fluoro substitution generates molecular tilting and thus produces smectic C phase which are essential for ferroelectric and antiferroelectric phase formation. Besides, fluoro substituted cyano compounds produce a large positive dielectric anisotropy which is used for low voltage switching in twisted nematic LCDs. Keeping these in view a number of achiral and chiral fluorinated compounds were therefore selected for investigation in the present dissertation. Their abbreviated names with molecular structures and transition temperatures are given in Table 1.1.

Table 1.1: Molecular structures and transition temperatures of the investigated compounds

ACHIRAL COMPOUNDS

Sl. No	Name	Molecular structure with transition temperature
1	2TP-3'F-4NCS	 Cr 102.5°C SmA 120.5°C N 188.2°C I
2	2TP-3',3F-4NCS	 Cr 80.2°C N 188°C I
3	4TP-3',3F-4NCS	 Cr 58.1°C SmA 96.9°C N 181.8°C I
4	3ccp-f	 Cr 90.0 (71.0) N 158.0 I
5	3ccp-ff	 Cr 45.6 N 123.8 I
6	3ccp-fff	 Cr 64.7 N 93.7 I
7	5ccp-f	 Cr 68.0 SmB 75.0 N 157.0 I
8	5ccp-ff	 Cr 47.0 (26.8) N 125.2 I
9	5ccp-fff	 Cr 87.3 N 101.2 I

CHIRAL COMPOUNDS

Sl. No	Name	Molecular structure with transition temperature
10	**4F3R**	 **Cr 79.8°C SmC* 134.1°C I**
11	**4F6R**	 **Cr$_1$ 46.7°C Cr$_2$ 60.0°C SmC$_A^*$ 86.5°C SmC* 128.3°C I**
12	**MPOBC**	 **Cr 48 SmG* 63 SmJ* 65 SmF* 67 SmI* 71 SmC* 81 SmA* 136 N* 139 BP* 140 Iso**

1.7 REFERENCES

[1] G. Durand and J. D. Lister; Ann. Rev. Mate. Sci., 23, 269 (1973), Recent advances in liquid crystals.

[2] T. J. Sluckin, D. A. Dunmur and H. Stegemeyer, Crystals That Flow: Classic Papers from the History of Liquid Crystals, History of Physics Group Newsletter, Institute of Physics (2006).

[3] O. Lehmann; Z. physik. Chem. 4, 462- 472 (1889), Fließende Kristalle.

[4] F. Reinitzer; Monatshefte fur Chemie., 9, 421-441(1888), Beitrage Zur Kenntnis des Cholesterins.

[5] G. Freidel; Ann. Physique (Paris), 18, 273 (1922), Les états mésomorphes de la matiére.

[6] V. Vill; Liq. Cryst 3.4 Database, LC publisher GmbH, hamburg, May (2000).

[7] H. Kelker and R. Hatz; Verlag Chemie, Chapter 1 (1980), Hand Book of Liquid Crystals.

[8] H. Kelker; Mol. Cryst. Liq. Cryst., 21, 1 (1973), History of liquid crystals.

[9] H. Kelker and P. M. Knoll; Liquid. Cryst. 5(1), 19 (1989), Plenary Lecture: Some pictures of the history of liquid crystals.

[10] G. W. Gray; Mol. Cryst. Liq. Cryst., 63, 3 (1981), Comments on some recent development in the field of liquid crystals.

[11] G. W. Gray; Liq. Cryst., 24(1), 5 (1998), Reminiscences from a life with liquid crystals.

[12] P. J. Coolings and M. Hird, Introduction to Liquid Crystals Chemistry and Physics, Taylor & Francis (1998).

[13] G. W. Gray and H. Finkelmann in Polymeric Liquid Crystals, ed. A. Ciferri, W. R. Krigbaum and Robert B. Meyer, AP, chap-1 and chap-2 respectively (1982).

[14] D. Demus; Mol. Cryst. Liq. Cryst., 364, 25 (2001), One century liquid crystal chemistry: from Vorlander's rods to disks, stars and dendrites and G. W. Gray in Handbook of Liquid Crystals. Vol. 1 (Fundamentals), Ed. D. Demus, J. W. Goodby, G. W. Gray, H.-W. Spiess and V. Vill, Introduction and Historical Development, WILEY-VCH, Verlag GmbH, Weinheim, FRG (1998).

[15] S. Chandrasekhar, B. K. Sadashiva and K. A. Suresh; Pramana, 9, 471- 480 (1977), Liquid crystals of disc-like molecules.

[16] J. Billard, J. C. Dubois, T. H. Nguyen and A. Zann; Nouveau J. Chim. 2, 535-540 (1978), Une mésophase disquotique.

[17] Liquid Crystals Application and Uses Vol. 1-3. Ed. B. Bahadur, World Scientific, (1990-1992).

[18] G. W. Brown, J. W. Doane and V. D. Neff, A Review of the Structure and Physical Properties of Liquid Crystals. CRC Press, Cleveland, Ohio (1971).

[19] J. W. Goodby; Liq. Cryst. 24, 25-38 (1998), Liquid crystals and life.

[20] P. G. de Gennes; "The Physics of Liquid Crystals", Clarendon Press, Oxford (1974); P. G. de Gennes and J. Prost, 2nd ed. Clarendon Press, Oxford (1993).

[21] L. A. Madsen, T. J. Dingemans, M. Nakata, E. T. Samulski; Phys. Rev. Lett. 92 (14) (2004), Thermotropic Biaxial Nematic Liquid Crystals.

[22] A. de Vries; Mol. Cryst. Liq. Cryst., 10, 31 (1970), Evidence for the Existence of More Than One Type of Nematic Phase.

[23] A. de Vries; Mol. Cryst. Liq. Cryst., 10, 219 (1970), X-Ray Photographic Studies of Liquid Crystals I. A Cybotactic Nematic Phase and A. de Vries, in Proc. of the International Liquid Crystal Conference, Bangalore, December, Pramana Supplement I, 93 (1973), X-Ray Studies of Liquid Crystals: V. Classification of Thermotropic Liquid Crystals and Discussion of Intermolecular Distances.

[24] P. E. Cladis; Phys. Rev. Lett., 35, 48-51 (1975), New Liquid-Crystal Phase Diagram.

[25] G. W. Gray, Molecular Structure and the Properties of Liquid Crystals, Academic Press, London (1962).

[26] P. S. Pershan, Structure of Liquid Crystals Phases, World Scientific Lecture Note in Physics, Vol 23, World Scientific, Singapore (1988).

[27] G. W. Gray and J. W. Goodby, Eds., Smectic Liquid Crystals, Textures and Structures, Leonard‑Hill, Philadelphia (1984).

[28] A. J. Leadbetter in Thermotropic Liquid Crystals, Critical Reports on Applied Chemistry, Vol. 22, G. W. Gray(Ed.),Wiley, Chichester, p1 (1987).

[29] A. de Vries in Liquid Crystals, The Fourth State of Matter (Ed. F. D. Saeva), Marcell Dekker, New York, p1 (1972).

[30] A. de Vries, Mol. Cryst. Liq. Cryst., 63, 215(1981), A Structural Classification of Smectic Liquid Crystals.

[31] J. Doucet in The Molecular Physics of Liquid Crystals, Eds. G. R. Luckhurst and G. W. Gray, Academic Press, London, p317 (1979).

[32] L. V. Azaroff, Mol. Cryst. Liq. Cryst., 60, 73(1980), X-Ray Diffraction by Liquid Crystals.

[33] D. Demus, J. W. Goodby, G. W. Gray and H. Sackmann, Mol. Cryst. Liq. Cryst., 56, 311(1980), Recommendation for The Use of The Code Letters G And H for Smectic Phases.

[34] J. W. Goodby and G. W. Gray, Mol. Cryst. Liq. Cryst., 41, 145-150 (1978), Some New Smectic F Materials.

[35] R. M. Richardson, A. J. Leadbetter and J. C. Frost, Mol. Phys., 45, 1163 (1982), A comparative study of the molecular motions in the three smectic phases of isobutyl 4(4′ phenylbenzylideneamino) cinnamate using incoherent neutron scattering.

[36] A. J. Leadbetter, J. C. Frost, J. P. Gaughan, and M. A. Mazid, J. Phys. (Paris), 40, C3-185-C3-192 (1979), The structure of the crystal, smectic E and smectic B forms of IBPBAC.

[37] J. W. Goodby in Handbook of Liquid Crystals, Eds. D. Demus, J. Goodby, G.W. Gray, H.-W. Spiess and V. Vill, Vol. 2A, Wiley-VCH, Verlag GmbH, Weinheim, FRG, p7 (1998).

[38] F. Hardouin, A. M. Levelut, J. Bennattar and G. Sigaud; Solid State Comm., 33, 337-340 (1980), X-rays investigations of the smectic A1 - smectic A2 transition.

[39] A. J. Leadbetter, J. L. Durrant and M. Rugman; Mol. Cryst. Liq. Cryst. Lett., 34, 231 (1977), The Density Of 4 n-Octyl-4-Cyano-Biphenyl (8CB).

[40] A. J. Leadbetter, J. C. Frost, J.P. Gaughan, G.W. Gray and A. Mosley; J. Phys. (Paris), 40, 375-380 (1979), The structure of smectic A phases of compounds with cyano end groups.

[41] F. Hardouin, G. Sigaud, N. H. Tinh, A.F. Achard; J. Phys. (Paris) Lett., 42, 63-66 (1981), A fluid smectic A antiphase in a pure nitro rod-like compound.

[42] J. Prost; Advances in Physics, 33, 1-46 (1984), The smectic state.

[43] P. S. Pershan, Structure of Liquid crystals, World Scientific, Singapore (1988).

[44] B. R. Ratna, R. Shashidhar and V. N. Raja, Phys. Rev. Lett.; 55(14), 1476 (1985), Smectic-A phase with two collinear incommensurate density modulations.

[45] S. T. Wang, S. L. Wang, X. F. Han, Z. Q. Liu, S. Findeisen, W. Weissflog and C. C. Huang; Liq. Cryst., 32, 5, 609–617 (2005), Optical studies on two tilted smectic phases of meta-substituted three-ring liquid crystal compounds.

[46] A. L. Tsykalo, Thermophysical properties of liquid crystals, Gordon and Breach Science Publishers (1991).

[47] R. Pindak, D. E. Moncton, S. C. Davey and J. W. Goodby; Phys. Rev. Lett., 46, 1135 (1981), X-Ray Observation of a Stacked Hexatic Liquid-Crystal B Phase.

[48] D. E. Moncton and R. Pindak in Ordering in Two Dimensions (Ed. S. K. Sinha), North Holland, New York, p83 (1980).

[49] A. J. Leadbetter, J. C. Frost, M. A. Mazid; J. Phys. (Paris) Lett., 40, 325-329 (1979), Interlayer correlations in smectic B phases.

[50] P. S. Pershan, G. Aeppli, J. D. Litster and R. J. Birgeneau; Mol. Cryst. Liq. Cryst., 67, 205(1981), High-Resolution X-ray Study of the Smectic A-Smectic B Phase Transition and the Smectic B Phase in Butyloxybenzylidene Octylaniline.

[51] D. E. Moncton, and R. Pindak; Phys. Rev. Lett., 43, 701(1979), Long-Range Order in Two- and Three-Dimensional Smectic-B Liquid-Crystal Films.

[52] P. A. C Gane, A. J. Leadbetter and P.G. Wrighton; Mol. Cryst. Liq. Cryst., 66, 247-266 (1981), Structure and Correlations in Smectic B, F and I Phases.

[53] S. Diele, D. Demus and H. Sackmann; Mol. Cryst. Liq. Cryst. Lett. , 56, 217 (1980), X-Ray Studies in the n-Pentyl 4-[4-n-Dodecyl-Oxybenzylidene-Amino]-Cinnamate in the S_I Phase.

[54] J. J. Benattar, F. Moussa, M. Lambert; J. Phys. (Paris) Lett., 42, 67-70 (1981), Two kinds of two-dimensional order : the SmF and SmI phases.

[55] A. M. Levelut, J. Doucet and M. Lambert; J. Phys., (Paris), 35, 773-779 (1974), X-ray study of the nature of the smectic B mesophases and of the solid-smectic B phase transition.

[56] J. Doucet, P. Keller, A.M. Levelut and P. Porquet; J. Phys. (Paris), 39, 548-553 (1978), Evidence of two new ordered smectic phases in ferroelectric liquid crystals.

[57] A. J. Leadbetter, M. A. Mazid, R. M. Richardson, in Liquid Crystals, Ed. S. Chandrasekhar, Heyden, London, p65 (1980).

[58] J. L. Fergason; Sci. Am., 211, 76-85 (1964), Liquid Crystals.

[59] D. Demus, J. Goodby, G.W. Gray, H.-W. Spiess and V. Vill, Handbook of Liquid Crystals, Ch. IV and V, Vol. 2A, Wiley-VCH, Verlag GmbH, Weinheim, FRG (1998).

[60] F. D. Saeva; Mol. Cryst. Liq. Cryst., 23, 171-177 (1973), On the Relationship between Cholesteric and Nematic Mesophases.

[61] T. Nakagiri, H. Kodama and K.K. Kobayashi; Phys. Rev. Lett., 27, 564-567 (1971), Helical Twisting Power in Mixtures of Nematic and Cholesteric Liquid Crystals*.

[62] I. G. Chistiyakov; Sov. Phys. Usp., 9, 551-573 (1967), Liquid Crystals.

[63] A. Saupe; Angew. Chem. Intnl. Edn. 7, 97-112 (1968), Recent Results in the Field of Liquid Crystals.

[64] A. Hochbaum, Fluorescent Guest-Host in Scattering Liquid crystals and New Physical Phenomena in Thin Liquid Crystal Films (Ph.D. Thesis), Temple University, p.5 (1980).

[65] J. J. Wysocki, J. Adams and W. Hasse; Phys. Rev. Lett., 20, 1024-1025 (1968), Electric-Field-Induced phase change in cholesteric liquid crytals.

[66] H. Baessler and M. M. Labes; Phys. Rev. Lett., 21, 1791-1793 (1968), Relationship Between Electric Field Strength and Helix Pitch in Induced Cholesteric-Nematic Phase Transitions.

[67] O. Lehmann; Z Phys. Chem, 56, 750 (1906).

[68] Harry J Coles, Pivnenko, N. Mikhail; Nature 436 (7053), 997–1000 (2005), Liquid crystal 'blue phases' with a wide temperature range.

[69] Jun Yamamoto, Isa Nishiyama, Miyoshi Inoue, Hiroshi Yokoyama; Nature, 437 (7058): 525 (2005), Optical isotropy and iridescence in a smectic blue phase.

[70] R. M. Hornreich and S. Shtrikman; J. Physique, 41, 335-340 (1980), A body-centered cubic structure for the cholesteric blue phase.

[71] H. Kikuchi, M. Yokota, Y. Hisakado, H Yang, T. Kajiyama; Nature Materials, 1 (1): 64–8 (2002), Polymer-stabilized liquid crystal blue phases.

[72] R. B. Meyer, L. Liebert, L. Strzelecki and P. Keller; J. Phys. Lett. 36, L69-L71 (1975), Ferroelectric liquid crystals.

[73] S. Pirke and M. Glogorova in Ferroelectric – Physical Effects; Ed, M. Lallart, INTECH, Rijeka, Croatia (2011).

[74] S. Pirkl and M. Glogarova; Intech, Croatia (2011), Ferroelectric liquid crystals with high spontaneous polarization.

[75] R. B. Meyer; Mol. Cryst. Liq. Cryst., 40, 33-48 (1977), Ferroelectric liquid crystals: A review.

[76] Yu. P. Panarin, O. Kalinovskaya & J. K. Vij; Liquid Crystals, Vol. 25, No. 2, 241- 252 (1998), The investigation of the relaxation processes in antiferroelectric liquid crystals by broad band dielectric and electro-optic spectroscopy.

[77] A. D. L. Chandani, E. Gorecka, Y. Ouchi, H. Takezoe, and A. Fukuda; Jpn. J. Appl. Phys. 28(7), L1265 (1989), Antiferroelectric Chiral Smectic Phases Responsible for the Trislable Switching in MHPOBC.

[78] H. Hiraoke, A. D. L. Chandani, E. Gorecka, Y. Ouchi, H. Takezoe and A. Fukuda; Jpn. J. Appl. Phys. 29(8), L1473 (1990), Electric-Field-Induced Transitions among Antiferroelectric, Ferrielectric and Ferroelectric Phases in a Chiral Smectic MHPOBC.

[79] J. P. F. Lagerwall, P. Rudquist, S. T. Lagerwall and F. Gieβelmann; Liq. Cryst., 30, 399-414 (2003), On the phase sequence of antiferroelectric liquid crystals and its relation to orientational and translational order.

[80] K. Miyachi and A. Fukuda, in Handbook of Liquid Crystals, Eds. D. Demus, J. Goodby,

G.W. Gray, H.-W. Spiess and V. Vill, Vol. 2B, Wiley-VCH, Verlag GmbH, Weinheim, FRG, Ch. 3 (1998).

[81] J. Dijon in Liquid Crystal Application and Uses (Ed. B. Bahadur), Vol. I, World Scientific, Singapore, p 305 (1990).

[82] N. A. Clark and S. T. Lagerwall; Appl. Phys. Lett., 36, 899-901(1980), Submicrosecond bistable electrooptic switching in liquid crystals.

[83] D. Armitage, J. I. Thakara and W. D. Eades; Ferroelectrics, 85, 291-302 (1988), Ferroelectric liquid-crystal devices and optical processing.

[84] M. Hird; Liq. Cryst., 38, 1467–1493 (2011), Invited topical review (Ferroelectricity in liquid crystals - materials, properties and applications).

[85] A. N. Cammidge and R. J. Bushby in Handbook of Liquid Crystals, Eds. D. Demus, J.

Goodby, G.W.Gray, H.-W. Spiess and V. Vill, Vol. 2B, Wiley-VCH, Verlag GmbH, Weinheim, FRG, Ch.VII (1998).

[86] S. Kumar; Liquid Crystals, 31, 1037-1059 (2004), Recent developments in the chemistry of triphenylene-based discotic liquid crystals.

[87] M. Schadt and W. Helfrich; Appl. Phys. Lett. 18(4), 127 (1971), Voltage-dependent optical activity of a twisted nematic liquid crystal.

[88] T. J. Scheffer and J. Nehring; Appl. Phys. Lett. 45(10), 1021 (1984), A new, highly multiplexable liquid crystal display.

[89] H. Xu, D. Hartono and K. -L. Yang, Liquid Crystals, 37 (10), 1269–1274 (2010), Detecting and differentiating Escherichia coli strain TOP10 using optical textures of liquid crystals.

[90] J. Akaogi, Y. Koizumi, M. Ono and H. Furue; Mol. Cryst. Liq. Cryst., 596, 106–112 (2014), Application of Ferroelectric Liquid Crystals to Optical Devices.

[91] J. S. Patel and Seong-Woo Suh; Journal of the Korean Physical Society, 32, S1048-S1051 (1998), Ferroelectricity in Liquid Crystals and Its Applications.

[92] C. L. Khetrapal in Liquid Crystals in the Nineties and Beyond, Ed. S. Kumar, World Scientific, p 435 (1995).

[93] B. Bahadur in Handbook of Liquid Crystals,Eds. D. Demus, J. Goodby, G.W. Gray, H.-W. Spiess and V. Vill, Vol. 2A, Wiley-VCH, Verlag GmbH, Weinheim, FRG, p257 (1998).