1. Introduction

It has been recognized that, under appropriate conditions of temperature and pressure, matter may exist in three possible states of aggregation the solid, the isotropic liquid and the gas. The molecule in a solid possesses positional order. The liquid state is quite different in that the molecules neither occupy a specific average position nor remain oriented in particular way. When a solid melts to isotropic liquid, both types of order are lost completely; the molecules move and tumble randomly. However, in certain compounds while the thermal energy received at a definite stage is able to cause flow making the domain structure loosened to an extent, yet it is not enough to shatter the order of crystallinity completely. A sort of residual orderly orientation of molecules persists until another temperature is reached which totally eliminates regularity of structure altogether. Between these two transitions, both being definite the properties displayed are unique indeed. This state of existence is independent within the definite temperature range and is neither totally crystallinity nor completely liquid, but has properties of both. The state is known as “mesophase” or “mesomorphic state”. This term, derived from the Greek, *mesos,* between or intermediate and phasis, a state or phase, does stress the intermediate nature of these state of matter. The phenomenon is known as “mesomorphism”; the compounds that exhibit this unique property are called “Liquid Crystals” or “mesomorphs” or “mesogens”. Liquid Crystals, as their name suggests are a phase of matter that is intermediate between an isotropic liquid and a crystalline solid. Schematic representation of solids, liquid crystals and liquid is given in Figure 1.1. Liquid crystals exhibit optical properties of solid and mechanical properties of a liquid. The degrees of molecular order in liquid crystalline state are intermediate between those of ordered crystals and disordered liquids.

The molecules in the liquid crystal phase are free to move about in much the same fashion as in a liquid, but as they do so they tend to remain oriented in a certain direction. Liquid crystals are self – organizing anisotropic fluids whose properties can be changed by the application of electric or magnetic fields. This allows them to be used in display devices such as laptop computer screens. The liquid crystalline state can be divided into a number of mesophase (or sub-mesophase) and many liquid crystals have a number of phase transitions between these mesophases.

1.1 History of Liquid Crystals

Liquid crystals are well known today to a broad community in vital range of widest vista. The liquid crystals discovered in 1888 by an Australian botanist named Friedrich Reinitzer [1]; when Reinitzer observed the melting behavior of cholesteryl benzoate and he found a phenomenon of double melting point; on heating this ester, the solid first melted to an opaque liquid exhibiting pictorial color, which, on further heating transformed to an optically clear liquid, on cooling pictorial colours reappears to an opaque liquid. It is followed by Lehmann [2] who striked the word ‘Liquid Crystals’ to describe the phenomenon. Soon after, Gatterman and Ritchke [3] and vorlander [4] investigated several liquid crystalline compounds. The apogee of all these efforts is the classification scheme by Friedel in 1922 [5]. Friedel and Friedel [6] proposed the term ‘mesomorphic state’ as the phase is an intermediate of a crystalline solid and an isotropic liquid. Brown and Shaw [7] used the term ‘mesomorphism’ for the title of their first review. Studies on the physical properties of liquid crystals are carried out in 1930’s; after which work on this field slowed down. Shortly before 1960, it once again gained momentum and then the progress is swift and highly substantial.

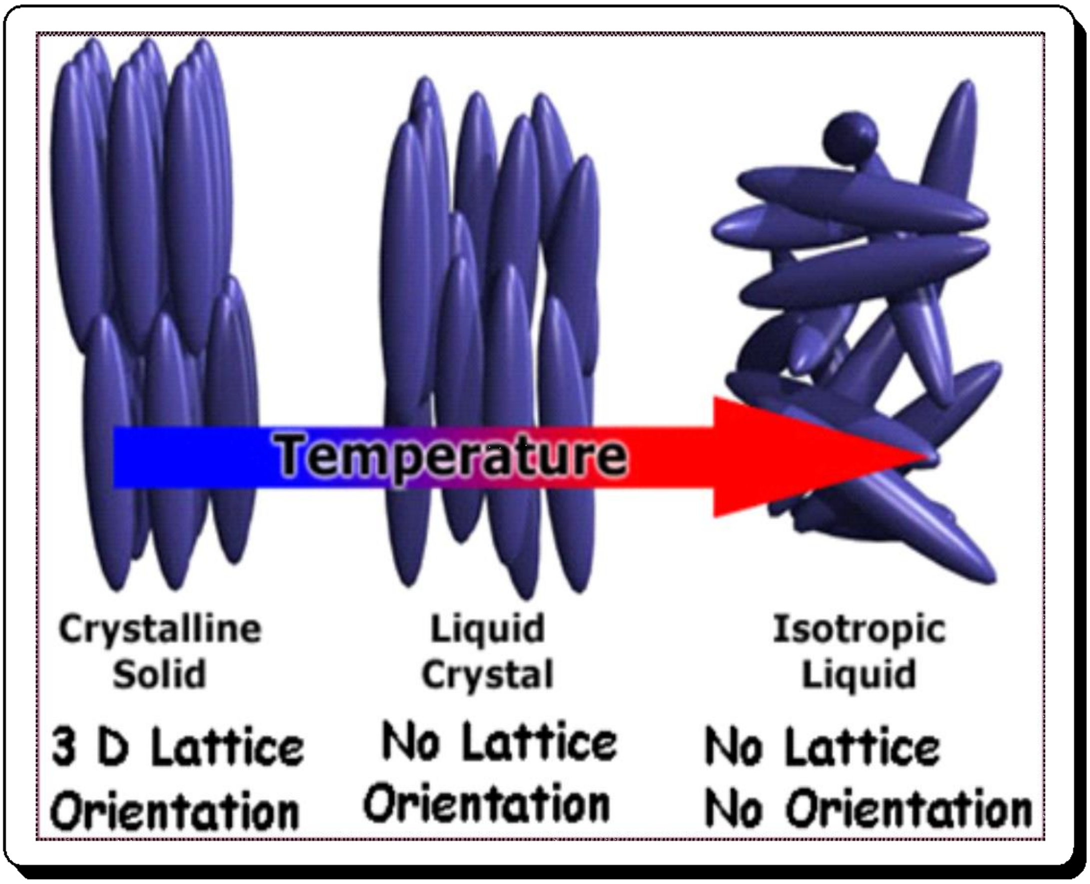

Figure 1.1: Schematic representation of solid, liquid crystals and liquid

1.2 Classification of Liquid Crystals

Liquid crystals are classified into two main categories according to the manner in which they are obtained.

(1) Thermotropic liquid crystals (2) Lyotropic liquid crystals

Liquid crystalline property is exhibited either by action of heat or by action of solvents. In thermotropic liquid crystals the change in the molecular ordering is brought about by variation in temperature whereas in lyotropic liquid crystals this is brought about by the effect of solvent on suitable substrates. Gray [8] classified lyotropic and thermotropic liquid crystals as amphiphilic and non-amphiphilic mesogens, respectively.

1.3 Thermotropic Liquid Crystals

Mesophases in thermotropic liquid crystals are most commonly observed when a suitable compound is heated to a temperature above that at which the crystal lattice is stable this type of mesomorphism is termed as thermotropic mesomorphism.

The thermal motions of the molecules within the lattice increase and eventually the vibrations become so intense on heating a fully ordered molecular crystal, which broken do the regular arrangement with the loss of range of orientational and positional order to give disorganized isotropic liquid. However for many compounds, this process occurs by way of one or more intermediate phases as the temperature is increased; form anisotropic fluids these phases are know mesophases.

On heating, liquid crystals exhibits first mesophase and then change into an isotropic liquid on further heating, which is reversible. On cooling, isotropic liquid changes to liquid crystalline phase and on further cooling solidifies; however many times super cooling takes place. The mesomorphic transition which occurs on heating the sample and reverses in opposite order on cooling is termed as enantiotropic mesomorphic state and the mesomorphism is known as enantiotropic mesomorphism (Figure 1.2). The sequence of changes of state for a compound which exhibits enantiotropic mesophases may be illustrated as below.

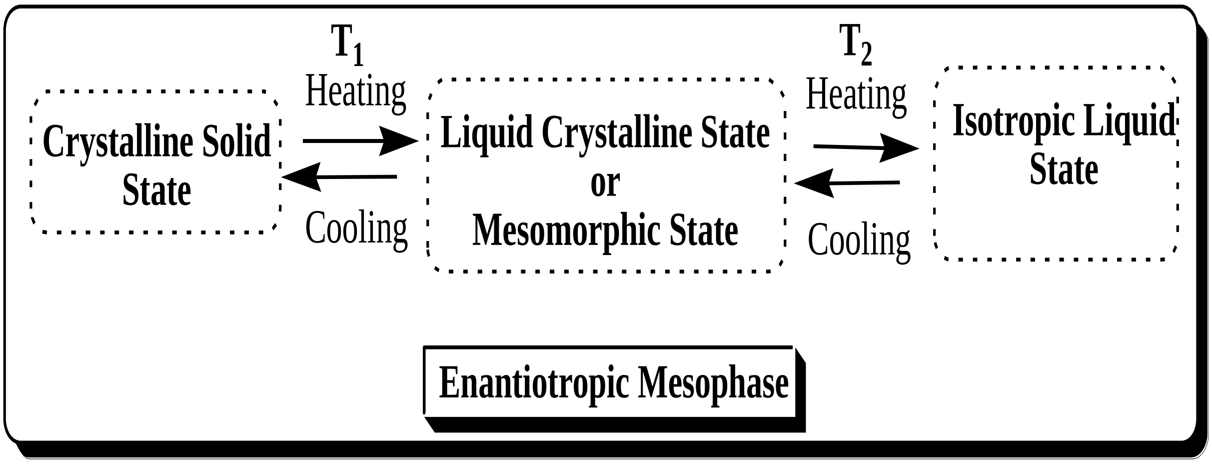

Figure 1.2: Enantiotropic mesomorphism

However, when a crystalline compound melts normally to give the isotropic liquid on heating, but on cooling the isotropic liquid exhibits a mesophase, before crystallization is known as monotropic mesomorphism. This kind of mesophase is termed as monotropic mesomorphic state. The sequence of changes of state for a compound which exhibits monotropic mesomorphism **(**Figure 1.3) may be illustrated as below.

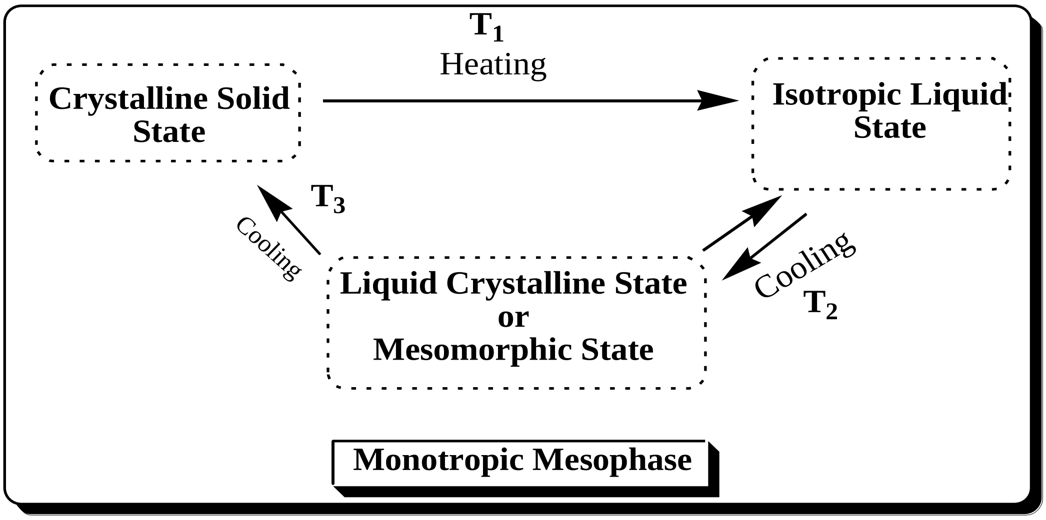

Figure 1.3: Monotropic mesomorphism

Most of the liquid crystals fall into the category of thermotropic liquid crystals. The vast majority of thermotropic liquid crystals are composed of rod like molecules and according to a modern proposal [9] may also be called calamitic liquid crystals', (In Greek – calamos means rod). They are classified broadly into three types: Smectic, Nematic and Cholesteric. Liquid Crystalline compounds may either exclusively be smectic or nematic or smectic and nematic or smectic and cholesteric. They may exhibit polymesomorphism. The transition temperatures are always definite and define the stability of different mesophases. Schematic representation of phase sequence for liquid crystals is given in Figure 1.4. The changes with increasing may be represented as;

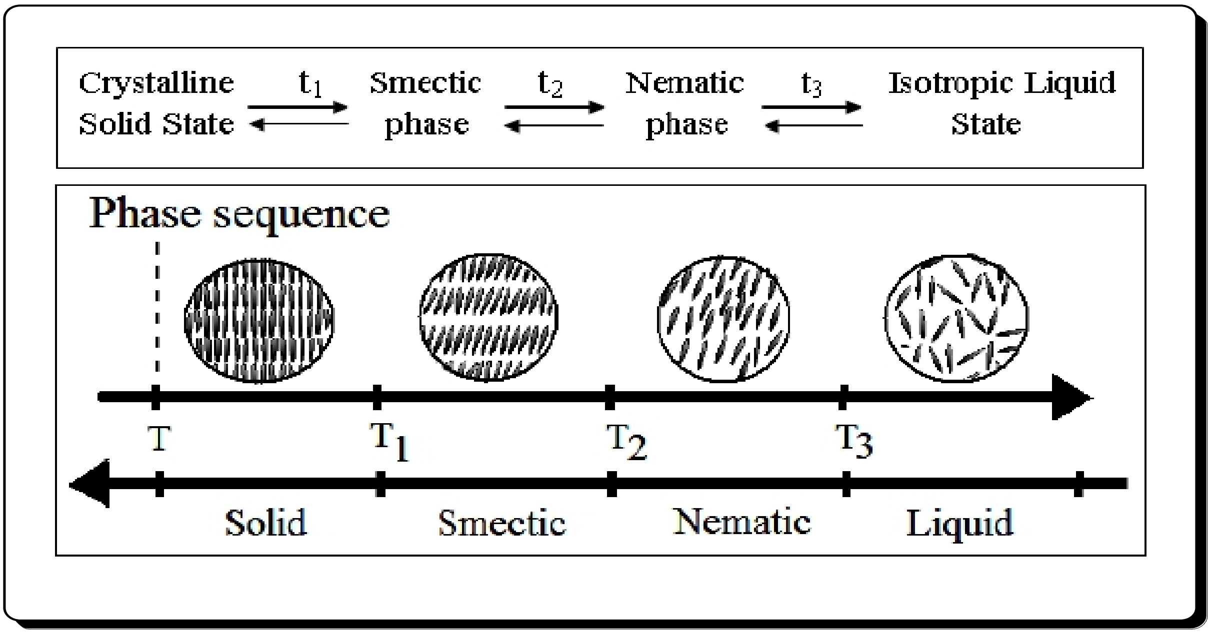

Figure 1.4: Schematic representation phase sequence for calamitic liquid crystals

1.3.1 Smectic Liquid Crystals

The smectic word derived from the Greek word ‘smectose’ for soap. Smectic mesophase is the most ordered one, which is turbid and viscous. The melting process disruptsthe end to end molecular cohesion, but the energy received at the temperature at which the smectic mesophase is stable is not sufficient to break down lateral cohesion. Evidently while the substance gets loosened and acquires a little flow, the lateral adhesion and layers remain essentially intact eventually retaining a two dimensional order. Thus the smectic state is another distinct mesophase of liquid crystal substances. Moloecules in this phase show a degree of translation order not present in the nematic. In the smectic state, the molecules maintain the general orientation order of nematic , but also tend to align themselves in layers or planes. Motion is restricted to within these planes and separate planes are observed to flow past each other. The increased order means that the smectic state is more “solid – like” than the nematic.

Hermann [10] and saupe [11] have classified the smectic phases in to two classes; smectic phases with unstructured layers and smectic phases with structured layers. The extensive work of Sackmann and Demus [12] has revealed some of the detailed arrangements of these phases and classified smectic phases according to the texture observed in the mesophase. (Table 1.1); Moreover, de Vries [13,14] has classified smectic into three main classes on the basis of X-ray studies. The class first contains smectic A, C, F and D , the class second contains smectic E, G and H , the class third contains the smectic B. Levelut et at [15] have designated smectic O phase in 1-(methyl)-heptyl-terephthalidene-bis-amino cinnamate. Bennemann et al [16] have reported some mesogenic chiral compounds, which show a smectic Q phase just below the clearing point. Bennemann, Beppke and Lotzsch [17] have carried out structural investigation of smectic Q phase. Schematic representation of different smectic phases is given in Figure 1.5.

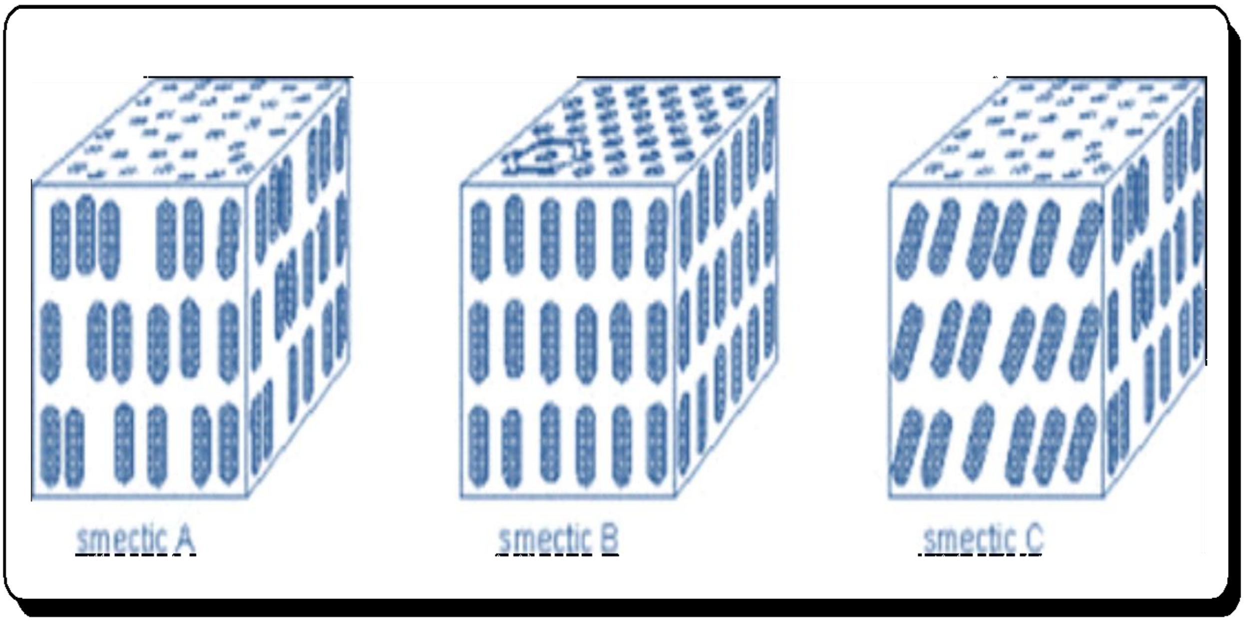

Figure 1.5: Schematic representation of smectic phases

Table 1.1: Texture classification of smectic phases

Type of smectic phase	Structure	Texture
Smectic A	Planar	1. Stepped drops 2.Oily streaks 3. Homeotropic
	Non-Planar	1.Simple Diagonal 2. Simple Fan shaped 3. Focal conic fan shaped 4. Batonnets 5. Bubble texture
	Cylinders	1.Myelinic Texture
Smectic C	Planar	1.Homogeneous 2.Stepped Drops 3.Schlieren
	Non-Planar	1.Broken polygonal 2.Broken fan shaped 3.Batonnets
	Twisted	1.planar 2.Schlieren 3.Straited fan shaped
Smectic F	Planar	1. Schlieren 2. Stepped Drops
	Non-planar Dupin Cyclides	1.Stipped broken fan
Smectic B	Hexagonal	1. Mosaic 2.Homeotropic 3.Stepped drops 4. Batonnets 5.Ovals 6.Lacets
	Non-planar Dupin Cyclides	1.Focal conic fan shaped
	Tilted	1. Mosaic 2. Planar
Smectic E	Planar	1.Mosaic 2.Stepped
	Non-Planar	1.Straited 2.Stripped fan shaped
Smectic G	Planar	1. Mosaic 2.Stepped drops
Smectic D	Cubic bands	1. Isotropic Mosaic

1.3.2 Nematic Liquid Crystals

The nematic Liquid Crystal phase is characterized by molecules which have no positional order but tend to point in the same direction. The word "Nematic" is derived from a greek word 'Nema' meaning threads as the phase exhibits threaded schlieren texture. The molecules in phase are arranged with their long axis parallel to each other but they are not separated in layers. de vries [18] proposed classification of nematic phase based on X-ray diffraction pattern as follows:

1. Skewed cybotactic Nematic.
2. Normal Cybotactic Nematic
3. Classical Nematic

Schematic representation of nematic phase is given in Figure 1.6, which shows that the molecules point vertically but are arranged with no particular order.

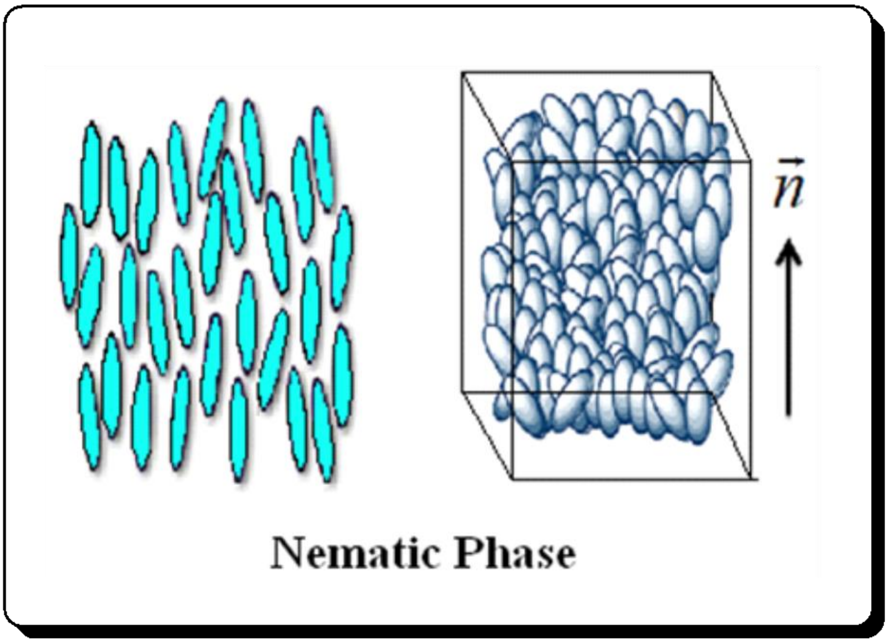

Figure 1.6 : Schematic representation of Nematic phase

The molecules in the nematic phase exist in the form of groups, each group consisting about 1,00,000 parallel molecules. These groups are referred to as swarms, The 'Swarms theory' was first proposed by E. Bose [19] in 1909, to explain the molecular arrangement and order in the nematic phase.

Nematic liquid crystals are optically positive and can be formed by compounds which are optically inactive or by recemic modification. A new type of mesophase is obtained by Zimmer and White [20], during the process of carbonisation and is termed ascarbonaceous mesophase. This phase was later studied in detail by Gasparoux [21]. Number of workres have reported re-entrant nematic below the smetic phase [22,23], which is generally exhibited by a few compounds possessing a nitro or cyano end group with positive dielectric anisotropy.

1.3.3 Cholesteric Liquid Crystals

The phase which, in, most regards, is similar to the nematic phase but with chiral structure is known as the cholesteric phase. This phase is exhibited by compounds composed of chiral molecules or if chiral dopants [24-26] are added to a non - chiral (regular) nematic. The name is based on the fact that derivatives of the infamous cholesteryl benzoate [1] are initially found to exhibit this phase. In this phase molecules are arranged themselves in a helical structure. The phase can be described as being made up of nematic planes helically piled over one another so that the director is rotating uniformally about the director normal. Certain cholesteric compounds can selectively scatter light into different colours. The colours of the reflected light can be determined by (a) a pitch of helix (b) by temperature (c) the angle of incident beams. Physical effects, which wind or unwind the helix such as temperature, mechanical disturbance like pressure or shear traces of organic vapors results in various color changes. Schematic representation of Cholesteric phase and helical structure is shown in Figure 1.7.

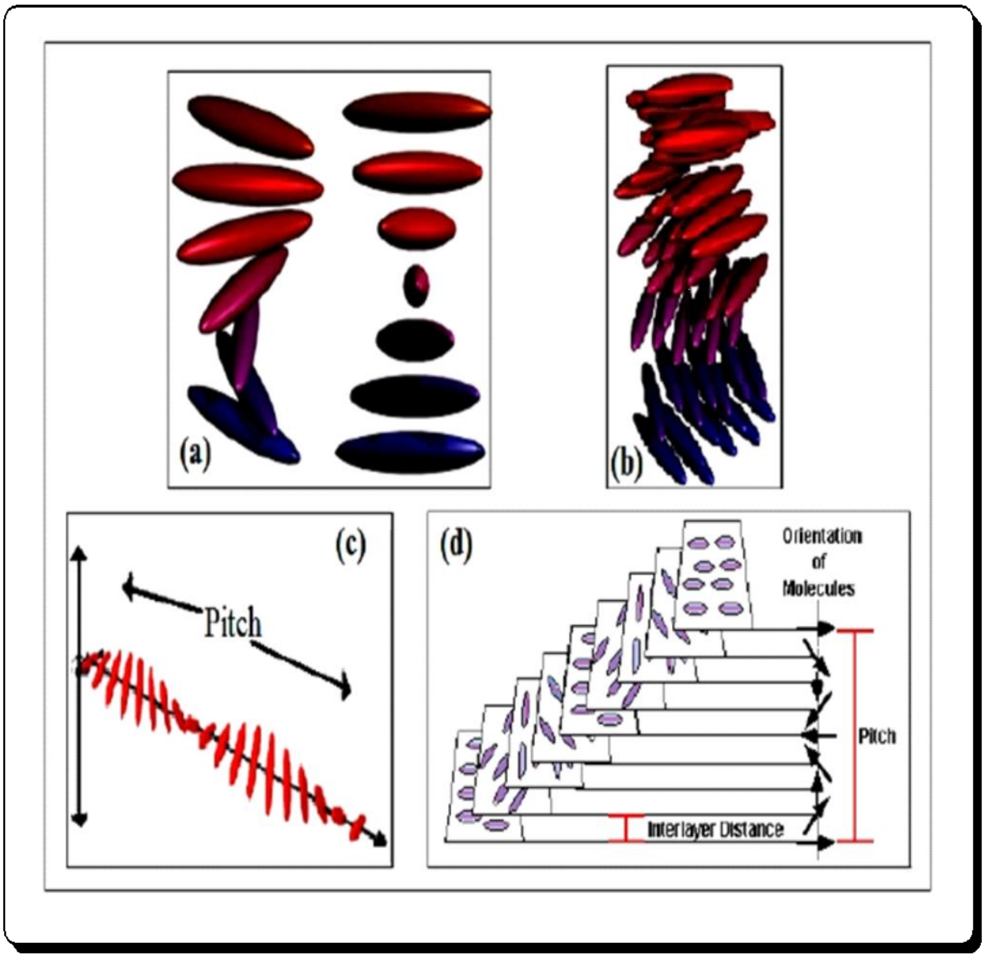

Figure 1.7: (a) and (b) Schematic representation of Cholesteric phase (c and (d) Schematic representation of helical structure

1.3.4 Blue Phase

In Liquid crystals; it has been the discovery of defect phases. These defects have several specific geometries and are energetically unfavoured. There are two common examples of these defects (1) Blue phases [BP] (2) The twist gain boundary phases [TGB].

Blue phase occurs when the pitch is large or the chirality is low. The defect phase's posses simple cubic, body centered cubic, and amorphous structures . Usually these phases occur only over a small temperature range between the isotropic liquid and the chiral nematic phases and are called blue phases because the first discovered phase appeared blue in reflected light.

Chiral liquid crystals have the tendency to form cholesteric - like helical director field; On the other hand, the molecular interactions may favour a smectic layers structure. The competition between these two structural features can results in frustrated structures containing a regular lattice of grain boundaries, which in turn consist of a lattice of screw dislocations. This phase is known as the twist gain boundary phase (TGB) and was theoretically predicted by Renn and Lubensky [27] and almost simultaneously experimentally observed by Goodby et al [28].

Blue phase appears over a narrow temperature range between the chiral nematic phase (N*), which has a relatively short helical pitch, and the isotropic phase [29,30]. The defect phase may have simple cubic, body centered cubic, and amorphous structures [31,32]. Blue phase are considered to consists of a double –twist- cylinder (DTC) structure and are classified into three categories depending on the assembly structure of the DTC: BP I, BP II and BP III, listed in the order of increasing temperature [33,34]. M. Lee et al [35] investigated blue phases of a nematogenic achiral bent bent – core molecules doped with chiral additives.

1.3.5 Twist Grain Boundary [TGB] Phases

Chiral liquid Crystals have the tendency to form cholesteric – like helical director field; on the other hand, the molecular interactions may favor a smectic layer structure. The competition between these two structual features can result in frustrated structures containing a regular lattice of grain boundaries, which in turn consists of lattice of screw dislocations. This phase is known as the twist grain boundary phase (TGB). In Renn and Lubensky [36] developed a specific model of this structure of TGB phase. A short time later, in 1989, Goodby et al [37] reported the discovery of the TGBA phase existing between the SmA* and the isotropic phases. X-ray studies performed by srajer et al [38] confirmed that the essential features and the physical properties of the TGBA phase are very well described by the Renn- Lubensky model. Nagappa et al. have observed the TGB-A phase in mixtures of cholesteric with nematic [39] and with [40] compounds. Some instresting research work for TGB phases are reported [41-44].

1.3.6 Ferroelectric and Anti- ferroelectric Liquid Crystals

If a compound made up of chiral molecule exhibits amectic C phase or a smectic C phase of nonchiral molecules is doped with a chiral dopants then that phase is called as chiral smectic C phase. The tilted molecule is doped with a chiral dopants then that phase is called as chiral Smectic C phase. The tilted molecules presses from one layer to another giving rise to a helical structure similar to the cholesteric liquid crystals. The helical structure of the chiral smectic C phase had been recognized in the early 1970s [45-46]. The tilted director rotates from layer to layer forming a helical structure (Figure 1.8). Various ferroelectric liquid crystalline materials are developed by Goodby et al [47-48]. The ferroelectric phase has an alternating tilted structure. The alternation is not symmetrical and more layers are tilted in one direction (Figure 1.8 d.). In antiferroelectric arrangement the adjacent layers of the molecules are oppositely tilted (Figure 1.8 e.) and alternation of molecules is symmetrical. Some compounds having antiferroelectric liquid crystalline properties are reported [49-52].

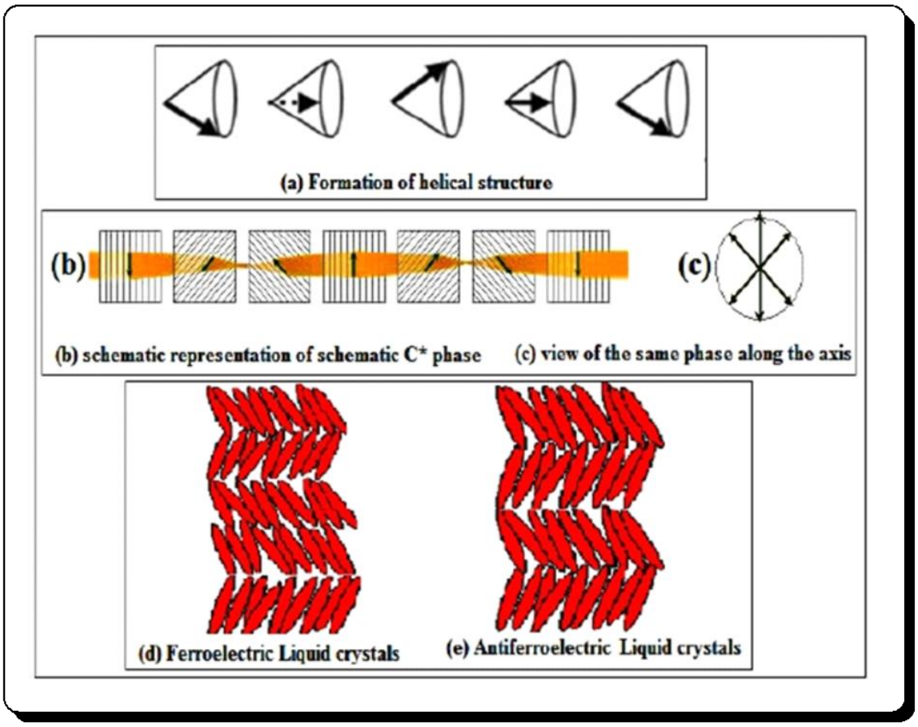

Figure 1.8: Formation of ferroelectric and antiferroelectric liquid crystals

1.3.7 Discotic Liquid Crystals

The mesophases exhibited by compounds composed of disc like molecules are known as discotic liquid crystals. The first discotic liquid crystals is synthesized and identified by Chandrashekhar at al in 1977 [53]. Discotic phase may be classified into two fundamental types: Columnar and nematic. In columnar phases, the molecules are stacked one upon another to form columns which may be arranged in hexagonal, tetragonal, rectangular or tilted arrays. Schematic representation of columnar discotic liquid crystals is given in Figure 1.9.

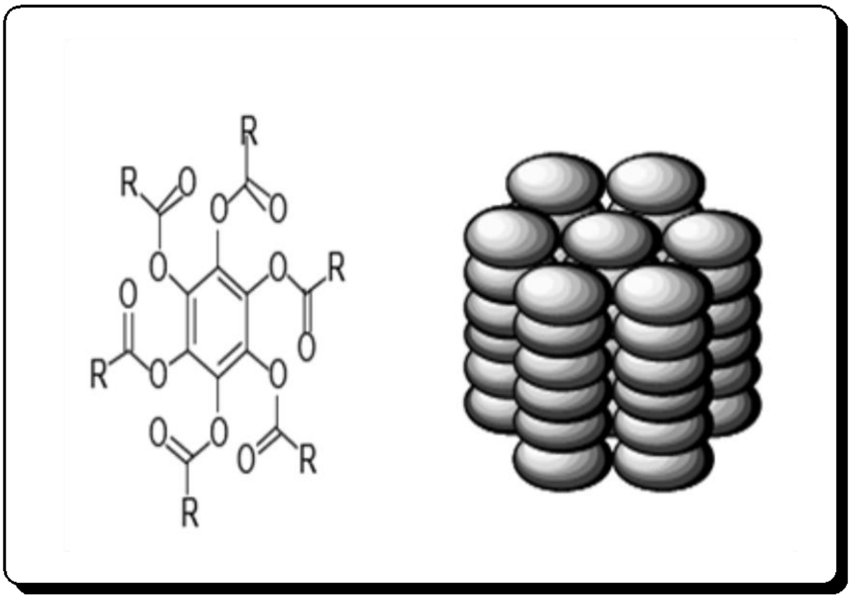

Figure 1.9: Schematic representation of Columnar discotic liquid crystals

The nematic phases are anisotropic fluids with a single order pararrieter with a tendency to align the disc- shaped molecules parallel to each other. Triphenylene based compounds showing columnar phase devloped by Boden et al [54]. Room temperature columnar phase is iobserved in polyalkynyl benzene based disc shaped molecules by Varshney et al [55]. Swen Mahlstedt at al, have reported a novel donor acceptor mesogen [56]. Discotic liquid crystals having crown ethers as central units are synthesized by M. Kaller et al [57] and C. Zhang et al [58]. Banana shaped discotic liquid crystals are reported by S. Kumar et al [59]. Recently, K. C. Majumdar et al [60] observed columnar phases from non disk- shaped mesogens. Some interesting discotic liquid crystals are reported by various reserchers. [58-64].

1.3.8 Sanidic Liquid Crystals

Compounds between the rod like and disc like molecules are the lath like species. They are generally fused or twin compounds derived from Greek word ‘Sanidic’ means broad. These phases are called sanidic and are first found in polymeric liquid crystals reported by Ringsdord et al in 1986 [65]. The board like molecules of this compound can form a nematic phase, however countrary to the behavior in “normal” nematic phases; the rotation around the molecular long axis is strongly hindered. Therefore the structure of these phases is characterized by translational period in accordance with length , breadth, thickness of scatterinf maximum. Sanidics can be considered as a class of liquid crystals intermediate between discotic columnar and calamatic liquid crystals. Photoconductive behavior is found in a series of sanidic liquid crystals materials by D. Haristoy et al [66].

1.4 Lyotropic Liquid Crystals

This class of mesophase is induced by the effect of solvent on amphilic molecules; the solvent generally being water. At a critical concentration the solution exhibits liquid crystalline properties.

Lehmann [67] is the first to recognize the mesomorphic state of ammonium oleate in aqueous solution. Lyotropic substances are strongly birefrigent. Mesophase in binary systems of amphiphiles and water may be classified as (a) the neat phase (b) the middle phase (c) the viscous isotropic phase (d) the isotropic phase and (e) the inverse phase [68]. Lyotropic substances with other solvents are also studied [69-71]. Lyotropic liquid crystals are also affected by temperature changes. Hysteresis is observed in the properties of a ternary lyotropic liquid crystals systems [72]. Lyotropic liquid crystals of hydrated phopholipids are studied [73] as model medium for studies of antimicrobial agent activity. The gradual breakdown of the crystals lattice by addition of water or in general solvent may be represented as Figure 1.10.

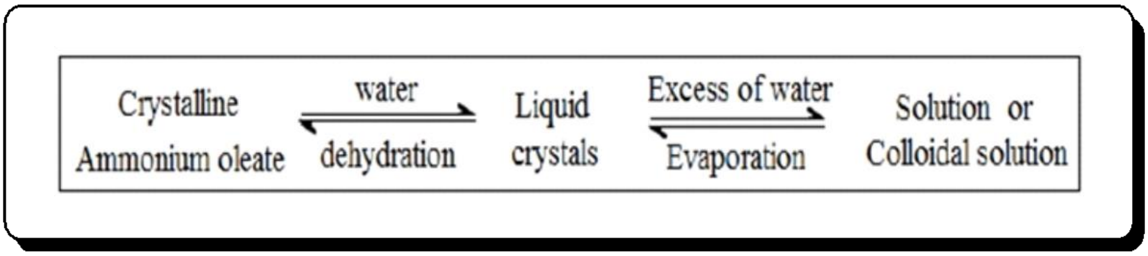

Figure 1.10: Lyotropic liquid crystals

In lyotropic liquid crystals, mesomorphism exists only in mixtures consisting of compounds with a relatively high polarity (amphiphillic compounds) and certain solvents. The necessary condition for the existence of lyotropic liquid crystals is a strong interaction of the polar compounds with molecules of the solvents. Certain compounds are able to form thermotropic as well as lyotropic liquid crystals; they are called “amphotropic”.

1.5 Influence of molecular structure on mesomorphism

The association between molecular structure and the mesomorphic properties of calamatic liquid crystals has beenm rigorously studied by Gray [74-75]. Demus et al. [76-78] have given quite a detailed account of effect of chemical constitution on mesomorphism. The majority of thermotropic liquid crystals are aromatic in naturer consisting of polarizable planer benzene rings linked with one another and having terminal alkyl or alkoxy group [79]. Merely suitable structural geometry may not turn the compound to behave as a liquid crystals; intermolecular forces also play a very important role. These iontermolecular forces are are of three types.

1. Dipole – dipole attractions between premanent dipoles in the molecules.
2. Induced dipole attractions arising from the mutual polariazation of the molecules by their permanent dipole moments.
3. Dispersion forces – the interction between instananeous dipoles produced by spontaneous oscillations of the electron clouds of the molecules.

The majority of thermotropic liquid crystla are aromatic in nature consisting of polarisable and planar rigid aromatic rings linked with one another through linking groups like –N=N-, -CH=N-, -COO-,

-CH_2COO-,-COO-CH_2-CH_2-O-, -CH=CH- etc. [79]. The increase in number of benzene rings increases the stability of the mesophases. The general structure can be represented as follows Figure 1.11.

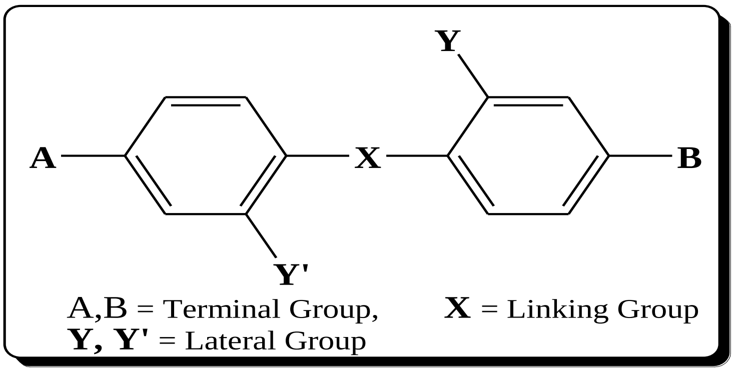

Figure 1.11: General molecular structure

1.5.1 Effect of terminal substituents on mesomorphism

Terminal groups present in the molecules have their own importance because of their polarity. It has been found that terminal substituted compounds exhibit more stable mesophases compared to unsubstituted mesogenic compounds. However, for smectic liquid crystals certain terminal groups lengthened the tendency of depressing the melting point is increased. Liquid crystals of moderate chain length of the carbon chain gives both smectic and nematic mesophases and of very long chain length usually exhibits only smectic phases. Gray [80] has discussed in detail, the effect of increase in alkyl chain in a mesogenic homolous series. sadashiva et al [81] have synthesized terminally swallow tail type of compounds and established that by selecting proper geometry of molecules the liquid crystalline property can be maintained in such system.

Branching in terminal chain often reduces liquid crystal phase stability [82] but is known to introduce tilted smectic thermal stability. Chain branching also provides the opportunity to use a chiral alkyl chain and thereby produce a chiral smectic C phase (Sc*)[83].

The terminal group efficiency order which has been compiled [85] for smectic phase in rod like aromatic system is

Ph > Br > Cl > F > NMe_2 > Me > H > NO_2 > OMe > CN.
The nematic group efficiency order is
Ph > NHCOMe > CN > OMe > NO_2 > Cl > Br > NMe_2 > Me > F > H.

1.5.2 Effect of lateral substituents on mesomorphism

The effect of introducing lateral substituents into the elogated molecules of mesogenic compounds are considered. This type of structural changes has been made systematically for a few types of compound by introducing a range of lateral substituents into the aromatic ring of core parts of the molecules [84] Figure 1.12.

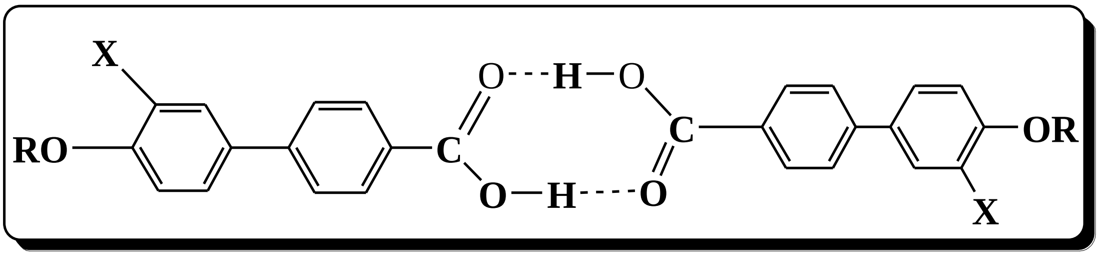

Figure 1.12: General molecular structure

The substituents X will have two effects;

(1) The long molecular axes may be forced apart by the substituents, reducing intermolecular forces of attraction and thus lowering liquid crystals thermal stability. Since lateral interactions will be most effected, the thermal stability of the smectic mesophase should decrease more than that of the nematic mesophase.

(2) The change from a ring-H to a ring-X bond will increase the molecular polarizability and possibly also the molecular dipolarity. This should increase lateral intermolecular attractions, enhancing liquid crystals thermal stability, particularly that of the smectic mesophase.

Lateral Substituents may force apart the molecules and may thus reduce the intermolecular lateral cohesion but at the same time lateral substituents may increase the intermolecular attractions. Normally the first effect predominates i.e. a lateral substituents decrease the mesophase thermal stabilities. However, if the substituents do not have full breadth increasinf effect as in the case of the 5-substituted 6-n-alkoxy-2-naphthoic acids [85], then the second effect predominates i.e. the thermal stability of substituted mesogens increases.

Common lateral substituents are halogens , methyl, ethyl, cyano, and other smaller groups [86-88]; however, liquid crystals having large lateral substituents are also known [89-93]. Every lateral substitution leads to an increase in the breadthof the molecule and thus a reduction in length to breadth ratio which in turn usually reduces the clearing temperatures.

The effect of lateral substitution of a type which, in addition to broading the molecule, increases its thickness by imposing its steric effect on the system i.e. by causing a twisting about one of the bonds, So that parts of the molecules are related out of the plane of the remainder of the molecule are also reported [94, 95]. A combination of both breadth and steric effects greatly reduces the thermal stabilities of the ordered arrangement of molecules in the liquid crystals. There are compounds in which the lateral substituents are shilded so that they are less effective in broadining the molecules and at the same time improve the thermal stability [96]. This gives rise to notably high clearing temperatures. Demus et al [97] have studied the effect of long lateral substituents having aromatic rings.

The lateral group efficiency order which has been compiled [98] for smectic phase is,

$I > Me > NO_2 > Br > Cl > F > H$

The lateral group efficiency order which has been compiled [98] for nematic phase is,

$NO_2 > I > Br > Cl > Me > F > H$

1.6 Mesomorphism in homologous series

For a homologous series, when the mesomorphic trnsition temperatures e.g. nematic-isotropic , smectic- istropic , smectic- nematic or smectic-smectic are plotted against the number of cartbon atoms in the alkoxy groups smooth curves may be drawn for like or related transitions. Usually the crystal- mesomorphic transitions do not exhibit regular trends. The mesomorphic –isotropic temperatures lie on two falling curves; the upper one for even and lower one for odd number of carbon atoms in the n-alkoxy chain. The odd-even effect usually becomes less marked as the series is ascended and the two curves merge later in the series. The smectic – nematic transition temperatures usually do not alternate and lie on a smooth curves, which rises steeply at first, then levels off and may or may not merge with the falling nematic –isotropic, smectic-isotropic curves.

1.7 Banana Shaped Liquid Crystals [409-410]

Liquid crystals have a long-range orientational order; i.e., molecular symmetry axes, the long axes of the rod like molecules and the disc normal of the disc like molecules align on average in a particular direction. This average molecular direction is called a *director*, and the orientational order parameter is defined by the molecular orientational distribution around the director. Since the rotation about the Symmetry axis does not affect the order parameter, liquid crystal molecules normally rotate freely along this symmetry axis, unless there is no symmetry requirement. From this viewpoint, molecules with shapes deviating from a rod, such as board or bent shape, have been thought of as bad molecules for forming liquid crystals. If such molecules freely rotate about their long molecular axes, the excluded volume becomes large and violates the liquid crystallinity. For these reasons, only a very few bent-core molecules have been synthesized before the discovery of their polar switching. It should be noted, however, that Vorlander [99,100] who is a pioneer in the field of liquid crystal synthesis [101,102] synthesized several bent-core liquid crystals and reported their mesogenic properties in 1929, mentioning that the thermal stability of the mesophase is low compared with that of the straight-core analogues. After a long time, Matsunaga and coworkers [103–106] revived the synthesis of bent-core mesogens in 1991. One of the molecules, 1, 3-phenylene bits-[4-(4-*n*-octyloxyphenyliminomethyl)-benzoate], opened a new era of liquid crystal science, although they did not realize the physical importance of this molecule before the discovery of polar switching in this molecule.

Another important aspect of this class of molecules is chirality. Groups in Colorado and Berlin opened the door of chirality. Link *et al*. [107] realized the introduction of opposite chirality by tilting an achiral bent-core molecule in the opposite direction in a smectic layer, as shown in Figure 1.13. The Berlin group [108] and Sekine *et al.*[109, 110] were the first to realize spontaneous chiral resolution in a non tilted phase. Particularly, the Berlin group [108] pointed out that otherwise indistinguishable domains appear to be bright and dark with slightly decrossing polarizers, and they were interchanged by decrossing the polarizers in opposite directions. Since then, similar phenomena have been observed in several phases. The use of polarizers under decrossed conditions became a standard method of confirming chiral segregated domains.

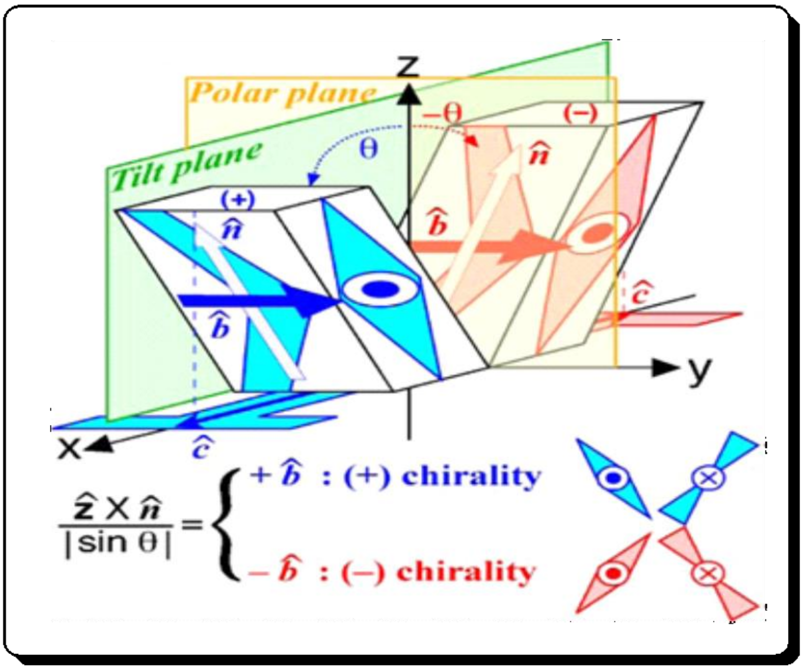

Figure 1.13: Definition of chirality in tilted smectic phase of bent-core molecules.

The first compound with a bent molecular geometry exhibiting mesogenic properties is synthesized by Vorlander and his group [99, 100] and explorerd the structure property relationship. These materials form new smectic and two – dimensional phases, which are unlike those obtained from normal calamatic molecules [111]. A real breakthrough in bent core liquid crystals came in 1996, when Niori et al [112] reported ferroelectricity in a smectic phase formed by an achiral banana shaped compound. In 1997, Skine at al reported [109, 110] a spontaneous helix formation in the smectic phase of an achiral bent core compound. The origin of the helix is discussed in view of the twisted molecular conformation and the escape from microscope polarization. In the last few years hundreds of compounds composed of bent core molecules have been synthesized [113-121] with a view to understand the relationship between structure and the mesomorphic properties exhibited by such compounds. At least seven of these phases have been described [122] and preliminarily designated by the code letters B1 – B7. The general formula and different possibilities for variation of the chemical structure can be be seen in Figure 1.14.

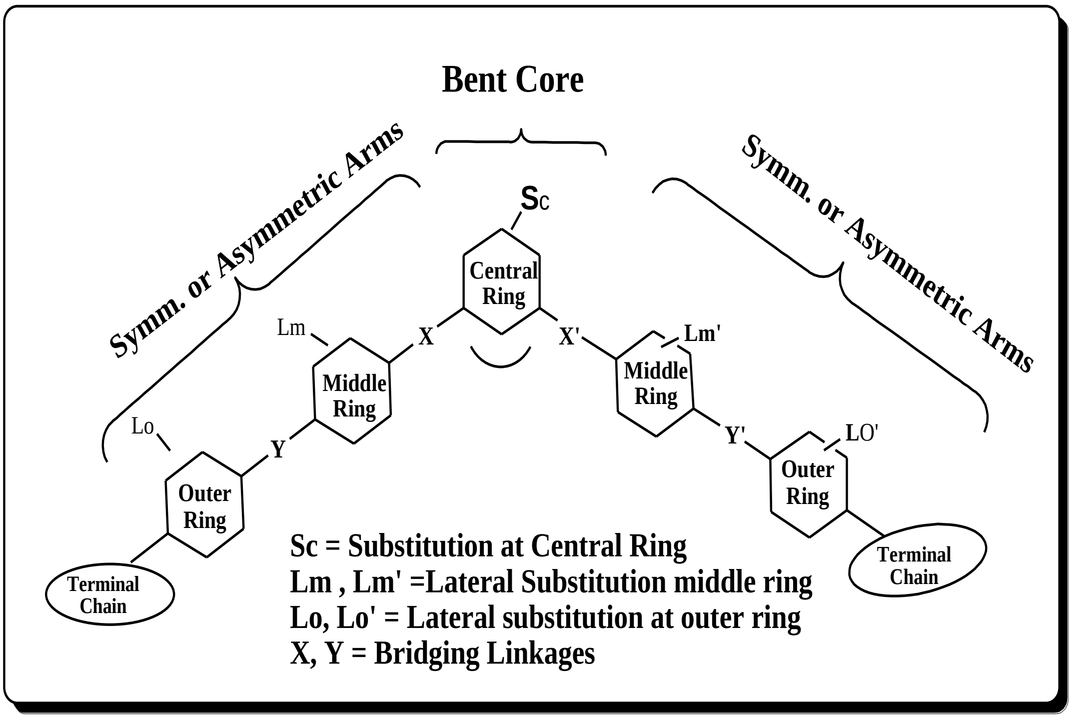

Figure 1.14: General structure of Banana-shaped mesogens

1.7.1 Structural property relationship of Banana mesophases

Ever since the beginning of the extensive research on banana –shaped liquid crystals and their special properties in 1996 [123] about 1000 new bent-core mesogens have been synthesized in that time. Of course, long before 1996 several molecules with bent shapes had been synthesized [124, 125, 126], but the observed mesophases were at that time not recognized as being extraordinary. In systematic studies a fixed aromatic central bent core is taken while the terminal alkyl tail lengths are varied. Most banana-shaped compounds that exhibit B-phases have five aromatic rings. Four [127 - 132], Five [172, 487], Six [133, 134, 135, 136, 137, 138-146] and seven [147, 148, 149, 150-155], aromatic rings in banana-shaped mesogens are also known and the mesophase range seems to increase upon increasing the number of rings [156]. In some cases six-ring compounds form conventional smectic phases in addition to banana-phases [157]. The influence of lateral substituents on the mesophase behavior of banana shaped LCs have also been studied intensively. Chlorine [148, 158, 138, 155, 156, 159-165], nitro [167, 158, 156, 161, 164-169], fluorine [170, 171, 148, 172, 149, 137, 173, 141-143, 146, 151, 154-156, 160, 174-175, 165, 168-169, 176-179], bromine [158, 180, 181, 159, 165, 179], methyl [170, 148, 149, 138, 156, 161, 175, 164, 165, 179], hydroxyl [182,153], cyano [138, 151, 154, 156, 165, 166, 169, 183], methoxy [158, 175], ethyl [133, 149], ethoxy [175], acetyl [133], dodecyloxy [158], pentyl [158, hexyl [133, 158], COOC$_8$H$_{17}$ [158] and CF$_3$ [156] groups have been used as lateral substituents to one or more of the rings, but small polar groups like fluorine seem to be most effective in retaining the desired B-phases.

The position of the substituents plays a highly important role in determining the liquid crystalline properties of bent-core mesogen [172]. In several cases the liquid crystalline properties completely disappear upon introduction of lateral substituents. In general, melting points are lowered upon introduction of lateral substituents. Bulky substituents can suppress the liquid crystalline properties completely and sometimes interesting changes in switching behavior can be observed upon introduction of small polar substituents [148].

Despite their Achiral molecular structure, bananas can form chiral mesophase domains due to two symmetry –breaking events. However bananas with chiral carbon atoms in the terminal tails have also been studied. In most cases the chirality is caused by methyl-branched terminal tails [184 – 187, 188, 189], but propyl –branched tails were also reported [190]. In these cases transition temperatures are lowered [184, 185] and ferroelectricity is induced [186,192, 188, 189].

Some more exotic banana-shaped liquid crystals have also been studied; polycatenar bent-shaped mesogens [191], molecules with a combination of rod-like and banana mesogenic groups [150], hydrogen-bonded banana mesogens [192] and bananas incorporated in dendritic systems [193]. Light-emitting bent-shape liquid crystals were also designed, but B-phases were not observed for these compounds [194].

1.7.2 Electro-optical Properties

A mesophase with a permanent polarization in the absence of an electric field is called a *ferroelectric* mesophase. In order to have a bulk polarization, molecules have to exhibits spontaneous polarization (Ps). Hindered rotation around the molecular long axis plays an essential role in the emergence of Ps. The director of a molecular assembly with spontaneous polarization can be changed by the application of an appropriate electric field. In most ordinary liquid crystalline phases (N, SmA, SmC), the symmetry is so high that rotation around the long molecular axis prevents the occurrence of ferroelectricity. To find ferroelectricity the symmetry has to be lowered further, for example in chiral tilted smectics (SmC*).

Ferroelectricity was discovered in the beginning of the 20th century in crystals by Valasek and later also in liquid crystals for a SmC* phase by Meyer *et al* [195]. Since the director of a SmC* phase rotates from layer to layer, helical arrangement is present and therefore the system escapes from macroscopic polarization. The SmC* phase can be driven towards the ferroelectric state by applying an external electric field. In that case the helix unwinds and the molecules in all layers orient in the same direction. By applying an electric field of opposite sign the polarized phase (*ferroelectric*) will switch to the other ferroelectric state (Figure 1.15). This behavior is often referred to as bistable switching.

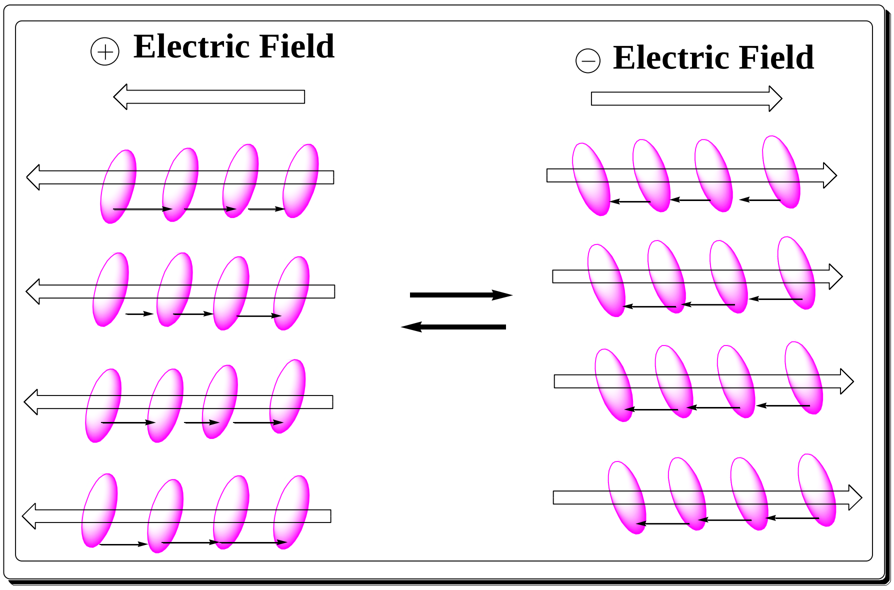

Figure 1.15: Bistable switching under the influence of electric field

The main advantage of these smectic materials, compared to conventional nematogens is their relatively fast switching properties [196]. The reorientation of the molecules does not require much energy when compared to nematogens. This is mainly caused by the fact that the molecules rotate collectively around a cone.

Apart from the *ferroelectric layer* organization, in which the direction of polarization (and also tilt) is the same in all layers, there is also the antiferroelectric (tristable) structure in which the tilt alternates from layer to layer when no field is applied. In the intermediate ferri-electric phases the tilts randomly alternate (with preference for one direction). Thus, as we move from the ferroelectric to the antiferroelectric phase, this usually occurs via the ferroelectric state.

Apart from *symmetry breaking* through a combination of chirality and tilt, the symmetry of the phases can also be broken by a combination of tilt and a polar component perpendicular to the director of the molecules. This is for example found in columns of bowl-shaped molecules [197]. These columnar phases are stabilized by the one-directional stacking of molecules in the columns [198]. This can generate a ferroelectric or antiferroelectric packing of the columns. This is also found for liquid crystalline phases of banana, bent-core or bow-shaped molecules. Just like the classical

SmC*compounds, banana-shaped compounds can order in to ferroelectric and antiferroelectric arrangements as shown in Figure 1.16.

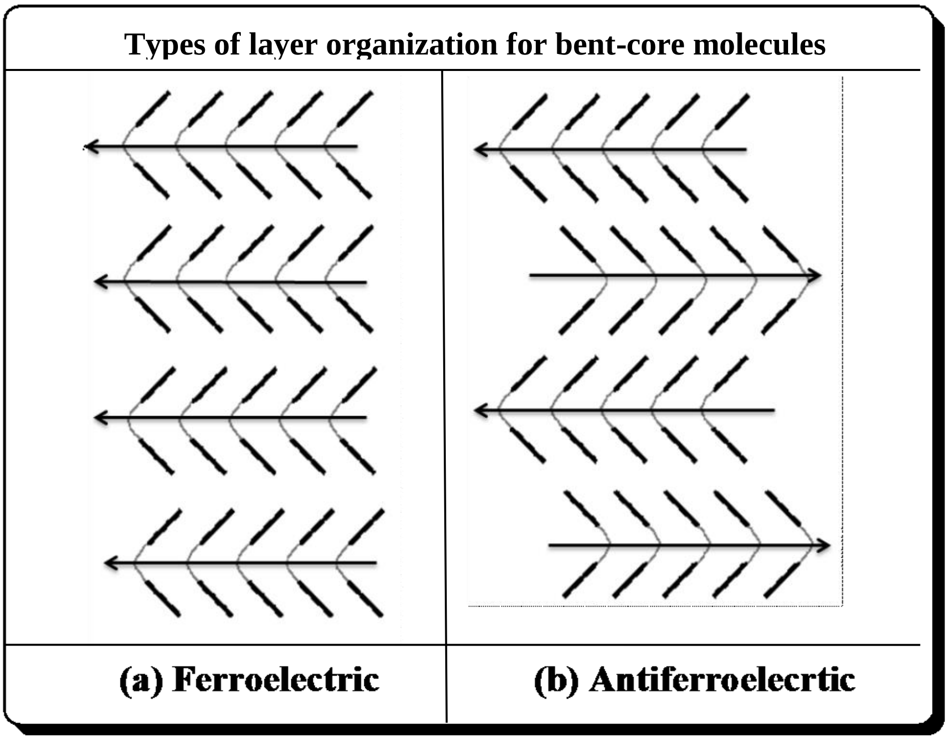

Figure 1.16: Types of layer organization for bent-core molecules

The switching process in banana-shaped mesogens under the influence of an electric field has always been thought to be linked with the strong π→π stacking of the aromatic cores that result in a restricted molecular rotation around the long axes. Therefore, the field – induced reorientation should take place via rotation of the molecules around the tilt cone and the chirality in the layer remains the same (tilt and polar direction reversed). Recently, however, field – induced switching of chirality was also detected [136,144, 163, 199]. In this case the polar switching is not caused by rotation of the director around the tilt cone, but by a collective rotation of the molecules around their long axes, Figure 1.17.

The ground state of a liquid crystalline phase can sometimes be changed from antiferroelectric to ferroelectric upon introduction of fluorine substituents in the outer rings (*ortho* to the terminal tails) [172, 171, 200], or by branching of the terminal tails [186,188-189]. The reason for this behavior might be related to dipolar interactions [172], or intermolecular interactions at the interlayer interfaces [201].

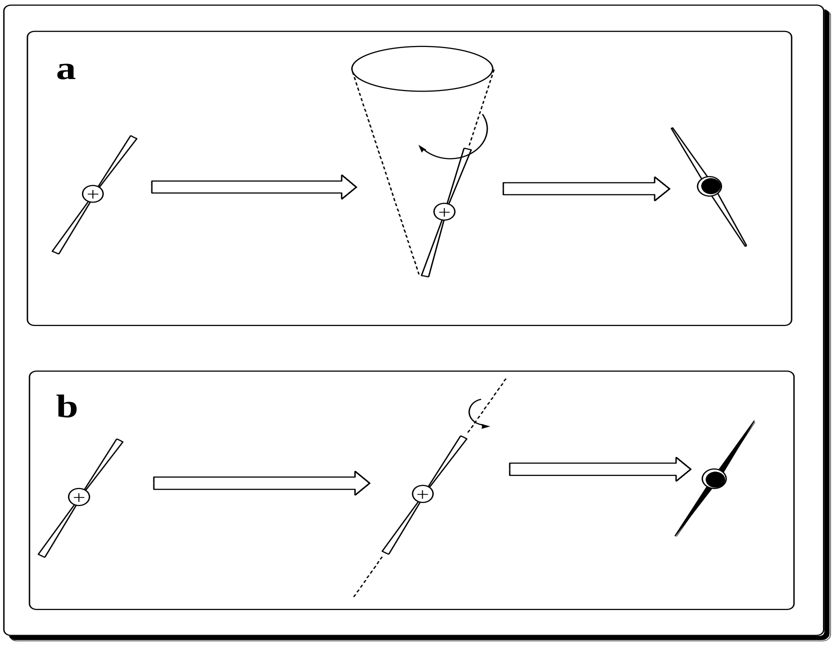

Figure 1.17: Types of polar switching (a) around cone (b) around the molecular long axis Open and filled molecule symbol represents layers of opposite chirality

Occasionally, a change in switching behavior was found depending on the length [199] or the parity [202] of the terminal alkyl tails. The short-tailed compounds in reference [199] showed an antiferroelectric ground state and the compounds with the longer tails a ferroelectric. According to the Reddy R. *et al* [199], this can be explained in terms of interlayer interactions: they could be strong for the analogues with short chains, which would clear favor the formation of an antiferroelectric polar structure. Lee *et al* [202] have studied alternating ferroelectric behavior for even and antiferroelectric behavior for odd terminal chain lengths. Also in this case interlayer steric interactions play a major role in the odd-even effect described for these compounds.

1.7.3 Classification of Banana phases

The mesogenic phases identified in bent-core compounds are classified (Table 2), and their phase structures determined by X-ray diffraction and other techniques are described. At an early stage of the discovery of the bent-core liquid crystals, seven mesogenic phases were identified and simply designated as B1–B7, where ‘‘B’’ stands for bent, banana, bow, or boomerang. All these phases together with another phase discovered later (B8) are sometimes called ‘‘banana phases’’, as specific phases different from conventional phases found in calamitic (rod like) mesogens.

Table 1.2 Summary of the typical feature of B1–B7 banana phases.

Bn	Other Symbols	Phase Type	Characteristic Properties	Switching Behavior
B1	Col_r	Columnar mesophases(ribbon phases),Different phase textures are possible	X-Ray: 2D lattice, mosaic texture (spherulatic textures)	Non-switching
B2	SmCP_A C_B2	Tilted smectic phase, monolayer structure, Polar order	X-ray: layer reflection, $L<d>L/2$, Diffuse wide angle scattering, Schlieren texture, non-specific broken fan texture	AF
	SmAP_A SmCP_F	Tilted smectic phase, Monolayer structure, Polar order	X-ray: layer reflections, $L < d > L=2$, diffuse wide angle scattering, dark texture with domains of opposite handedness, sometimes bluish appearance, often high viscosity	AF FE
	SmAP_A C_PA	Orthogonalsmectic phase mono-layer structure, polar order, polar axis parallel to the layer planes	X-ray: layer reflections, $L < d > L=2$, diffuse wide angle scattering on the equator, Schlieren texture, fan texture	AF
B3		Crystalline lamellar mesophase, tilted	X-ray: layer reflections, numerous sharp reflections in the wide angle region	Non-switching
B4	SmBlue	Soft crystal, non-tilted , double twisted TGB like structure	X-ray: layer reflections, numerous reflections in the wide angle region, but fewer and less sharp reflection compared to the B3 phase, transparent blue color, regions with opposite chirality, SHG active in the ground state	Non-switching
B5		Tilted smectic phase, monolayer structure, polar order, short range 2D lattice within the layers, non-correlated layers	X-ray: layer reflections, $L < d > L=2$; 3 maxima in the wide angle region, Schlieren texture, nonspecific broken fan texture	AF FE
B6	Sm_int SmC	Intercalated smectic mesophase	X-ray: layer reflections, $d < L=2$, diffuse scattering in the wide angle region, fan texture and Schlieren texture	Non-switching
B7		Modulated layer structures	Typical textures: screw-like growth, helical superstructures, fibres can be drawn, X-ray: complex diffraction pattern (sometimes layer structure?), diffuse wide angle scattering	Non-switching FE(AF)

1.7.3a B1 phase

The B1 phase is categorized as a columnar (Col) phase because of its columnar structure [203–208], typical mosaic textures under a polarizing microscope are observed, as shown in Figure 1.18, which is similar to those in the Col phase in discotic liquid crystals. Dendric like growth of domains in B1 was discussed by Chan and Dierking [209]. According to the NMR measurements of homologous compounds reported by Weissflog *et al*., [210] the orientational order parameter is 0.84 and the molecular bending angle is ca. 120°, both of which are independent of temperature.

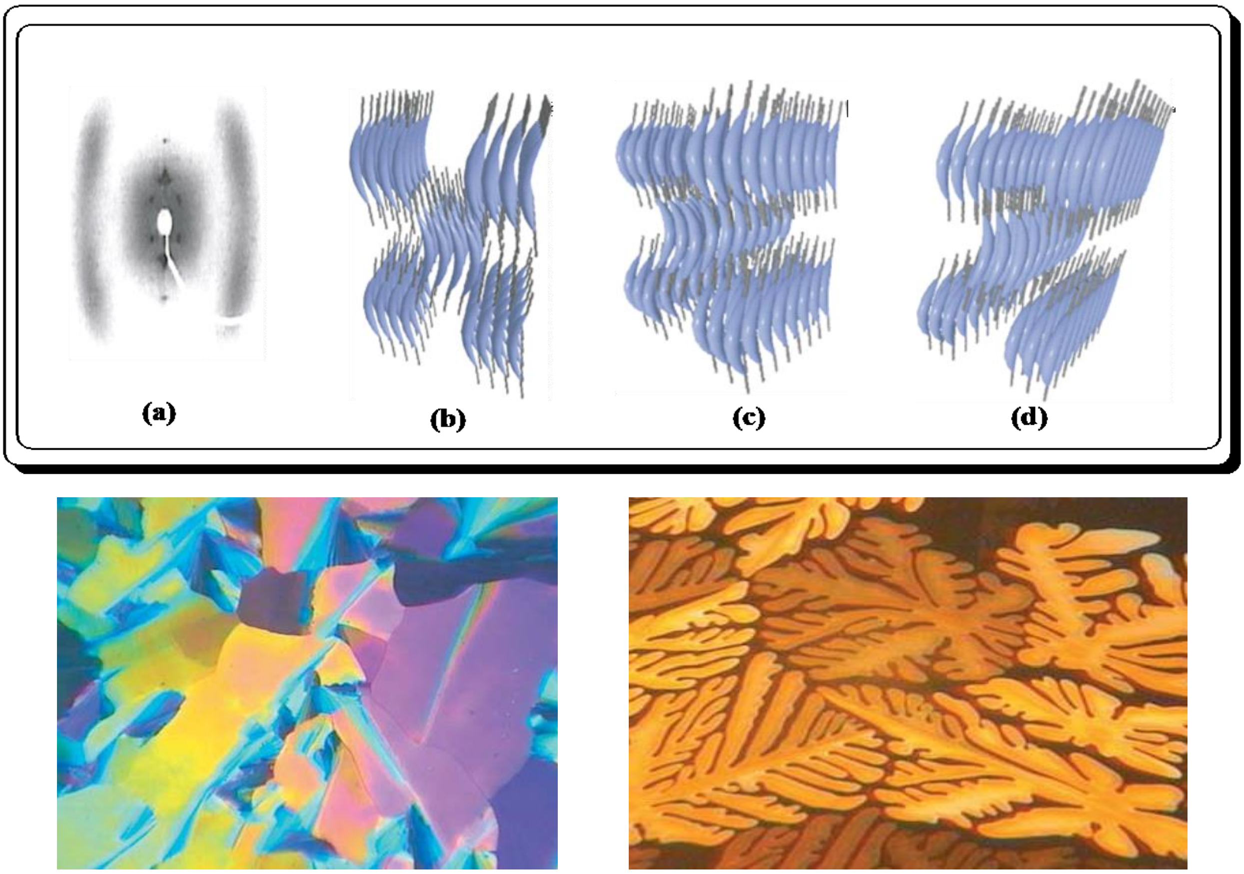

Figure 1.18: (a) X-ray pattern for B1 phase, (b), (c) and (d) are the layer organization of B1, B_{rev} and $B_{revtilt}$ phase respectively and textures of B1 phase

A 2D modulated phase different from conventional B1 was reported, without suggesting any concrete structures [211-212]; Considering the electroptic switching behavior at low field and high field and X-ray study Szydlowska *et al* [213] concluded Bx forms the new modulated structure B1rev and Bx1 is the tilted version of $B1_{rev}$ and $B1_{revtilt}$. Szydlowska *et al* [213] also suggested the existence of a 3D modulated structure, although decisive evidence has not been obtained, complete classification of the B1 related phases is a subject for future research

1.7.3b B2 Phase

The B2 phase Figure 1.19, is the most extensively studied banana phase. Niori et al.[133] first observed the ferroelectric-like switching current due to spontaneous polarization and explained the polar order based on close packing of molecules in a smectic layer with a unique bending direction along a C2v symmetry axis. The appearance of polar switching properties despite the molecules being achiral is one of the reasons why many researchers seize upon this phase.

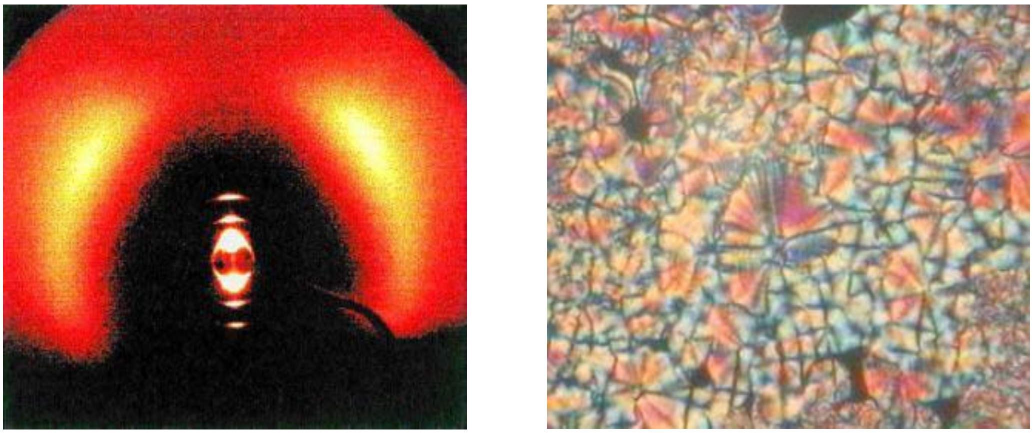

Figure 1.19: X-ray pattern and texture for B2 phase

1.7.3c B3 Phase

The B3 phase, for which there is less information on its structures and properties than for other Bn phases, frequently appears between B2 and B4. The texture obtained by rapid cooling from the B2 phase shows a texture similar to that in the B2 phase, as shown in Figure 1.20, but the domain is broken by slow cooling. Although a ferroelectric-like switching current indicating large spontaneous polarization up to 150 nC/cm^2 was observed in spite of no electro-optic response was reported [214], this is doubtful because the second-harmonic generation (SHG) activity initially reported [215] was not confirmed[216], and the dielectric constant was low [133].

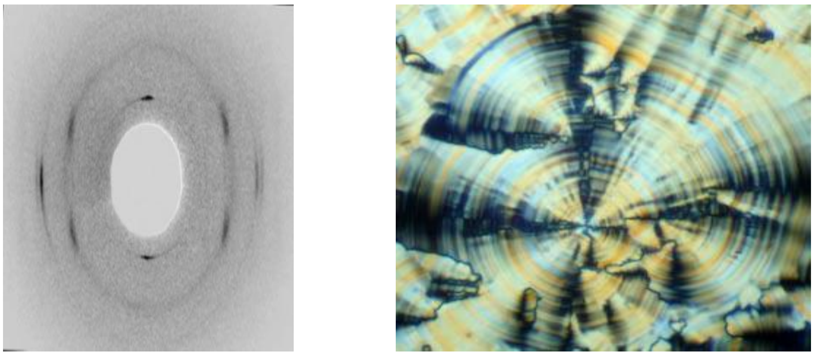

Figure 1.20: X-ray pattern and texture for B3 phase

1.7.3d B4 Phase

The B4 phase has been studied extensively, particularly from the viewpoint of system chirality. It is a mesogenic phase appearing in the lowest temperature region in bent core molecular systems. Textures in the B4 phase Figure 1.21 under a polarizing microscope appear as transparent dark-blue colored domains this brightness change is attributed to the optical rotation, suggesting that the B4 phase has a chiral structure.

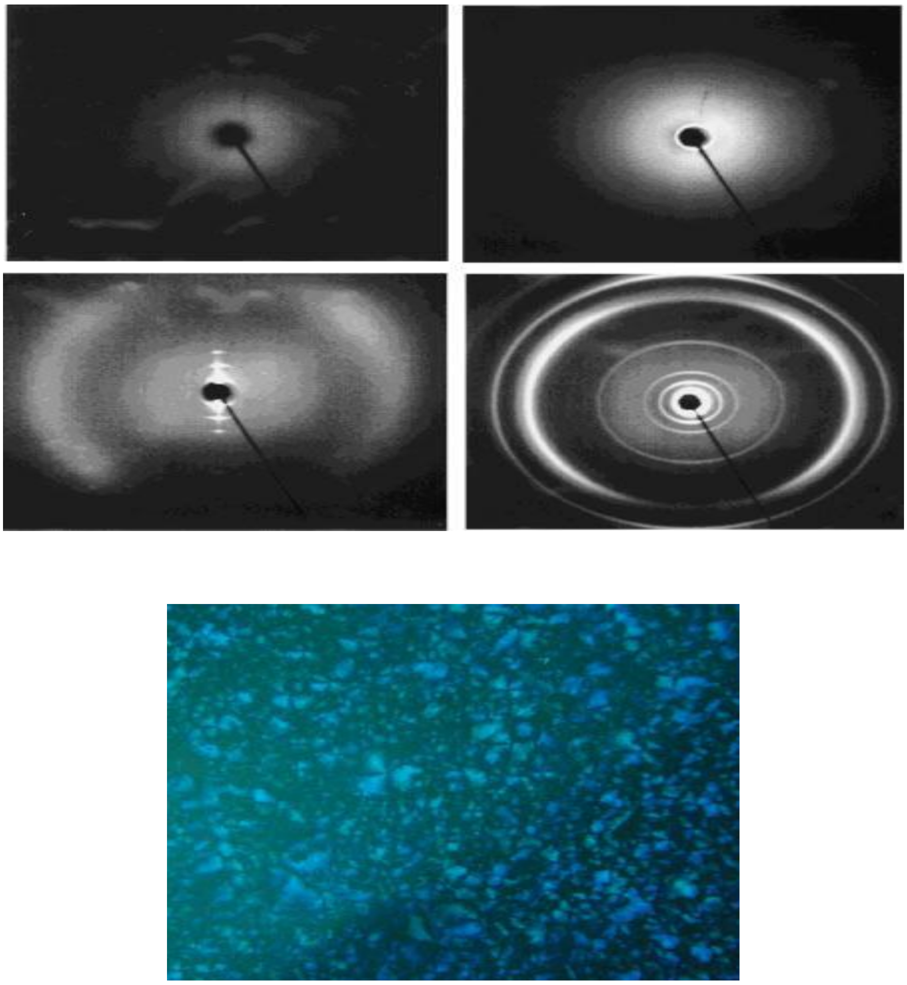

Figure 1.21: X-ray pattern and texture for B4 phase

1.7.3e B5 Phase

Although the B5 phase was first observed in 1998, only a few reports have thus far appeared [133,138,217,171] This phase appears below the B2 phase, and the transition enthalpy between them is small [133,138,217,171]. In this phase, electro optic responses as observed in the B2 phase were confirmed. The texture and electro optic response in the B5 phase Figure 1.22 is similar to those in the B2 phase.

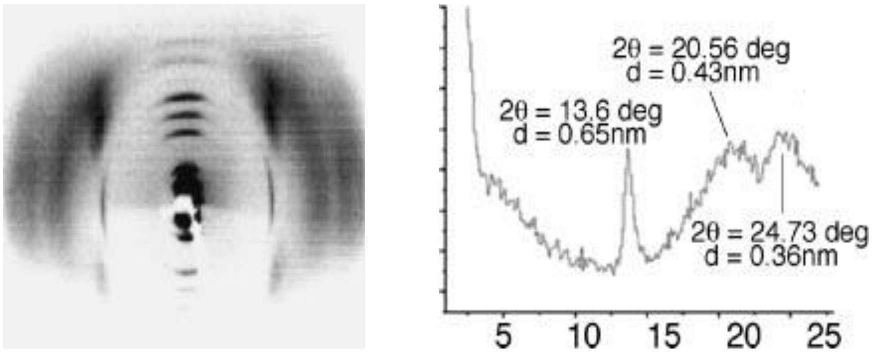

Figure 1.22: X-ray pattern and texture for B5 phase

1.7.3f B6 Phase

Only a few compounds showing this phase have been identified. In the B6 phase, long fan-shaped textures as observed in the SmA of rod like molecules are frequently observed; 2D X-ray pattern was obtained from a sample oriented by a magnetic field, as shown in Figure 1.23 [133,218]. Only one reflection corresponding to a periodicity smaller than half the molecular length appears in the small-angle region. This periodicity strongly indicates that the B6 phase has the intercalated structure shown in Figure 1.23. In addition, molecules are tilted in a layer, and the tilt angles are estimated to be about 25° [133] and 10° [219] in reported compounds. In the bent-core molecular system, the phase sequence tends to change from B6 to B1 and B2 as the terminal chain length of the homologues increases [149,218-219], although the B1–B2 sequence in a single compound is extremely rare [139, 178, 141) The origin of this change was explained by considering the relation between free volume space and terminal chain length based on a calculation of electrostatic potential [149].

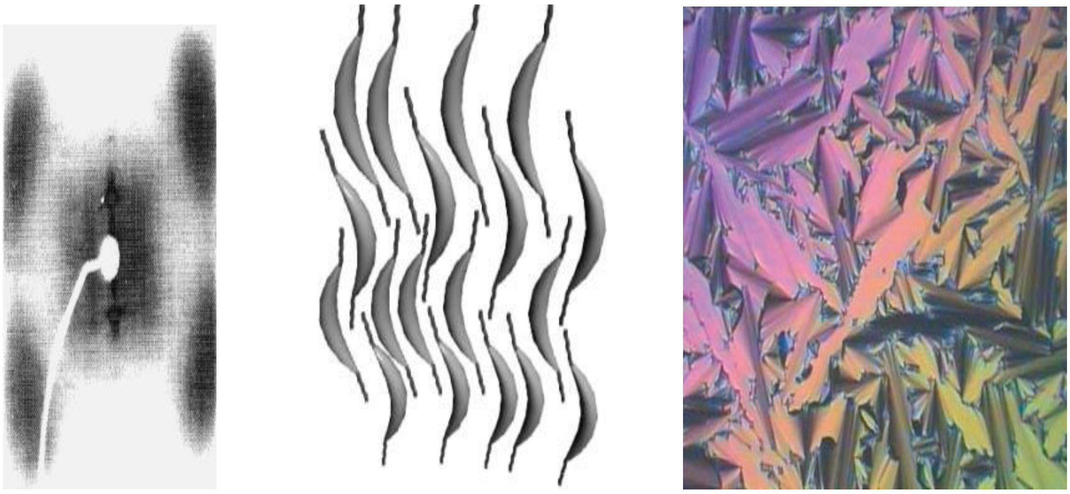

Figure 1.23: X-ray pattern and texture for B6 phase

1.7.3g B7 Phase

The B7 phase has attracted considerable attention because of its characteristic texture. The texture observed in the B7 phase is very characteristic, and a variety of textures are reported, as shown in Figure 1.24 [220, 225, 226]. The most typical texture is a spiral filament as shown in Figure 1.24 (a). Jakli et al. showed that left handed and right-handed spirals exist equally, and that the spiral texture consists of smectic filaments, forming single, double or triple coils [220]. Chiral micro mosaic domains are observed with different optical rotations as observed in the B4 phase, as shown in Figure 1.24 (b) [220] In addition, myelinic like, accordion-like, checker-board-like, banana-leaf-like, and circular domain textures are also observed, as shown in Figure 1.24 (c) and (g). Among them, the fan-shaped texture has different colors, both dark and bright. These are observed simultaneously under the same conditions [221-224].

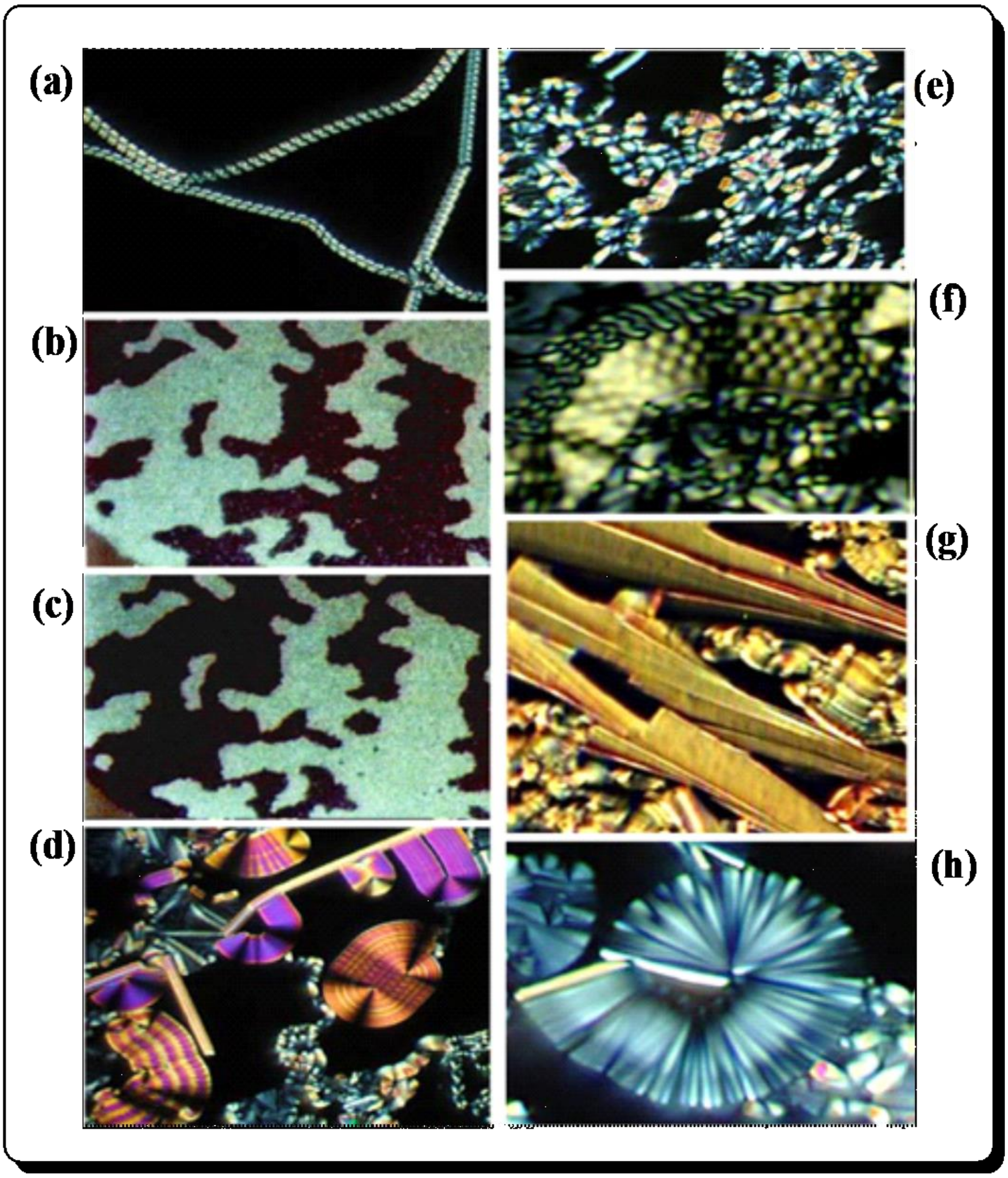

Figure 1.24: X-ray pattern and texture for B7 phase

1.7.3h B8 Phases

This phase was found considerably later than the other Bn phases. B8 are symmetric bent core molecules with decyl chains, as shown in Figure 1.25 (a) [227]. The homologues of this compound with shorter end chains do not show the B8 phase. In this phase, the layer spacing is 46.5 Å (q = 0:135 $Å^{-1}$), and from this value, the tilt angle is estimated to be 25°. On the other hand, in the B8 phase of this compound, another diffraction peak appears at a smaller angle. This diffraction corresponds to q=2 (= 0:068 $Å^{-1}$), suggesting that the B8 phase has a bi layer structure. This is the first and only report on the B8 phase thus far, and further investigations are expected.

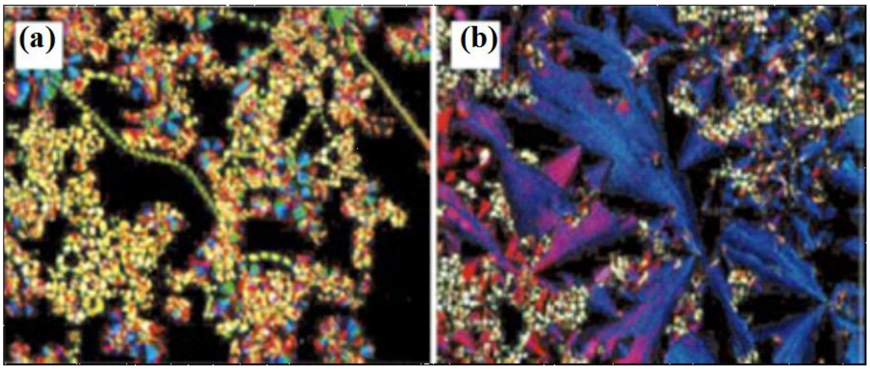

Figure 1.25: X-ray pattern and texture for B7 phase

Most of the compounds reported so far contain at least five phenyl rings. The angle results from a central 1,3- phenylene unit. The 2,7 – disubstituted naphthalene unit is also a suitable central unit for banana shaped molecules [228]. The compounds with six or seven aromatic rings have also been reported [229,230]. The transition temperature increase with increasing number of phenyl rings. The exchange of phenyl rings with six member heterocyclic rings like pyridine or pyridimidine is reported for seven ring compounds [198]. The substitution of the central ring by a five member heterocyclic ring such as 2,5- disubstututed -1,3,4- thiadidazole or 1,3,4 - oxadizole results in nematic or smectic mesophase, typical of calamatic liquid crystals [231-232].

1.8 Mesogenicoligomers having flexible spacers : Dimers, Trimers, tetramers

Liquid crystalline oligomers, which consists of molecules composed of semi rigid mesogenic or nonmesogenic units interconnected via flexible spacers, have attracted considerable interest [233-234]. Mesogens containing two, three or four mesogenic or non mesogenic connected by flexible spacers are called as dimers, trimers or tetramers respectively. Liquid crystal dimers, trimers and tetramers are also of interest as models for main chain liquid crystal polymers [235-239].Schematic representation of dimers, trimers and tetramers is shown in Figure 1.26.

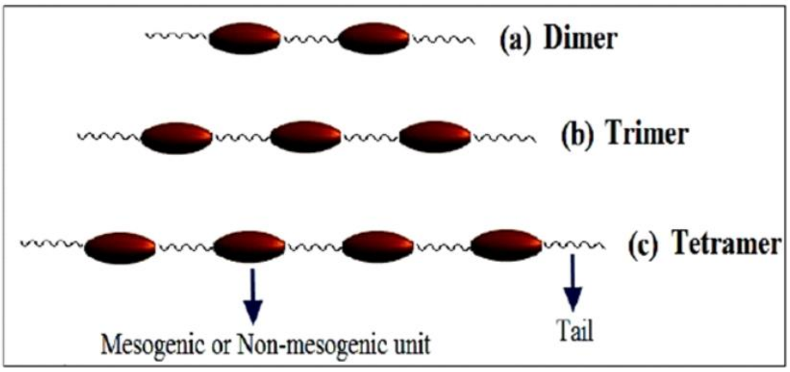

Figure 1.26: Schematic representation of mesogens with flexible spacers

1.8.1 Mesogenic Dimers

The first mesogenic dimer made of rod like unit is reported [235] by vorlander long ago. Interesting mesophases exhibited by the dimeric system [236-239] depending upon the variation in structure. The first liquid crystalline dimer composed of banana shaped mesogenic units are reported by Dantlgraber *et al* [240]. Recently, Kosata *et al* reported [241] symmetric dimers showing columnar phase. Several H- shaped dimmers [242-244] with different spacers are reported. Prasad *et al* [245] synthesized anthraquinone based discotic dimers exhibiting columnar mesophases. Majumdar *et al* [246] synthesized and characterzed cholesterol based liquid crystalline dimers.

1.8.2 Mesogenic Trimers

The significant findings on the dimers have prompted researchers to also synthesize its longer counterpart with three mesogenic groups connected by two spacers which are known as the trimers or trimesogens [247]. The trimers show different mesomorphic properties as compared to those of the dimers. A few chiral trimeric liquid crystals are reported [248-249]. Variety of trimers are synthesized with different mesogenic or non- mesogenic units and different flexible spacers or terminal chain lengths [250-255]. Trimers containing three biphenyl groups are reported by Itahara *et al* [256].

1.8.3 Mesogenic Tetramers

Liquid crystalline tetramers are prepared by many groups of researchers [257-259]. These compounds exhibits a remarkable odd-even effect in their trnsition properties, depending on the length and part of the flexible spacers [260-261]. The variation in smectic behavior of mesogenic tetramers containg four mesogenic tetramers containings four mesogenic units and three flexible spacers is studied [262-263].

1.9 Polymer Liquid crystals

After the initial discovery of liquid crystallinity in polymeric solutions by oster [264] and Robinson [265] number of liquid crystalline polymers have been reported. The high strength, high modulus fibers have given an impetus in the study and synthesis of liquid crystals, yet retain many of the useful and versatile properties of polymers. The molecular structure and mesomorphic character of liquid crystal polymers is discussed in detail by Finklemann [266] and ober [267].

The classification of lquid crystal polymers is based on the mesogens used in the construction of the liquid crystal polymer, which can be rod like, disc like or amphiphilic [268]. They are broadly classified into main chain liquid crystal polymers. Figure 1.27 shows the molecular geometry of liquid crystal polymers.

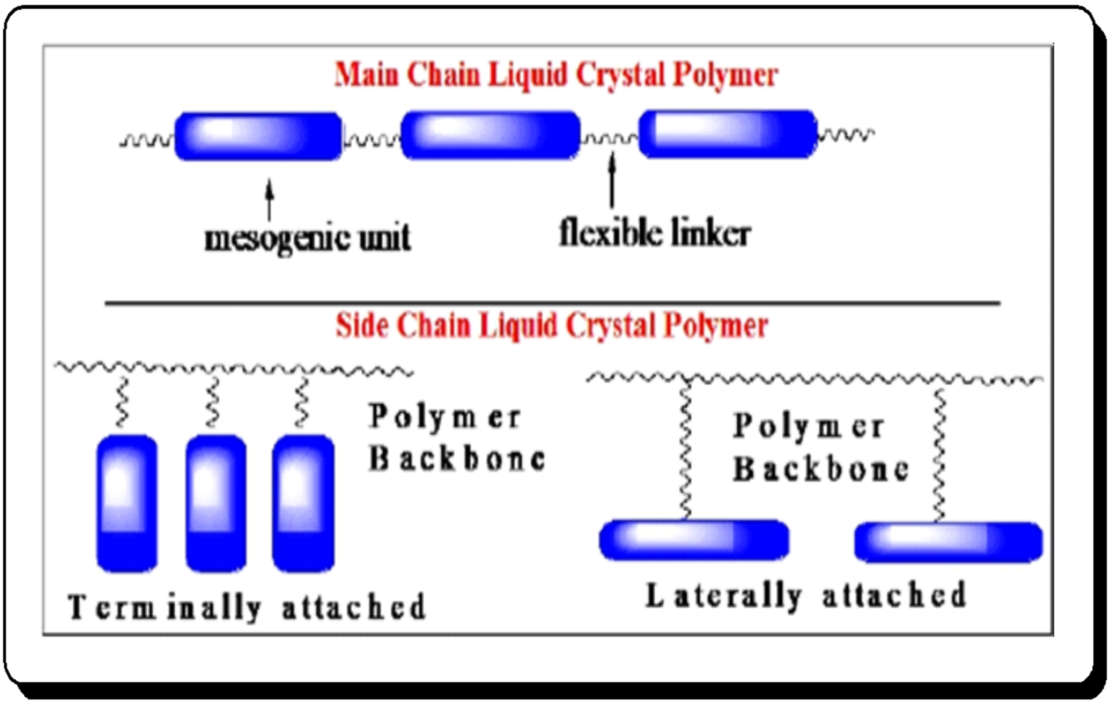

Figure 1.27: Molecular geometry of liquid crystal polymers

1.9.1 Main Chain Polymer Liquid crystals (MC- PLCs) (Figure 1.27)

Main chain liquid crystal polymers are formed when rigid elements are incorporated into the backbone of normally flexible polymers. These stiff regions along the chain allow the polymer to orient in a manner similar to ordinary liquid crystals, and thus display liquid crystal, characteristics.

There are two distinct groups of MC – PLCs differentiated by the manner in which the stiff regions are formed. The group of main chain polymer liqquid crystals is characterized by stiff, rod like monomers. These monomers are typically made up of several rings, which provide the necessary size. The second and more prevalent group of main chain polymer liquid crystals is different because it incorporates a mesogens directly into the chain. Main chain liquid crystal polymers are reported by various workres [269-273].

1.9.2 Side Chain Polymer Liquid crystals (SC - PLCs) (Figure 1.27)

It has been demonstrated that main chain polymer liquid crystals often cannot show mesogenic behavior over awide temperature range. Side chain polymer liquid crystals, however, are able to expand this scale. These materials are formed when mesogenic units are attached to the polymer as side chains; which are very well summarized by Blumstein and Hsu [274] and Ciferri *et al* [275].
Generally acrylates or methacrylates which form a vinyl backbone are prepared as polymerizable groups [276]. Side chain cholesteric mesogenic polymers having isosorbide chiral agent are synthesized by He *et al* [277]. The first side chain polymer liquid crystals with incorporated bent core

mesogens is reported by Keith et al [278]. Numbers of side chain liquid crystalline polymer are reported by various researchers [279-283].

1.10 Metallomesogens

In recent years, there is a growing interest in synthesis of liquid crystals containing metal atoms. These have been termed as metallomesogens (Figure 1.28). Metallomesogens have combination of properties of both of organic liquid crystalline ligand and metal atom [284]. Coordination of liquid crystalline ligands to metal ions can give variety of molecular shapes and phase changes [285]. The first thermotropic metal containing liquid crystals are reported by Vorlander [286] in 1910. He found that the alkali metal carboxylates –$(CH_2)_n$-COONa forms classical lamellar phase on heating. Many thermotropic metallomesogens have been prepared over the years and many of these are discussed in the review articles by Pucci [287] and Espinet et al [288]. Both the rod like [289-291] and disc like [291-292] metallomesogens are known and examples of all the main mesophase types have been observed. Varieties of monodentate ligands, such as distilbazole [293], 4- substituted pyridines [294], Ferrocenes [295-296] etc. Synthesis of macrocyclic liquid crystalline ligands and their complexes are reported by C. R. Jejurkar et al [297]. A literature survey shows that several metallomesogens containing different metal atoms are synthesized [298-306].

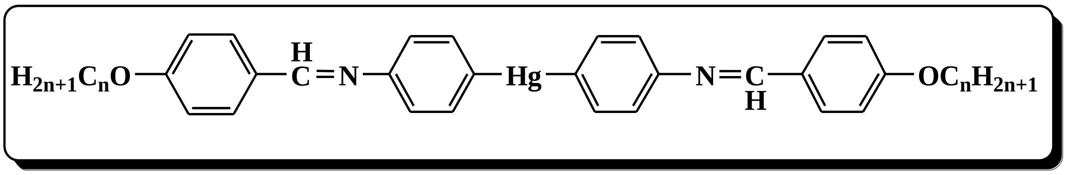

Figure 1.28: General molecular structure for metallomesogens

1.11 Mixed Mesomorphism

When mesomorphs are mixed, their melting points as well as transition temperatures depress in the usual way following more or less the law of mixtures. Different types of mixtures where none, one or both the components are mesomorphs have been investigated. Tamman [307], Lehmann [308], Schenck [309] and Schenck and Schneider [310] reported long back that nematic – isotropic temperature of p-azoxyanisole is lowered by the addition of other substances. The extent of mixed mesophase and the effect of terminal substituents in the exhibition of mixed mesomorphism have been studied in greater details by Dave and Dewar [311]. Dave and Lohar [312], Dave and Vasanth [313], Lohar and Shah [314], Lohar and Patel [315], Lohar and Mashru [316], Lohar and Jayrang Dave [317], Jayrang Dave and Menon [318] and Jayrang Dave and Pratik Patel [319]. Many researchers have given a detailed account on the studies of mixed mesomorphism [320-324].

Much earlier Bagojawlensky and Winogrodow [325] deduced from their study of mixed mesomorphism the latent transition temperatures of non-mesomorphic substances by extrapolation method. Walter [326] reported similar cases. Dave and Dewar [311], however, criticized the extrapolation method since they obtained different Values for latent trtansition tem,peratures of a non-mesomorphic substance depending upon whether the liquid crystalline component was p-azoxyanisole or p-azoxyphenetole. Later on Dave and Lohar [312] found better evidence in favour of the accuracy of the extrapolation method; Lohar and shah [314], Dewar and Goldberg [327], Lohar and Patel [315], Lohar and Mashru [316] and Lohar and Jarang Dave [317] have brought out more evidences in support of the extrapolation method, prescribing certain conditions for better reliability.

De kock's [328] contention that there should exist a range of temperature over which two liquid phases- one isotropic and another anisotropic co-exist has been questiones by Dave and Dewar [311] who re-examined the system stuidided by de kock. Showing that the mixed liquid crystalline region is a single homogeneous phase. Dave and Dewar [311] and Dave and Lohar [312] obtained quite intersting results by mixing p-azoxy anisole with different Schiff's base and deduced an order of efficiency of the terminal groups for exhibiting nematic mixed mesophases.

Sackmann *et al* [329] have identified smectic mesophase on the basis of miscibility criteria and texture phenomena. Madhusudana [330] synthesized some liquid crystals made of banana – shaped molecules and studied their binary mixtures with rod-like molecules.

1.12 Physical Properties of Liquid Crystals

Large volume of work to study the physical properties of liquid crystals has been carried out by scientists in early days of liquid crystals. Van der lingen [331], and Huckel [332], Dabrowski et al [333], Yang et al [334] and Iida et al [335] carried out X-ray studies. NMR and DSC studies are carried out by Tanaka et al [336] Domenici et al [337] and Lippmann et al [338-339] and Saupe and Englert [340]. The stuidies of Ultra violet and Infrared Spectroscopy are carried out by a number of researchers like sun et al [341] and Khoo et al [342]. Viscosity are done by Schafer [343].

The use of liquid crystals as stationary phase in chromatography is initiated by Dewar et al [344] and Kelker [345] used few liquid crystalline compounds as stationary phase in gas chromatography. Many other researchers worked in this field [346-349]. Number of reviews and books are published where detailed studied of physical properties are discussed [350-351]. The study of physical properties is important as it decides the applicability of liquid crystals so that can be exploited for practical advantages.

1.13 Biological Systems

Mesomorphic property in the form of Myelin in biological system is first shown by Virchouw [352] in 1854. Biological systems are multi component and contain numerous types of macromolecules, organic ions etc. One of the first demonstrations of liquid crystalline phenomenon in a well characterized biological systems is given by Bernal and Faukuchen [353] who used X-ray diffraction to investigate solutions of tobacco mosaic virus. A definite claim that liquid crystals entered the structure of living cells and tissues is made in 1959 [354] when it is shown that complex lipids present in adrenal cortex, ovaries , myelin and also in atheromatous arteries existed at body temperature in a characteristic mesophase. Stewart [355] studied in detail the mesomorphism is observed in biologiocal systems. Liquid crystals are abundant in nature and intrinsically linked to a multitude of biological processes, as discussed in several reviews [356-357]. Jewell discussed in detail on living systems and liquid crystals [358]. The lung liquid crystals droplets are capable of phase transitions between liquid crystals, Crystal, and isotropic phases which are dependent on the rate of temperature change as in liver, Kideny and other major tissues of the embryo [359]. The exploration of liquid crystalline materials at the interface between physics, chemistry and biology is particularly lucrative, providing a greater insight into the mechanisms by which living systems function as well as leading to new biomedical applications in the understanding, diagnosis and treatment of diseases [360]. Naturally occuring biological materials that spontaneously form liquid crystal phases in vivo include DNA [361-362], chromosomes [363] and collagen [364] as well as the lyotropic phases formed by protiens in the production of spidersilk [365] and lipids in the membrane of living cells.

1.14 Applications of Liquid Crystals

From the application point of view, ‘liquid crystals’ are one of the most developing and fascinating fields of current research. Liquid crystalline compounds have found ways for numerous potentials applications because of their characteristic physical and optical properties. Now a days liquid crystals are used in many fields, particularly in the fields of electro-optical applications [366] and in biological systems.

1.14.1 Display applications of Liquid crystals

Liquid crystals displays (LCDs) [367] had a humble beginning with wrist watches in the seventies. Continued research and development in this multidisciplinary field have resulted in displays with increased size and development in this multidisciplinary field have resulted on deisplays with increased size and complexity. After three decades of growth in performance, LCDs now a formidable challenge to Cathode Ray Tube (CRT). Liquid Crystal Displays (LCDs) have many advantages over other displays types. They are flat and compact, process extremely low power consumption (Microwatts per square centimeter in the case of the twisted nematic display).

For simple calculator and watch displays TN (twisted Nematic) mixtures based on cyanobiphenyls are used. These materials are first invented by G. W. Gray 39 years ago [368-369]. Broad range TN mixtures with improved viewing angle using phenylcyclohexanes [370-371] are then used for automotive applications. The introduction of STN displays required materials with large dielectric anisotropy, eg. Cyaesters with lateral fluro substitution [372]. Thin filmtechnology (TFT) display require liquid crystalline materails with high stability like fluorinated liquid crystals [373-378]. Kim et al [379] has fabricated a novel switchable transmitive and reflective (STR) LCD based on dual gap TN (Twisted Nematic) mode.

1.14.2 Non display application of Liquid crystals

1.14.2.1 Thermal mapping and non-destructive testing

A film of cholesteric liquid crystal may be applied to large uneven area. This makes it an ideal tool for thermal mapping and non-destructive testing [379-380]. The great deal of flexibility in the colour play range allows for a great diversity in potential applications ranging from food processing to electronics and space applications e.g. thermochromic paints have been used on printed circuit boards to examine overheating of components. Liquid crystal thermography is used non – destructive testing and continuously growing due to the development on new chiral nematic materials to offer improved performance over the cholesteryl esters used in early applications.

1.14.2.2 Liquid crystals lenses

The ability to control the refrective index of a liquid crystal allows the implementation of liquid crystal lenses. The refractiveindex profile in these devices acts as a curved surface of a glass and hence acts as a lens [381].

1.14.2.3 Medical Thermography

Thermochromic liquid crystals are extensively used in medical application [382], Forehead thermometers also known as ‘fever strips’ are based on different thermochromic liquid crystal materials. Thermal mapping of various areas of the body has been used as a diagnostic technique for a wide ranging group of the body has been used as a diagnostic technique for a wide ranging group of medical condition in which a temperature defferential near the skin surface may be related to the disorder. Subcutaneous and intracutaneous malignant tumors are typically 0.9-3.3°C warmer than the surrounding tissues. Therefore, thermography is an interesting candidate for cancer Screening.

1.14.2.4 Radiation detection

Films containing cholesteric liquid crystals are inexpensive and versatile tools for visualizing invisible radiation[383].

1.14.2.5 Liquid crystals in gas (GLC) liquid chromatography

The molecular structure of liquid crystals allows for their application in gas and liquid chromatography as highly selective stationary phase. A number models have been developed to describe more quantitatively the enhancement in selectivity that is obtained the anisotropic orientation ordering of liquid crystals [384-386]. Earlier uses of liquid crystals as statinary phases in gas chromatography are avalibale [387-389]. Statinary phases can be prepared from either monomeric or side chain polymeric liquid crystal.

1.14.2.6 Liquid crystals as solvents in spectroscopy

Liquid crystalline media, particularly nematic, provide the bulk molecular orientation necessary for observation of spectroscopic details analogous to those obtained in solid state experiments. These have been widely used as solvents in NMR, EPR and Optical spectroscopic studies on oriented molecules. A few general reviews ion this area of applications have appeared [390,391].

1.14.2.7 Liquid crystals as solvents in chemical reactions

Thermotropic liquid crystals have been used as solvents to alter course or rates of uni and bi-molecular thermal and photochemical reactions. The unique anisotropic properties of liquid crystals are utilized to control the efficiency and specificity I microsynthesis elucidation of reaction mechanism etc. Factors that are important in defining the ability of liquid crystals to control solute reactivity have been reviewed to be able to choose the liquid crystals of proper morphology as a solvent [392-394].

1.14.2.8 High – Strength Fibers

An application of polymer liquid crystals that has been successfully developed for industry is the area of high strength fibers e.g. Kevlar fibers, which are used to make such things as helmets and bulletproof vests, is just one example of the use of polymer liquid crystals in applications calling for strong light weight materials [395].

1.14.2.9 Optical Applications

The use of liquid crystalline polymer in the display is an exciting area of research. A twisted nematic polymer liquid crystal cell can be used to make energy efficient displays. Highly polarizable thiophene derivatives are used in nonlinear optical applications [396-398]. Nematic triphenylenes have found applications as the principle components in optical compensation films to improve the viewing angle of liquid crystal display [399]. Liquid crystalline polymers contaning azo group have been widely studied overall in the field of optical materials. [400-401].

1.14.2.10 Discotic liquid crystals for solar cells

Discotics liquid crystals have very high cherge carrier mobility in columnar mesophases which offers potentials applications as charge transport materials in a variety of devices like conductors, field – effect transistors, photovoltaic solar cells etc. [402]. Some other studies on charge and energy migration in discotic liquid crystals [403-404] lead us closer to a long desired goal of achieving cheaper , clean, eco friendly energy for the benefit mankind. The application is of great importance to developing countries.

1.14.2.11 Thermotropic Liquid Crystals as lubricating agent

The mechanism of lubrication is based on the creation of adsorbed layer by a lubricating agent [405-408]. Such compounds have polar groups which let the adsorption on the metal surface and formation of protecting ordered layers. Different liquid crystalline are tested as lubricating agents to check the influence of chemical structure and the mechanism of action these substances.