

**“FINAL REPORT OF THE MINOR RESEARCH  
PROJECT”**

**SYNTHESIS AND CHARACTERIZATION OF  
SOME NOVEL LIQUID CRYSTALS COMPOUNDS**

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# **INTRODUCTION**

Liquid crystals are a state of order between crystals and liquids. They have imperfect long-range orientational and / or positional orders. Thus, they can be fluid like a liquid and can have anisotropic properties like crystals. The liquid crystals have a predominating orientational order. They also exhibit rheological behaviour similar to those of liquids and anisotropic physical properties similar to those of crystalline solids in the same thermodynamically stable phase.

### History of Liquid Crystals:

The study of liquid crystals began in 1888 when an Austrian botanist [1] named Friedrich Reinitzer observed that cholesteryl benzoate had two distinct melting points, first melting at 145.5 °C to give a coloured cloudy fluid which, on further heating changes into a clear, transparent liquid at 178.5 °C. The phenomenon is reversible. Because of this early work, Reinitzer is often credited with discovering a new phase of matter – the liquid crystal phase, however, Otto Lehman [2] was the first to make a systematic study of such substances and proposed the name 'Liquid Crystals' for such compounds.

Daniel Vorlander [3] in 1908 was able to establish a rule that liquid crystalline compounds must have a molecular shape as linear as possible. In 1906, he had detected the phenomenon of liquid crystalline polymesomorphism i.e. a given compound exhibits more than one liquid crystalline phases.

G.Friedel [4] for the first time gave rational explanation for the pictures observed under the polarizing microscope and concluded from his observations on the structure of three phases as follows.

- a) Nematic phase normally exhibited threaded texture.
- b) Smectic phase normally exhibited focal conic fan shaped texture.
- c) Cholesteric phase exhibited focal-conic or plane texture with vivid colours.

Onsagar [5] tried to explain this state of matter based on model of long stiff rods, pointing at the dominant role of repulsive forces, while Maier and Saupe [6] indicated the importance of the dispersion forces in the liquid crystalline state.



S. Chandrasekhar [7] in 1977, for the first time, could show that not only rod-like molecules, but compounds, with disc-shape molecules are also able to form liquid crystals of different phase structures.

Liquid crystallinity since then has been observed in different classes of compounds such as fullerenes, calixarenes, metallomesogens, dendrimers, banana shape molecules, etc.

### What are Liquid Crystals?

2 ✓ The distinguishing characteristic of the liquid crystalline state is the tendency of the molecules (mesogens) to point along a common axis, called the director. This is in contrast to molecules in the liquid phase, which have no intrinsic order. In the solid state, molecules are highly ordered and have little translational freedom. The characteristic orientational order of the liquid crystal state is between the traditional solid and liquid phases and this is the origin of the term mesogenic state, used synonymously with liquid crystal state. 1

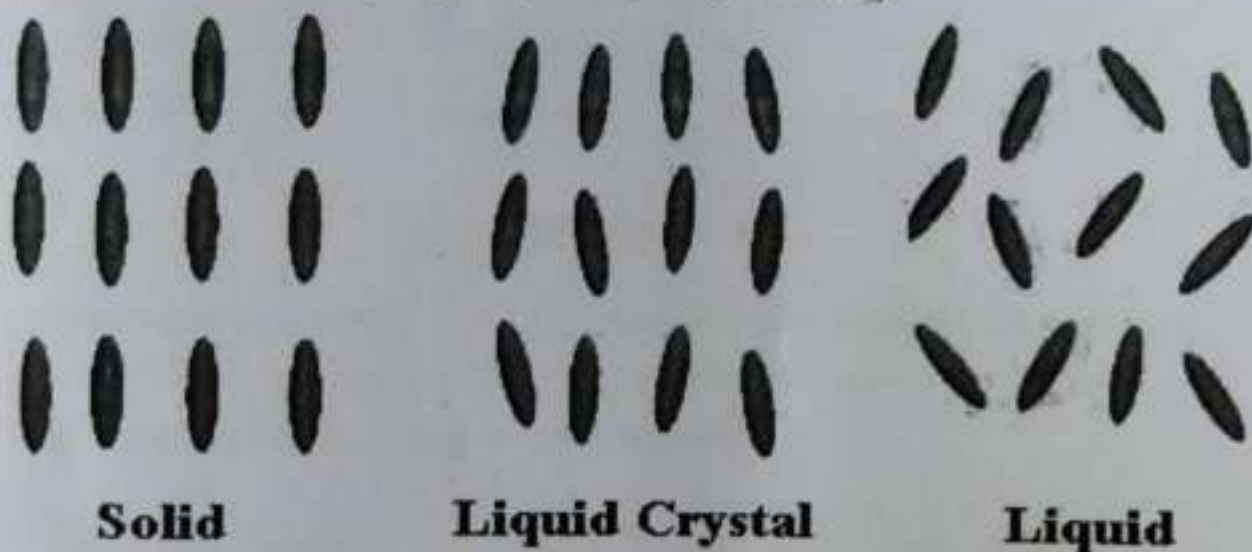


Figure-1      Molecular arrangement in solid, liquid crystal and liquid

It is sometimes difficult to determine whether a material is in a crystal or liquid crystal state. The crystalline materials demonstrate long-range periodic order in three dimensions. By definition, an isotropic liquid has no orientational order. The substances that are not as ordered as a solid, yet have some degree of alignment are properly called liquid crystals.

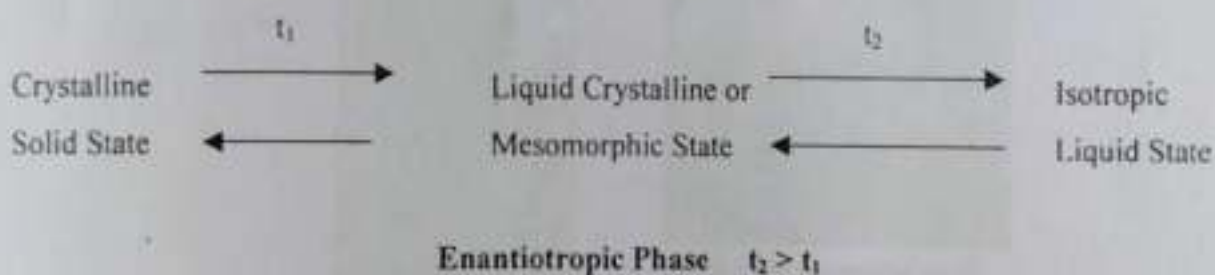
## CLASSIFICATION:

Liquid crystals are classified into two distinct types depending on the manner in which these are obtained.

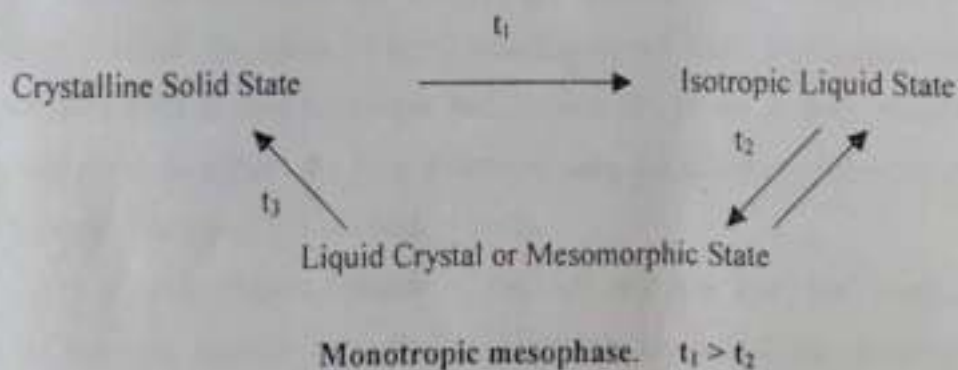
- I) Thermotropic liquid crystals
- II) Lyotropic liquid crystals

## THERMOTROPIC LIQUID CRYSTALS:

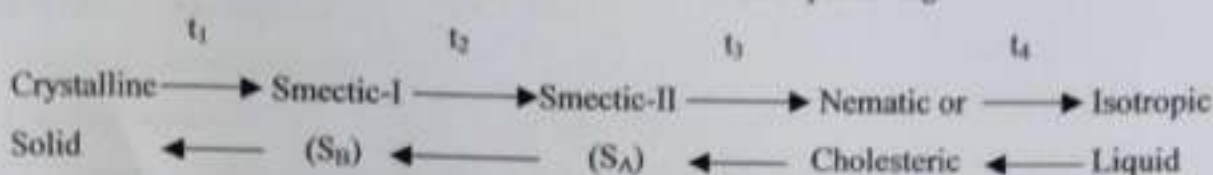
This class of liquid crystals is formed by the application of heat. A compound exhibiting thermotropic liquid crystalline phases on heating, changes to an isotropic liquid on further heating. This phase change is reversible. On cooling isotropic liquid changes to liquid crystalline phase and on further cooling solidification takes place, however many a times super cooling takes place. Such a phase is designated as enantiotropic liquid crystalline phase.



There are many compounds, which on heating do not exhibit mesophase and directly pass to an isotropic liquid, but on cooling they exhibit a mesophase, before crystallization. Such metastable mesophases are termed as monotropic mesophases.



Liquid crystalline compounds may either be exclusively smectic or nematic or may exhibit smectic and nematic or smectic and cholesteric phases. They may exhibit polymesophases. There may be different types of one phase. This phenomenon is known as polymorphism and is commonly observed for smectic mesophase. e.g.



### Nematic mesophases:

The nematic liquid crystal phase is characterized by molecules that have no positional order but tend to point in the same direction (along the director). The following diagram shows that the molecules point vertically but are arranged with no particular order.



A schematic representation of the nematic phase (left) and a photo of a nematic liquid crystal (above).

*Photo courtesy Dr. Mary Neubert ICI-KSU*

Figure-2

Under the polarizing microscope, the nematic phase is seen as a threaded schlieren texture and hence the name ('Nema' meaning thread like). The optical effect of the nematic threads have been studied by Zocher and Birstein [8]. In the nematic phase the molecules have rotational freedom around the long molecular axis, the effective molecular shape is not flat, but may be better described by a rotating cylinder.

The nematic phases, because of the high mobility, have low viscosities very similar to those of isotropic liquids. Nematic liquid crystals are anisotropic with respect to the optical properties, viscosity, electrical and magnetic susceptibility, electrical and thermal conductivity.



De Vries [9] proposed the classification of nematic phases based on X-ray diffraction pattern:

1. Skewed cybotectic nematic.
2. Normal cybotectic nematic.
3. Classical nematic.

Nematic liquid crystals are optically positive and can be formed by compounds, which are optically inactive, or by racemic modification.

Alben [10], Onsager [5] and Dreyer [11] suggested that it is reasonable to expect that there might be negative nematics with planar molecules aligned with their shortest axis parallel to each other. A new type of nematic mesophase was obtained by Zimmer and White [12], during the process of carbonization and is termed as carbonaceous mesophase. Gasparoux [13] has studied the carbonaceous mesophase in detail and reviewed its properties.

### **Smectic Mesophase:**


The word "smectic" is derived from the Greek 'Smectose' meaning soap like. Molecules in this phase show a degree of translational order not present in the nematic phase. In the smectic state, the molecules not only maintain the general orientational 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 [14] and Saupe [15] have classified the smectic phases into two classes.

1. Smectic phases with unstructured layers
2. Smectic phases with structured layers.

Much work on the classification of smectic liquid crystals has been done by Sackmann and Demus (Table-1) [16]. De Vries and Fishel [17] have reported the  $S_{11}$  smectic phase, moreover, de Vries [18] on the basis of X-ray studies has classified the smectic phases into three main classes  $\alpha$ ,  $\beta$  and  $\gamma$ . Class  $\alpha$  consists of smectic A, C, F and D, class  $\beta$  consists of smectic B and class  $\gamma$  consists of smectic E, G and H.

Destrade et al. [19, 20] have studied homologous series showing re-entrant phenomenon in smectic mesophases. Bennemann et al. [21] have reported some mesogenic chiral compounds showing smectic Q phase just below the clearing point. Bennemann, Heppke and Lotzsch [22] have carried out structural investigation of smectic Q phase. As suggested by Gray and Goodby [23] the thermodynamic ordering of known smectic polymorphic forms is as follows:

A D C F B H E G 

Thermal stability decreases.

**Table – 1**  
**Texture Classification of Smectic Phases**

Type of Smectic Mesophase	Structure	Texture
Smectic - A	Planar	i) Stepped drops ii) Oily Streaks iii) Homeotropic
	Non – Planar (Dupin Cyclides)	i) Simple polygonal texture ii) Simple fan shaped texture iii) Batonnets iv) Bubble textures
	Cylinders	i) Myelinic textures
Smectic - C	Planar	i) Homogenous texture ii) Stepped drops iii) Schlieren texture
	Non – Planar (Dupin Cyclides)	i) Broken polygonal texture ii) Broken fan shaped texture iii) Batonnets
	Twisted	i) Planar texture ii) Schlieren texture iii) Straited fan shaped texture
Smectic - F	Planar	i) Schlieren texture ii) Stepped drops
	Non – Planar (Dupin Cyclides)	i) Stripped broken fan shaped textures
Smectic - B	Hexagonal Planar	i) Mosaic texture ii) Homeotropic texture iii) Stepped drops iv) Batonnets v) Ovals vi) Lancets
	Non – Planar (Dupin Cyclides)	i) Focal conic texture (paramorphosis)
	Tilted	i) Mosaic texture ii) Stepped texture
Smectic - E	Planar	i) Mosaic texture ii) Stepped texture
	Non – Planar	i) Straited ii) Stripped fan shaped texture
Smectic - G	Planar	i) Mosaic texture ii) Stepped drops
Smectic - D	Cubic bands	i) Isotropic mosaic texture

In **smectic-A** mesophase, the director is perpendicular to the smectic plane and there is no particular positional order in the layer. The **smectic B** mesophase orients with the director perpendicular to the smectic plane, but the molecules are arranged into a network of hexagons within the layer. In **smectic C** mesophase, molecules are arranged as in the smectic A mesophase, but the director is at a constant tilt angle measured normally to the smectic plane.

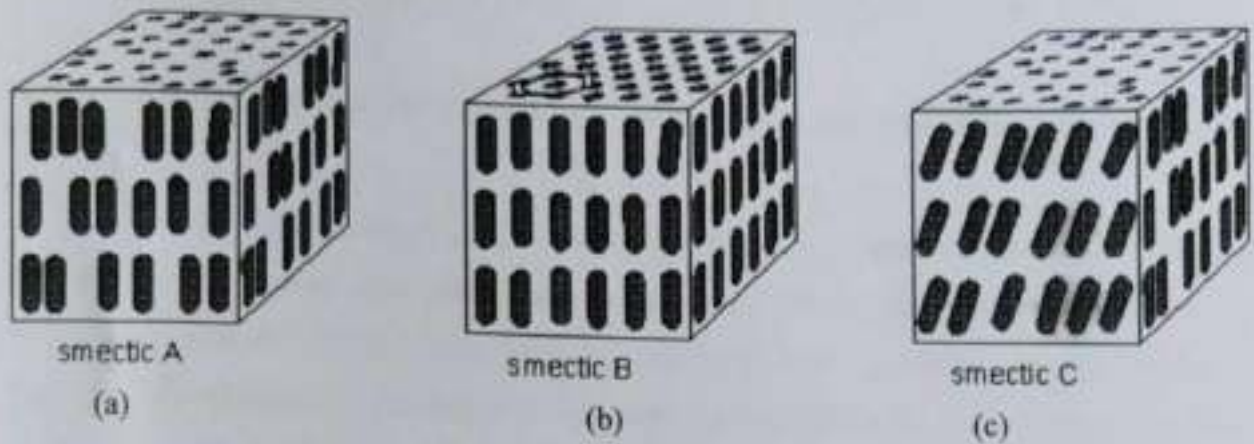


Figure - 3 Different Textures of Smectic Phases



Figure-4 Schematic Representation of Smectic A phase



Photo courtesy of Dr. Mary Neubert LCI-KSU



Photo courtesy Dr. Mary Neubert

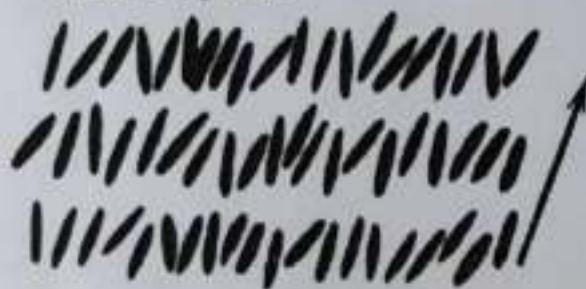


Figure-5 Schematic representation of Smectic C phase



Photo courtesy Dr. Mary Neubert LCI-KSU



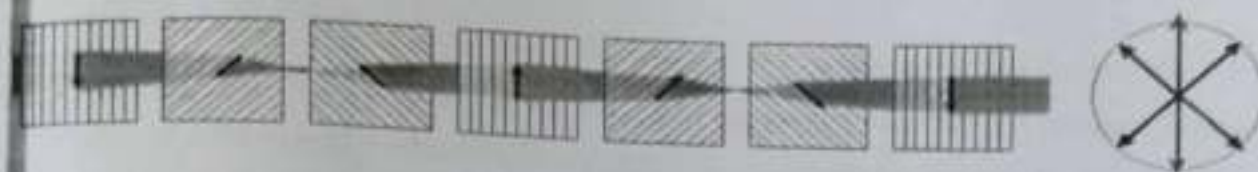


Figure - 6 A schematic representation of a smectic C\* phase (left), and a view of the same phase, but along the axis (right).

As in the nematic, the smectic C mesophase has a chiral state designated C\*, consistent with the smectic C phase, the director makes a tilt angle with respect to the smectic layer. The difference is that this angle rotates from layer to layer forming a helix. In other words, the director of the smectic C\* mesophase is not parallel or perpendicular to the layers but it rotates from one layer to the next. The green arrows represent the twist of the director in each layer in figure-6.

### Cholesteric mesophase:

The cholesteric (also called chiral nematic phase) [24-26] liquid crystal phase is typically composed of nematic mesogenic molecules containing a chiral center, which produces intermolecular forces that favour alignment between molecules at a slight angle to one another. This leads to the formation of a structure, which can be visualized as a stack of very thin 2-D nematic-like layers with the director in each layer twisted with respect to those above and below. In this structure, the directors actually form in a continuous helical pattern about the layer normal as shown in figure 7.

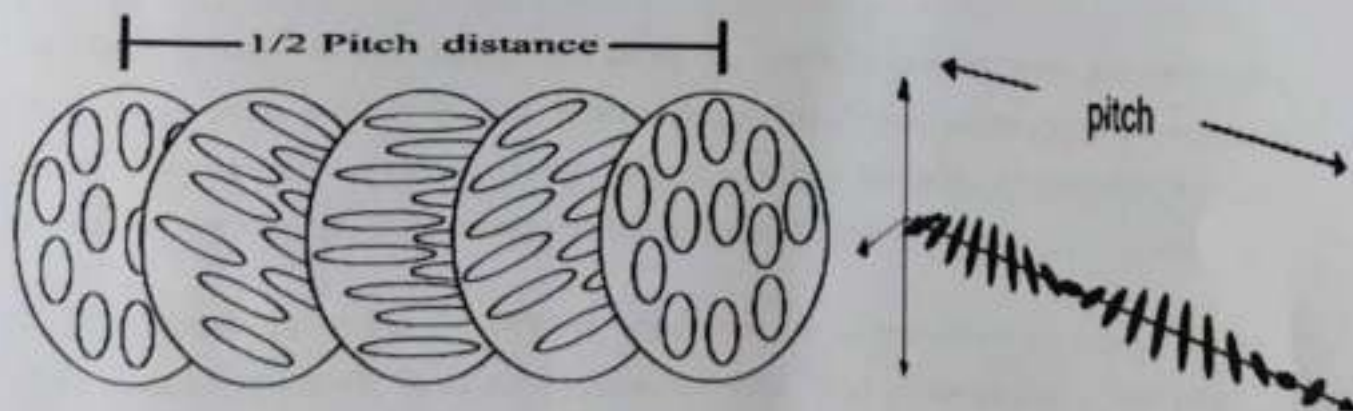


Figure - 7 A Schematic representation of cholesteric phase

The black arrow represents director orientation in the succession of layers along the stack. The molecules shown are merely representations of the many chiral nematic mesogens lying in the slabs of infinitesimal thickness with a distribution of orientation around the director. This is not to be confused with the planar arrangement found in smectic mesophases.

The mesomorphic behaviour of cholesteryl esters has been studied by Gray [27] and Dave and Vora [28]. Cholesteric liquid crystals behave in a unique and striking way not observed in other types of liquid crystals i.e. reflection of iridescent colours. An important characteristic of the cholesteric phases is the pitch. The pitch,  $p$ , is defined as the distance it takes for the director to rotate one full turn in the helix. The cholesteric compounds can selectively scatter light into different colours. The colour of the reflected light can be determined by (a) pitch of helix (b) by temperature (c) the angle of incident beam. Physical effects, which wind or unwind the helix such as temperature, mechanical disturbance like pressure or shear and traces of organic vapours result in various colour changes. Re-entrant cholesteric phases have been reported in polar mesogens by Destrade et al. [29].

In contrast to smectic and nematic compounds, cholesteric liquid crystals are optically negative. They generally have three types of textures.

- i) **Focal Conic Texture:** When an isotropic liquid is cooled, the texture obtained is focal conic. The term is derived from the conic sections that are usually observed in case of smectics. The focal conic texture nucleates in discrete points from where it grows in all the direction i.e. radial growth until whole film is covered.
- ii) **Plane Texture:** In this texture, the sample is uniformly aligned with the twist axis perpendicular to the plane of the film. However, alignment discontinuities can show reflected colours. For perpendicular incidence the wavelength of light at the centre of the reflection band is equal to the wavelength of the pitch multiplied by refractive index.
- iii) **Blue Phases:** On cooling the isotropic liquid some cholesteric mesogens exhibit a phase which is visible to the eyes in reflected light over a small range of temperature. This phase is known as blue phase and its possible structure was determined by NMR spectroscopy [30]. The



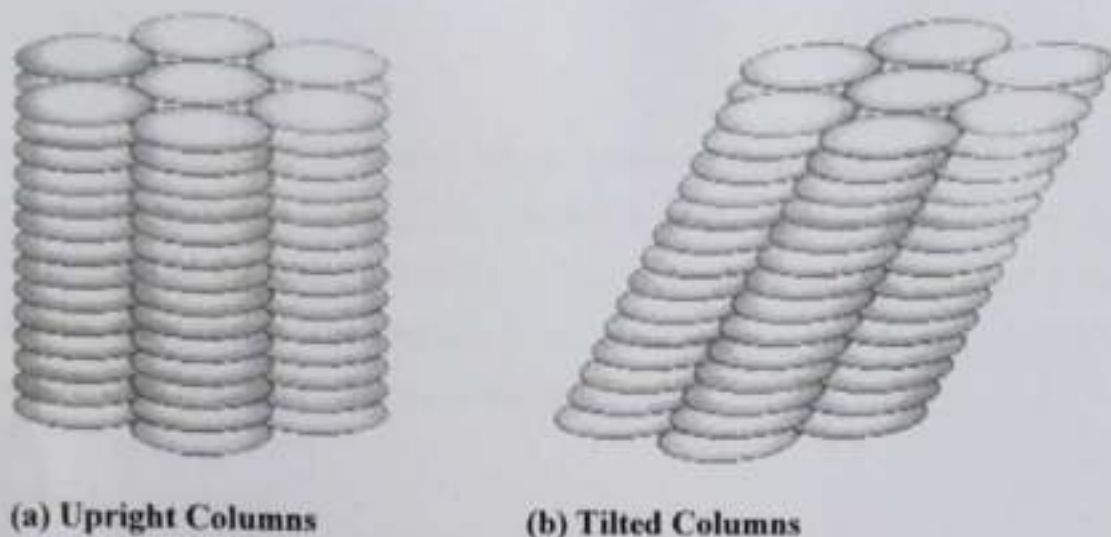
colour of light reflected by a blue phase sample indicates a cubic structure having a lattice parameter about the same as the pitch of the cholesteric phase.

Bergmann and Stegemeyer [31] have confirmed the blue phase of chloesteryl nonanoate by calorimetric and microscopic studies and reported the existence of two polymorphic forms of blue phases. These phases are optically isotropic and exhibit Braggs (light) scattering. Monocrystals may be grown showing distinct crystal faces. Siegemeyer et al. [32, 33] have observed two thermodynamically stable phases (Blue phase I and blue phase II). It was suggested by Saupe [34] that these blue phases (I and II) have cubic structure. Crooker [35] has suggested possible amorphous "fog" phase (Blue phase III) besides cubic phases (Blue phases I and II).

A number of workers [36-39] studied the physical properties and their results provide further evidences that blue phase is a three dimensionally ordered system [36] and confirmed the cubic structure [37]. Kitzerow [40] has presented an experimental review on electric field effects on blue phases.

### **Discotic Mesophase:**

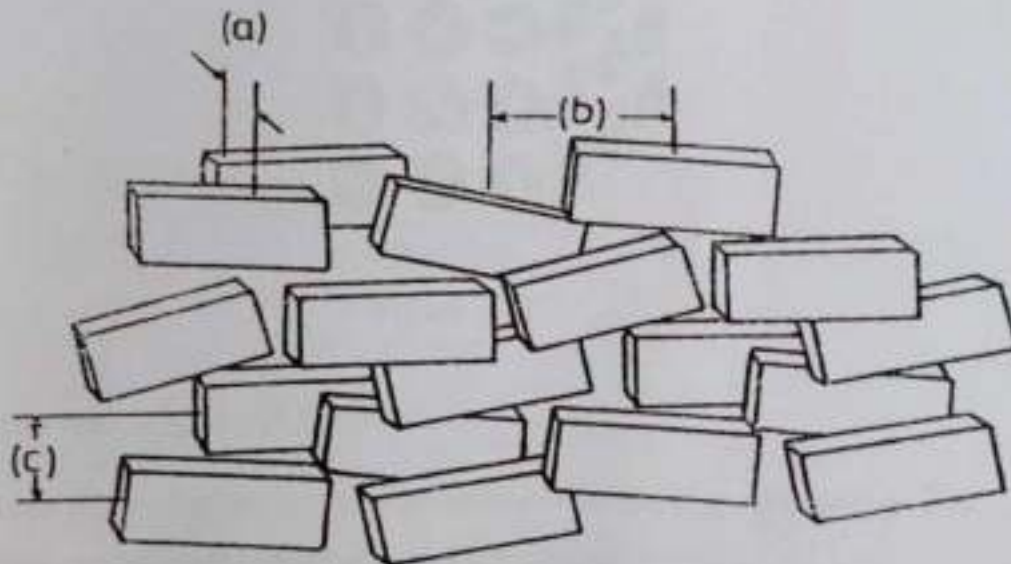
The first liquid crystals of disc shaped molecules were synthesized and identified by Chandrasekhar et al. [7] in 1977. These phases are formed from molecules with nearly flat aromatic cores, possessing four or six lateral substituents with at least five carbon atoms. This mesophase is characterized by stacked columns of molecules. The columns are packed together to form a two-dimensional crystalline array. The arrangement of the molecules within the columns and the arrangement of the columns themselves lead to new mesophases. Structurally, most of them fall into two distinct categories; **the columnar and nematic**, with a number of variants for the columnar [41]. The thermodynamic, optical and X-ray studies [42] have led to the conclusion that these compounds are entirely new class of liquid crystals [43-47]. Sandeep kumar et al. have reported a room temperature electron deficient new discotic system of branched chain tricycloquinazoline [48]. Re-entrant phenomenon in disc like molecules is reported by Destrade et al. [49]. Schematic representation of discotic mesophase is given in figure - 8.



**Figure – 8** A schematic representation of discotic mesophase

### Sanidic Liquid Crystals:

Sanidic liquid crystals are the lath like molecules having molecular geometry between the rod like and disc like molecules [50]. The term is derived from Greek word meaning board like and these phases were first observed in polymeric liquid crystals by Ringsdorf et al. in 1986 [51]. They are generally fused or twin compounds.



**Figure 9** Structure model of the sanidic nematic phase: a, b, c are the lattice parameters according to X-ray data



### Cubic Mesophases:

This phase is optically isotropic and its structure has been derived from X-ray investigations, which indicate a cubic lattice. There is three-dimensional long-range order with respect to the position of the lattice units [52]. On the molecular level, the structure is liquid-like with 'molten' alkyl chains. The viscosity of the cubic phase is very high. Lyotropic liquid crystals are also known to exhibit cubic mesophases.

### Plastic Crystals:

Liquid crystals are solid like liquid while Plastic crystals are liquid like solids. Generally liquid crystalline compounds are long, rigid and rod-like, whereas, plastic crystals are usually globular and compact. In plastic crystals positional order is maintained but orientational order is lost. Plastic crystals are also called orientationally disordered crystals (figure-10). Various physical properties of plastic crystals have been studied [53-56].



Figure - 10

### Physical Properties of Liquid Crystals:

The study of physical properties is important as it decides the applicability of liquid crystals so that they can be exploited for practical advantages.

Large volume of work has been carried out by scientists in early days of liquid crystals to study the various physical properties of liquid crystals. Van der Lingen [57], Huckel [58], de Broglie and Friedel [59], Cladis et al. [60] and Brown et al. [61], carried out X-ray studies. NMR studies were carried out by Spence et al. [62, 63], Lippmann et al. [64], and Saupe and

Englert [65]. The studies of ultra violet and infrared spectroscopy were carried out by a number of researchers [66,67]. Viscosity studies were carried out by Schenk [68] and Porter and Johnson [69].

The use of liquid crystals as stationary phases in chromatography was initiated by Dewar et al. [70] and Kelker [71]. Vora et al. [72] and others [73-75] used few liquid crystalline compounds as stationary phase in gas chromatography. A number of research papers have appeared recently in the literature, where scientists have reported ferroelectric, antiferroelectric and ferrielectric properties of liquid crystalline materials [76-80]. Linear and non-linear optical studies of liquid crystalline materials is also reported [81,82]. Perkin et al. have reported physical properties of some novel nematic bimesogens for the flexoelectric effect [83].

### **Mixed Mesomorphism:**

Just as the melting points of the solids are depressed by the additions of other substances, so are the transition temperatures of liquid crystals lowered by the addition of foreign substances. When a mesomorphic compound is mixed with another mesomorphic or non-mesomorphic component, the solid-mesomorphic and mesomorphic-isotropic transitions may be depressed and the degree of depression will depend upon the nature and the concentration of the added component in the mixture.

In early 1950's, Dave and Dewar [84] examined the problem of studying the behaviour of mixtures of varying compositions and they reached to several interesting conclusions. Based on their study they deduced a group efficiency order [84-86]. The study of exhibition of induced mesophases in binary systems where one or both components are non-mesogenic is a recent trend in liquid crystal research as these provide liquid crystalline materials at comparatively low temperatures and from relatively cheap and easily available materials.

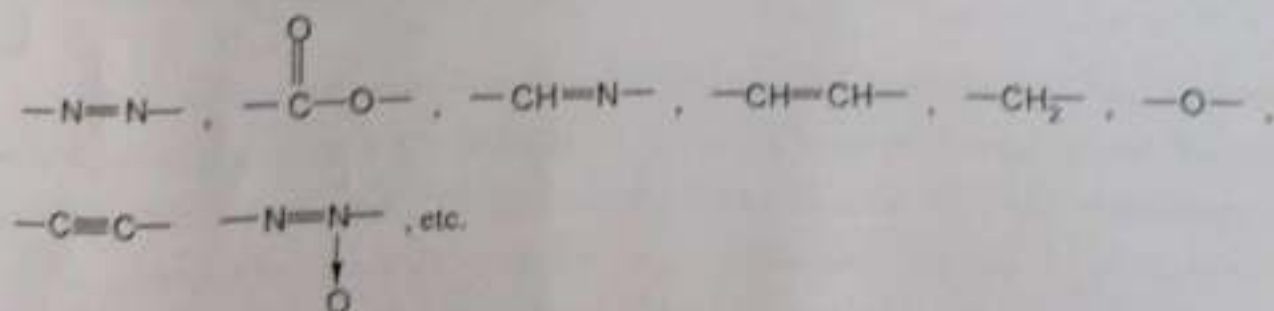
Padmini et al. [87] reported induced nematic phases in a binary system consisting of a polymorphic smectogen and non-mesogenic schiffs bases. Arora et al. [88] and Neubert et al. [89] have reported creation of nematic mesophase by addition of the second component, which is also a mesogen. Mahajan et al. [90] for the first time have reported the induction of smectic and nematic phases in binary systems of non-mesogens where one of the component is 1,2,4-

trisubstituted benzene derivatives. Mahajan et al. [91] also have reported intermolecular hydrogen bonding in binary system and discussed its role in the exhibition of mixed mesomorphism. Vora and co-workers [92] have studied binary systems of mesogens and non-mesogens exhibiting induced smectic and nematic phases. Sackmann and Demus [16] identified smectic mesophases on the basis of miscibility criteria and texture phenomena. Chiral smectic liquid crystal mixtures containing 1,3-difluoro naphthalene derivatives and compounds with fluorinated side chains have been studied by wolfgang et al. [93].

### The Effect of Chemical Constitution on Mesomorphism:

A close relationship exists between the structure of the molecules and its capacity to form liquid crystals. Considerable interest has been shown from the very beginning to find out the correlation between chemical constitution and mesomorphism. The majority of thermotropic liquid crystals are aromatic in nature consisting of polarizable and planar benzene rings linked with one another and having terminal alkyl or alkoxy groups. Gray [94,95] and Demus et al. [96-99] have given quite a detailed account of effect of chemical constitution on mesomorphism.

The major anisotropy of molecules necessary for their mesomorphic properties, results from the cores, which also are responsible for relatively high melting temperatures. Due to large conjugated aromatic ring systems the intermolecular attractions of the molecules are very large resulting in high melting temperatures. The core consists of rings that are connected to one another either directly or by linking groups. The mesogenic properties of the compound and the stability of the mesophase increase with the increase in the number of linearly connected rings. The central rigid linking groups are as under:

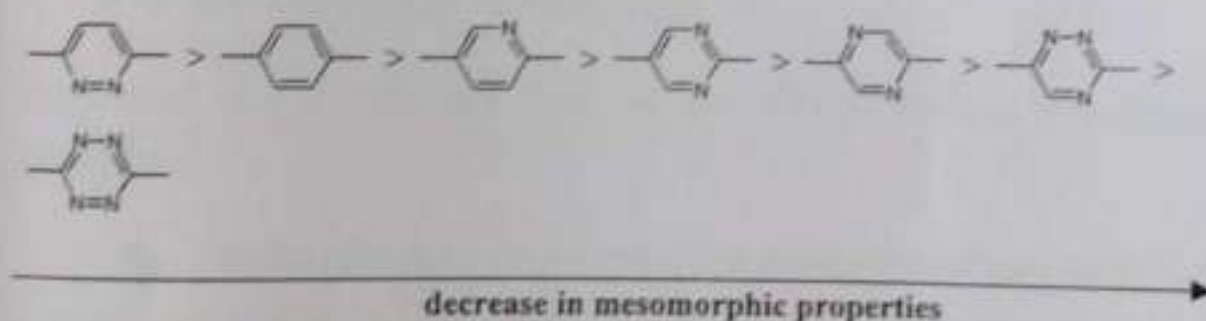




The cyclohexane ring is non-aromatic and flexible as compared to benzene ring. Dewar and Goldberg [100] have replaced the aromatic rings by saturated alicyclic rings and have studied its mesomorphic properties. The flexibility of central alicyclic ring has some negative influence on mesomorphic properties, however, cyclohexane derivatives belong to the most important class of substances for the application of liquid crystals in displays.

If a  $-CH-$  group in a ring is replaced by 'N' atom, the shape of the ring is only slightly altered but the electronic properties are changed and large electric dipoles are induced which change the intermolecular attractions. Vorlander successfully used heterocyclic six and five membered rings for synthesis of liquid crystals [101]. In addition, he applied several other heterocyclic rings, without obtaining liquid crystalline compounds [102]. Weygand and Lanzendorf in 1938 prepared the homologous series of the di-alkylphenyl-pyridazines, showing nematic and smectic phases [103]. It has been Schubert with his group, who systematically elaborated new families of mesogenic compounds using different six and five membered heterocyclic rings like thiadiazoles, pyridazines, pyrimidines and tetrazoles [104 - 108].

Much work has been reported by researchers on the liquid crystalline behaviour of heterocyclic compounds [109, 110]. Zaschke and Wiss [111] have given the order of efficiency of nitrogen heterocycles on mesomorphism as under:



### The Effect of Terminal Substituents on Mesomorphism:

Early reviews state that molecules of mesogenic compounds should contain moderately polar terminal groups, (X and Y in figure - 11) and it is important to establish the function of such substituents more clearly. Evidences will be put forward to show that replacement of a terminal hydrogen in a molecule by another substituent enhances the potential of the system to form liquid crystals. If the unsubstituted compound will form liquid crystals, then the substituted



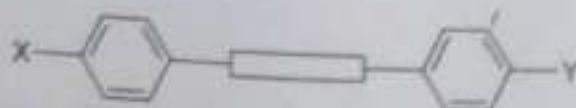


Figure - 11

compound will form liquid crystals which are, in the majority of cases, more thermally stable; only for smectic liquid crystals do certain terminal substituents reduce thermal stability. The role of the terminal substituent is not therefore simply to lower the melting point and reveal liquid crystal behaviour latent in the parent system. Indeed, terminal substituents usually raise melting points, but they increase liquid crystal thermal stability even more.

Liquid crystals of moderate chain lengths normally exhibit only nematic phase, increasing the length of the carbon chain gives both smectic and nematic mesophases and very long chain lengths usually exhibit only smectic phases. Gray and Winsor [112] have reviewed and compared the effects of terminal substituents on the mesogenic systems. The average terminal group efficiency order for nematic phase in rod like aromatic system is

$$\text{Ph} > \text{NH.CO.Me} > \text{CN} > \text{OMe} > \text{NO}_2 > \text{Cl} > \text{Br} > \text{NMe}_2 > \text{Me} > \text{F} > \text{H}. \quad [112]$$

and the average terminal group efficiency order for smectic phase is

$$\text{Ph} > \text{Br} > \text{Cl} > \text{F} > \text{NMe}_2 > \text{Me} > \text{H} > \text{NO}_2 > \text{OMe} > \text{CN}. \quad [112]$$

These orders give a broad idea about the probability of obtaining a particular type of mesophases.

Gray [94] and Dave and Vora [113] have studied the effects of substitution in chloesteryl benzoates and obtained a group efficiency order for the different substituents in chloesteryl systems. Demus et al. [96] have synthesized terminal swallowtail type compounds and established that by selecting proper geometry of molecules, the liquid crystalline property can be maintained in such systems. The systematic studies by Gray and Harrison [114] on alkyl-4-(p-substituted benzyldeneamino) cinnamates, indicate that all the branched chain esters have lower mesophase stabilities than the unbranched chain ester. Vora and Gupta [115] for the first time reported mesogenic homologous series having lateral and terminal phenolic groups. Recently,

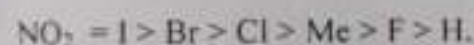
Ogawa [116] has reported the effects of terminal mesogens on thermal properties of dimeric, trimeric and tetrameric model compounds for main chain liquid crystalline polymers.

### The Effect of Lateral Substituents on Mesomorphism:

Lateral substituents may force apart the molecules and may thus reduce the intermolecular lateral cohesions but at the same time substituents may increase the intramolecular attractions. Normally, the first effect predominates i.e. a lateral substituent decreases the mesophase thermal stabilities, however, if the substituents do not have fullest breadth increasing effect as in the case of the 5-substituted-6-n-alkoxy-2-naphthoic acids [117] then the second effect predominates i.e. the thermal stabilities of substituted mesogens increases. The lateral group efficiency order [112] for smectic phase is



and the nematic group efficiency order is



The increased molecular breadth has three pronounced effects.

- i) Lowering of the temperature at which mesophase appears.
- ii) Decreasing the stabilities of the mesophases.
- iii) Destroying any smectogenic property regardless of alkoxy or alkyl group chain length.

Vora et al. [118, 119] have studied number of homologous series with bulky methoxy group as a lateral substituent. They have found that contrary to common observations, lateral methoxy group does not depress the crystal-mesomorphic transition temperatures to a greater extent but the mesomorphic-isotropic transitions are drastically reduced.

Demus et al. [97-99] have reported compounds with long chain lateral substituents and have established new molecular concept for liquid crystalline materials. They have found that the nematic state is mainly stabilized by steric repulsions and that the attractive forces play only a secondary role.

Bayle et al. [120] have reported influence of a lateral aromatic chain on the ordering in some nematic compounds. The metallomesogens [121] having lateral branched alkoxy chain and still exhibiting a large nematic phase range have been reported. It is also reported [122] that in laterally substituted nematogens, there is a change in conformation of the lateral chain in the solid and nematic phases. Weissflog and Hehmuth [123] for the first time have reported the two ring system mesogens and corresponding polysiloxanes having a lateral aromatic branch.

### **Lytotropic Liquid Crystals:**

Lytotropic liquid crystals belong to a class of substances called amphiphilic compounds. The phase transitions of thermotropic liquid crystals depend on temperature, while those of lyotropic liquid crystals depend on both temperature and concentration.

Lytotropic liquid crystals were actually discovered long before their thermotropic counterparts. In 1854, the lyotropic texture was noticed in a mixture of myelin and water. The molecules that make up lyotropic liquid crystals are surfactants, consisting of two distinct parts: a polar, often ionic head and a non-polar, often hydrocarbon tail. The polar end is attracted towards water (hydrophilic) while the non-polar end is attracted towards hydrocarbons (lipophilic). The amphiphilic molecules which have the greatest tendency to form liquid crystalline systems with water are those in which the hydrophilic and lipophilic units are strong and rather equally matched. In systems, which form lyotropic liquid crystals, order arises as a consequence of selective interactions among two or more molecular species. Typical hydrophilic groups are  $-\text{OH}$ ,  $-\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$ ,  $-\text{CO}_2\text{H}$ ,  $-\text{CO}_2\text{Na}$ ,  $-\text{SO}_3\text{K}$ ,  $-\text{NMe}_3\text{Br}$ ,  $-\text{PO}_4\text{CH}_2\text{CH}_2\text{NH}_3^+$  and typical lipophilic groups are  $-\text{C}_n\text{H}_{2n+1}$ ,  $\text{C}_n\text{H}_{2n+1}-\text{O}_2\text{C}-\text{CH}=\text{CH}-\text{CO}_2-\text{C}_n\text{H}_{2n+1}$ . The amphiphilic compounds, as a consequence of their dual character, have striking solubility characteristics. As they show miscibility in both water and organic solvents, they show marked co-solvent effects.

At low concentrations, the solution looks like any other particles of solute distributed randomly throughout the water. When the concentration gets high enough, the molecules began to arrange themselves in hollow spheres, rods, and disks called micelles.





**Figure 12**

Bruce, et al. [124] has reported lyotropic mesomorphism in some thermotropic, polycatenar complexes of silver (I) and of rare-earth trisalkylsulphates in the water-ethylene glycol systems. The use of lyotropic smectic phase on the flory lattice is reported [125]. The structures and properties of induced lyotropic cholesteric phase are also reported by Dieter et al. [126].

Soaps and detergents form lyotropic liquid crystals when they combine with water. Most importantly, biological membranes display lyotropic liquid crystalline behaviour.

### **Mesomorphism in Biological Systems:**

Liquid crystals play an important role in nature. The mesomorphic properties in biological system, in the form of myelin, were first reported in 1854 by Virchow [127]. The senses such as smell may be involved with substances exhibiting mesomorphic properties [128]. This is based on the possible presence of cholesterol ester sensitive to small amount of vapours. Birefringence in the case of muscle was noted by Murali and Edsall in 1930 [129].

From a study of structure of Hemoglobin, Perutz et al. [130] concluded that it could assume liquid crystalline form in the red blood cell. No reports of the presence of liquid crystalline compounds in plants could be found in literature till 1970. Knapp and Nicholas [131] reported the isolation of tetracyclic triterpene ester exhibiting smectic and cholesteric mesophases, from banana peels and from the seeds of strychnine producing plants. Livolant [132] has observed the cholesteric phase of DNA in vitro and in vivo. He also has reported the electron microscopic analysis of the highly concentrated liquid crystalline phase of DNA [133].



## Ferroelectric Liquid Crystals:

The smectic C\* phase of liquid crystals first appeared in literature in 1933 [134], however, it was not realized until 1974 that the phase ought to be ferroelectric, meaning that the phase has a permanent polarization without the need for an electric field. This was discovered by Robert Meyer and co-workers in 1975 [135].

The literature survey indicates that in 1980 Clark and Lagerwall [136] have produced a fast electro-optical switching device based on the influence of an external field on the spontaneous net polarization in the chiral smectic C phase. The existence of this net polarization parallel to the layers and the evidences from the work of Keller and co-workers [137] implies that there must be a slowing down in the rotation of the molecules about their long axes at the point of dipole alignment which could aid the tilting of the molecules. Gray and McDonnell [138] and Goodby, Gray and McDonnell [139] did however show that racemic systems related to chiral systems exhibiting chiral C phases form equivalent achiral C phases. Therefore, although the spontaneous polarization may aid tilting, it is not a primary factor in the formation of the phase but plays a secondary role, i.e. it develops as a result of tilting.

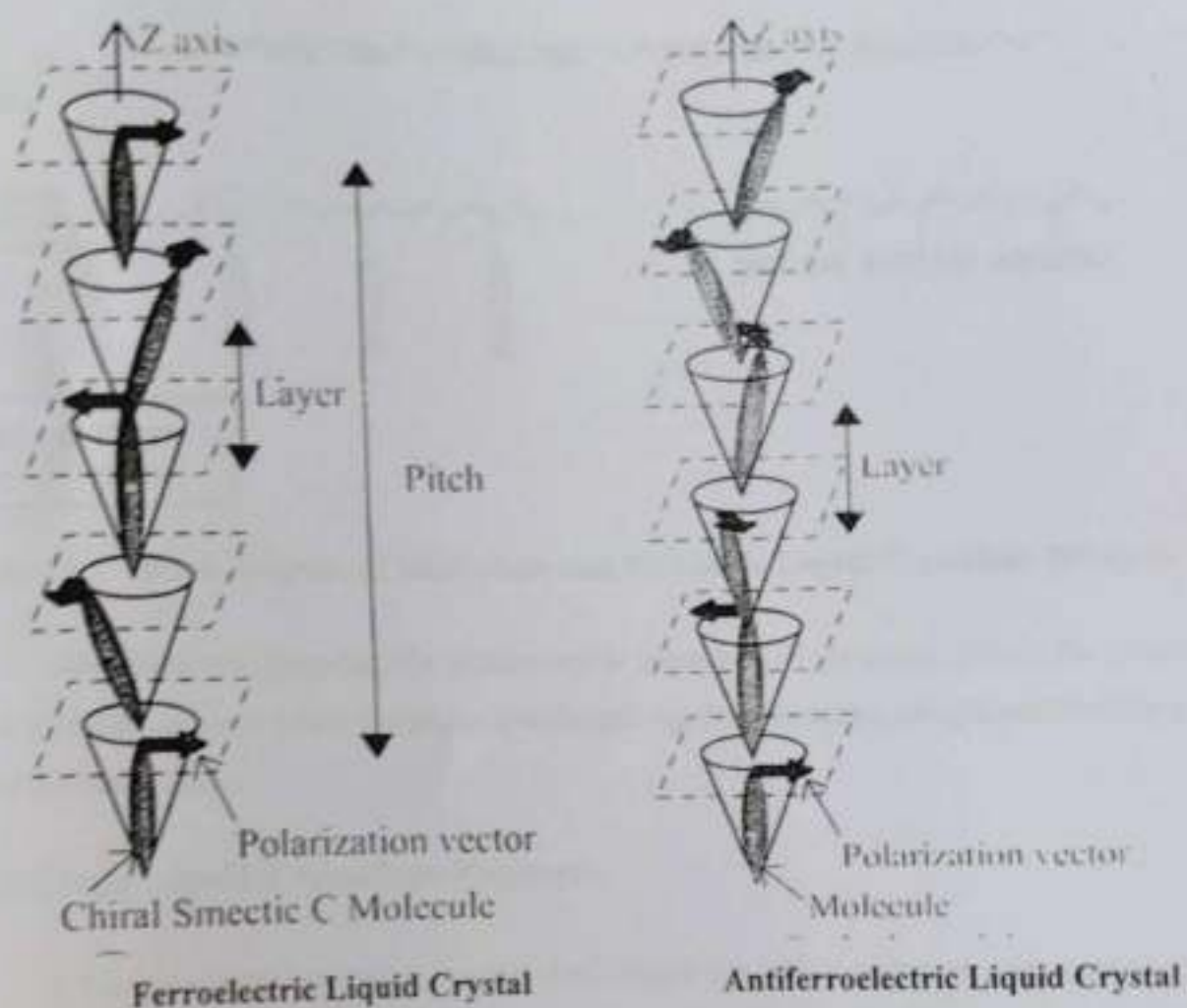


Figure - 13

The chiral smectic C\* phase, because of its unusual structure, exhibits a number of microscopic textures different from those of the achiral smectic C phase.

### Liquid Crystal Polymers:

Liquid crystal polymers are a class of materials that combine the properties of polymers with those of liquid crystals. These "hybrids" show the same mesophases characteristic of ordinary liquid crystals, yet retain many of the useful and versatile properties of polymers. In order for normally flexible polymers to display liquid crystalline characteristics, rod-like or disk-like elements (called mesogens) must be incorporated into their chains. The placement of the

**Main-chain liquid crystalline polymers** are formed when the *mesogens* themselves are the part of main chain of a polymer. Conversely, **side-chain liquid crystal polymers** are formed when the mesogens are connected as side chains to the polymer by a flexible "bridge" (called the spacer.)

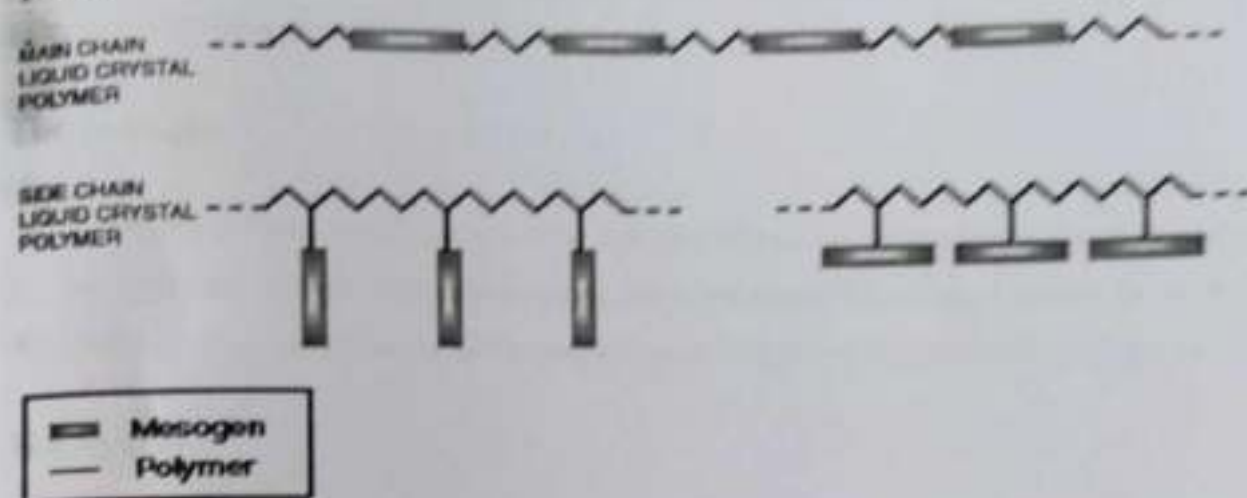


Figure-14 Block diagram of Main-chain and Side-chain Liquid Crystalline Polymers

Other factors influencing the mesomorphic behaviour of polymers include the presence of long flexible spacers, a low molecular weight and regular alternation of rigid and flexible units along the main chain.

### Side-Chain Liquid Crystalline Polymers:

It has been demonstrated that main chain liquid crystalline polymers often cannot show mesogenic behaviour over a wide temperature range. Side chain liquid crystal polymers, however, are able to expand this scale. These polymers have three major structural components: the backbone, the spacer, and the mesogen.

### The Backbone

The backbone of a side chain liquid crystalline polymer is the element that the side chains are attached to. The structure of the backbone is very important in determining the extent of liquid crystallinity exhibited by the polymer. Polymers with rigid backbones typically have high



glass transition temperatures and thus liquid crystalline behaviour is often difficult to observe. In order to lower this temperature, the polymer backbone can be made more flexible.




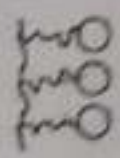


### **The Mesogen**

Perhaps the most important part of a side chain liquid crystalline polymer is the mesogen. It is the alignment of these groups that causes the liquid crystal behaviour. Usually, the mesogen is made up of rigid core of two or more aromatic rings joined together by a functional group.

### **The Spacer**

The mesogens attached as side groups to the backbone of side chain liquid crystal polymers are able to orient because the spacer allows for independent movement. The structure of the spacer is an important determining factor in side chain liquid crystal polymers. Generally, the spacer consists of two to six methylene ( $\text{CH}_2$ ) groups attached together in a linear fashion. Accordingly, the spacer length has profound effect on the temperature and type of phase transitions. Usually, the glass transition temperature decreases with increasing spacer length. Short spacers tend to lead to nematic phases, while longer spacers lead to smectic phases. The classification of liquid crystal polymers are given in chart 1.

25

MONOMER UNIT	AMPHIPHILIC 	NONAMPHIPHILIC 	DISCOTIC 
POLYMER			
	SIDE CHAIN	SIDE CHAIN	SIDE CHAIN
	MAIN CHAIN	MAIN CHAIN	MAIN CHAIN
	LYOTROPIC	THERMOTROPIC	THERMOTROPIC
PHASE BEHAVIOUR	LYOTROPIC	THERMOTROPIC THERMOTROPIC LYOTROPIC	THERMOTROPIC

CLASSIFICATION OF LIQUID CRYSTALLINE POLYMERS

CHART 1

### Banana shaped or Bent core liquid crystals:

Recently a new feature [140] is added to the organisations of rigid molecules of liquid crystalline materials. Compounds incorporating a bent rigid core (known as **bow shaped** molecules, **banana shaped** molecules, **V shaped** molecules, etc.) have been synthesized and investigated. The credit for the synthesis of the first compound with a bent molecular geometry exhibiting mesomorphic properties has been attributed to Vorlander [141]. The term "banana shaped mesogens" is used as a synonym for a new class of liquid crystals, which was established by the corresponding paper of Takezoe [142]. He reported ferroelectric properties of a new type of mesophases, which is formed by non-chiral bent mesogens. This discovery was the beginning of a lot of activity to investigate the structure and properties of these new mesophases, which are not comparable with smectic phases formed by calamitic mesogens. A little later Link et al. [143] demonstrated that the chirality arising in these smectic layers is due to the tilting of the molecules about the "arrow" directions of the bows, thus breaking the achiral symmetry of the layers. There has been intense research activity in this field and in the last few years hundreds of compounds composed of bent-core molecules have been synthesized [144-153] 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 [154] and preliminarily designated by the code letters B1 - B7.

### The structure-property relationship of banana-shaped mesogens:

The specific synthesis of bent mesogens was started [142] only a few years ago. As shown by different research groups, the relationship between the chemical structure of bent molecules and their mesomorphic behaviour are not comparable to those known from calamitic mesogens. The general formula and different possibilities for variation of the chemical structure can be seen in Chart 2.

Most banana-shaped liquid crystals described in the literature correspond to this general formula and they 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 [155]. The compounds with six or seven aromatic rings have also been



reported [153,154,156,157]. The transition temperatures increase with increasing number of phenyl rings. Four-ring compounds seem not to be able to form B-phases. The exchange of phenyl rings with six-member heterocyclic rings like pyridine or pyrimidine was reported for seven-ring compounds [157]. The substitution of the central ring by a five-membered heterocyclic ring such as 2,5-disubstituted-1,3,4-thiadiazole or 1,3,4-oxadiazole results in nematic or smectic mesophases, typical of calamitic liquid crystals [158-159]. The reason for this is still not clear.

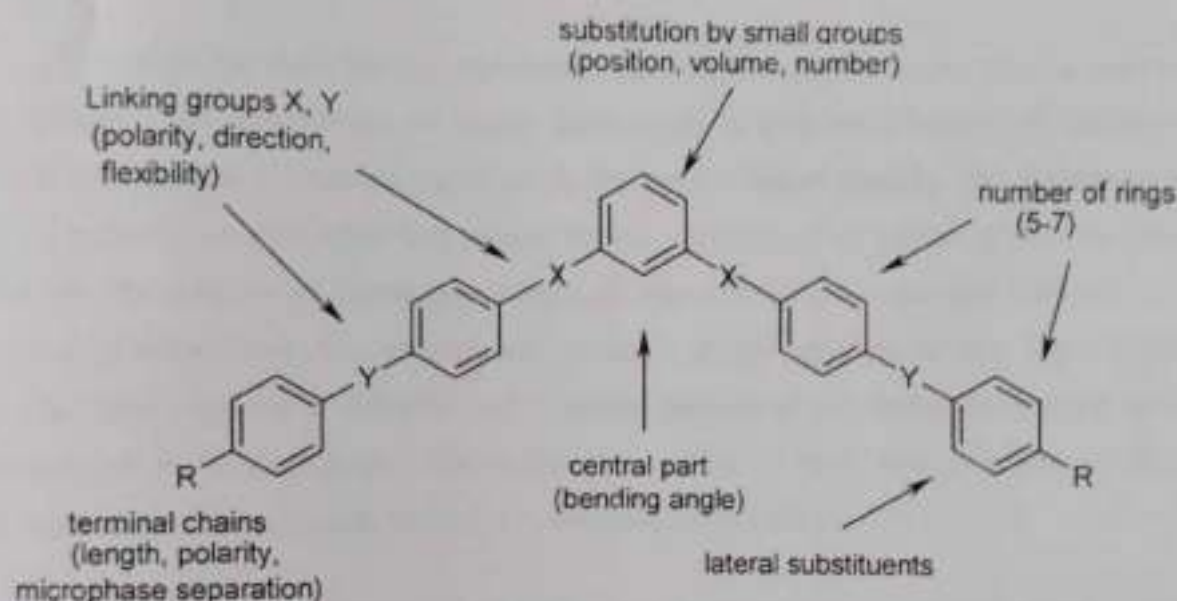


CHART - 2

On the other hand, Dingerms et al. [160] have found new mesophases for boomerang-shaped mesogens containing five-membered heterocyclic units. The phase type could not be assigned because of the high transition temperatures. In most of the cases of banana-shaped mesogens, alkyl and alkoxy chains were used as terminal groups. Only a few complete homologous series have been synthesized and reported till date. The trend of the clearing points is very different in these series.

The effects of the connecting groups X and Y on the liquid crystalline behaviour of banana-shaped compounds is unusually strong as compared to calamitic mesogens [144]. The simple inversion of the linking groups X or Y resulting in isomeric compounds, may affect the mesophase stability markedly and may even lead to the loss of liquid crystalline properties. This

behaviour cannot be explained in terms of our knowledge of rod-like mesogens [161], however, one possible explanation could be that it is a result of special packing of the bent molecules within the layers. According to Bedel et al. [149] an alternating distribution of the electron density throughout the molecules preferentially leads to B-phase. As reported by Shen et al. [146] for m-terphenyl derivatives and other compounds, the removal of two connecting groups reduces the conformational flexibility, which seems to disfavour B-phase formation. The linking of two three-ring fragments by means of single units like  $\text{CH}_2$ , CO, S, O was investigated by Thisayukta et al. [162]

To change the mesomorphic behaviour, the transition temperatures and the structure of the mesogens, the introduction of lateral substituents at different positions of calamitic and discotic mesogens is a common procedure in the field of liquid crystals. The depression of the melting points is another important reason for the introduction of lateral groups. In rod-shape molecules, the presence of lateral substituents decreases the length-to-breadth ratio and therefore the clearing temperature. The enlargement of lateral groups may lead to new liquid crystalline materials resulting from a different and a special packing of the molecules leading to a non-conventional molecular shape. The molecular packing is such that it enhances the layer formation and the smectogenic tendency in the compounds [163].

Depending on the number of aromatic rings, banana-shaped mesogens can be substituted laterally by atoms or small groups only in a limited way. One has to distinguish between the substitution at the central phenylene ring or at the outer rings and in both the cases the position of lateral substituents exerts a great influence on the mesomorphism. These two substitutions are basically different, because the substituents near the linking groups of the central part can change the bending angle between the two legs of the molecules.

Generally, the substituents attached to the central aromatic unit make it possible to vary the bending angle in a delicate way, thus, for the first time the phase sequences SmA SmC B2 and N SmA SmC B2 were observed with 4-cyano-substituted resorcinol derivatives [152,164]. The introduction of fluorine or chlorine atoms near the terminal wing groups was reported by Heppke et al. [165] Lee and Chien [166,167] and Bedel et al. [149]. Beside halogen atoms methoxy group was also attached at the same position by Kwon et al [168]. Recently Ninri et al.



[169] studied the influence of the positions of the lateral substituents on the mesomorphic properties of non-symmetrical banana-shaped liquid crystals. By increasing the number of aromatic rings of the mesogenic core, the possibilities of substitution without the loss of the liquid crystalline properties can be increased.

Sadashiva et al. [151,153] have reported that the influence of chlorine and methyl lateral groups, having nearly the same van der Waals' volume, on bent molecules is different from those known for calamitic mesogens. Sadashiva et al. [170] have reported biaxial smectic A phase in homologous series of compounds composed of highly polar unsymmetrically substituted bent-core molecules.

### **Ferroelectric, Ferrielectric and Antiferroelectric properties in Banana shaped molecules:**

Ferroelectricity in liquid crystals has been [171] known since the pioneering work by R.B.Meyer et al. [134]. Recently Reddy and Sadashiva reported [172] the ferroelectric properties in the achiral banana shaped molecules having a fluoro substituent. Chirality in a tilted  $\text{SmC}^*$  phase introduced by chiral dopants or by chirality of the constituting molecules themselves results in breaking of mirror symmetry. In such chiral tilted phases the symmetry group is reduced to  $C_2$ , hence, it permits the appearance of the spontaneous electric polarization  $P_s$  in each layer of the  $\text{SmC}^*$  phase, however, in bulk, the equilibrium structure will be twisted into a helix so that the polarization of the layers precesses around the layer normal and in a macroscopic sample the spontaneous polarization averages to zero and a surface-stabilization is required to obtain bistable ferroelectric (FE) switching. Later antiferroelectric (AFE) and ferrielectric (FI) smectic phases were also discovered in such materials [173,174].

Several theoretical concepts were developed in order to obtain ferroelectric smectic phases built up by achiral molecules. Compounds that exhibit these properties were first reported in 1989 by Chandani et al. [173]. Prost and Barois [175] and Petschek and Wiefeling [176] predicted a ferroelectric  $\text{SmA}$  phase where the spontaneous polarization is directed along the normal of the smectic layers. A very successful concept for ferro- or antiferroelectric smectic phase is based on achiral bent-shaped molecules [177]. Because of the close packing of bent



molecules and high rotational hindrance about the long molecular axis, an in-layer polar order emerges despite the achiral nature of the molecules.

The detailed electro-optical investigations by Link et al. [143] gave evidence that the packed polar molecules are tilted with respect to the layer normal. This combination of tilt and polar order in the smectic layers leads to a chirality of the smectic layers as a whole. Recently Nguyen et al. [147] reported achiral five-ring banana-shaped compounds with fluorine substituents at the terminal rings exhibiting four switchable smectic phases. Weissflog et al. [171] have reported ferroelectric and antiferroelectric "banana-phases" of new fluorinated five-ring bent-core mesogens. Mathru et al. [178] have reported the synthesis and characterization of (S)-4'-(1-methylheptyloxycarbonyl)biphenyl-4-yl and 5-(4-n-decyloxyphenyl)thiophene-2-carboxylate and studied the ferro-, ferri and antiferro electric behaviour.

Rouillon et al. [179] have reported new banana-shaped thiobenzoate liquid crystals with B6, B1 and B2 phases. A bow-phase mesogen showing strong, robust analog electro-optics has been reported by Clark et al. [180]. Goodby et al. [181] have reported synthesis and properties of novel banana-shaped liquid crystals containing 1,5-disubstituted 2,3,4-trifluorophenyl unit. New variants of polymorphism in banana-shaped mesogens with cyano-substituted central core have been reported [182]. Pelzl et al. [152] have reported the designing of banana-shaped liquid crystals without schiff's base units in m-terphenyls, 2,6-diphenylpyridines and V-shaped tolane derivatives. The same author has reported [183] spontaneous chiral ordering in the nematic phase of an achiral banana – shaped molecules.

### **Applications of Liquid Crystals:**

Liquid crystal technology has had a major effect in many areas of science and engineering, as well as device technology. Applications for this special kind of materials are still being discovered and continue to provide effective solutions to many different problems. Applications of liquid crystals are divided in two parts A) Display and B) Non-display

## A) Liquid Crystal Displays:

The most common application of liquid crystals is in displays devices (LCDs). This field has grown into a multi-billion dollar industry and many significant scientific and engineering discoveries have been made. From the ubiquitous wristwatches and pocket calculators to an advanced VGA (Video Graphics Array) computer screen, the types of displays have evolved into an important and versatile interface. A liquid crystal display consists of an array of tiny segments (called pixels) that can be manipulated to present information. This basic idea is common to all displays, ranging from simple calculators to a full colour LCD television.

### Why are liquid crystal displays important?

- Size factor
- LCD consists primarily of two glass plates with liquid crystalline material between them. There is no bulky picture tube. This makes LCDs practical for applications where size (as well as weight) is important.
- LCD uses much less power than their cathode-ray tube (CRT) counterparts.
- Many LCDs are reflective, i.e. they use only ambient light to illuminate the display.
- Even displays that do require an external light source (i.e. computer displays) consume much less power than CRT devices.

There are many types of liquid crystal displays, each with unique properties. The most common LCD that is used for everyday items like watches and calculators is called the twisted nematic (TN) display. Twenty-five years ago G.W.Gray [184] invented TN mixtures based on cyanobiphenyls. The broad range TN mixtures and TN mixtures with improved viewing angle using phenylcyclohexanes [185] were then used for automotive applications. The introduction of STN (Super Twisted Nematic) displays required materials with large dielectric anisotropy, e.g. cyanoesters with lateral fluoro substitution [186]. Thin film transistor (TFT) displays require liquid crystalline materials with high stability like fluorinated liquid crystals.

A major contribution to the growth of LCD technology has come from the development in addressing techniques used for driving matrix LCDs. There are several approaches, like

passive matrix addressing, active matrix addressing and plasma addressing to drive a matrix display. Passive matrix LCD has a simple construction and uses the intrinsic non-linear characteristic of the LCD for driving. Active matrix LCDs and STN LCDs are leading display technologies for portable applications such as notebooks, computers etc.

A review [187] of the uses of ferroelectric liquid crystals for display devices appeared in the literature. Takehara et al. [188] have reported the design, synthesis and physical properties of new liquid crystalline materials containing saturated and aromatic ring systems, for active matrix LCD. The physical properties of new liquid crystalline materials and mixtures designed for active matrix LCD are reported by Iwashita et al. [189]. Nematic thiophenes and highly birefringent nematic liquid crystals for STN-LCDs and flexoelectric LCDs are also reported [190].

#### **Optical Imaging:**

An application of liquid crystals that is only now being explored is optical imaging and recording. In this technology, a liquid crystal cell is placed between two layers of photoconductor. Light is applied to the photoconductor, which increases the material's conductivity and causes an electric field to develop in the liquid crystal corresponding to the intensity of the light. The electric pattern can be transmitted by an electrode, which enables the image to be recorded. This technology is still being developed and is one of the most promising areas of liquid crystal research. Full colour image has been demonstrated on a high frame rate, binary, ferroelectric liquid crystal display or spatial light modulator (SLM) by Rankyn et al. [191].

**Liquid crystalline polymers** have been intensively investigated with respect to their non-linear optical properties. Chiral polymers [192] are used for photo-optical and optoelectronic applications. The polymers possessing coumarin side-chain being used for liquid crystal photo alignment layers are reported by Kelly et al. [193]. Main chain liquid crystalline polymers are used essentially as high performance materials



The search for fullerene based new materials has attracted much attention [194] ever since the first fullerene containing thermotropic liquid crystal was reported [195]. Nano-, pico- and femtosecond study of fullerene-doped polymer-dispersed liquid crystals are reported [196] for holographic recording and optical limiting effect.

## **B) Non-display Applications of Liquid Crystals:**

There are many nondisplay applications of liquid crystals. Some of the most developed applications that are currently being researched are in optical correlators, optical interconnections, wavelength filters, and optoelectronic neural networks. Most of these systems use liquid crystal spatial light modulators (SLMs). The interaction has been described by Jones [197]. The display devices based on nematic liquid crystals, notably small liquid crystal televisions, are used as SLMs due to their increased availability [198].

### **Three-Dimensional Video:**

This application of liquid crystal technology may not seem to fit into the category of non-display applications, but the actual use of the liquid crystal is not in the display of the images, rather it is used to perform the angular multiplexing which grows to make up the three dimensional image [199]. The display itself is autostereoscopic, with no external optics, such as 3-D glasses, required. The viewer can see the 3-D image over a viewing angle of 40° with the naked eye.

### **In-fiber Liquid Crystal Devices:**

Liquid crystal materials have been used in a variety of fiber-based applications, such as liquid crystal wave-guides and liquid crystal interactions with tapered fibers [200]. The inclusion of liquid crystals in hollow fiber tubes has created a new class of hybrid electro-optical devices with applications in telecommunications and fiber-based sensor systems. The liquid crystal waveguides were also demonstrated as being able to produce  $TE_{01}$ , (transverse electric) and  $TM_{01}$ , (transverse magnetic) modes in an optical fiber [201]. A variety of waveguides has been produced containing FLC materials to improve the modulation and decrease loss. The results so

far have demonstrated in-fiber modulation of light at speeds of up to 100 KHz, with good modulation depth [202].

### **Liquid Crystals Lenses:**

The ability to control the refractive index of a liquid crystal allows the implementation of liquid crystal lenses. In these devices, a gradient of refractive indices is set up in the liquid crystal by addressing patterned ITO (indium-tin-oxide) electrodes [203]. The refractive index profile acts as a curved surface of glass and hence acts as a lens. By tuning the structure of the refractive index profile, it is possible to alter dynamically the performance of the lens. A novel form of liquid crystal 'lens' is the switchable hologram [204]. The exact functionality of the device depends on the design of the pattern.

### **Thermography Using Liquid Crystals:**

The dramatic variation of liquid crystalline properties with respect to temperature has resulted in the widespread use of cholesteric (chiral nematic) liquid crystals for thermography. The property that has been exploited most in liquid crystal thermography is the critical temperature dependence of the selective reflection from cholesteric liquid crystals, though other temperature dependent properties of mesophases have been utilized (e.g. the birefringence of nematic systems and selective reflection from other chiral phases). Oron et al. [205] found that including certain nematic materials in mixtures of cholesteryl esters substantially reduced the angular dependence of the selective reflection.

The use of cholesteric liquid crystals for thermography was reviewed by Elser and Ennulat [206], and in the commercial literature of Hallcrest [207]. Amongst the substances with the largest temperature coefficient are cholesteryl oleyl carbonate [208] and s-cholesteryl esters [209], which are capable of showing temperature variations of the order of a milli kelvin detectable to the human eye.

The application of liquid crystals to thermography is widespread, and covers areas as diverse as infant bath and feed temperature indicators, medical screening and diagnostics, nondestructive testing, aerodynamics research, thermometers for fish tanks and refrigerators, battery testing, jewellery, advertising and art.

### **Medical Thermography:**

The thermochromic liquid crystals have found extensive uses in medical applications. A different device structure is produced by Sharn Inc. [210], in which the liquid crystal is incorporated into the device in a single strip and treated such that the temperature is displayed as a narrow colour band that may move continuously across the device. Device structures range from the application of neat material on to the skin [211], to including the liquid crystal in its microencapsulated form as a paint or embedded in rigid or flexible substrates. The first example of the use of liquid crystals to indicate skin temperature was reported in 1964 [212].

The use of liquid crystals in evaluating deep vein thrombosis is described by several authors [213-219]. Sandler and Martin, for example [220], consider liquid crystals thermography as a screening test for deep-vein thrombosis. The location of veins [221-224] and the study of arterial disease [225,226] using liquid crystal thermography is also common. The prediction of fast ulceration in diabetic patients through thermal mapping using liquid crystal technology is described by Benbow et al. [227].

Liquid crystal thermography has been extensively used in the area of oncology, especially breast cancer [228-237]. Subcutaneous and intracutaneous malignant tumours are typically 0.9-3.3 °C warmer than the surrounding tissue [238], making thermography an interesting candidate for cancer screening. Thermography has proved useful in the study of temporal variations in breast temperatures [239, 240]. The use of liquid crystal thermography has also been reported for the determination of the extent of basal cell carcinomas [241] and cancer in other parts of the body [242-246].

Other medical applications include the use of liquid crystal thermography in diagnosing acute paraproctitis [247], localization of undescended testicles [248], the diagnosis of infertility [249], and varicocele, the most common form of male infertility, proved to be easily



detectable by this technique. The diagnosis of scaphoid fractures using liquid crystal thermography has been suggested [250].

Indeed liquid crystal thermography has found use in areas as diverse as core body temperature measurements in anesthetic recovery [251], headache clinic setting [252], investigation of spinal root syndromes [253-257], lower back syndrome [258], chronic [259] and low [260] back pain, scrotal temperature in cases of spinal cord injury [261], knee joint stress [262], evaluation of the diabetic foot [263], the thyroid [264], lacrimal tract inflammation [265], as a diagnostic test in acute [266] and destructive [267] lactation mastitis, acute appendicitis [268], chronic liver disease [269], placental localization [270, 271], skin allergy [272-274] and carpal tunnel syndrome [275, 276]. Liquid crystal thermography in ophthalmologic practise is discussed by several authors [277-279].

#### **Engineering and Aerodynamic Research:**

The use of liquid crystals to observe shear stresses in wind tunnel models was first demonstrated by Klein [280] in 1968, who applied an unprotected liquid crystal solution to a test object in order to view the location of laminar and turbulent layers in aerodynamic models. To develop the principle of making quantitative measurement of stress visually, Klein and Margozzi [281, 282] exploited the sensitivity of certain mixtures of cholesteric liquid crystals to stress.

The micro encapsulation technique avoids many of the problems associated with the use of neat liquid crystal. Elderry [283] used microencapsulated material to study flat plates placed in a supersonic air stream, to produce a colour display that had relatively low angular dependence. Ogden and Hendricks [284] used this technique for the study of turbulent flow around the body and reported that it results in more rapid cooling rates due to higher heat transfer rates. Similar materials were used in water tunnels by Maughan and Incropera [285], though shear sensitive unsealed mixtures have been used successfully to visualize hydrodynamic flow on surface with both steady and unsteady boundary layer separation and transition characteristics [286].

The use of thermochromic liquid crystals in qualitative studies of heat transfer is relatively common [287-291]; hot and cold regions are discriminated, but precise temperatures

are not necessarily deduced from the results. Quantitative measurements were first made by Cooper et al. [292, 293], who evaluated the variation of the Nusselt number around a heated cylinder in cross-flow.

The local heat transfer coefficients for plates in air jets have also been measured [294] and the temperature shift of the colour band due to the shearing action of the air flow have been determined [295]; this is particularly important in making quantitative measurements from exposed liquid crystals in wind tunnels.

### **Thermal Mapping and Nondestructive Testing:**

Liquid crystal thermography has been used to observe time dependent temperature patterns on an electrically heated surface during boiling [296]. The time dependent aspects of nucleate boiling have also been studied by Bergez [297] which showed that existing heat transfer models are inadequate for water under conditions of saturation, atmospheric pressure and low heat flux. A bibliography of non-destructive testing using thermochromic liquid crystals is also published [298].

In composite materials flaws, bonding faults and internal defects have all been examined using liquid crystal thermography, [299-306]. Surface and subsurface flaws have been detected, including regions of unstable plastic flow in aluminium alloys (luder lines) [307], faults in welded metals [308], and cracks, voids and leaks in pressure vessels [309, 310]. The potential fracture sites have been determined in metals [311], together with defects in springs [312]. The other applications examine shrinkage cavities in metal castings [313], thermal isolation of aluminium rivets [314] and thermal gradients on the surface of heating coils [315].

Scientists have studied cholesteric liquid crystals for thermal mapping of both ordinary [316-318] and multilayer [319] printed circuit boards. Cholesteric liquid crystals are used to detect short circuits in field effect transistors [320]. The defects in toroidal transformers and the temperature variation of other electrical components are visualized by using cholesteric liquid crystals [321-323]. The other applications include the study of deposits on thin film resistors [324], in homogeneities in the sapphire windows of infrared detectors [325], switching phenomena in deposited metal films and junctions [326-328]. Breaks in electrical conductors



embedded in windscreens [329], heat leaks in refrigerator doors [330], and heat patterns generated by piezoelectric and ultra high frequency devices [331, 332] have also been studied via liquid crystal thermography. There are several examples of the uses of cholesteric liquid crystals as temperature indicators in low gravity and to estimate heat flow through textiles [333] in the space programme aboard Apollo 14 [334, 335] and Apollo 17 [336].

#### **Radiation Detection:**

The technical details of the construction and operation of the detectors are readily available in the patent literature [337-341]. Membrane devices, including a thin layer of carbon black, are often used for infrared radiation detection and visualization [342, 343] and such detectors are particularly useful in the observation of the modes and emission parameters of infrared lasers [344-349]. A thermal imaging device that offers the possibility of night vision has also been described [350].

It has been shown that the shift in the selective reflection band is linear with respect to  $\gamma$ -ray dosage, and that the temperature response remained stable after exposure [351-354]. There have been suggestions that thermochromic liquid crystals may be used for the detection of elementary particles [355], heavy moving ions [356] and for monitoring the frequency of UHF electromagnetic fields [357].

#### **Liquid Crystals as Solvents for Spectroscopic, Chemical Reaction and Gas Chromatographic Applications:**

The fundamental principles involved in the use of thermotropic liquid crystals for such applications and the literature related to these areas, are covered in detail in the 1<sup>st</sup> Edition of the Handbook [358]; Several reviews of NMR spectroscopy in liquid crystals are reported [359-363]. The number of studies of the uses of thermotropic liquid crystals as solvents to alter the course or rates of uni- and bimolecular thermal and photochemical reactions has increased dramatically. To be useful for these purposes it is imperative to be able to predict accurately the specific effects that an anisotropic environment will have on a given reaction and to be able to choose a liquid crystal of the proper morphology as a solvent to give the desired outcome. For these reasons the majority of studies over the past two decades have been directed at elucidating



the factors that are important in defining the ability of liquid crystals to control solute reactivity. Several critical reviews summarizing the progress in this area have appeared in the literature [364-371].

Liquid crystals have found widespread use as stationary phases in gas chromatographic applications due to the benefits of coupling the usual analytical strengths of gas chromatography with the unique structure and shape selective properties of the liquid crystalline phase. A number of models have been developed to describe quantitatively the enhancement in selectivity that is obtained from the anisotropic, orientational ordering of liquid crystalline stationary phases; most notable in this regard is the work by groups of Janini [372, 373], Luffer [374], Martire [375-378], and Wise [379,380]. Several reviews outlining the fundamentals and applications of liquid crystal stationary phases in both packed and capillary columns are available [381-386]. The sheer number of liquid crystalline stationary phases employed precludes their summary here, but many are based on substituted biphenyl or terphenyl derivatives, isothiocyanates, Schiff bases, or azo- or azoxy derivatives. A few liquid crystalline stationary phase columns are commercially available [387].

The dramatic variation of liquid crystalline properties with respect to temperature has resulted in the increasing use of cholesteric (chiral nematic) liquid crystals for the jewelry, fashion garments and cosmetics. The 'Mood Ring' so very popular few years ago, uses the same principle and changes the colour with the change in the temperature or the pressure. The garments painted with liquid crystals that can change the colour with the variation of temperatures during the day are becoming popular. The cosmetic industry is also experimenting with liquid crystals to develop a single product giving various shades depending on the time of the day it is being used. The possibilities are endless.

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# AIMS AND OBJECTIVES

## Aims and Objectives

Chemistry of liquid crystal compounds is becoming more interesting looking to the structural variations and exhibition of mesomorphism. New applications of liquid crystals in different fields also induces synthetic variations in compounds which exhibit desired properties in new mesogens.

Lately bent – core molecules have attracted attention of researchers. They exhibit chirality on application of electric field even though they are achiral in nature. The exhibition of smectic phases by such bent core molecules also have generated interest in the research to study them extensively.

It was proposed to synthesize number of homologous series with biphenyl methane bent core with lateral substituents and different central linkages to evaluate the effect of such variations on mesomorphism.

Trisubstituted benzene derivatives have been of interest because many of them exhibit smectic C mesophases at comparatively low temperatures. It was proposed to synthesize a few trisubstituted homologous series to evaluate the effect of such substituents on mesomorphism.

Heterocyclic moiety induces rich mesomorphism in the system as compared to carbocyclic moiety. Piperazine moiety may induce useful property in the mesogenic compounds. With this in view a homologous series would be synthesized and mesogenic properties evaluated.

The study of binary systems of non-mesogens exhibiting induced mesophases has been ever interesting. In the present work it is proposed to study a few binary systems with trisubstituted benzene derivatives as one of the components with an expectation of exhibition of induced mesophases. A few systems will be studied by taking a chiral non-mesogen with mesogens.

## CHARACTERIZATION OF MESOPHASES

### Determination of transition temperatures

The phase assignment and transition temperatures were determined by thermal polarized light microscopy using a Leitz Laborlux 12 POL polarizing microscope equipped with a Koffler heating stage and a thermostat. The microscope was standardized by taking transition temperatures of known, pure compounds like 4-n-alkoxy benzoic acids, 4-azoxy anisole, etc.

**Procedure:** A small quantity of the sample to be observed under the polarizing microscope was placed on a glass slide. The slide was heated till the substance just melted. A cover slip was then placed on the molten sample taking care that no air bubbles form between the cover slip and the slide. The sample was allowed to cool down slowly so crystallization could take place.

To determine the various transition temperatures, a glass slide with the sample was inserted into the specimen chamber of the heating stage and the temperature raised slowly ( $3^{\circ}\text{C} / \text{min}$ ) to find approximate transition temperatures. The observations were repeated and near the transition to be observed, the heating rate was controlled carefully so as to observe the changes in the texture at an accurate temperature.

All observations were repeated several times and in case of any doubt, the compounds were purified again and then observed under the microscope. In compounds which decomposed at high temperatures, fresh slide was prepared each time to record correct transition temperatures.

Photographs of textures of mesophases observed under the polarizing microscope for liquid crystal compounds have been taken using the Leica photomicrography system mounted on the microscope. Magnification factor is  $50 \times 10X$ .

### Characterisation of Smectic phases

The mesophases can be identified based on the texture observed under the polarizing microscope, however, in certain cases, especially in the case of smectic mesophases, the change in texture is so subtle that identification becomes difficult. Therefore, miscibility studies are



## Smeectic Textures

The smectic phases exhibit either focal conic texture or schlieren texture. The focal conic texture is observed in smectic A phase whereas, schlieren texture is seen in Smectic C phase.

### Electro-Optical Investigation:

Electro-optical investigations were carried out in a joint programme in the physics laboratory of Prof. K.K. Raina, Patiala, India.

The cells were constructed with conducting plates and having uniform thickness. The cells were pretreated with polyimide and rubbed unidirectionally to obtain homogeneous alignment. The sample of the compound was filled by capillary action at about 100 °C. The temperature was controlled to an accuracy of 0.1 °C / min. in Linkam temperature controller model TP94 and THMS. 600. The observations were made through Olympus polarizing microscope model BX51P at 10X. The whole setup was interfaced with computer and textures were recorded using LINsys software. The sample was cooled, heated and cooled at the rate of 0.1 °C from isotropic liquid and heated at the rate of 3-5 °C. On applying a triangular voltage, at a relatively high threshold the electric field shows some switching on the material. The spontaneous polarization is very small hence could not be measured.

The sample shows SmA phase at 135 °C and then chiral smectic (ferroelectric) phase is obtained. The compound exhibits SmA phase even in applied electric field it shows switching effect and ferroelectric behaviour, however, spontaneous polarization value is very small.

## CHARACTERIZATION OF COMPOUNDS

### Elemental Analysis

Number of homologues of each series were subjected to elemental analysis. Coleman USA-CHN analyser was used for the purpose.

### IR Spectral Study

Representative members of each series were characterized by IR spectroscopy. The mesogenic materials were screened by using KBr pellets in the range of infra-red frequency. This helped in confirming the functional groups present in the synthesized compounds. The purity of the compounds could also be confirmed by IR spectroscopy. The samples were analysed on FTIR-Shimadzu and 8400 Perkin Elmer 16PC.

### NMR Spectral Study

Proton NMR spectra of representative compounds of each homologous series were used for characterization.  $\text{CDCl}_3$  was used as a solvent and TMS as an internal standard. The technique helped in assigning the molecular structure of the synthesized compounds. The samples were analyzed on DPX 200 and DPX 400.

### Differential Scanning Calorimetry

To study the thermodynamic aspects of mesophases, calorimetric study was carried out on a Mettler TA 4000 system. Thermograms for few representative derivatives were recorded to confirm the microscopic reading and also to observe the enthalpy change with respect to phase transitions. The principle involved is that the DSC curve peak is directly proportional to the enthalpy change.

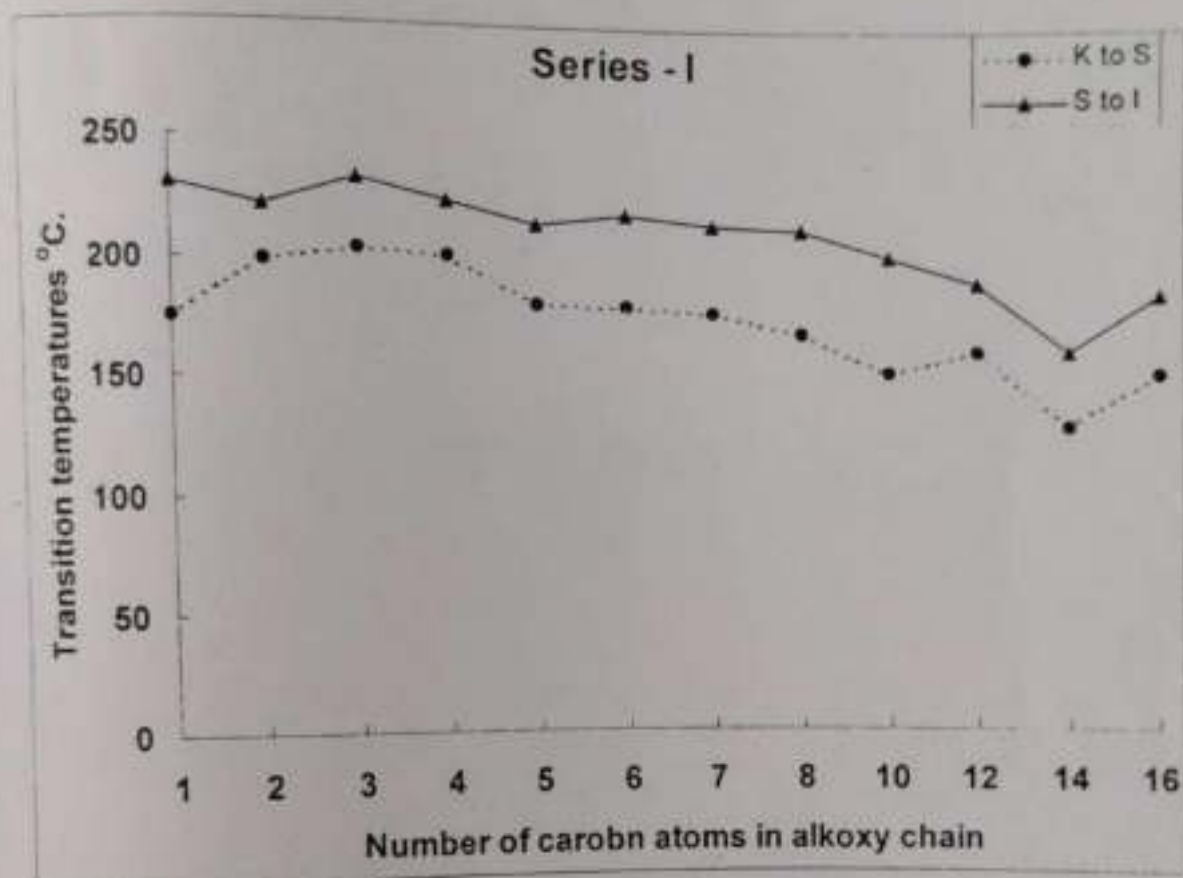
$$\text{Area} = K \Delta H_m$$

Where K is calibration constant and independent of temperature.

$\Delta H_m$  is enthalpy change.

From the texture and the contact studies the smectic phase appears to be of the smectic A type. The plot of transition temperatures versus the number of carbon atoms in the alkoxy chain is given in fig.4.

Figure-1





## EXPERIMENTAL

Complete study is thought to be done in a scientific manner with the following synthesis.

Synthesis of N, N' bis [4'-(4"-n-alkoxy benzoyloxy) benzylidene] biphenyl sulphone.

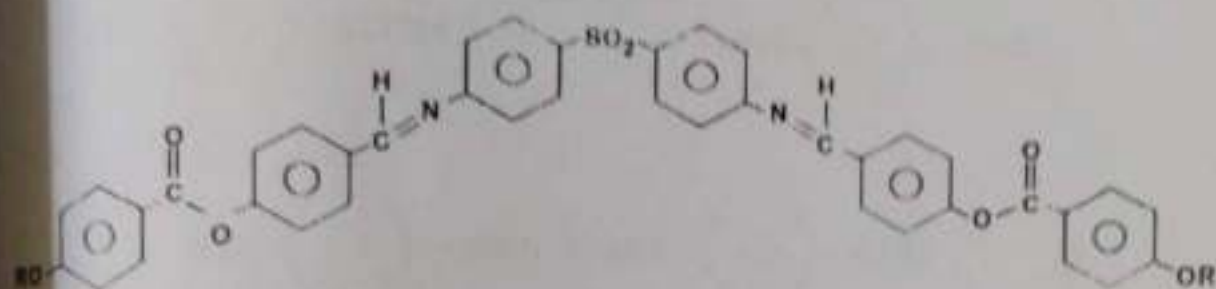
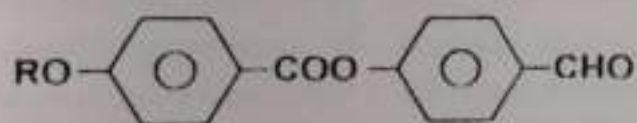
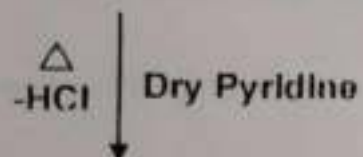
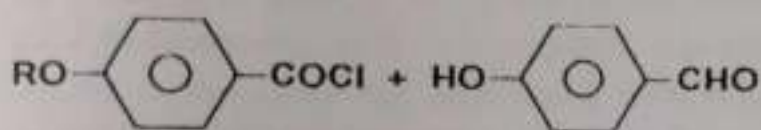
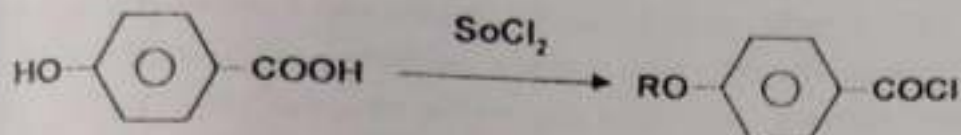
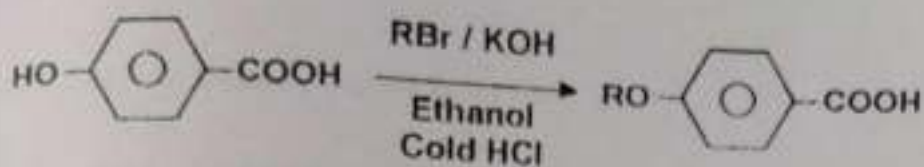


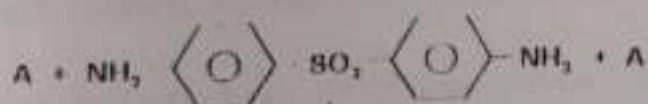
Table - I

Sr.No.	R = n-alkyl group
1.	Methyl
2.	Ethyl
3.	n-Propyl
4.	n-Butyl
5.	n-Pentyl
6.	n-Hexyl
7.	n-Heptyl
8.	n-Octyl
9.	n-Decyl
10.	n-Dodecyl
11.	n-Tetradecyl
12.	n-Hexadecyl

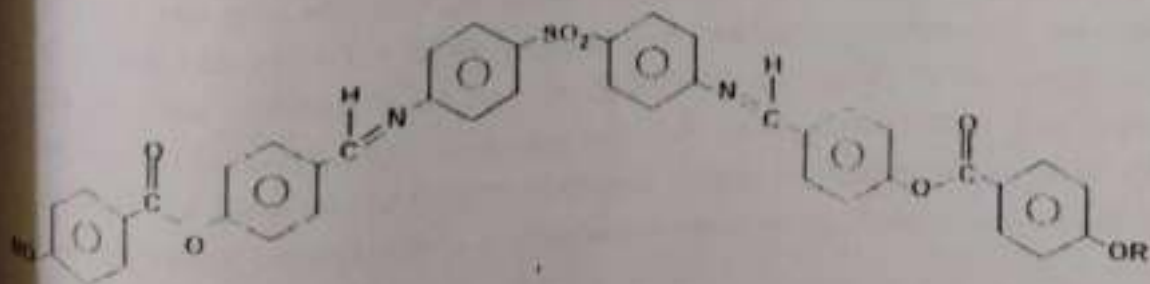
# SCHEME



A



Ethanol / Reflux 3 Hr.



## Synthesis of N, N' bis [4'-(4"-n-alkoxy benzoyloxy) benzylidene] biphenyl sulphone

### Synthesis of 4-n alkoxy benzoic acids.

4-hydroxy benzoic acid (0.1 mole), appropriate n-alkyl bromide (0.12 mole) and potassium hydroxide (0.25 mole) were taken in 100 ml ethanol in a round bottom flask. The reaction mixture was refluxed on sand bath for 6 to 7 hours. 10% (25ml) aqueous potassium hydroxide solution was added to the reaction mixture and the reflux continued for further 1 hour. The reaction mixture was allowed to cool to room temperature and was then acidified using 1:1 cold hydrochloric acid to precipitate 4 n-alkoxy acid. The crude acid was filtered at the pump and crystallized from ethanol or glacial acetic acid till constant transition temperatures were obtained.

### Synthesis of 4-n-alkoxy benzoyl chlorides

4-n-alkoxy benzoic acid (0.01 mole) was treated with excess of thionyl chloride in a round-bottom flask. The reaction mixture was heated on a water bath till evolution of hydrochloric gas ceased (about two and half hours). The excess of thionyl chloride was distilled off under reduced pressure. The acid chloride left behind as a residue was used in the next step without further purification.

### Synthesis of 4(4'-alkoxy benzoyloxy) benzaldehydes

4-Hydroxy benzaldehyde (0.01 mole) dissolved in 10 ml dry pyridine was added portion wise with stirring to appropriate cold 4-n-alkoxy benzoyl chloride (0.01 mole). The reaction mixture was heated on a water bath for 30 minutes and was allowed to stand overnight. The reaction mixture was then acidified with cold 1:1 hydrochloric acid and the precipitates obtained were filtered and washed with water followed by cold 10% aqueous sodium hydroxide solution and then again with cold water. The aldehydes were crystallized from methanol till constant transition temperature were obtained. The transition temperatures are in good agreement with those reported in the literature.



Synthesis of N, N' bis [4'-(4"-n-alkoxy benzoyloxy) benzylidene] biphenyl sulphone

4(4'-n-alkoxy benzoyloxy) benzaldehydes (0.01mole) and 4-4' Diamino biphenyl Sulphone (1.24 gm, 0.005 mole) were condensed in 20 ml ethanol. The reaction mixture was refluxed on a sand bath for three hours. On cooling, the schiffs bases as solids, which were filtered. The schiffs bases were crystalized from ethanol at constant transition temperatures were obtained. The purity of the mesogens was checked by TLC (Merck). The transition temperature, elemental analysis, DSC data and spectral data are recorded.

Table - I

Sr.No.	R = n-alkyl group	Transition Temperature in °C	
		Smectic	Isotropic
1.	Methyl	----	209.00
2.	Ethyl	(190.00)	203.00
3.	n-Propyl	(192.00)	200.00
4.	n-Butyl	140.00	180.00
5.	n-Pentyl	144.00	203.00
6.	n-Hexyl	130.00	176.00
7.	n-Heptyl	136.00	173.00
8.	n-Octyl	115.00	185.00
9.	n-Decyl	124.00	180.00
10.	n-Dodecyl	132.00	174.00
11.	n-Tetradecyl	113.00	173.00
12.	n-Hexadecyl	111.00	168.00

Table - II

Sr. No.	Homologee	Required Percentage (%)			Found Percentage (%)		
		C	H	N	C	H	N
1	n-Butyl	74.45	5.83	3.40	72.10	5.40	2.90
2	n-Pentyl	75.50	6.62	3.10	75.00	6.10	2.83
3	n-Hexyl	76.10	7.10	2.51	75.66	6.79	2.17
4	n-Octyl	77.00	8.00	2.60	76.58	7.63	2.37

Table - III

Transitions		MicroScope reading in °C	DSC Peak Temperature °C	ΔH J/G	ΔS J/G °K
K	S	144.00	155.2	11.751	0.02745
N	I	203.00	184.00	4.7761	0.01045

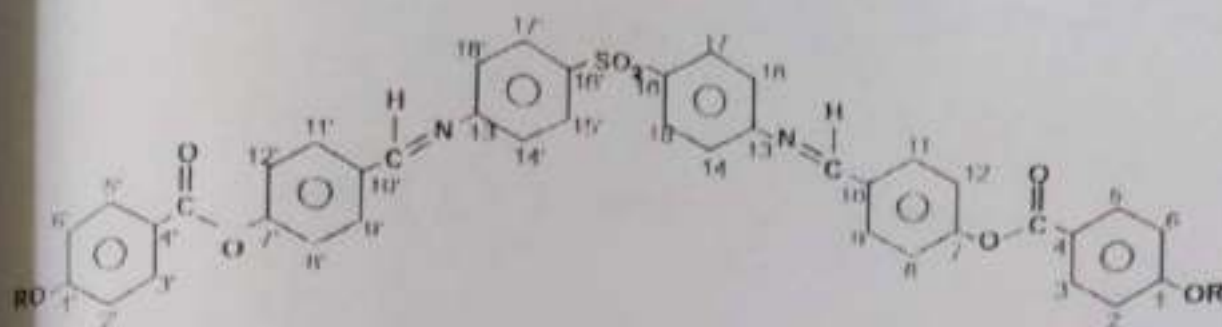


Table - IV Spectral Data

**Proton NMR - Spectra  $\text{CDCl}_3$ , 200 MHz,  $\delta$  ppm, Standard TMS)**

0.9  $\delta$  (t, 6H, 2 x  $\text{CH}_3$  of alkoxy chain at  $\text{C}_1$  and  $\text{C}_1'$ )

1.2-1.9 d (m, 12H, 6 x  $\text{CH}_2$  of alkoxy chain at  $\text{C}_1$  and  $\text{C}_1'$ )

3.66 - 4.15 d (m, 6H, 2 x  $\text{OCH}_2$  of alkoxy chain at  $\text{C}_1$  and  $\text{C}_1'$  overlapped with two central methylene protons).

7.0  $\delta$  (d,  $J = 8.9$  Hz, 4H of  $\text{C}_2$ ,  $\text{C}_6$ ,  $\text{C}_2'$  and  $\text{C}_6'$ )

7.08-7.16  $\delta$  (m, 4H of  $\text{C}_{14}$ ,  $\text{C}_{14}'$ ,  $\text{C}_{14}''$  and  $\text{C}_{14}'''$ )

7.35  $\delta$  (d,  $J = 8.5$  Hz, 4H of  $\text{C}_8$ ,  $\text{C}_{12}$ ,  $\text{C}_8'$  and  $\text{C}_{12}'$ )

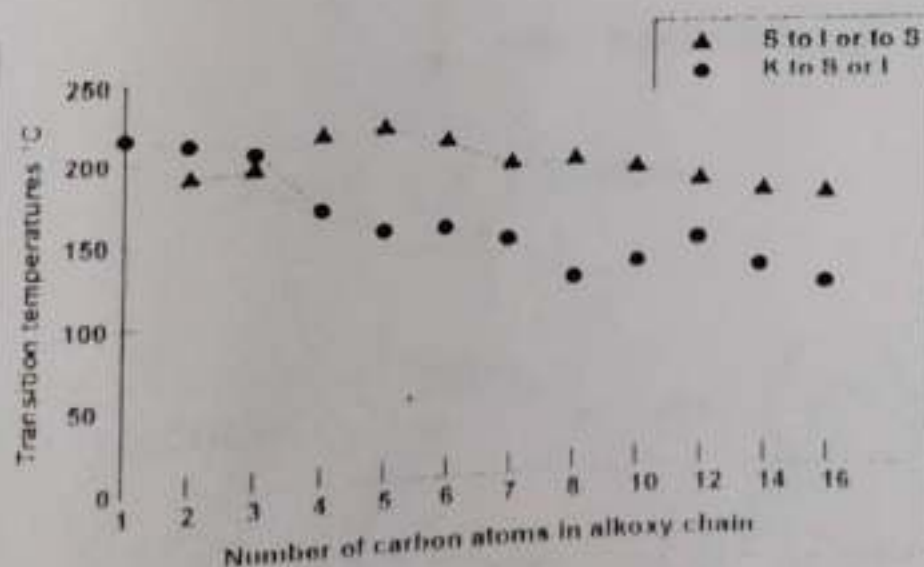
8.0  $\delta$  (d,  $J = 8.6$  Hz, 4H of  $\text{C}_4$ ,  $\text{C}_{12}$ ,  $\text{C}_4'$  and  $\text{C}_{12}'$ )

8.15  $\delta$  (d,  $J = 8.8$  Hz, 4H of  $\text{C}_6$ ,  $\text{C}_8$ ,  $\text{C}_6'$  and  $\text{C}_8'$ )

8.54  $\delta$  (s, 2H of two azomethine protons)

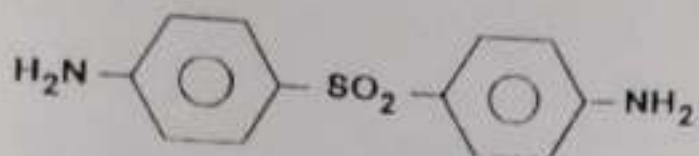
**FTIR (KBr) Spectra - Bending and stretching vibrations ( $\text{cm}^{-1}$ ).**

3414.35, 2933.20, 1712.73, 1630.52, 1605.45, 1509.99, 1318.11, 1258.32, 1203.36, 1170.58, 1115.62, 1071.26, 1014.37, 882.27, 845.63, 587.61, 516.83.

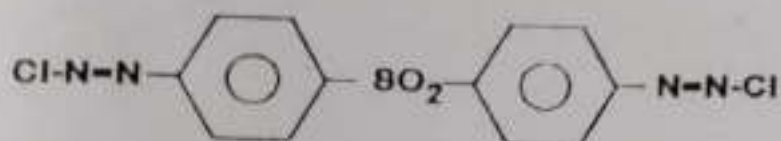


# SET-II

STEP - I

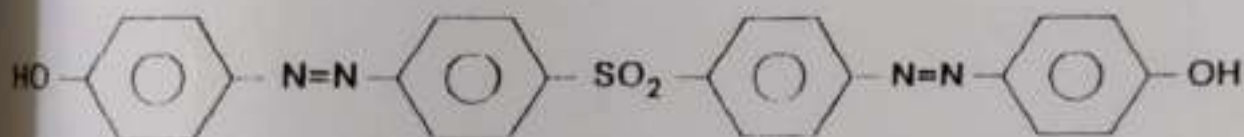


Diazotization  
0-5°C NaNO<sub>2</sub>/HCl



0-5°C

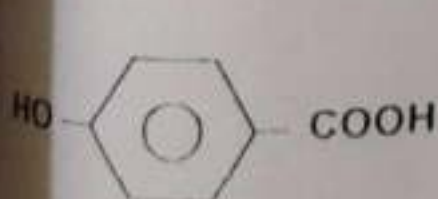
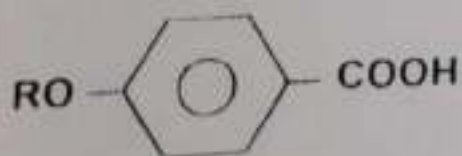
Couple with β-Naphthol  
10% NaOH



STEP - II



RBr / KOH / Ethanol

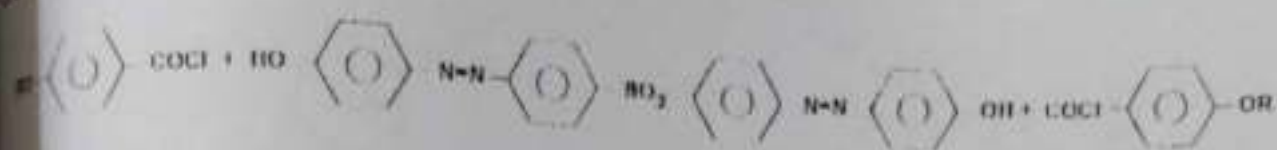


SOCl<sub>2</sub>

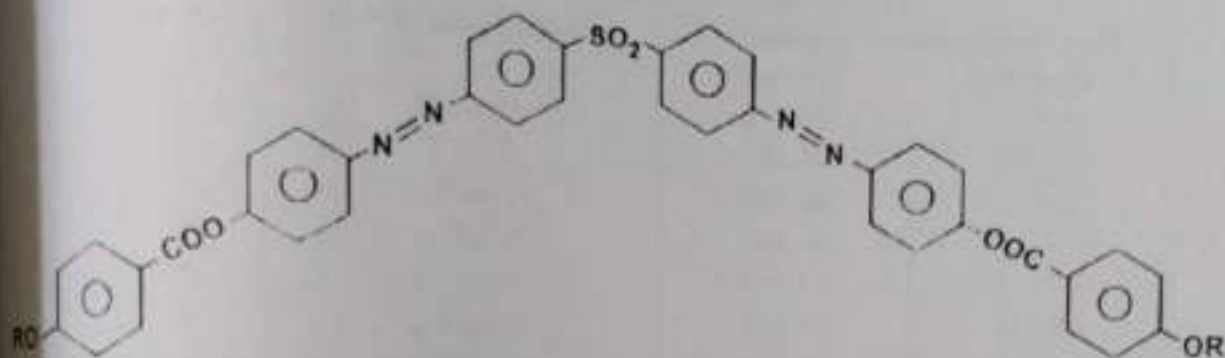


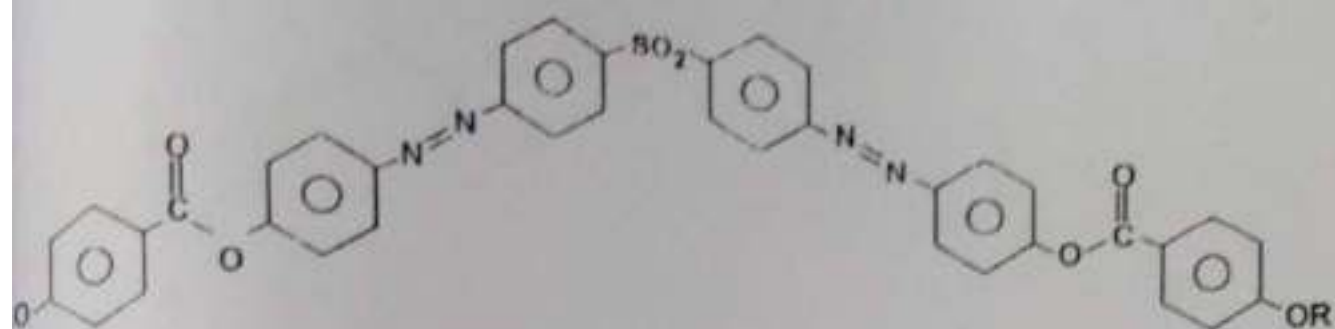


STEP-III



↓ Coupling  
- HCl





**Table - I Transition Temperatures**

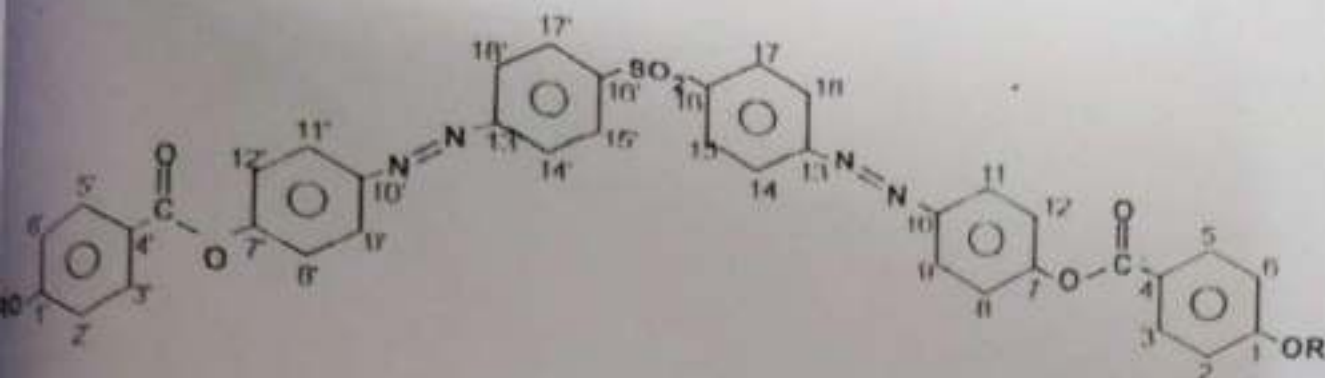
Sr.No.	R = n-alkyl group	Transition Temperature in °C	
		Smectic	Isotropic
1.	Methyl	172.00	229.00
2.	Ethyl	196.00	219.00
3.	n-Propyl	201.00	230.00
4.	n-Butyl	198.00	221.00
5.	n-Pentyl	179.00	212.00
6.	n-Hexyl	177.00	217.00
7.	n-Heptyl	175.00	213.00
8.	n-Octyl	167.00	210.00
9.	n-Decyl	150.00	198.00
10.	n-Dodecyl	158.00	188.00
11.	n-Tetradecyl	126.00	158.00
12.	n-Hexadecyl	147.00	182.00

**Table - II Elemental Analysis**

Sr. No.	Homologue	Required Percentage (%)			Found Percentage (%)		
		C	H	N	C	H	N
1	n-Propyl	72.79	5.47	7.65	72.31	5.25	7.43
2	n-Butyl	74.20	5.79	7.37	73.47	5.66	7.32
3	n-Pentyl	74.62	6.10	7.11	73.87	6.37	6.78
4	n-Hexyl	75.00	6.37	6.86	74.62	6.45	6.75
5	n-Heptyl	75.36	6.64	6.64	74.98	6.60	6.85
6	n-Octyl	75.69	6.88	6.42	75.18	6.68	6.36
7	n-Dodecyl	76.83	7.72	5.69	76.18	7.57	5.96
8	n-Tetradecyl	77.74	8.39	5.11	76.95	8.71	5.21

**Table - III DSC data of n-Pentyloxy homologue**

Transitions	MicroScope reading in °C.	DSC Peak Temperature °C	ΔH J/G	ΔS J/G °K
		184.20	13.186	0.03074
K - S	179.00	204.10	1.5947	0.00337
S - I	213.00			



### Spectral Data

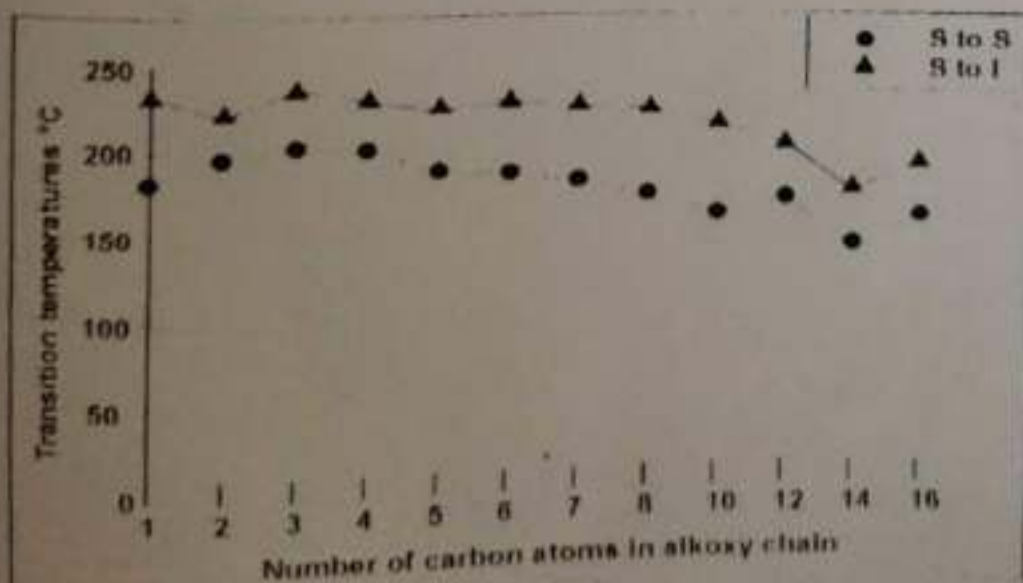
**Proton NMR** Spectra ( $\text{CDCl}_3$ , 200 MHz,  $\delta$  ppm, Standard TMS)

- 0.898  $\delta$  (t, 6H, 2 x  $\text{CH}_3$ , of alkoxy chain at  $\text{C}_1$  and  $\text{C}_1'$ )
- 1.27-1.95  $\delta$  (m, 40H, 20 x  $\text{CH}_2$ , of alkyl chain at  $\text{C}_1$  and  $\text{C}_1'$ )
- 4.0  $\delta$  (t, 6H, 2x $\text{OCH}_2$ ,  $\text{C}_4$  and  $\text{C}_4'$  and two central methylene protons)
- 6.95  $\delta$  (d, 4H of  $\text{C}_{15}$ ,  $\text{C}_{15'}$ ,  $\text{C}_{16}$  and  $\text{C}_{16'}$ )
- 7.35  $\delta$  (d, 4H of  $\text{C}_5$ ,  $\text{C}_5'$ ,  $\text{C}_6$  and  $\text{C}_6'$ )
- 7.85  $\delta$  (d, 4H of  $\text{C}_{14}$ ,  $\text{C}_{14'}$ ,  $\text{C}_{15}$  and  $\text{C}_{15'}$ )
- 8.00  $\delta$  (d, 4H of  $\text{C}_8$ ,  $\text{C}_{13}$ ,  $\text{C}_9$  and  $\text{C}_{13'}$ )
- 8.05  $\delta$  (d, 4H of  $\text{C}_2$ ,  $\text{C}_8$ ,  $\text{C}_2'$  and  $\text{C}_8'$ )
- 8.15  $\delta$  (d, 4H of  $\text{C}_6$ ,  $\text{C}_{12}$ ,  $\text{C}_6'$  and  $\text{C}_{12'}$ )

**FTIR (KBr) Spectra** - Bending and stretching vibrations ( $\text{cm}^{-1}$ ).

1429.2, 1062.7, 2954.7, 2931.6, 2871.8, 1724.2, 1604.7, 1510.2, 1492.8, 1463.9, 1417.6, 1384.8, 1253.6, 1222.8, 1201.6, 1168.8, 1151.4, 1078.1, 1008.7, 970.1, 889.1, 848.6, 821.6, 759.9, 692.4, 657.7, 551.6

1175.2, 1280.7, 2925.8, 2854.5, 1728.1, 1604.7, 1510.2, 1492.8, 1463.9, 1417.6, 1388.7, 1255.6, 1222.8, 1199.6, 1168.8, 1066.6, 1008.7, 887.2, 846.7, 819.7, 759.9, 721.3, 692.4, 657.7, 549.7





## SUMMARY

Liquid crystals find applications in different fields. This has given impetus for the development of new liquid crystalline materials. Lately bent - core mesogens have gained importance for their potential in application and interesting geometrical variations.

The present work involves the synthesis of liquid crystalline materials with bent core molecules and other varying unconventional geometry.

### 1. Liquid crystals with biphenyl methane bent core.

Seven homologous series with biphenyl methane bent core has been synthesized. One of the series has no lateral substituent (Series I). Series II to series VII have different lateral substituents, except series VII, which has four methyl group as lateral substituent. The bent - core molecules with such lateral substituents have provided unique opportunity to compare the mesogenic properties with unsubstituted bent core molecules and rod - shaped molecules.

One of the compound of these series was tested for its electro - optical properties.

### 2. Liquid crystals with 1,2,4-trisubstituted benzene derivative.

The conventional mesogenic compounds have rod-shaped geometry, while molecules with trisubstituted benzene nucleus deviate from conventional geometry. Series VIII has phenyl ring as lateral substituent joined by an ester linkage and having para n-alkoxy group. Series IX has hydroxyl group as lateral substituent.

### 3. Liquid crystals with piperazine moiety

Heterocyclic rings induce reach mesomorphism, however, introduction of saturated heterocycles are less studied as one of the component of the molecules. Such nucleus affects the geometry of the molecules and also impart higher polarizability.

Binary systems with achiral and chiral components.

Four achiral binary systems have been studied by incorporating non-mesogenic substituted benzene derivatives with classical rod shaped non-mesogens. Two binary systems having one non-mesogenic chiral component and other components exhibiting nematic and smectic phases are studied.

Seven homologous series I to VII with biphenyl methane bent core exhibited smectic phases. The lateral substituents did have adverse effect on smectic mesophases compared to unsubstituted mesogens. However, one would not have expected exhibition of smectic mesophase in laterally substituted systems. It seems that molecules pack in smectic layer in such a way that adverse effect of lateral substituent decreases.

The lateral substituents also have brought down solid-smectic as well as smectic-isotropic transition temperatures. Due to this reason the exhibition of smectic phases are at relatively lower temperature increasing their applicability potential.

Bent core molecules are known to exhibit chiral properties, even though they are achiral on application of electric field. One of the compound from above series was evaluated for its electropirical property. At higher temperature it exhibits switching effect, gives chiral smectic C\* phase and also exhibits spontaneous polarization normally exhibited by chiral smectic C\* phases.

Trisubstituted mesogenic compounds are of interest as unconventional molecules. Series VIII exhibits monotropic smectic phases below 100 °C. Lower members of series IX exhibit nematic mesophases.

Series X, with piperazine moiety exhibits smectic phases. Smectic phases with piperazine moiety are known to conduct electric current. Present study has provided number of smectogens for such studies.

Binary systems with non-mesogens having trisubstituted component and rod-shaped molecules have induced nematic and smectic phases. The induction of these phases is for large concentration of non-mesogens.



The chiral non-mesogen induces chiral nematic N\* and chiral smectic C\* phases in binary systems, however the exhibition of mesophases is up to 30 % concentration of chiral non-mesogen in the mixtures.

The compounds were characterised by TLC, elemental analysis, IR and NMR spectroscopy. Mesogenic properties were evaluated by using polarizing microscope with heating stage and by DSC. The type of mesophases were ascertained by miscibility studies and contact method.

The study has provided bent - core mesogens exhibiting smectic mesophases which would exhibit chiral smectic phases under electric field as per the study of one such compound. These compound have good potential for application.

Study also provided useful information regarding effect of lateral substitution on such molecules. They reduced the melting point also which result in the exhibition of smectic mesophases at lower temperatures.

The hydroxyl group as lateral substituent does not affect mesophases adversely. The other trisubstituted compounds exhibit smectic C phases at relatively lower temperatures.