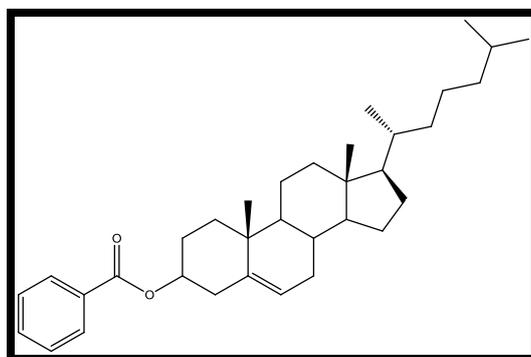


## 1.1 Liquid Crystals

The solid, liquid and gaseous states, the common states of matter differ primarily by the types and order found in the state. The molecule into crystalline solid, possessing high order has positional order and orientation order. When most solids melt at specific temperatures in an isotropic liquid, both orders are completely lost; the molecules move and tumbel randomly. Certain substances, however, have intermediate states having more order than in liquids, but less order than in typical crystals. These orderly fluids are termed liquid crystals. A liquid crystal substance in this state is highly anisotropic in some of its properties like birefringence associated with crystalline solids and yet has the flowing property like liquids. In the LC state, molecules tend to point to a common axis, named the director [1].

## 1.2. History of Liquid Crystals

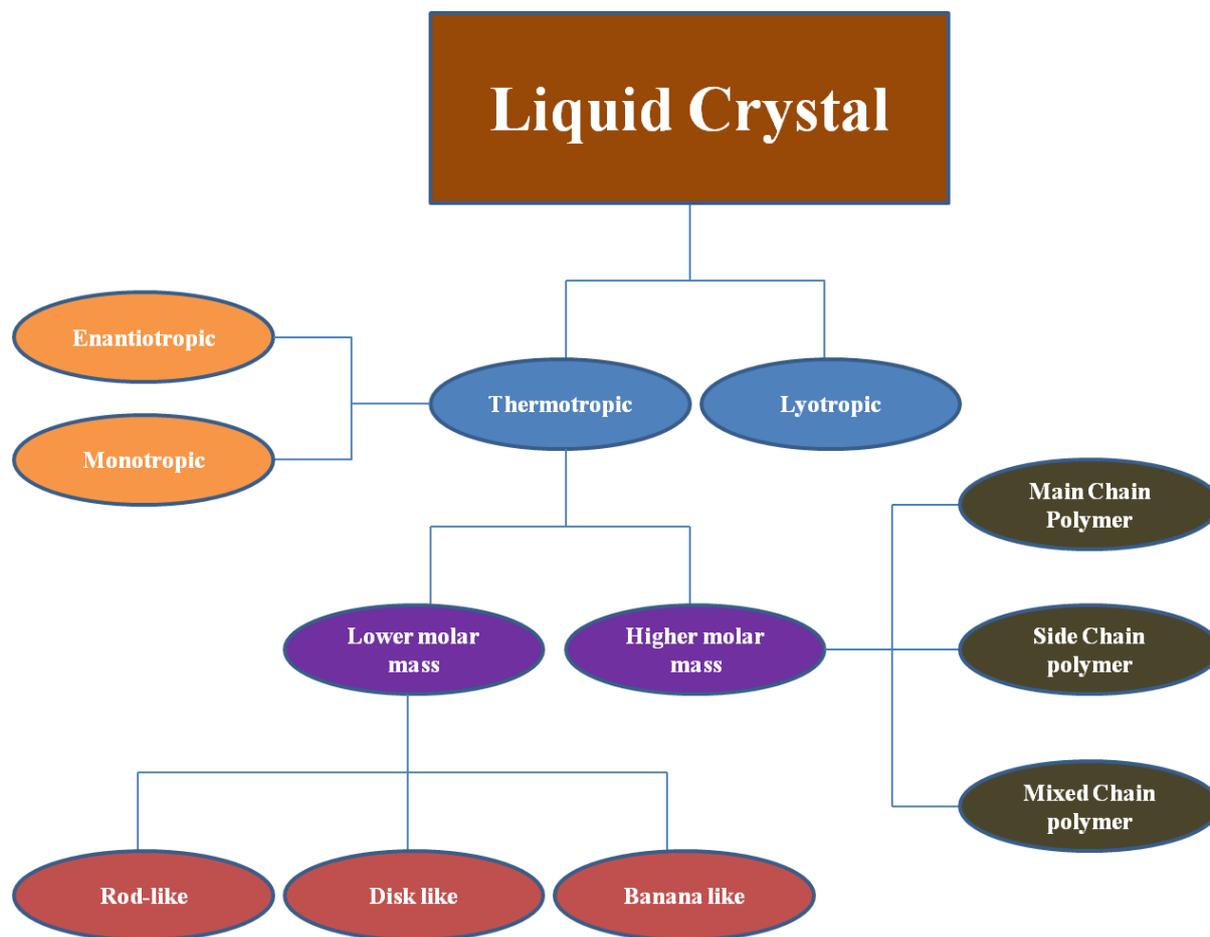
In 1888, the Austrian botanist Friedrich Reinitzer noted the unusual melting behavior of cholesterol benzoate (**Figure 1**), exhibited two melting points on heating. The solid ester first melted at 145.5 °C to form a turbid liquid, which, when further heated to 178.5 °C, disappeared and became a clear isotropic liquid [2]. Reinitzer sent the material to Otto-Lehman. Lehmann observed the substance of Reinitzer with the help of the polarising microscope and confirmed the existence of the new physical state of matter [3]. He proposed the term "liquid crystal" for the new intermediate state between the crystalline solid and the isotropic liquid.



**Figure 1.** Cholesteryl benzoate

In 1908, Vorlander undertook a systematic study of the relation between the molecular structure and the properties of liquid crystals [4]. Several research groups have systematically modified the structure of the aromatic nucleus and studied many homologous series, and found that the systematic changes in the transition temperature always occur within the series [5-8]. In 1977, Chandrasekhar and colleagues reported on the formation of liquid crystals by disc-like molecules [9]. They synthesized the hexa-substituted benzene derivatives, which exhibited discotic nematic phase. A brief overview of the progress in this area, with particular emphasis on the structural aspects provided by S. Chandrasekhar in his discotic liquid crystal review [10]. Progression of triphenylene-based discotic liquid crystals reported by S.K Pal et.al [11]. An interesting review on discotic liquid crystals reported by Tobias Wöhrle et al. [12]. Niori et al. states the unusual ferroelectrical behaviour of banana-shaped liquid crystals. [13]. The main concepts of a banana-shaped liquid crystal are reviewed by M. Blanca Ros et.al. Michael Hird reported review on Banana-shaped and other bent-core liquid crystals. [15] It was believed that the possibility of formation of liquid crystal phase in polymeric materials is difficult to achieve, because the polymer chain unusually adopts a statistical coil conformation, whereas LC phases possess an orientational and/or a positional long-range order. Flory, in 1956, predicted that rod-like polymer solutions could also exhibit liquid crystal behavior [16]. Mahmoud A. Hussein et al. reported review on liquid crystalline polyazomethines polymers [17]. Recently Lyu X et al. reported detail review on liquid crystalline polymers [18].

## 1.3. Classification of Liquid Crystals



**Figure 2.** Classification of Liquid Crystal

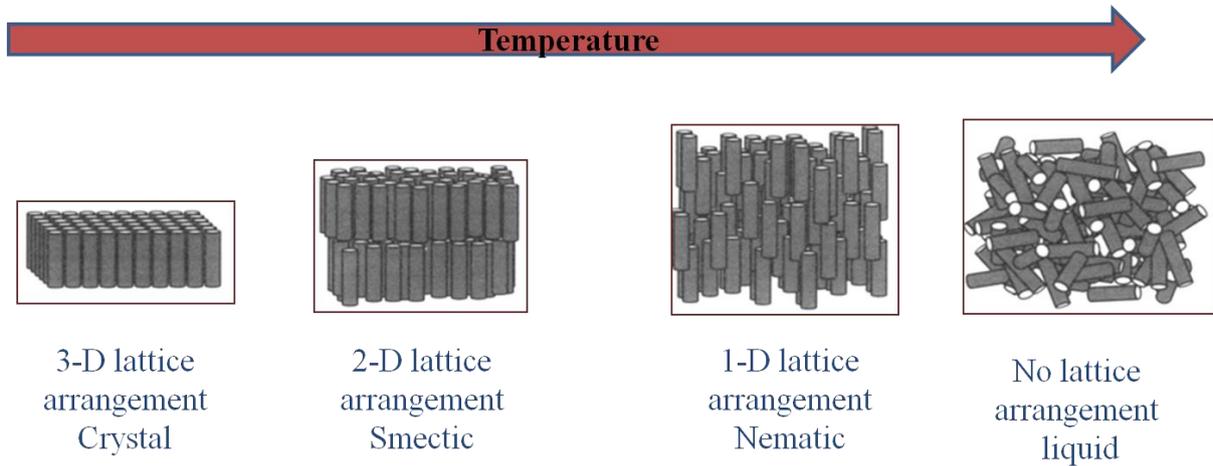
The broad classification of liquid crystals is depicted in **Figure 2**. The most widely used classification of liquid crystals is in two broad categories, thermotropic liquid crystals and lyotropic liquid crystals according to the way they are obtained.

**(A) Thermotropical liquid crystals:** When a compound has a liquid crystalline state as a primary function of temperature, the behavior of the liquid crystal is referred to as thermotropic [19].

**(B) Lyotropic liquid crystals:** When phase transitions are induced by the concentration of the liquid crystal in a solvent at a different temperature, the behavior is called lyotropic [20].

**(A) Thermotropic liquid crystal:**

Thermotropical fluid crystals occur within a certain temperature range. If the temperature increase is too large, the thermal motion will destroy the order of the molecules, forcing the material into an isotropic fluid [1, 21] **(Figure 3)**.



**Figure 3.** Thermotropic liquid crystal

There are two types of thermotropic liquid crystal.

**(i) Enantiotropic Liquid Crystals:**

This can be transformed into a liquid crystalline state by reversibly heating the solid and cooling the liquid; this phenomenon is considered to be enantiotropy, and the substance is considered to be enantiotropic.

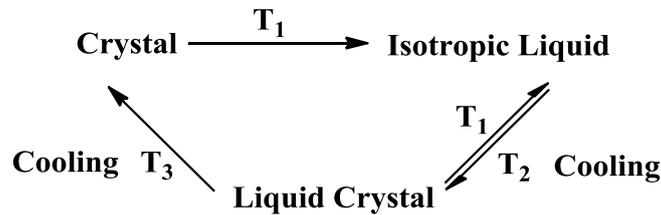


Where,  $T_2 > T_1 > T_3$

**(ii) Monotropic Liquid Crystals:**

This mesomorphic behavior observed only during cooling is referred to as monotropic. In this case, when the crystalline solid is heated, it will directly melt into the isotropic liquid, but when the same isotropic liquid cools, it shows a liquid crystal phase

before crystallization. Therefore, the mesogenic behavior that happens only during cooling is called monotropic.



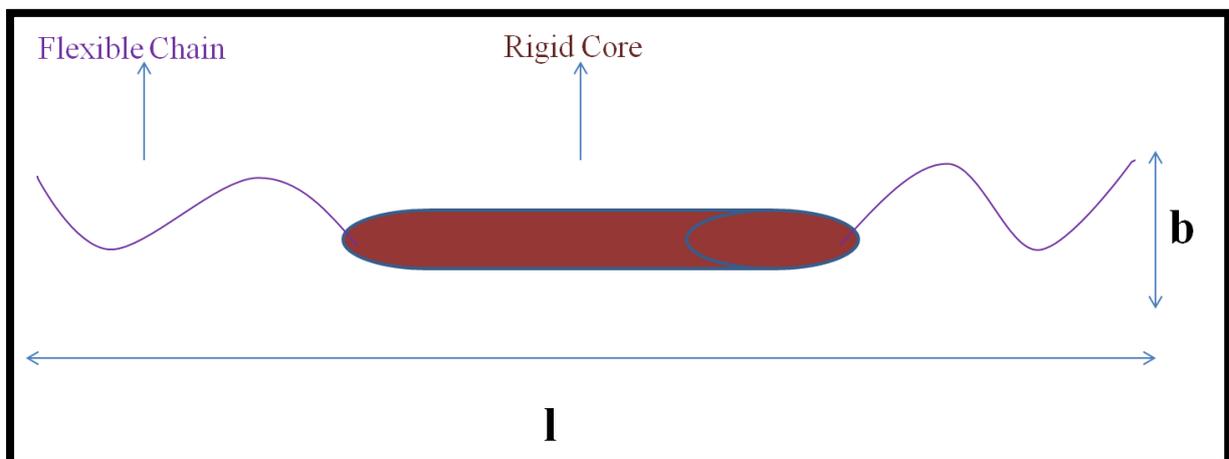
Where,  $T_1 > T_2 > T_3$

Depending on the molecular form of the mesogens, thermotropic liquid crystals are divided into three classes:

- 1) Rod-like
- 2) Disc-like
- 3) Banana-like

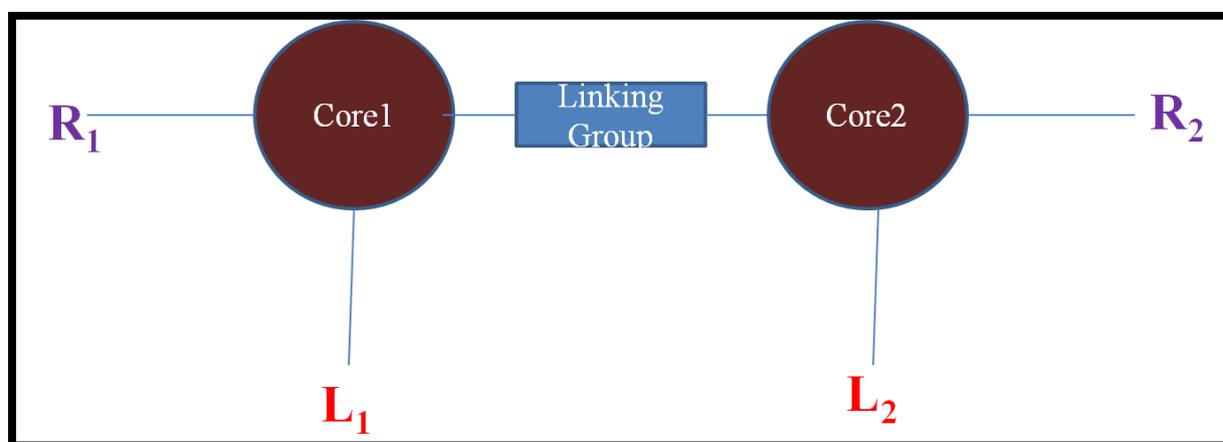
**1) Rod-like**

The most common liquid crystal molecules forming the phase are rod-shaped molecules, where the length and width of the molecules differ considerably, thereby providing the required anisotropy (**Figure 4**). These compounds are referred to as calamitic liquid crystals.



**Figure 4.** Dipiction of a calamitic liquid crystal

A typical calamitic mesogen consists of a rigid central core, since it must remain elongated to produce directional interaction. In addition to the flexible side chains which provide a stabilizing effect, there are also rigid linking groups. The rigid core is essentially aromatic, but it may also be alicyclic, and the polar group is also commonly used. Most rod-like liquid crystal compounds are made up of two or more rings, which are either directly connected to each other or connected by a linking group. The chemical structure of several mesogens may be depicted by the general formula in **Figure 5**. Where,  $R_1$  and  $R_2$  are terminal units, whereas  $L_1$  and  $L_2$  are side substitutes.



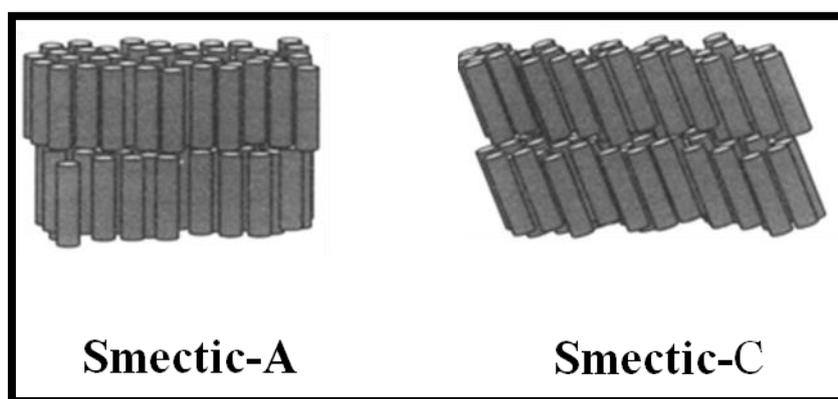
**Figure 5.** General chemical structure formula for a calamitic liquid crystal

Depending on the arrangement of the molecules in different mesophases, calamitic liquid crystal may be divided into two types: (a) Smectic phase (b) Nematic Phase.

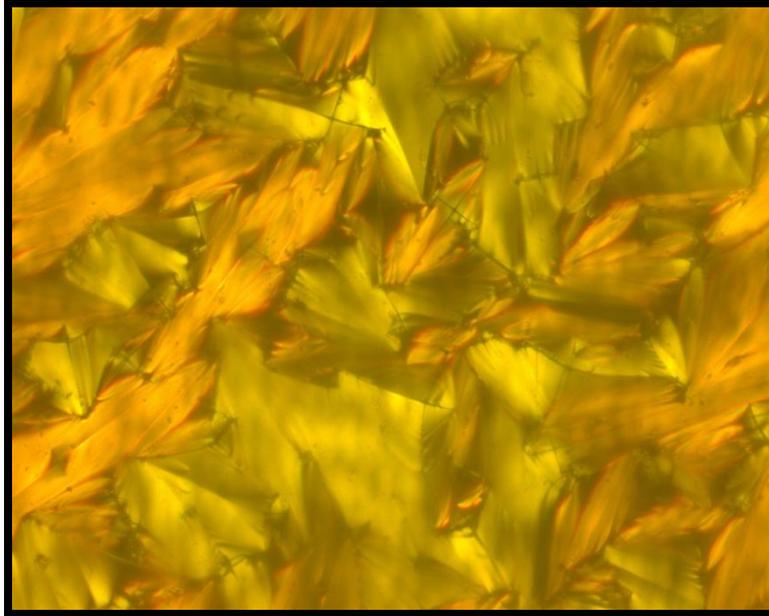
### (a) Smectic Phase

The word smectic is derived from the Greek word smectose, which means soap, created by Friedel because the smectic mesophase is a thick turbid liquid with soapy properties [22]. Of all the liquid crystal phases, smectic mesophase is the most orderly. The smectic mesophase has a layered structure; the long molecules are adjacent to each other, parallel and arranged in a row of layers, and their longitudinal axis is approximately perpendicular to the layer plane. When placed on a horizontal surface, it has a tendency to form a series of layers or terraces. These terraces are known as the plain of Granjana [23]. The liquid character of

this phase is due to the sliding between the superior and inferior adjacent layers, and the smectic phase produces a focal cone texture. It diffuses through the sample and looks like a fan-shaped when inspected under polarized light. When the smectic liquid crystal is heated, molecular cohesion is disrupted, which is not sufficient to break the lateral binding, and the layers remain virtually intact. After cooling, the smectic phase looks like particles of rod-shaped birefringent droplets. The number of these rods increases as the temperature decreases, and they have a focal cone texture, which is characteristic of the smectic mesophase [24, 25]. There are different types of smectic liquid crystals, which vary according to the type of layer, namely SmA, SmB, SmC, SmF, SmI, and so on. The smectic mesophase appears in the following order:  $A \rightarrow C \rightarrow B$ , as the temperature drops. However, the most studied smectic phases are SmA and SmC (**Figure 6**). In the smectic-A, the molecules of each layer are arranged vertically, and the centre is unequally arranged such that in a liquid state. The lateral forces between the molecules are strong with respect to the inter layer attraction. Consequently, these layers can glide relatively easily. As a result, this phase has fluid properties (**Figure 7**). The smectic-C is a tilted form of smectic-A. The molecules are inclined with respect to the layer.



**Figure 6.** Smectic liquid crystals

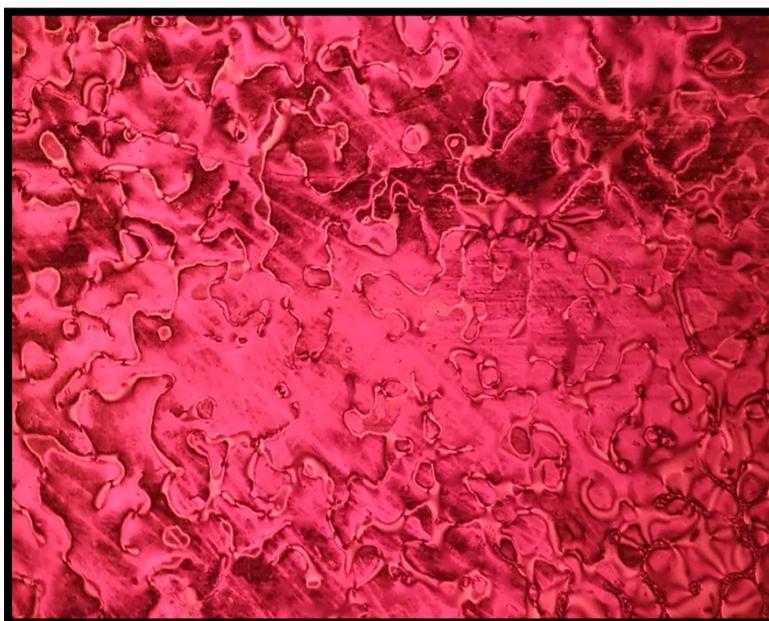


**Figure 7.** Focal cone texture of smectic-A Phase

## **(b) Nematic Phase**

The word "nematic" comes from the Greek word "nema", which means thread since the phase has a thread-like schlieren texture. In this phase, the molecules are arranged parallel to the long axis but are not stratified. Molecules are found in groups and each group contains approximately 100,000 parallel molecules. These groups were known as "Swarms". The group theory was first proposed by E. Bose [26] in 1909 to explain the molecular structure and order in the nematic phase. The optical properties of the nematic phase indicate that the molecules are in constant motion, so the swarms will not remain constant, but the molecules will constantly exchange with each other. The arrangement of the swarms is nonrigid and will be affected by mechanical deformation. The nematic phase has a low viscosity because of its great fluidity. They are anisotropic from the point of view of optical properties, viscosity, electrical and magnetic susceptibility, electrical conductivity and thermal conductivity [27]. Nematic substances separate into spherical droplets in the melt, which coalesce to give the threaded structure. The least ordered mesophase is the nematics phase, in which the molecules have only an orientational order. The long molecular axis, on average, points to a

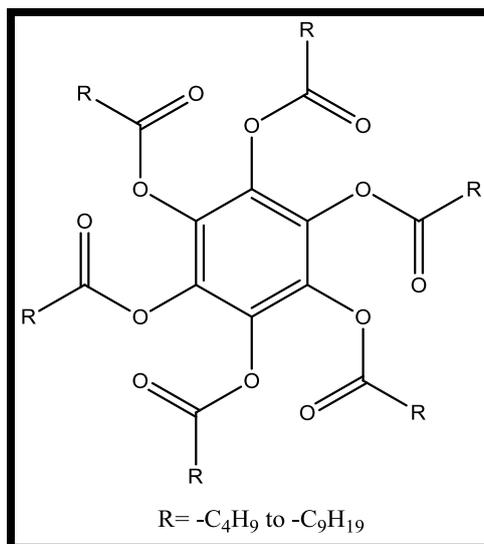
avored direction called the director [28]. When observed under POM, the nematics compound shows the threaded texture, as shown in **Figure 8**. Nematic fluid has the same fluidity as isotropic fluid, but can be readily aligned with external electric or magnetic fields. Aligned nematics have the optical properties of uniaxial crystals, making them very useful for liquid crystal displays (LCD) [1].



**Figure 8.** Thread-like texture of nematic phase

## (2) Disk-like

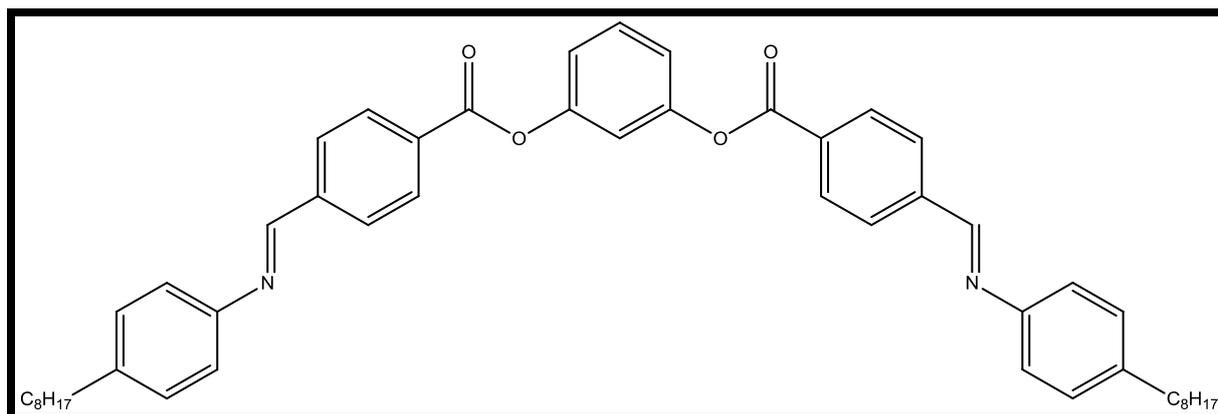
Disc-shaped mesogens are called discotic liquid crystals. In 1977, the Indian scientist S. Chandrasekhar et al. discovered the disc-shaped mesophase [9] described for the first time (**Figure 9**). A typical discoid mesogens usually consists of a central aromatic functionalized core with three to eight flexible chains. The two major types of discotic liquid crystals are the nematic phase and the columnar phase. The discotic nematics has a similar structure to the calamitic nematics, although in this case, the axis of the disc is more or less in the same direction. In the columnar phases, the Penny Stack columns are arranged in a regular two-dimensional network.



**Figure 9.** Discotic liquid crystal: Benzenehexa-n-alkanoate derivatives

### 3) Banana-like

The liquid crystal phase consisting of bent molecules is called banana liquid crystal. These compounds usually comprise a bicentric aromatic moiety (such as 1, 3-disubstituted benzene) and two flexible tails. First, Vorlander [29] synthesises the bent-core LC. Niori et al. reported the ferroelectric properties of 1,3-phenylene bis[4(4-n-octyliminomethyl) benzoate] [13] (**Figure 10**). Because these mesophases are not miscible with known phases of thermotropic liquid crystals, the symbol "B" is designated to indicate the shape of the molecule. Several intermediate phases were identified and, consequently, the symbol was assigned. They are closely related to the smectic phase. In the B2 mesophase; the molecules are tilted like SmC. Banana-shaped mesogens form a complex, layered structure because of their curved shape and molecular polarity, and are the only substance with increased non-linear secondary optical susceptibility in liquid crystals.



**Figure 10.** Banana shape Liquid Crystal

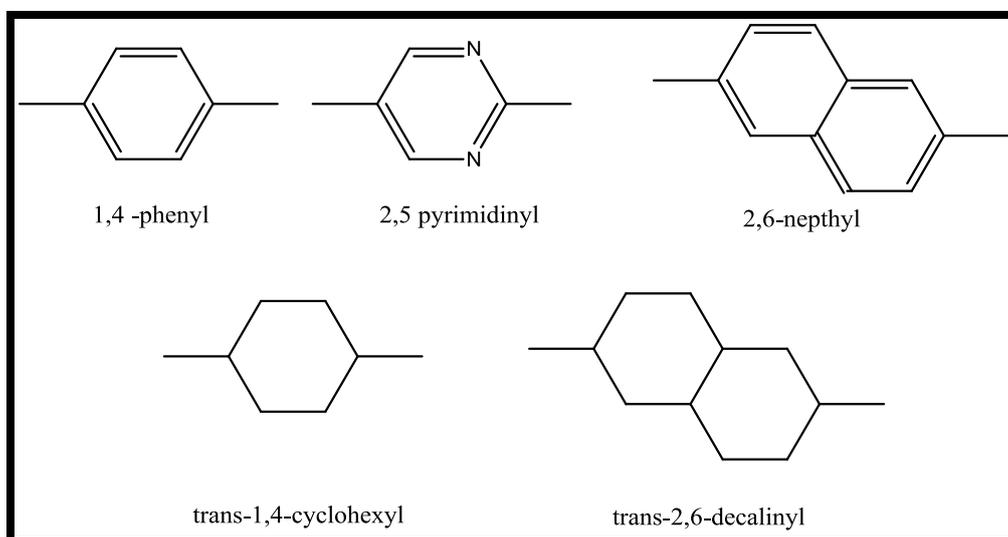
**(B) Lyotropic liquid crystals:**

If a phase with a long-ranged orientation is induced by the addition of a solvent, the liquid crystal material is referred as lyotropic. The lyotropic liquid crystalline phase is made up of amphiphilic molecules [30]. The molecules are characterized by a hydrophilic polar head and a nonpolar tail. Typical hydrophobic groups are saturated or unsaturated hydrocarbon chains. When dissolved in an appropriate solvent, they self-assemble to micelle. Three different types of lyotropic liquid crystal phase structures are familiar. This refers to the cubic phase, the hexagonal columnar phase and the lamellar phase. The formation of different phases of lyotropic liquid crystals is thought to be a function of cohesive forces and water affinity [31].

## 1.4 Structure-property relation in thermotropic liquid crystal.

### (i) Core

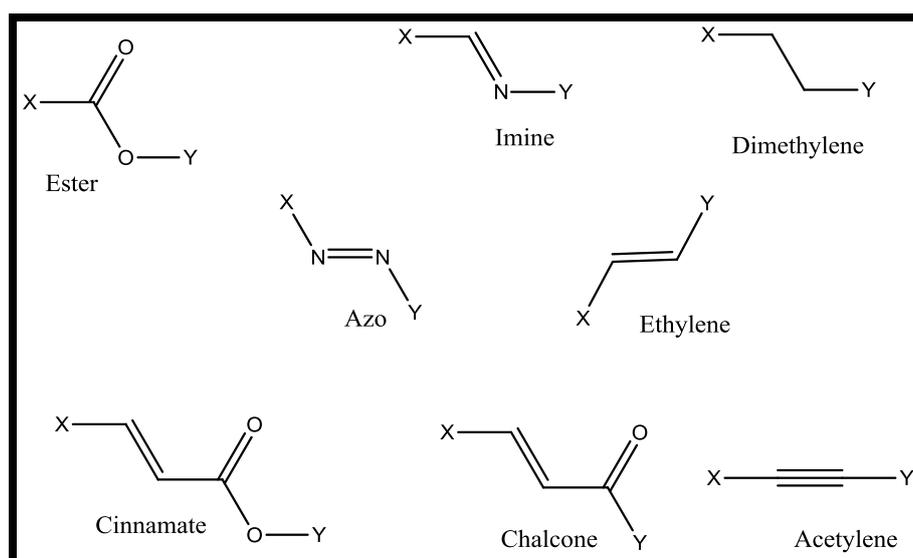
The molecular anisotropy required for its mesogenicity is primarily due to the core, which is also the cause of the comparatively high melting point. The core rings are connected either directly or by linking groups, along with lateral substituent. Calamitic liquid crystals generally have aromatic rings such as 1,4-phenyl, 2,5-pyrimidin, 2,6-naphthalene and alicyclic rings such as trans-1,4-cyclohexyl and trans-2,6-decahydronaphthyl (**Figure 11**) [1]. An increase in benzene rings will generally result in an increase in the melting point. Furthermore, the mesogenicity of the compound increases as the number of linearly connected rings increases. When the CH group in the ring is replaced by an N atom, the shape of the ring changes little, but the electronic properties change, and a considerable electric dipole is generated, which changes the intermolecular attraction.



**Figure 11.** Different core units

**(ii) Linking groups**

The different linking groups used in liquid crystal molecules are depicted in **Figure 12**. A linking group is a structural unit that connects one part of the core to another part of a liquid crystal molecule. The linking group increases the length of the molecule while maintaining the linear shape, also increases the polarization anisotropy of the molecular core, and improves the stability of the liquid crystal phase. The effect of linking groups for aromatic and non-aromatic compounds can be significantly different because there is no conjugating effect for non-aromatic compounds. The ester group is the most commonly used linking group in liquid crystals because it is relatively stable, easily synthesized and can produce useful low-melt liquid crystals. Ethylene is a fully conjugated linking group that can improve longitudinal polarization and lengthen the molecule while preserving linearity. Acetylene retains the rigidity, linearity and polarization of the core and increases the length of the molecule. Schiff bases, imine functional groups ( $\text{CH} = \text{N}$ ), are widely used as linking groups for rigid base fragments. It offers greater stability and promotes mesophase formation, although it produces a staggered central structure [32].



**Figure 12.** Different linking groups

**(iii) Terminal Group**

The terminal group that exists in the molecule are important because of their polarity. Polar groups may produce significant intermolecular attraction forces to stabilize the molecular orientation. The terminal substituted compound was found to have a more stable mesophase than the non-substituted mesogenic compound. The choice of end groups is critical for the formation of a particular type of liquid crystal phase. The theory of Mayer and Saupe [33] showed that the nematic-isotropic transition temperature of a compound is related to the molecular polarization of the molecule, and the molecular polarization is always related to the terminal group and its influence on the intramolecular conjugation. In smectic liquid crystals, some terminal groups reduce thermal stability. When the alkoxy or alkyl carbon chain increases, the trend towards a lower melting point increases. These chains are responsible for the orientation necessary for stabilizing the liquid crystal. Most of the liquid crystals with medium chain length are pure nematic phases. Increasing the length of the carbon chain causes smectic and nematic mesophases, whereas very long chains generally have only smectic phases. For  $T_{N-I}$  trend values, odd-numbered chains produce higher  $T_{N-I}$  values than even-numbered chains. This effect is called the odd-even effect, which can be explained by the fact that the extra carbons constituting the chain even deviate from the most suitable linear structure as trans chain conformation. As the length of the end chain increases, the smectic tendency increases, and the nematic phase is eventually eliminated. This is because the long chains are attracted and entangled together, which facilitates the laminar stacking required to form the smectic phase. In the rod-shaped aromatic system, the order of effectiveness of the terminal group of the smectic phase is [34] Ph > -Br > -Cl > -F > -NMe<sub>2</sub> > -Me > -H > -NO<sub>2</sub> > -OMe > -CN and the nematic group efficiency order is -Ph > -NHCOCH<sub>3</sub> > -CN > -OCH<sub>3</sub> > -NO<sub>2</sub> > -Cl > -Br > -N > (CH<sub>3</sub>)<sub>2</sub> > -CH<sub>3</sub> > -F > -H.

### (iv) Lateral substitution

A lateral substituent is a substituent away from the linear axis of the molecule, generally on the side of the aromatic nucleus. Many different liquid crystal systems contain a various lateral substituents, including F, Cl, CN, NO<sub>2</sub>, CH<sub>3</sub>, and CF<sub>3</sub>. Lateral substitution separate molecules and reduce lateral adhesion between molecules, but at the same time they can enhance molecular attraction. Regardless of the chain length of the alkoxy or alkyl group, they will destroy any smectogenic properties, lower the temperature at which the mesophase occurs, and reduce the stability of the mesophase. In addition to the broadening of the molecule, the lateral substitution also increases its thickness and imposes a steric effect on the system, that is, it causes a twist around one of the bonds, causing part of the molecule to rotate out of plane [35]. The combination of broadening and steric effects significantly reduces the thermal stability of the ordered arrangement of molecules in the liquid crystal, which is more for the smectic phase than the nematic phase. Mesogens substituted by *o*-hydroxyl are an exception to the general rule above because intermolecular hydrogen bonds enhance the overall polarizability of the molecule [36]. The most common lateral substituent used is fluorine. It is very small in size, has a steric effect, and extremely polar. Chlorine substituents form larger dipoles than fluorine substituents. Since the bond with carbon is longer, however, the large size of the chlorine substituent makes it unsuitable as a lateral substituent in the liquid crystal compound because of poor liquid crystal phase stability and high viscosity. The decrease of  $T_{N-I}$  caused by the side group substituents, regardless of their polarity, is proportional to the size of the substituents. However, if the side substituents are the polar, the reduction in the stability of the smectic phase caused by the side substituents can be partially offset; the layered packaging is interrupted by a large size but enhanced by a greater polarity [1].

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