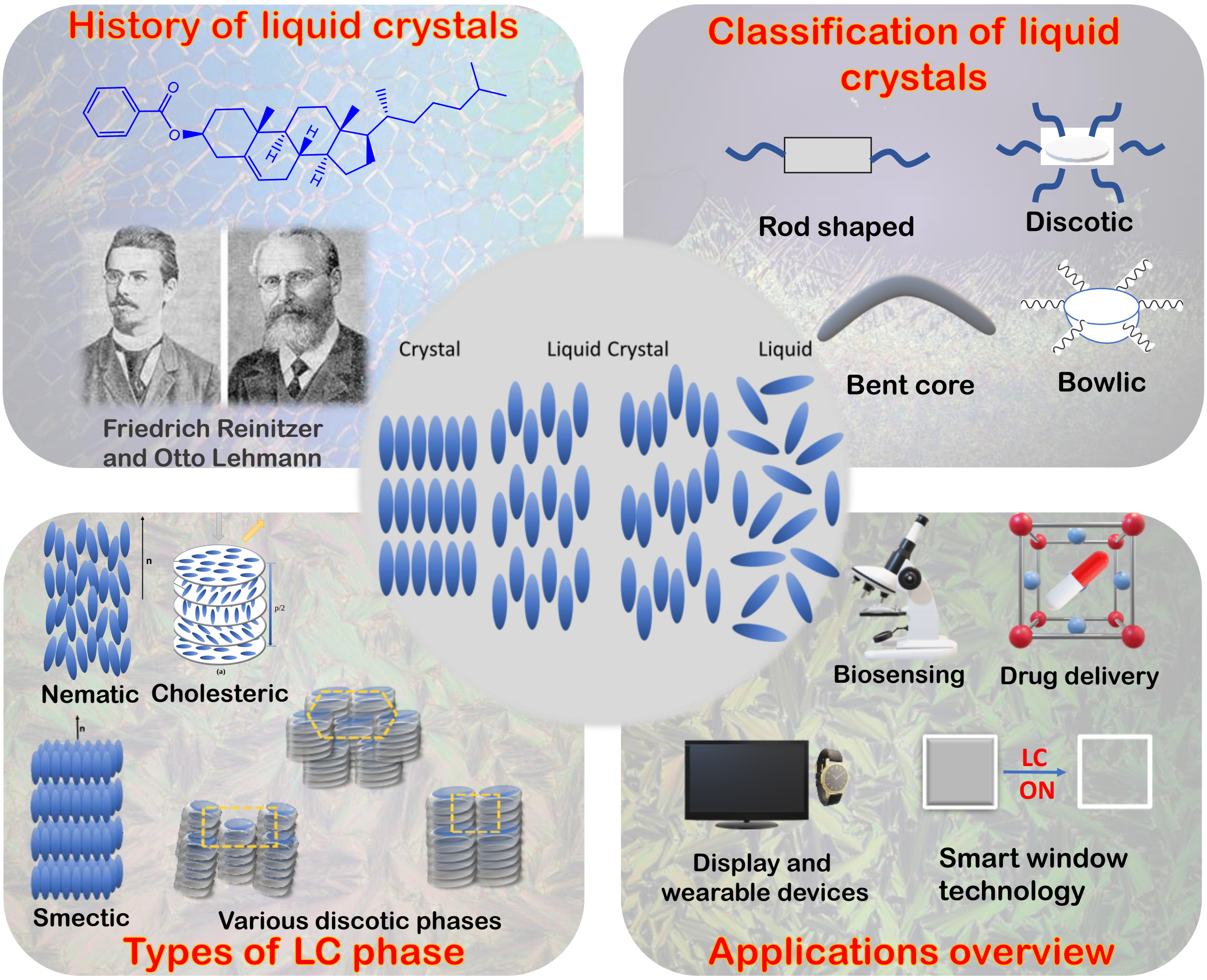
CHAPTER 1

Introduction



1.1. General introduction

Liquid crystals (LCs) represent a distinct state of matter, often referred to as the fourth state of matter, characterized by properties that fall between those of conventional liquids and crystalline solids [1–5]. For instance, the molecules in a liquid crystal may be orientated in the same direction as those in a solid, yet the crystal itself may flow like a liquid.

The three different states of matter that exist conventionally are solid, liquid and gas. Crystalline solids have both positional and orientational order, meaning that the molecules that make up the solid are restricted to specific points within the lattice and to specific directions with their molecular axes. Owing to this rigid configuration of molecules, the majority of crystalline materials exhibit optical anisotropy, usually possessing both orientation and three-dimensional positional orders. Liquids have an optically isotropic condition in which the molecules randomly propagate across the container with their molecular axes moving wildly, which results in the loss of positional and orientational order. In nature, there are phases with a lower order than solids but a greater order than liquids. More specifically, solids often exhibit both positional and orientational order, meaning that molecular axes and centres of mass are oriented in specified directions. Since molecules disperse in all directions, the centre of mass of a liquid's molecules changes and has no fixed position. Thus, this condition is known as an isotropic state as its physical characteristics are independent of direction. Generally considered, mesogens are anisotropic ordered fluids, also referred to as "orientationally ordered liquids" or "positionally disordered crystals". These material states have been categorised and given the name "liquid crystals" (LCs). The liquid crystalline phases known as the nematic and smectic phases, shown in **Figures 1.1.(b)** and **1.1.(c)**, are characterized by molecules that retain a preferred orientational direction (referred to as the director and denoted by the letter "n"). Compared to a crystal, a liquid crystal has a very minimal degree of order. Molecules show only a slight inclination to favour one direction over others or to prefer certain positions over various alternatives.

A molecule exhibiting a liquid crystalline state is referred to as a "mesogen" and shows "mesomorphism." The "mesophase" (*mesos* = between) is the intermediate phase between solids and liquids [6–8]. The word '*liquid*' is derived from the Latin words '*liquere*' or '*liquidis*,' which translate into '*flowing*' or '*capable of flowing*'. The term '*crystal*' originated after the Greek word '*krústallos*' that translates into *'clear ice'* [9]. It should be noted that there is another phase of matter known as plastic crystals that lacks orientational organization but has positional order [10]. This lack of orientational order distinguishes plastic crystals from liquid crystal phases of matter, which have long-range orientational order [11].

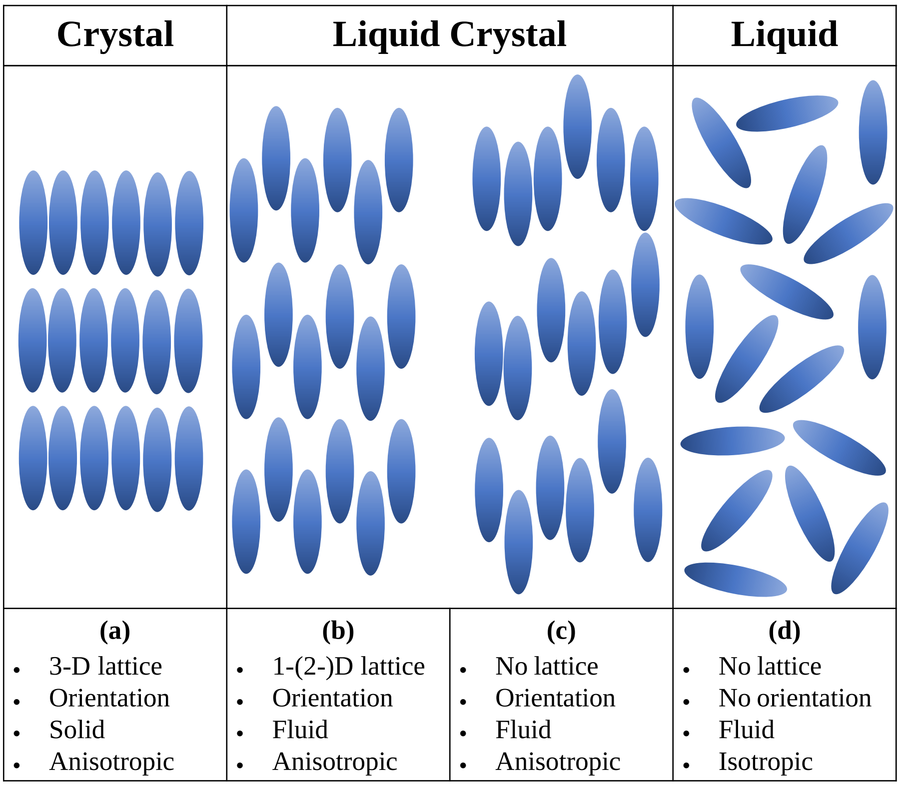


Figure 1.1: Fundamental structural variations among crystalline solids, liquid crystals and isotropic liquid

With contrast to solids, molecules in LC phases exhibit increased intermolecular and intramolecular mobility [12]. The increased intermolecular interactions in the LC phase allow for greater mobility, leading to optically anisotropic properties and unique dynamics. The transmitted light has distinct velocities in different directions. As a result, they have distinct birefringent properties and produce dramatic colour patterns when viewed via crossed polarizers. The birefringence of liquid crystals is highly dependent on temperature and thickness, and it decreases with increasing temperature [13]. These patterns are known as textures, and they are unique to each LC phase.

1.2. Historical developments in liquid crystals

Liquid crystals were first discovered serendipitously by an Austrian botanist and chemist Friedrich Reinitzer (1857–1927) around the end of 1800s at the Karl Ferdinands Universität, while studying the cholesterol derivatives [14]. While studying the properties of cholesterols extracted from carrots, he discovered that cholesteryl benzoate (i.e. $C_{34}H_{50}O_2$) **(Figure 1.2)** had not one, but two melting points, with the compound melting initially from solid crystal to hazy intermediate liquid at 145.5 °C and then tending to melt back to a transparent liquid at 178.5 °C, which were associated with 'birefringence' and vivid iridescent colour changes. Reinitzer explored the remarkable phenomenon of two unique melting points that were also totally reversible with German scientist Otto Lehmann at Aachen University. Otto Lehmann (1855–1922) [15] was one of the pioneers who coupled a Polarizing Optical Microscope (POM) with a heated stage to demonstrate the unique phenomena of two melting points. Nowadays, the hot stage and polarized optical microscope are considered basic equipment in liquid crystal research. Lehmann also proposed the term "*liquid crystals*," which has since been utilized to refer to these compounds. It is worth noting that researchers as early as the 1850s experimented with liquid crystals but did not publish their findings [16–19].

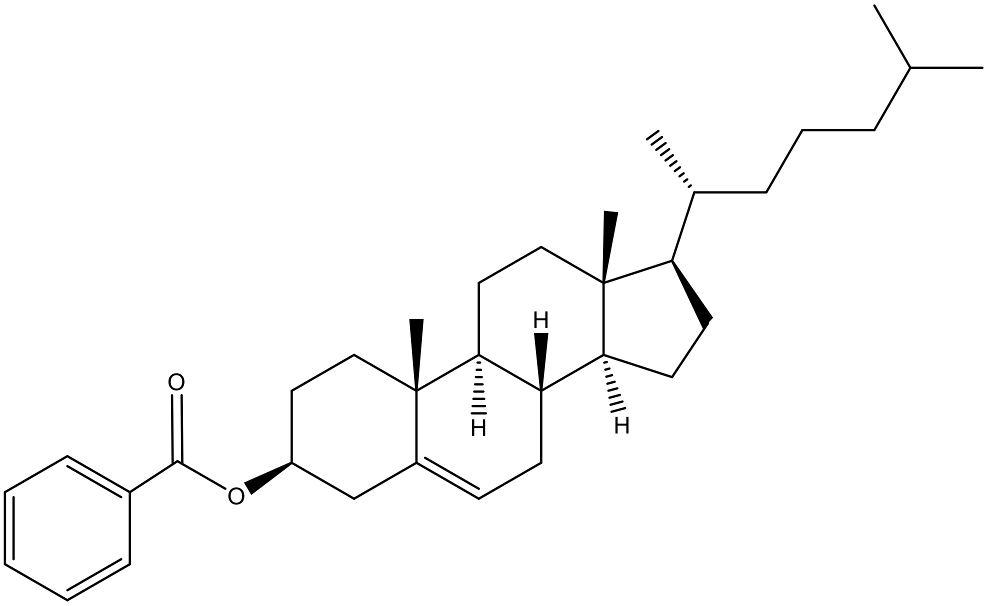
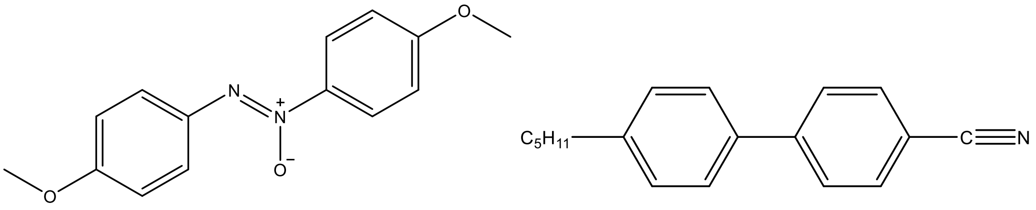


Figure 1.2: Structure of cholesteryl benzoate

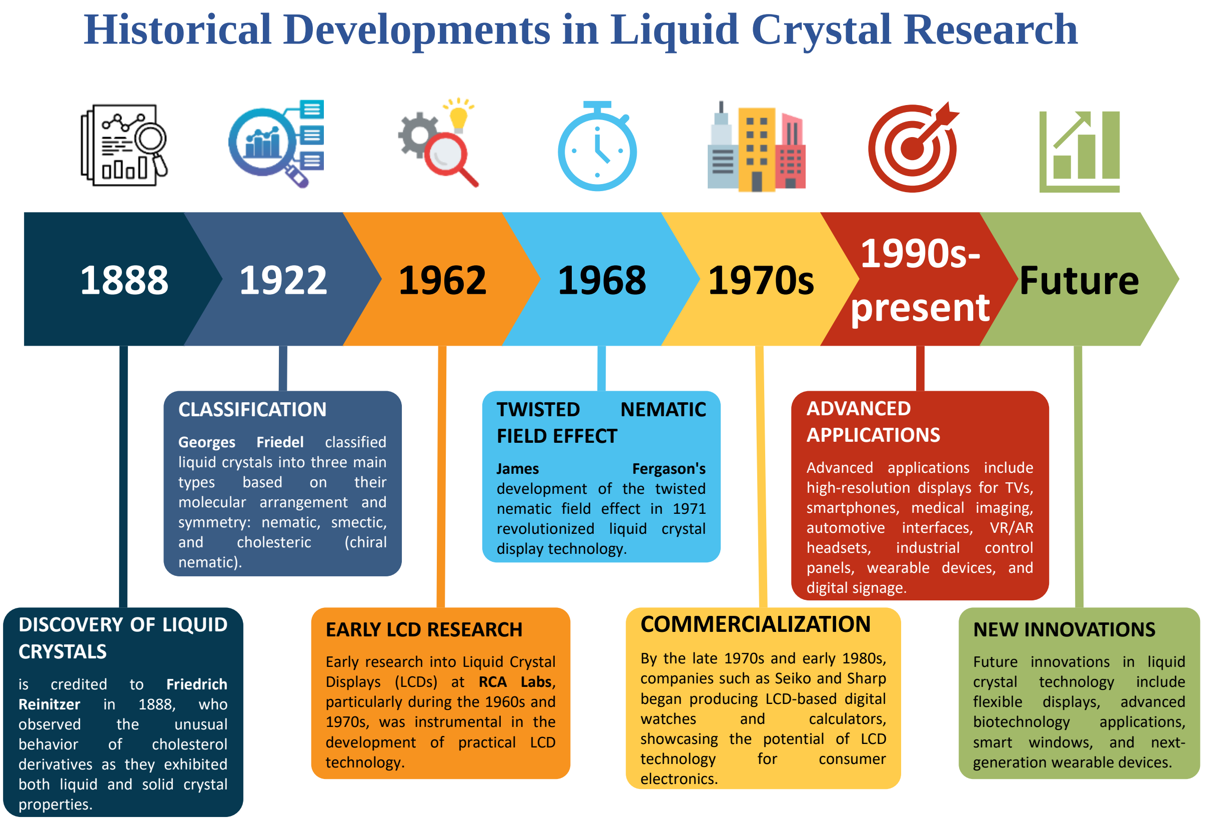
Beyond the natural compounds like cholesteryl esters Lehmann started studying some purely synthetic materials, synthesised by different scientists, namely azoxy ethers **(Figure 1.3 (a))**, p-methoxy cinnamic acids, ethyl p-azoxy benzoates, etc. [20,21]. Chemists made the most significant advancements in the first half of the twentieth century, developing new types of liquid crystal molecules. In the early twentieth century, Daniel Vorlander, a chemistry professor at the University of Halle, began systematic synthetic effort to discover the structure mesophase relationship, and by 1935, he had synthesized over 1100 liquid crystalline compounds in his lab alone [22]. Georges Friedel was the first to give the nomenclature of LC [23].



(a) (b)

Figure 1.3: Structure of **(a)** para-azoxy anisole and **(b)** 4-pentyl-4’-cyanobiphenyl

The period 1925-1960 considered as second phase for LC development witnessed lower progress. Major developments which contributed during this period includes; the impact of external fields on liquid crystals, the orienting influences of surfaces, measurements of the anisotropic physical properties, the array of new liquid crystal materials and structure/property relationships, the progress of theories of the liquid crystal state ranging from the swarm theory to the emerging continuum theory, increased awareness of the value of polarizing optical microscopy for the identification of mesophases, the determination of transition temperatures, and gaining greater knowledge of defect textures [24].



Historical Developments in Liquid Crystal Research

1888 | 1922 | 1962 | 1968 | 1970s | 1990s-present | Future

DISCOVERY OF LIQUID CRYSTALS
is credited to **Friedrich Reinitzer** in 1888, who observed the unusual behavior of cholesterol derivatives as they exhibited both liquid and solid crystal properties.

CLASSIFICATION
Georges Friedel classified liquid crystals into three main types based on their molecular arrangement and symmetry: nematic, smectic, and cholesteric (chiral nematic).

EARLY LCD RESEARCH
Early research into Liquid Crystal Displays (LCDs) at **RCA Labs**, particularly during the 1960s and 1970s, was instrumental in the development of practical LCD technology.

TWISTED NEMATIC FIELD EFFECT
James Fergason's development of the twisted nematic field effect in 1971 revolutionized liquid crystal display technology.

COMMERCIALIZATION
By the late 1970s and early 1980s, companies such as Seiko and Sharp began producing LCD-based digital watches and calculators, showcasing the potential of LCD technology for consumer electronics.

ADVANCED APPLICATIONS
Advanced applications include high-resolution displays for TVs, smartphones, medical imaging, automotive interfaces, VR/AR headsets, industrial control panels, wearable devices, and digital signage.

NEW INNOVATIONS
Future innovations in liquid crystal technology include flexible displays, advanced biotechnology applications, smart windows, and next-generation wearable devices.

Figure 1.4: Timeline depicting historical developments in liquid crystal research

The 1960 to present time is the period where there has been rapid expansion in this field. During the first ten years, significant advancements in liquid crystals, such as the mean field theory proposed by Maier and Saupe, promoted research [25,26]. The knowledge of liquid crystal phases was enhanced by the contributions of de Vries and Diele via their advancements in novel materials and X-ray research [27,28]. The International Liquid Crystal Conferences (ILCCs), which were started by Glenn Brown in 1965, cultivated a dynamic scientific community. The research conducted by Heilmeier et. al., [29] at RCA in 1968 was an important event that ultimately resulted in the successful implementation of liquid crystal displays in the 1980s. The discovery of cyanobiphenyls facilitated the development of superior liquid crystal displays, leading to a significant transformation in the industry **(Figure 1.3 (b))** [30]. The display options were further expanded by the introduction of ferroelectric and in-plane-switching technologies. Additionally, the synthesis of disc-shaped molecules by S. Chandrashekar et.al. in 1977 [31] and the subsequent synthesis of cone or bowl-shaped molecules (predicted by Lui Lam in China in 1982 and synthesized in Europe in 1985) [32] led to the discovery of new liquid crystal phases.

These results prompted a significant increase in interest in the field of liquid crystal research, which persists up to the present day. By 1992, the quantity of liquid crystalline minerals had expanded to over 50,000. Over one hundred thousand liquid crystalline compounds have been found in the existing literature.

1.3. Classification of Liquid Crystals

Figure 1.5 illustrates the classification of LC, which can be categorized in several ways. Primarily, liquid crystal mesophases are achieved either by adding a solvent (lyotropic) or by changing the temperature (thermotropic). Based on the molar mass of their constituent molecules, these materials are classified into lower molar mass (such as monomeric and oligomeric) and higher molar mass (polymeric) liquid crystals. Additionally, classification depends on the nature of the constituent molecules (organic, inorganic, and organometallic), their geometric profile (calamitic, discotic, bent core, etc.), and the molecular prearrangement within the liquid crystal mesophase (nematic, cholesteric, smectic, frustrated phases, columnar mesophases, blue phases, etc.).

Liquid crystalline compounds are commonly classified into 2 main categories:

(a) Thermo-tropic liquid crystal, where the occurrence of mesophase is influenced by temperature, and

(b) Lyo-tropic liquid crystal, where the occurrence of mesophase is influenced by the solvent and its concentration.

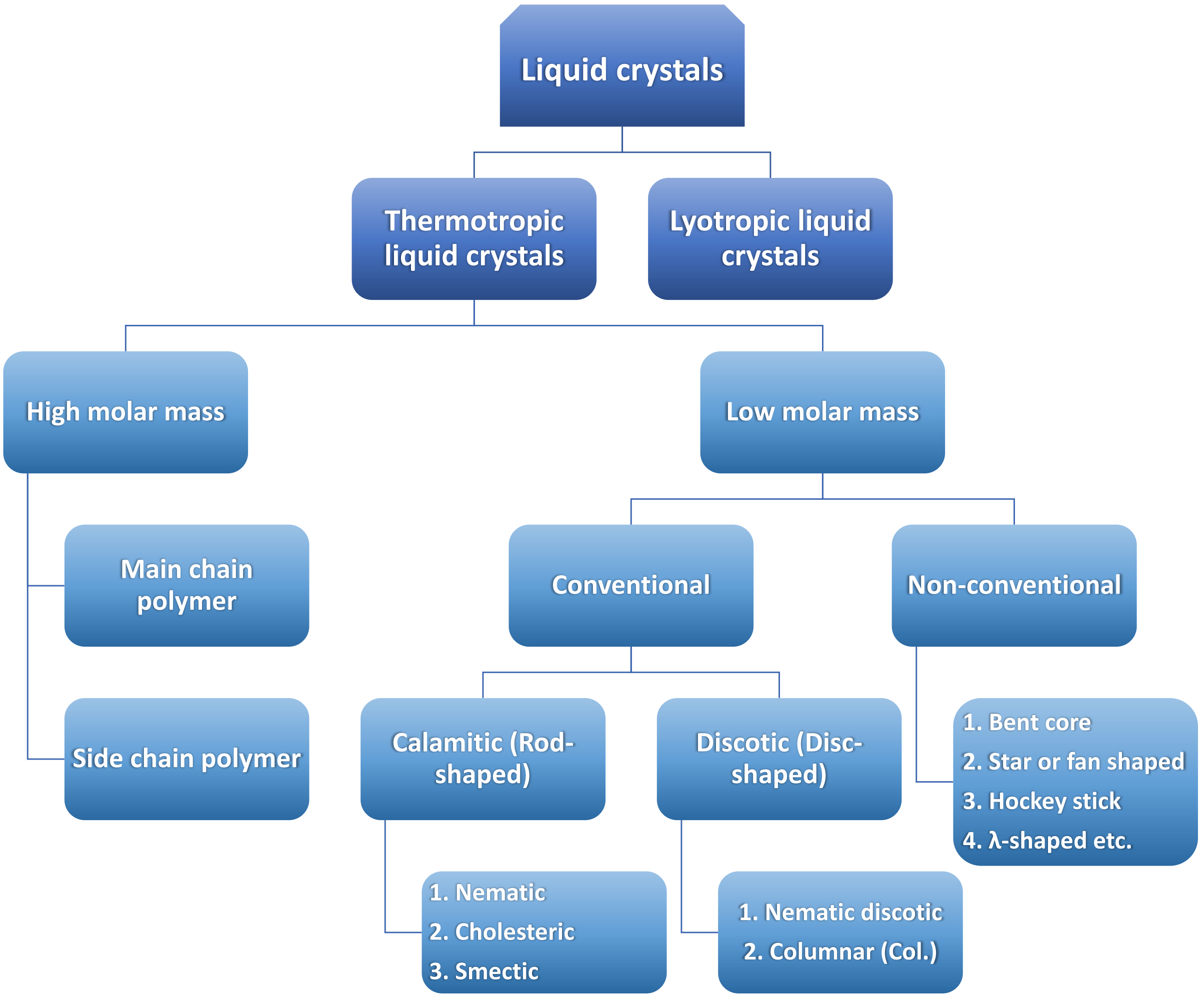


Figure 1.5: Classification of LC Compounds

An ampho-tropic LC is a substance that exhibits both thermo-tropic as well as lyo-tropic LC phases [33]. Considering the focus of this thesis on thermo-tropic liquid crystalline materials, a concise overview of lyo-tropic LC is provided below owing to their overall biological importance in addition to their significant function in biological systems [34].

1.3.1. Lyotropic liquid crystal

Lyotropic LC are a specific kind of liquid crystals that arise when amphiphiles (such as surfactants) and solvents, such as detergents and water, are combined. These entities possess the ability to modify their attributes in response to changes in temperature and concentration. Amphiphilic compounds possess two different components: a hydro-philic "head" and a hydro-phobic "tail". Illustrations of these types of molecules include soaps (depicted in **Figure 1.6**

(a)) and different phospholipids, such as those found in cell membranes (shown in **Figure 1.6 (b)**)[35].

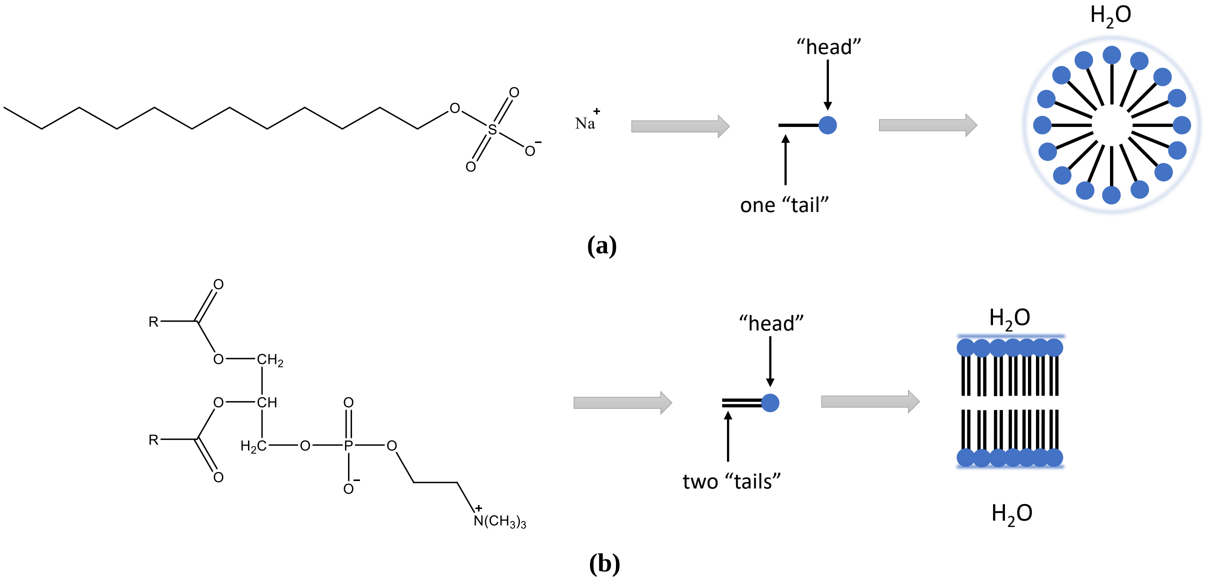


Figure 1.6: (a) Illustration of sodium dodecylsulfate (soap) forming micelles and **(b)** illustration of phospholipids forming bilayer lyotropic LC as present in cell membranes

Lyotropic liquid crystals exhibit a diverse range of phases based on their concentration, unlike thermotropic liquid crystals. The four main types of phases are hexagonal, lamellar, reversed hexagonal and cubic. These lyotropic liquid crystals need certain conditions of concentration, temperature, and pressure in order to form. Lyotropic liquid crystals encompass common mixes such as soap and water. They possess many uses, including their use in display materials, information storage materials, optical couplers, optical waveguides and also drug delivery and biomedical applications [36–40].

1.3.2. Thermotropic Liquid Crystals

Upon heating, the majority of crystals undergo a direct transformation into the liquid phase, resulting in the simultaneous disruption of the long-range positional and orientational order of the molecules. Nevertheless, if the individual molecules possess pronounced anisotropy of shape, the loss of the extended translational pattern in the crystal may occur before the decline of the extended orientational order in one, two, or three dimensions. These compounds undergo multiple transitions, instead of a single one, as they transform from a solid to liquid (isotropic) state. These transitions involve liquid crystal (LC) phases that have mechanical and symmetry properties that are in between those of a liquid and a crystal. The transition from a crystalline state to a mesophase is referred to as the phase transition temperature, whereas the transition from the mesophase to the isotropic liquid state is known as the clearing point.

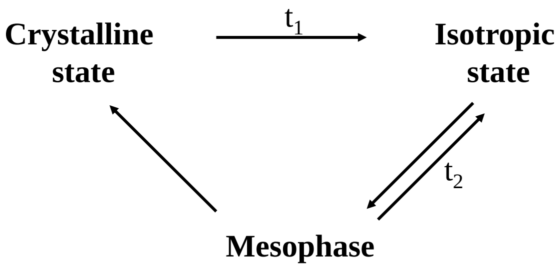
Nevertheless, several compounds exhibit liquid crystalline properties at room temperature. Only the clearing point is seen for molecules of this kind. Certain compounds exhibit many types of crystal or liquid crystal structures. These systems exhibit Cr-to-Cr, Cr-to-phase, and/or phase-to-phase shifts, which are determined by different interactions.

Enantiotropic Liquid Crystals

The word "enantiotropic" is used to describe phases that are thermodynamically stable and may be detected both during heating and cooling. The transitions t_1 and t_2 occur at distinct and well-defined temperatures and are completely reversible. The diagram illustrates the enantiotropic mesophase.

Monotropic Liquid Crystals

Monotropic liquid crystals are a type of thermotropic liquid crystals that can transition into the liquid crystal state from either an increase in the temperature of a solid or a decrease in the temperature of a liquid, but not both. The graphic illustration aimed at monotropic mesophase is shown below:



Polymorphism

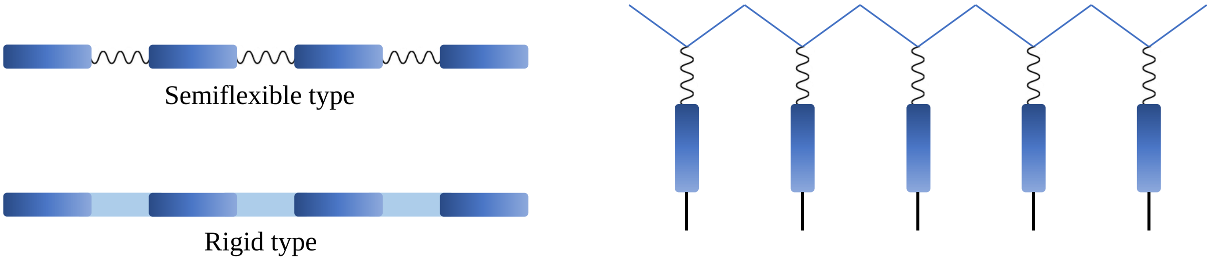
Polymorphism in liquid crystals relates to the ability of some LC compounds to exist in numerous separate stable liquid crystalline phases, each distinguished by a distinctive molecular arrangement. These distinct stages can display differences in molecular arrangement, orientation, and symmetry. We can infer, as a rough guideline, the following possible phase sequence upon cooling from the isotropic melt in achiral molecules (while ignoring different chiral phases) [41]:

Iso—N—SmA—SmC—SmB—SmM—SmI—SmF—Crystal B—J—G—E—K—H—Cr

and Iso—BP—N*— TGB—SmA— SmC*— SmI*—SmF* for chiral LCs.

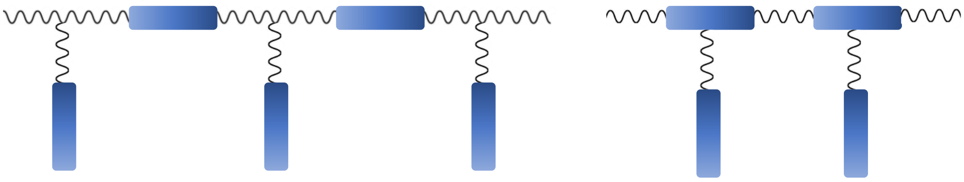
It is evident that no one compound displays all of the mentioned phases. However, studies on various materials have indicated that their individual phase sequences generally align with this hypothetical sequence, excluding any phases that are absent. In some substances, it has been discovered that upon cooling below a thermodynamically stable phase with lower symmetry, a rare occurrence takes place when a high temperature phase with higher symmetry reappears. The occurrence of this behaviour is referred to as "re-entrant" and was initially observed by Cladis in a cyano compound exhibiting the phase sequence Iso-N-SmA-N_{re}-Cr [42]. Subsequently, several further studies were published in the upcoming years, involving many other mesophases [43]. Some mentioned causes discussed for this phenomenon includes frustration of molecular structure, complex steric factors, confirmational changes and competing interests [44].

1.3.2.1. High-molar mass



(a) Main chain LC polymers

(b) Side chain LC polymers



(c) Combined main-chin/side chain LC polymers

Figure 1.7: Different types of LCPs

a) Main chain polymer

Main chain liquid crystal polymers (LCPs) are a type of polymers that have liquid crystal components incorporated into its main polymer framework. These liquid crystal units are commonly found among the polymer chain's repeating units [45,46] **(Figure 1.7 (a))**.

b) Side chain polymer

Side chain liquid crystal polymers (SCLCPs) belong to a distinct category of polymers whose liquid crystal components are integrated as pendant or side chains along the primary polymer backbone [47,48] **(Figure 1.7 (b))**.

Also, hybrid main-chain/side-chain LCPs **(Figure 1.7 (c))** have been studied extensively [49,50].

1.3.2.2. Low molar mass

Low molar mass liquid crystals are liquid crystal materials consisting of small molecules with relatively low molecular mass. Classification of liquid crystals based on their structural shapes is given below.

1.3.2.2.1. Conventional

Conventional liquid crystals are a class of materials with linear or rod-like molecular structures that exhibit well-established phases, such as the nematic, smectic, and cholesteric phases. They can be classified as follows:

a) Calamitic

Calamitic liquid crystals, sometimes referred to as rod-shaped, belong to a category of liquid crystal molecules that display an elongated, rod-like molecular configuration. Typically, these molecules are composed of a rigid, elongated core or mesogenic unit, accompanied by flexible side chains or substituents. A general representative structure for calamitic LC is given below **(Figure 1.8)** where length of the molecules is much higher than the breadth of the molecule (i.e. $l >> b$).

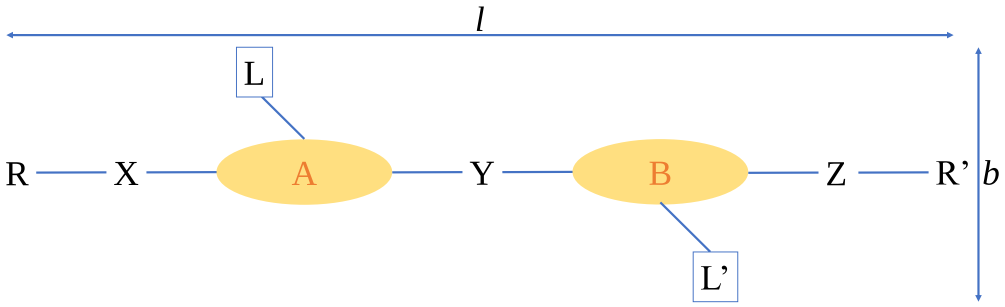
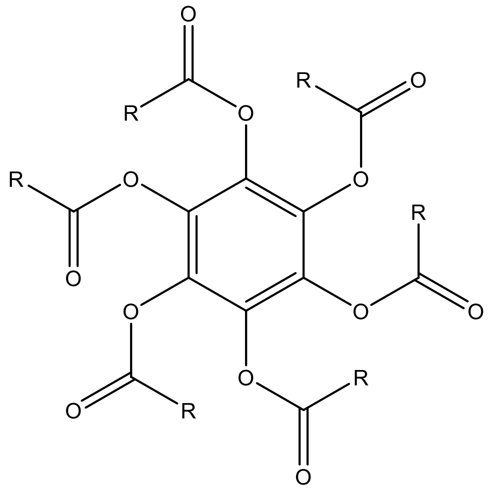


Figure 1.8: General representation of calamitic LCs

Where; A and B = core units (p-benzene, p-biphenyl, cyclohexane, heterocyclic rings, etc.), X, Y, Z = linking units (-CH=N-, -CO-CH=CH-, -N=N-, -CONH-, -COO-, etc.), R & R' = flexible chains (alkyl or alkoxy chain, -CN, $-CF_3$, etc.) and L & L' = lateral substitution ($-OCH_3$, $-OC_2H_5$, $-NO_2$, -F, etc.).

b) Discotic

Discotic liquid crystals are a kind of liquid crystal molecules that have a molecular structure resembling to a disc [51,52].



R = n-C_4H_9 and n-C_9H_{19}

Figure 1.9: First discotic LC synthesised by S. Chandrasekhar et.al.

S. Chandrasekhar et.al. first documented the discovery of mesomorphism in discotic materials in 1977 [31]. Calamitic liquid crystals differ from discotic liquid crystals in terms of their structural composition. While calamitic liquid crystals have rod-like structures, discotic liquid crystals have a flat, discoidal shape **(Figure 1.9)**. They are characterised by a central aromatic or conjugated core and typically include flexible periphery substituents. These molecules have distinctive liquid crystalline properties, generating organised phases that are different from those seen in calamitic liquid crystals.

c) Bent-core

Bent-core liquid crystals, in contrast to rod-like (calamitic) or disc-like (discotic) liquid crystals, distinguished by their distinctive bent or banana-shaped molecular structure possess a curved form that imparts curvature to the molecular structure. These types of LCs were first reported by Niori et al. [53] when they synthesized 1,3-phenylene derivative and studied its ferroelectric properties. These thermotropic liquid crystals offer new smectic-like phases named "B" phases, numbered from B_1 to B_8 based on their discovery date. Typically, LC compounds with a banana shape conform to the structural formula depicted in **Figure 1.10**. Many bent core LC with variety of bending cores have been reported [54,55].

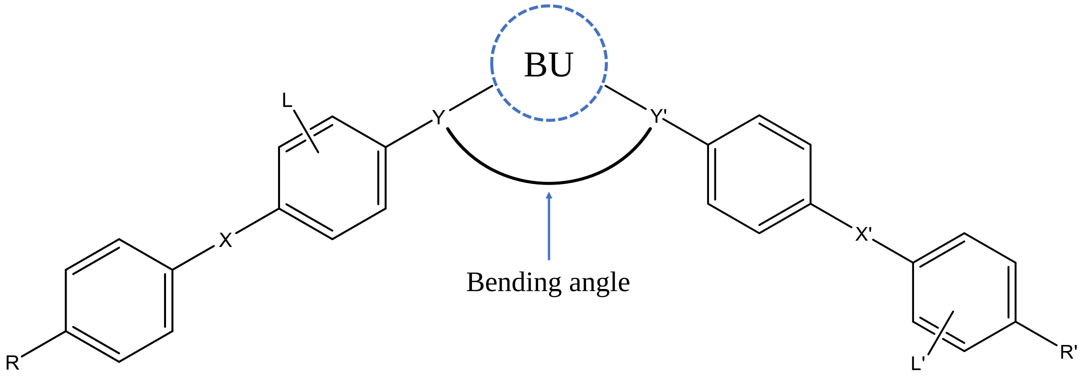


Figure 1.10: General representative structure of bent-core LC

Where, BU = bent units (2,5-disubstituted thiadiazole/oxadiazole, 1,3- disubstituted benzene, etc.), X & Y = linking units, R & R' = terminal chains and L & L'= lateral substitutions.

1.3.2.2.2. Non-conventional

Non-conventional LCs, on the other hand, constitute a larger and more diversified class of materials having molecular architectures that are different from the normal calamitic LC. This category contains many types of liquid crystals such as star shape, hockey stick shape etc. which are discussed below.

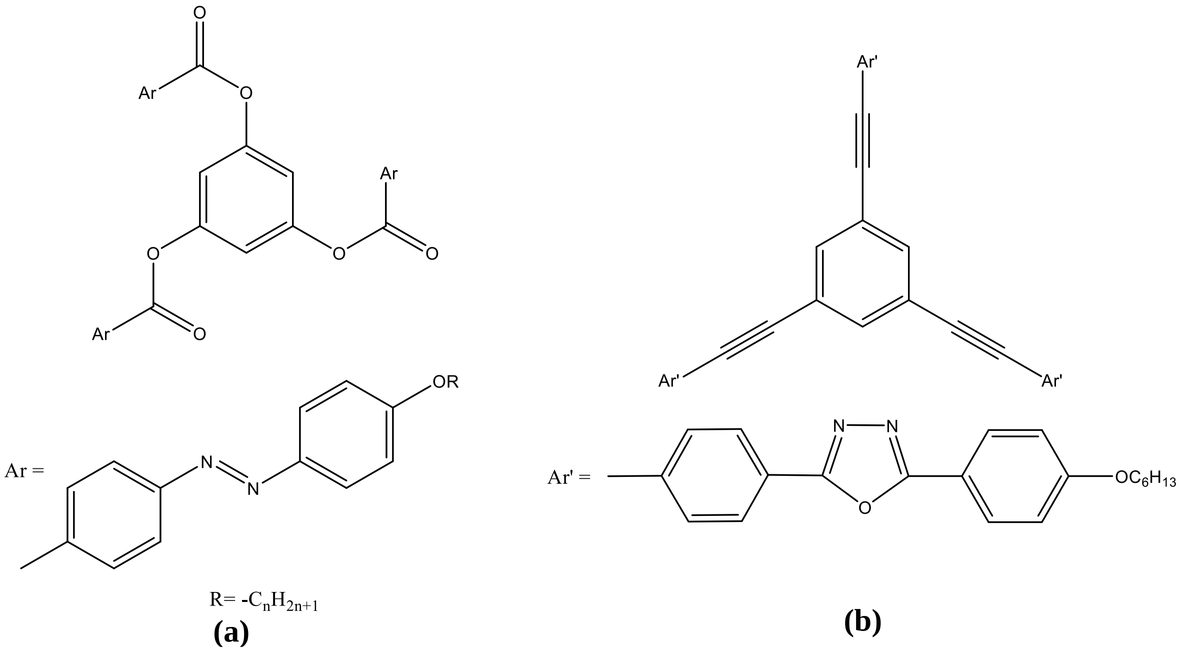


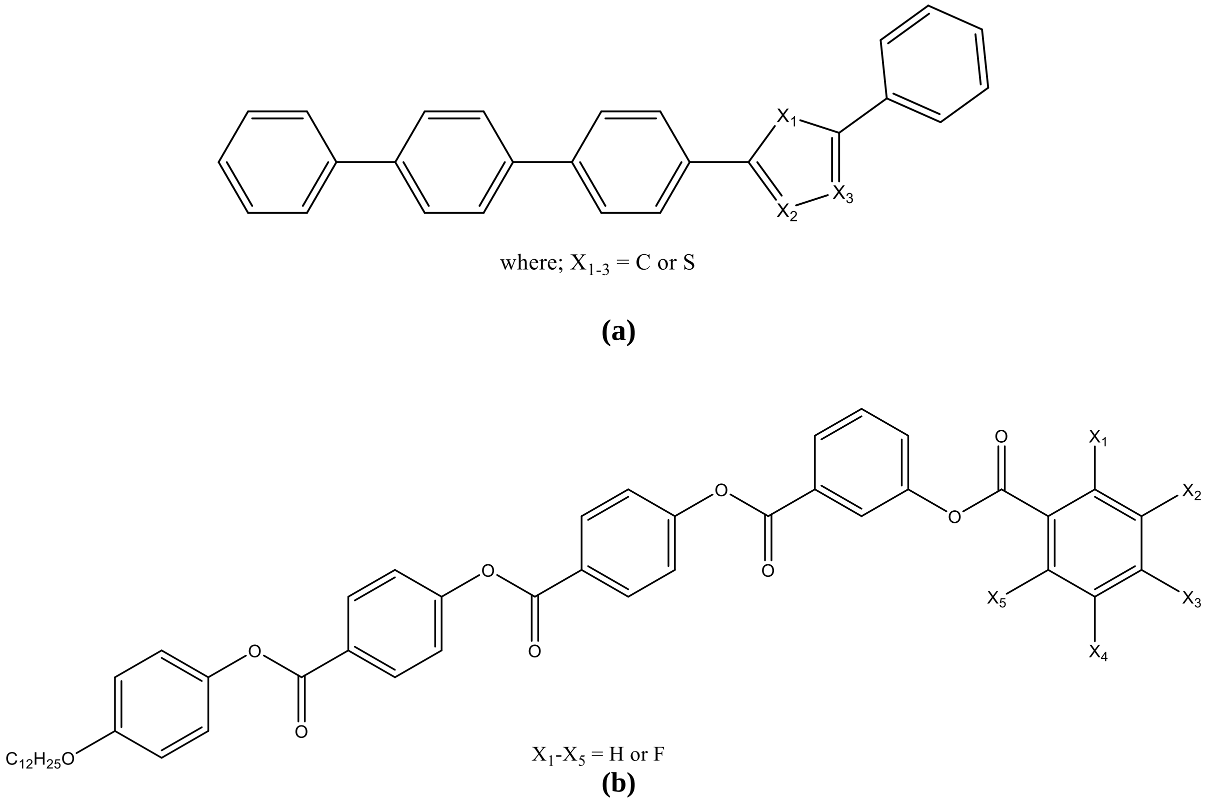
Figure 1.11: Illustrative examples of some reported star shaped LCs

a) Star shaped

Star-shaped liquid crystals, also called dendritic or starburst liquid crystals, are a distinct category of liquid crystal molecules characterised by a central core from which many flexible arms or branches emerge radially, mimicking the form of a star. The presence of mesogenic units in these arms frequently contributes to the molecule's LC nature. Many star-shaped LCs have been reported so far [56–58] **(Figure 1.11)**.

b) Hockey sticks shaped

"Hockey stick-shaped liquid crystals" is a term used to describe a class of liquid crystal molecules with a molecular structure that resembles the shape of a hockey stick. These molecules typically consist of a rod-like or calamitic core with a flexible tail or side chain, giving them a shape reminiscent of a hockey stick. Extensive study has been reported for these types of LCs in the literature [59–61] **(Figure 1.12)**.



where; $X_{1\text{-}3}$ = C or S

(a)

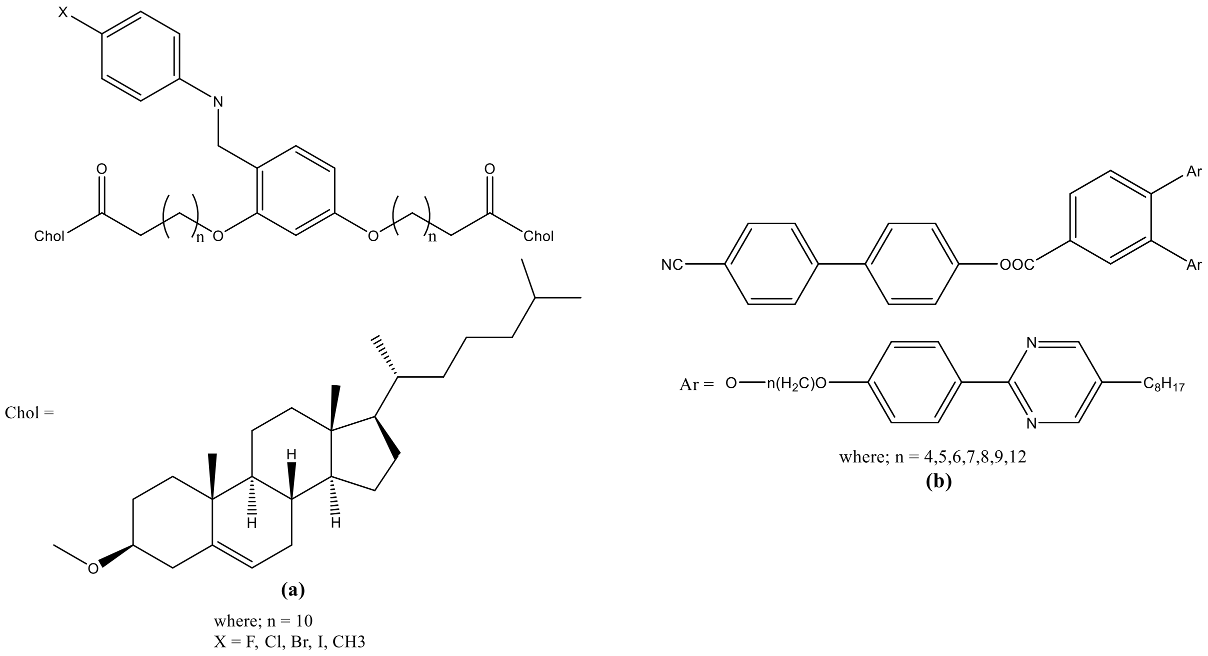
X_1-X_5 = H or F

(b)

Figure 1.12: Illustrative examples of hockey stick shaped LCs from literature

c) λ-shaped

This LC presumably refers to a liquid crystal molecule with a structure like the Greek letter lambda (λ). The word can refer to a specific arrangement of functional groups or mesogenic units that resemble the letter λ. Some examples reported are given below [62–64] **(Figure 1.13)**.



(a)

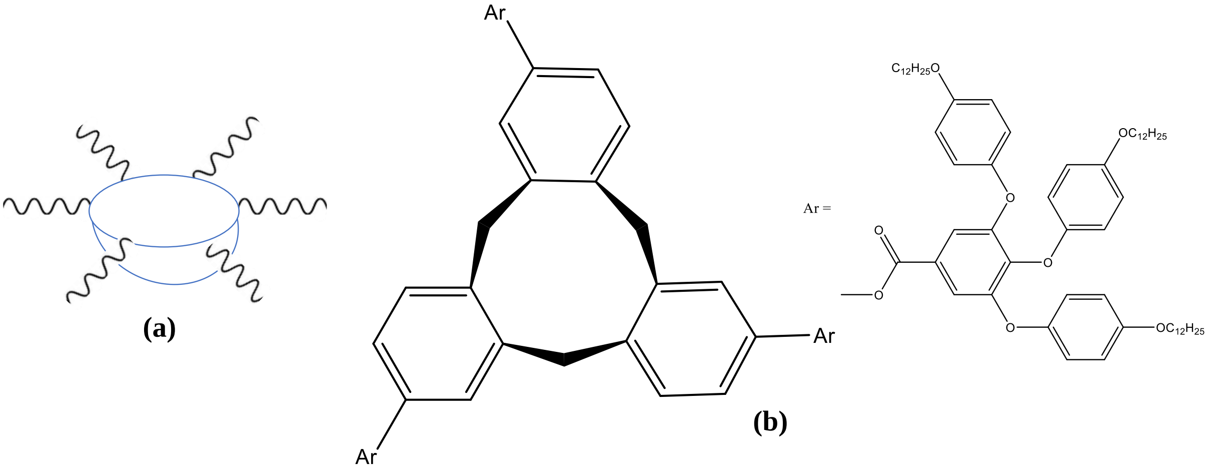
where; n = 10
X = F, Cl, Br, I, CH3

where; n = 4,5,6,7,8,9,12
(b)

Figure 1.13: Some examples of λ-shaped LC

d) Bowl shaped

"Bowl-shaped liquid crystals" are a group of liquid crystal molecules that have a three-dimensional, concave, or bowl-like molecular structure. Typically, these molecules have a central core that is curved or bowl-shaped. Some reported illustrations foe this type of LC is [65–67] with general structure are given in **Figure 1.14**.



(a)

(b)

Figure 1.14: (a) Representative image and **(b)** Example of bowl-shaped LC

e) Other non-conventional LCs

Additional non-conventional liquid crystals (LCs) encompass cones, shuttlecocks, dendrimers, dendrons, supramolecular mesogens (e.g., metallomesogens and hydrogen-bonded mesogens), rod-dendrons, and rings, which have attracted greater attention [68–70].

1.4. Classification of liquid crystalline phase

A diverse range of liquid crystal (LC) phases have been discovered, which may be attributed to factors such as the chemical structure, shape of the component molecules and external conditions like temperature and pressure. This section focuses on the discussion of different types of mesomorphism displayed.

1.4.1. Nematic phase (N)

The most basic kind of liquid crystal phase is known as the nematic phase, which occurs just below the isotropic phase and has a viscosity similar to that of isotropic liquids. It exhibits a long-range orientational order and short-range positional disorder [71]. Within this phase, the individual molecules exhibit a significant degree of arrangement in a shared direction, known as the director axis (n), while still displaying characteristics similar to that of a fluid. The N phase displays schlieren, droplets, marble and pseudo-isotropic textures, which vary depending on the surface conditions. **Figure 1.15** depicts the molecular arrangement in the nematic phase. Despite the fact that the molecules' preferred orientation differs at different points in the medium, a uniformly aligned sample exhibits optical uniaxiality (N_u) and birefringence [13]. However, biaxial nematic phases (N_b) having additional degrees of freedom, with molecules oriented along two orthogonal axes is also known.

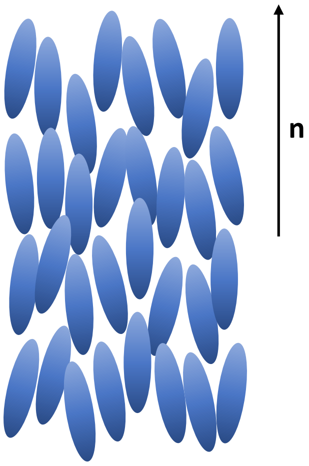


Figure 1.15: Diagram illustrating the molecular arrangement in the N phase

1.4.2. Chiral nematic or Cholesteric phase (N*)

Cholesteric LC is similar to nematic LC and so it is also known as chiral nematic liquid crystal denoted by N* [72]. The main difference of N* is its helical superstructure. The molecules in the chiral nematic phase exhibit a helical arrangement along the director axis, as opposed to the uniaxial alignment seen in typical nematic phases. The formation of this helical structure is a result of the existence of chiral molecules, which are molecules that have asymmetry, within the liquid crystal molecule. Addition of nematic LC with optically active compounds can also yield N* LC. Within these systems, there exists a subtle inclination for adjacent molecules to orient themselves at a tiny angle relative to one other. The local director forms a helix with a pitch beyond the size of a single molecule in space.

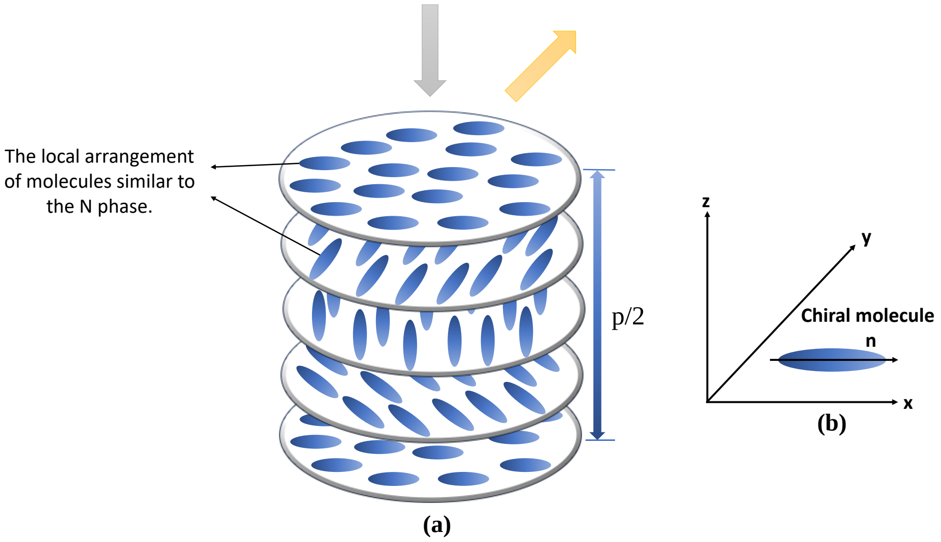


Figure 1.16: (a) Helical super structure of the chiral nematic mesophase, **(b)** director lies in xy coordinates and rotates in plane that defines its structure.

The N* phase structure is shown in **Figure 1.16**. This helical configuration is responsible for the phase's distinctive optical features, including selective reflection [73]. N* phase displays focal-conic, oily streaks, droplets, fingerprint textures depending on surface conditions.

1.4.3. Smectic phase

In smectic mesophase, molecules constituting LC are grouped in layers, where each layer is composed of molecules arranged in a 2-D lattice structure. The molecules in each layer display positional order, indicating that they are usually fixed in their position within the layer yet still retain some level of mobility [74]. Smectic mesophases are categorized into distinct categories based on the molecular arrangement inside the layer and the degree of inter-layer connections. The smectic phases have been assigned code letters A, B, C, etc., based on the sequence in which they were discovered. The several smectic LC phases identified so far are SmA, SmB, SmC, SmF and SmI. Also, chiral variants of these phases are known which are formed when the molecules consist chiral elements. These phases include chiral SmA, SmC*, SmI*, and SmF*. The SmA and SmC phases, together with their chiral variations, are the most often encountered and intensively studied phases, as discussed below.

<u>Smectic A (SmA) and chiral SmA phases</u>: In Smectic A mesophase, LC molecule remain layered parallel to one other. In contrast to the disorganized isotropic liquid phase, molecules in each layer are relatively fixed. There is no long-range spatial order between layers, therefore the substance flows like a liquid.

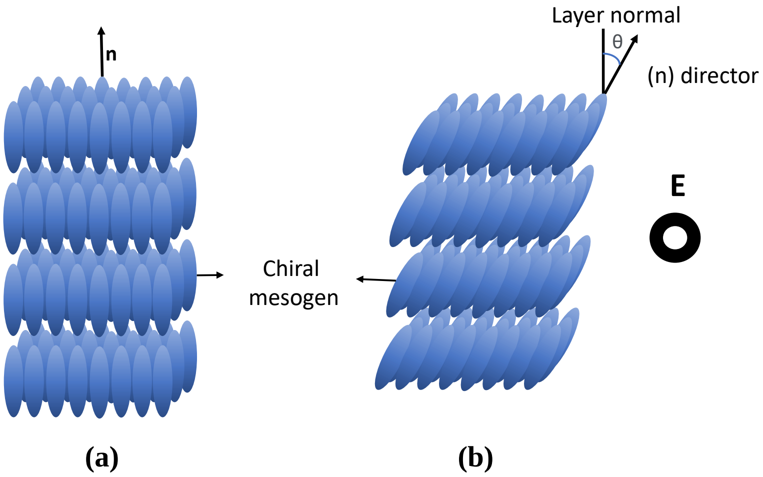


Figure 1.17: Diagram illustrating the formation of the SmA phase by chiral rod-like anisometric molecules: **(a)** orthogonal layered geometry; **(b)** tilted layered geometry

Similar to biaxial nematic phase, SmA phase can also have biaxial symmetry, known as biaxial smectic A (SmA_b) phase [75]. Despite being chemically identical to achiral SmA, the chiral smectic A phase found with optically active molecules has decreased symmetry from $D_{\infty h}$ to D_{∞} due to molecular chirality. When an electric field is applied orthogonally to the layer normal direction in the SmA phase **(Figure 1.17(a))**, it causes the long molecular axes of the molecules to tilt with respect to the layered plane **(Figure 1.17(b))**. Tilt angle varies linearly with field at low applied fields. Both SmA and chiral SmA phases show focal-conic textures in planar oriented slides and a black field of vision in homeotropic oriented slides.

<u>Smectic C (SmC) and chiral smectic C (SmC*) phases</u>: The SmC phase varies from the SmA phase by having a layer director inclined at an angle to the layer normal and the same angle for all layers **(Figure 1.18(a))** [76]. Unlike the SmA phase, the SmC phase is optically biaxial. In this phase, the tilt angle varies with temperature and often increases steadily with decreasing temperature. In this phase, the symmetry components align with the point group C_{2h}. The chiral smectic C (SmC*) phase, generated by optically active molecules, features a helical arrangement of molecules. The helix is formed by a progressive shift in molecule tilt direction (n) from layer to layer, perpendicular to layer planes **(Figure 1.18(b))**. The SmC* phase exhibits reduced C_2 symmetry owing to chiral compounds.

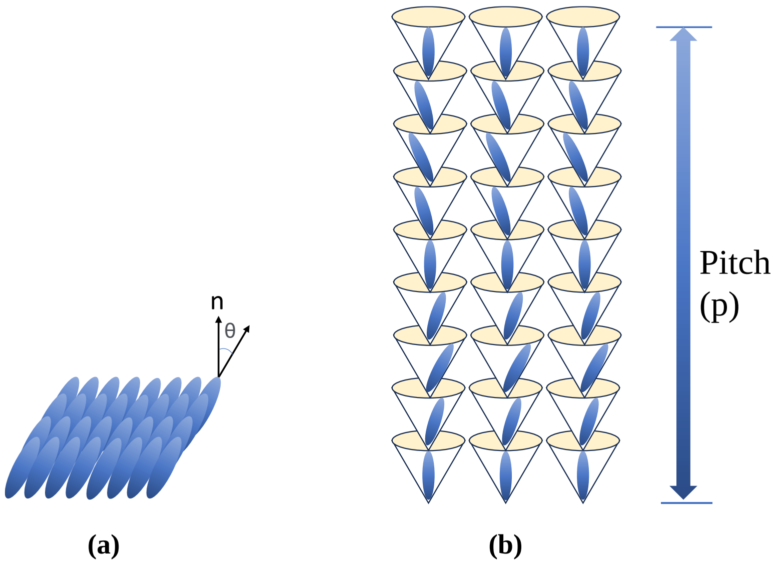


Figure 1.18: (a) Structure of the SmC phase; **(b)** SmC* phase with helical macroscopic structure, where the successive layers rotate around the normal axis of the layer.

1.4.4. Discotic liquid crystalline phases

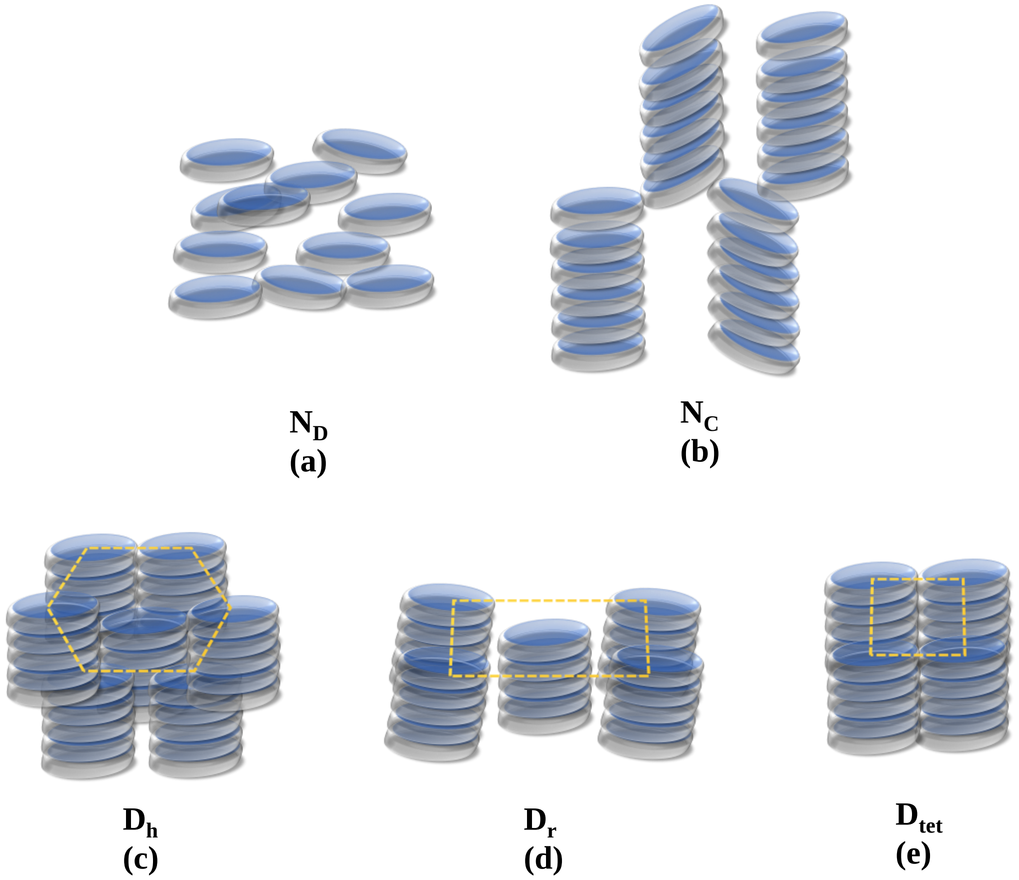


Figure 1.19: Schematic representation of discotic phases :**(a)** N_D, nematic discotic; **(b)** N_C, columnar nematic; **(c)** D_h, discotic hexagonal **(d)** D_r, discotic rectangular; **(e)** D_{tet}, discotic tetragonal

Liquid crystalline materials with disk-like molecular structure can form layers called discotic nematic phases. When discs form stacks, the phase generated is discotic columnar. Columns can be arranged in rectangular or hexagonal arrays. Chiral discotic phases, like chiral nematic phases, are also seen. Not all molecules are disc-shaped, although they can still produce discotic phases.

Using the word "discotic" for mesophases does not always mean the molecules are disc-like [51,77]. There are various types of discotic columnar mesophases, including hexagonal (Col_h), rectangular (Col_r), oblique (Col_{ob}), plastic (Col_p), helical (H), square (tetragonal), and lamellar (Col_L). In the discotic nematic phase (N_D), the arrangement of disc-like molecules resembles that of calamitic molecules (**Figure 1.19**).

In the N_C phase, the columnar superstructure behaves like rod-like molecules, similar to the nematic calamitic phase. Other times, columns create a periodic two-dimensional array when parallel. There are hexagonal, rectangular, and tetragonal columnar discotic phases, as well as orthogonal and tilted ones, comparable to calamitic mesophases.

The key findings from the aforementioned phases may be shown in **Figure 1.20**, which visually depicts the behaviour of a typical thermotropic calamitic liquid crystalline sample, regardless of the exact material being studied.

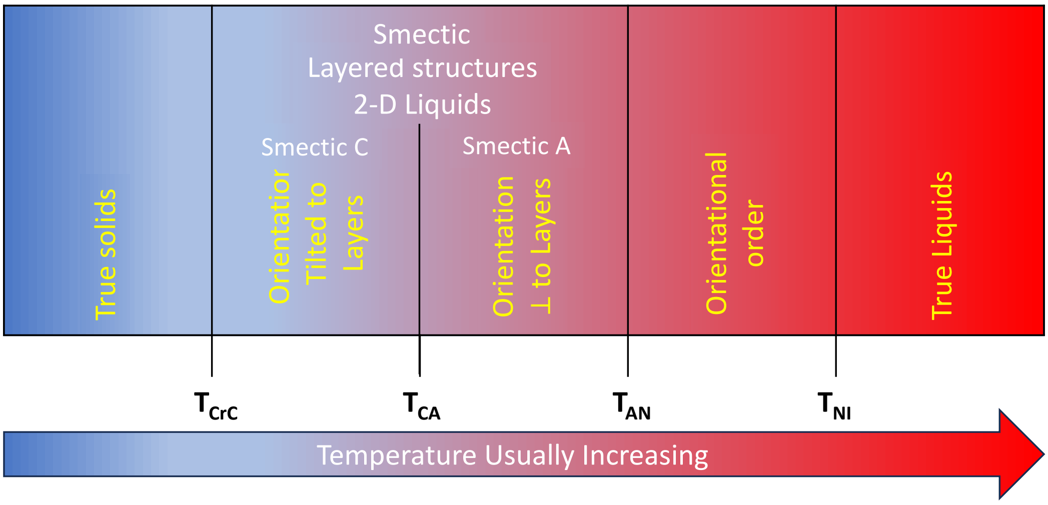


Figure 1.20: Summary of typical thermotropic LC phases.

1.4.5. Chirality induced phases / Frustrated phases

The presence of chirality in liquid crystal molecules results in an asymmetry that affects how they are arranged and how mesophases are formed. This alteration frequently results in the occurrence of frustrated phases, particularly the Blue Phase (BP) and Twist Grain Boundary

(TGB) phases [78,79]. The emergence of these phases is a result of the interaction between chirality, which encourages the formation of helical superstructures, and thermodynamics, which prefers low-temperature phases with increased organization and decreased symmetry. Consequently, frustrated phases, characterized by competing molecular arrangements, are stabilized. However, this competition restricts their existence to narrow temperature ranges. The structures of these phases are discussed below.

Twist grain boundary (TGB) phases: The TGB$_A$ phases often occur during the phase transition from the SmA or SmC* phase to the N* or isotropic phase [78–80]. Short pitch chiral LC may face a conflict between helical molecule packing and layered phase formation. To alleviate frustration, molecules form the twist grain boundary phase, consisting of smectic layer blocks twisted at a constant angle to create a helical shape with an axis perpendicular to the layer normal direction. To prevent continuous twisting, smectic layers are separated by screw dislocations, resulting in periodic grain boundaries and stacking, as well as helical twist. Smectic blocks of A, C, or C* can result in three forms of TGB phases: TGB$_A$, TGB$_C$, and TGB$_C$* [81]. The TGB$_C$* phase has a more intricate structure compared to the TGB$_A$ and TGBC phases. Empirically, it has been noted that this phase displays a consistent (square or hexagonal) grid pattern imposed on the flat structure. A schematic representation of the TGB$_A$ structure is depicted in **Figure 1.21**.

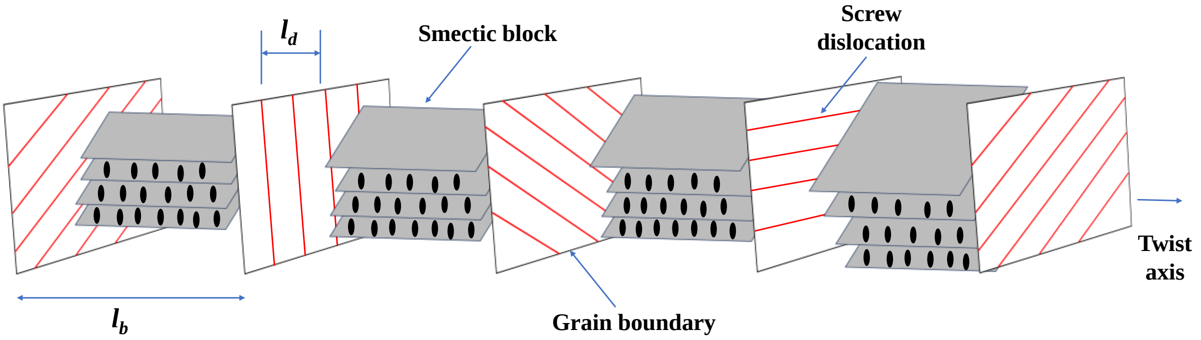


Figure 1.21: The TGB$_A$ phase structure is depicted schematically. The distances separating two dislocations and two grain boundaries are denoted as l_d and l_b, respectively.

Blue phase: Chiral nematic LCs, consisting of single component optically active rod-like mesogens or mixtures of achiral and optically active mesogens, exhibit distinct thermodynamic phases in a narrow temperature range between cholesteric and isotropic phases in short pitch (< 5000 Å) chiral nematic LCs [78,79]. These liquid crystal systems exhibit the Blue Phase (BP), a fascinating state of matter with a 3-D periodic pattern of helical structures. It is a chiral liquid crystal phase that appears bright blue under crossed polarizers, thus its name.

Reinitzer observed the blue phase first [14]. Three blue phases BPI, BPII, and BPIII occur in the same order with increasing temperature. These phases are called blue because their Bragg reflections at blue wavelengths indicate a partly periodic structure with several hundred nm lattice parameters. Today, blue phases reflect other visible colors too.

Bragg reflection investigations show that BPI has a body-centered cubic lattice, BPII a simple one, and BPIII likely amorphous [82]. BP directors have a twin cylinder radial twist. However, this double-twisted structure cannot stretch properly into three dimensions. **Figure 1.22(a)** & **(b)** illustrates the spaghetti model of BPIII, which has randomly arranged wriggling double twist cylinders. Geometrical models of cubic blue phases (BPI and BPII) include cubic networks of double twist cylinders divided by disclination lines **Figure 1.22(c)**. Thus, the BP are optically isotropic, meaning that they lack linear birefringence. The visual appearance of the cubic BP is quite distinctive, typically exhibiting a platelet-like texture. The distinguishing feature of amorphous BPIII is its opaque or hazy appearance.

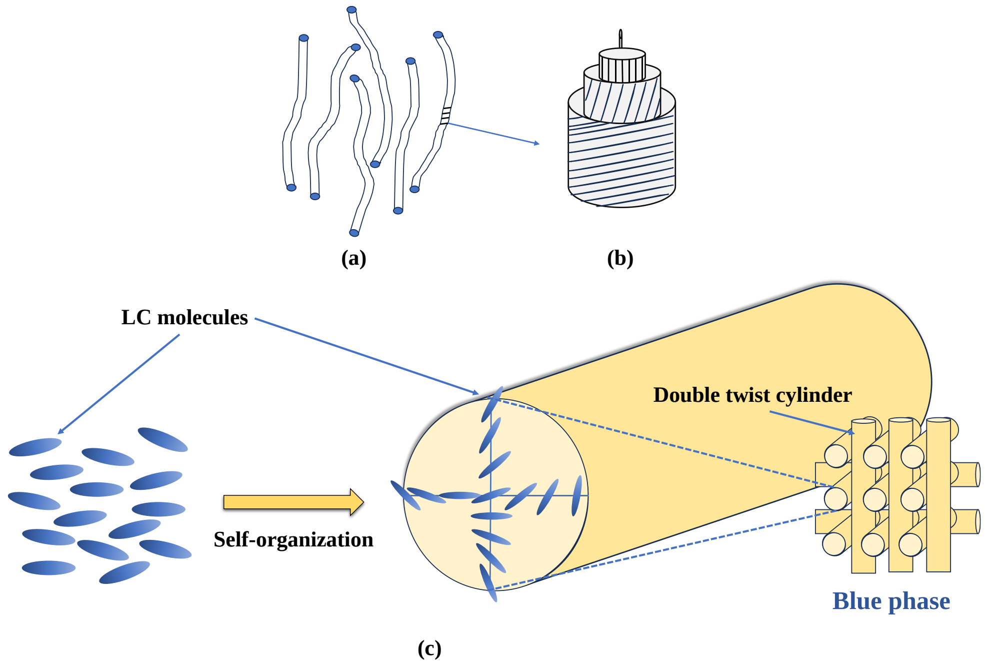


Figure 1.22: **(a)** Schematic representation of the theoretical spaghetti model of BPIII, **(b)** having randomly oriented squirming double twist tubes, **(c)** Geometrical models of cubic blue phases (BPI and BPII)

1.5. Identification of liquid crystals and liquid crystalline phases:

The characterization of liquid crystal phases may be accomplished by employing a number of diverse techniques, such as Polarized Optical Microscopy (POM), Differential

Scanning Calorimetry (DSC), and X-ray Diffraction (XRD). Each of these approaches offers distinct insights on the structural and thermal characteristics of liquid crystal phases.

1.5.1. Polarized Optical Microscopy (POM):

The characterisation approach relies on a mesophase's birefringence, which splits light rays into two directions according on their polarization throughout the liquid crystalline phase [83]. The standard method for studying liquid crystals using "crossed-polarizers" is depicted in **Figure 1.23**. The little sample is inserted between two microscope cover slips and placed on a controlled hot-stage with an optical path. The hot-stage is connected to the microscope's working stage. The mesophase birefringence method uses a first plane polarized light impinge on the sample and a second polarizer at 90° between the sample and objective. Light becomes elliptically polarized when two refracted rays interact in the mesophase, resulting in unique interference patterns. In contrast, when the material is isotropic, the sample looks black between cross polaroids due to only one refractive index. Textures, which indicate specific mesophases, are most evident during a cooling cycle. POM can identify different LC phases based on their characteristic textures. It is widely used to study phase transitions, defect structures and texture evolution in LC systems.

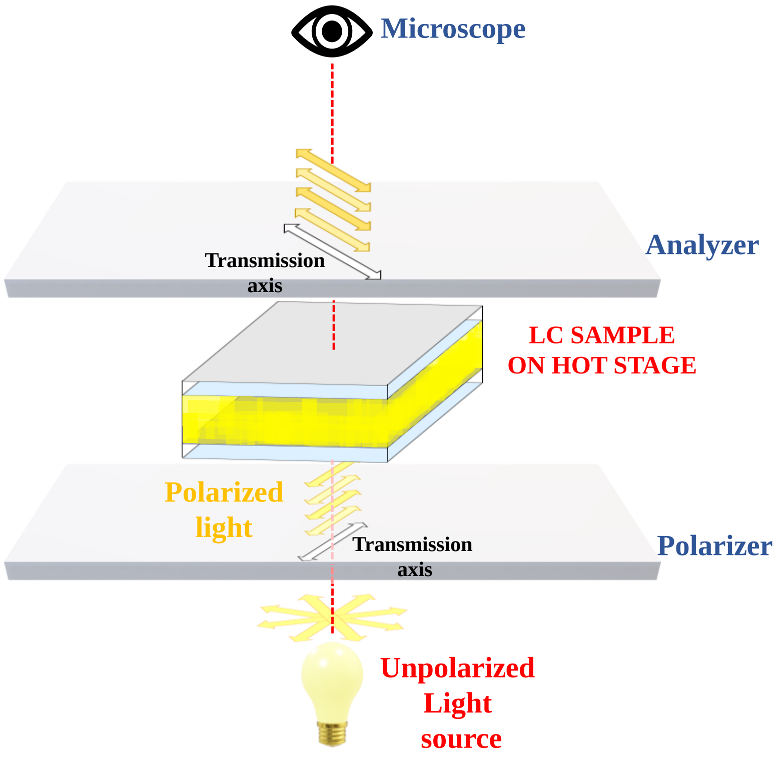


Figure 1.23: The standard method for studying liquid crystals using "crossed-polarizers"

1.5.2. Differential scanning calorimetry (DSC):

It quantifies the amount of heat released or absorbed during thermal changes in a sample, considering the temperature variations. The provided information encompasses phase transitions in LC, melting points, enthalpy changes and transition temperatures. DSC is capable of identifying phase transitions occurring between distinct liquid crystal phases, such as the transition from isotropic to nematic or from nematic to smectic [84]. This is achieved by observing alterations in heat capacity and enthalpy. The peaks observed in the DSC curve are indicative of phase transitions, and the magnitude of the peaks yields quantitative data on the enthalpy of the transition. It is employed to ascertain phase diagrams, investigate thermal stability, and evaluate the thermal properties of liquid crystal materials.

The DSC measurement complements optical microscopy, however not all changes in optical texture indicate a change in mesophase type. Additionally, not all changes in phase recorded in DSC thermograms result in a visible change in texture. DSC traces should be compared to optical examinations continuously to ensure a reliable result.

1.5.3. X-ray diffraction (XRD) analysis:

XRD is a highly effective method for examining the crystallographic order of materials. The process involves subjecting a sample to X-rays and quantifying the resulting diffraction pattern generated by the crystal lattice. X-ray diffraction (XRD) can yield insights into the molecular configuration and the degree of organization across extended distances in liquid crystal phases [85]. Distinct phases display distinctive diffraction patterns, enabling the detection of phase transitions and changes in structure. X-ray diffraction (XRD) is employed to ascertain the molecular arrangement, distance between layers, and distribution of orientations in different phases of liquid crystals. Powder XRD provides some insight into phase nature, but cannot discriminate reflections from intercolumnar and intracolumnar order. Thus, extrusion of macroscopically orientated samples for structural examination is necessary. When filaments are positioned perpendicular to the incident beam, wide angle X-ray scattering (WAXS) measurements produce 2-dimensional diffractograms that show the arrangement of columns in both vertical and horizontal directions. When 3D correlation exists, diagonal reflexes arise. The dispersed intensity distributions can be studied in several directions, such as equatorial (e) or meridional (m), or integrated throughout the azimuthal angle. It is highly advantageous for examining organized phases, such as smectic and columnar phases.

Additional experimental approaches, including electro-optic measurements and nuclear magnetic resonance (NMR) spectroscopy, are employed to characterize mesophases.

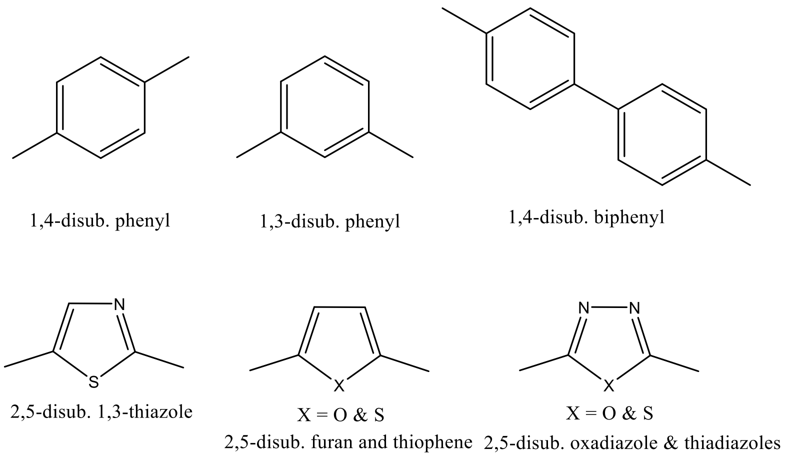
1.6. Effect of chemical constituents

The features of LC molecules are influenced by their chemical constituents. The potential of molecules to form LC phases and their stability are influenced by factors such as size, molecular structure, and functional groups. Phase stability, solubility, and surface anchoring are influenced by polar groups, alkyl chains, and halogenated moieties. Introducing chirality to LC molecules by including asymmetrical centres or substitutions can result in the formation of chiral nematic or twist-bend N phases. Modifying LC molecules by chemical functionalization alters their properties to suit various applications. Functional groups have the capacity to enhance polymer compatibility, improve thermal properties, boost photo responsiveness, enhance electroactivity, and promote surface anchoring and other devices. Little quantities of dopants, stabilizers, or reactive compounds have the ability to alter the properties of liquid crystals. Chiral dopants induce the formation of chiral phases or enhance the electro-optical properties, whereas stabilizers enhance thermal stability and prevent degradation. The process of combining different molecules to create LC combinations allows for the customization of their features and performance. The combination of mesogens, additives, and polymers can have a synergistic effect on enhancing response time, phase stability, and operating temperature limits.

A close correlation exists between a compound's molecular structure and its mesomorphic nature. Nevertheless, defining the specific structure of a molecule that signifies its mesomorphic state is a challenging task. Assessing the impact of constituents on the characteristics of liquid crystals is crucial for the rational design and optimization of LC materials for diverse applications, such as displays, including LCDs, e-readers, and smart devices, for their responsive optical properties. Some of the important structural variations effecting the molecular structure which in turn effect the mesogenic property of LC materials have been discussed.

1.6.1. Effect of core of the molecule

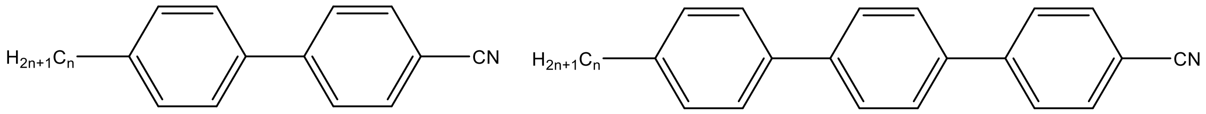
The core in liquid crystal molecules is the core or central part of the molecule that displays ordered arrangement, leading to anisotropic features. It often includes connecting groups and lateral substituents related to the rings. Different types of cores exist based on their geometric shape and molecular structure as discussed in section **1.3**. Some common types of cores found in liquid crystal molecules are 1,4-phenyl, 1,3-phenyl, 1,3,4-phenyl, biphenyls, triphenylene, naphthalene, pyrimidine etc. and some heterocyclic molecules including pyridine, pyrimidine, triazoles, 2,5 substituted-thiophenes and furans, 2,5 substituted-thiazoles, 2,5 substituted-oxadiazoles, 2,5 substituted-thiadiazoles, etc. **(Figure 1.24)**.



1,4-disub. phenyl
1,3-disub. phenyl
1,4-disub. biphenyl
2,5-disub. 1,3-thiazole
X = O & S
2,5-disub. furan and thiophene
X = O & S
2,5-disub. oxadiazole & thiadiazoles

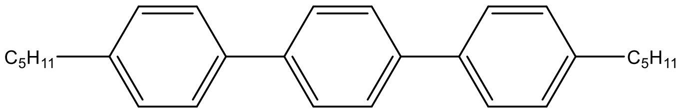
Figure 1.24: Some common core units of LC molecules

The effect of core of the molecules can further be understood by discussing some examples. Conjugation of aromatic core plus the terminal cyano (CN) group results in positive dielectric and significant optical anisotropy (birefringence). Their low viscosity as well as chemical and photochemical stability are noteworthy. These materials remain effective in fundamental watches and calculators like twisted N display technolgies. The 4,4'-disub. biphenyls as key component are utilized now. Anti-parallel correlations within this core increase the actual molecule length and enable highly stable nematic phase (T_{N-I}). The alkyl cyanobiphenyls **(Figure 1.25 (a))** [86] were the first commercially feasible nematic LCs for display systems. These substances have elevated T_{N-I} values with low melting points. As reported by G. Gray the n-pentyl to n-nonyl derivatives exhibited average N-Iso stability 39.67 °C where only n-octyl and n-nonyl show Smectic mesophase. Adding a third aromatic ring system yields a greater length-to-breadth ratio, enhanced polarizability anisotropy, and a significant rise in T_{N-I} **(Figure 1.25 (b)),** where the compound displays very high average N-Iso thermal stability i.e., 235.0 °C. This compound extends T_{N-I} in commercialized biphenyl nematic combinations. Strong smectic phase stability is also seen in the three-ring system compound **(Figure 1.25 (c))** .[5]



(a)
where n = 4-9

(b)
where n = 3-8



(c)
Cr 192.0 SmA 213.0 Iso

Figure 1.25: Molecular structures depicting effect of core on phase transition

1.6.2. Effect of linking groups

Liquid crystal molecules' polarity, polarizability, and flexibility are highly affected by connecting groups. Some common connecting groups in LCs include azomethine (-CH=N-), azo (-N=N-), ester (-COO-), chalcone (-CO-CH=CH-), aliphatic chains, such as methylene (-CH_2-) or ethylene (-CH_2CH_2-), ether (-O-), amide (-CONH-) and carbonates (-O-COO-). These groups restricts the free rotation, conjugate with phenylene rings to improve anisotropic polarizability, lengthen molecules, and preserve molecules rigidity. Selecting connecting groups is critical for developing LC materials having desirable phase and characteristics.

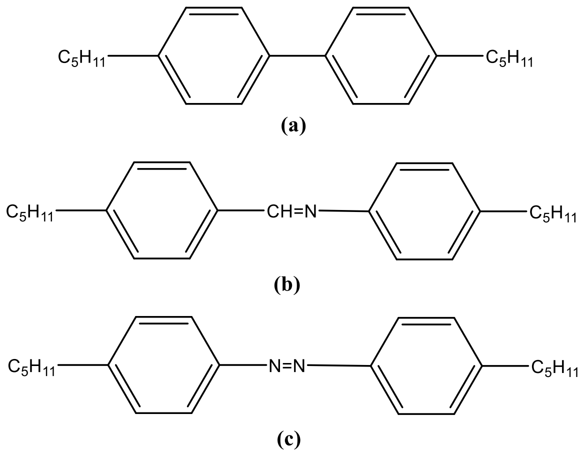


Figure 1.26: Molecular structures of compounds with different linking units

Linking groups ensures basic linearity and structural compatibility. By increasing the length of the molecule core or polarizability anisotropy, these compounds improve mesophase stability and melting point, resulting in larger mesophase range. For example, compound **(Figure 1.26 (a)),** which have no linking group shows only smectic phase with clearing temperature of 52.2 °C. When an azomethine **(Figure 1.26 (b))** and azo group **(Figure 1.26 (c))** is introduced in between the phenyl rings a significant change in mesophases as well as thermal stability of the molecule is observed. With the introduction of azomethine linkage an additional nematic phase appears and the clearing temperature of the compound is reduced to 43.7 °C. Moreover, with introduction of azo linkage the smectic phase completely disappears and the molecules shows only monotropic nematic phase with clearing temperature of 49.5 °C.

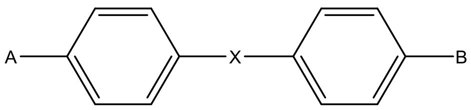
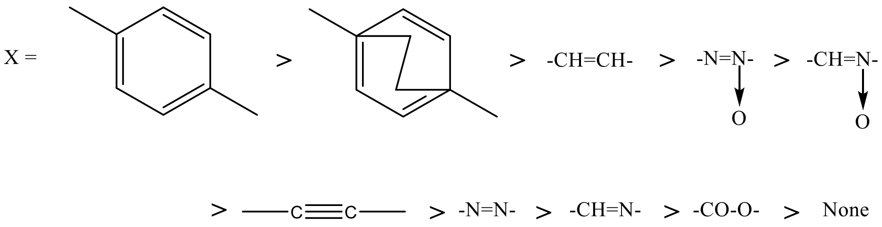


Figure 1.27: Low melting mesogen with different terminal and linking groups

An average efficiency ordering for central group X in enhancing N-I transition temperature may be determined based on published values [87] and the statistical data provided by Kanak et al. [88] for the molecule with the structure illustrated in **Figure 1.27**. The sequence may vary somewhat depending on the end groups A and B, with small exceptions and is as follow.



In this thesis, substantial amount of work has been done on molecules containing carbonate and azomethine linking groups.

1.6.3. Effect of terminal substitution

Terminal groups are chemical moieties or functional groups at the terminals of liquid crystal molecules. The liquid crystal material's characteristics and behaviour depend on these terminal groups. They affect molecule alignment, intermolecular interactions, phase transitions, viscosity, stability, as well as optical properties. The terminal group in a liquid crystal molecule can greatly influence its phase behaviour, determining whether it forms smectic, nematic, chiral nematic, or discotic phases, and can also impact its applicability in displays, sensors, or photonic devices. Some commonly used terminal groups include alkyl or alkoxy chains, such as methyl or methoxy ($-CH_3$ or $-OCH_3$), ethyl or ethoxy ($-CH_2CH_3$ or $-OCH_2CH_3$), or longer aliphatic chains, fluorinated groups, like trifluoromethyl ($-CF_3$) or perfluorinated alkyl chains, cyano (-CN), chiral groups, like cholesteryl or biphenyl-2-yloxy groups, polar groups, such as hydroxyl (-OH), amino ($-NH_2$) groups or nitro ($-NO_2$), etc.

Maier and Saupe's [89] ideas propose that the transition temperature from nematic to isotropic phase of a LC is linked to the molecules polarizability, that is consistently influenced by the end group as well as its impact on coupling inside molecules. As chain length increases, melting points decrease due to flexibility, but extreme "van der Waals" forces to hold molecule together raise melting temperature. A balance is needed for lowering the melting temperatures.

The $T_{N\text{-}I}$ values fall through longer chains, nevertheless increases with long terminal chains of chemicals. As terminal chain length increases, smectic tendency emerges, finally eliminating the nematic phase. Long chains attract and interweave, enabling lamellar filling for generation smectic mesophase.

Branching of the chains significantly impacts the LC mesophase characteristics of a molecule. Branching of the chains introduces chirality in the molecules. Terminal chain branching disrupts molecular packing, usually lowering melting temperatures and liquid crystal (N and Sm) thermal stability. Branches near the core cause significant disturbance, resulting in low melting temperatures.

The average terminal group competence order cited for nematic mesophase may be expressed as per [87].

$$\mathrm{Ph} > \mathrm{NH\text{-}COCH_3} > \mathrm{C{\equiv}N} > \mathrm{O\text{-}CH_3} > \mathrm{NO_2} > \mathrm{Cl} > \mathrm{Br} > \mathrm{N\text{-}(CH_3)_2} > \mathrm{CH_3} > \mathrm{F} > \mathrm{H}$$

Therefore, higher N-I temperatures result from the terminal replacement of H with any of these substituents; the effect is (i) most pronounced for groups that significantly contribute to axial polarizability and/or possess the ability to form strong conjugative bonds; (ii) least pronounced for small substituents (CH_3, F), weakly conjugating substituents (F, Br), or substituents with an off-axial dipole moment, such as $N(CH_3)_2$. Cholesteric terminal group efficiency orders have previously been obtained for fewer systems [87,90], but they seem to be comparable with the nematic order corresponding to the identical substituent group. This is predicted as optically active isomers' Ch-I transition temps match the racemic modification's N-I temperature.

Lateral attractions play a significant role in Smectic phases, leading to an alternate group efficiency order compared to nematic mesophase. The sequence to SmA mesophases can be given as [87].

$$\mathrm{Ph} > \mathrm{Br} > \mathrm{Cl} > \mathrm{F} > \mathrm{N\text{-}(CH_3)} > \mathrm{CH_3} > \mathrm{H} > \mathrm{OCH_3} > \mathrm{CN}$$

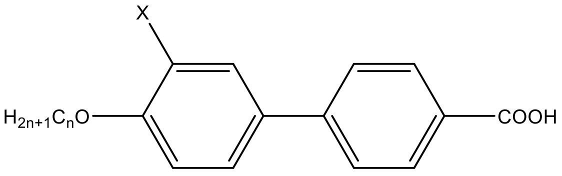
1.6.4. Effect of lateral substitution

Laterally substituted LC system involves replacing molecular components or functional groups along the side of the main molecular axis. In other words, it includes changing the side groups or substituents associated to the core structure of a liquid crystal molecule. Typical side groups found in liquid crystal molecules include methoxy and ethoxy (-OCH_3 and -OC_2H_5), methyl (CH_3), chloride (Cl), cyanide (CN), fluoride (F), nitro (NO_2), etc. Lateral substitution is employed in alicyclic structures also, with the lateral group situated at the end of the terminal alkyl chain at axial position. Alkyl chain comprising laterally substituted units are likewise present in LC molecules. Impact of lateral groups on the rod-shaped molecules of liquid crystals is analyzed based on many categories, mainly because the molecular structure is influenced differently depending on the specific molecule and the location of the group.

While lateral substitution is crucial in both N and SmA systems, it frequently diminishes the stability of the smectic mesophase to a greater extent than that of the nematic mesophase due to the lamellar packing disruption. It is possible for a polar lateral group to partially counteract the effect of a lateral substituent making the smectic phase less stable. Increased size disrupts lamellar packing, but polarity enhances it.

Research has shown [87] that lateral substituents have consistent impacts on various mesogens. It has been observed that a substituent reduces N-I transition temperatures more significantly in shorter molecules, likely due to a greater impact on the anisotropy of molecular polarizability. Additionally, a substituent decreases S-N or S-I temperatures more in shorter molecules, with less dependence on molecular length compared to nematic thermal stabilities. This may align with the impact of substituent dipoles in offsetting their size-related effects. Although some exceptions do exist.

The broadening impact of a lateral group is most apparent when it is placed in the central core of the structure without causing any steric effects, allowing the substituent to fully exert its influence. Experimental findings have been gathered for many types of mesogens. The 4'-n-alkoxybiphenyl-4-carboxylic acids [91,92] have been extensively studied, showing N and Sm C phases. The impact of various 3'-substituents with different sizes and dipolarities on the thermal stabilities of the mesophases was examined. For example, structure in **Figure 1.28** with X= F, Cl, Br, I, NO_2, and CH_3.



where X = F, Cl, Br, I, NO_2 and CH_3

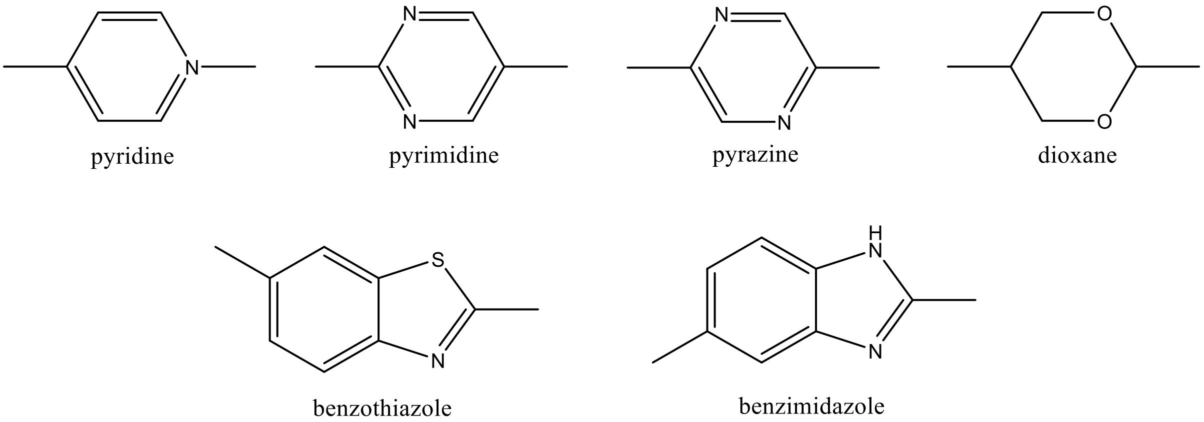
Figure 1.28: Molecular structure of laterally substituted 4'-n-alkoxybiphenyl-4-carboxylic acids

The substituent enhances long-axis polarizability and also lowers molecular anisotropy, while it promotes axial-separation, diminishing intermolecular attraction.) As predicted, replacing 3'-H with a different group lowers N-I temperatures. Regardless of bipolarity, compound in **Figure 1.28,** N-I temperatures decreased with substituent X size. The inefficacy of substituent dipole aligns with the Maier-Saupe hypothesis [25,26,89]. For SmC thermal stability, it was more complicated. A highly dipolar lateral group X had a lesser influence on S-N or S-I temperatures than a less dipolar one of same size. Hence, dipole moments promote lamellar smectic ordering and restrict substituent size to smectic transition temperature relationships.

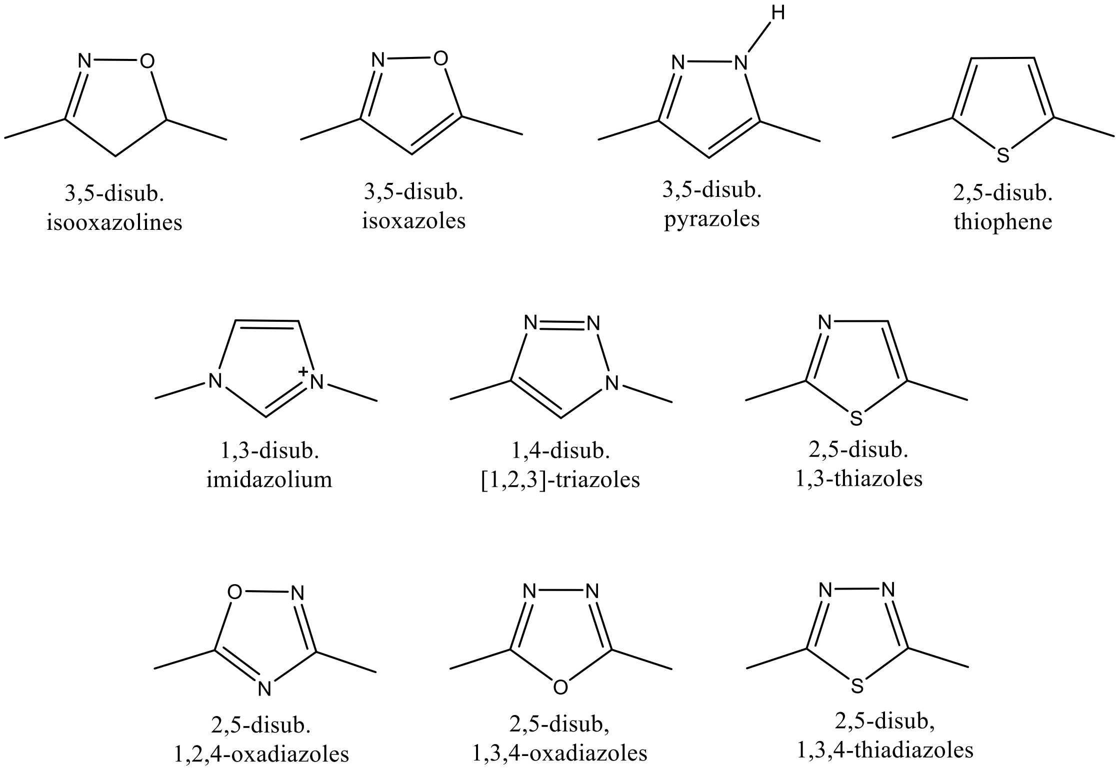
1.6.5. Effect of heterocyclic rings

Heterocycles are essential for determining the properties and behaviour of liquid crystals. Several kinds of heterocycles have been investigated for their impact on liquid crystal characteristics. Within the field of liquid crystals, there has been a strong emphasis on five-membered heterocycles, although six-membered heterocycles also have a notable impact on liquid crystalline characteristics. Some of the most commonly employed six membered heterocycles in liquid crystal **(Figure 1.29 (a))** includes pyridine, pyrimidine, pyrazine, dioxane, benzothiazole, benzimidazole, etc. Some commonly employed five membered heterocycles used in LC **(Figure 1.29 (b))** include 1,2,4-triazoles, 1,3,4-thiadiazoles, 1,3,4-oxadiazoles, 1,2,4-oxadiazoles, thiazoles, isoxazolines, pyrazolines, isoxazoles, thiophenes, pyrazoles, imidazoles, 1,2,3-triazoles, etc.

Schubert et. al. [87,93,94] studied several compound **Figure 1.30** with heterocyclic rings X and two alkyl or alkoxy groups in the terminal positions. Notably, the di-n-pentyl series pyridyl and pyrimidinyl derivatives have low melting points. The non mesomorphic features of 4,4"-diethyl-p-terphenyl, the purely smectic properties of 4,4"-di-n-pentyl-p-terphenyl, and the phase type changes within each series make mesophase thermal stabilities difficult to measure.



(a) Examples of some six membered and fused heterocyclic rings



(b) Examples of some five membered heterocyclic rings

Figure 1.29: Illustrative examples of five, six membered and fused heterocycles used in LC

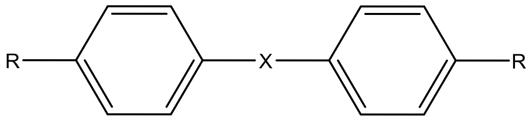
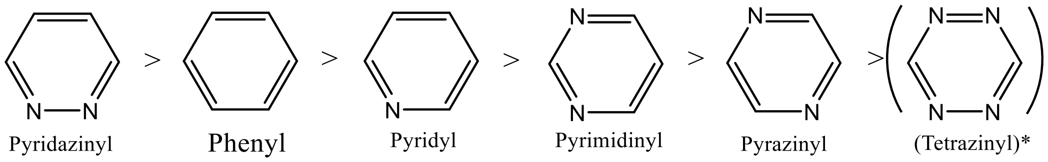


Figure 1.30: Molecular structure of compounds studied by Schubert et. al.

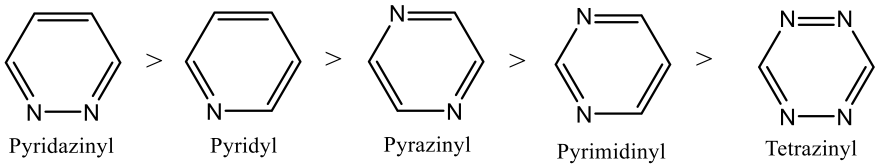
The findings suggest that the center ring promotes mesophase thermal stability in the following order:

Smectic:



* Nematogen

Nematic:



Recent study has shown a significant rise in the investigation of the uses of five-membered LC heterocycles in photovoltaic devices [95–97], organic light-emitting technologies [98–101], and biological systems [101–104], etc.

When a five-membered heterocyclic ring is added to a LC molecule, it may cause a bend or curve in its molecular arrangement. This bend plays a crucial role in liquid crystal materials by impacting the fundamental molecular geometry and configuration in the phase. It also induces flexibility and distortions in the linear backbone of the LC molecule, leading to a bent conformation. This curvature causes a disturbance in the arrangement of neighbouring molecules in the LC phase, resulting in the emergence of a bent-core or banana-shaped mesophase. The influence of different heterocyclic group on the mesophase have been studied extensively in literature by varying the heterocyclic moiety in the molecular structure [105–108].

The heterocyclic ring within the central core impacts the mesophases and physical characteristics due to the higher polarizability of heteroatoms like nitrogen, oxygen, and sulfur compared to that of carbon [109–111]. In addition, they possess good optical, electronic and liquid crystalline properties [112,113]. Thus, developing a molecule with high potency for liquid crystal applications is a fascinating area of study, considering even a little alteration in the molecular structure may lead to significant changes in the LC phases.

1.7. Applications overview

LCs are used across numerous fields (**Figure 1.33**) because of their distinctive optical, mechanical, and electrical characteristics. Key uses of liquid crystals have been discussed in brief below:

1. Display Technology: Within liquid crystal displays (LCDs), LCs are placed between transparent electrodes and polarizing filters to control the transmission of the light. Electric fields applied to the LC layer may change the alignment of molecules, thus controlling the transmission of light. Such precise control allows for the development of graphics and text on the displayed screens. **Figure 1.31.** shows working of a typical Transmissive LCD Display. LCDs provide benefits like as high resolution, low power consumption, and functionality with a range of electronic devices like TVs, PC monitors, cellphones, and tablets [114–117].

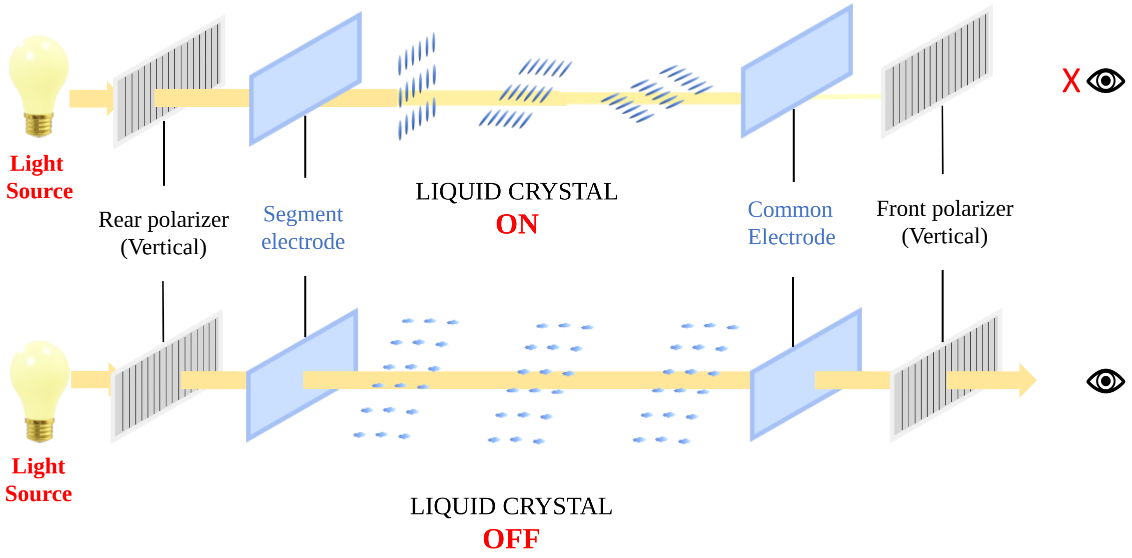


Figure 1.31: Working of Transmissive LCD Display

2. Optical Devices: LCs are useful for optical switches, modulators, and attenuators because of their controllable optical behaviour. Electric fields or mechanical stress may modify LC alignment, enabling quick and accurate light transmission modification. Telecommunications as well as data transmission networks use LC-based optical switches due to their quick switching times and minimal power consumption. LC modulators offer flexible illumination, polarization, and phase regulation for imaging, sensing, and laser systems. In addition, LC attenuators offer tunable optical dampening for signal processing and optical power control. The adaptability and tunability of LC make them essential in current optical devices, advancing photonics, telecommunications, as well as optical sensing [118–120].

3. Photonics and Telecommunications: LCs play an essential part in photonics and telecommunications by offering distinctive optical characteristics and adaptable functions. Devices using LC technology, such as optical modulators, polarization controllers, and selective wavelength filters, allow accurate manipulation of light's polarization, intensities, and wavelengths. LCs are used in optical communication network, wavelength division multiplexing, and spectroscopic research [121–123].

<u>4. Biomedical Applications</u>: LCs are used across multiple biological applications because of their distinctive features. They are used for drug deliveries, biosensors, and tissue engineering. Liquid crystals impart targeted drug release, precise biosensing, and serve as a suitable structure for tissue regrowth. Their adaptability and ability to work well with biological systems stimulate progress in healthcare and biotechnology [37,101–104].

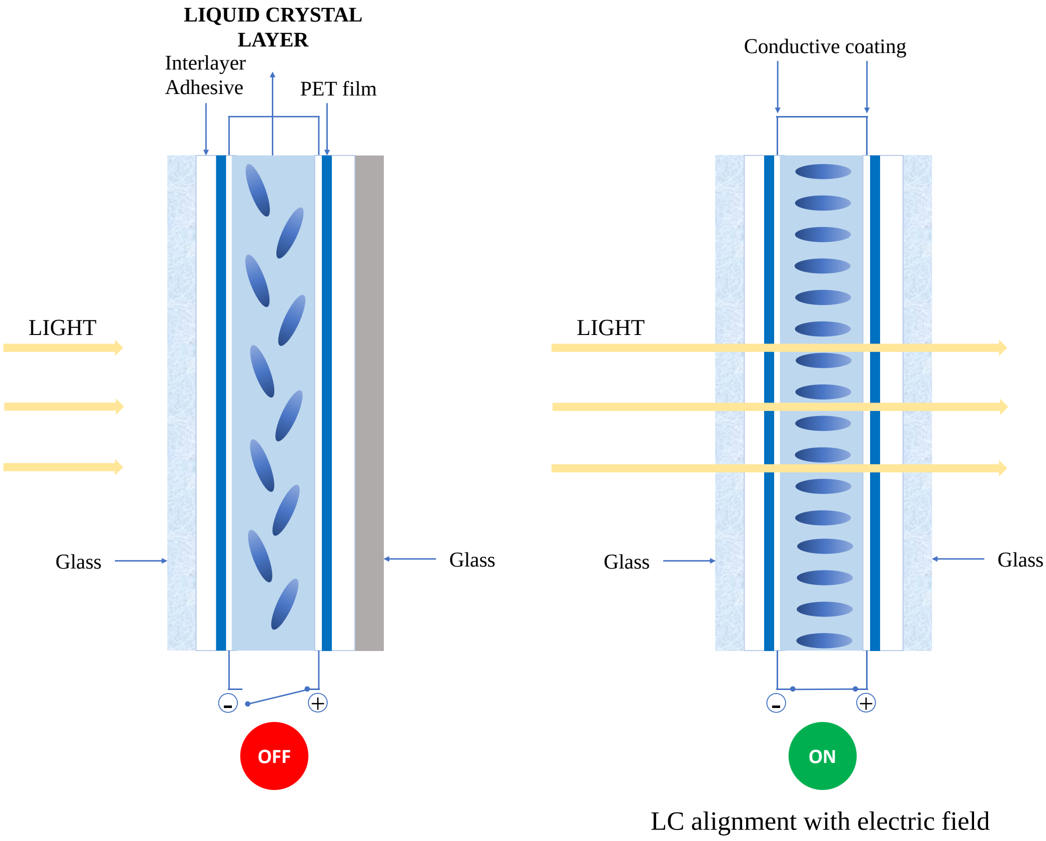


Figure 1.32: Representative diagram for working of smart window based on PDLC

<u>5. Smart Windows and Privacy Filters</u>: LC-based smart windows switch across transparent and opaque states, offering adaptable shade. Illustrative diagram of working of PDLC is an active smart glass technology is shown in **Figure 1.32**. LC-based private filters provide customizable transparency levels to ensure privacy in different circumstances. LCs provide UV protection, thermal insulation, as well as glare reduction, improving comfort and conserving energy inside. Their adaptability is crucial for the advancement of smart material development [124–126].

<u>6. Sensors and Detectors</u>: Sensors and detectors use LCs due of their optical and sensitive features. The sensitive and precise detection of gases, biomolecules, and contaminants is possible using LC-based sensors. LCs may alter structure in response to temperature, pH, or chemical interactions, affecting optical characteristics including colour, polarization, and light dispersion. Accessible applications benefit from LC-based detectors' fast reaction times, high sensitivity, and compactness. Environmental surveillance, medical diagnosis, food safety, and security screening use LC sensors and detectors to develop sensing technologies and address social concerns [127–129].

7. Energy Storage and Conversion: Liquid crystals (LCs) are currently studied for energy storage and conversion. LC materials' unique characteristics make them promising for electrical capacitors, batteries, and photovoltaics. Enhancing charge transfer and stability using LCs improves batteries performance. New materials for electrodes and interface using LCs improve energy storage systems. LCs regulate light and carry charge in photovoltaic devices, improving efficiency. Renewable energy and portable electronics benefit from LC-based systems' high electrical efficiency and quick charge or discharge frequencies. Optimization of LC-based energy systems for sustainability continues to be the course of study [130–132].

8. Liquid Crystal Elastomers (LCEs): LC elastomers combine the properties of LC with elastomers, providing distinctive mechanical features like reversible deformations and controlled actuation. LCEs are used in soft robotics, biomedical devices, and adaptive optics, demonstrating their capability in developing sophisticated smart materials with various functions [133,134].

9. Liquid Crystals in Cosmetics: Lipsticks, and lip glasses with cholesteric LCs uses LC materials Cosmetics are gradually utilizing LCs for their versatility. LCs improve active ingredient durability and cutaneous delivery. They make skincare products smoother and more luxurious. LCs provide brightness and shine to cosmetic compositions. They stabilize emulsions and suspensions, maintaining skincare product uniformity and effectiveness. Sunscreen compositions use LCs to boost photoprotection and water resistance. Contemporary cosmetics utilize LCs' effectiveness, stability, and sensory qualities [135,136].

10. Chemical Reactions and Spectroscopy: Due to their unique features affecting molecular interactions and optical responses, LCs are used in chemical processes and spectroscopy. They provide precise conditions for chemical reaction, kinetics and processes. They are used in spectroscopy to study molecule structures, dynamics, and photophysical characteristics including luminescence and absorption. Spectroscopic methods based on LC also highlight structural organisation and phase transitions, advancing the field of materials and chemistry [137,138].

11. Industrial Applications: LC polymers are attracting attention in numerous industrial sectors because of their distinctive features, such as strong heat resistance, exceptional mechanical strength, and intrinsic flame retardancy. They are often used to provide fire-resistant coatings for optical cables. LCPs are valued for their capacity to improve the elastic modulus in molding applications. Manufacturers may enhance the mechanical characteristics and accuracy of molded products by integrating it into material composites or using them as reinforcements in thermoplastic moulding techniques [139–141].

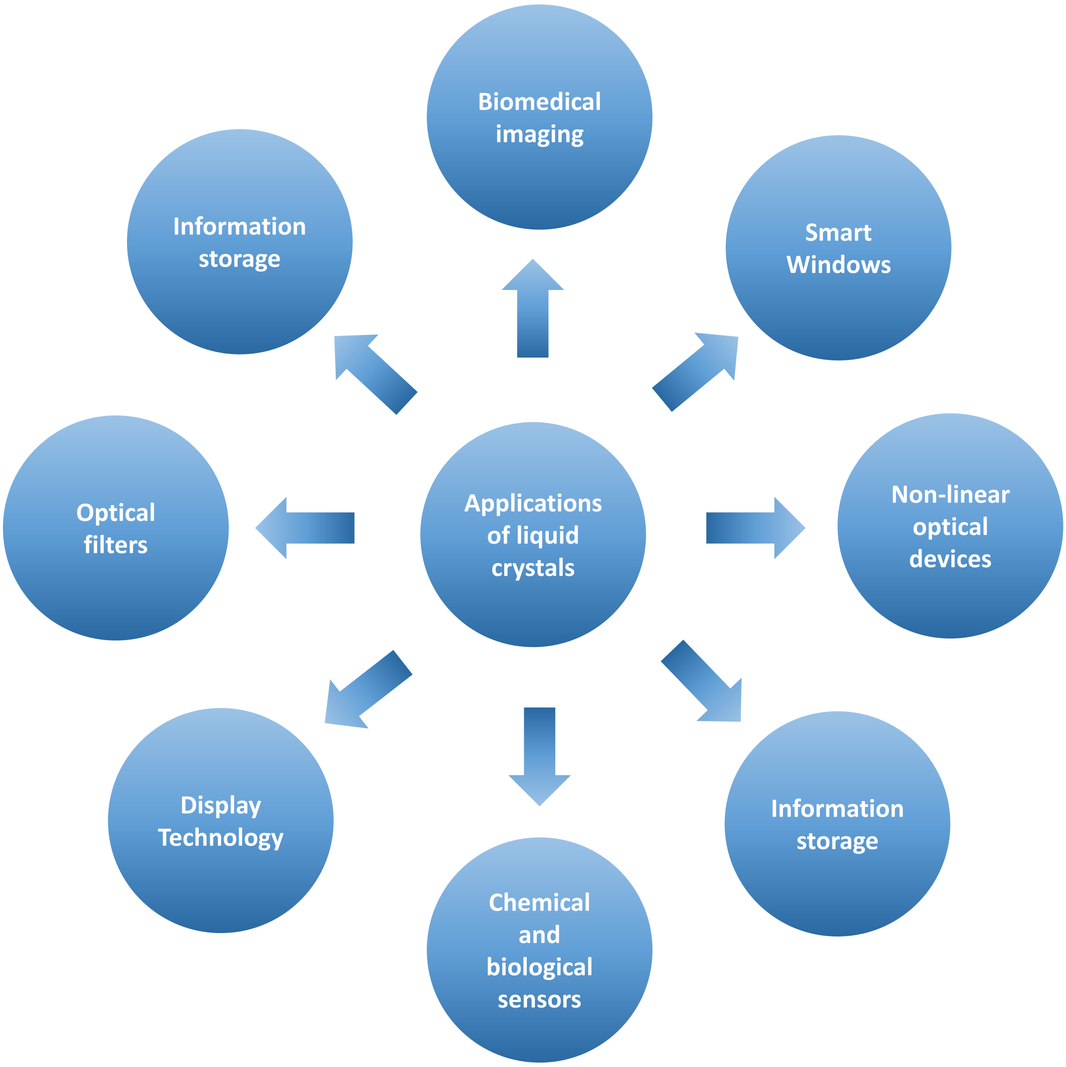


Figure 1.33: Various applications of Liquid Crystals

Overall, liquid crystals provide various features that make them suitable for a wide range of technical applications, including consumer electronics, sophisticated materials, biomedical devices, etc. Continuous research and development contribute to extending the scope of applications and enhancing the efficiency of liquid crystal-based technologies.

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Aims and Objectives

The overarching aim of this thesis is to design new molecular structures and synthesize liquid crystalline compounds, mainly focusing on cholesterol and heterocyclic moieties. Molecular design techniques, novel synthetic pathways, and the factors influencing phase behaviour can all be investigated to gain a thorough grasp of the molecular structure underpinnings of liquid crystalline phenomena. Also to evaluate the mesomorphic, thermal, and photophysical properties of synthesized compounds. Additionally, the study includes an evaluation of their antioxidant properties and biological activities. The utilization of Density Functional Theory (DFT) calculations is integrated into the research to gain theoretical insights into the electronic structure and properties of the synthesized compounds.

Objectives:

- To design and synthesize a diverse range of novel homologous liquid crystal compounds, including cholesterol-based Schiff's base derivatives with carbonate linkage, azo-based biphenyl liquid crystals, series of Schiff's base derived from cholesteryl carbonate and thiadiazole moiety, unsymmetrical 1,3,4-oxadiazole based LC and cholesterol-based Schiff's base derivatives with thiazole moiety.
- To characterize the synthesized compounds using a comprehensive set of analytical techniques, including elemental analysis, spectroscopy techniques such as FT-IR, ^{1}H-NMR, ^{13}C-NMR, microscopy, and thermal analysis, to elucidate their molecular structure, physical properties, and mesomorphic behaviour.
- To investigate the photophysical properties of the synthesized compounds, including photoluminescence and photoisomerization, to assess their potential applications in optoelectronic devices and materials.
- To evaluate the antioxidant properties of the synthesized liquid crystal compounds using DPPH assays, aiming to explore their potential as antioxidants in various applications.
- To assess the biological activities of the synthesized compounds against bacteria and fungi to investigate their potential as antimicrobial agents.
- To perform Density Functional Theory (DFT) calculations to provide theoretical insights into the electronic structure, optical properties, and molecular behaviour of the synthesized liquid crystal compounds, aiding in the interpretation of experimental results and guiding further research directions.

- To compare previously reported mesogens with synthesized mesogens, summarize and analyze the experimental and computational findings to elucidate the structure-property relationships and potential applications of the investigated liquid crystal materials.
- To discuss the implications of the research findings, propose future research directions, and provide recommendations for the development of novel liquid crystal materials with enhanced properties and diverse applications in fields such as optoelectronics, materials science, and biomedical engineering.

To present a comprehensive summary, conclusion and outlook for future research in the field of liquid crystal chemistry, highlighting the significance of the study and its contributions to the scientific community.