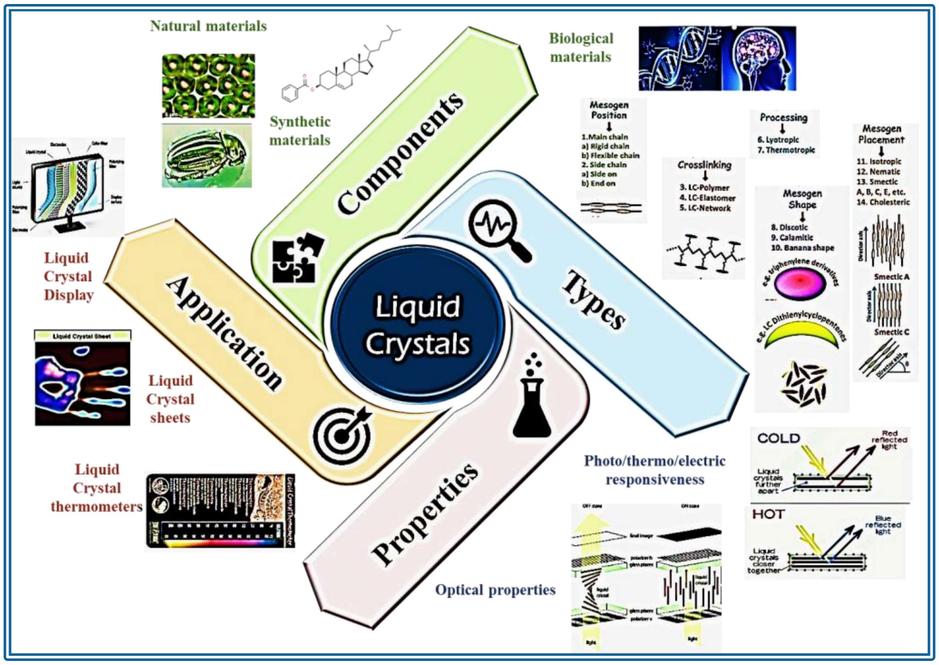
CHAPTER 1

INTRODUCTION OF THE LIQUID CRYSTALS



1.1 General Introduction of Liquid Crystals

Liquid Crystals (LC) represent an intriguing state of matter positioned between solids and liquids, showcasing properties of both. Liquid crystals, often termed as orientationally ordered liquids, possess unique properties like flow combined with long-range orientational order.[1] These materials exhibit phases transitioning from solid-like to liquid-like behaviour under varying conditions, leading to their designation as mesogens. Their mesomorphic state, characterized by intermediate molecular order, offers a rich area for scientific investigation.[2] The versatility of liquid crystals arises from their anisotropic elasticity, dielectric susceptibilities, and optical properties. They exhibit responsiveness to the external stimuli like magnetic as well as electric fields, making them adaptable for diverse applications including temperature sensors and liquid crystal lasers.[3,4]

Liquid crystals have transformed the landscape of display technology, offering advantages such as reduced power consumption, enhanced contrast ratios, and flexibility in design.[5,6] Beyond displays, they find utility in diverse domains including optical devices, medical diagnostics, and non-destructive testing.[7,8] Understanding the structure-property relationships of LCs is crucial to maximize their performance through optimization. These substances are pivotal in modern technology, evident in various everyday devices such as clocks, computer displays, and televisions.[9] The exploration of LCs spans various disciplines including physics, material science, optics, and engineering, showcasing their interdisciplinary nature. From ancient times to modern applications, liquid crystals have played crucial roles in everyday life and scientific exploration.[10]

In summary, liquid crystals represent a fascinating category of substances possessing distinctive characteristics that serve as a bridge between solids and liquids. Their applications in technology and science continue to expand, driven by ongoing research and interdisciplinary collaboration. Understanding their behaviour and harnessing their properties opens avenues for innovation across multiple fields.

1.2 Liquid Crystals: “Fourth State of Matter”

LCs are a unique state of matter characterized by both fluidity and order, displaying properties distinct from those of traditional solids and liquids.[2] The term "liquid" originates from the Latin word "*liquere*," meaning to flow, while "crystal" is derived from the Greek word "*kristallos*," signifying "clear ice." Unlike conventional crystals with three-dimensional lattice structures, liquid crystals lack such ordered arrangements and exhibit anisotropic properties.[11,12] **(Fig. 1.1)**

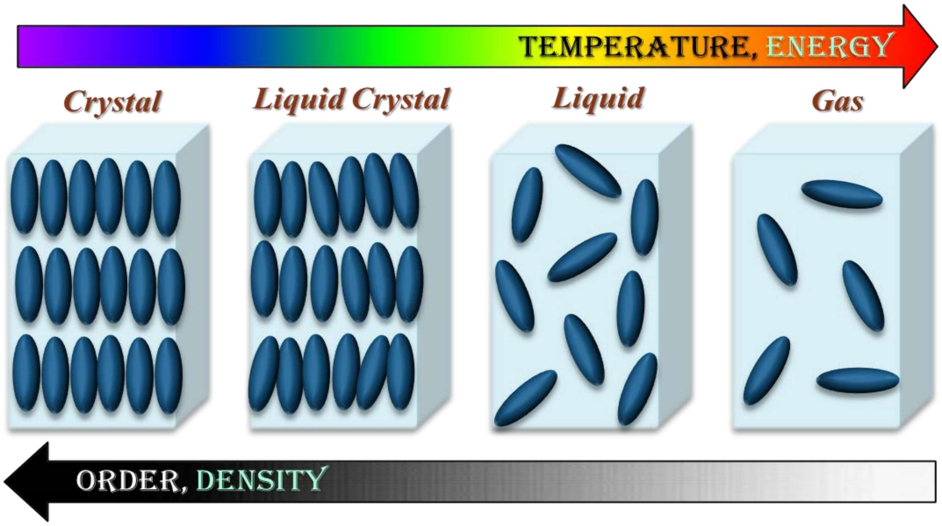
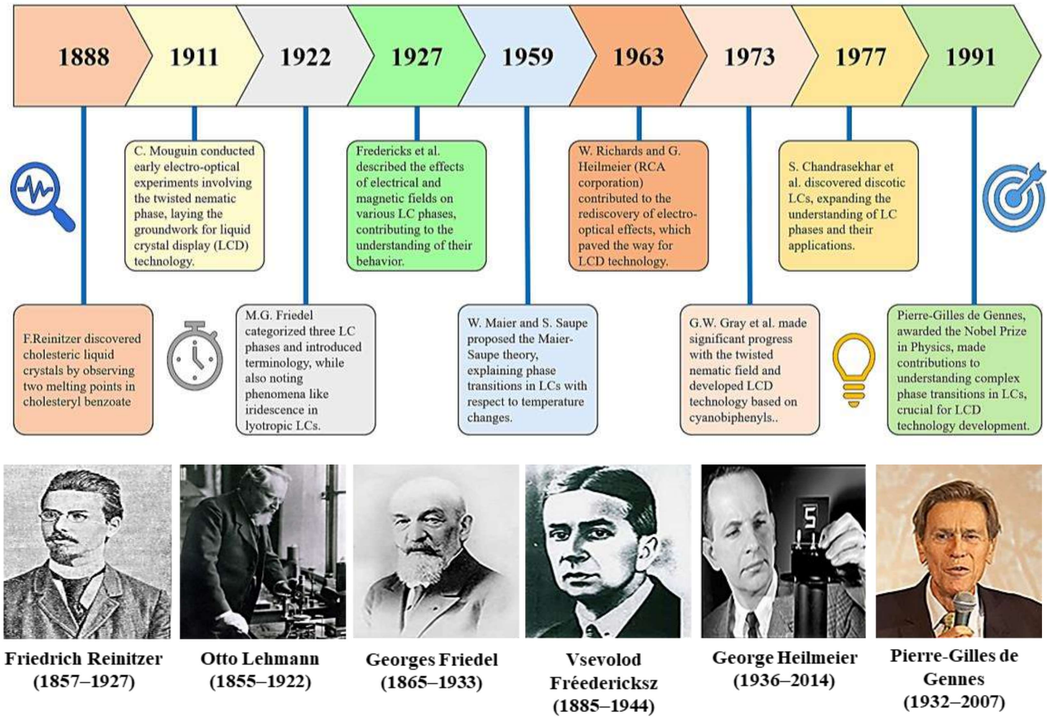


Fig. 1.1: Different state of Matter

Liquid phase (Isotropic) is identified by random molecular distribution without positional or orientational order, with molecules moving in arbitrary directions. In contrast, liquid crystals demonstrate a tendency for molecules, or mesogens, to align along a single axis called the director (n), which distinguishes them from isotropic liquids. Unlike solids, which exhibit rigid molecular arrangements and definite shapes, liquid crystals lack long-range order but retain some degree of orientational order observed in crystals. This orientational ordering distinguishes them from isotropic liquids, allowing for unique physical properties such as anisotropy. Unlike gases, which lack any order, liquid crystals demonstrate intermediate order, making them an intriguing phase of matter commonly known as "**fourth state**." Transitioning from crystalline solids to liquid crystals involves breaking intermolecular bonds and losing specific molecular orientations due to increased thermal energy. Liquid crystals are often termed "solid-like liquids" due to their simultaneous possession of characteristics from both crystalline solids and isotropic liquids.[13]

1.3 History of Liquid Crystals

Working at the Charles University (Institute of Plant Physiology), Prague, F. Reinitzer was examining derivatives of cholesterol when he stumbled upon an unusual phenomenon. Specifically, he noticed distinct colour changes in cholesteryl benzoate when it was cooled just above its freezing temperature. Upon closer investigation, it was observed that cholesteryl benzoate displayed dual melting points: initially at 145.5°C, leading to the formation of a turbid liquid, followed by another at 178.5°C, resulting in the liquid. This observation marked the first recorded documentation of the "Liquid Crystal phase," a phenomenon that F. Reinitzer suggested represented a new state of matter.[14] **Fig. 1.2** describes the timeline for the history of liquid crystals.



1888 — F.Reinitzer discovered cholesteric liquid crystals by observing two melting points in cholesteryl benzoate

1911 — C. Mouguin conducted early electro-optical experiments involving the twisted nematic phase, laying the groundwork for liquid crystal display (LCD) technology.

1922 — M.G. Friedel categorized three LC phases and introduced terminology, while also noting phenomena like iridescence in lyotropic LCs.

1927 — Fredericks et al. described the effects of electrical and magnetic fields on various LC phases, contributing to the understanding of their behavior.

1959 — W. Maier and S. Saupe proposed the Maier-Saupe theory, explaining phase transitions in LCs with respect to temperature changes.

1963 — W. Richards and G. Heilmeier (RCA corporation) contributed to the rediscovery of electro-optical effects, which paved the way for LCD technology.

1973 — G.W. Gray et al. made significant progress with the twisted nematic field and developed LCD technology based on cyanobiphenyls..

1977 — S. Chandrasekhar et al. discovered discotic LCs, expanding the understanding of LC phases and their applications.

1991 — Pierre-Gilles de Gennes, awarded the Nobel Prize in Physics, made contributions to understanding complex phase transitions in LCs, crucial for LCD technology development.

Fig. 1.2: Major discoveries in the history of Liquid Crystals

F. Reinitzer's initial discovery, however, remained somewhat obscure until he sought assistance from German physicist O. Lehmann. In March 1888, F. Reinitzer reached out to O. Lehmann regarding his findings. Upon examining the intermediate cloudy liquid, concluded that it exhibited liquid crystalline properties. He coined the phrase "Liquid Crystal," characterizing it as an intermediate state between a liquid and a solid.[15–17]

1.4 Properties of Liquid Crystals

The main physical properties of liquid crystals include:

1. **Anisotropy**: LCs exhibit different physical properties in different directions due to their anisotropic molecular arrangement.

2. **Phase Transition**: Liquid crystals undergo phase changes at specific temperatures, transitioning from solid to liquid crystal and then to ordinary liquid as temperature increases.
3. **Birefringence**: They display birefringent behaviour, meaning they can split light into two polarized components with different refractive indices.
4. **Response to External Stimuli**: Liquid crystals can respond to changes in temperature, pressure, electric fields, or chemical environment, leading to phase transitions or alterations in optical properties.
5. **Optoelectronic Properties**: Liquid crystals can be optically transparent or opaque depending on their molecular arrangement, making them suitable for use in display technologies.[18]

1.5 Classification of Liquid Crystals

Liquid crystals exhibit various orders that classify their molecular arrangements**.** **Orientational Order** measures the tendency of molecules to align along a specific direction known as the director (n), extending over considerable distances. **Positional Order** refers to the degree of translational symmetry observed among average molecules or molecular sets within the material. **Bond Orientational Order** characterizes the alignment of molecules along a line connecting their centers, without requiring uniform spacing along that line, indicating a form of extended order.

Liquid crystals (LCs) are categorized in various ways, including

- Molar mass
- Method of formation,
- Nature of constituent molecules,
- Types of phases they exhibit.

G. Friedel introduced the initial classification of liquid crystals in 1922, which included the categories of nematic, smectic, and cholesteric.[19] Over time, this classification system has expanded to encompass more intricate and diverse types of liquid crystals. As a result, the parameters used for classifying liquid crystals have undergone considerable expansion. These now include considerations such as molar mass, formation methods, symmetry, shape, chemical composition, and various other factors.[20,21] Despite this diversity, the most common classification criterion is the means of formation, resulting in three main categories. The general classification of liquid crystals is depicted in **Fig. 1.3**.

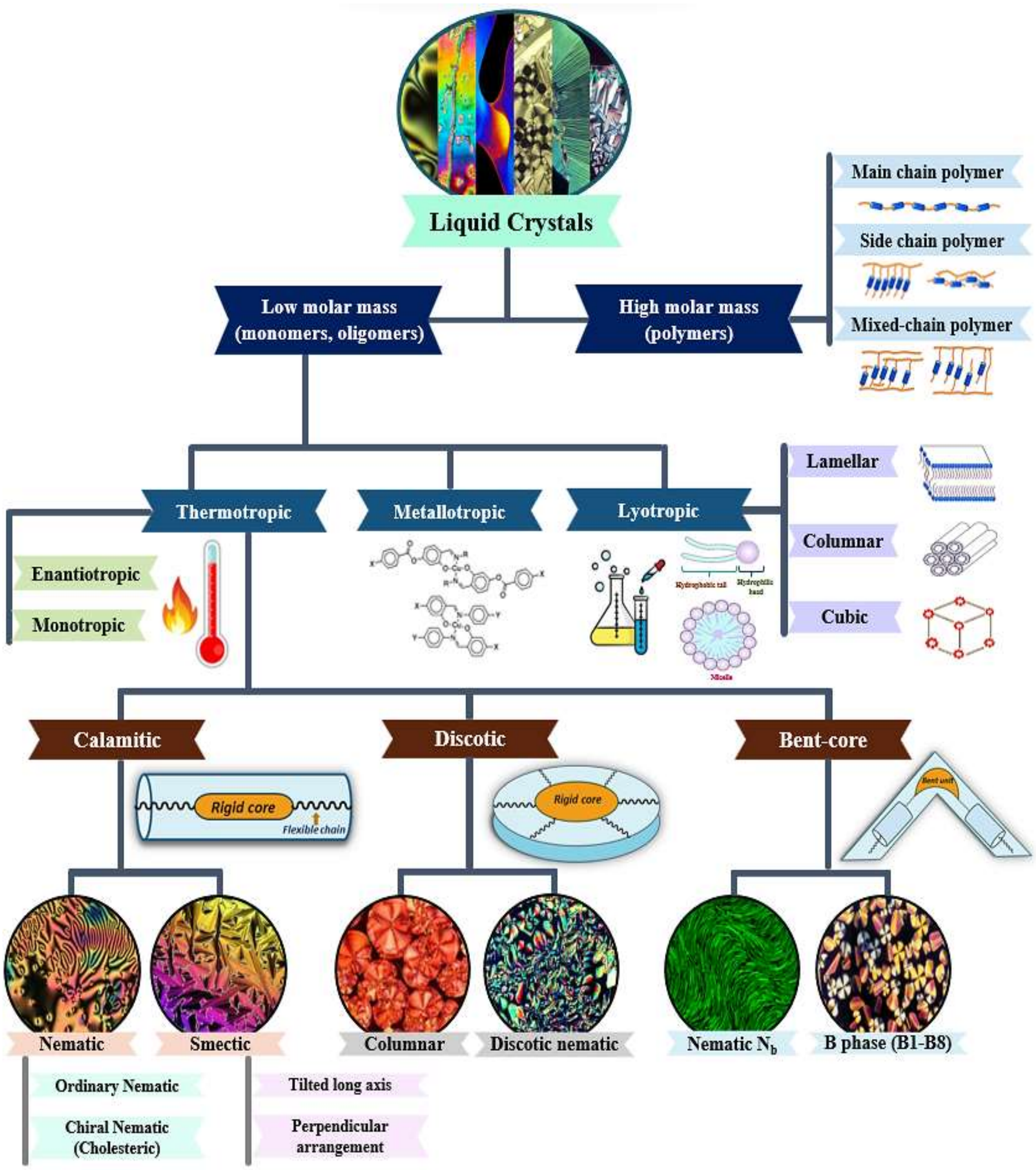


Fig. 1.3: General Classification of Liquid Crystals

1.5.1 Lyotropic Liquid Crystals

Lyotropic LCs (LLCs) are created by dissolving amphiphilic compounds in appropriate solvents within a defined concentration range and are composed of two or more components. These compounds contain both hydrophilic polar heads and hydrophobic nonpolar tails. Lyotropic liquid crystals are also called anisotropic solutions and examples include soap solutions and various phospholipids. At low concentrations, the solute molecules are randomly dispersed within the polar solvent. Below a critical concentration, LLCs do not form. Once the critical concentration is reached, the molecules organize into structures like spheres, rods, or discs, known as micelles, illustrated in **Fig. 1.4**. Consequently, various lyotropic mesophases emerge, including lamellar, hexagonal, and cubic phases.[22,23] Additionally, amphotropic LCs exhibit both thermotropic and lyotropic behaviours.

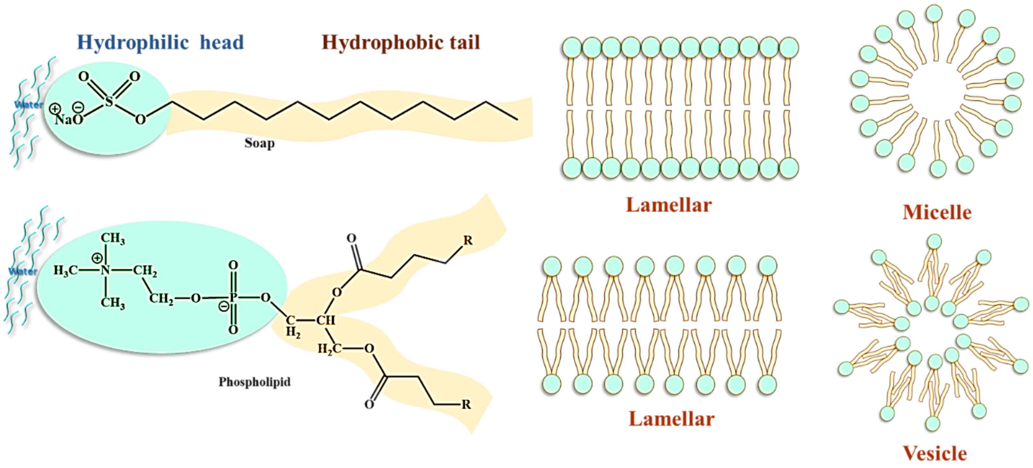


Fig. 1.4: Lyotropic Liquid Crystals

1.5.2 Metallotropic Liquid Crystals

Metallomesogens, metal complexes with liquid-crystalline properties, exhibit diverse mesophases like nematic, smectic, and even cubic forms. They can be covalent or ionic, with various low molar mass thermotropic and some lyotropic examples. Recent focus has expanded to metallomesogenic polymers, offering a wide array of structural possibilities. Their introduction of metals allows for unique coordination geometries via polydentate ligands, potentially leading to new mesophases and molecular organizations, promising novel functionalities and device applications.[24,25]

1.5.3 Thermotropic Liquid Crystals

Thermotropic liquid crystals demonstrate distinct phases within defined temperature ranges, which can be achieved by altering temperatures. Elevated temperatures can disrupt the partial ordering of the liquid crystal phase, causing a transition into a conventional isotropic liquid phase. Conversely, when the isotropic liquid phase is cooled to very low temperatures, most liquid crystal materials undergo various phases before transitioning into a conventional crystal structure. Thermotropic liquid crystals typically consist of single-component systems.[26] Given the focus on thermotropic liquid crystals in this research, we delve deeper into this category. Thermotropic liquid crystals exhibit various phases and physical properties, largely influenced by molecular shape. Different geometrically anisotropic molecules like rod-like, disc-like, banana-shaped, etc., form different liquid crystal phases.

❖ **Classification based on the behaviour of LC phases to temperature changes:**

The transition from the crystalline state to the mesophase is termed as the "melting point," whereas the shift from the mesophase to the isotropic liquid phase is referred to as the "clearing point." These classifications are based on how liquid crystal phases respond to alterations in temperature.

1.5.3.1 Enantiotropic Phase

Enantiotropic mesophase refers to a state of matter where liquid crystalline phases which is thermodynamically stable are attained both upon heating and cooling (**Fig. 1.5**), with transitions occurring in opposite directions during both of these processes.

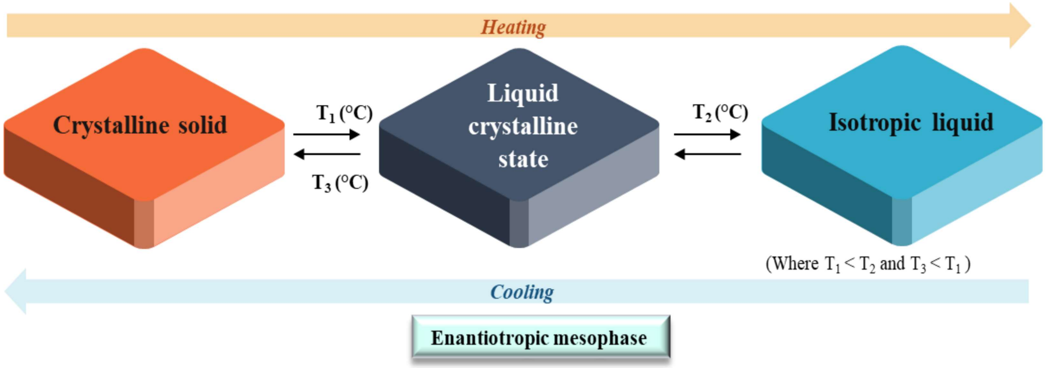


Fig. 1.5: Representation of phase transitions for enantiotropic mesophase

1.5.3.2 Monotropic Phase

In the monotropic phase, the mesophase forms solely during the cooling stage of the isotropic liquid (**Fig. 1.6**). This phase is classified as metastable as the transition to the mesophase happens below the melting point.

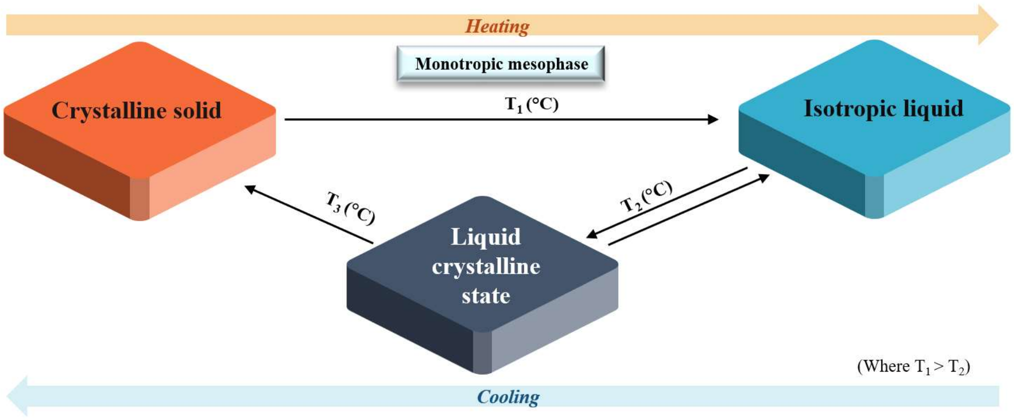


Fig. 1.6: Representation of phase transitions for Monotropic mesophase

❖ **Classification based on Shapes:**

Thermotropic liquid crystals are categorized into three primary groups based on the shape of the mesogenic molecules: Calamitic (rod-shaped), bent-core (including boomerang, and banana-like), and discotic (disk-like) liquid crystals.

1.6 Calamitic Liquid Crystals

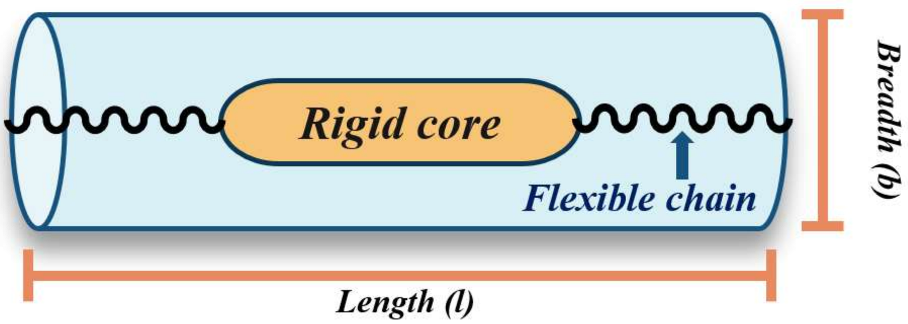


Fig. 1.7: Representation of a calamitic liquid crystals; (*l* > *b)*

Calamitic liquid crystals refer to molecules with a rod-like structure that frequently exhibit thermotropic mesophases. Typically, these compounds exhibit an elongated structure (**Fig. 1.7**) characterized by a notable contrast between their length (l) and breadth (b). The majority of calamitic liquid crystalline compounds are characterized by a central rigid core, typically formed from two or more ring structures.[27] These rings have the option of being bonded directly or linked through intermediary groups. Additionally, these compounds commonly include flexible hydrocarbon chains at their terminals and occasionally have lateral substituents. **Fig. 1.8** illustrates the typical molecular constitution and shape of calamitic LCs.

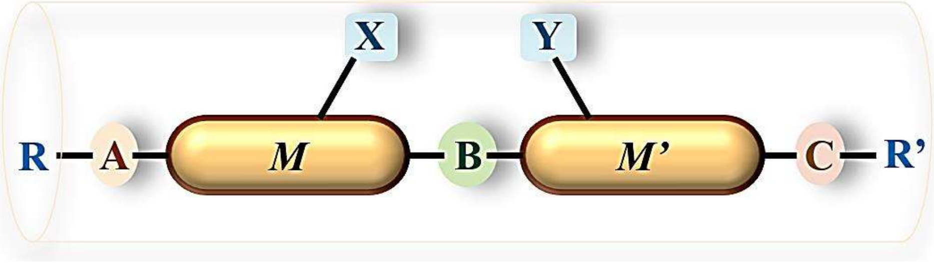


Fig. 1.8: General template for calamitic LC molecules

In the given context, M and M' symbolize core units, which can be aromatic like benzene, naphthalene, biphenyl or alicyclic or heterocyclic. Meanwhile, R and R' represent flexible components, often comprising normal or branched alkyl groups. In molecular structures, A and C serve as connecting groups linking the terminal chains to the core units, while X and Y typically denote small lateral substituents like halogen -X (-F, -Cl, -Br), methyl (-CH_3), nitro (-NO_2), methoxy (-OCH_3), cyano (-CN) etc. B serves as a linking group to the core units which can be azo, azomethine, ester, ether, flexible chain, etc. The mesophase morphology and physical properties of calamitic LCs are notably influenced by their composition, encompassing the central core, linking groups, and lateral substituents. This composition exerts a significant impact on the structure and characteristics of the liquid crystal phases.[28,29]

1.7 Discotic Liquid Crystals

In 1977, at the Raman Research Institute (RRI, India), S. Chandrasekhar and his team achieved a significant breakthrough by observing the initial occurrence of thermotropic mesomorphism in pure, single-component disc-shaped systems. Their study focused on investigating mesomorphism in benzene hexa-n-alkanoates[30], characterized by their simple, disk-like molecular structure, through innovative design and synthesis approaches. Through thermodynamic and optical investigations, they validated the formation of a new class of liquid crystals. These materials were distinguished by molecules arranging themselves in stacked columns, forming a 2D hexagonal structure. Discotic liquid crystals typically feature a central discotic core with flexible saturated chains comprising different methylene units (**Fig. 1.9**). Mesomorphism in discotic liquid crystals arises from:

- The promotion of crystalline properties arises from the interaction among conjugated discotic cores.
- The introduction of liquid characteristics is attributed to the presence of saturated flexible alkyl chains.

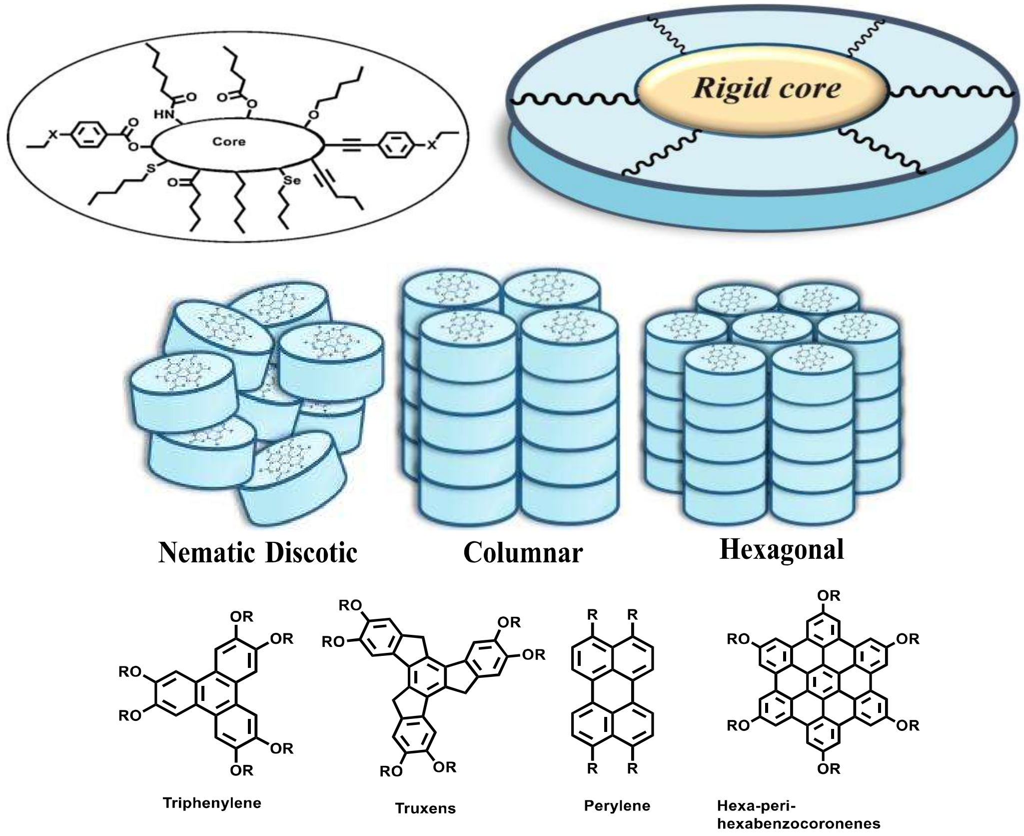


Fig. 1.9: General template for discotic LCs and Different types of discotic LCs

Molecules with discotic arrangement, naturally assemble into one-dimensional columns, facilitating convenient alignment and inherent self-repair capabilities. This unique arrangement allows for the seamless correction of structural flaws, distinguishing it from crystalline materials. By tailoring the shape, size, and characteristics of the central core and attached side chains, compounds with diverse abilities to self-organize into various mesophase morphologies can be created.[31,32] Disk-shaped molecules primarily categorized into four types of mesophases (i) nematic, (ii) smectic, (iii) columnar, and (iv) cubic.[33]

1.8 Bent-Core Liquid Crystals

Molecular structures with a bent or banana-like shape introduce a distinctive category of thermotropic liquid crystals. These compounds can manifest traditional nematic and/or smectic phases, along with distinct smectic-like phases denoted as "B" phases. The B phases are assigned numerical designations based on the order of their discovery, spanning from B1 to the latest B8. Their molecular structure typically consists of an angular central core, along with two linear rigid cores and terminal chains (**Fig. 1.10**).

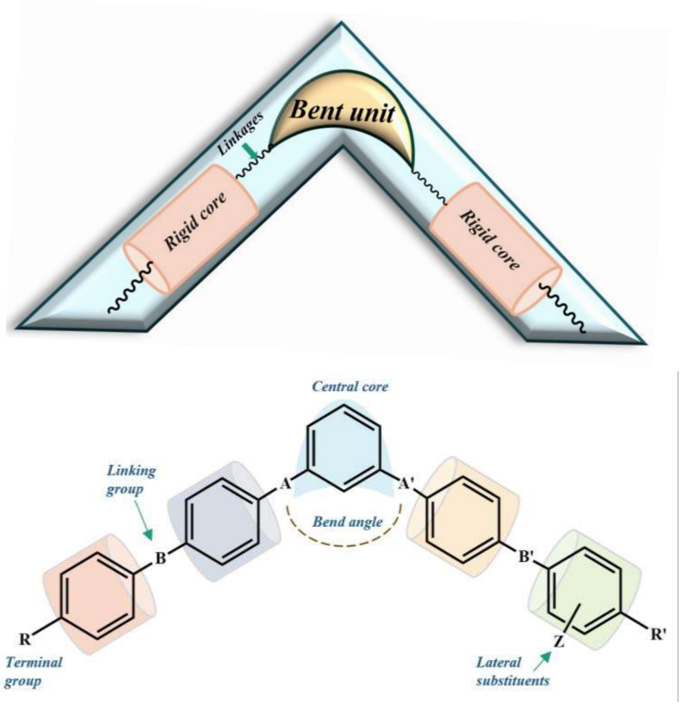


Fig. 1.10: General template for bent-core LC compounds

The curvature found in the central region of banana-shaped compounds decreases rotational disorder along their longitudinal axes, thus promoting organized packing within layers. The organized packing encourages polar alignment parallel to the smectic layers. Adjustments in layer arrangements to prevent macroscopic polarization give rise to novel mesophase morphologies. Bent-core molecules serve as leading instances demonstrating the possibility of antiferroelectric switching with significant spontaneous polarization in a liquid crystal phase composed of non-chiral materials. This advancement highlights the importance of bent-core liquid crystals in broadening our comprehension of liquid crystal behaviour and their possible applications.[34,35]

❖ Different Types of Thermotropic Mesophases

1.9 Smectic Phase (Sm):

The term "smectic" comes from the Greek word "smēktikos," meaning "capable of being smeared," which reflects the slippery nature of these materials. The smectic phase displays high order with both short-range positional and orientational order of rod-like molecules, distinguishing it from the nematic phase which only has orientational order. The smectic phase is denoted by the symbol "Sm". Smectic typically forms at lower temperatures than nematic. In the smectic mesophase, molecules arrange in layers with distinct interlayer spacing. While lacking uniform spacing within layers like crystals, these layers can smoothly glide, granting the phase its fluidity. This fluidity arises from weak interlayer attractions compared to lateral forces between molecules, resulting in higher viscosity than the nematic phase. Various classes of smectic mesophases have been identified, distinguished by differences in molecular arrangements within and between layers. Some liquid crystalline molecules exhibit multiple smectic mesophases, with up to twelve classes recognized depending on the director's orientation relative to the layers and the degree of in-plane and inter-layer correlations. These phases are typically labelled with letters of the alphabet, such as SmA, SmC, SmF, SmI, and SmB.[36–38]

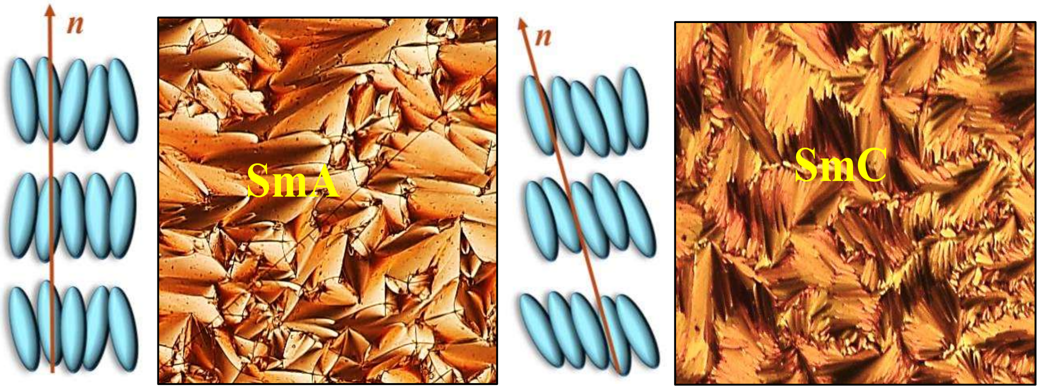


Fig. 1.11: Orientation of the molecules in Smectic A and Smectic C phase and its respective textures

In the SmA phase, molecules align parallel to each other and arranged upright in each layer, with their long axes perpendicular to the layer planes. While there's no positional correlation between layers, molecules within each layer exhibit short-range positional ordering. Upon cooling from the SmA phase, a more ordered SmC phase is obtained, where molecules are similarly arranged within layers but are tilted with respect to the layer normal (**Fig. 1.11**). Smectic phases often form "batonnets" when cooling from the isotropic liquid phase, appearing as elongated birefringent particles. These particles coalesce into a focal conic structure, maintaining their thickness even as the layers become distorted in the melt. The distortions in layer arrangement give rise to the characteristic optical properties of the smectic phase, observable as a fan-line appearance under polarized light microscopy.[39] Typical textures formed by smectic phases are depicted in **Fig. 1.11**.

1.10 Nematic Phase (N)

The term "nematic" originates from the Greek word "*nema*", which translates to thread-like. In the nematic phase, molecules display significant long-range alignment along their long axes without having a specific long-range positional arrangement. Within this phase, molecules tend to align parallel or nearly parallel to each other. However, unlike in the smectic phase, molecules in the nematic phase do not demonstrate layer flow due to the lower degree of order, resembling the isotropic liquid state. This phase is symbolized by 'N'.[40,41]

When certain nematogens are heated and observed under polarized light using a microscope, they exhibit thread-like textures emerge due to defects which occurs between the ordered regions. In the nematic phase, the predominant average alignment of the molecules' long axes, indicated by a prominent arrow (**Fig. 1.12**), is referred to as the "director (*n*)." The fluidic nature of the mesophase stems from the molecules' ability to move past each other along their long axes.[42]

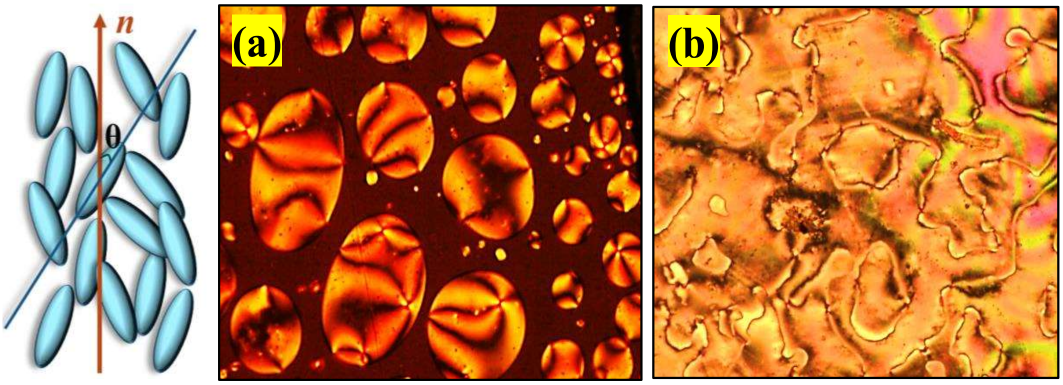


Fig. 1.12: Orientation of the molecules in nematic phase along its director (*n*) and its respective textures (a) nematic droplets (b) schlieren structures

The idealized equilibrium configuration of nematic LCs is seldom observed optically. Various typical textures of nematic phases are depicted in Fig. 1.12. The first texture (a) represents a nematic droplet, while the second texture (b) depicts thread-like schlieren structures, which are notable structural perturbations from which nematics derive their name.

1.11 Chiral Nematic Phases (N*) (Cholesterics)

Originally discovered by botanist F. Reinitzer in 1888 in cholesterol derivatives, the phase now recognized as the chiral nematic phase (N*) is commonly referred to as the cholesteric liquid crystal phase.[14] This phase was historically referred to as the "cholesteric phase" due to its discovery in cholesterol-based materials. However, it's important to note that today, the N* phase can be exhibited by various chiral materials unrelated to cholesterol. Therefore, a more appropriate term for this phase is the chiral nematic liquid crystal, where "chiral" denotes a twisted structure.[43] Similarly, introducing optically active molecules, even if they are not liquid crystalline, into a nematic structure can transform it into a cholesteric liquid crystal. In a cholesteric liquid crystal, the helical macrostructure is formed by a chiral dopant inducing chirality in otherwise achiral molecules. This asymmetry causes the director, the average molecular orientation, to adopt a twisted configuration throughout the medium (**Fig. 1.13**).

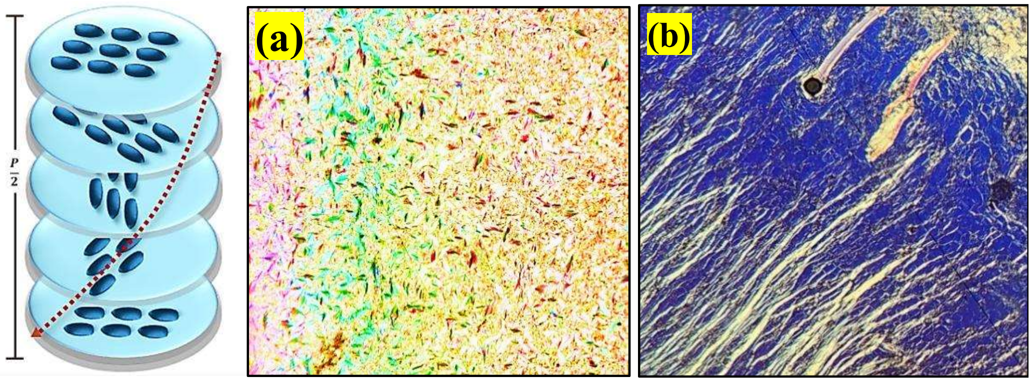


Fig. 1.13: Orientation of the molecules in nematic phase along its director (*n*) and its respective textures (a) Chiral nematic phase (b) schlieren structures

The gradual rotation of the director along a single axis, results in a macroscopic helix, with local ordering resembling that of the nematic phase. The pitch of this helix, varying with temperature, determines the length along the helix where the director completes a full 360° rotation. The spiral arrangement of the chiral nematic phase selectively reflects light, resulting in fascinating optical characteristics. In some liquid crystal systems, when the helical pitch length aligns with the wavelength of visible light, specific colours are preferentially reflected, and due to the temperature-dependent nature of the pitch length, the reflected colour alters accordingly. This characteristic is exploited in various commercial applications.[44]

1.12 Criteria for showing LC property

The ability of a compound to exhibit a mesophase depends not only on its molecular shape but also on factors such as the position and strength of polar groups, overall polarizability, and the presence of chiral centres.

Key factors influencing liquid crystallinity are given below:

- **Rigid Core:** Liquid crystalline compounds often feature aromatic, alicyclic or heterocyclic rings as rigid cores, providing molecular rigidity and facilitating stretching. Phenyl rings, biphenyl, terphenyl, cyclohexane, salicylaldimine, diphenylbutadiene, and complex structures like cholesterol.[45]
- **Linking Group:** Linking groups connect stiff cores, enhancing mesomorphic characteristics and thermal stability. Groups like ester, chalcone, azo, azomethine, ether, amide, chalcone, stilbene, and tolane etc. are commonly used in liquid crystalline materials.
- **Terminal Group:** Terminal substituents significantly influence properties and behaviour, with choices like cyano, nitro, alkyl, alkoxy, perfluoroalkoxy, halogen, amino, hydroxy, etc. allowing tailored properties for specific applications.
- **Lateral Group:** Substitutions attached to aromatic rings or stiff cores affect material properties, influencing dimensions and clearing temperature. Each lateral substitution increases breadth, altering the length-to-breadth ratio and often lowering the clearing temperature, thereby influencing mesomorphic behaviour. [46]

1.13 Characterization of Liquid Crystals

Identification of liquid crystals through experimental methods is a crucial aspect of research in this field. Among the various techniques available, optical polarizing microscopy, differential scanning calorimetry (DSC), and X-ray diffraction (XRD) studies are commonly employed (**Fig. 1.14**). These experimental methods play complementary roles in identifying and characterizing liquid crystals.

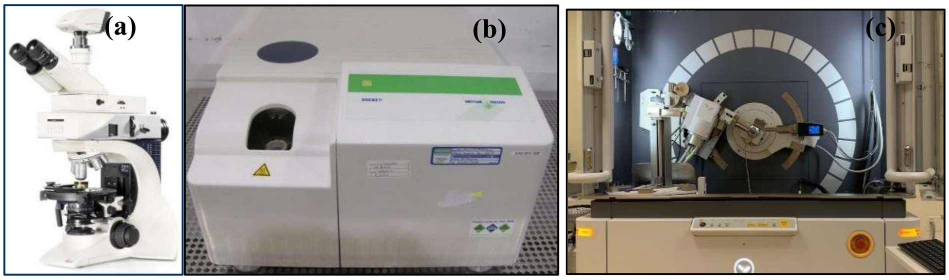


Fig. 1.14: Various instruments for characterizing Mesomorphic properties: (a) Polarized Optical Microscopy (POM), (b) Differential Scanning Calorimetry (DSC), and (c) X-ray Diffraction (XRD).

1.13.1 Polarizing Optical Microscope (POM)

The optical polarizing microscope with a hot stage is a valuable tool for identifying textures of liquid crystals at specific temperatures. To prepare samples for examination under the microscope, sample is mounted individually on slide and after placing a coverslip on top with light pressure. The procedure involves gradually heating the sample until it becomes a clear liquid, and allowing it to cool.[47] By gently warming the sample with a controlled heating rate, changes in texture can be observed over a range of temperatures.

1.13.2 Differential Scanning Calorimetry (DSC)

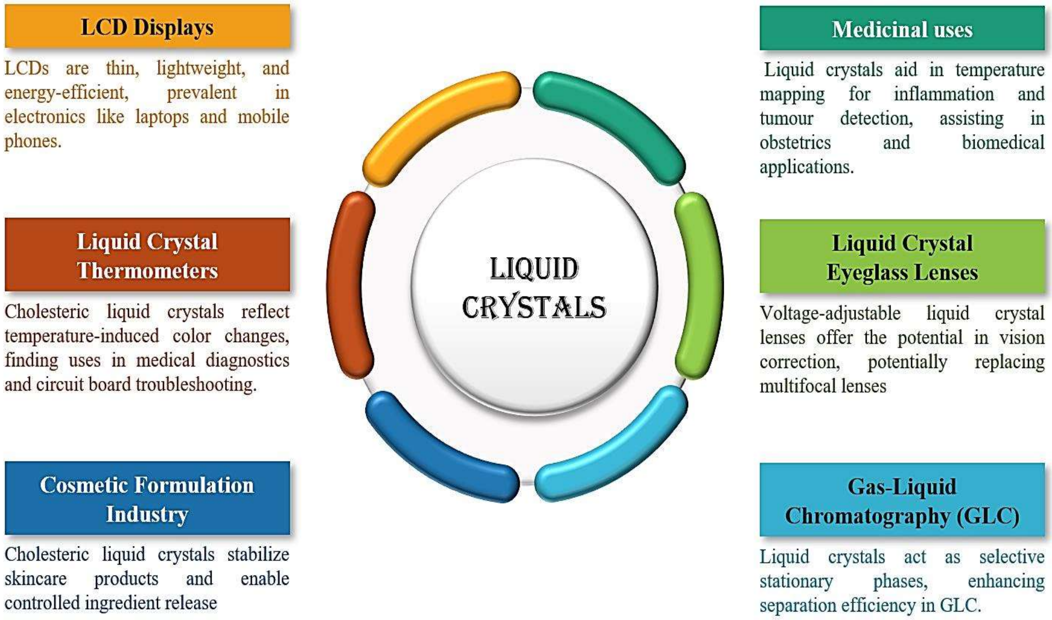
DSC is a thermal analytical method used to determine the transition temperatures of components. DSC enables rapid identification of transitions and calculation of enthalpy changes for all phases present in a mesomorphic compound.[48]

1.13.3 X-ray Diffraction Study (XRD)

XRD investigation is employed to determine the molecular arrangement, positional order, orientation, and translational order of molecules in liquid crystalline materials. It utilizes X-ray diffraction patterns to assess the phase of the material based on the value of theta (θ). XRD is a powerful technique for gaining insights into the structural properties of liquid crystals and understanding their behaviour.[49]

1.14 Applications of Liquid Crystals

The sensitivity of LCs to minute changes in temperature, electromagnetic radiation, and mechanical stress renders them indispensable in numerous applications.[50,51] (**Fig. 1.15**)



LCD Displays

LCDs are thin, lightweight, and energy-efficient, prevalent in electronics like laptops and mobile phones.

Liquid Crystal Thermometers

Cholesteric liquid crystals reflect temperature-induced color changes, finding uses in medical diagnostics and circuit board troubleshooting.

Cosmetic Formulation Industry

Cholesteric liquid crystals stabilize skincare products and enable controlled ingredient release

Medicinal uses

Liquid crystals aid in temperature mapping for inflammation and tumour detection, assisting in obstetrics and biomedical applications.

Liquid Crystal Eyeglass Lenses

Voltage-adjustable liquid crystal lenses offer the potential in vision correction, potentially replacing multifocal lenses

Gas-Liquid Chromatography (GLC)

Liquid crystals act as selective stationary phases, enhancing separation efficiency in GLC.

Fig. 1.15: Different Applications of Liquid Crystals

Some notable applications include:

- Liquid Crystal Thermometers
- LCD Displays
- Cosmetic Formulations
- Medicinal Uses
- Solvents in Spectroscopy and Chemical Reactions
- Gas-Liquid Chromatography (GLC)
- Liquid Crystal Eyeglass Lenses
- Liquid Crystal Polymers (LCP) Applications

1.15 Liquid Crystal Oligomers

In the realm of liquid crystals (LCs), the molecular arrangements play a crucial role in determining their properties and behaviour. Among these arrangements, oligomers and dimers hold significant importance.

Oligomers, consisting of short molecular chains with a few monomer units, occupy a unique position between monomers and polymers. Despite their smaller size, oligomers can exhibit many characteristics similar to polymers, often with enhanced strength and durability. In the context of liquid crystals, oligomers serve as fundamental building blocks for the creation of liquid crystal polymers (LCPs). These LCPs find widespread use in technologies like liquid crystal displays (LCDs) and electrical devices due to their combination of liquid crystalline and polymeric properties. Within liquid crystal formulations, oligomers function as mesogens, molecules responsible for imparting ordered structure to the liquid crystal. Through the careful selection of oligomers based on their size, shape, and chemical composition, researchers can tailor the parameters of the liquid crystal, including viscosity and melting point, to suit specific applications.

Dimers, on the other hand, represent pairs of molecules joined by weak attractive interactions that form liquid crystals. These dimers play essential roles in both nematic and smectic liquid crystals. In nematic liquid crystals, dimers typically consist of long, rod-like molecules that align parallel to each other within columns held together by weak van der Waals interactions. This alignment allows dimers to freely spin along their long axis, facilitating the flow and shape alteration of the liquid crystal. Dimers can vary in their molecular geometries, with even- and odd-membered dimers exhibiting differences in behaviour. Liquid crystal dimers, specifically, consist of two mesogenic groups joined by a flexible spacer. The arrangement of these dimers significantly influences the smectic behaviour of the liquid crystal, with bent dimers exhibiting distinct characteristics compared to their linear counterparts.

Understanding the roles and characteristics of oligomers and dimers in liquid crystal formulations is crucial for designing advanced materials with tailored properties for various applications. Researchers continue to explore novel oligomer and dimer structures to unlock new possibilities in liquid crystal technology, paving the way for advancements in displays, electronics, and beyond.

1.15.1 Liquid crystal dimers

A. Griffin and T. Britt pioneered the synthesis of materials composed of molecules featuring two mesogenic units linked by a polymethylene chain, displaying liquid crystalline behaviour.[52] These molecules, termed twins or bimesogens, consist of a highly flexible core and a semi-rigid core with anisometric properties.[53]

Researchers have been intrigued by dimers for several reasons:

i. The transition properties of liquid crystalline materials containing dimers rely on the parity properties of mesogens.
ii. Traditional low molar mass liquid crystals feature a single mesogenic group, posing challenges to our current understanding of self-assembly in condensed phases.
iii. The transitional properties of dimers are influenced by the length and parity of the terminal and mesogenic linking flexible spacer, resembling observations made for semi-flexible main chain polymers.

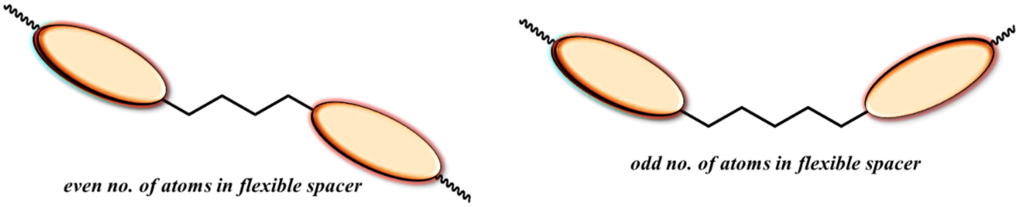


Fig. 1.16: Odd-even effect in the liquid crystal dimers

The behaviour disparity between odd and even spacer dimers in liquid crystals can be attributed to their molecular shape. In odd dimers, the mesogenic groups are inclined, while in even dimers, they are antiparallel when the spacers are in an all-trans conformation (**Fig. 1.16**). This difference affects their compatibility with the nematic phase molecular organization. Even dimers, with their linear structures, align well with the nematic phase, leading to larger transitional entropy. However, they behave akin to monomers due to their linear structure. Odd dimers, with bent structures, exhibit weaker transitions and behave more like monomers. The flexibility of the spacer allows for a range of conformations, but the relative proportion of linear to bent conformers differs between odd and even dimers. This conformational distribution affects the orientational order of the nematic phase.[54,55]

Types of Liquid Crystal dimers:

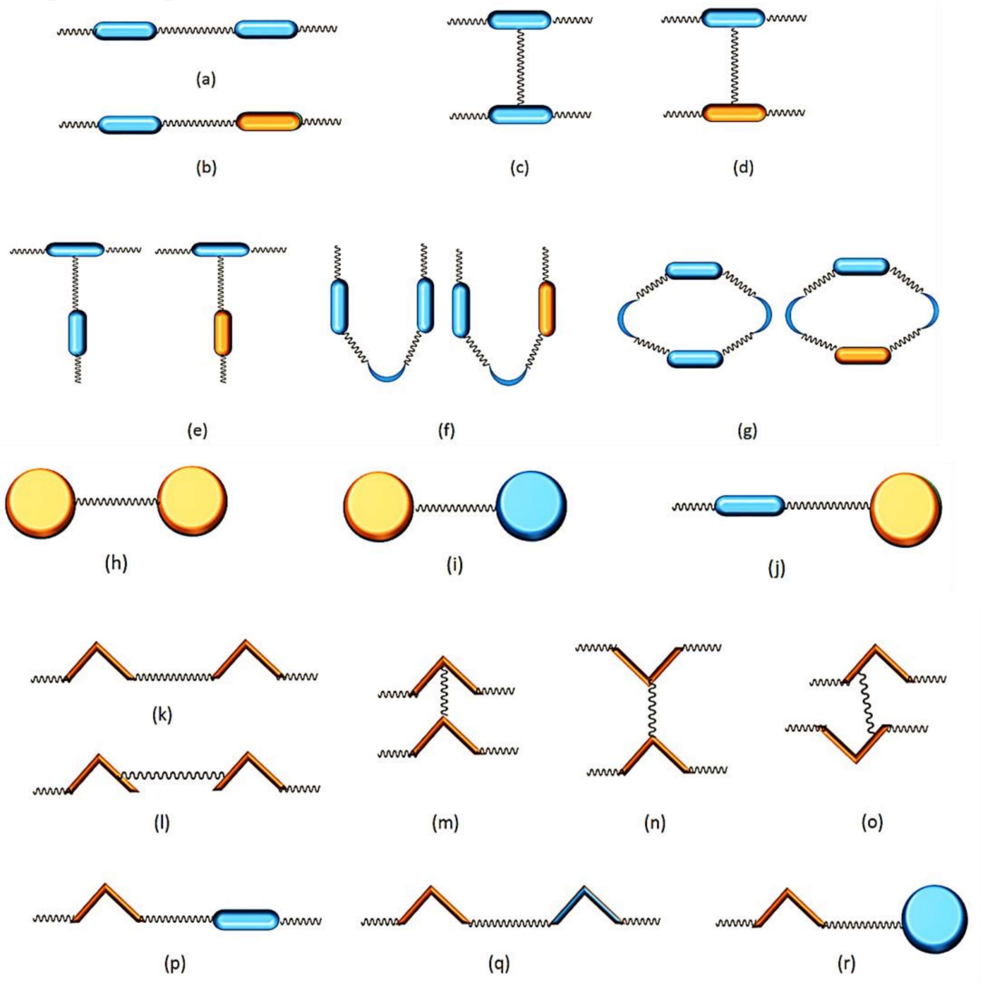


Fig. 1.17: Schematic representation of various types of dimers (a) Symmetric linear calamitic LC dimers; (b) Non-symmetric linear calamitic LC dimers; (c) Symmetric H-shaped calamitic LC dimers; (d) Non- symmetric H-shaped calamitic LC dimers; (e) T-shaped, (f) U-shaped, (g) O-shaped symmetric and non-symmetric LC dimers; (h) Symmetric discotic LC dimers; (i) Non-symmetric discotic LC dimers; (j) Calamitic-Discotic LC dimer (k) end to end connected bent core dimers (l) lateral-lateral connected bent core dimers (m, n) apex apex connected bent core dimers (o) side by side connected bent core dimers (p) Non-symmetric calamitic-bent dimer (q) Non symmetric bent core dimers (r) Non symmetric discotic-bent dimer

Liquid crystalline dimers encompass a diverse array of molecular architectures (**Fig. 1.17**), each characterized by unique mesophase behaviour and optical properties. Here are several types of liquid crystalline dimers:

1. **Linear Calamitic Dimers**:
- Symmetric: Two rod-shaped mesogens connected via a flexible spacer.[56]
- Non-symmetric: Asymmetric arrangement of rod-shaped mesogens and spacers.[57]
2. **H-shaped Calamitic Dimers**:
- Symmetric: Two rod-shaped mesogens connected laterally via a flexible spacer.[58]
- Non-symmetric: Asymmetric lateral connection between rod-shaped mesogens.
3. **T-shaped Calamitic Dimers**:
- Symmetric: Two rod-shaped mesogens connected in a transverse fashion via a flexible spacer.
- Non-symmetric: Asymmetric transverse connection between rod-shaped mesogens.[59]
4. **U-shaped Calamitic Dimers**:
- Symmetric: Two rod-shaped mesogens forming a U-shape connected by a semiflexible spacer.
- Non-symmetric: Asymmetric U-shaped configuration of calamatic mesogens.[60]
5. **O-shaped Calamitic Dimers**:
- Symmetric: Two rod-shaped mesogens forming a cyclic structure.
- Non-symmetric: Asymmetric cyclic arrangement of rod-shaped mesogens.[61]
6. **Discotic Dimers**:
- Symmetric: Two disc-type mesogens connected via a flexible spacer.
- Non-symmetric: Asymmetric arrangement of discotic mesogens and spacers.[62]
7. **Calamitic-Discotic Dimers**: Combination of rod-like and discotic mesogens connected via a flexible spacer.[63]
8. **Bent Core Dimers**:
- End-to-end connected; Lateral-lateral connected; Apex-apex connected; Side-by-side connected.
9. **Calamitic-Bent Dimer**: Combination of rod-shaped and bent-core mesogens connected via a flexible spacer.[64]
10. **Discotic-Bent Dimer**: Combination of discotic and bent-core mesogens connected via a flexible spacer.

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