Chapter-1

General introduction
to liquid crystals
Introduction

1.1. Liquid Crystals
Liquid crystals (LCs) represent a unique state of matter having dual properties of both crystals (order) and liquid (fluidity and disorder) [1-4]. The combination of these properties is of importance for the application of liquid crystalline materials in different areas such as from LC displays technology to biomedical application. The liquid crystal display technologies have significantly changed our daily life because they have found their ways in many products of utility that we use today from tiny mobile display to giant display screen. Moreover, LCs displays are important due to light and low energy consuming organic electronic materials. The other applications of LC materials, in LC polymers, for example, can form high strength fibers (e.g. Kevlar). Chiral LCs is well known as temperature sensors, polarized light reflectors and photonic band-gap materials. Ferroelectric and pyroelectric liquid crystals are useful as light modulators, sensor applications, etc. In the 21st century, major research efforts are presently being made in utilizing the liquid crystalline materials for optical data storage, volumetric and holographic storage, self-assembled semiconducting organic materials for photovoltaic cells, organic transistors and organic light emitting diods (OLEDs), polarized light emitting OLEDs for security labels, electron conducting materials, direction dependent ion conducting materials [5-6]. Recently, self-assembled and self-organized systems of lyotropic liquid crystals (viz; amphiphilic LC) added a new dimension due to their biomedical applications [7-8]. The fundamental understanding of the basic structure-property relationship is essential for their utility in the development of new display devices as well as in biomedical applications. Hence the development of new LC materials is the need of the hour.

What are liquid Crystals: Molecules in crystal lattice possess both orientational and positional order. A perfect crystal shows anisotropic behavior i.e. the physical properties depend on the direction in which they are measured. When a crystal is heated, the orientational and positional orders are retained while the heating effect increases the vibrational energy of the
concerned molecules. On further heating the compound attains its melting point. At this point, all the long-range order is suddenly lost and the solid crystal is slowly transformed into anisotropic liquid state. This simple phenomenon is not possessed by all compounds. Due to the presence of some special structural features the compounds of this class exhibit multi-step melting process in between the normal crystalline state and liquid state. They possess one or more intermediate steps between the ordered crystalline and disordered liquid state. Such intermediate state is referred as “mesophase”. In general, the molecules with rod-like shape (also known as calamitic molecules), disc-like shape (also called discotic molecules) and banana shape (also called bent core liquid crystals) show typical liquid crystalline behavior, although many exceptions are there [9-12]. When a crystal consisting of such molecules are heated, at the melting temperature, the molecules lose their 3D positional order, but not all they orientational order. Such phase with partial orientational order is referred as “liquid crystalline state” and compounds forming such liquid crystalline state are termed as “liquid crystals” (or mesomorphic compounds or mesogens) [1-2]. LCs has been defined as “orientationally ordered” liquids or “positionally disordered” crystals [13] and combine properties of both the crystalline state (e.g. optical and electrical anisotropy) and the liquid state (molecular mobility and fluidity).

1.2. Brief history of thermotropic liquid crystals
The discovery of thermotropic liquid crystals was attributed to an Austrian botanist Friedrich Reinitzer about 125 years ago. In 1888, he discovered double melting points when cholesteryl benzoate [14] was heated to isotropic phase. Cholesteryl benzoate (1) was to found to melt at 145.5 °C from solid to cloudy or opaque liquid followed by the transformation of opaque liquid to isotropic clear liquid at another temperature, 178.5 °C.

![Figure 1.1: Chemical structure of cholesteryl benzoate.](image)
This strange unusual “double melting” phenomenon and colour behavior of cholesteryl benzoate was explained by the German physicist Otto Lehmann [15] by optical textures using polarizing optical microscopy. He first referred them as “soft crystals” and later he coined the term “crystalline fluids”. The opaque phase was a uniform phase of matter exhibiting dual properties of both liquids and solids, and later coined them as “liquid crystals”.

In the beginning of twentieth century Daniel Vorlander, a Professor of Chemistry at the University of Halle started systematic synthetic work in order to find out structure-mesophase relationship and by mid of twentieth century almost 1100 liquid crystalline compounds were prepared in his laboratory. Most of the compounds synthesized in his laboratory have rod-like shape and asserted that only rod-like molecules exhibit liquid crystalline phases. In 1963, Fergason reported [16] the first practical application of cholesteric liquid crystals as temperature indicators in the non-destructive testing of materials and in medical diagnostics applications. In 1968, Heilmeier et al. [17] reported the application of room temperature liquid crystalline material (2) with negative dielectric anisotropy in display devices.

![Figure 1.2](image1.png)

**Figure 1.2:** Chemical structure of N-(4-methoxybenzylidene)-4-methyl aniline.

In 1975, Meyer predicted [18] ferroelectricity in chiral smectic C phases exhibit by chiral Schiff base (3).

![Figure 1.3](image2.png)

**Figure 1.3:** Chemical structure of N-(4-n-decyloxybenzylidene)-2-methylbutyl-4′-aminocinnamate.
In 1977, Chandrasekhar et al. reported [19] the discotic mesomorphism in compounds with disc-like molecular shape (4). The phases exhibited by disc shaped molecules are different from the rod shaped molecules.

Figure 1.4: Chemical structure of hexa ester of 1,2,3,4,5,6-hexahydroxybenzene.

In 1996, Niori et al. reported the polar order in achiral bent-core molecules (5) [20] exhibiting liquid crystalline phases followed by supramolecular chirality in similar bent core compounds.

Figure 1.5: Chemical structure of 1,3-phenylene bis[4-(4-octyloxyphenyl iminomethyl) benzoate.

1.3 Classification of liquid crystals

The liquid crystals can be classified in different ways:

(i) Depending on the molar mass of the constituent molecules
   a) Low molar mass liquid crystals: monomeric and oligomeric liquid crystals.
   b) High molar mass liquid crystals: polymeric liquid crystals.

(ii) Depending on how the liquid crystalline phase has been achieved
   a) By adding solvent: lyotropic liquid crystals.
   b) By varying the temperature: thermotropic liquid crystals.

However, the liquid crystals had been widely classified as
(a) Thermotropic liquid crystals: Mesophase formation is temperature dependent,
(b) Lyotropic liquid crystals: Mesophase formation is solvent and concentration dependent. If a compound displays both thermotropic and lyotropic liquid crystalline phases then it is called *amphitropic* liquid crystal. On the basis of geometrical shape of molecule, thermotropic liquid crystal is further classified into

a) Rod-like: *Calamitic liquid crystals*
b) Disc-like: *Discotic liquid crystals*
c) Bent core: *Banana shaped or V-shaped liquid crystals*

### 1.3.1 Calamitic liquid crystals:

The word calamitic was derived from the Greek, *colomos* means rod. The calamitic molecules are rod shaped molecules. These molecules possess an elongated shape i.e. the molecular length (l) is significantly greater than the molecular breadth (b) as presented figure 1.6.

![Figure 1.6: Representation of Calamitic molecule (l>>b).](image)

This class of liquid crystalline compounds is highly investigated and most important with respect to practical applications. The majority of thermotropic liquid crystals are composed of rod-like molecules.

In 1922, George Friedel [21-23] a French mineralogist and crystallographer proposed a classification scheme based on the molecular structural arrangement where he named different liquid crystal systems as nematic, smectic and cholesteric.

### (a) Nematic Phase:

The word “nematic” is derived from the Greek word for “*thread*” as thread like textures were observed under the polarizing microscope as presented in figure 1.7a. The nematic phase has a high degree of long-range orientational
order of the molecules, but no long range positional order. This is the least ordered mesophase and closest to the isotropic liquid state as shown in figure 1.7b.

**Figure 1.7a:** Thread like texture of nematic phase.

**Figure 1.7b:** Model structure of nematic Phase.

**b) Smectic Phases:**

The word “smectic” is derived from the Greek word means “soap”. In addition to the orientational order, the molecules are arranged in layers to possess short range positional order and then such a phase is called as smectic phase. On the basis of different molecular arrangements within and between the layers, smectic mesophases are of different types have been defined as SmA, SmB, SmC, SmF, SmI etc. However, SmA and SmC mesophases are commonly found in calamitic liquid crystals. In SmA phase the molecules form layers with their long molecular axes and hence the director parallel to the layer normal as presented in figure 1.8a and under polarizing optical microscopy, SmA phase are represented as batonnets texture as presented in figure 1.8b.

**Figure 1.8a:** Model structure of SmA phase.

**Figure 1.8b:** Batonnets texture of SmA phase.
The SmC phase has the same layer structure of the SmA, but the molecules are tilted with respect to the layer normal as presented in figure 1.9a and under polarizing optical microscope SmC texture show schlieren texture as presented in figure 1.9b.

1.3.2 Discotic liquid crystals:
Discotic liquid crystals are composed of disk-like molecules. Billard et al. [24] proposed the word "discotic" to describe the mesomorphism exhibited by disk-like molecules. The discotic molecules exhibit two distinct classes of phases, the discotic nematic and the columnar. The nematic phase formed by disk-like molecules, designated by the symbol \( N_D \) is a fluid phase showing schlieren textures similar to those of the classical nematic phase of rod-like molecules. The arrangement of discotic molecule in a discotic nematic phase is presented in figure 1.10a and optical texture is presented in figure 1.10b.
The discotic molecules assemble and stack in a column to exhibit a discotic or columnar liquid crystalline phase. The molecular arrangement of the discotic molecules in a columnar phase is presented in figure 1.11a and the optical texture is presented in figure 1.11b.

1.3.3 Bent core liquid crystals:
Bent-core or banana-shaped liquid crystals refer to new subfield of liquid crystals [25] whose molecular shapes resemble the bananas or a bow with a bend at the centre of the molecules. The bend in the rigid cores of the banana shaped liquid crystalline compounds leads to a reduction of the rotational disorder of the molecules about their long axes. The reduced symmetry of the rigid segments of such molecules favors smectic packing of the molecules within layers. In order to escape from a macroscopic polarization, the layer structures are modified, and this leads to new mesophase morphologies. Bent core molecules are the first examples of achiral liquid crystal materials which have experimentally shown that antiferroelectric switching with large spontaneous polarization. Majority of the bent-core molecules contain bending unit such as an aromatic 1,3-disubstituted phenyl ring or 2,7-disubstitued naphthalene moiety derivatives. The general structure of the bent core molecules is presented in figure 1.12.
Figure 1.12: General structure of bent core molecule.

The angle between two linking arms ranges from 100° to 140°. The first bent-core liquid crystal was synthesized by Vorlander group in 1923 [26] but the mesogenic properties of the compound were not reported. Even though in 1932, the observation of mesophases in bent-core compounds appeared in literature for the first time [27] the identified nomenclature of banana phases was unknown at that time. After almost 60 years, latter Matsunaga et al. [28-29] reported banana-shaped molecules exhibiting mesomorphism similar to calamitic molecules. In 1996, bent-core molecules have received special attention to scientific community due to pioneering work by Takezoe presentation at an International Liquid Crystal conference at Kent in 1996 [20]. They first reported achiral bent core molecules exhibiting new and intriguing polar mesophases with large spontaneous polarization. In 1997, Clark et al. demonstrated supramolecular chirality [30] in banana phases. The macroscopic chirality is due to appearance of tilt and polar order of some of the banana phases. The generation of macroscopic polar order [31] and chirality motivated great interest and has emerged as a major topic of liquid crystal research [32-35]. The typical bent core molecule exhibit banana phases (B₁-B₉). The physical properties of mesophases of bent core mesogens are distinctly different from that of smectic phases exhibited by calamitic (rod-like)
molecules except layer ordering. Hence most of the research efforts had been focused on the bent-core smectics because nematic phases were meagre.

1.4. Bent core mesogens: Nematic Phases

Bent-core mesogens exhibit the conventional nematic and smectic phases of rod-shaped molecules along with several novel lamellar and columnar phases depending on the bend angle, chemical moieties, and molecular dipoles. The prediction of molecular biaxiality in a bent core mesogen is due to bending angle \( \alpha \) between the rigid molecular frames. Theoretically, occurrence of biaxial nematic phase \( (N_b) \) in the bent core mesogens depends on the bending angle. The bending angle for the appearance of the \( N_b \) phase should occur within a small bending angle range (~1–2\(^\circ\)) close to the tetrahedral angle of 109\(^\circ\) [36-40]. This magnitude of the bending angle can be achieved if a \(-\text{CH}_2-\) group (with a tetrahedral C-atom) is used as the central bent unit [41-43]. Recently, there has been a surge of interest in the nematic phases of banana mesogens at both experimental and theoretical levels. The nematic phase occurring in bent-core systems is more conducive to the formation of the biaxial \( (N_b) \) phase due to the biaxial molecular shape [44-45]. However, the most often used bending unit used in bent core mesogens are 1,3-disubstituted aromatics rings, 2,6-disubstituted pyridine ring, a 2,7-disubstituted naphthalene unit or a 1,3,4-oxadiazole unit having large angle of 120\(^\circ\) or more. A typical bent-core molecule strongly prefers the formation of smectic and modulated smectic phases due to their kink molecular shape and there are relatively few examples of bent-core mesogens with nematic phases. The formation of nematic phases in bent core mesogen having bending angle of 120\(^\circ\) or more did not meet the theoretical requirements of phase biaxiality.

Prasad et al. reported [46] unsymmetrical bent core molecule derived from 2-methyl-3-aminobenzoic acid (table 1.1) exhibiting uniaxial nematic to biaxial nematic phase with other smectic phases.
**Table 1.1:** Chemical structure of bent core compounds exhibiting uniaxial nematic to biaxial nematic phase.

<table>
<thead>
<tr>
<th>R</th>
<th>R'</th>
<th>Phase transition temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OC₈H₁₇</td>
<td>C₁₂H₂₅</td>
<td>Cr 88.6 SmY 103.1 SmX 107.7 SmC 132.5 Nₙ 162.5 Nₜ 189.5 Iso</td>
</tr>
<tr>
<td>C₈H₁₇</td>
<td>C₁₂H₂₅</td>
<td>Cr 82.8 SmY 93.4 SmX 104.3 SmC 118.5 Nₙ 149.0 Nₜ 176.5 Iso</td>
</tr>
</tbody>
</table>

Here, Nₙ = Uniaxial nematic phase, Nₙ = Biaxial nematic phase, SmC = tilted Smectic phase, SmX and SmY = unidentified Smectic phase.

Five-ring bent core compounds derived from 4,6-dichlororesorcinol as a bending unit [47] have also been reported. The polar fluoro- or chloro-substitution at the outer ring with short carbon chain length (n = 3, 5, 6, 8) display either monotropic or enantiotropic nematic phase (N) with lower temperature SmA, SmC and SmCPₐ (antiferroelectric polarized tilted SmC) phases whereas presence of H atom at the outer ring display enantiotropic N phase with lower temperature columnar oblique phase (Col₀b) and SmC phase as presented in table 1.2.
Table 1.2: Influence of outer ring substituents on the phase behaviour of the bent core molecule.

<table>
<thead>
<tr>
<th>n</th>
<th>X</th>
<th>Phase sequence</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>H</td>
<td>Cr-Col_{ob} - N-Iso</td>
</tr>
<tr>
<td>7</td>
<td>H</td>
<td>Cr-Col_{ob} - N-Iso</td>
</tr>
<tr>
<td>8</td>
<td>H</td>
<td>Cr-Col_{ob} - N-Iso</td>
</tr>
<tr>
<td>9</td>
<td>H</td>
<td>Cr-Col_{ob} - N-Iso</td>
</tr>
<tr>
<td>10</td>
<td>H</td>
<td>Cr-Col_{ob} - N-Iso</td>
</tr>
<tr>
<td>12</td>
<td>H</td>
<td>Cr-Col_{ob} - SmC - N-Iso</td>
</tr>
<tr>
<td>3</td>
<td>F</td>
<td>Cr-N-Iso</td>
</tr>
<tr>
<td>8</td>
<td>F</td>
<td>Cr-SmCP_{A} - SmA - N-Iso</td>
</tr>
<tr>
<td>5</td>
<td>Cl</td>
<td>Cr-N-Iso</td>
</tr>
<tr>
<td>6</td>
<td>Cl</td>
<td>Cr-N-Iso</td>
</tr>
<tr>
<td>7</td>
<td>Cl</td>
<td>Cr-N-SmC - Iso</td>
</tr>
<tr>
<td>8</td>
<td>Cl</td>
<td>Cr-N-SmC - SmCP_{A} - Iso</td>
</tr>
</tbody>
</table>

Keith *et al.* reported homologous series of unsymmetrical bent-core mesogens obtained from alkyl substituted 4-cyanoresorcinol bisbenzoates as presented in figure 1.13. The bent core mesogens exhibit wide range of nematic phase (enantiotropic and monotropic), some of them long-term metastable at ambient temperature and without smectic low temperature phases. Short chain compounds exhibits only nematic phases which can be cooled to ambient temperature whereas long chain compounds display SmC-type cybotactic clusters. These cybotactic nematic phases (NcybC) can be regarded as strongly fragmented SmC phases [48].
Francescangeli et al. reported ferroelectric response in a low molar mass bent core nematic material as presented in figure 1.14 and electric field induced biaxiality. The nematic phase exhibited by bent core molecules consists of a conglomerate of nano-sized cybotactic groups featuring short-range SmC-like ordering. Each group exhibits local biaxial and polar (i.e., ferroelectric) ordering due to the cooperative alignment of the molecules with their short axes and electric dipoles parallel to each other. In the absence of an electric field (E), the orientations of the domains are randomly distributed in space and, as a result, the macroscopic polarization Ps averages to zero. Applying electric field above a certain threshold converts this non-polar phase into a polar nematic in which the cybotactic groups are on the average aligned with their dipoles parallel to the applied field over macroscopic volumes. A net bulk polarization is then induced and its direction can be reversed by changing the sign of electric field. Once the polar state has settled, this switching can simply take place through the cooperative rotation of the bent molecules (BM) of each group about the long molecular axis (with the local biaxial order persisting during field reversal) and does not necessarily involve further rotation of the clusters [49].

Kang et al. reported some bent-core mesogens derived from oxadiazole (figure 1.15) exhibiting nematic phase along with other smectic phases. The nematic
phase appears at high temperature and the thermal range of nematic phase is ~ 4 °C [50].

![Chemical structure of unsymmetrical 1,3,4-oxadiazole bent core molecule.](image)

**Figure 1.15:** Chemical structure of unsymmetrical 1,3,4-oxadiazole bent core molecule.

Lee *et al.* reported a homologous series of bent-shaped molecules with a low bent angle of about 60° using a 1,7-naphthalene as a bent core unit, a long side wing in which one phenyl ring is attached to the classical wing via an ester linkage and alkoxy tail groups with numbers of carbons of 4 to 14 (figure 1.16). All the compounds except higher homologue (14) display nematic phase along with polar smectic A and B$_4$ phase. On increasing chain length, nematic phase disappeared and smectic phases appeared.

![Chemical structure of seven ring bent core molecule.](image)

**Figure 1.16:** Chemical structure of seven ring bent core molecule.

Dimitrova *et al.* reported thiadiazole based three ring bent core liquid crystal as presented in figure 1.17 exhibiting high temperature nematic phase figure [51].

![Chemical structure of three ring 1,3,4-thiazole bent core molecule.](image)

**Figure 1.17:** Three ring 1,3,4-thiazole bent core molecule.
Lehmann et al. reported 1,3,4-oxadiazole based bent core mesogen bearing rigid laterally alkyl substituted oligo(phenyleneethinylene) wings as presented in figure 1.18 exhibit monotropic nematic phase [52].

![Five ring 1, 3, 4-oxadiazole based bent core molecule bearing lateral alkoxy chain.](image1.png)

**Figure 1.18:** Five ring 1, 3, 4-oxadiazole based bent core molecule bearing lateral alkoxy chain.

Lehmann et al. reported [53] bent core molecules bases on fluorenone bending unit with hexyloxy chain as lateral substituents display nematic phase as presented in figure 1.19.

![Fluorenone based five ring bent core molecules.](image2.png)

**Figure 1.19:** Fluorenone based five ring bent core molecules.

Bent core mesogens having 1,3,4-oxadiazole ring as a bent core unit possess large bending angle of 135 ° exhibits nematic phase at high temperature along with the unidentified smectic phases. The presence of the different alkyl chain length on the both end of oxadiazole bent core mesogen did not influence transition temperature and phase behavior. The position of lateral fluoro-substituent did not influence the phase sequences whereas the bulky lateral siloxane substituent have substantial influence on the phase sequence and the transition temperature as presented in table 1.3. The introduction of the large silyl group decrease the transition temperature and display monotropic nematic phase.
Table 1.3: Influence of the outer ring substitution of the five ring 1,3,4-oxadiazole bent core molecules.

<table>
<thead>
<tr>
<th>m</th>
<th>n</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
<th>Phase sequence</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>12</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>SmX 182 N 210 Iso</td>
</tr>
<tr>
<td>9</td>
<td>12</td>
<td>F</td>
<td>H</td>
<td>H</td>
<td>SmX 168 N 205 Iso</td>
</tr>
<tr>
<td>9</td>
<td>12</td>
<td>F</td>
<td>F</td>
<td>H</td>
<td>SmX 197 N 210 Iso</td>
</tr>
<tr>
<td>7</td>
<td>7</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>SmX 173 N 222 Iso</td>
</tr>
<tr>
<td>12</td>
<td>12</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>SmX 193 N 204 Iso</td>
</tr>
<tr>
<td>11</td>
<td>8</td>
<td>H</td>
<td>H</td>
<td>-O(CH₂)₄Si(Me)₂OSi(Me)₃</td>
<td>Cr 65 N 63 Iso</td>
</tr>
</tbody>
</table>

Schroder et al. reported piperazine based bent core liquid crystal resembling a hockey stick shaped liquid crystal (figure 1.20) display nematic phase and monotropic unusual nematic phase and columnar phase [54-58].

Lesac et al. reported bent core mesogen having bending core unit dicyclohexylmethanes with bending angle in between 116° and 139° form...
nematic phase at high temperature with nematic columnar and lamella columnar phases as presented in figure 1.21 [42].

\[ X = H \text{ and } OH \]

**Figure 1.21:** Six ring dicyclohexylmethanes containing bent core molecules.

Vaupotic *et al.* reported bent core molecule bearing long lateral alkyl chain and benzyl group connecting the aromatic cores with the bent central unit display nematic phase with smectic A phase as presented in figure 1.22 [59].

\[ \text{Figure 1.22: Seven ring bent core molecule.} \]

Seltmann *et al.* reported non-symmetrically substituted thiadiazole, whose chemical structure is shown in figure 1.23 contains extra hydrocarbon chains attached at similar ring positions on each arm of the core. These lateral chains stabilize the nematic phase over a wide range, encompassing an enantiotropic region (90–154 °C) and a monotropic regime that extends on cooling down to ambient temperature [60].

**Figure 1.23:** Non-symmetrical seven ring 1,3,4-thiadiazole bent core molecule.

Mehl *et al.* reported [61] unsymmetrical four or five rings bent core molecules with bent 1,3,4-oxadiazole ring as bending unit and flanked at the end of the
molecular long axis with alkyl chain exhibit monotropic N phase as presented in table 1.4.

**Table 1.4:** Four ring 1,3,4-oxadiazole bent core molecule.

<table>
<thead>
<tr>
<th>R</th>
<th>Phase sequence</th>
</tr>
</thead>
<tbody>
<tr>
<td>C&lt;sub&gt;11&lt;/sub&gt;H&lt;sub&gt;23&lt;/sub&gt;-O-</td>
<td>Cr-N-Iso</td>
</tr>
<tr>
<td>C&lt;sub&gt;11&lt;/sub&gt;H&lt;sub&gt;22&lt;/sub&gt;O&lt;sub&gt;-&lt;/sub&gt;</td>
<td>Cr-N-Iso</td>
</tr>
</tbody>
</table>

Shanker *et al.* reported [62] first examples of unsymmetrically substituted 1,2,4-oxadiazole based bent-core LC incorporating cyclohexane unit(s) (figure 1.24) exhibiting cybotactic nematic phases composed of SmC-like clusters (N<sub>cybC</sub> phases) or nematic to SmC transition over broad temperature ranges.

**Figure 1.24:** Five ring unsymmetrical 1,2,4-oxadiazole bent core molecule.
Wirth et al. [63] reported lateral polar cyano-substituent in the central phenyl ring and hexyloxy end chain of five ring bent core molecule (figure 1.25) exhibiting N-SmA-SmC-SmCP phase sequence whereas lower and higher homologue did not display N phase.

![Figure 1.25: Five ring cyano substituted bent core molecule.](image)

Weissflog et al. [64-66] also reported five-ring bent-core molecules bearing lateral polar cyano or chloro substituent in the central phenyl ring and ester linking groups exhibiting nematic and polar smectic C phases and are presented in table 1.5.

**Table 1.5:** Influence of length of alkyl chain length and the polar group in the central phenyl ring of a five ring bent core molecule.

<table>
<thead>
<tr>
<th>n</th>
<th>X</th>
<th>Phase sequence</th>
</tr>
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<td>CN</td>
<td>Cr-N-Iso</td>
</tr>
<tr>
<td>7</td>
<td>CN</td>
<td>Cr-Col-N-Iso</td>
</tr>
<tr>
<td>10</td>
<td>CN</td>
<td>Cr-SmCP(^{2}_A)-SmCP(^{2}_A)-N-Iso</td>
</tr>
<tr>
<td>12</td>
<td>CN</td>
<td>Cr-SmCP(^{2}_A)-SmCP(^{2}_A)-SmCP(^{2}_A)-N-Iso</td>
</tr>
<tr>
<td>12, 16</td>
<td>Cl</td>
<td>Cr-SmCP-N-Iso</td>
</tr>
</tbody>
</table>

Tschierske et al. reported [67] five-ring bent-core compounds derived from 4-cynoresorcinol bearing terminal alkyl groups in the molecule. They exhibit nematic phase, with molecular arrangement as in smectic C phase and abbreviated as cybotactic nematic phase, and tilted smectic phases (table 1.6).
Table 1.6: Influence of the terminal alkyl chain length on the cyano-substituted bent core molecule.

<table>
<thead>
<tr>
<th>n</th>
<th>m</th>
<th>Phase sequence</th>
</tr>
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<td>2,3,4,5</td>
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<td>Cr-N-Iso</td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>Cr-NcybC-Iso</td>
</tr>
<tr>
<td>7,8,9</td>
<td>7,8,9</td>
<td>Cr –SmC-CybC-NcybC-Iso</td>
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<td>10, 11, 12, 14</td>
<td>Cr –SmC’-SmC-CybC-NcybC-Iso</td>
</tr>
<tr>
<td>6</td>
<td>12</td>
<td>Cr –SmC-CybC-NcybC-Iso</td>
</tr>
</tbody>
</table>

Sadashiva et al. reported [68] the influence of lateral substituent in six-ring bent-core liquid crystals, bearing polar cyano group at one end and alkyl chain length at other end of the molecule. These compounds exhibited nematic and polar smectic phases (table 1.7).

Table 1.7: Unsymmetrical six-ring bent-core compounds bearing terminal polar cyano group and lateral substituents.

<table>
<thead>
<tr>
<th>n</th>
<th>A</th>
<th>B</th>
<th>Phase Sequence</th>
</tr>
</thead>
<tbody>
<tr>
<td>8, 9</td>
<td>H</td>
<td>H</td>
<td>Cr-SmA&lt;sub&gt;d&lt;/sub&gt;P&lt;sub&gt;A&lt;/sub&gt; -N-Iso</td>
</tr>
<tr>
<td>9, 14</td>
<td>F</td>
<td>H</td>
<td>Cr-SmA&lt;sub&gt;d&lt;/sub&gt;P&lt;sub&gt;A&lt;/sub&gt; -N-Iso</td>
</tr>
<tr>
<td>9, 14</td>
<td>H</td>
<td>F</td>
<td>Cr-SmA&lt;sub&gt;d&lt;/sub&gt;P&lt;sub&gt;A&lt;/sub&gt; -SmA&lt;sub&gt;d&lt;/sub&gt;-N-Iso</td>
</tr>
</tbody>
</table>

Weissflog et al. reported [69] five-ring bent-core molecules derived from 4-chlororesorcinol with a polar fluoro substituent at the outer phenyl rings (figure 1.26) display N-SmCP<sub>A</sub> transition.
Sadashiva et al. [70-71] reported bent-core compounds derived from 2,7-dihydroxynaphthalene having cinnamate moiety in the leg exhibit nematic phase with Colr and SmCP\textsubscript{A} phases depending on the length of the alkyl chain, position of the polar substitution on the lateral position and methyl group at the cinnamate moiety as presented in Table 1.8.

Weissflog et al. [72-73] reported unsymmetrical bent-core compounds where the bending of the molecule is achieved by carbonyl group linked to one of the nitrogen atoms of a central piperazine ring. These compounds exhibit nematic, Sm\textsubscript{A}, SmCP\textsubscript{A} and Colr phases depending upon the outer linking group and the alkyl chain length (Table 1.9).

**Table 1.8:** Symmetrical six ring bent core molecule based on 2,7-dihydroxynaphthalene having cinnamate linkage.

<table>
<thead>
<tr>
<th>n, m</th>
<th>A, B, C</th>
<th>Phase sequence</th>
</tr>
</thead>
<tbody>
<tr>
<td>5,6</td>
<td>H, F, H</td>
<td>Cr-Colr- B\textsubscript{6}-N-Iso</td>
</tr>
<tr>
<td>7,8</td>
<td>H, F, H</td>
<td>Cr-Colr- N-Iso</td>
</tr>
<tr>
<td>9, 10, 12, 14</td>
<td>H, F, H</td>
<td>Cr-Col\textsubscript{ob}-N-Iso</td>
</tr>
<tr>
<td>4-9</td>
<td>H, F, CH\textsubscript{3}</td>
<td>Cr-Colr- N-Iso</td>
</tr>
<tr>
<td>11, 12, 14</td>
<td>H, F, CH\textsubscript{3}</td>
<td>Cr-SmCP\textsubscript{A}- N-Iso</td>
</tr>
<tr>
<td>12</td>
<td>F, H, CH\textsubscript{3}</td>
<td>Cr-Colr- N-Iso</td>
</tr>
<tr>
<td>13,14</td>
<td>F, H, CH\textsubscript{3}</td>
<td>Cr-SmCP\textsubscript{A}- N-Iso</td>
</tr>
<tr>
<td>2-8</td>
<td>H, F, CH\textsubscript{3}</td>
<td>Cr-Colr- N-Iso</td>
</tr>
<tr>
<td>9,10</td>
<td>H, F, CH\textsubscript{3}</td>
<td>Cr-SmCP\textsubscript{A}- N-Iso</td>
</tr>
</tbody>
</table>
Table 1.9: Unsymmetrical piperazine based bent core molecule and their phase sequence.

<table>
<thead>
<tr>
<th>n</th>
<th>L1</th>
<th>L2</th>
<th>Phase sequences</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>-CH=N-</td>
<td>-N=CH-</td>
<td>Cr-SmA-N-Iso</td>
</tr>
<tr>
<td>8</td>
<td>-CH=N-</td>
<td>-N=CH-</td>
<td>Cr-SmCP_A-N-Iso</td>
</tr>
<tr>
<td>4</td>
<td>-COO-</td>
<td>-OOC-</td>
<td>Cr-Nx-N-Iso</td>
</tr>
<tr>
<td>5</td>
<td>-COO-</td>
<td>-OOC-</td>
<td>Cr-Nx-N-Iso</td>
</tr>
<tr>
<td>6</td>
<td>-COO-</td>
<td>-OOC-</td>
<td>Cr-Colr- Nx-N-Iso</td>
</tr>
<tr>
<td>8</td>
<td>-COO-</td>
<td>-OOC-</td>
<td>Cr-SmCP_A-N-Iso</td>
</tr>
</tbody>
</table>

Kang et al. [74] reported five-ring bent-core compounds derived from 4-bromoresorcinol bearing terminal butyloxy and pentyloxy chains (figure 1.27) and exhibit unusual nematic and columnar phases.

Niori et al. [75] reported unsymmetrical six-ring bent-core compounds bearing four chloro substituents (figure 1.28) in lateral positions to exhibit nematic phase only.

Figure 1.27: Chemical structure of bromo-substituted bent core molecule.

Figure 1.28: Chemical structure of unsymmetrical six ring bent core molecule.
Nguyen et al. reported [76] five-ring bent-core compounds with a thioester linkage (figure 1.29) between the outer rings and display nematic phase.

![Figure 1.29:](image) Chemical structure of symmetrical five ring bent core molecule having thioester linking group.

Tschierske et al. reported [77] reported seven-ring bent-core compounds (figure 1.30) exhibiting N-B$_1$ phase variant.

![Figure 1.30:](image) Chemical structure of terphenyl based bent core molecule.

Weissflog et al. reported [78] three-ring bent-core compounds derived from 2-methyl-isothalic acid exhibiting nematic, smectic A and smectic C phases as shown in table 1.10.

<table>
<thead>
<tr>
<th>R</th>
<th>n</th>
<th>Phase sequence</th>
</tr>
</thead>
<tbody>
<tr>
<td>-OC$<em>n$H$</em>{2n+1}$</td>
<td>1-8</td>
<td>Cr-N-Iso</td>
</tr>
<tr>
<td></td>
<td>9-10</td>
<td>Cr-SmC-N-Iso</td>
</tr>
<tr>
<td>-COC$<em>n$H$</em>{2n+1}$</td>
<td>1-6</td>
<td>Cr-N-Iso</td>
</tr>
<tr>
<td>-C$<em>n$H$</em>{2n+1}$</td>
<td>8,9,12</td>
<td>Cr-N-Iso</td>
</tr>
<tr>
<td>-OOC$<em>n$H$</em>{2n+1}$</td>
<td>7</td>
<td>Cr-N-Iso</td>
</tr>
</tbody>
</table>
Novotna et al. [58] reported hockey-stick shaped compounds consisting central naphthalene unit with a methyl substituent at the 2-position and is elongated by two asymmetric arms, containing the ester linkages (figure 1.31). The shorter arm possesses only one and the longer arm has three benzene rings. The nematic–synclinic smectic C–anticlinic smectic C (N–SmCS–SmCA) phase sequence was observed.

![Figure 1.31: Hockey stick shaped bent core molecule.](image)

Lehmann et al. reported [79] bent core molecules derived from benzodithiophene as a bending unit exhibiting monotropic nematic phase as presented in table 1.11.

**Table 1.11:** Chemical structure and phase sequence of bent core molecules derived from benzodithiophene.

<table>
<thead>
<tr>
<th>R</th>
<th>R'</th>
<th>X</th>
<th>Y</th>
<th>Y'</th>
<th>Phase sequence</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆H₁₃</td>
<td>C₆H₁₃</td>
<td>p-CN</td>
<td>H</td>
<td>S</td>
<td>Cr-N-Iso</td>
</tr>
<tr>
<td>C₆H₁₃</td>
<td>C₆H₁₃</td>
<td>m-CN</td>
<td>H</td>
<td>S</td>
<td>Cr-N-Iso</td>
</tr>
<tr>
<td>C₆H₁₃</td>
<td>C₅H₁₁</td>
<td>m-CN</td>
<td>H</td>
<td>S</td>
<td>Cr-N-Iso</td>
</tr>
<tr>
<td>C₆H₁₃</td>
<td>C₆H₁₃</td>
<td>p-CN</td>
<td>S</td>
<td>H</td>
<td>Cr-N-Iso</td>
</tr>
<tr>
<td>C₆H₁₃</td>
<td>C₆H₁₃</td>
<td>m-CN</td>
<td>S</td>
<td>H</td>
<td>Cr-N-Iso</td>
</tr>
</tbody>
</table>
References:


