Our study of examining effect of polar as well as non polar substituents on the central bent core unit as well as on side wings of an Achiral five ring banana shaped molecule. Additionally the observation of chiral phase in a triply bent W-shaped azo based compound will also be detailed.
5.1 Five ring bent-core Liquid Crystals:

From the molecular structural aspect the bent-core liquid crystal based on five phenyl rings connected via different linking groups are well studied [1-6]. This stems from the basic convention that the parent series of bent-core liquid crystals 1,3-phenylene-bis-[4-(4-n-alkylphenyliminomethyl)benzoates] and 1,3-phenylene-bis[4-(4-n-alkyloxyphenyliminomethyl) benzoates] was based on five aromatic benzene rings. Weissflog et al. later modified the basic structure of parent series of compound by introducing substituents at the central core. They observed that generally, the introduction of small substituents into the central 1,3-phenylene ring proved to be a possibility for synthesizing mesogens with novel B phases and for shifting the existence range of B phases to lower temperatures.

In this work the influence of the substituents in the central as well as in the lateral benzene rings in a five ring bent-core liquid crystal as well as the swapping of linking groups between the lateral phenyl rings with the linking groups between the central core and side wings on the mesomorphic behaviour have been studied and the details are presented. The effect of substituents on the bent core liquid crystals was studied in regards to:

1. Effect of polarity, position, size, etc of the substituent’s on the mesomorphic property of synthesized mesogens.
2. Effect of aforementioned parameters on the switching characteristics of the SmCP phase observed in the synthesized mesogens.
3. Effect of the substituents on the induction of chiral nature in the mesophase.

5.2 Effect of Substituents on Bent-core Liquid Crystals:

The liquid crystalline phase behaviour of bent or banana-shaped compounds is dependent upon several factors, namely the size of the molecule and the number of aromatic rings, the position as well as the magnitude of the bent angle, the size, number, position and nature of the substituents, the nature and direction of linkage groups and the length and nature of the terminal alkyl chains. In general, any minor change in these structural elements leads to drastic changes in the phase behaviour. One of the important aspects is the nature and size of the substituent in the central core, which largely influences the mesophase behaviour [7-11]. Several research
groups studied the influence of the lateral substituents on the mesophase behaviour either in the central core or the outer rings [7-17]. However, the introduction of a small substituent into the central 1,3-phenylene ring leads to the possibility of synthesising new mesogens with novel banana phases [14-19]. Moreover, it was found that mesophase behaviour is much more strongly influenced by substituents at the central core than by these at the outer ring [20-23]. The influence of fluorine substitution depending upon its position in banana-shaped molecules revealed several interesting factors. The two important characteristics of a fluorine atom [24-27] are its size and its electro-negativity. The size of the fluorine atom (1.47 Å) which is slightly larger than the hydrogen atom (1.2 Å) contributes towards the steric intermolecular interactions. Further the electro-negativity of the fluorine atom exhibit a strong influence on the intermolecular interactions reflecting in the local dipole moments, electron density of the phenyl ring system, which in turn influences the π–π stacking of phenyl rings, π–H–C electrostatic interactions between phenyl rings, polarisation and polarizability of the entire molecular conjugated system [24-27]. Moreover, the molecular conformation which is dependent upon linking groups being influenced by the steric, stereo-electronic and polar effect reflects in the molecular conformation and minimisation of rotational energy of these molecules. In fact, the bulky and electronegative 4-chloro substitution in bent shaped molecules influenced the mesomorphism not only by a decrease in the clearing temperatures and mesomorphic range but also suppressed the B3 and B4 phases [15]. Similarly the 4-cyano substitution leads to the appearance of calamitic phases (smectic A (SmA) and smectic C (SmC)) with suppression of B3 and B4 phases and enhanced B2 phase [17]. Hence, the substitution with a highly polar substituent, particularly F on the central 1,3-phenylene core, is of special interest owing to its distinct influence on the properties of bent core mesogens. The majority of banana-shaped liquid crystals usually comprise 1,3-phenylene-bis-benzoates incorporating at least one Schiff base unit [14-17, 28-32] because of the ease of synthesis and promesogenic-promoting character of this particular linkage. However, the important limitations of the compounds possessing the imine linkage are thermal, hydrolytic and photochemical stability. These limitations can be addressed with an ortho hydroxyl group to imine linkage which stabilises the compound. Hence, as part of our work on substituted banana-shaped mesogens with an ester–imine combination, we report a new class of banana-shaped mesogens with a fluoro substituent on the central core.
and a lateral hydroxyl group ortho to imine linkage which participates in intramolecular or intermolecular H-bonding to stabilise the imine linkage and thereby promoting non-covalent self-assembly with a hope for new findings about the influence of highly polar substituents especially via new combination of linking group and lateral substituents.

5.3 **Ferroelectricity and Antiferroelectricity in Bent-core LC’s:**

Since their discovery, ferroelectric liquid crystals have attracted particular attention of scientists and applied researchers [33-37]. First, ferroelectric order in liquid crystals has been discovered in a tilted chiral smectic phase (SmC*). In a single layer, the polar order occurred as a result of broken mirror symmetry and the tilt of the molecules. However, the spontaneous polarization in the bulk of SmC* phases is averaged out by a helical winding. SmC* phases confined between two boundaries in surface stabilised states show a clear bistable switching with a spontaneous polarization in the range from a few nC/cm² to several hundreds of nC/cm² [37]. This kind of behaviour has found a wide range of applications in science and technology. Apart from commensurate ferroelectric SmC* phases, antiferroelectric and a number of incommensurate ferrielectric phases have been reported till now [38–40]. The discovery of a new class of liquid crystals formed by bent-shaped molecules [41] considerably expanded the variety and complexity of phenomena encountered in thermotropic liquid crystals [10, 42–44]. The smectic phases formed by bent-core molecules are found to exhibit polar liquid crystalline phases and polar switching. The polar order of smectic phases results from the sterically induced packing of the molecules in bent direction of the molecule. Bent molecules in the polar smectic phases are arranged either parallel (SmAP phases) or tilted (SmCP phases) to the layer normal and the abbreviation A and C represent the orthogonal or tilted arrangement of molecules as defined in SmA or SmC phase respectively while P stands for the polar order in the phase structure. Thus, in contrast to calamitic chiral SmC* phases, the spontaneous polarization in bent-shaped smectics can appear independently of tilt [45]. However, polarization and tilt coupling is still present [46]. Interestingly, in these tilted polar smectic phases chirality of the smectic layers is observed even when the constituent molecules are achiral [47-49]. Majority of these SmAP and SmCP phases are found to be antiferroelectric (SmCPA) [10, 18, 41–43, 50]. The preferred antiferroelectric ground state of these phases is
due to energetic effects, i.e. by the escape of the macroscopic polar order as well as entropic effects promoted by interlayer fluctuations. There are also SmCP phases with a ferroelectric ground state (SmCP$_f$) which have been observed in bent-core compounds with end branched chiral alkyl chains, with terminal oligo(siloxane) or oligo(carbosiloxane) units, furthermore in compounds with non-branched alkoxy chains adjacent to fluorine substituents (see references in [41]) as well as in laterally non-substituted compounds [51]. The ferro- and/or antiferroelectric nature of the SmCP phase is well studied by the triangular-wave voltage method [52]. Ferroelectric states are characterized by one peak per half-period of the applied triangular voltage, whereas in the antiferroelectric ground state two current peaks per half-period are recorded. In the present work the influence of substituent and the change in position of the substituent in the central core of bent core molecules on the mesomorphic properties and related electrical characteristics had been investigated.

5.4 Spontaneous Polarization, Layer Chirality:

Chirality has been one of the attractive subjects in chemistry since Pasteur first observed organic crystal conglomerate formation in one of the most famous experiments [53]. Achiral bent shaped mesogens have opened up a new era in liquid crystal science with respect to polarity and chirality. The influence of chirality on the phase behaviour of bent-core liquid crystals is another interesting topic in recent years. Bent core compounds even without the introduction of non-centrosymmetric moieties into the molecular structure manifest the helically twisted structures. Chiral "banana phases" by achiral bent-core mesogens [44, 54] have been one of the most extensively investigated topics because of a variety of unusual chirality-related phenomena; i.e., large optical rotation (OR) [55,56] and huge chiral nonlinear optic (NLO) effect [57, 58], enhanced twisting power [59-61], and induced blue phase [62] by doping conventional chiral systems with achiral bent-core molecules. Typically banana shaped mesogens viz., B2 and B4 phases are found segregate into two assembling chiral domains in which the molecules are believed to possess the chiral conformations [43, 47, 54, 63-65]. The spontaneous chirality in the B2 phase originates from symmetry breaking due to the tilt of banana-shaped molecule from the layer normal. On the other hand, in the B4 phase, conformational molecular chirality is believed to be nucleated, resulting in some helical superstructures such as a twist-grain-boundary (TGB) structure with the helix parallel to the layer.
The sign of spontaneous polarization is defined using the direction of the tilt and polarization, i.e., the sign is plus when $\mathbf{P}$ points to the same direction of $\mathbf{z} \times \mathbf{n}$ (where $\mathbf{z}$ points along the layer normal and $\mathbf{n}$ is parallel to the molecular long axis). In the case of ferroelectric SmC* phase or antiferroelectric SmCA* phase of rod-like molecules, spontaneous polarization is originated from breaking of mirror symmetry by introduction of chirality. Hence, at any given temperature, all of the layers in these chiral smectic phases have a uniform sign of spontaneous polarization that is completely determined by the handedness of molecules. In the tilted polar smectic phases (SmCP phases) of *Achiral* bent-core molecules, two types of layers exist, and one of which is the mirror image of the other [Figure 5.1a]. Then as in the case of the SmC* phase of rod-like molecules, the spontaneous polarization of each layer is uniquely defined. However, the situation is little complicated because molecules in each layer have a bent-direction $\mathbf{b}$. $\mathbf{P}$ and $\mathbf{b}$ are assumed to be parallel but their directions are not always the same. Further the layer chirality, instead of the sign of spontaneous polarization, is defined [47] using the molecular tilt direction $\theta$ and $\mathbf{b}$. The handedness of a layer (layer chirality) is defined as plus (+), when $\mathbf{b}$ points along the same direction as ‘$\mathbf{z} \times \mathbf{n}$’ as shown in Figure 5.1b.

**Figure 5.1:** (a) Geometry for smectic layers and layer stacking in tilted smectic phase of bent-core molecules (b) In one smectic layer with layer normal along the z-axis composed of bent-core molecules with polar order along $\mathbf{b}$ parallel to the y-axis, two possible layer structures one of which is mirror image of the other, are defined by the director $\mathbf{n}$ tilting by $\theta$ either along the positive or negative to x-axis. The two dimensional $\mathbf{c}$-director (nail) is defined by the projection of $\mathbf{n}$ onto a layer surface with the head of the nail indicating which end of the molecule is closest the top surface.

It is difficult to determine the direction of $\mathbf{P}$ and $\mathbf{b}$ experimentally. The director $\mathbf{b}$ points in the same direction (or opposite direction) to the electric field when $\mathbf{P}$ and $\mathbf{b}$
are parallel (or anti-parallel). The layer chirality (also the sign of spontaneous polarization) is completely defined by chirality of molecules. However, both handednesses of layers exist in the SmCP phase of achiral bent-core molecules since molecules are achiral. Hence existence of the molecules in the (+) and (-) layers of the achiral SmCP phase is attributed to the chirality of the molecules. Several reports point out that the conformation of the molecule is chiral and the molecules in the (+) and (-) layer are forming a chiral conformation which is the mirror image of that of molecules in layers of opposite handedness [66, 67].

As it is evident from the above discussion bent core molecule are well studied from the prospective of chemical structure–mesomorphism relationships. Occurrence of novel and intriguing polar mesophases, the induction of supramolecular chirality using Achiral molecules and the noticeable optical, ferroelectric and antiferroelectric responses shown by these materials are, among others, aspects of interest. In this chapter we chose a five-ring system designed and synthesized from substituted 1,3-phenylene diamine, containing the azomethine, ester and or azo linking groups. In some of the homologues series of compound we simultaneously substituted the phenyl rings of the arms of the bent-core molecules with hydroxyl group and examined the effect on mesomorphic properties on substitution. A total of 30 compounds belonging to 8 different homologous series that have been studied; these are shown in Figure 5.2.

Figure 5.2: Molecular structure of the different homologous series of compound synthesized for the present study.

Apart from these a triply bent W-shaped azo based bent core compound is also designed and synthesized in regards to study its absorption and emission properties along side liquid crystalline property.
5.5 \( \text{N,N'-bis[4-(4-n-alkyloxybenzoyloxy)salicylidene]-phenylene-} \)
4-fluoro-1,3-diamine, 4F\(-n\)OH:

5.5.2 Experimental Details:

The starting material in the present study 4\(-(4'\text{-n-alkyloxybenzoyloxy})\)
salicylaldehyde was prepared from 4-n-alkoxybenzoic acid by converting into acyl
chloride followed by condensation with 2,4-dihydroxy benzaldehyde. Even though
the condensation of acyl group with both the hydroxyl groups in 2- and 4- positions
of the phenyl moiety is possible, the reaction was carried out at low temperature
mainly to promote the condensation at 4- position ahead of the 2-hydroxyl group
which is bonded with the aldehyde oxygen through H-bonding. The condensation of
4\(-(4'\text{-n-alkyloxybenzoyloxy})\)salicylaldehyde with 4-fluoro-1,3-phenylenediamine in
the presence of a few drops of glacial acetic acid yielded the product of bent shaped
compounds \( \text{N,N'-bis[4-(4-n-alkyloxybenzoyloxy)salicylidene]-phenylene-} \)
4-fluoro-1,3-diamines, 4F\(-n\)OH \((n = 8, 10, 12, 14, 16 \text{ and } 18)\). To avoid the resulting side
products mainly the mono imine under cold conditions in solution, the precipitated
compounds were filtered when the solution was hot to yield pure compounds.
Repeated recrystallization of product was carried out to obtain the pure product with
constant transition temperatures. The formation of all of the compounds was
confirmed by \(^1\text{HNMR}\) and IR spectroscopy and the purity was established by
elemental analysis. The details of the experimental procedure along with the
spectroscopic data for all the homologous series of compounds are provided in
Chapter 3. The liquid-crystalline behaviour of the synthesised compounds had been
studied by optical microscopy and DSC.

5.5.2 Mesomorphic properties:

The transition temperatures, enthalpies and entropies of the homologous series 4F-
\(n\)OH as a function of number of the carbon atoms in the terminal alkyl chains from
DSC runs at a cooling rate of \(10\text{°C min}^{-1}\) are presented in Table 5.1. The enthalpy
changes corresponding to the clearing transition from mesophase to isotropic phase
in banana compounds (4F\(-n\)OH series) are usually larger than those observed in
calamitic compounds. The thermal data revealed that all of the compounds are
exhibiting identical enantiotropic phase transitions except 4F-8OH. As shown in
Figure 5.3, the clearing points increase moderately and the melting points decrease
with the increasing chain length of the terminal alkoxy chains.

Table 5.1: Transition Temperatures (°C), Enthalpies (italics kJ/mol) and entropies (italics in brackets J/mol/K) of homologous series 4F-nOH.

```
Table 5.1

<table>
<thead>
<tr>
<th>Compd.</th>
<th>R</th>
<th>Cr/ B4</th>
<th>Heating</th>
<th>Cooling</th>
<th>Sm X</th>
<th>Heating</th>
<th>Cooling</th>
<th>SmCP_A</th>
<th>Heating</th>
<th>Cooling</th>
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<td>[17.2, 39.9]</td>
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<td>[14.4, 33.6]</td>
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<td>[20.4, 46.8]</td>
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<td>•</td>
<td>108.9</td>
<td>•</td>
<td>121.3</td>
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<td>[18.8, 45.4]</td>
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<td>[23.3, 56.0]</td>
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<td>[17.0, 39.4]</td>
<td>[162.9]</td>
<td>[20.4, 46.8]</td>
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<tr>
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<td>[17.0, 39.4]</td>
<td>163.0</td>
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<td>114.0</td>
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<td>[18.4, 45.4]</td>
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<td>[8.1, 18.6]</td>
<td>160.3</td>
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<td>[8.1, 18.6]</td>
<td>[2.5, 6.7]</td>
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<td>[10.2, 23.6]</td>
<td>[162.8]</td>
<td>[20.4, 46.8]</td>
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<td></td>
<td>[19.3, 44.3]</td>
<td>162.4</td>
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<td>115.4</td>
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<td>[19.3, 44.3]</td>
<td>159.6</td>
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<td>•</td>
<td>[38.6, 98.4]</td>
<td>[18.5, 45.3]</td>
<td>[19.3, 44.3]</td>
<td>[38.6, 98.4]</td>
<td>[18.5, 45.3]</td>
<td>[19.3, 44.3]</td>
<td>[19.3, 44.3]</td>
<td>[19.3, 44.3]</td>
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</tbody>
</table>

All the reported temperatures are the peak recorded in DSC thermographs in the first heating and cooling cycles at the heating and cooling rates of 10 °C/min. Additional crystal to crystal transitions have been observed in the heating cycle (a) 100.4 [5.6, 15.0]; (b) 105.7 [15.9, 41.9], in cooling cycle (c) 103.8 [4.3, 11.3] [64, 66, 68, 69].

All of the compounds exhibited liquid-crystalline behaviour with an identical texture as shown in Figure 5.4a observed for 14OHF, characteristic of the SmCP_A phase, which is further confirmed from the electro-optical and X-ray studies. Further cooling of the sample 14OHF indicated another phase B_x, exhibiting a texture resembling the B4 phase which is yet to be confirmed (Figure 5.4c) [64, 66, 68, 69]. The SmCP_A to B_x phase transformation is shown in Figure 5.4b. The crystallisation from the B_x phase in general takes a longer duration of time, up to a few hours, and hence could not be detected. The supercooling effect of more than 15 K suggests that the B_x phase may be a B4 phase and further work by other experimental
investigations, namely atomic force microscopy of thin films, optical studies of free-standing films, freeze fracture transmission electron microscopy and synchrotron X-ray studies are in progress to confirm the phase structure.

All of the homologues exhibited an identical texture indicating an unknown B\textsubscript{X} phase, which is under further investigation. The homologue 80HF exhibits only a monotropic SmCP\textsubscript{A} phase. On cooling from the isotropic phase the circular domains appeared which are characteristic of SmCP\textsubscript{A} phase and the phase existence becomes broader for the longer chain homologues.

5.5.3 X-ray studies:

In order to identify the model structure of the liquid-crystalline phases formed by these compounds, we conducted preliminary X-ray diffraction measurements on 4F-140H homologue as a representative example using an image plate detector. Lindemann glass capillaries (1 mm diameter) were filled by a capillary action at high temperature without an alignment procedure to yield an unoriented sample and sealed under dry atmosphere. The capillary tube was introduced in an oven whose temperature stability was ±10 mK. The tube was vertical and perpendicular to the beam and the exposure times were maintained for 15 min. The X-ray diffraction experiments carried out on a non-oriented sample of the smectic phase of compound 4F-140H revealed the following features. In the small angle region one strong
reflection (Figure 5.4d) was observed at \( d = 4.10 \) nm revealing the layer structure. The value for the first reflection is considerably smaller than the length of the molecule (4F-14OH) \((L = 6.33 \) \( \text{nm}\)) as measured along the bow axis’ (also the director direction for the bent-core molecules) by assuming that the methylene chains are fully extended in the all-trans conformation (Figure 5.5).

![Intensity profile of the X-ray diffraction pattern in the small angle region at T = 154°C](image)

**a)** \( T = 158.0°C \)

![Intensity profile of the X-ray diffraction pattern in the small angle region at T = 154°C](image)

**b)** during transition at \( T = 114.0°C \)

![Intensity profile of the X-ray diffraction pattern in the small angle region during the transition at T = 114°C](image)

**c)** Smectic X phase at 113.2°C.

**d)** Intensity profile of the X-ray diffraction pattern in the small angle region at \( T = 154°C \)

**e)** Intensity profile of the X-ray diffraction pattern in the small angle region during the transition at \( T = 114°C \)

**f)** Intensity profile of the X-ray diffraction pattern in the small angle region at \( T = 92°C \)

*Figure 5.4:* Characteristic textures exhibited by 4F-14OH and intensity profiles of X-ray diffraction pattern.
The tilt angle (θ) of the molecules was estimated to be 49° which is little larger than the optical tilt angle (~46°) observed between the extinction brushes in the electro-optical measurements during the switching process. Such large tilt angles up to 56° are reported in literature in lateral fluoro substituted compounds exhibiting SmCP_A phases [14-17]. Further broad diffuse scattering maxima in the wide-angle region around 0.47nm indicated a liquid like in-plane order with no long-range positional order within the smectic layers. Further during the transition from SmCP_A to a low-temperature phase, with the disappearance of the existing peak and appearance of the strong reflection indicating another smectic phase with an increase in layer thickness (Figure 5.4e), 4.30 nm. On further cooling the peak grows stronger (Figure 5.4f) and continued until room temperature.

Figure 5.5: Molecular model of compound 4F-14OH in which the chains are in a fully extended all trans conformation.

5.5.4 Electro-optical investigations:

The mesophase exhibited by compounds nOHF shows electro-optical switching behaviour. The switching behaviour of the SmCP_A phase was observed using electro-optical measurements as well as simultaneous observation of changes in thin film of the compound under a polarizing microscope. The sample was filled in a freshly assembled 5 μm polyimide-coated homogenous cell in the isotropic phase and cooled slowly into the mesophase at a rate of 0.5°C min⁻¹. After the sample is cooled into the mesophase 5°C below the mesophase–isotropic phase transition temperature, the applied field is gradually increased to obtain aligned samples and saturated current peaks. The application of a sufficiently large triangular voltage yielded the current response peaks in each half period of the waveform. The current response of compound 4F-14OH (Figure 5.6a) shows two polarization current peaks for each half cycle on applying a triangular-wave electric field of about ±80 V, 50 Hz, at 145°C, indicating an antiferroelectric ground state structure in the mesophase, and the spontaneous polarization was found to be, 590 nC cm⁻², which is comparable
with the reported values in the SmCP phase of compounds possessing a lateral dipole moment. The variation of spontaneous polarization, which is found to be temperature dependent, is shown in Figure 5.6b. The electro-optical behaviour response of this sample was observed as textural changes by the application of an electric field. The influence of d. c. electric field on the molecular alignment, which is reflected in the optical textures of compound 4F-14OH filled in readymade unidirectional polyimide-coated 5 μm thin commercial cells purchased from Instec Inc., are as follows. On cooling the isotropic phase of the compound 4F-14OH in the absence of an electric field, it transformed into a SmCP-type liquid-crystalline phase at 158.2°C with the appearance of a characteristic striped texture with spherulitic growth (Figure 5.7a) and tends to grow fan-shaped domains (with horizontal and vertical Maltese crosses making an angle with the polariser) with a fringe pattern showing helical structure. The majority of the domains exhibited a striped pattern texture with equal spacing of the stripes. This texture is reminiscent of the ‘fingerprint’ texture expected for helical banana phase structures, with the molecular plane parallel to the cell surface and the tilted smectic layers, with a tilt equal to the director tilt angle, aligned perpendicular to the plane of the cell surface (bookshelf geometry). (The director is along the layer normal and the molecules can have either a synclinic or an anticlinic interlayer correlation.) Consistent with the helical structure, it is apparent that the stripes are oriented parallel to the layers in the focal conic texture.

Figure 5.6: a) Switching current response obtained for the compound 4F-14OH by applying a triangular wave electric field at (±80 Vpp, 50 Hz) at T = 145°C. Sample thickness 5 μm; spontaneous polarisation, PS, 528 nC cm⁻². b) Temperature variation of spontaneous polarisation in the SmCP phase of compound 4F-14OH.
It is apparent from the equally spaced striped lines that the layers are flat and parallel to each other and the curved complex patterns on the macroscopic length support the formation of the random focal conic fan texture. The switching behaviour of the SmCP_A phase of the compound 4F-140H under a d. c. electric field has been examined using a polarising microscope. On cooling from the isotropic phase the sample under the influence of an electric field ±6 V µm\(^{-1}\) exhibiting an equally spaced striped texture (Figure 5.7b), with a spherulitic growth in the entire region with homeotropic regions. Further increase in the strength of the electric field ±10 V µm\(^{-1}\) leads to the appearance of stable colourful stripes with a change in birefringence of the texture.

![Figure 5.7: Optical texture of the SmCP_A phase of compound 4F-140H under the influence of an electric field: spherulitic growth with coloured stripes. Thickness of cell = 5 µm. (a) Without an electric field. (b) Electric field = 6 V mm\(^{-1}\), T = 154°C. (c) Optical texture of the SmCP_A phase of the compound 4F-140H cooled from the isotropic phase under the influence of an electric field of 10 V and after the removal of the field, T = 154°C.](image)

The sample is cooled under the influence of a field (±6 Vµm\(^{-1}\)) and when the field is switched off the texture (Figure 5.7 e) becomes non-birefringent with more dark regions. These preliminary studies of optical textures confirm the identification of the mesophase as a SmCP_A phase which is similar to the fringe texture of the SmCP_A mesophase of PIMB series [70]. The detailed electro-optic measurements are in progress.
5.6 N,N′-bis[4-(4-n-alkyloxybenzoyloxy)salicylidene]-phenylene-2-methyl-1,3-diamines 2M-nOH:

5.6.1 Experimental Details:

The starting material in the present study 4-(4-n-alkyloxybenzoyloxy) salicylaldehyde was prepared as described in earlier section. The condensation of 4-(4′-n-alkyloxybenzoyloxy)salicylaldehyde with 2-methyl-1,3-phenylenediamine in presence of a few drops of glacial acetic acid yielded the product of bent shaped compounds N,N′-bis[4-(4-n-alkyloxybenzoyloxy) salicylidene]-phenylene-2-methyl-1,3-diamines, 2M-nOH (n = 6, 8-10, 12 14, 16 and 18). To avoid the resulting side products mainly the mono imine under cold conditions in solution, the precipitated compounds were filtered when the solution was hot to yield pure compounds. Repeated recrystallization of product was carried out to obtain the pure product with constant transition temperatures. The formation of all of the compounds was confirmed by ¹HNMR and IR spectroscopy and the purity was established by elemental analysis. The details of the experimental procedure along with the spectroscopic data for all the homologous series of compounds are provided in chapter 3. The liquid-crystalline behaviour of the synthesised compounds had been studied by optical microscopy and DSC. The structural details are determined using X-ray diffraction studies.

5.6.2 Mesomorphic properties, Differential Scanning Calorimetry and Thermal Microscopy studies:

The transition temperatures, enthalpies and entropies of the homologous series 2M-nOH as a function of number of the carbon atoms in the terminal alkyl chains from DSC runs at a cooling rate of 10°C min⁻¹ are presented in Table 5.2. The enthalpy changes corresponding to the clearing transition from mesophase to isotropic phase in banana compounds (2M-nOH series) are usually larger than those observed in calamitic compounds. The thermal data revealed that the higher homologue compounds are exhibiting identical enantiotropic phase transitions. The dependence of the mesomorphic properties of the homologous series of Bis-[4-(4′-n-alkyloxybenzoyloxy)-salicylidene]-phenylene-2-methyl-1,3-diamines, 2M-nOH, as function of number of carbon atoms in the alkyl chain length is shown in Figure 5.8. As shown in Figure 5.8, the clearing points are almost constant and the solid-liquid crystalline transition temperature decreased initially and later increased with
the increase in chain length of the terminal alkoxy chains. Two types of liquid crystalline phases viz., B1 and SmCP (B2) phases were observed in this series of compounds. The compounds with shorter chain length exhibit B1 phase whereas the homologues with long alkyl chains display the SmCP phase. The lower homologues exhibited C6 and C8 homologues exhibited characteristic textures of B1 phase. All the higher homologues viz. 2M-12OH to 2M-18OH exhibited liquid-crystalline behaviour with an identical texture resembling SmCP phase.

Table 5.2: Transition Temperatures (°C), Enthalpies (italics kJ/mol) and entropies (italics in brackets J/mol/K) of homologous series 2M-nOH.

All of the reported temperatures are the peak recorded in DSC thermographs in the first heating and cooling cycles at heating and cooling rates of 10°C min⁻¹. Additional crystal-to-crystal transitions have been observed in the heating cycle for 6 and 2M-8OH at (139.7 [5.2, 37.9]) and (115.0 [4.9, 43.0]) respectively.

-152-
5.6.3 Thermal microscopy of 2M-6OH:

The lower homologues 2M-6OH and 2M-8OH exhibit a mesophase which shows textural features similar to that of the two-dimensional B1 phase. The photomicrographs of the optical textures exhibited by 2M-6OH are shown in Figure 5.9. On cooling from the isotropic liquid state small batonets sometimes growing fern like domains are formed which subsequently transformed into branched lancets and finally coalesce to a structured mosaic-like texture with and without some spherulitic domains. However on slow cooling of a thin film of a 5μm sample of 2M-6OH dark pink or greenish yellow smectic domains grew from defect-like lines and transform into very long colourful banana leaf like patterns as well as spherulitic domains as shown in Figure 5.9c and d, suggesting a two-dimensional structure for the mesophase. These types of textures had been reported for a two dimensionally modulated frustrated smectic phase of short chain bent-shaped Schiff’s base molecule and was designated as B1 phase. The homeotropic orientations which can be obtained by shearing thin samples between glass plates exhibit always a distinct birefringence. No pseudo-isotropic regions can be obtained. Two dimensional rectangular lattice can be visualized [68] as follows. The molecular structure of 2M-6OH and the space filling model is shown in Figure 5.10. The molecular length assuming a bow shape of the molecule with a bending angle ca 120° and an all-trans conformation of the alkyl chains is 4.55 nm. Assuming a ribbon structure as
proposed earlier in other compounds the parameter $c$ should correspond to the thickness of the ribbons and $a$ may correspond to the diameter of the ribbons in the lateral direction. About seven molecules should be arranged side by side in the ribbons forming 2D lattice. The textural features indicated the mesophase could be columnar phase, which is also further supported by X-ray data.

![Optical photomicrograph](image)

**Figure 5.9:** Optical photomicrograph (crossed polarizers) of the Col$_r$ phase as obtained by cooling from the isotropic liquid a) mosaic texture b) lancet like texture c) banana-leaf like texture d) banana leaf and spherulitic texture at 170°C.

![Molecular structure](image)

**Figure 5.10:** Molecular structure and space filling model of 2M-60H.
5.6.4 X-ray studies of 2M-nOH:

As mentioned above the lower homologues exhibited B1 phase and the higher homologues exhibited B2 phase. As the clearing transition temperatures are relatively high the experimental limitations did not allow obtaining the oriented samples of the mesophase. In situ desired temperature experiment was performed by placing the sample in 1 mm diameter quartz capillary tubes and data were collected using a point detector mounted on a Huber four-circle goniometer at Cu K(α) radiation from a 8 kW Rigaku UltraX-18 rotating anode x-ray generator (Cu anode, wavelength = 1.54 Å). The sample was placed in an oven, providing a temperature control of 0.1K. The angular intensity profile of the mesophase of 2M-6OH is shown in Figure 5.13. The X-ray patterns of non-oriented samples for 2M-6OH compound at 170°C shows diffuse scattering in the wide angle region at 0.45 nm, indicating a liquid-like in-plane order. In the small angle region three sharp reflections at d1 = 2.73 nm d2 = 1.95 nm and d3 = 1.59 nm were obtained. The smallest and next smallest small angle peaks which did not exhibit any relation with the first and second X-ray diffractions corresponding to the smectic layer thickness, suggested a two dimensional frustrated layer structure. The spacing of the inner reflections as well as their diffraction geometry can well be explained [8-10, 32, 44, 55, 68, 71-80] by the two-dimensional lattice with a = 4.0 nm and c = 3.9 nm. The c axis length i.e., layer thickness corresponds to molecular length and the frustration i.e., unusual modulation takes place along the a axis. The a axis may correspond to the bent direction of molecules. In absence of the higher order reflections the density modulation along the layer is irregular. Hence the unusual density modulation is modulated is produced by the periodic structure with inversion walls such that the molecules in adjacent domains slide halfway along the layer normal after 2π rotation around the molecular axes. 2π rotation is necessary to achieve efficient packing of the banana-shaped molecules reported earlier. The length of the a axis indicates that 8 to 10 molecules on an average are included in a unit i.e., 4 to 5 molecules are included in each frustrated domain. These columnar phases have recently been investigated by means of X-ray scattering with aligned samples and it was shown that they are built up of ribbons of parallel aligned and non-tilted bent-core molecules as shown in Figure 5.11b and is in agreement with other reported results in literature [71-79].
Figure 5.11: a) X-ray angular intensity profile of the B1 phase of compound 2M-6OH at 170°C b) Two dimensional modulated structure as suggested for short chain bent core molecules exhibiting Col B1 phase. The molecules are non-tilted and the 2D lattice is in the plane of the polarization vectors. Only aromatic bent-core units are shown and the space the ribbons is filled by conformationally disordered terminal chains (not shown) a = 4.0 nm, c = 3.9 nm.

The compound 2M-10OH, on slow cooling from the isotropic phase, exhibited a fringe pattern texture with beautiful dendritic growth in the mesophase initially which further spread in the entire field of view on further cooling as shown in Figure 5.12. The texture is normally observed for an antiferroelectric SmCP phase [71].

Figure 5.12: Photomicrographs obtained for compound 2M-10OH showing the textural change on slowly cooling from the isotropic melt a) at 187°C b) at 165°C c) X-ray angular intensity profile of the mesophase of compound 2M-10OH at 160°C.
We also conducted X-ray diffraction measurements on 2M-10OH homologue using an image plate detector. The X-ray diffraction experiments carried out on a non-oriented sample of the smectic phase of compound 2M-10OH at 160°C revealed the following features. In the small angle region one strong reflection (Figure 5.12c) was observed at $d = 35.6\text{Å}$ revealing the layer structure. The value for the first reflection is considerably smaller than the length of the molecule (2M-10OH) ($L = 55.7\text{Å}$) as measured along the “bow axis” (also the director direction for the bent-core molecules) by assuming the methylene chains to be fully extended in the all-trans conformation (see Figure 5.13) and a tilt angle of about $50^\circ$ could be estimated for this compound. Such large tilt angles up to $56^\circ$ are reported in literature in lateral fluoro substituted compounds exhibiting SmCP$_A$ phases [14-17]. Further a broad diffuse scattering maxima was also observed in the wide angle region around 0.42 nm indicated a liquid like in-plane order with no long range positional order within the smectic layers.

Figure 5.13: Molecular model of compound 2M-10OH in which the chains are in a fully extended all trans conformation.

The DSC and microscopic studies on a representative compound 2M-14OH are presented here. 2M-14OH exhibited two transitions in the heating cycle at (122.7°C, $\Delta H = 79.1 \text{kJ/mol}$, $\Delta S = 199.8 \text{J/K/mol}$, melting point) and (192.8°C, $\Delta H = 17.8 \text{kJ/mol}$, $\Delta S = 38.2 \text{J/K/mol}$, clearing point). In the cooling cycle also it exhibited enantiotropic phase transitions at (190.7°C, $\Delta H = 17.1 \text{kJ/mol}$, $\Delta S = 36.8 \text{J/K/mol}$) and (90.6°C, $\Delta H = 66.1 \text{kJ/mol}$, $\Delta S = 181.7 \text{J/K/mol}$). The differential scanning calorimetry spectrum is presented in Figure 5.14. A thin film of the compound 2M-14OH melts at 122.7°C exhibiting isotropic like texture without any specific features and transforms into isotropic phase at 192.8°C. In the cooling cycle the compound exhibit mesomorphic behaviour between 190.7°C and 90.6°C with a mesomorphic range of 100°C. On cooling the sample 2M-14OH from the isotropic liquid phase to the mesomorphic phase a characteristic texture of large chiral domains appeared. Figure 5.15 shows two chiral domains that can be recognised by uncrossing the polarizers. In the figure a polarizer is slightly rotated clockwise, and then some of
the regions become dark while adjacent regions become bright. If we rotate the polarizer counterclockwise, bright and dark regions are interchanged. This optical property was observed in several bent-core materials [14, 15] being characteristic of spontaneous resolution of chiral domains. The formation of chiral domains resembling of the smectic phase shows a complete extinction between crossed polarizers. Even large drops (1–2 mm thick) appear completely dark indicating that the mesophase is optically isotropic. In thin sandwich cells of 5–10 μm optically active domains of opposite handedness can be distinguished when the polarizers are slightly decrossed.

![Figure 5.14: DSC spectrum of the compound 2M-14OH.](image)

**Figure 5.14:** DSC spectrum of the compound 2M-14OH.

![Figure 5.15: The texture observed on cooling of the SmCP phase of compound 2M-14OH (T = 165°C). In slightly uncrossed polarizers (right image +5° and left image –5°), optically active domains become visible in the form of black and grey patches. Those domains indicate a spontaneously broken achiral symmetry.](image)

**Figure 5.15:** The texture observed on cooling of the SmCP phase of compound 2M-14OH (T = 165°C). In slightly uncrossed polarizers (right image +5° and left image –5°), optically active domains become visible in the form of black and grey patches. Those domains indicate a spontaneously broken achiral symmetry.
5.7 N,N'-bis[4-(4-n-alkyloxybenzoyloxy)benzylidene]-phenylene-4-fluoro-1,3-diamine, 4F-nH:

5.7.1 Experimental details:

The starting material in the present study 4-(4'-n-alkyloxybenzoyloxy) benzaldehyde was prepared as described in earlier section. The condensation of 4-(4'-n-alkyloxybenzoyloxy)benzaldehyde with 4-fluoro-1,3-phenylenediamine in presence of a few drops of glacial acetic acid yielded the product of bent shaped compounds N,N'-bis[4-(4-n-alkyloxybenzoyloxy)-benzylidene]-phenylene-4-Fluoro-1,3-diamine 4F-nH (n = 8, 10, 12, 14 and 16). To avoid the resulting side products mainly the mono imine under cold conditions in solution, the precipitated compounds were filtered when the solution was hot to yield pure compounds. Repeated recrystallization of the products was carried out to obtain the pure product with constant transition temperatures. The formation of all of the compounds was confirmed by $^1$HNMR and IR spectroscopy and the purity was established by elemental analysis. The details of the experimental procedure along with the spectroscopic data for all the homologous series of compounds are provided in Chapter 3. The liquid-crystalline behaviour of the synthesised compounds had been studied by optical microscopy and DSC.

5.7.2 Mesomorphic properties:

The transition temperatures, enthalpies and entropies of the homologous series 4F-nH as a function of number of the carbon atoms in the terminal alkyl chains from DSC runs at a cooling rate of 10°C min$^{-1}$ are presented in Table 5.3. The enthalpy changes corresponding to the clearing transition from mesophase to isotropic phase in banana compounds (4F-nH series) are smaller than there hydroxyl substituted counterpart (4F-nOH series). The thermal data revealed that all of the compounds are exhibiting enantiotropic phase transitions except. As shown in Figure 5.16, the clearing points decrease and the melting points almost remain constant with the increasing chain length of the terminal alkoxy chains. The higher homologue compounds exhibited liquid-crystalline behaviour with an identical texture as shown in Figure 5.17, observed for 4F-14H, characteristic of the B2 phase. On slow cooling the sample they grow like a banana leaf like pattern characteristic of B2 phase. While the lower homologues 4F-8H and 4F-10H exhibit a mesophase which
shows textural features similar to that of B1 phase as seen in Figure 5.18.

Table 5.3: Transition Temperatures (°C), Enthalpies (italics kJ/mol) and entropies (italics in brackets J/mol/K) of homologous series 4F-nH.

<table>
<thead>
<tr>
<th>Compd.</th>
<th>R</th>
<th>Cr</th>
<th>Heating cooling</th>
<th>SmCP_A</th>
<th>Heating cooling</th>
<th>B1</th>
<th>Heating cooling</th>
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<td>4F-8H</td>
<td>C_8H_17</td>
<td></td>
<td>-</td>
<td>105.2</td>
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<td>[1.8, 4.6]</td>
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<tr>
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<td>C_10H_21</td>
<td></td>
<td>-</td>
<td>91.3</td>
<td>-</td>
<td>126.2</td>
<td>-</td>
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<td></td>
<td>[3.4, 9.3]</td>
<td>[1.5, 3.7]</td>
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<tr>
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<td>-</td>
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<td>-</td>
<td>120.2</td>
<td>-</td>
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<td></td>
<td>[7.4, 19.7]</td>
<td>[5.5, 14.0]</td>
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<tr>
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<td>-</td>
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<td>120.2</td>
<td>-</td>
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<td>[8.9, 24.1]</td>
<td>[4.1, 10.4]</td>
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<tr>
<td>4F-16H</td>
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<td>-</td>
<td>102.7</td>
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<td>[8.8, 23.8]</td>
<td>[1.8, 4.8]</td>
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</table>

All of the reported temperatures are the peak recorded in DSC thermographs in the first heating and cooling cycles at heating and cooling rates of 10°C min⁻¹. Additional crystal-to-crystal transitions have been observed in the heating cycle for 4F-14H at 89.8°C [0.6, 1.6]

Figure 5.16: Banana leaf like domain observed for 4F-14H at 90°C.
5.7.3 Structure–property relationship: Influence of the functional group

The molecular structures of different compounds A–D of five-membered ring molecular bent-core skeletons with a change in the substituent are depicted in Figure 5.19. The liquid-crystal properties and phase transition temperatures were greatly affected by the subtle changes in chemical structure. The unsubstituted homologous series, viz., \( \text{N,N'-bis[4-(4-n-alkyloxybenzoyloxy)benzylidene]-phenylene-1,3-diamines} \) (compound A, \( \text{nHH} \) without fluoro and ortho hydroxyl substituent analogues) lower homologues (with carbon chain length \( n = 1–4 \)) exhibited a B6 phase, while middle homologues (\( n = 7–10 \)) exhibited B6 and B1 phases. However, the higher homologues with \( n = 11 \) and 12 exhibited a monotropic B2 phase as
transient phenomena for a shorter duration which did not allow any experimental studies [80, 81]. In order to make a comparison with the compounds mentioned above we synthesised C-10 homologue of five (compound B-F) additional compounds listed in Figure 5.19.

![Chemical Structures](image)

Figure 5.19: Five-membered ring molecular bent-core skeleton with a change in substituent.

The compounds N,N'-bis[4-(4'-n-decyloxybenzoyloxy)salicylidene]-phenylene-1,3-diamine (10OH, B) and the corresponding compounds viz., N,N'-bis[4-(4-n-decyloxybenzoyloxy)-salicylidene]-4-methyl-1,3-phenylenediamine (4M-10OH), N,N'-bis[4-(4'-n-decyloxybenzoyloxy)salicylidene]-4-chloro-1,3-phenylenediamine (4Cl-10OH), N,N'-bis[4-(4'-n-decyloxybenzoyloxy)salicylidene]-4-nitro-1,3-phenyle-nediamine (4N-10OH), N,N'-bis[4-(4'-n-decyloxybenzoyloxy)salicylidene]-3,5-diaminobenzoic acid (5Ba-10OH) are studied for their mesomorphism by thermal microscopy and DSC (compound C-F respectively.). The compound B exhibited an unspecific grainy texture with enantiotropic phase transitions with higher thermal stability. Expecting a new sequence of polymorphism we synthesized the compound C with a methyl substituent in position 4 unlike its 2-substituted counterpart (4M-10OH) described in Chapter 3. It is quite remarkable to note that in this case compound bearing a methyl group in position 2, that is within the obtuse angle of the molecules is mesomorphic where as the compound with the methyl group in position 4 (compound C) is nonmesomorphic. This observation again strongly support the general believe that these angled molecules under investigation are very sensitive against the position of the substituted groups attached at the central ring. In order to
understand the effect of substituents at the 4-position of central phenyl ring we also synthesized the chloro and nitro counterpart of compound B. In case of chloro substituted product we obtain a higher order Sm phase in POM study, which is yet too identified by other complimentary techniques. In case nitro substituted product, we able to shift the existence range of B phases to lower temperatures compared to the unsubstituted one compound B (Figure 5.19). Furthermore, we also studied the effect of having a carboxylic group attached at the top of the bent molecules that is in position 5. As it was observed that even small groups (methyl, methoxy and cyano) attached at the top of the bent molecules, prevent the existence of mesophases [18]. In our case we do observe the existence of B phase in compound F, but unfortunately the compound is not thermally stable as it decomposes on keeping the sample near to isotopic to mesophase transition temperature.

![Photomicrograph of the B2 phase observed in 4N-10OH compound along with the corresponding X-ray intensity profile.](image)

Figure 5.20: Photomicrograph of the B2 phase observed in 4N-10OH compound along with the corresponding X-ray intensity profile.

The thermal instability of such compound attributed to the presence of bared carboxyl group at the top of the molecule. Our studies on 4F-nH series of compounds reveal that in case of 4F-10H, the introduction of a fluoro substituent at a lateral position of the central phenyl ring, not only changes the nature of mesomorphism from monotropic to enantiotropic phase behaviour, but also causes a moderate reduction in clearing temperatures when compared with the unsubstituted compounds A and B. The introduction of a fluoro group in the central core in addition to the ortho hydroxyl group stabilising the imine linkage in the lateral ring by intermolecular or intramolecular hydrogen bonding which resists hydrolysis (nOHF series) completely changed the mesophase behaviour of these compound. They exhibit SmCP_A and BX phases as compared with the B6, B1, B2 phases exhibited by unsubstituted compounds A and B.
5.7.4 Influence of the linkage group:

However, when the imine linkage at the central core is reversed the resulting unsubstituted homologues of 1,3-phenylene-bis-[4-(4'-alkoxybenzoyloxy)phenyliminomethane] family (Cn series) also exhibited B1 (C5–C9 lower homologues) and SmCP\textsubscript{A} (C10–C14 higher homologues) phases [82]. The C12 homologue G (Figure 5.21) exhibits a SmCP\textsubscript{A} phase and spontaneous polarisation is of the order of 350 nC cm\textsuperscript{-2}, which is smaller than the PS, 590 nC cm\textsuperscript{-2} that we found in 4F14OH of 4FnOH series of compounds. However, if the ester linkage and salicylideneimine linkage are swapped [83-88], then the resulting materials compound H (BCH) without a fluoro group in the central core also exhibited switchable B2 or B1 (PS, 500 nC cm\textsuperscript{-2} for a C10 homologue [84] or B7 (C16 homologue) phases depending on the end alkyl chain length, which indicates the importance of the ortho hydroxyl group and the position of linking groups. The homologues with chloro or nitro substituents in the central core exhibited a SmCP\textsubscript{A} phase.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5_21.png}
\caption{Bent-core molecular skeleton with reversed imine linkage G, or swapped imine and ester linkages H.}
\end{figure}

5.8 \textit{N,N'-bis[2-hydroxy-5-(4'-n-dodecyloxyphenylazo)benzylidine]-4-nitro-1,3-phenylenediamine}, 134NPD(OH)O12:

5.8.1 Design and Synthesis of azo based W-shaped molecule:

Molecular self-assembled organization relies heavily on two important factors, (a) the interactions of certain molecular subunits [89-92] viz., rigid aromatic cores, lateral substituent functional groups, terminal aliphatic chains or perfluorinated alkyl chains, and (b) the shape of the molecular structure, which determine the non-covalent intermolecular interactions leading to a distinct and persistent supramolecular assembly that permits the overall organization to be predicted. Reports in the literature have revealed that the majority (~90%) of the published work on bent, banana or V-shaped molecules (because many non-mesogenic
compounds whose phase structure is not clear have been synthesized but not been published), based on rigid central 1,3-phenylene and 2,7-naphthalene cores self-assemble to yield molecular structures that exhibit banana liquid crystalline polymorphism. However either modification of the central aromatic ring of the core itself or the position of linking groups in the central core with an angled polar substituent in the central core may yield novel or mixed mesophase variants. However selective molecular engineering of such structures with the proper interplay of molecular structural anisotropy and the shape factor with the required polarizability anisotropy can be achieved in bent shaped molecules that match the prerequisites of molecules that exhibit novel smectic phases. In attempting to devise a strategy for the synthesis of a triply bent W-shaped molecule we extended each of the arms of bent shaped molecules by substitution at the meta position rather than the usual para position, which can promote lateral dipole character as well as molecular self-organization. Further, a hydroxyl group ortho to an imine linkage participates in intra or inter-molecular H-bonding thereby promoting non-covalent self-assembly. Introduction of a nitro group in the central core also complies with the strategy of creating an angled dipole in the long axis of a bent molecule which in turn promotes the biaxial smectic phase in such system. The W-shaped azobenzene molecule was so designed to have high azobenzene content per single molecule and unique bent-core shape with a twisted molecular chirality. In addition the W-shape deviates significantly from the typical banana or V-shaped or bent core molecules. The molecular structure of the azo based compound under study, N,N’-bis[2-hydroxy-5-(4’-n-dodecyloxyphenylazo)benzylidene]-4-nitro-1,3-phenylenediamine possessing one nitro group in the central core and two hydroxyl groups is shown in Figure 5.22.

![Figure 5.22: Molecular structure of the W-shaped azo compound.](image)

The synthesis of the intermediate materials required in obtaining the product 134NPDO12 viz., 4-n-dodecyloxyaniline from 4-acetamidophenol by Williamson etherification followed by hydrolysis followed by diazotization of 4-n-dodecyloxyaniline in aqueous alcohol to yield 3-(4-n-dodecyloxyphenylazo)-
salicylaldehyde are described in detail in Chapter 3. The condensation of 3-(4-n-dodecylxyloxyphenylazo)-salicylaldehyde with 4-nitro-1,3-phenylenediamine in presence of a few drops of glacial acetic acid yielded the product of W-shaped compound \(N,N'-\text{bis}[2\text{-hydroxy-5-(4'-n-dodecylxyloxyphenylazo)benzylidene}]-4\text{-nitro-1,3-phenylenediamine}\). To avoid the resulting side products mainly the mono imine under cold conditions in solution, the precipitated compounds were filtered when the solution was hot to yield pure compounds. Repeated recrystallization of the products was carried out to obtain the pure product with constant transition temperatures. The formation of all of the compounds was confirmed by \(^1\text{H NMR}\) and IR spectroscopy and the purity was established by elemental analysis. The liquid-crystalline behaviour of the synthesised compounds had been studied by optical microscopy and DSC.

5.8.2 Mesomorphic properties:

The compound \(N,N'-\text{bis}[2\text{-hydroxy-5-(4'-n-dodecylxyloxyphenylazo)benzylidene}]-4\text{-nitro-1,3-phenylenediamine}\) has exhibited three enantiotropic phase transitions at 120.2\(^\circ\)C \([\Delta H = 26.3\text{kJ/mol}, \Delta S = 66.8\text{J/mol K}]\) 125.6\(^\circ\)C \([\Delta H = 1.86 \text{kJ/mol}, \Delta S = 4.67 \text{J/mol K}]\) and 190.2\(^\circ\)C \([\Delta H = 56.2 \text{kJ/mol}, \Delta S = 121.5 \text{J/mol K}]\) in the heating cycle and at 181.5\(^\circ\)C \([\Delta H = 53.0 \text{kJ/mol}, \Delta S = 116.7 \text{J/mol K}]\); 114.8\(^\circ\)C \([\Delta H = 2.84 \text{kJ/mol}, \Delta S = 7.33 \text{J/mol K}]\) and 108.3\(^\circ\)C \([\Delta H = 4.11 \text{kJ/mol}, \Delta S = 10.8 \text{J/mol K}]\) in the cooling cycle as shown in Figure 5.23. The large enthalpy change is generally associated with crystal to liquid or liquid crystalline phase transition. However in the present case large enthalpy of 56.2kJ/mol at 190.2\(^\circ\)C in the heating cycle and 53.2kJ/mole in cooling cycle indicates a phase transition associated with strong intermolecular forces such as H-bonding, strong dipolar interactions and a sudden transformation from ordered fluid to disordered isotropic liquid. In general H-bonding is associated with 20 -40 kJ/mole and the other enthalpy is not accountable. However liquid crystal to isotropic phase transition with such large change in enthalpy of the order 40-50 kJ/mol is reported in literature for banana shaped liquid crystals. The broadness of peak at 190.2\(^\circ\)C indicate the slow phase transition, which in turn indicate the complex structure of the phase and intramolecular hydrogen bonding in the molecule. The peak at a 114.8 \(^{0}\)C \((2.84\text{kJ/mol})\) in cooling cycle is due to liquid crystal to crystal transition indicated by small enthalpy change which was later confirmed by thermal microscopy and the results are presented below.
The liquid crystalline behavior of the synthesized compound has been confirmed by polarizing optical microscope study. The transition temperatures measured from thermal microscopy are in good agreement with the transition temperatures detected by DSC. The compound melted at 120°C and became isotropic at 195°C. The liquid crystalline texture shown by the compound seems to be unusual which is a grainy like textures with two domains which cannot be distinguished (Figure 5.24) while the analyzer and polarizers were crossed. However if one of the crossed polarizers is slightly rotated clockwise +5°, then one domain becomes dark and the other domain becomes bright. If we rotate the polarizer counterclockwise −5°, (Figure 5.24b and c) the bright and dark regions are interchanged. The W-shaped azobenzene molecules themselves spontaneously segregate into two chiral domains viz., the optically active darker and brighter domains in the liquid crystal and/or crystal phase. The texture observed from well-grown chiral domains separated by a defect line that are only recognized by uncrossing polarizers giving darker and brighter domains. Those domains indicate a spontaneously broken achiral symmetry. When the sample was cooled from the isotropic phase, the size of the domain was strongly dependent on the rate of cooling condition. This optical property has been
also observed in several bent-core materials [59, 61] which have molecular chirality. Thus, the bent-core molecules are regarded as racemic mixtures rather than an achiral system because of the spontaneous segregation into two chiral domains [93]. The unique shape of the molecules can play a key role in inducing chirality in this case. These results are supporting the earlier reported alkyl analogue of the same compound reported from our laboratory [94-96]. Further work is in progress to understand the molecular structure and the origin of chiral properties in these compounds.

![Figure 5.24: (a) The texture observed from well-grown chiral domains separated by a defect line that are only recognized by uncrossing polarizers giving darker and brighter domains. When the polarizers are uncrossed clockwise +5° and counter-clockwise –5°, the optically active darker and brighter domains are interchanged (b and c).](image)

5.8.3 Absorption & Emission characteristics:

The UV absorption and fluorescence spectroscopic properties of the compound 134NPDO12 in solution were studied in chloroform to obtain the information regarding absorption and emission maxima, and the Stokes shift of fluorescence. The variation of absorption with wavelength (UV-Visible spectra) and the emission spectra of the compound are presented in Figure 5.25. The compound exhibited UV absorption with a peak at 362 nm (3.42 eV, \( c \sim 95000 \text{ Lmol}^{-1}\text{cm}^{-1} \)). The absorption band with large molar absorption coefficient reflects the \( \pi - \pi^* \) transition of the highly \( \pi \)-conjugated system with substituted phenyl benzoate unit as the core. Further we investigated the fluorescence spectrum to observe the excited state characteristic features of the newly designed W-shaped molecule possessing two azo groups.
exhibiting liquid crystalline behaviour. The W-shaped compound in solution ($\lambda_{cm}$) is found to exhibit strong fluorescence on excitation at 365 nm (conc. $4.66 \times 10^{-6}$ M). The emission peak at 442 nm (2.80 eV) with a Stokes shift of the order of 80 nm (1.62 eV) was attributed to the formation of intermolecular excimer. The Stokes shift, which reflects the structural relaxation of the excited molecule, which is significantly larger than the reported push-pull systems [97-101] exhibiting liquid crystal behaviour, confirmed the molecular conformational changes upon excitation. These results are in good agreement with the reported results of molecular J-aggregates [102] in which the excitonic energy is delocalized as a result of intermolecular coupling within the head-to-tail arrangement of the molecules in the solution. We believe that the presence of two Schiff's base linkages and H-bonding in which the coplanar planes of the phenyl rings of aldehyde and aniline moieties may be contributing to the planar nature of the excimer and hence results in high fluorescence intensity in this compound.

Figure 5.25: The absorption and emission profile of the compound 134NPD(OH)O12.
5.9 Conclusion:

Thirty compounds belonging to eight different novel homologous series of achiral five-ring bent-core compounds derived from 1,3-phenylene diamine containing lateral substituents in central bent-core as well as in end side wings were synthesized and their mesomorphic properties investigated. These compounds exhibit a variety of B phases, some of this B phases show antiferroelectric switching characteristics and exhibit two dimensional lattice structure. We also find that the reported observation [103], regarding the influence of the fluoro atom in the 4- position of the central core, a derivative of isophthalic acid that does not modify the mesomorphic domain and the phase sequence in comparison with the compounds without a substituent, is always not true. The nature of the substituent, combination and the direction of different linking groups in each arm of the bent shaped molecule, the position of the substituent either on the central core or other rings of the molecule and the length of aliphatic end chains collectively play a very important role in deciding the nature of banana mesophases. In all the compounds with lateral hydroxyl group in the side wing, the hydrogen bonding may be intramolecular or intermolecular and the combination of a specific substituent such as a fluorine atom or nitro group replacing the H atom in the central core not only enhances the polarizability due to its large dipole moment, but also has a major influence on the mesophase behaviour leading to banana mesomorphism. Our work also support the general view that a minor change in the molecular structure in this system can lead to a drastic change of the associated mesophase and sometime result in suppressing the liquid crystalline behaviour as in the case of 4M-10OH compound.

In an aim to study the mesomorphic properties of a five ring Schiff base azo compound, a novel bent shape compound having a polar nitro group at 4-position of central core with bending angle ~120° has been synthesized. The polarizing optical microscopy study revealed that the compound can be a model example of an achiral banana shaped molecule exhibiting chiral phase. The differential scanning calorimetry studies also revealed that there is large change in enthalpy may be due to complicated phase structure or may be due to the presence of intra or inter molecular Hydrogen bonding. The presence of the chiral phase is a consequence of the polar order in combination with the tilt and layer ordering of the molecules.
References:


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