Our study of examining the effect of polar substituents on the central bent core unit of achiral four ring banana shaped molecules are detailed in this chapter. The phases exhibited by these compounds were confirmed by POM, DSC and XRD techniques.
5. Effect of polar substituents on mesomorphism of unsymmetrical four-ring bent-core compounds:

In the previous chapter it is successfully demonstrated that new asymmetric four-ring bent-core compounds exhibiting banana mesomorphism viz., 2D-polarization modulated layer undulated smectic phases (B1RevTilt phases). The majority of the reported four-ring bent-core compounds did not exhibit mesomorphism [1-5]. However Hird et al reported fluoro substituted bent–core compounds exhibiting monotropic nematic phase with chiral domains. The earlier reported four-ring molecules with a biphenyl moiety in the wing possessing fluoro substituents on the central ring viz. [(S)-1-methylheptyl-4-[2,3,4-trifluoro-5-(4'-dodecyloxy-biphenyl-4-ylcarbonyloxy)-phenylcarbonyloxy] benzoate] exhibited conventional SmA, ferro-, ferri-, and antiferroelectric SmC phases resulting from the molecular chirality and not due to the bent shape [6]. Weissflog et al recently reported asymmetric achiral four-ring bent-core mesogens derived from N-benzoylpiperazine and only few of them found to exhibit only calamitic phases. The introduction of a substituent in the side wings of the molecules also does not promote the mesomorphism [7]. They reported polar structures under the influence of electric field in these four-ring bent-core compounds exhibiting calamitic type smectic phases. Moreover they also exhibited switchable smectic I phase the first example of non-chiral ferroelectric SmI phase (SmIPr), which is attributed due to bent shape of the molecules. None of these four-ring compounds are found to spontaneously exhibit typical banana phases (SmAP, SmCP) because of weak steric interactions between the aromatic cores. Kang et al [8] reported a four-ring oxadiazole derivative exhibiting nematic-SmC-Bx phase variant. The Bx phase is found to be uniaxial, exhibited randomly distributed domains of opposite handedness and under the influence of electric field transformed to a homochiral SmCAPr phase with antiferroelectric response.
Figure 5.1: Molecular structures of reported four ring compounds
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 [9-13]. Several research groups studied the influence of the lateral substituents on the mesophase behaviour either in the central core or the outer rings [9-19]. 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 [16-21]. 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 [22-25]. Rich variety of banana phases was discovered by introducing lateral substituents in the central ring. In case of lateral substitution three major factors are involved depending on the size and polarity of the substituents namely inter- and intra molecular forces of attraction, repulsion of the substituents and the position of the substitution. These factor influence molecular conformation. Molecular conformation effects on molecular packing and vice versa. Consequently, lateral substitution has an impact on the liquid crystalline state, i.e. on the liquid crystalline behaviour. Systematic study of banana substance classes one by one, may advance understanding of this subject.

In this and next chapters unsymmetrical four ring banana shaped compounds substituted with Fluoro (F), Chloro (Cl) and Methyl (CH₃) at different positions of the aromatic ring of the central core will be discussed. This chapter is divided into three sections based on the substituents e.g. the first section is on the effect of fluoro substituent, the second and third section on the effect of chloro substituents at different positions.
Modified Structures of central bent core unit with a substituent

\[
\begin{align*}
5-3a & : \text{4'-aminophenyl-5-amino-2-fluorobenzoate} \\
5-3b & : \text{4'-aminophenyl-5-amino-2-chlorobenzoate} \\
5-3c & : \text{4'-aminophenyl-3-amino-4-chlorobenzoate}
\end{align*}
\]

Designed compounds

\[
\begin{align*}
\text{RN-n-6}'F : n & = 8, 9, 10, 11, 12, 13, 14, 16 \\
\text{RN-n-6}'Cl : n & = 10, 12, 14, 16
\end{align*}
\]

Figure 5.2: Modified Structures of central bent core unit with a substituent and designed compounds
5.1. Effect of Fluoro substituents:

The fluoro substituent in organic compounds is regarded as so interesting because of the combination of polar and steric effects, and the great strength of the C–F bond which confers stability on fluoro-substituted compounds. Fluorine has the highest electro-negativity of all the elements (3.98), and hence as a substituent confers a high dipole moment on the C–F bond. In an aliphatic or alicyclic environment the dipole moment is relatively large, e.g., 1.85 D in fluoromethane, however, in an aromatic environment the mesomeric effect causes a reduction in dipole moment, e.g., 1.50 D for fluorobenzene. Despite the high polarity, the fluoro substituent has a low polarizability which confers low intermolecular dispersion interactions. The fluoro substituent is the smallest, after hydrogen, of all possible substituents, and like hydrogen it is monoatomic. So although a fluoro substituent obviously causes a steric effect, the size influence is not too drastic, which enables it to be usefully incorporated into parent molecules for beneficial modification of properties. Lateral substituents, particularly fluoro, are frequently employed in liquid crystal structures to modify melting point, liquid crystal transition temperatures and mesophase morphology and to modify the physical properties of liquid crystals to enable their use in applications. Fluoro substituents have been so successfully and usefully incorporated into liquid crystal molecules because of the combination of small size and high polarity [26-28] and because the high strength of the C–F bond confers excellent stability. The relatively small size of a fluoro substituent means that it does not unduly alter the necessary stylized structure, which helps to maintain the existing liquid crystalline nature of the compound. However, the important attributes of the fluoro substituent discussed above, ensures that subtle, but significant, modifications are frequently encountered in respect of melting point, mesophase morphology, transitions temperatures, and the many essential physical properties of liquid crystals, such as optical, dielectric, and visco-elastic properties. Such alterations to the attributes of liquid crystals are of great significance in terms of fundamental academic structure–property relationships, and crucial to the development of commercially-successful liquid crystal displays. The structure of this series of compound is shown in figure 5.2.
5.1.1. Synthesis:

The starting material in the present study 4-n-alkyloxysalicylaldehyde was prepared by Williamson etherification of 2,4-dihydroxybenzaldehyde with appropriate n-alkyl bromide. The central bent core moiety 4'-aminophenyl-5-amino-2-fluorobenzoate (5-3a) was prepared as follows. 2-Fluoro-5-nitrobenzoic acid was converted into its acyl chloride followed by condensation with 4-nitrophenol using phase transfer reaction. The resultant 4'-nitrophenyl-2-fluoro-5-nitrobenzoate was subjected to 10% Pd-C catalysed reduction to get the desired di-amino bent-core compound. The condensation of 4-n-alkylox salicylaldehyde with 4-aminophenyl-5-amino-2-fluorobenzoate in presence of a few drops of glacial acetic acid yielded the target bent shaped compounds [4-(N-4'-n-decyloxysalicylidene)-aminophenyl]-[5-(N-4'-n-decyloxysalicylideneamino)-2-fluorobenzoate (RN-n-6'F, n = 10). To avoid the formation of side products, the precipitated compounds were filtered when the solution was hot to yield the pure compounds. The compounds were further recrystallized repeatedly to get the pure samples. The formation of all of the compounds was confirmed by \(^1\)H-NMR and IR spectroscopy and the purity was established by elemental analysis. The other homologues with n = 8, 9, 11, 12, 13, 14 and 16 were also synthesized following the same procedure and characterized. The details of the experimental procedures along with the spectroscopic data for all the homologous series of compounds are presented in the experimental part of Chapter 3. The liquid-crystalline behaviour of the synthesised compounds had been investigated by optical microscopy and differential scanning calorimetry (DSC).

5.1.2. Mesomorphic properties:

The transition temperatures, enthalpies and entropies associated with the phase transitions of all the compounds of the homologous series RN-n-6'F (n = 8 to 14 and 15) as a function of number of the carbon atoms in the terminal alkyl chains obtained from DSC at a scan rate of 5°C min\(^{-1}\) in the second heating and first cooling scans are presented in Table 5.1. All the compounds of the homologous series RN-n-6'F exhibit banana liquid crystalline behaviour over a moderate temperature region. The differential scanning calorimetric thermogram of representative compounds RN-14-6'F and RN-8-6'F are presented in Figure 5.3. RN-14-6'F exhibited two transitions in the heating cycle at 126.63°C (\(\Delta H = 31.58 \text{ kJ/mol, } \Delta S = 79.02 \text{ J/K/mol}\), melting
point and 144.45°C (ΔH = 56.95 kJ/mol, ΔS = 136.42 J/K/mol) clearing point. In the cooling cycle also it exhibited enantiotropic phase transitions at 138.37°C (ΔH = 19.13 kJ/mol, ΔS = 46.50 J/K/mol), 99.75°C (ΔH = 19.80 kJ/mol, ΔS = 53.11 J/K/mol).

Figure 5.3: DSC thermogram of RN-14-6'F and RN-10-6'F.

A plot of phase transition temperatures as a function of number of carbons in the end alkoxy chain is depicted in Figure 5.4. All the compounds were found to exhibit one mesophase only exhibiting almost same texture. The mesophase range increases with the increasing n-alkoxy chain length initially and for the number of carbon atoms 10 and more the mesomorphic range is almost constant (Figure 5.5). The clearing transition temperatures for the mesophase in a homologous series follow a smooth curve.
Table 5.1: Transition Temperatures (°C), Enthalpies (Italic, kJ/mol) and entropies (Italic, J/mol/K) of homologous series RN-n-6'F.

![Chemical structure](image)

<table>
<thead>
<tr>
<th>Compound</th>
<th>R</th>
<th>Cr Heating</th>
<th>Cooling</th>
<th>Colr Heating</th>
<th>Cooling</th>
<th>I</th>
<th>ΔT</th>
</tr>
</thead>
<tbody>
<tr>
<td>RN-11-6'F</td>
<td>C₁₁H₂₃</td>
<td>● 124.67 [16.8, 42.2] 106.69 [29.1, 76.6]</td>
<td>● 149.28 [40.4, 95.7] 138.59 [10.0, 24.3]</td>
<td>● 24.61</td>
<td>• 31.90</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RN-12-6'F</td>
<td>C₁₂H₂₅</td>
<td>● 126.70 [18.8, 47.2] 103.56 [31.8, 84.5]</td>
<td>● 147.46 [36.6, 87.0] 138.71 [13.4, 32.6]</td>
<td>● 20.76</td>
<td>• 35.15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RN-14-6'F</td>
<td>C₁₄H₂₉</td>
<td>● 126.63 [31.6, 79.0] 99.75 [19.8, 53.1]</td>
<td>● 144.45 [56.5, 41.7] 138.37 [19.1, 46.5]</td>
<td>● 17.82</td>
<td>• 38.62</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RN-16-6'F</td>
<td>C₁₆H₃₃</td>
<td>● 111.73 [76.0, 197.5] 101.68 [27.1, 72.5]</td>
<td>● 141.95 [50.8, 122.4] 137.47 [16.2, 39.6]</td>
<td>● 30.22</td>
<td>• 35.79</td>
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</table>
Figure 5.4: Plot of phase transition temperatures as a function of number of carbons in the end alkoxy chain for the compounds of series RN-n-6F in the cooling cycle.

Figure 5.5: Influence of the number of carbon atom at the end alkoxy chain upon the liquid crystalline properties of RN-n-6F series.

The compounds of the homologous series exhibit only one mesophase. The thin film of these samples examined by polarizing optical microscopy highly spherulitic growth was observed from the isotropic melt upon cooling. The typical microphotographs of the textures exhibited by different compounds are shown in
Figure 5.6. On slow cooling the isotropic melt of compound RN-14-6'F, B1 phase grows as dendritic nuclei which coalesce into a typical mosaic texture with large domains of uniform birefringence characterising the phase as columnar phase (Figure 5.6c). The texture of the mesophase (Figure 5.6a, b) is dominated by defects growing from spherulitic nuclei into banana-leaf or lancet-like defects. The observed POM textures resemble the textures of B1 phase reported in other bent core compounds [11, 29-34]. The XRD studies also confirmed the phase as B1. A comparison of the mesomorphic behaviour of these compounds with that of parent unsubstituted compounds reveals that a) a strong super cooling in the Isotropic-B1 phase transition temperatures, b) rectangular columnar phases instead of 2D modulated reversible tilted phases.

Figure 5.6: Optical photomicrograph (crossed polarizers) of the Col, phase of RN-14-6'F in a 5.0 μm cell as obtained by cooling from the isotropic liquid a) growing of columnar mesophase from isotropic liquid at 138 °C b) columnar phase at 125.5 °C c) texture of the compound RN-10-6'F contained between glass plate and cover slide at 120°C. d) Columnar phase of RN-11-6'F at 132 °C
5.1.3. X-Ray Studies:

To confirm the mesophase structures X-ray diffraction studies are performed on a representative compound belonging to the homologous series RN-n-6'F. X-Ray measurements were performed on unaligned (powder) samples in a 0.5 mm diameter Lindeman capillary tube (sealed at both ends) with Cu Kα (λ = 1.5418 Å) radiation using the P Analytical X’Pert PROMP X-ray diffractometer consisting of a focusing elliptical mirror and a fast resolution detector (PIXCEL). A typical diffraction pattern obtained for the compound RN-10-6'F at 134°C is shown in Figure 5.7. The diffraction pattern indicated a strong reflection at 2θ = 1.95° corresponding to 45.2 Å. This corresponds to the molecular length n which is slightly lower than the estimated molecular length of 48.7 Å (Figure 5.8) in all trans conformation indicated a tilted layer with a tilt angle 21°. Another broad diffuse peak at 2θ = 5.776° corresponding to 15.3 Å in conjunction with the peak at 45.2 Å suggest a 2D columnar phase. In addition to these reflections a broad diffuse wide angle reflection at 2θ = 19.21° corresponding to 4.62 Å reflects the spacing between the aliphatic chains indicative of a liquid-like in-plane order of the fluid phase. Based on the POM texture, X-ray studies and large enthalpy values associated with the phase transition the mesophase in these compounds is identified as B1 columnar phase. These observations are in agreement with the reported results on compounds exhibiting B1 columnar phases [18, 30, 35-36].

![Figure 5.7: X-Ray angular intensity profile obtained for the B1 mesophase of compound RN-10-6'F at 134°C diffraction spectrum.](image-url)
5.1.4. UV-Visible and Fluorescence studies:

As already described in previous chapter the emission properties of organic liquid crystals (LCs) are currently an active area of research because of their potential applications in the area of optoelectronics. Emissive liquid crystals (LCs) are intriguing systems for materials research because they couple molecular self-assembly with intrinsic light generation capabilities. The importance of the substituent on the central core plays an important role in the modification of electronic characteristics of the molecules. Hence the absorption and emission properties of the compounds are studied and the results are presented in this section.

The UV absorption and fluorescence spectroscopic properties of compound RN-10-6'F in solution were studied in various solvents of different concentrations to obtain information regarding absorption and emission maxima and the Stokes shift of fluorescence. The UV-Visible and Fluorescence spectra of a representative compound RN-10-6'F are shown in figure 5.9. The UV-visible spectra in these homologous compounds exhibited strong absorption peaks at ~344 nm with a large molar extinction coefficient (3.60 eV for RN-10-6'F, ε ~ 107800 Lmol⁻¹cm⁻¹, concentration = 10⁻⁵ M solution in CHCl₃). The strong absorption band reflects the π-π* transition of the highly π-conjugated system having the substituted phenyl benzoate unit as the core. Additionally, we investigated the fluorescence spectrum to observe the characteristic features of the excited states of RN-10-6'F. The fluorescence emission spectrum of RN-10-6'F was examined in chloroform solution (conc. 1.0 x 10⁻⁵ M) and it was found to exhibit a strong fluorescence on excitation at 344 nm. The emission maximum (λ_em) at 510 nm (2.4 eV) for compound RN-10-6'F originate from with a large Stokes shift (λₛ) of 166 nm (ΔE = 1.17 eV) was attributed
to the formation of intermolecular excimers. This Stokes shift, which reflects the structural relaxation of the excited molecule, is significantly larger than in reported push-pull systems exhibiting liquid crystal behaviour [37-41] indicating that the molecular conformation changes upon excitation. These results are in good agreement with the reported results of molecular J-aggregates [42] 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. The optical band gap investigations of thin films in LC phase and solid state for their possible applications and Fluorescence confocal polarizing microscope studies to detect the polarization dependent fluorescence in mesophase of these compounds are currently in progress.

![UV-Visiblc and fluorescence spectra of RN-10-6'F](image)

**Figure 5.9: UV-Visible and fluorescence spectra of RN-10-6'F**

5.2. **Effect of Chloro substituents:**

Chloro substitution is less studied compared to fluoro substitution [43-45]. The size of chlorine atom (atomic radius = 0.97Å) is larger than fluorine atom (atomic radius = 0.57Å). Because of larger atomic size of the chloro substituent than the hydrogen and fluorine substituents, it exerts a steric effect on the organization of molecular structures and in turn mesomorphic characteristics.
5.2.1. Synthesis of \([4-(N-4\text{-tetradecyloxysalicylidemino})\text{phenyl}]\)-\([5-(N-4\text{-tetradecyloxysalicylidemino})\text{-2-chlorobenzoate}]\), RN-14-6'Cl:

The starting material 4-n-tetradecyloxy salicylaldehyde was condensed with the unsymmetric central core 4/-aninophenyl-5-amino-2-chloro benzoate to get the final compound, \([4-(N-4\text{-tetradecyloxysalicylidemino})\text{phenyl}]\)-\([5-(N-4\text{-tetradecyloxysalicylidemino})\text{-2-chlorobenzoate}]\). The compound was further recrystallized repeatedly to get the pure sample. The formation of the compound was confirmed by \(^1\text{H}-\text{NMR}\) and IR spectroscopy and the purity was established by elemental analysis. The details of the experimental procedures along with the spectroscopic data for compound are presented in the experimental part of Chapter 3.

5.2.2. Mesomorphic properties:

To investigate the liquid-crystalline behaviour of the synthesised compound, RN-14-6'Cl, optical microscopy and differential scanning calorimetric (DSC) studies were carried out. The DSC thermogram, phase transition temperatures and enthalpy associated with the transitions are presented in Figure 5.10.

![Figure 5.10: DSC thermogram, transition temperatures and enthalpies of phase transition of compound RN-14-6'Cl.](image)

(Heating): K 98.1°C (11.0) K1 130.7°C (35.9) Col, 134.7°C (7.1)

(Cooling): K 92.4°C (7.7) K1 109.6°C (40.7) Col, 133.6°C (12.7)

Figure 5.10: DSC thermogram, transition temperatures and enthalpies of phase transition of compound RN-14-6'Cl.
On slow cooling from the isotropic phase the mesophase grows within the isotropic liquid as telephone-wire structures that are shown in Figure 5.11a. On further cooling, the material enters completely to a structured columnar fan like texture under the polarization microscope. It exhibits pseudo-broken fans or circular domains with extinction brushes directed along polarizing directions. On further cooling the sample, low birefringent stripes appears across the blades of the columnar fan and finally becomes completely low birefringent without changing the columnar texture before it crystallizes. The polarising optical microscopic textures of the compound RN-14\textsubscript{6}\textsuperscript{C1} in a 5.0 \textmu m cell are shown in Figure 5.11.

**Figure 5.11:** Microphotographs of the compound RN-14\textsubscript{6}\textsuperscript{C1} in a 3.5\textmu cell. Photographs shows (a) helical spiral formation from the isotropic phase to mesomorphic phase at 133.6\textdegree C (b) dendritic growth at 133.6\textdegree C (c) fully developed columnar texture (d) phase transition appearance of POM texture of the transient transition bars of arcs across the fans at 125.0\textdegree C after 3 minutes (d) after 5 minutes and (e) columnar texture of phase at 133.5\textdegree C with a change in colour at 124\textdegree C.
5.2.3. X-Ray diffraction studies:

However, the growth of the mesophase in telephone-wire structures has been widely related to the existence of 2D periodic structures such as columnar or smectic undulated phases [46-48]. In order to clarify this point, small angle X-ray diffraction experiments were carried out. The measurements were performed at different temperatures within the mesophase on an unaligned sample.

In powder X-ray diffraction measurements the diffuse broad hump observed in the wide angle region (2θ ~ 15°~25° with a maximum at 4.63 Å) from in-plane molecular positional correlations indicating that the layers in this phase is two-dimensional liquid like order (Figure 5.12). In contrast several sharp peaks at (1) 70.11 Å, (2) 63.22 Å, (3) 47.46 Å, (4) 40.44 Å, (5) 32.79 Å and (6) 24.41 Å in the small angle region (Figure 5.13) are observed in the mesomorphic phase of RN-14-6'C1 at 130°C. The first and second peaks in the small angle region have no relation to the first and second order diffraction peaks corresponding to the smectic layer and hence a two dimensional (2D) frustrated layer structure can explain the reflections. Following the hypothesis proposed for 2D rectangular lattices, it is reasonable to assign the most intense peak at 47.46 Å corresponding to layer periodicity and is found to be less than the molecular length of 58.4 Å in most extended conformation shown in Figure 5.14 although it is likely that somewhat more bent conformation is adopted in the smectic phase. Typical bent core tilt angle of the molecules (tilt angle θ ~ 35°) and the measured layer spacings would imply an effective molecular length ~58 Å. The reflection in the low angle region (~ 2θ ~ 1.26°) indicative of in-plane modulation of the smectic layers of wavelength λ ~70.1 Å associated with the 2D polarization splay modulated layer undulated structure, a structural feature associated with the B7 and the B1_{RevTiled} phases with a 2D lattice of a ~ 70.1 Å (along the layer) and c (layer thickness) ~ 47.4 Å. The helical filament textures, the multiple peak reflections at low angles, the tilt in molecular layering and non-switchable phase structure are indicative of a B1_{RevTiled} phase structure and suggest that the phase represents 2D polarization splay modulated layer undulated molecular structure of SmCPU family. Further work of electro-optical experiments is in progress to compliment the x-ray results and to assign the reflections and to identify the exact phase structure. The temperature variation of layer thickness is presented in Figure 5.15 and found only small variation from 47.45 to 47.92 Å.
Figure 5.12: X-ray diffraction pattern of RN-14-6'Cl at 130°C

Figure 5.13: X-ray diffraction pattern of RN-14-6'Cl at 130°C in the low angle region
5.2.4. UV-Visible and fluorescence studies:

The UV absorption and fluorescence spectroscopic properties of compound RN-14-6\textsuperscript{6}Cl in solution were studied in various solvents of different concentrations to obtain information regarding absorption and emission maxima and the Stokes shift of fluorescence. The UV-Visible and Fluorescence spectra of a representative compound RN-14-6\textsuperscript{6}Cl are shown in figure 5.16. The UV-visible spectra in these homologous compounds exhibited strong absorption peaks at ~344 nm with a large molar extinction coefficient (3.60 eV for RN-14-6\textsuperscript{6}Cl, \( \varepsilon \approx 216000 \text{ Lmol}^{-1}\text{cm}^{-1} \), concentration = 10\textsuperscript{-5} M solution in CHCl\textsubscript{3}) and shoulders at 283 nm, 398 nm and 423 nm. The strong absorption band reflects the \( \pi-\pi^* \) transition of the highly \( \pi \)-conjugated system having the substituted phenyl benzoate unit as the core.
Additionally, we investigated the fluorescence spectrum to observe the characteristic features of the excited states of RN-14-6Cl. The fluorescence emission spectrum of RN-14-6Cl was examined in chloroform solution (conc. $1.0 \times 10^{-5}$ M) and it was found to exhibit a strong fluorescence on excitation at 344 nm. The emission maximum ($\lambda_{em}$) at 462 nm (2.68 eV) for compound RN-14-6Cl originate from with a large Stokes shift ($\lambda_s$) of 115 nm ($\Delta E = 0.92$ eV) was attributed to the formation of intermolecular excimers. This Stokes shift, which reflects the structural relaxation of the excited molecule, is significantly larger than in reported push-pull systems exhibiting liquid crystal behaviour [37-41] indicating that the molecular conformation changes upon excitation. These results are in good agreement with the reported results of molecular J-aggregates [42] 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. The optical band gap investigations of thin films in LC phase and solid state for their possible applications and Fluorescence confocal polarizing microscope studies to detect the polarization dependent fluorescence in mesophase of these compounds are currently in progress.

![Figure 5.16: UV-Visible and fluorescence spectra of 2-14-6Cl in chloroform (10^-5M)]](image-url)
5.2.5. Synthesis of [4-(N-4-decyloxy salicylideneimino)phenyl]-[3-(N-4-decyloxy salicylideneimine)-4-chlorobenzoate], RN-10-4′Cl:

The starting material in the present study 4-n-decyloxy salicylaldehyde was prepared by Williamson etherification of 2,4-dihydroxybenzaldehyde with n-decyl bromide. The central bent core moiety 4′-aminophenyl-3-aminoo-4-chlorobenzoate (5-3c) was prepared as follows. 4-Chloro-3-nitrobenzoic acid was converted into its acyl chloride followed by condensation with 4-nitrophenol using phase transfer reaction. The resultant 4′-nitrophenyl-4-chloro-3-nitrobenzoate was subjected to 10% Pd-C catalysed reduction to get the desired di-amino bent-core compound. The condensation of 4-n-decyloxy salicylaldehyde with 4-aminophenyl-3-amino-4-chlorobenzoate in presence of a few drops of glacial acetic acid yielded the target bent shaped compounds [4-(N-4′-n-decyloxy salicylidene)-aminophenyl]-[3-(N-4′-n-decyloxy salicylideneamino)-4-chlorobenzoate (RN-10-4′Cl)]. To avoid the formation of side products, the precipitated compounds were filtered when the solution was hot to yield the pure compounds. The compounds were further recrystallized repeatedly to get the pure samples. The formation of all of the compounds was confirmed by ¹H-NMR and IR spectroscopy and the purity was established by elemental analysis.

The other homologues with n = 12, 14 and 16 were also synthesized following the same procedure and characterized. The details of the experimental procedures along with the spectroscopic data for all the homologous series of compounds are presented in the experimental part of Chapter 3. The liquid-crystalline behaviour of the synthesised compounds had been investigated by optical microscopy and differential scanning calorimetry (DSC).

5.2.6. Mesomorphic properties:

All the compounds of the homologous series (RN-n-4′Cl) show mesomorphic behaviour for a moderate temperature range. The lower homologues of the series (RN-10-4′Cl and RN-12-4′Cl) show B1 mesophases whereas higher homologue (RN-14-4′Cl and RN-16-4′Cl) shows B7 phases. The differential scanning thermograms of all the compounds of the homologous series show enantiotropic phase transition. The transition temperatures, enthalpies and entropies associated with the phase transitions of all the compounds of the homologous series RN-n-4′Cl (n = 10, 12, 14 and 16) obtained from DSC at a scan rate of 5°C min⁻¹ in the second...
heating and first cooling scans are presented in Table 5.2. Mesomorphic range for the series of compounds in heating and cooling scan are presented in Figure 5.17. All the compounds are enantiotropic with a short mesophase range in heating and long range in cooling. DSC thermogram of a representative compound RN-14-4’Cl shows two transitions in heating cycle at 131.33 (melting point, \( \Delta H = 47.78 \text{ kJ/mol}, \Delta S = 118.17 \text{ J/K/mol} \)) and 137.45 (clearing point, \( \Delta H = 17.04 \text{ kJ/mol}, \Delta S = 41.51 \text{ J/K/mol} \)) and two transition in cooling cycle at 136.73 (\( \Delta H = 16.53 \text{ kJ/mol}, \Delta S = 40.34 \text{ J/K/mol} \)) and 111.87 (\( \Delta H = 42.85 \text{ kJ/mol}, \Delta S = 111.33 \text{ J/K/mol} \)). Other transitions at 99.48, 104.6 in heating cycle and 94.94 and 91.71 in cooling cycles are crystal to crystal transitions. (Figure 5.18).

<table>
<thead>
<tr>
<th>Compound</th>
<th>R</th>
<th>Cr</th>
<th>Heating</th>
<th>Cooling</th>
<th>B1/ B7</th>
<th>Heating</th>
<th>Cooling</th>
<th>I</th>
<th>( \Delta T )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-10-4’Cl*</td>
<td>C(<em>{10})H(</em>{21})</td>
<td>•</td>
<td>127.76</td>
<td>[20.2, 50.4]</td>
<td>102.23</td>
<td>•</td>
<td>129.53</td>
<td>127.31</td>
<td>[8.5, 21.2]</td>
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<td>C(<em>{12})H(</em>{25})</td>
<td>•</td>
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<td>[37.1, 91.4]</td>
<td>110.61</td>
<td>•</td>
<td>134.88</td>
<td>132.98</td>
<td>[6.3, 15.6]</td>
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<tr>
<td>2-14-4’Cl</td>
<td>C(<em>{14})H(</em>{29})</td>
<td>•</td>
<td>131.33</td>
<td>[47.8, 118.2]</td>
<td>111.87</td>
<td>•</td>
<td>137.45</td>
<td>136.73</td>
<td>[16.5, 40.3]</td>
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<td>2-16-4’Cl</td>
<td>C(<em>{16})H(</em>{33})</td>
<td>•</td>
<td>130.03</td>
<td>[41.2, 102.2]</td>
<td>108.73</td>
<td>•</td>
<td>132.40</td>
<td>131.34</td>
<td>[6.9, 17.2]</td>
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Figure 5.17: Mesomorphic range (ΔT, °C) for the series of compounds in heating and cooling scan.

Figure 5.18: DSC thermogram of RN-14-4'Cl on second heating and cooling at a scan rate 5 °C min⁻¹

Polarising optical microphotographs of the compounds of the homologous series are presented in Figure 5.19. Upon very slow cooling the isotropic liquid, the mesophase defect textures exhibited by RN-16-4'Cl (Figure 5.19a-f) resembles the
B7 phase [33,47-58] texture of fascinating long spiral domains. The microscopic texture of the B7 phase is extraordinary and not comparable with the textures of other B7 phases. If the isotropic liquid is cooled down very fast, the B7 phase appears as a cluster of thin thread-like or straight lancet-like nuclei which coalesce to an unspecific texture. On very slow cooling, variety of texture variants is obtained, but these mostly occur simultaneously within the same preparation. Also, on slow cooling of the isotropic liquid, the B7 phase frequently forms elongated germs such as straight lancet-like or irregular thread-like germs. But frequently these germs have clearly a spiral or double-spiral character. Figure 5.19g shows the growth of a spiral germ. The handedness of the screw-like nuclei could be determined by adjusting the focus of the microscope. The B7 phase frequently grows as oval or sometimes as circular domains. Such domain (shown in figure 5.19a, b, f) exhibits equidistant stripes.

Figure 5.19: Polarising optical microphotographs of various features of B7 textures of compounds RN-16-4Cl sandwiched between glass plate and cover slip (a-g). (h) RN-16-4Cl in a 5μm cell at 132°C. (i) texture of RN-10-4Cl at 134.2°C.

In nylon 6,6 treated cell of the compound RN-14-4Cl, straight lancet like or spiral germs appears when slowly cooled the sample below isotropic temperature. On further cooling the germs coalesce to banana leaf, ribbons and fanlike textures with
equidistant stripes. HTAB treated film appears as blue fan on slow cooling the isotropic liquid. On further cooling, pink stripes appears across the blades of the fan and finally becomes completely pink in colour. In some part of the cell, B7 texture appears as weakly birefringent fan shaped texture which reminds one of the corresponding texture of a SmA phase (Figure 5.20d). Sometimes, but not always, within the fans equidistant black stripes are visible between crossed polarizers. [47]

Figure 5.20: Polarising optical photographs of RN-14-4’Cl on a HTAB treated cell at a)133.2 °C, b) 124.8 °C, C) Nylon 6,6 treated cell at 131 °C, d) Different side of HTAB treated cell at 124.8 °C.

5.2.7. X-Ray Diffraction study:

RN-10-4’Cl

To confirm the mesophase structures X-ray diffraction studies are performed on a representative compound belonging to the homologous series RN-n-4’Cl. A typical diffraction pattern obtained for the compound RN-10-4’Cl at 120° C is shown in Figure 5.21. The diffraction pattern indicated a strong reflection at 2θ = 1.95° corresponding to 45.2Å. This corresponds to the molecular length n which is slightly lower than the estimated molecular length of 48.7 Å (Figure 5.22) in all
trans conformation indicated a tilted layer with a tilt angle 16°. In the small angle region (2θ = 1 - 8°) there are other low intense peaks as observed for the 2D polarization splay modulated layer undulated structure, a structural feature associated with the B7 and the BlRevtilted phases with a 2D lattice. In addition to these reflections a broad diffuse wide angle reflection at 2θ = 19.21° corresponding to 4.51 Å reflects the spacing between the aliphatic chains indicative of a liquid-like in-plane order of the fluid phase. The formation of stripes on focal conic textures, the multiple peak reflections at low angles, the tilt in molecular layering and non-switchable phase structure are indicative of a BlRevtilted phase structure and suggest that the phase represents 2D polarization splay modulated layer undulated molecular structure of SmCPU family. Further work of electro-optical experiments is in progress to compliment the x-ray results and to assign the reflections and to identify the exact phase structure.

Figure 5.21: X-ray diffraction pattern of RN-10-4’Cl.
5.2.8. UV-Visible and Fluorescence study:
The UV absorption and fluorescence spectroscopic properties of compound RN-10-4′Cl in solution were studied in various solvents of different concentrations to obtain information regarding absorption and emission maxima and the Stokes shift of fluorescence. The UV-Visible and Fluorescence spectra of a representative compound RN-10-4′Cl are shown in Figure 5.23. The UV-visible spectra in these homologous compounds exhibited strong absorption peaks at ~344 nm with a large molar extinction coefficient (3.60 eV for RN-10-4′Cl, ε ~ 98300 Lmol⁻¹cm⁻¹, concentration = 1 X 10⁻⁵ M solution in CHCl₃) and shoulders at 283 nm, 398 nm and 423 nm. The strong absorption band reflects the \(\pi-\pi^*\) transition of the highly \(\pi\)-conjugated system having the substituted phenyl benzoate unit as the core. Additionally, we investigated the fluorescence spectrum to observe the characteristic features of the excited states of RN-10-4′Cl. The fluorescence emission spectrum of RN-10-4′Cl was examined in chloroform solution (conc. 1.0 x 10⁻⁵ M) and it was found to exhibit a strong fluorescence on excitation at 344 nm. The emission maximum (\(\lambda_{em}\)) at 450 nm (2.7 eV) for compound RN-10-4′Cl originate from with a large Stokes shift (\(\lambda_S\)) of 106 nm (\(\Delta E = 0.84\) eV) was attributed to the formation of intermolecular excimers. This Stokes shift, which reflects the structural relaxation of the excited molecule, is significantly larger than in reported push-pull systems exhibiting liquid crystal behaviour [37-41] indicating that the molecular conformation changes upon excitation. These results are in good agreement with the reported results of molecular J-aggregates [42] 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. The optical band gap investigations of thin films in LC phase and solid state for their possible applications and Fluorescence confocal polarizing microscope studies to detect the polarization dependent fluorescence in mesophase of these compounds are currently in progress.
5.3. Conclusion:

The influence of polar (fluoro and chloro) substitution at the bent aromatic core was investigated with respect to its effects upon the structures of the mesophases formed by 4-ring bent-core molecules. It was found that, formation of different mesophases is not solely determined by the types of substituent but also by their position. Substitution by chloro and fluoro group on the four ring system produced liquid crystals with a wide variety of mesophases.

Combining the XRD data with DSC and POM results provide unequivocal identification of the mesophase of RN-n-6′F series as B1 columnar phase. Chloro substituted homologues series of compounds, RN-n-6′Cl (n=14) and RN-n-4′Cl (n = 10, 12, 14, 16) belong to the class of compounds exhibiting polarisation modulated layer undulated (PMLU) phase and show B1_{Rev.Tilted} and B7 phase like textures. Because of the possible free rotation of the central ester linkage, all the rings are at different plane with respect to each other. The twisted conformation of the molecule and the hydroxyl groups in the side wings of these molecule participate in inter and or intra molecular H-bonding which in turn give rise to the formation of this kind of undulated and modulated smectic phases. Additionally, all the materials described in this chapter have interesting intrinsic light generating capacity in the region 450-580 nm still retaining their banana polymorphism which could be of use in applications; they are thermally and hydrolytically stable.

Figure 5.12: UV-Vis and Fluorescence curve of 2-10-4′Cl in chloroform solution (10^{-5} M).
References:


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