Chapter 6

Six-ring Bent Core Mesogens

Systematical study of the symmetrical and unsymmetrical bent-core compounds composed of six benzene rings is described. To gain an insight into the structure property relationship in such system, two isomeric series of compound were synthesized without altering their atomic count. It was achieved by changing the direction of ester linking on the central bent core platform.
6.1 Six-ring Bent core Liquid Crystals:

The banana mesomorphism with polar order which is exhibited by bent core molecules is dominated by five ring systems all these years even though four ring bent dimers of two rod like mesogens separated by an alkyl spacer [1,2], few six [3,4] and seven phenyl ring systems [5] appeared in literature. The five ring symmetric and unsymmetrical bent molecules are reported in literature [6-17]. The bent molecule consists of the central bent unit linked to two rod like wings. In these molecules the bending angle a (i.e., the opening angle between the two rod-like wings) is about 120°, but adjacent linking groups connecting the central bent core moiety with the two rod-like wings can introduce some flexibility. The prominent linking groups between the rod like side wings or between the central core and rod like wings are ester, imine or ethylene but few other linkages like acetylene, CH₂O, (CH₂)n are also reported [1]. The length of this bent-core and the bending angle of the central unit are most important for the formation of polar ordered mesophases. In majority of the five rings bent core compounds the central core is phenyl or hetero-aromatic (pyridine) rings are used as unsubstituted or substituted central core. However, broad mesomorphic range is realized in less symmetric biphenyl derivatives [7]. The increasing size of the rigid bent unit also increase the transition temperatures because of aromatic character in order of phenyl, biphenyl, naphthalene, m-terphenyl rings,1,3-bis(phenylethynyl)benzene derivatives, 1,3-bis(4-hydroxyphenyl)benzene derivatives and leads to stabilization of columnar phases [5]. The first banana-shaped six-ring compounds derived from a central core of 3,4'-dihydroxybiphenyl leading to a unsymmetrical bent-shaped molecule [3] exhibiting banana phases is shown in Figure 6.1. These compounds form B1 and/or B2 phases depending on the length of the terminal chains and exhibited remarkable switchable B2 phase at relatively low temperatures.

![Figure 6.1: Molecular structure of the first six ring bent core compound.](image-url)
The seven-ring banana-shaped mesogens with seven rings [5] possessing either only phenyl rings or also with heterocyclic rings exhibited B1 phases. The modification of molecular structures can be realized either by the introduction of a substituent in the central six ring core or heterocyclic five membered rings and hence the bending angle from 100–140° to realize different novel mesophases.

6.2 Structure of the bent-core unit:

The occurrence of polarity and chirality in the mesophases of bent-core molecules strongly depends on the molecular structure and intermolecular interactions. As already mentioned in the Chapter 4, there are three basic structures of Bent-core molecules one of which having the central bent unit (BU) is rather rigid, typically a 1,3-disubstituted benzene ring, a 2,6-disubstituted pyridine ring, a 2,7-disubstituted naphthalene unit or a 1,3'-disubstituted biphenyl unit, to mention only the most often used. The number of reports about six ring compounds mostly based on the last two bent core platform. Those bent core molecules with six benzene rings are known for their highest thermal stability since with an increasing number of rings the transition temperatures increase, although the broader mesomorphic ranges were obtained with the less symmetric biphenyl derivatives. The mesophases with highest thermal stability can also be realised with bent-core units (BU) comprising three aromatic rings giving rise to seven ring banana shaped compounds. Figure 6.1 shows the bent core platform employed to study six and seven ring banana shaped molecule. Generally, increasing the size of the rigid bent unit (biphenyl < naphthalene < m-terphenyl < Tol1 < Tol2) Figure 6.2, increases the transition temperatures and leads to a stabilisation of rectangular columnar phases. For such compounds longer terminal chains are required to suppress the columnar phases and to obtain polar smectic phases.

Figure 6.2: The structure of various bent-core platform and positions of structural substituents.
So the bent shape of these molecules having six or seven aromatic rings mostly results from the central unit listed above. Nonetheless, most banana-shaped liquid crystals reported up to now with six-benzene ring based on 2,7-naphthylene or unsymmetrical substituted biphenyl central unit.

Thus, the design of novel, stable and low-melting banana-shaped mesogens based on six benzene rings is a topical subject in liquid crystal research to explore our understanding on structure property relation in this class of liquid crystals. It seems that, although the minimum number of rings required for obtaining polar order is four which is the classical case of bent dimers [2] of two calamitic mesogens apart from that there is no other report of bent-core molecule with four ring system possessing polar order Sm phases. But after successfully materializing the liquid crustal behaviour in the four ring compound based on 3-amino phenyl-4-amino benzoate and 4,4'-diamino benzophenone bent core platform discussed in Chapter 4 in this chapter we will focus on our work in bent shaped molecule comprising of six benzene ring. To achieve the successful synthesis of six ring compound described in this chapter Table 6.1, we have combined different rigid or flexible angular central units such as a 3-aminophenyl-4-aminobenzoate, 4-aminophenyl-3-aminobenzoate and 4,4'-diaminobenzophenone with 4-n-alkoxybenzoyloxysalicylaldehyde and 4-n-alkoxybenzoyloxybenzaldehyde based side wings. In all the homologous series we have kept Schiff’s base moiety as one of the linking unit as it was observed that it entail mesomorphism. Owing to the high melting temperature of these homologues series of compounds phase identification remains in many cases remain uncertain with other complimentary techniques.

Table 6.1: List of six ring bent core Compounds designed and synthesized for the present study.

Table 6.1: List of six ring bent core Compounds designed and synthesized for the present study.

\[ \text{[3-(N-4-(4'-n-alkyloxybenzoyloxy)salicylidene)-aminophenyl]-[4-(N-4-(4'-n-decyloxybenzoyloxy)-salicylideneamino)-benzoate, (34-nOH-6), } n =10,12 \text{ and } 14 \]
6.3.1 Experimental Details:

The new homologous series of unsymmetrical six ring banana-shaped compounds were synthesized according to the reaction pathway shown in Scheme 23 of chapter 3. The synthetic details of preparation of intermediate compounds viz., central bent core moiety 3-aminophenyl-4-aminobenzoate, 4-n-decyloxybenzoic acid, 4-n-decyloxybenzoylsalicylaldehyde and the six ring product 34-nOH-6 are described in chapter 3. 4-n-decyloxybenzoic acid was obtained from 4-hydroxyethylbenzoate by Williamson etherification followed by hydrolysis. Further 4-n-decyloxybenzoic acid was reacted with thionyl chloride to obtain 4-n-decyloxybenzoylchloride, which was dissolved in dichloromethane and added drop wise to a stirred suspension of aqueous 2,4-dihydroxybenzaldehyde in presence of potassium carbonate and catalytic amount of tetrabutylammoniumbromide by a phase transfer reaction to yield the 4-n-decyloxybenzoylsalicylaldehyde. The condensation of 4-n-decyloxybenzoylsalicylaldehyde with 3-aminophenyl-4-aminobenzoate in presence of a few drops of glacial acetic acid yielded the target bent shaped compounds [3-(N-4-(4'-n-decyloxybenzoyloxy)salicylidene)-aminophenyl]-[4-(N-4-(4'-n-decyloxybenzoyloxy)-salicylideneamino)-benzoate (34-nOH-6). The materials are labelled 34-nOH-6, where n is the number of carbon atoms in the terminal alkoxy chain and 6 for the
number of phenyl rings in the molecule. To avoid the formation of side products under cold conditions in the solution, 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 CHN analysis, $^1$HNMR and IR spectroscopy and the purity was established by elemental analysis. The other homologues with $n = 12$ and 14 were also synthesized following the same procedure and characterized. The purity of all compounds was checked by thin-layer chromatography. The presence of ortho hydroxyl group to form a hydrogen bond with the nitrogen atom of the imine linkage increases the thermal stability and modifies the mesophases thus formed. The liquid-crystalline behaviour of the synthesised compounds had been investigated by optical microscopy and differential scanning calorimetry (DSC).

6.3.2 Mesomorphic properties:

The transition temperatures, enthalpies and entropies associated with the phase transitions of all the compounds of the homologous series 34-nOH-6 ($n = 10, 12$ and 14) as a function of number of the carbon atoms in the terminal alkyl chains obtained from DSC at a scan rate of $10^0\text{C min}^{-1}$ in the second heating and cooling scans are presented in Table 6.2.

Table 6.2: Transition Temperatures ($^\circ\text{C}$), Enthalpies (italics kJ/mol) and entropies (italics in brackets J/mol/K) of homologous series 34-nOH-6.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$R$</th>
<th>Cr</th>
<th>Heating</th>
<th>Enthalpies</th>
<th>Heating</th>
<th>Cooling</th>
<th>Entropies</th>
</tr>
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<tr>
<td>34-10OH-6</td>
<td>C$<em>{10}$H$</em>{21}$</td>
<td>✓</td>
<td>177.2</td>
<td>[77.7, 172.7]</td>
<td>197.8</td>
<td>[19.6, 41.6]</td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>139.9</td>
<td>[61.6, 149.2]</td>
<td>191.2</td>
<td>[9.7, 20.9]</td>
<td></td>
</tr>
<tr>
<td>34-12OH-6</td>
<td>C$<em>{12}$H$</em>{25}$</td>
<td>✓</td>
<td>175.7</td>
<td>[63.3, 141.2]</td>
<td>195.7</td>
<td>[14.6, 31.3]</td>
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<td>[35.7, 87.6]</td>
<td>185.3</td>
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<tr>
<td>34-14OH-6</td>
<td>C$<em>{14}$H$</em>{29}$</td>
<td>✓</td>
<td>172.3</td>
<td>[79.2, 177.9]</td>
<td>198.0</td>
<td>[16.8, 35.7]</td>
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<td></td>
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<td>142.4</td>
<td>[35.8, 86.3]</td>
<td>189.1</td>
<td>[4.3, 9.2]</td>
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</tr>
</tbody>
</table>
All the compounds of the homologous series 34-\textit{nOH-6} exhibit banana liquid crystalline behaviour over a moderate temperature region. The phase transition temperatures as a function of number of carbons in the end alkyl chain length is depicted in \textbf{Figure 6.3}. All the compounds had exhibited mesomorphic range approximately \(\sim 20^\circ\text{C}\) in the heating cycle and \(\sim 50^\circ\text{C}\) in the cooling cycle. All the compounds were found to show one mesophase only exhibiting an identical texture. The observed optical textures exhibited by a representative compound \([3-(N-4-(4'-n-decyloxybenzoyloxy)-salicylidene)-aminophenyl]-[4-(N-4-(4'-n-decyloxybenzoyloxy)-salicylideneamino)]-benzoate, 34-\textit{10OH-6}\) are presented in \textbf{Figure 6.4}. On very slow cooling the representative compound \textit{34-10OH-6} from the isotropic liquid, a large variety of texture arises. These texture variants frequently occur at different places within the same sample preparation. Some typical examples are displayed in \textbf{Figure 6.4}. Different kinds of spiral germ with equally spaced stripes are observed indicating a helicoidally arranged molecular structure and ribbons with helix frequently appear. Sometime, very beautiful two-dimensional periodic pattern are visible.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure6.3.png}
\caption{Phase transition temperatures as a function of number of carbons in the alkyl chain length.}
\end{figure}
6.3.3 X-ray studies:

Because of the high melting temperature of the compounds of this series, unoriented powdered sample was used for the variable temperature X-ray diffraction analyses. 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).

Figure 6.4: Growth of circular domains and of elongated germs or nuclei giving domains like a) and b) different spiral nuclei.

Figure 6.5: X-ray intensity profile of 34-10OH-6 at 160°C.
The scattered radiation was detected using high sensitivity scintillation detector (Crismatec). The sample was placed in an oven, providing a temperature control of 0.1K. We have conducted X-ray diffraction studies on C-10 (see Figure 6.5) and C-14 homologues; the X-ray patterns of them show sharp Bragg reflections corresponding to the length of the molecule giving evidence of a layer structure. In addition, a broad diffuse scattering in the wide angle region indicate a fluid smectic phase with no long range positional order within the layers. The layer structure of the phases as determined for 34-10OH-6 from the X-ray patterns in reciprocal space recorded at 160°C (Figure 6.5) exhibited one sharp peak at 4.57nm using the equation \( q = \frac{2\pi}{d} \), where layer thickness, \( d = L \cos(\theta) \), \( L \) being the molecular length and \( \theta \) the tilt angle. The temperature variation of layer thickness of compound 34-10OH-6, which is found to be constant, is shown in Figure 6.6.

The smectic layer spacing observed for compound 34-10OH-6 corresponds to a tilt angle of about 30° which is calculated assuming the molecule has the conformation shown in Figure 6.7 in which the methylene chains unit of the aliphatic chains are in a fully extended all trans-conformation. Such patterns are consistent with a smectic phase with tilted molecules without in plane order within the layers. Although from the textural observation it seems to be the typical case of a B7 phase but the other characteristics peaks for B7 in the small angle region was not observed in the X-ray pattern for both the compounds.

![Figure 6.6: Plot of layer spacing vs Temperature for 34-10OH-6.](image-url)
This may be due to the fact that the results obtained are in an unoriented sample rather than in a mono-domain sample and hence the observed peaks are too weak to be detectable. Nevertheless, our POM textures share some common characteristics features with those observed in a reference compound for B7 phase [18].

Figure 6.7: Molecular model of compound 34-10OH-6 in which the chains are in a fully extended all trans-conformation.

6.4 [4-{(N-4-{4'-n-alkyloxybenzoyloxy)salicylidene}-aminophenyl]-[3-(N-4-{4'-n-alkyloxybenzoyloxy}-salicylideneamino)-benzoate, 43-nOH-6:

6.4.1 Experimental Details:

The isomeric compounds 4-(N-4-{4'-n-alkyloxybenzoyloxy)-salicylidene}-aminophenyl]-[3-(N-4-{4'-n-alkyloxybenzoyloxy}-salicylideneamino)-benzoate (43-nOH-6) differ from the 34-nOH-6 homologous series of compounds only by the direction of ester linkage in the central bent unit. The new homologous series of unsymmetrical six ring banana-shaped compounds were synthesized according to the reaction pathway shown in Scheme 24 of chapter 3. The synthetic details of preparation of intermediate compounds viz., central bent core moiety 4-aminophenyl-3-aminobenzoate, 4-n-decyloxybenzoicacid, 4-n-decyloxybenzoylsalicyldehyde and the six ring product 43-10OH-6 are furnished in chapter 3. The condensation of 4-n-decyloxybenzoyl-salicylaldehyde with 4-aminophenyl-3-aminobenzoate in presence of a few drops of glacial acetic acid yielded the target bent shaped compounds [4-(N-4-{4'-n-decyloxybenzoyloxy)-salicylidene)-aminophenyl]-[3-(N-4-{4'-n-decyloxybenzoyloxy}-salicylideneamino)-benzoate (43-10OH-6). The materials are labelled 43-nOH-6, where \( n \) is the number of carbon atoms in the terminal alkoxy chain and 6 for the number of phenyl rings in the molecule. To avoid the formation of side products under cold conditions in the solution, the precipitated compounds were filtered from the hot solution 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 CHN analysis, $^1$HNMR and IR spectroscopy and the purity was established by elemental analysis. The other homologues with $n = 12$ and 14 were also synthesized following the same procedure and characterized. The purity of all compounds was checked by thin-layer chromatography. The presence of ortho hydroxyl group to form a hydrogen bond with the nitrogen atom of the imine linkage increases the thermal stability and modifies the mesophases thus formed. The liquid-crystalline behaviour of the synthesised compounds had been investigated by optical microscopy and differential scanning calorimetry (DSC).

6.4.2 Mesomorphic properties:

The phase transition temperatures, enthalpies and entropies associated with the phase transitions of all the compounds of the homologous series 43-$n$OH-6 ($n = 10, 12$ and $14$) as a function of number of the carbon atoms in the terminal alkyl chains obtained from DSC at a scan rate of $10^0$C min$^{-1}$ in the second heating and cooling scans are presented in Table 6.3.

![Table 6.3: Transition Temperatures ($^0$C), Enthalpies (italics kJ/mol) and entropies (italics in brackets J/mol/K) of homologous series 43-$n$OH-6.](image)

<table>
<thead>
<tr>
<th>Compound</th>
<th>R</th>
<th>Cr</th>
<th>Heating</th>
<th>SmCP</th>
<th>Cooling</th>
</tr>
</thead>
<tbody>
<tr>
<td>43-10OH-6</td>
<td>C$<em>{10}$H$</em>{21}$</td>
<td>178.7</td>
<td>[30.8, 68.3]</td>
<td>221.8</td>
<td>[19.1, 38.6]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>149.6</td>
<td>[24.4, 57.8]</td>
<td>215.9</td>
<td>[9.8, 20.1]</td>
</tr>
<tr>
<td>43-12OH-6</td>
<td>C$<em>{12}$H$</em>{25}$</td>
<td>176.8</td>
<td>[29.3, 65.1]</td>
<td>219.7</td>
<td>[16.6, 33.6]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>146.5</td>
<td>[23.7, 56.4]</td>
<td>216.3</td>
<td>[8.2, 16.7]</td>
</tr>
<tr>
<td>43-14OH-6</td>
<td>C$<em>{14}$H$</em>{29}$</td>
<td>173.4</td>
<td>[28.4, 63.8]</td>
<td>218.4</td>
<td>[14.3, 29.1]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>144.6</td>
<td>[27.4, 65.7]</td>
<td>215.6</td>
<td>[8.8, 18.0]</td>
</tr>
</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 $10^0$C/min. Additional crystal to crystal transitions have been observed in the 43-$n$OH-6 series of compound.
All the compounds of the homologous series 43-\(n\)OH-6 exhibit banana liquid crystalline behaviour over a moderate temperature region. The phase transition temperatures as a function of number of carbons in the end alkyl chain length is depicted in Figure 6.8. All the compounds had exhibited mesomorphic range approximately \(\sim 45^\circ C\) in the heating cycle and \(65\sim 70^\circ C\) in the cooling cycle and found to show one mesophase only exhibiting an identical texture. The change in direction of ester linkage and the position of ester group influences not only the mesomorphic range but also the thermal stability of the compounds. The observed optical textures exhibited by a representative compound [4-(N-4-(4'-n-decyloxybenzoyloxy)-salicylidene)-aminophenyl]-[3-(N-4-(4'-n-decyloxybenzoyloxy)-salicylideneamino)-benzoate, 43-10OH-6 are presented in Figure 6.9. On very slow cooling the representative compound 43-10OH-6 from the isotropic liquid, a large variety of texture arises. Some typical examples are displayed in Figure 6.9. On cooling the sample from isotropic melt the mesophase appear as a lath or coloured banana leaf like texture with stripes pattern. The stripes are indicative of smectic polar SmCP type phases.

![Figure 6.8: Phase transition temperatures as a function of number of carbon atoms in the alkyl chain length.](image)
On rapid cooling the texture appear as circular focal conic domains and indicates that a smectic mesophase exist. Different kinds of spiral germ with equally spaced stripes are observed indicating a helicoidally arranged molecular structure and ribbons with helix frequently appear. Sometime, very beautiful two-dimensional periodic pattern are visible. Although from the textural observation it apparently appears as the typical case of a polar SmCP phase, further work is necessary to
confirm the phase characteristics by X-ray diffraction, electro-optical and other studies. Efforts in this direction are in progress to characterize the phase characteristics.

6.5 N,N'-bis[4'-4'-n-alkyloxybenzyloxy]benzyldene]-4,4'-diamino-benzophenone, BP-nH-6:

6.5.1 Experimental Details:

The homologous series of compounds N,N'-Bis[4-(4-n-alkyloxybenzoyloxy)-benzyldene]-4,4'-diaminobenzophenone BP-nH-6 differ from the 34-nOH-6 and 43-nOH-6 homologous series of compounds by the linkage moiety viz., carbonyl rather than ester linkage in the central bent core unit and hydroxyl groups in the side wings. The new homologous series because of such a linkage became symmetrical rather than unsymmetrical six ring banana-shaped compounds described in the earlier sections. The homologous series of compounds were synthesized according to the reaction pathway shown in Scheme 25 of chapter 3. The synthetic details of preparation of intermediate compounds viz., 4-n-dodecyloxybenzoic acid, 4-n-dodecyloxybenzoylbenzaldehyde and the six ring product BP-nH-6 are furnished in chapter 3. The condensation of 4-n-decyloxybenzyloxybenzaldehyde with 4,4'-diaminobenzophenone in presence of a few drops of glacial acetic acid yielded the target bent shaped compounds N,N'-Bis[4-(4-n-dodecyloxybenzoyloxy)-benzyldene]-4,4'-diaminobenzophenone BP-12H-6. The materials are labelled BP-nH-6, where BP benzophenone central link, n is the number of carbon atoms in the terminal alkoxy chain and 6 for the number of phenyl rings in the molecule. To avoid the formation of side products under cold conditions in the solution, the precipitated compounds were filtered from the hot solution 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 CHN analysis, 1H NMR and IR spectroscopy and the purity was established by elemental analysis. The other homologues with n = 14 and 16 were also synthesized following the same procedure and characterized. The purity of all compounds was checked by thin-layer chromatography. The liquid-crystalline behaviour of the synthesised compounds had been investigated by optical microscopy and differential scanning calorimetry (DSC).
6.5.2 Mesomorphic properties:

The phase transition temperatures, enthalpies and entropies associated with the phase transitions of all the compounds of the homologous series \( \text{BP-}n\text{H-6} \) \( (n = 12, 14 \text{ and } 16) \) as a function of number of the carbon atoms in the terminal alkyl chains obtained from DSC at a scan rate of \( 10^0 \text{C min}^{-1} \) in the second heating and cooling scans are presented in Table 6.4.

Table 6.4: Transition Temperatures (\(^0\text{C}\)), Enthalpies (italics kJ/mol) and entropies (italics in brackets J/mol/K) of homologous series \( \text{BP-}n\text{H-6} \).

<table>
<thead>
<tr>
<th>Compound</th>
<th>R</th>
<th>Heating</th>
<th>Cooling</th>
<th>Col</th>
<th>Heating</th>
<th>Cooling</th>
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</thead>
<tbody>
<tr>
<td>( \text{BP-12H-6} )</td>
<td>( \text{C}<em>{12}\text{H}</em>{25} )</td>
<td>( 178.0 )</td>
<td>( 207.9 )</td>
<td>( 134.5 )</td>
<td>( 200.0 )</td>
<td>( 35.7, 87.6 )</td>
</tr>
<tr>
<td>( \text{BP-14H-6} )</td>
<td>( \text{C}<em>{14}\text{H}</em>{29} )</td>
<td>( 197.3 )</td>
<td>( 204.8 )</td>
<td>( 188.9 )</td>
<td>( 202.2 )</td>
<td>( 29.2, 62.1 )</td>
</tr>
<tr>
<td>( \text{BP-16H-6} )</td>
<td>( \text{C}<em>{16}\text{H}</em>{33} )</td>
<td>( 199.3 )</td>
<td>( 204.3 )</td>
<td>( 188.4 )</td>
<td>( 199.3 )</td>
<td>( 23.0, 48.7 )</td>
</tr>
</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 \( 10^0 \text{C/min} \). Additional crystal to crystal transitions have been observed in the \( \text{BP-}n\text{H-6} \) series of compound.

All the compounds of the homologous series \( \text{BP-}n\text{H-6} \) exhibit banana liquid crystalline behaviour above \( 150^0 \text{C} \) temperature region. The phase transition temperatures as a function of number of carbons in the end alkyl chain length is depicted in Figure 6.10. The lower \( \text{C12} \) homologue exhibited mesomorphic range \( \sim 29^0 \text{C} \) in the heating cycle and \( 66^0 \text{C} \) in the cooling cycle while the other two higher homologues exhibited mesomorphism over a narrow temperature region. All the compounds show one mesophase only exhibiting identical textures. The changes in linking group and variation in chain length had pronounced influence on the phase behaviour, mesomorphic range and thermal stability.
Figure 6.10: Phase transition temperatures as a function of number of carbon atoms in the alkyl chain length.

The observed optical textures exhibited by a representative compound [N,N'-Bis[4-(4-n-dodecyloxybenzoyloxy)-benzylidene]-4-4'-diaminobenzophenone BP-12H-6 are presented in Figure 6.11. On cooling the representative compound BP-12H-6 from the isotropic liquid, the columnar phase appears as circular focal conic domains textures with uniform birefringence. On very slow cooling the texture appear as circular focal conic domains occupying the entire area under observation and indicates that a smectic mesophase exist. Although from the textural observation it apparently appears as the typical case of a polar columnar phase, further work is necessary to confirm the phase characteristics by X-ray diffraction, electro-optical and other studies. Efforts in this direction are in progress to characterize the phase characteristics.

Figure 6.11: Growth of a) banana leaf like and focal conic domains with homeotropic regions and b) circular focal conic domains with uniform birefringence.
6.6 Conclusion:
The work carried out in this chapter and in general in thesis adds new structural features for bent core molecules capable of forming B7 and columnar phases. The six-ring series of compounds 43-nOH-6 34-nOH-6 had no structural counterparts of unsymmetrical molecules exhibiting B7 mesomorphism. The homologous series of compound discussed in this Chapter give evidence of the subtle relationship between the chemical structure and mesomorphic properties of banana compounds. The subtle variation in the direction of the ester linking group in the central bent core of 43-nOH-6 homologous series to realize the isomeric 34-nOH-6 homologous series of compound without altering their atomic count was achieved. Even though it appears as a minor modification, had a pronounced change in the mesomorphic behaviour viz., mesomorphic range, and nature of mesomorphic phases i.e., layered SmCP phase/ two-dimensional B7 mesophase like, thermal stability etc. of these compounds. It is evident from the above examples that the direction of the ester linkage in central bent core is also one of the parameters in deciding the direction of polarization of the bent molecules which in turn determine their polar organization.
References:


