Chapter V

Four ring Bent-Core Mesogens: Azo based 2,6-disubstituted toluene derivatives
5.1. Bent-core mesogens with ester, imine and azo linking groups:

This chapter is basically focused on two things; one is linking group and another one is presence of substitutions on the bent shaped compound. From the molecular structural aspect the bent-core liquid crystal based on five phenyl rings connected via four linking groups are well studied [1-6]. Weissflog et al. [7] 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 banana phases and for shifting the thermal range of banana phases to a lower temperature.

In this chapter the influence of the substituents in the central benzene ring in an achiral unsymmetrical substituted four ring bent-core molecules as well as the change in the linking group between the lateral phenyl rings in one of the side wings on the mesomorphic behaviour have been studied and the details are presented below. The effect of linking group on the bent core liquid crystals viz; azo (-N=N), can form cis-trans isomerism of the molecule, though the trans form is more stable. The position of ester group (-COO or -OOC) can change the phase behaviour and isotropic transition temperature.

5.2. Influence 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, 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 [12-17]. However, the introduction of a small substituent into the central 1,3-phenylene ring leads to the possibility of synthesizing 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 methyl substitution depending upon its position in banana-shaped molecules revealed several interesting factors. The one important factor is that the compound with a methyl substitution in the central phenyl exhibited large thermal nematic phase range [24].

However recent results [25-27] on bent core liquid crystals exhibiting nematic phase with a signature of four-spot in small angle X-ray diffraction pattern confirm the existence of short range cybotactic clusters in that phase. The self assembly and self organization of a group of molecules in a nematic phase, in a smectic C (SmC) or smectic A (SmA) like arrangement is called as cybotactic cluster. SmC type of cluster in nematic phase is called nematic cybotactic C (NcybC) cluster. Interestingly X-ray diffraction small angle four-spot pattern on both side of the meridian and equator in low temperature region evidenced the cluster formation of skewed cybotactic supramolecular structure with temperature dependent tilt angle. High resolution X-ray studies confirmed the presence of cybotactic clusters of SmC like ordering in low temperature region in lower homologue of ODBP [25] exhibiting nematic phase only. Further the two-spot pattern in high temperature region of the nematic phase is similar to that of the uniaxial nematic (N_{u}) phase of conventional calamitic molecules. Polarizing Optical Microscopy (POM) studies [28] evidenced the biaxial nematic to uniaxial nematic phase transition confirming the signature of four-spot to two-spot pattern [24] in X-ray studies.

Moreover, the fluid smectic liquid crystal phases with spontaneously growing chiral and polar layers (SmCP phases) including the polarization splay modulated and layer undulated (PMLU) B_{7}/B_{1Rev/Tilted} phases variants in four ring bent system [29]. The four ring molecule possesses two -OH groups in two wings, located in unsymmetrical positions, which deviates significantly from the typical symmetrical and/or V-shape of other bent core molecules. Further, helical structures have been observed in these four ring achiral systems and this phenomenon is the strong evidence of the origin of the chirality in this system viz. ferro/antiferroelectricity and twisted structures is related to the twist conformation of these molecules. The modification of angular 3,4'-disubstituted biphenyl unit [30] with the introduction of an ester linkage viz., COO moiety between the phenyl units, reduction of phenyl
rings and proper choice of a substituent and its position in the central core leads to structural variation of polar groups in bent core molecules and hence can promote a broad range of interesting variations in their mesogenic properties [29]. Any substituent ortho to ester linkage separating the two phenyl rings may substantially change the conformation of the molecule depending on the size, polarity and direction of substituents and hence can contribute to the formation of novel phases. So the central core was modified with the introduction of methyl substituent in the bay position of the central bent core. Further the four-ring molecule possess an unequal distribution of aromatic rings in the two wings which manifest the unsymmetrical bent shaped molecule and hence can be regarded as a true hockey stick molecule bordering the bent core and calamitic molecules. The designed and synthesized compounds n-12 (n = 7, 8, 10 and 14) are depicted below.

![Chemical structures of compounds 7-12 to 14-12](image-url)
5.3. Results and Discussion

5.3.1. POM and DSC studies:

The four ring system consists of three different types of linkage units (azo -N=N-, ester -COO- and salicylidene -CH(-C(-OH)=N-) bridging the phenyl rings to each other. The designed molecules and synthetic details are presented in Scheme 5.1. The synthetic details of the compounds are presented in chapter 3. The molecular structure and the associated thermodynamic data of the phase transitions of the first examples of achiral four ring asymmetric bent-core compounds of 2,6-disubstitued toluene derivatives 7-12, 8-12 and 10-12 exhibiting enantiotropic 1-N-SmC-Cr phase transition are presented in Table 5.1. However the compound 14-12 exhibits 1-N-SmA-Cr phase transition and the relevant data is also presented in Table 5.1. The compound 8-12 exhibits broad mesomorphic range with clearing temperatures below 140°C. The DSC spectrum for 8-12 is shown in Figure 5.1.
With increasing alkyl chain length (n) the Smectic range gradually increases whereas Nematic range decreases. The optical textures of sample 8-12 using three different preparation methods (i) untreated glass plate with coverslip (ii) aligned planar cell (HG) and (iii) homeotropic cell (HT) are studied. The POM textures of
the samples 8-12 contained between glass slide and a coverslip are shown in Figure 5.2. 8-12 on cooling from the isotropic phase exhibited distinctly well known characteristic textures of nematic phase viz. 2- and 4-brush Schlieren texture with threads as boundaries throughout the nematic phase temperature range. The growth of schlieren texture is accompanied by Brownian motion. The lower temperature phase exhibited SmC phase which is different from SmA phases for the compound 14-12.

![Figure: 5.2: Defect texture of the compound 8-12 on a glass slide and coverslip during cooling from isotropic phase (a) majority 2-brush defect texture at 135°C; (b) 133°C at same site; (c) during nematic- smectic phase transition (SmC) of compound 8-12 at 112.8°C; (d) nematic-SmA transition at 126.5°C for the compound 14-12.](image)

In an anti-parallel rubbed homogeneous cell was filled with the sample 8-12, change in birefringence with decreasing temperature when the stage of sample 8-12 in extinction position was rotated by 10° from crossed polarizers. The birefringence in high temperature phase increased with the decreasing temperature (Figure 5.3). The low birefringence in the PI coated cell can be explained due to a small film thickness of approximately 5.0 μm.

PI coated (AL-1254) antiparallel rubbed sandwich cell filled with the sample 8-12 to get homeotropic alignment. However when the director (optic axis) of the
nematic phase was aligned with one of the polarizer’s direction in POM studies, the sample appeared black (Figure 5.4a), a defect free planar texture, such that the high temperature phase resembled a birefringent plate of a crystal with the optic axis in the plane of the substrate. With the variation of the sample in azimuthal angle the transmitted light intensity between crossed polarisers continuously increased to a maximum (Figure 5.4b), when the optic axis was oriented at 45°. The nematic phase was confirmed by characteristic flickering upon tapping the sample caused by Brownian motion. On further cooling the nematic phase transformed into another mesomorphic phase by a very slow growth of two types of spiral textures (Figure 5.4c) of opposite twist resembling the filament textures of B7 phase or knitting instability, which later transformed into cluster like regions with complimentary colours in adjacent domains and with a strong increase in birefringence as shown in Figures 5.5a-e.

![Figure 5.3: Change in birefringence with decreasing temperature when the rubbing direction of sample 8-12 is kept at an azimuthal angle 20° with one of the polarizer.](image)

![Figure 5.4: (a) texture of director orientation of a uniform planar uniaxial nematic phase between crossed polarizers in extinction position; (b) maximum transmittance at 45° with respect to polarizer/analyzer and (c) growth of two types of adjacent spiral regions during phase transformation at 111.8°C of compound 8-12.](image)
Photomicrographs of the sample 8-12 in a planar cell oriented for maximum extinction of the domains in the lower temperature SmC phase (a) in crossed polariser and analyser arrangement (b) polarizer rotated clockwise 10° (c) polarizer rotated anticlockwise 10°, (d) sample rotated clockwise 10° and (e) sample rotated anticlockwise 10° are shown in Figures 5.5a-e.

Figure: 5.5: Photomicrographs of the sample 8-12 in a planar cell (AL-1254) oriented for (a) maximum extinction of the domains in the lower temperature Smectic like phase Stable adjacent regions of complimentary colours and stripes with fluidity. (b) polarizer rotated clockwise (c) polarizer rotated anti-clockwise (d) sample rotated clockwise 10° and (e) anticlockwise 10°. The distinct regions are appearing identical and the difference in orientation of the molecular arrangement in each domain indicates the molecular alignment either parallel or perpendicular to the polarizer respectively. (f) 4-brush defect of second phase in homeotropic (JALS-204 coated) cell.

There is a difference in orientation of the molecular arrangement in each domain which indicates the molecular alignment either parallel or perpendicular to the polarizer respectively. There is occurrence of dark and bright regions when the sample is rotated between crossed polarisers and hence it is apparent that the orientation of the layer direction is perpendicular to the stripes as usually observed for SmC phases. The stripe patterns and the orientation of the stripes are the distinct characteristics of the banana shaped molecules and they differ from the conventional Smectic phase. In homeotropic cells with alignment layers like JALS-204, the nematic phase shows extinct, when polarisers are perpendicular to each other. From that it reveals that the character
of molecule is uniaxial. On transition from nematic to smectic phases, it shows some defects in HT cell because SmC are tilted as compared to SmA as illustrated in Figure 5.5f.

The sample 14-12, in homogeneous PI coated cell, when the director (optic axis) of the nematic phase was aligned with one of the polarizer’s direction in POM studies, the sample appeared as nematic droplets Figure 5.6a, which was confirmed by tapping. On further cooling the SmA phase appears which shows typical fan-shaped texture Figure 5.6c, the transition between the phases inducing a change in colour shown in Figure 5.6b reflecting an increase in birefringence.

![Figure 5.6: Photomicrographs of the sample 14-12 in a planar cell oriented for (a) texture of nematic droplet between crossed polarizers (b) transition from Nematic-smectic phase (c) smectic phase at 125.9°C.](image)

5.3.2. X-Ray diffraction (XRD) investigations of magnetically aligned samples: XRD was carried out of compound 8-12, oriented in a magnetic field of strength \( B = 0.267 \) T, cooling rate \( 0.5^\circ \text{C min}^{-1} \). Figure 5.7 shows the 2D small-angle X-ray scattering (SAXS) patterns of magnetically aligned sample of 8-12 at different temperatures.

In the XRD study at \( T=133^\circ \text{C} \) (phase-1), the SAXS pattern as shown in Figure 5.7a are centered on the equator indicating a fluid nematic phase. Cooling the sample to \( 133^\circ \text{C} \), a change in diffuse SAXS pattern with clear maxima besides the meridian resembling a dumb bell shape as shown in Figure 5.7b reflects different molecular alignment. The intensity of the SAXS is significantly higher than that of the diffuse wide angle scattering (Figure 5.8). The \( \chi \)-scans over the small angle regions patterns are shown in Figure 5.9. The experimental value is smaller than the molecular length of 46.4 Å as evidenced from the energetically optimized preferred molecular structure of 8-12 shown in Figure 5.10 in gaseous phase which was
obtained from density functional theory studies at the B3LYP/6-31G(d) level basis set performed using ground state restricted ab initio calculations. Temperature variation of $2\theta$ scan as a function of intensity in small angle region confirms different molecular arrangements in lower and higher temperature regions of the nematic phase. The SAXS patterns in the region $120\sim130^\circ C$ (Figure 5.9), confirmed molecular arrangement resembling SmC type cybotactic clusters (hereafter abbreviated as $N_{cybc}$), different from that of molecular arrangement of classical nematic phase in high temperature region $>130^\circ C$.

Figure: 5.7: Small angle diffraction patterns of magnetically samples (direction of magnetic field, $B$ is shown as red arrow) in the nematic and smectic phases of compound 8-12 at different temperatures (a) – (f). The pattern (g) and (h) wide angle scattering at respective temperatures and crystal (i) at 106°C.
The organization of molecules in a cybotactic nematic phase with SmC type clusters (N_{cybC}) aligned under a magnetic field B parallel to the molecular long axis is shown in Figure 5.11. Repeated DSC scans at different heating/cooling rates (2, 5 and 10 °C/min) also could not detect the N-N_{cybC} transition with any noticeable transition enthalpy (Figure 5.1). At lower temperatures below this transition temperature (~130°C) one could observe the diffuse small angle scattering maxima besides the meridian (dumbbell shape as shown in Figure 5.9c at 125°C, Figure 5.9d at 120°C and the 2θ scans over the small angle diffraction having maxima at d = 44.8 Å shown in Figure 5.8, is smaller than the molecular length of 46.4Å. The χ scans over the small angle region clearly indicated four symmetrically located diffuse maxima as shown in Figures 5.9b-c, tilt angle ~9.4° which confirmed this phase to be a cybotactic nematic phase with SmC type clusters.

On reducing the temperature cybotactic C cluster in nematic phase is transformed into another mesomorphic phase (phase-2), the position, shape and intensity of the wide angle scattering do not change, with a maximum at diffuse peak (D) = 5.42 Å corresponding to the mean lateral distance between the molecules, confirming the retention of fluidity of the liquid crystalline phase. However the SAXS patterns transformed into sharp Bragg peak is shown in Figures 5.9e-f with maxima at the
meridian and has its maximum at \( d = 44.8 \) Å comparable with the molecular length \( L = 46.4 \) Å with tilt angle \( \sim 16.8^\circ \). This is consistent with a transition to a SmC phase indicating the orthogonal molecular alignment of the director. On further cooling the sample below 105°C transformed into a crystalline phase with sharp peaks at wide and small angle diffraction scatterings.

**Figure: 5.9:** \( \chi \)-scans over the small angle regions for 8-12 at temperatures 133°C, 130°C, 125°C, 120°C, 112°C and 108°C.
Figure 5.10: Optimised molecular structure of 8-12.

Figure 5.11: Organisation of the molecules in a skewed cybotactic nematic phase (N_{cybc} phase) aligned under a magnetic field B parallel to the molecular long axis.

5.3.3. UV-Visible study:

UV-Visible spectra of all the compounds of the homologous series $n$-12 ($n = 7, 8, 10$ and $14$) at $10^{-5}$ M concentrations were recorded in dichloromethane ($\text{CH}_2\text{Cl}_2$). Absorption peak of all compounds appearing at $\sim 340$ nm ($3.6$ eV, $\varepsilon = 64000$ Lmol$^{-1}$cm$^{-1}$ for the compound 8-12) is due to the $\pi-\pi^*$ transition of the highly $\pi$-conjugated system having the substituted phenyl benzoate unit as the core. UV-Visible spectra of $n$-12 homologues series are shown in Figure 5.12.
5.3.4. Electro-optical investigations:

To investigate the polar properties of the mesophase, electric field experiments were carried out on the compound 8-12. The switching behaviour was investigated in transparent sandwich type capacitor cells (5 μm) consisting of two indium-tin oxide (ITO) coated glass plates. In presence of electric field the compound 8-12 in HT cell exhibited extinction crosses and coincide with direction of the crossed polarizers when frequency is 1 kHz and voltage is zero. Further when the strength of electric field across the cell was increased, birefringence was changed from dark orange texture to green texture Figure 5.13a-c. However the ferroelectric switching process can be clearly seen in the electro-optical investigations study in HG cell. There are some patterns in Figure 5.13e-g, when frequency is 60 Hz and applied voltage is ~ 6-10 volt. This electro conventional pattern can be explained due to the hydrodynamic instability of the compound [31]. Organization of the molecules 8-12 in presence of electric field is shown in Figure 5.14.
Figure: 5.13: The applied voltage and frequency on 8-12 are (a) 60Hz 10V, HT at 125°C; (b) 60Hz 1V, HG at 130°C; (c) 60Hz 6V, HG at 130°C; (d) 60Hz 7V, HG at 130°C; (e) 60Hz 10V, HG at 130°C and (f) 60Hz 18V, HG at 130°C.

Figure: 5.14: (a) molecular structure of 8-12; (b) crossed/uncrossed positions of polarisers and (c) effect of electric field on the alignment of the molecules.
5.3.5. Density Functional Theory (DFT):
Quantum chemical calculation based on density functional theory (DFT) study has been performed to give more insight into the molecular electronic properties of 8-12. Full geometry optimizations have been carried out without imposing any constraint using Gaussian 09 program package [32]. Spin-restricted DFT calculations were carried out in the framework of the generalized gradient approximation (GGA) using Becke3-Lee-Yang-Parr hybrid functional (B3LYP) exchange-correlation functional and the 6-31G (d, p) basis set [33, 34].

Table 5.2:

<table>
<thead>
<tr>
<th>Comp</th>
<th>Energy (eV)</th>
<th>ΔE (eV)</th>
<th>Dipole moment (Debye)</th>
<th>Bend angle (°)</th>
<th>Bond length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HOMO</td>
<td>LUMO</td>
<td>μₓ</td>
<td>μᵧ</td>
<td>μz</td>
</tr>
<tr>
<td>8-12</td>
<td>-5.77</td>
<td>-2.06</td>
<td>3.71</td>
<td>2.33</td>
<td>0.40</td>
</tr>
</tbody>
</table>

Figure: 5.15: a) Optimized geometry b) HOMO and c) LUMO diagram

The HOMO and LUMO energies are calculated and presented in Table 5.2. The HOMO–LUMO energy separation can be used as a measure of kinetic stability of the molecule and could indicate the reactivity pattern [35, 36]. A large HOMO–
LUMO gap implies a high-kinetic stability and low chemical reactivity, because it is energetically unfavourable to add electrons to a high-lying LUMO or to extract electrons from a low-lying HOMO [36]. The HOMO–LUMO energy gap for 8-12 is found to be 3.71eV suggesting that the compound is fairly stable. Further, the electron density of the molecular orbital i.e. HOMO and LUMO of the compound is mainly concentrated in the aromatic region of the molecules. Dipole of the compound has been calculated along the three Cartesian directions.

5.3.6. Discussion:

Majority of the four-ring bent core compounds reported so far in literature do not exhibit banana mesomorphism. However in some compounds [37] SmA, SmC and SmI phases can be transformed into polar structures under the influence of electric field. Another four-ring compound derived from oxadiazole [38] exhibits a nematic, a SmC and optically isotropic phase (chiral Bx) with randomly distributed domains of opposite handedness. Classical Four-ring system derived from 1,3-phenylene moiety [39] substituted with three fluoro substituents exhibited chiral SmA* and SmC* phases while the unsubstituted compound do not show mesomorphism. It is remarkable that the exhibition of banana mesomorphism in an earlier communication and nematic and smectic phase with distinctly different molecular orientation presented in this work respectively, by the classical four-ring bent-core system with modifications of bridging groups or substituents, demonstrated the importance of these materials and is therefore of high priority. The importance of substituents, influence of bridging groups, steric and Vander Waals interactions etc have origins in basic structure–property relationships and the observed smectic mesophases and polar structures in these materials research opened lot of intriguing questions which requires further systematic investigations. Experimental examples of orientationally ordered but spatially homogeneous liquid phases are rare among the bent-core molecules.
5.3.7. **Conclusion:**

In conclusion the synthesised four-ring bent core systems are able to form traditional polar banana phases [29] as well as nematic phase with classical molecular alignment of calamitic type as well as cybotactic nematic (N_{Cybc} type) and the lower phase is smectic phase, depending on the nature and position of substituents, linking group and its direction. X-ray and different other experimental studies confirm the phase sequence as N-N_{Cybc}-Sm-Cr in the four-ring bent core system of hockey stick shaped molecules under investigation. Hence the four-ring bent core systems n-12 are of great importance as their study form the boundary between calamitic and banana shaped compounds of five- and six- ring compounds.


