Chapter-4
Part-A
Oligomers: Bent-core liquid crystals
(bent core dimers)
4.a.1. Introduction:
Over the last two decades, bent-core liquid crystals consider as a sub-branch of thermotropic liquid crystals have gained prominence due to the observed fascinating properties such as polar phases and chiral phases exhibited by achiral bent core molecules [1-2]. Excellent reviews [3-6] appeared in literature in recent years indicating the importance of such materials as future thrust areas of research. The bent core molecules reported in literature are either symmetrical or unsymmetrical composed of in general five ring connected via linking groups (such as \(-\text{COO}, -\text{CH}=\text{N}-, -\text{N}=\text{N}-\) etc.) and containing aliphatic chains at the terminal position of the bent core molecules. The liquid crystal dimer composed of calamitic as well as discotic liquid crystalline monomers are reported in literature and investigated in detail [7-10] have proved to be a rich source of new and unusual smectic phases including the intercalated phases and also exhibiting nematic phase draw the special attention of the researcher. Moreover, dimers can be used to stabilize the blue phase which is technologically important as fast light modulators, tunable photonic crystals [11-12]. The dimers can be subdivided in two categories such as symmetrical dimers and unsymmetrical dimers depending on the mesogenic unit connected via flexible spacers. Flexible spacers within the molecule may control the molecular shape and phase behaviour depending on the length and parity of the spacer connecting the mesogenic groups. Dimers having an odd-membered spacer show a bent average shape while those with an even-membered spacer are linear. The linking units between two monomers (liquid crystalline molecules) are generally flexible alkylene spacers and siloxane or carbosiloxane as spacers. The mesogenic behaviors of dimers are greatly influenced by the nature, parity, structure and length of the spacers. Liquid crystalline dimers obtained from five ring bent core mesogenic unit as monomer are relatively new and few reported in literature. The different possible types of symmetrical and non-symmetrical bent core dimers are pictorially represented in figure 4.a.1.
The first liquid crystalline dimers consisting of two banana-shaped mesogenic units connected by flexible oligosiloxane spacer units exhibit ferroelectric optically isotropic phase (i.e. dark conglomerate phase) SmCPF* phase and antiferroelectric polarizable tilted smectic phase SmCP_A depending on the parity of flexible dimethylsiloxane unit in the spacer length [13]. Liquid crystalline dimers composed of bent core (BC) mesogenic units, which are terminally linked using alkylene spacer did not display liquid crystalline phases, using tetraethylene glycol spacer form columnar phase and insertion of siloxane unit into spacer results in polar smectic phase [14]. The influence of lateral fluoro substituents, terminal chain length, length of the alkylene spacer on the dimer composed of bent core mesogenic unit did not affect mesomorphic behavior and exhibit columnar polar phase with an oblique lattice showing ferroelectric characteristics (Col_{ob}P_F) [15]. The first laterally connected bent core dimers exhibiting enantiotropic and monotropic nematic phase [16]. Symmetrical dimer composed of five ring bent core mesogen which are connected at the apex position through flexible alkylene spacer via ether or ester linkages exhibit smectic A and or smectic A' (variant of SmA phase) [17]. The bent core dimers with an alkylene spacer exhibit liquid crystalline behavior only when terminal chain lengths are relatively long. Theoretical studies have shown that mixtures of rods and discs can exhibit the biaxial nematic phase [18-19]. The mixture of rod and disc shaped liquid crystals can be achieved by non-symmetrical rod-disc dimer that fulfills the
molecular arrangement of rod and disc mixture. Non-symmetrical dimers obtained from disc-rod shaped mesogen linked via flexible alkyl chain spacer resembles model compounds exhibit the biaxial nematic phase [20-22]. Recently, four ring bent core molecules considered as hockey stick shaped liquid crystals due to the unequal distribution of the phenyl ring in both side of a molecule. The molecular architect of four ring bent core molecule is border line between the calamitic (rod like) and typical bent core molecule leads to interesting phase behaviour which is quite different from either calamitic or bent core molecule. The occurrence of nematic phase in a bent core molecule is scarce. Bent core materials exhibiting nematic phase is considered to be of immense interest due to the bent shape of the molecule may leads to phase biaxiality in a nematic phase (N_b phase). The N_b phase is of fundamental interest for fundamental soft mater physics as well as use in display application with much faster switching response time than uniaxial nematic phase. Since then researcher reported bent core materials exhibiting nematic phase but none of the molecule display true biaxial nematic phase. The solid proof existence of biaxial nematic phase was provided by polymeric liquid crystals [23-25] and laterally connected oligo-mesogen [26-27]. The high viscosity of polymeric mesogen and oligomer restrict these materials for further physical studies and application. The bent core mesogenic dimers possibly provide combine feature of polymers/oligo mesogen with those of low molar mass mesogenic unit but still relatively low molecular masses and viscosity.

Therefore, we describe the design, synthesis and liquid crystalline properties of new bent core dimer as presented in figure 4.a.2 wherein the individual monomeric units are connected at the end of the BC molecules via flexible alkylene spacers. The extreme terminal ends are substituted with methoxy moieties. The four-ring bent-core molecule is designed to possess three linkages viz., photochromic azo linkage, followed by an ester linkage and an imine linkage formed with 4-hydroxy benzaldehyde. 4-hydroxyl moieties of two monomers are linked by alkylene spacer. The molecules possessing the azo linkage (\(\text{N=N}\)), undergo cis-trans isomerisation in the presence of UV light. In this section the results of the bent-core dimers and with methyl
substituent in lateral position are also presented. These compounds are found to exhibit a wide range of nematic phase as evidenced by the optical textures observed with the help of polarizing optical microscopy (POM) and small enthalpy values at the nematics-isotropic phase transformation recorded in differential scanning calorimetry (DSC) studies.

<table>
<thead>
<tr>
<th>Compound designed and synthesized</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Compound</strong></td>
</tr>
<tr>
<td>1,9-OM</td>
</tr>
<tr>
<td>1,9-o-OM</td>
</tr>
<tr>
<td>1,9-m-OM</td>
</tr>
</tbody>
</table>

**Figure 4.a.2:** Molecular structures of bent core dimers

4.a.2. Synthesis:

The starting material in the present study 1,9-bis(4-formylphenoxy)nonane was prepared by Williamson etherification of 4-hydroxybenzaldehyde with appropriate 1,9-dibromalkane. 2-methyl-3-nitrobenzoic acid was converted into corresponding amine by reduction using 5% Pd-C, which was condensed with 1,9-bis(4-formylphenoxy)nonane in presence of few drops of glacial acetic acid to get 1,9-bis(4-(2-methyl-3-phenyliminomethyl)phenoxy)nonane in good yields. 1,9-bis(4-(2-methyl-3-phenyliminomethyl)phenoxy) nonane was further esterified with 4-methoxy azophenol/2-methyl-4-methoxy
azophenol/3-methyl-4-methyloxy azophenol using DCC-DMAP reaction to yield the designed products 1,9-OM, 1,9-\textit{o}-OM and 1,9-\textit{m}-OM. The compounds were further recrystallized repeatedly to get the pure samples. All the compounds were characterized by FTIR, UV-Vis and \textsuperscript{1}H NMR studies. The detailed experimental procedures along with the spectroscopic data for all the homologous series of compounds are presented in the experimental section of Chapter III. The liquid-crystalline behaviour of the synthesized compounds had been investigated by optical microscopy and differential scanning calorimetry (DSC).

**Scheme 4.a.1:** Synthetic details of bent core dimers 1,9-OM, 1,9-\textit{o}-OM and 1,9-\textit{m}-OM. Reagents and Condition: (i) Dry acetone, KHCO\textsubscript{3}, Br(CH\textsubscript{2})\textsubscript{9}Br, KI (ii) 5\% Pd /C, H\textsubscript{2}, EtOAc stirring 48h (iii) \textsuperscript{Na}NO\textsubscript{2}, 0-5 \textdegree C, Phenol (v) DCC, DMAP, DCM, stirring 48h.

4.a.3. Results and Discussion

4.a.3.i. Mesomorphic properties: Polarizing optical microscopy and differential scanning calorimetry

The transition temperatures, enthalpies and entropies associated with the phase transitions of the dimers 1,9-OM, 1,9-\textit{o}-OM and 1,9-\textit{m}-OM are obtained from
DSC at a scan rate of 5 °C min\(^{-1}\) in the second heating and second cooling scans are presented in table 4.a.1.

Table 4.a.1: DSC data of the compounds 1,9-OM, 1,9-o-OM and 1,9-m-OM.

Phase transition temperatures (°C) and mesomorphic thermal range of the recorded for second heating (first row) and second cooling (second row) cycles at 5°C/min from DSC and confirmed by polarized optical microscopy. The enthalpies (ΔH in kJ/mol) and entropies (ΔS in J/mol/K) respectively are presented in parentheses.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Phase transition temperatures in °C (enthalpy kJ/mol, entropy J/mol/K)</th>
<th>N phase Range °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,9-OM</td>
<td>Cr 165.7 [28.9,65.9] N 227.4 [2.54,5.07] I</td>
<td>61.6</td>
</tr>
<tr>
<td></td>
<td>Cr 126.1 [41.2,103.9] N 218.0 [0.21,0.43] N</td>
<td>100.5</td>
</tr>
<tr>
<td></td>
<td>[1.41,2.84] I</td>
<td></td>
</tr>
<tr>
<td>1,9-o-OM</td>
<td>N 187.1 [2.3,5.0] I</td>
<td>-----</td>
</tr>
<tr>
<td></td>
<td>Cr* &lt;RT N 186.4 [2.24,4.88] I</td>
<td>&gt;150</td>
</tr>
<tr>
<td>1,9-m-OM</td>
<td>Cr 118.7 [99.4,253.7] N 201.9 [5.27,11.1] I</td>
<td>83.1</td>
</tr>
<tr>
<td></td>
<td>Cr*&lt;RT N 199.7 [5.36,11.3] I</td>
<td>&gt;170</td>
</tr>
</tbody>
</table>

Cr = Crystalline phase, N = Nematic phase, I = Isotropic liquid and Cr* indicates crystallization below room temperature. Heating and cooling rates are 5°C min\(^{-1}\) for the melting and clearing transitions.

All the compounds 1,9-OM, 1,9-o-OM and 1,9-m-OM exhibit enantiotropic nematic phase.

1,9-OM:

Compound 1,9-OM, exhibits two transitions in the heating cycle, crystal transform to nematic phase at 165.7 °C (ΔH = 28.9 kJ/mol, ΔS = 65.9 J/mol/K) and nematic phase transform to isotropic phase at 227.4 °C (ΔH = 2.54 kJ/mol, ΔS = 5.07 J/mol/K). In the cooling cycle, it exhibited three phase transitions, nematic phase exhibit at 226.7 °C (ΔH = 1.41 kJ/mol, ΔS = 2.84 J/mol/K) another transition from nematic to nematic phase at 218.0 °C (ΔH = 0.21 kJ/mol, ΔS = 0.43 J/mol/K) and solidified at 126.1 °C (ΔH = 41.2 kJ/mol, ΔS = 103.9 J/mol/K). The DSC thermogram of compound 1,9-OM is presented in figure 4.a.3.
Further transition temperature and phase was confirmed by polarized light microscopy. On slow cooling the sample from isotropic liquid, 2- and 4-brushes schlierien texture or thread like texture appears at 226.7 °C confirms nematic phase as presented in figure 4.a.4 a, b which on further cooling secondary defect line defect appears on the thread like texture at 218 °C shown in figure 4.a.4c. Such transition was observed by DSC with very small enthalpy and entropy change indicates that the molecular organization of the phase is similar with nematic phase. Therefore, such phase is designate as N′ phase. On further cooling, crystallization occurs at 126.1 °C as presented in figure 4.a.4d. Further phase conformation by small angle X-ray diffraction is to be carried out to confirm the phase.
optical textures of 1,9-OM under crossed polarizers. a) Nematic schlieren texture at 226.7 °C appeared from isotropic liquid; b) thread like texture of nematic phase at 226 °C; c) secondary thread like texture appeared on the thread like nematic texture at 218 °C; d) transition to crystalline phase at 126.1 °C.

1,9-o-OM:

Compound 1,9-o-OM also exhibit enantiotropic nematic phase. 1,9-o-OM, exhibited one transitions in the second heating cycle at 187.1°C ($\Delta H = 2.30$ kJ/mol, $\Delta S = 5.0$ J/mol/K). In the second cooling cycle it exhibited nematic phase at 186.4 °C ($\Delta H = 2.24$ kJ/mol, $\Delta S = 4.88$ J/mol/K), and no crystallization occurred in the cooling cycle. The DSC thermogram of compound 1,9-o-OM is presented in figure 4.a.5.

Figure 4.a.4: Optical textures of 1,9-OM under crossed polarizers. a) Nematic schlieren texture at 226.7 °C appeared from isotropic liquid; b) thread like texture of nematic phase at 226 °C; c) secondary thread like texture appeared on the thread like nematic texture at 218 °C; d) transition to crystalline phase at 126.1 °C.

Figure 4.a.5: DSC thermogram of 1,9-o-OM.
Further transition temperature and phase was confirmed by polarized light microscopy. On slow cooling the sample from isotropic liquid, nematic droplet texture or thread like texture appears at 179.6 °C figure 4.a.6a. The thread like nematic texture super cooled to room temperature figure 4.a.6b. Further phase conformation by small angle X-ray diffraction is to be carried out to confirm the phase.

![Figure 4.a.6: Optical textures of 1,9-o-OM under crossed polarizers. a) Nematic droplet texture at 179.6 °C appeared from isotropic liquid; b) thread like texture of nematic phase at room temperature.](image)

1,9-mOM:

Compound 1,9-m-OM exhibits three transitions in the second heating cycle at 118.7 °C (ΔH = 99.4 kJ/mol, ΔS = 253.7 J/mol/K), 132.9 °C (ΔH = 0.72 kJ/mol, ΔS = 0.72 J/mol/K) and at 201.9 °C (ΔH = 5.27 kJ/mol, ΔS = 11.1 J/mol/K). In cooling cycle only one transition is observed at 199.5 °C (ΔH = 5.34 kJ/mol, ΔS = 11.3 J/mol/K). The DSC thermogram of 1,9-m-OM is presented in figure 4.a.7.
Figure 4.a.7: DSC thermogram of 1,9-m-OM.

On slow cooling the sample from isotropic liquid, 2- and 4- brushes schlieren texture appears at 199.5 °C figure 4.a.8a. On further cooling the thread like nematic textures appear supercooled to room temperature figure 4.a.8b. Further phase conformation by small angle X-ray diffraction is to be carried out to confirm the phase.

Figure 4.a.8: Optical textures of 1,9-m-OM under crossed polarizers. a) two- and four brushes schlieren texture at 199.5 °C appeared from isotropic liquid; b) two- and four brushes schlieren at room temperature.

The large enthalpy value associated with the crystal to nematic (Cr–N) phase transition in the heating cycle indicate strong inter-actions (van der Waals type) between the end chains of neighbouring molecules. These strong interactions (van der Waal type) between end chains of neighbouring molecules keep them
static in the crystalline phase before the transition to LC state in the heating cycle. However these interactions are totally disrupted in the nematic phase allowing the end chains to freely rotate. In the substituted dimeric compounds the nematic to isotropic phase transition temperature decreases from the unsubstituted parent compound because of the weak interactions between the end chains of the neighbouring molecules. The small enthalpy changes observed at the liquid crystalline nematic phase possessing orientational order to isotropic liquid with random ordering of molecules are indicative of smaller changes in the molecular ordering. The nematic to isotropic phase transition temperature in the heating as well as in the cooling cycle are almost same.

![Phase transition temperature of the compounds 1,9-OM, 1,9-o-OM and 1,9-m-OM in heating and cooling cycle.](image)

**Figure 4.a.9**: Phase transition temperature of the compounds 1,9-OM, 1,9-o-OM and 1,9-m-OM in heating and cooling cycle.
Figure 4.a.10: Entropy of the compounds 1,9-OM, 1,9-o-OM and 1,9-m-OM in heating and cooling cycle.

Figure 4.a.11: Enthalpy change during nematic-isotropic transition of the compounds 1,9-OM, 1,9-o-OM and 1,9-m-OM in heating and cooling cycle.

4.a.3.ii. Photo-physical properties

Photochromic low-molar mass and polymer systems have drawn attention of many research groups due to the possibility of manipulating the molecular shape and the supramolecular structure and the possibility of a wide range of
promising applications in photonics, optoelectronics, optical data storage, etc. [28-30]. The dimers containing photochromic azo functional group are interesting optical materials because of their trans-cis or cis-trans isomerisation and occurs due to external stimuli for example irradiation by UV light, mechanical stress, electrostatic simulation or recovering the thermodynamic stability. This unique photochemistry and change in material properties during irradiation with UV- light leads to materials with variety of application such as lithography, non-linear optical devices, optical switches and data storage.

The UV-visible absorption spectra of dimers (1,9-OM, 1,9-o-OM, 1,9-m-OM) (c = 10^{-5} M solution in CHCl₃) as shown in figure 4.a.12, revealed two strong absorption ~ 290 nm and ~346 nm with a large molar extinction coefficient (ε =~50,000-70000 Lmol^{-1}cm^{-1}), which reflected the symmetry allowed π-π* transition of azomethine (-CH=N-) and (-N=N-) group in the molecule respectively [31]. However a weak absorption in the visible region ~ 437 nm (ε = ~3340 Lmol^{-1}cm^{-1}) corresponding to symmetry forbidden n-π* transition [32-33] was also observed.

![Figure 4.a.12: UV-Visible absorption spectra of dimers 1,9-OM, 1,9-o-OM and 1,9-m-OM in chloroform at c = 1x10^{-5}M.](image-url)
The UV-Vis absorption spectra of 1,9-OM were obtained in 1x10^{-5} M solutions using CHCl₃ as solvent in three different conditions viz., (a) virgin sample solution, (b) solution after exposure to UV light for 2h and (c) solution kept in dark for 12 h shown in figure 4.a.13. From the analysis of the spectra it can be readily seen that there is change in absorption intensity and peak position of each compound from virgin sample solution to UV light irradiated solution and solution kept in dark for 12h. The high and low intense absorption bands centred at ~291 nm, ~346 nm and ~431 nm are due to the π-π* and n-π* electronic transitions, respectively [34-36]. The freshly prepared dilute solution of the azo compounds when irradiated with UV light for 2 h, the resulting UV-Vis spectra illustrated that the π-π* transition band is shifted to lower wavelength, blue shifted (~20 nm) with a decrease in intensity of the band and appears as shoulder. The blue shift in the absorption band is due to breaking of π electron conjugation in a cis (Z-form) isomer. The intensity of the band decreases indicate the trans (E-form) isomer is converted to a cis isomer. However the opposite phenomenon occurred in case of n-π* band due to increase in the cis isomer. The intensity of the n-π* band of the freshly prepared solution is less than for the UV irradiated solution. When the solution was kept in dark for 12h the peak position of the high intense π-π* band and intensity of n-π* band were gradually shifted and the UV-Visible spectra appeared closer to the UV spectra of virgin solution.
Figure 4.a.13: UV-Visible absorption spectra of 1,9-OM in CHCl₃ (c = 1x10⁻⁵ M) and the changes in the absorption spectrum with respect to exposure time to UV light and in absence of light.

As expected, the symmetry allowed high intense π→π* absorption band decreased progressively while the symmetry forbidden low intense n→π* absorption band increased after UV irradiation due to the trans→cis photo-induced isomerisation. If we consider only the azobenzene moiety the symmetry for trans [E-isomer] azobenzene is C₂ᵥ and for cis [Z-isomer] azobenzene is C₂ and hence the symmetry is breaking down from trans to cis isomer indicating a less conjugation as shown in figure 4.a.14.
Figure 4.a.14: Molecular structure of \textit{trans} (E) and \textit{cis} (Z)-isomers of the compound.

Thus it is obvious that after UV irradiation there should be shift of $\pi-\pi^*$ band towards the lower wavelength. As the symmetry is transformed from \textit{trans} to \textit{cis} isomer, an increase in the intensity of $n-\pi^*$ band was observed. Actually the $n-\pi^*$ transition occurs from the non-bonding ($n$) electrons of nitrogen atom shift to the $\pi^*$ orbital of the molecule. The change in absorbance with respect to the time exposed to UV-light irradiation is only because of \textit{trans-cis} isomerization.

The similar photo-physical behaviours are observed for methyl substituted bent core dimers (1,9-\textit{o}-OM and 1,9-\textit{m}-OM) as presented in 4.a.15 and 4.a.16 respectively. The photo-physical properties of liquid crystal bent core dimers in chloroform is summarized presented in table 4.a.2.
Figure 4.a.15: UV-Visible absorption spectra of (1,9-\(\alpha\)-OM) in CHCl\(_3\) (c = 1x10\(^{-5}\)M) and the changes in the absorption spectrum with respect to exposure time to UV light and in absence of light.

Figure 4.a.16: UV-Visible spectra of 1,9-\(\alpha\)-OM in CHCl\(_3\) (c = 1x10\(^{-5}\)M) and the changes in the absorption spectrum with respect to exposure time to UV light and in absence of light.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Wavelength (nm) and corresponding molar extinction coefficient (Lmol⁻¹ cm⁻¹)</th>
<th>Types of transition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Without UV exposure</td>
<td>12 h in dark</td>
</tr>
<tr>
<td>1,9-OM</td>
<td>291 (50000)</td>
<td>285 (53400)</td>
</tr>
<tr>
<td></td>
<td>346 (68100)</td>
<td>347 (40000)</td>
</tr>
<tr>
<td></td>
<td>432 (1760)</td>
<td>441 (3430)</td>
</tr>
<tr>
<td>1,9-(\alpha)-OM</td>
<td>287 (52700)</td>
<td>285 (53200)</td>
</tr>
<tr>
<td></td>
<td>344 (58900)</td>
<td>339 (45500)</td>
</tr>
<tr>
<td></td>
<td>431 (3090)</td>
<td>436 (3110)</td>
</tr>
<tr>
<td>1,9-(\beta)-OM</td>
<td>292 (50600)</td>
<td>286 (59700)</td>
</tr>
<tr>
<td></td>
<td>346 (66300)</td>
<td>340 (53000)</td>
</tr>
<tr>
<td></td>
<td>437 (1620)</td>
<td>439 (3810)</td>
</tr>
</tbody>
</table>
4.a.4. Conclusion:
New azo functionalized dimers derived from achiral four ring unsymmetrical bent core mesogens with alkylene spacer were synthesized. The four-ring bent-core units are connected end to end with alkylene spacer. The dimers exhibit wide range of the nematic phase (~60-100 °C). The presence of lateral methyl substitution on outer phenyl ring decreases the melting temperature and isotropic temperature and the nematic phase become supercooled to room temperature. The compounds exhibit interesting photochromic behavior due to presence of azo group in molecules. The presence of wide range of the nematic phase and the photochromic behaviour in a material has potential application in optical data storage.
References:


