

## DECLARATION

I, **Nirmalangshu Chakraborty**, bearing Registration Number Ph.D/457/2007 dated 01/05/2007, hereby declare that the subject matter of the thesis entitled **“CHIRALITY IN ACHIRAL BENT-SHAPED MOLECULE” SYNTHESIS AND CHARACTERIZATION OF BANANA LIQUID CRYSTALS** is the record of work done by me and that the contents of this thesis did not form the basis for award of any degree to me or anybody else to the best of my knowledge. The thesis has not been submitted in any other University/Institute.

This thesis is being submitted to Assam University for the degree of Doctor of Philosophy in Chemistry.

Nirmalangshu Chakraborty

Place: Silchar

Candidate

Date: 28/04/2012



## Contents

<b>Chapter -1: General Introduction- Brief introduction of bent shaped liquid crystals and its associated mesophases.....</b>	<b>1</b>
Introduction.....	2
1.1 Liquid Crystals .....	2-5
1.2. Symmetry in Liquid Crystal Phases .....	5
1.3 Ferroelectricity and Antiferroelectricity in Liquid Crystals .....	6
1.3.1 Ferroelectric Liquid Crystals and Surface Stabilization .....	6-8
1.3.2 Antiferroelectric Liquid Crystal Phase and Smectic-C* Sub-phases .....	8-9
1.4.Liquid Crystal Phases of Bent-core Molecules.....	9-15
1.5Thermotropic properties of Bent-core liquid crystals.....	15-23
1.6 Spontaneous Polarization, Layer Chirality, and Molecular Chirality.....	24-25
References.....	26-30
<b>Chapter-2: Survey of Literature- Survey about bent shaped liquid crystals in quest for chirality in achiral molecules followed by proposed plan of research work.....</b>	<b>31</b>
2. Banana shaped Liquid crystals: till date from the beginning.....	32
2.1. Chirality in Achiral Molecules: ferroelectricity and antiferroelectricity.....	32-34
2.2. Materials suitable for ferroelectricity.....	34
2.3. Design of the molecules.....	34-40
2.4. Influence of terminal chain lengths.....	40-43
2.5. Effect of linking groups in bent core molecules.....	43-50
2.6. W-shaped compounds.....	50-51
2.7. Effect of substituents on banana shaped mesogens.....	51-55
2.8 Calamitic compounds with a spacer in the central unit.....	55-56
2.9. Four-ring bent shaped liquid crystals.....	56-58
2.10. Nematic phases in bent core mesogens.....	58-61
2.11. Cybotactic clusters in the nematic phases.....	61-62
2.12 Stripe patterns and elastic constants in the nematic phases.....	62-63
2.13 Density Functional Theory study.....	63
Motivation of this work.....	64

References.....	65-72
<b>Chapter-3: Methodology- Describes the synthetic procedure towards the target compounds.....</b>	<b>73</b>
3. Experimental: Synthetic strategy and Methodology.....	74
3.1. Commercially available compounds.....	74
3.2. Intermediate compounds.....	75-76
3.3. Final compounds.....	76
3.4. Synthesis of intermediates.....	77
3.4.1. Synthesis of alkoxysalicylaldehyde.....	77-81
3.4.2. Synthesis of alkoxyaniline.....	81
3.4.3. Synthesis of alkoxyphenylazo phenol.....	82-83
3.4.4. Synthesis of 2-Methyl-3-aminobenzoic acid.....	83
3.4.5. Synthesis of 3-[N-(4/-n-alkyloxysalicylideneamino)]-2-methylbenzoic acid.....	83-84
3.5 Synthesis of central core.....	84
3.5.1 Synthesis of 3-fluoro-4-nitrophenyl 3-nitrobenzoate.....	84-85
3.5.2 Synthesis of 4-amino-3-fluorophenyl 3-aminobenzoate.....	85
3.6. Synthesis of the target designed compounds.....	86
3.6.1 Synthesis of 4-((E)-(4-(decyloxy)phenyl)diazenyl)phenyl 3-((E)-(4-(alkyloxy)-2-hydroxybenzylidene)amino)-2-methylbenzoate.....	86-89
3.6.2 Synthesis of 3-fluoro-4-((E)-(2-hydroxy-4-(alkyloxy)benzylidene)amino)phenyl 3-((E)-(2-hydroxy-4-(alkyloxy)benzylidene)amino)benzoate.....	89-92
3.7. Experimental techniques.....	92
3.7.1. Infrared Spectroscopy.....	92
3.7.2. <sup>1</sup> H NMR.....	93
3.7.3. CHN analysis.....	93
3.7.4. UV-visible spectroscopy.....	93
3.7.5. Fluorescence Studies.....	93
3.7.6. Texture Observation Using an Optical Polarized Microscope.....	93
3.7.7. Differential Scanning Calorimetry.....	94
3.7.8. X-ray Diffraction Studies.....	94-95

3.7.9. Density Functional Theory study.....	95
References.....	96-97
<b>Chapter-4 (PartA): Results and discussion- Design, synthesis and characterization of novel 4-ring achiral bent core liquid crystals by POM, DSC and XRD studies.....</b>	<b>98</b>
4A.1. Introduction.....	99-103
4A.2. Experimental.....	103
4A.3. Results and Discussion.....	103
4A.3.1. POM and DSC studies.....	103-112
4A.3.2. X-Ray diffraction (XRD) investigations of magnetically aligned samples.....	112-125
4A.3.3 Absorption and Emission characteristics.....	125-128
4A.4. Conclusion.....	129
References.....	130-133
<b>Chapter-4 (PartB): Results and discussion- Study of stripe domains, freedricksz transition and the elastic constants in the nematic phase.....</b>	<b>134</b>
4B.1. Introduction.....	135-136
4B.2. Results and Discussion.....	136-138
4B.3. Influence of UV-Visible light on the stripe formation in Nx phase...	138-141
4B.4. Dielectric investigations of 7CB, mixtures 5M and 7M.....	141-143
4B.5. Elastic constants of 7CB, mixtures 5M and 7M.....	143-147
4B.6. Conclusion.....	147-148
References.....	149-151
<b>Chapter-4 (PartC): Results and discussion- Conformation of nematic phase by electric field, magnetic field and free standing film studies.....</b>	<b>152</b>
4C.1. Introduction.....	153
4C.2. Results and Discussion.....	153-156
4C.3. Electric field study in Al spacer-IPS cell.....	156
4C.4. Electric field in HT cell.....	156-157
4C.5. Free standing film study.....	157-159
4C.6. Conclusion.....	159
References.....	160

<b>Chapter-5: Results and discussion- Influence of polar substituent in the central bent core unit of four ring bent liquid crystals on mesomorphism.....</b>	<b>161</b>
5.1. Introduction.....	162-163
5.2. Effect of Fluoro substituents.....	163-165
5.3. Synthesis.....	165-166
5.4. Mesomorphic properties.....	166-171
5.5. Density Functional theory study.....	172-173
5.6. Absorption and emission spectral analysis.....	173-175
5.7. Electro-optical study.....	175-176
5.8. Conclusion.....	177
References.....	178-181

## List of Tables and Figures

<p><b>Figure 1.1.1.</b> Examples of liquid crystal phases. (a) Nematic, (b) Sm-<i>A</i>, (c) Sm-<i>C</i>, (d) discotic nematic, (e) the columnar phase of bent-shaped molecules and (f) the lamella phase organized with lipid and water .....</p>	3
<p><b>Figure 1.1.2.</b> Examples of layer structure of smectic phases. (a) Sm-<i>A</i>, (b) Sm-<i>C</i>, (c) Sm-<i>CA</i>, (d) Sm-<i>B</i>, (e) Sm-<i>I</i> and (f) Sm-<i>IA</i>. In the phases, (a)-(c), molecules have no in-plane positional order in a smectic layer, while in the hexatic phases on (d)-(f) molecules have the short range positional order even in a plane of smectic layer .....</p>	5
<p><b>Figure 1.3.1</b> Helical super structure in the Sm-<i>C</i>* phase .....</p>	6
<p><b>Figure 1.3.2.</b> The helical structure and the surface stabilized state of ferroelectric Sm-<i>C</i>* phase. In a thick planar cell, molecules wind helix with its axis parallel to the surface. (a) top-view and (b) side view of the deformed-helical ferroelectric liquid crystal cell (DHFLC). However the cell thickness is thin around the helical pitch, the helix is unwound by surface interactions and molecules uniformly align as shown in (c) and (d) or (e) and (f); (c) and (e) are top view and (d) and (f) are side view of the surface stabilized ferroelectric liquid crystal cell (SSFLC).....</p>	7
<p><b>Figure 1.3.3.</b> Molecular orientation in the antiferroelectric Sm-<i>CA</i>* phase. (a) top-view and (b) side view of the antiferroelectric Sm-<i>CA</i>* phase in a planar cell. Spontaneous polarization in each smectic layers is canceled out because of anticlinic orientation of molecules. However the spontaneous polarization re-orientes and uniformly aligns along an external electric field direction when the electric field is applied ((c) and (d) or (e) and (f)). These two states (d) and (f) are having the same molecular orientation which observed in the Sm-<i>C</i>* phase and only stable under application of an external field, so that these states are called as field-induced Sm-<i>C</i>* state. ....</p>	9
<p><b>Table 1.4.1.</b> Liquid crystal phases of bent-core molecules. “Polar” indicates that the phase shows responses to an applied electric field or not. “Tilting in a layer” indicates that the average molecular long axis in a smectic layer is tilted with respect to the smectic layer normal direction or not tilted. ....</p>	10
<p><b>Figure 1.4.2.</b> (a-c) Three proposed structures of the B1 phase[34,35]. (d) Photomicrograph of the B1 phase, P6OPIMB in a 4-micron thick cell. (e) Photomicrograph of the B1 phase, W503 in a 4-micron thick cell.....</p>	11

**Figure 1.4.3.** Photomicrograph of the B3 phase, P8OPIMB in a 6-micron thick cell.....12

**Figure 1.4.4.** Photomicrographs of the B4 phase, P8OPIMB in a 6-micron thick cell. (a) Under crossed polarizers the texture looks dark because of low birefringence. Blue color is often observed in this texture. Two domains of opposite optical rotation exist and these domains are clearly observed in (b) and (c) by uncrossing polarizer and analyzer, where polarizer rotated clockwise 5-degree in (b) and counter-clockwise 5-degree in (c).....13

**Figure 1.4.5.** (a) Photomicrograph of the B6 phase, 6OAm5AmO6 in a 6-micron thick cell and (b) molecular orientation in the phase.....14

**Figure 1.4.6:** Typical textures observed in B7 phase, (a), (b) In a 4-micron thick cell, (c) Racemic MHO-Bow in a 6-micron thick cell and (d)-(f) Chiral MHO-Bow in a 8-micron thick cell.....14-15

**Figure 1.4.7:** Microphotographs of texture observed in B8 phase at (a) 181<sup>0</sup>C, (b) 175<sup>0</sup>C and (c) 166<sup>0</sup>C.....15

**Figure 1.5.1:** Molecular structure of typical bent-core liquid crystals: (a) typical molecular structure of a bent-core liquid crystal; (b) first bent-core liquid crystal synthesized by Vorländer[51]; (c) first recognized bent-core liquid crystal in 1994.....17

**Figure 1.5.2:** Schematic representation of the structures of polar smectic banana phases.

⊗ and ⊙ indicate that the in-plane layer polarization component (Pt) points outward (inward) from the plane of the drawing. ⊥ and ⊤ : upper (lower) part of the director tilt toward the observer. ↑ and ↓ indicates that out-of-plane polarization component Pn points down (up).....19

**Figure 1.5.3:** First experimentally proved SmAP bent-core mesophase[55] (a). Molecular structure of 4CN-3F-OPIMB , which shows SmAP mesophase[55]; (b) SmAP type of arrangement of bent-core molecules in smectic layer[55]; (c) polarization of 4CN-3FOPIMB at the function of electric field[55]. (d) polarization of 4CN-3F-OPIMB at the function of temperature[55]; (e) corresponding textures under cross-polarized microscope at 170<sup>0</sup>C-SmA (f) 130<sup>0</sup>C-SmAP.....20

**Figure 1.5.4:** handedness and chirality of SmCP: P is polarization of layer, n is the layer normal. (c) is the side view of bent-core molecules in a layer structure. ⊗ and ⊙ indicate that the in-plane layer polarization component (Pt) points inward (outward) from



the plane of the drawing. Chirality is defined according to the left /right hand rule shown in (a). SmCsPA is racemic, with synclitic tilting, and antiferroelectric with the chirality of layer different in alternate layers.....22

**Figure 1.5.5:** Typical textures between crossed polarizers of SmCsPA (b) at ground state and switched to SmCaPF (a).....23

**Figure 1.6.1.** (a) Geometry for smectic layers and layer stacking in tilted smectic phase of bent-core molecules. (b) In one smectic layer with layer normal along the **z**-axis composed of bent-core molecules with polar order along **b** parallel to the **y**-axis, two possible layer structures one of which is mirror image of the other, are defined by the director **n** tilting by  $\theta$  either along the positive or negative to **x**-axis. The two dimensional **c**-director (nail) is defined by the projection of **n** onto a layer surface with the head of the nail indicating which end of the molecule is closest the top surface.....25

**Figure 2.1:** Molecule in which Takezoe et al found ferroelectricity.....33

**Figure 2.2:** Skeleton of a banana shaped liquid crystal (top). Central bent core C (a-j), linking groups X,Y (k-s) and end chain R (t-w) (bottom) used so far in designing banana shaped liquid crystal.....35

**Figure 2.3:** Reported molecule containing ester and imine as linking group.....37

**Figure 2.4a:** Modification of molecule in fig.2 with an O-hydroxyl group.....37

**Figure 2.4b:** Five ring compound containing nitro group as substituent.....38

**Figure 2.4c:** Five ring compound reported by Rao et al containing fluoro group as substituent.....38

**Figure 2.5:** Lee et al reported five ring compound containing chiral carbon in the terminal chains.....41

**Figure 2.6:** Tschierske et al reported several bent core compound without imine linkage.....42

**Table 2.1:** Comparison of the mesophases shown by compounds containing different types of terminal chains.....43

**Table 2.2:** Influence of direction of ester linkage on mesophase behaviour.....44

**Figure 2.7:** Five rings bent core system reported by Weissflog et al.....45

<b>Figure 2.8:</b> Homologous series of five ring compound reported by Gomola et al.....	46
<b>Figure 2.9:</b> Five ring bent molecule with ethylene linkage reported by Gomola et al....	47
<b>Figure 2.10a-e:</b> Nguyen et al, Weissflog et al reported various five ring compounds; <b>f:</b> Pelzl <i>et al.</i> reported a novel chiral banana shaped mesogens, derived from 4-chloro resorcinol; <b>g:</b> Kovalenko <i>et al.</i> reported first examples of achiral banana shaped compound possessing perfluoroalkyl chain in the terminal position; <b>h:</b> Vorlander's compound in which B6 phase was reported by Pelzl et al.....	49
<b>Figure 2.11:</b> Prasad et al reported first examples of five ring bent core molecules linked by an azo linkage.....	50
<b>Figure 2.12a:</b> Kumar et al reported W-shaped molecule.....	50
<b>Figure 2.12b:</b> Rao et al reported W-shaped molecule with an azo linkage.....	51
<b>Figure 2.13a-d:</b> Watanabe et al reported banana leaf like textures in dimeric systems.....	52-56
<b>Figure 2.14:</b> Sadashiva et al reported five ring system containing polar group in the terminal chain.....	52-53
<b>Figure 2.15:</b> Kang et al four ring molecule containing oxadiazole moiety.....	57
<b>Table 2.5:</b> Chemical structure and mesophase behaviour of bent core four ring mesogens reported in the literature.....	57-58
<b>Figure 2.16:</b> Weissflog et al reported asymmetric four ring compound derived from N-benzoylpiperazine.....	58
<b>Figure 2.17:</b> Some banana shaped liquid crystals exhibiting nematic phase.....	60-61
<b>Figure 2.18:</b> Tschierske et al reported compounds with cybotactic clusters in nematic phase.....	61
<b>Figure 2.19:</b> Tschierske et al reported cybotactic clusters in nematic phase in compounds with oxadiazole moiety.....	62
<b>Figure 2.20:</b> Dhara et al reported K11 and K33 in nematic phase of a bent core liquid crystal.....	63
<b>Table 3.1.</b> Commercially available compounds.....	74
<b>Table 3.2.</b> Intermediate compounds.....	75-76

<b>Table3.3.</b> Final compounds.....	76
<b>Figure.4A.1</b> Nematic phases of bent core molecules: (a) unrestricted rotation around the molecular long axis $n$ leads to an uniaxial nematic phase(Nu); (b) restricted rotation around $n$ , but without polar order, leads to the simplest type of biaxial nematic phase(Nb) with orthorhombic $D_{2h}$ symmetry ( $N_{bo}$ phase); (c) biaxial nematic phase with monoclinic $C_{2h}$ symmetry ( $N_{bm}$ phase) as for example possible by the organization of the molecules in SmC clusters with frozen rotation around $n$ ; (d) rotationally disordered biaxial clusters, where the rotational disorder of the clusters around $z$ leads to macroscopic uniaxiality;(e) phase biaxiality due to field or surface- induced or spontaneous alignment of the biaxial clusters.....	100
<b>Table4A.3.1:</b> Phase transition temperatures ( $^{\circ}C$ ) of the compounds, recorded for second heating (first row) and second cooling (second row) cycles at $5^{\circ}C/min$ from DSC. The enthalpies ( $\Delta H$ in kJ/mol) and entropies ( $\Delta S$ in J/mol/K) respectively are presented in parentheses.....	104-105
<b>Figure4A. 3.1. 2:</b> DSC spectrum of <b>12-10</b> recorded in the second heating/cooling cycle at @ $5^{\circ}C/minute$ .....	105
<b>Figure 4A.3.1.3:</b> Defect texture of the nematic phase of compound <b>12-10</b> on cooling from isotropic phase (a) majority 2-brush defect texture at $147^{\circ}C$ (b) at $145^{\circ}C$ at different site (c) during nematic- another mesomorphic phase transition at $121.8^{\circ}C$ (d) at $120.5^{\circ}C$ on a untreated glass slide and coverslip.....	106-107
<b>Figure 4A.3.1.4:</b> The phase transformation from N-another mesomorphic phase is accompanied by ripples which slowly spreads over a period of time indicating the segregation of molecular assemblies followed by organization in adjacent domains.....	107-108
<b>Figure 4A.3.1.5:</b> Finger-print texture or undulation lines in cells with different reagents treated for homotropic alignment.....	108
<b>Figure 4A. 3.1.6:</b> Change in birefringence with decreasing temperature when the stage of sample <b>12-10</b> in extinction position was rotated by $10^{\circ}$ from crossed polarizers.....	109
<b>Figure 4A. 3.1.7</b> (a) texture of director orientation of a uniform planar uniaxial nematic phase between crossed polarizers in extinction position and (b) maximum transmittance at $45^{\circ}$ with respect to polarizer/analyzer (c) growth of two types of adjacent spiral regions during phase transformation at $125^{\circ}C$ .....	110
<b>Figure4A. 3.1.8:</b> Photomicrographs of the sample <b>12-10</b> in a planar cell 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 anticlockwise (d) sample rotated clockwise  $10^0$  and (e) anticlockwise  $10^0$ . 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.....110-111

**Figure 4A.3.1.9** (a) texture of director orientation of a uniform planar uniaxial nematic phase of **18-10** between crossed polarizers in extinction position at  $136^{\circ}\text{C}$ , (b) growth of two types of adjacent spiral regions during phase transformation at  $130^{\circ}\text{C}$ , (c) smecticA like phase at  $115^{\circ}\text{C}$ , (d) polariser rotated anti-clockwise at  $120^{\circ}\text{C}$  (e) Stable adjacent regions of complimentary colours and stripes with fluidity at  $120^{\circ}\text{C}$ , (f) polariser rotated clockwise at  $120^{\circ}\text{C}$ .....112

**Figure 4A.3.2.10:** 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 **12-10** at temperatures (a)  $140^{\circ}\text{C}$ , (b)  $135^{\circ}\text{C}$ , (c)  $132^{\circ}\text{C}$ , (d)  $130^{\circ}\text{C}$ , (e)  $127^{\circ}\text{C}$ , (f)  $125^{\circ}\text{C}$  (g)  $110^{\circ}\text{C}$  and (h) wide angle scattering at  $95^{\circ}\text{C}$ .....113

**Figure 4A.3.2.11:**  $2\theta$ -scans over the small and wide angle scatterings at temperatures  $135^{\circ}\text{C}$ ,  $130^{\circ}\text{C}$ ,  $125.5^{\circ}\text{C}$ ,  $125^{\circ}\text{C}$  and  $110^{\circ}\text{C}$ .....114

**Figure 4A.3.2.12:**  $\chi$ -scans over the small angle regions for **12-10** at temperatures  $135^{\circ}\text{C}$ ,  $130^{\circ}\text{C}$ ,  $128^{\circ}\text{C}$  and  $125^{\circ}\text{C}$ .....114-115

**Figure 4A.3.2.13:** Optimised molecular structure of **12-10**.....115

**Figure 4A.3.2.14:** Smectic C cluster in the small angle diffraction.....116

**Figure 4A.3.2.15:** Organisation of the molecules in a skewed cybotactic nematic phase ( $N_{\text{cybc}}$  phase) aligned under a magnetic field **B** parallel to the molecular long axis.....116

**Figure 4A.3.2.16:** Comparison of  $\chi$ -scans over the small angle regions for **12-10** at temperatures  $130^{\circ}\text{C}$  and  $125^{\circ}\text{C}$  indicating the presence of coexistence of SmA and SmC cybotactic cluster in the nematic phase.....118

**Figure 4A.3.2.17:** (a) Intensity profile of  $2\theta$ -scan in SAXS in the coexistence region ( $125^{\circ}\text{C}$ ), (b) temperature dependence of d-values from SAXS and (c) temperature dependence of azimuthal angle ( $\chi$ -values) from SAXS.....119-120

**Figure 4A.3.2.18(a):** Intensity profile of q-scan at nematic, Smectic and crystalline temperature of **18-10**.....121

**Figure 4A.3.2.18(b):** Temperature dependence of d-values and intensity of **18-10**....121

**Figure 4A.3.2.19:** Various intensity vs  $q^{-1}$  profile showing the nematic phase, SmA phase and crystalline phase in SAXS and WAXS.....122-124

**Figure 4A.3.3.20:** UV-Visible spectra of **12-10**.....126-127

**Figure 4A.3.3.21:** Theoretical and experimental UV spectra of **12-10**.....127

<b>Figure 4A.3.3.22:</b> HOMO and LUMO of 12-10.....	127-128
<b>Figure 4A.3.3.23:</b> Fluorescence spectra of 12-10 in benzene at various excitation wavelengths.....	128
<b>Figure 4B.1:</b> Chemical structure of the compound 12-10.....	136
<b>Figure 4B.2.2:</b> Observed stripe pattern in homeotropically aligned cells treated with different alignment agents (a) Silane coupling (b) Cytope (c) SE-1211 (d) JALS-204, T = 125°C.....	136-137
<b>Figure 4B.2.3:</b> (a) Variation of stripe period <b>D</b> as a function of cell thickness <b>d</b> and (b) square of stripe period <b>D</b> <sup>2</sup> as a function of cell thickness <b>d</b> , T = 124.5°C.....	138
<b>Figure 4B.3.4:</b> Azobenzene photoisomerization, <i>trans</i> -form can be converted to <i>cis</i> -form using UV light (300 ~ 400 nm) and <i>cis</i> -form can be converted to <i>trans</i> -form by visible light.....	139
<b>Figure 4B.3.5:</b> Stripe pattern periodicity ( <b>D</b> ) variation as a function of Intensity of UV-Visible light, T = 124.5°C.....	139
<b>Figure 4B.3.6:</b> (a) The DFT optimised energy minimised molecular structure of (a) N1210, (b) magnified image of molecular conformational structure of N1210 with coordinates and dipole-moment (the end alkyl chains are not shown in the figure for clarity), (c) 7CB (d) Schematic representation of alignment of bent-core molecules. The direction of the resultant dipole moment and the large polarizability directions are denoted by $\mu$ and P, respectively. $\mu$ and P are mutually perpendicular in materials with $\Delta\epsilon < 0$ (upper one). Planar alignment of the director with $\Delta\epsilon < 0$ (lower one).....	140-141
<b>Figure 4B.4.7:</b> Variation of dielectric anisotropy $\Delta\epsilon$ as a function of relative temperature in 7CB, 5M and 7M, $f = 1$ kHz.....	142
<b>Figure 4B.4.8:</b> (a) Mutual alignment of rod-like and bent-core molecules in nematic phase. Schematic representation of (b) splay and (c) bent distortion of the director in the mixtures.....	143
<b>Figure 4B.5.9:</b> Variation of capacitance as a function of voltage for the 7CB, 5M and 7M at T = 36°C, $f = 1$ kHz.....	144
<b>Figure 4B.5.10:</b> Variation of (a) splay and (b) bend elastic constants of pure 7CB and two mixtures 5M and 7M on the relative temperature scale.....	146
<b>Figure 4C.2.1:</b> Chemical structure of the compound 12-10.....	154
<b>Figure 4C.2.2:</b> Configurations of cells used in optical study (a) homeotropic cell, cell gap = 5 $\mu\text{m}$ , (b) homeotropic cell, antiparallel rubbing, cell gap = 5 $\mu\text{m}$ . Arrows point to the rubbing direction.....	154

<b>Figure 4C.2.3:</b> Textures of the unrubbed homeotropic cell for temperatures of 135 <sup>0</sup> C, cell gap = 5μm, (a) E=0Vpp and (b) E= 150Vpp, 1 kHz square wave, A denotes analyzer, P denotes polariser, E denotes electric field.....	154-155
<b>Figure 4C.2.4:</b> Textures of the rubbed homeotropic cell for temperatures of 135 <sup>0</sup> C, cell gap = 5μm, (a) E=0Vpp and (b) E= 150Vpp, 1 kHz square wave, A denotes analyzer, P denotes polariser, E denotes electric field and R denotes the rubbing direction.....	155
<b>Figure 4C.2.5:</b> Textures of homeotropic alignment of molecules at temperature of 135 <sup>0</sup> C, (a) with and (b) without magnetic field, arrow denotes the direction of magnetic field.....	156
<b>Figure 4C.3.6:</b> Textures of homeotropic alignment of molecules in Al spacer-IPS cell.....	156
<b>Figure 4C.4.7:</b> Effect of electric field in the nematic phase in homeotropic alignment of molecules.....	157
<b>Figure 4C.5.8:</b> Textures of nematic phase in droplets of glycerol.....	158
<b>Figure 4C.5.9:</b> Free standing film textures of 12-10 in a plate with hole of 1mm diameter; (a) 140 <sup>0</sup> C, film of less thickness, 4-brush defects (uv power of 154μW/cm <sup>2</sup> ) (b) 140 <sup>0</sup> C, combined with reflectance mode (c) 4-brush defects at 130 <sup>0</sup> C (d) film of maximum thickness at 130 <sup>0</sup> C (e) N-SmC transition (f) after transition at SmC, 120 <sup>0</sup> C, (g) induced N-Sm transition. (h) Strong UV power (1925μW/cm <sup>2</sup> ).....	158-159
<b>Figure 5.2.1:</b> Modified Structures of central bent core unit with a substituent and designed compounds.....	165
<b>Table 5.4.1:</b> Phase transition temperatures ( <sup>0</sup> C) of the compounds <b>2-14-2F</b> , recorded for second heating (first row) and second cooling (second row) cycles at 5 <sup>0</sup> C/min from DSC. The enthalpies (ΔH in kJ/mol) and entropies (ΔS in J/mol/K) respectively are presented in parentheses.....	167
<b>Figure 5.4.3:</b> DSC thermogram of 2-14-2F.....	167
<b>Figure 5.4.4:</b> Optical microphotographs of <b>2-14-2F</b> under crossed polarizers in different regions (a) developable domains at T = 135 <sup>0</sup> C, (b) telephone wire like spiral texture and checkerboard patterns T = 132 <sup>0</sup> C, (c) circular domains and spiral texture with banana leaf like T = 125 <sup>0</sup> C, (d) developable domains as well as spiral textures T = 122 <sup>0</sup> C, (e) banana leaf like textures T = 118 <sup>0</sup> C, and (f) transition to Cr phase T = 116 <sup>0</sup> C.....	168-169

<b>Figure 5.4.5:</b> Optical microphotographs of <b>2-11-2F</b> of an uncovered drop of B7phase at T =135°C, 130°C and 120°C respectively.....	169
<b>Figure 5.4.6:</b> Optical microphotographs of <b>2-11-2F</b> under crossed polarizers in different regions.....	169-170
<b>Figure 5.4.7:</b> Optical microphotographs of <b>2-12-2F</b> under crossed polarizers in different regions (a) telephone wire like spiral texture at T = 135 <sup>0</sup> C (b) developable domains at T = 132 <sup>0</sup> C, (c) circular domains with banana leaf like T = 122 <sup>0</sup> C.....	170
<b>Figure 5.4.8:</b> Optical microphotographs of <b>2-13-2F</b> of an uncovered drop of B7phase at T =138°C, 129°C and 118°C respectively.....	170
<b>Figure 5.4.9:</b> Optical microphotographs of <b>2-14-2F</b> of an uncovered drop of B7phase at T =137°C, 132°C respectively.....	171
<b>Figure 5.4.10:</b> Myelinic domains observed between crossed polarisers in a free drop of B7 in 2-14-2F about 5 ° below I-B7 transition temperature. The pattern is interpreted as splay-bend regions.....	171
<b>Figure 5.4.11:</b> Squared portion in figure 1.10 (positive and negative splay).....	171
<b>Figure 5.5.12:</b> Optimised molecular structure of 2-14-2F.....	172
<b>Figure 5.5.13:</b> HOMO of 2-14-2F.....	172
<b>Figure 5.5.14:</b> LUMO of 2-14-2F.....	172
<b>Figure 5.6.15:</b> UV-Visible (a) theoretical and experimental UV) and fluorescence spectra of <b>2-14-2F</b> in CHCl <sub>3</sub> .....	174-175
<b>Figure 5.6.16 :</b> Fluorescence spectra of the series at 10 <sup>-3</sup> M concentration chloroform solution.....	175
<b>Figure 5.7.17 :</b> Textures of the effect of electric field in B7 phase.....	176

## Preface

*“Imagination is more important than knowledge”*

--- *Sir Albert Einstein*

The bent shape in an organic molecule promotes layer ordering and hence do not promote mesomorphism unless sufficient anisotropy is manifested in the molecule. For obtaining mesomorphism in bent core compounds, the proper design of ligand is important. The exhibition of nematic and smectic phases by such compounds is experimentally challenging. Due to strong tendency for smectic layering generated by the close packing of the kinked molecules promoted by aromatic core interactions the manifestation of nematic phases among the mesophases in materials of bent core molecules is relatively scarce. Nematic phase is largely realized in five-ring bent core compounds, the derivatives of 1,3-disubstituted phenyl ring with a substituent in 2- or 4- positions. However, reduction of the molecular bent at the apex by the replacement of 1,3-substituted 6-membered phenyl ring by a 2,5-substituted 5-membered heterocycles like oxadiazole, or thiadiazole or unsymmetrical hockey stick molecules or dimesogens comprised of rod-like and bent units (with a overall reduction in bent angle) yielded the nematic phases at high temperatures above the layered smectic or columnar phases. In this thesis, an extensive study on the design, synthesis and characterisation of novel achiral bent-core molecule based on four benzene rings are presented and the influences of substituents on these materials are highlighted to explore some general structure–property relationships. Additionally, physical studies like stripe periodicity, elastic constants, electro-optical study and dielectric investigation on nematic phases are realized. The organized body of thesis is as follows:



**Chapter 1** deals with the general attributes of bent shaped and its associated mesophases. In addition, orientation of molecules in different mesophases of bent core compounds determined by X-ray diffraction and other techniques are described.

**Chapter 2**, gives the survey about banana-shaped liquid crystals of different molecular structures reported in the literature in quest for chirality followed by proposed plan of research work. This chapter also gives an idea about the current research work in the field of banana shaped liquid crystals.

**Chapter 3**, describes the elegant synthetic steps towards the successful synthesis of the desired compound. Chemical characterization methods like FT-IR, <sup>1</sup>H-NMR, UV-visible, Fluorescence spectroscopy with spectral data of the synthesized compound and procedure involved for the synthesis are mentioned. A brief outline about the experimental set up with working principles and methods involved for studying the phase behaviours and other associated physical properties of liquid crystals are also detailed. These methods include DSC, POM X-ray diffraction measurements, Stripe periodicity and elastic constants.

**Chapter 4 (Part A)** describes the detailed study of the design, synthesis and characterization of novel 4-ring achiral bent core liquid crystals by POM, DSC and XRD studies. The most elusive nematic phase observed in this type system is discussed elaborately. It is found that nematic mesomorphism can be realized with reduced ring system containing a substituent at the bay position.

**Chapter 4(PartB)** deals with study of stripe domains, Freedricksz transition and the elastic constants in the nematic phase.

**Chapter 4(PartC)** describes the conformation of nematic phase by electric field, magnetic field and free standing film studies.

**Chapter 5**, exhibited the study of examining effect of polar substituents on the central bent core unit in unsymmetrical achiral four ring banana shaped molecule. We observed that a specific substituent (also its polarity and position) in the

central core in such system has a major influence on the banana mesomorphism. The mesomorphic behaviour and emission profile of the compounds are studied.

### **Acknowledgement**

“Knowledge can only be got in one way, the way of experience, there is no other way”

--- Swami Vivekananda.

The present thesis is an outcome of the years of experience, ideas generated in the form of knowledge.

In the over six years of my research career I have been supported and assisted by a large number of people, in regards to whom I want to convey my couple of words for heartfelt thanks. Foremost, I would like to thank Prof. Nandiraju V S Rao whose enthusiasm and creativity has motivated all of the work in this thesis. He has given me an extraordinary amount of freedom to be creative and to work on the problems that have interested me. I've spent countless hours discussing research and ideas in science as well as life in general with him. He always cheerfully made time to answer any theoretical questions that I may have had. Without his patience and guidance, I would not have finish this work. It was one of the best choices I have ever made to choose him as my supervisor. He is the only person who used to make me feel the sayings, “If you rest, you will rust”. His good sense of humour had contributed greatly to the positive environment and had been playing as mitochondria in enriching my academic as well as personal life.

My special thanks to our mother university, Assam University, Silchar for providing her lap and stay in her heart to gain the ray of knowledge to every students irrespective of good or bad, caste, creed, religion etc.

I express my deepest sense of gratitude and heartfelt thanks to the Honourable Vice-Chancellor of my time, Prof. T Bhattacharjee, Controller of Examination, Dr. P Debnath and respected Dean of School of Physical Sciences, Prof. D Biswas for their support.

The long hours of Ph D programme were made easier by the companionship of Dr. M K Paul who has paved me the way to know, understand and synthesize the liquid crystal molecules and their properties; I am greatly indebted to him.

I would like to thank all of the professors who taught me the courses. It is my honour and pleasure to express my sincere gratitude to our Retd. Professor, Prof. M R Islam for his moral support all throughout my university career. I also value the influence of fatherly assistance of Prof. S B Paul which flourished a unique atmosphere in my long hours at department. His genuine concern in the teachings of organic chemistry is evident in the synthesis of my liquid crystal molecules. I am greatly indebted to Prof. C R Bhattacharjee for his support and endeavour which made my path easy to understand the behaviour of interactions of organic ligands and metals.

My heartfelt gratitude and thanks to Dr. P. Mandal, Dr. Sk. Jashimuddin, Dr. P.C Paul, Dr. H. Acharya, Dr. D. Sengupta, , Dr. S. K Ghosh.

The liquid crystal research would not have been accomplished without the support of Dr. S Choudhury. I cannot forget his smile coming from pure kindness for all of which I am greatly indebted to him.

My special thanks are due to my supervisor at Tokyo Tech, Japan Prof. Ken Ishikawa and Prof. Hideo Takezoe for providing me the platform to work there and have taste of liquid crystal research in Physics. I also want to express my thanks and gratitude to my foreign friends and collaborators who went out their way to provide me assistance- Asstt. Professor Dr. Fumito Araoka for managing the things at time, Dr. Khoa V Le for helping me in elastic constant study, Mr. S Aya for teaching me how to run the XRD machine and providing me the experimental datas and Cao Huanqi, for with me there all the time during my stay

at Japan and also I cannot forget Mrs. H Takahashi, Secretary to GCOE for been instrumental in making things work during my stay at Japan.

Of course nothing would function properly without our gifted non-teaching staffs, I specially acknowledge to Mr. P. R Ramesh, Mr. S. Bhattacharjee, and Mr. B. Nath, Md. J. A. Borbhuiya for their help and support. I am also thankful to office staff Md. Jamil Borbhuiya for his cooperation.

I also want to remember the endless contribution from my senior colleague, Dr. Rajdeep Deb, who was there with me all the time, discussing on topics starting from research to life. He had always given me the kind and correct answers even though my poor asking. I have also benefited from the experience and ideas of Dr. T D Choudhury and Dr R K Nath in this long span of years starting from my master's programme to the end of my Ph D.

I would like to give special acknowledgment to my friend Rahul Deb with whom I spent many long hours working in the lab, planning in the lawn of department and in the midst of Irongmara valley for organising everything which we faced in the long run. He has thrown Frisbee with me nearly every sunny day for long years and who commiserated with me during the concurrent developing and writing of my thesis.

The tight- knit community formed by Dipika during and beyond laboratory hours have been a constant source of insight and support and I am very grateful for her friendship.

God will not forgive me if I forget the great influence of my friend Atiqur in my research career. He was there supportive with me all the time starting from research to administrative activities; I am greatly indebted to him.

I realize again that when something is done however small it is, it is not done by alone. I express my deep sense of gratitude to all my junior research colleagues like Gayatri, Kalpana, Venkatesh, Srikant, Nazma and Golam in the development of my thesis.

My special thanks are due to Somen for being supportive at any situational demands.

The class of master students with whom I entered University specially Bimolendu, Kaushik, Biswajit, Meenakshi and Hemoprabha for being my friend, supportive and encouraging all throughout.

I would like to acknowledge CLRI, Chennai, Tamil Nadu and CIL, Assam University, Silchar for providing me the NMR spectra whenever it is felt necessary.

Apart from academic activities, there are lots of emotional activities related to the compiling of my thesis. I can't deny the motherly atmosphere which I got from Mrs. Anantha Lakshmi, my heartfelt thanks to her.

My science career really began many years ago with the patience that my parents Mr. Himangshu and Mrs. Radha Rani Chakraborty showed in answering my constant questions. They encouraged me to pay attention to the world around me and to wonder why and how things work. I express my sincere thanks to my younger brother Binayak, who is there with me being supportive all the time irrespective of situations.

My deep sense of gratitude to my maternal grandfather Late Rajani K. Bhattacharjee and my maternal uncle Mr. Srikanta Bhattacharjee for being with me all the time starting from the beginning of my educational career.

I express my heartfelt thanks to my paternal uncle and auntie Mr. Sitangshu Chakraborty and Mrs. Meera Chakraborty; for spending endless efforts throughout my life.

Finally, during the beginning of my research career I have been gifted with the love and companionship of my wife Lopamudra. She has put up with endless discussions of my work and has always been supportive and encouraging, no matter what circumstances demanded. The life with her is always like a safe and quite harbour where I can anchor. My heartfelt acknowledgement is due to her.

I would like to acknowledge the financial support from UGC, India for helping me to carry out research in the host institute and also GCOE for providing me funds and support of necessities which helped my research at Tokyo Institute of Technology, Japan.

