

Liquid crystals are condensed phases, which possess some properties of a crystalline solid as well as an isotropic liquid. These intermediate phases are also known as mesophases and a compound which exhibits such a phase is called a mesogen. Liquid crystals may be broadly classified into two types: (i) Thermotropic liquid crystals –which are obtained by the action of heat on certain pure organic compounds or their mixtures and (ii) Lyotropic liquid crystals – which are formed by the action of a solvent on suitable substrates. Thermotropic liquid crystals may be further divided into: (i) Calamitic liquid crystals (ii) Discotic liquid crystals and (iii) Banana-shaped liquid crystals, depending on the shape of the constituent molecules. The investigations carried out and described in this thesis are low molar mass thermotropic liquid crystalline compounds composed of banana-shaped or bent-core molecules.

Ferroelectricity in liquid crystals was discovered by Meyer *et al.* [1] in 1974, who postulated and proved the polar ordering in chiral smectics. In such materials, the system escapes from macroscopic polarization by the formation of a helix. This helix can be unwound by the application of any external electric field. In 1989, Chandani *et al.* [2] discovered an antiferroelectric smectic phase in a chiral compound namely, 4-(1-methylheptyloxy-carbonyl)phenyl-4'-octyloxybiphenyl-4-carboxylate (MHPOBC). In antiferroelectric phases, the molecules in the successive layers tilt in opposite directions, so that the dipole moments cancel out within two adjacent layers. These tilt directions precess around the smectic layer normal which results in a helical structure. Around the same time, Goodby *et al.* [3] discovered a theoretically predicted defect stabilized intermediate phase, namely twist grain boundary smectic A ( $TGB_A$ ) phase in a variety of optically active phenyl propiolates. In 1977, Chandrasekhar *et al.* [4] discovered liquid crystalline behaviour in a new class of compounds composed of disc-like molecules. The disc-shaped molecules are found to stack one above the other forming columnar mesophases. All these discoveries have stimulated the search for new materials and new mesophases.

In 1930's, Vorlander and Apel reported [5] a few compounds with non-linear molecular structure and exhibiting mesomorphic properties. However, they could not characterize the mesophases. In 1991, Kuboshita *et al.* [6] investigated in detail the mesomorphic properties of such compounds, whose constituent molecules are non-linear in shape. They synthesized compounds derived from 1,2-dihydroxybenzene and also the corresponding 3- and 4-methyl-1,2-phenylene derivatives. The mesophases obtained were characterized as nematic, smectic A and

smectic B. In 1993, Matsuzaki and Matsunaga reported [7] the 2,3-naphthalene analogues. Akutagawa *et al.* [8] extended this work and carried out the synthesis and studied the mesomorphic properties of achiral non-linear materials derived from resorcinol. On the basis of microscopic observations, X-ray powder diffraction measurements and miscibility studies, the mesophases shown by these compounds were identified as N and SmC. Electro-optical switching measurements were not carried out for these materials simply because the mesophases obtained were from achiral molecules.

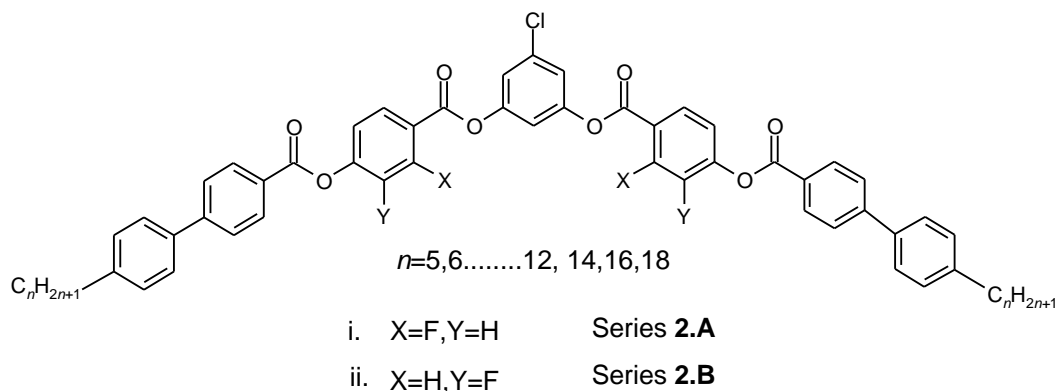
Until 1996, ferro- and / or antiferro-electricity in liquid crystal phases were believed to be observed only in compounds composed of chiral molecules. A real breakthrough in liquid crystals came in 1996, when Niori *et al.* reported [9] ferroelectricity in a smectic phase formed by achiral banana-shaped compound, viz. 1,3-phenylene bis [4-(4-*n*-octylphenyliminomethyl)benzoate]. Since then, banana-shaped mesogens, whose constituent molecules have a bent-core (BC) structure, have become a subject of intense investigations. The ferroelectricity observed in the mesophases of these compounds is ascribed to the  $C_{2v}$  symmetry resulting from the packing of banana-shaped molecules into layers. Because of the intrinsic shape, these molecules adopt dense packing in the layers and are all aligned in the bend direction, which restrict the rotation around the long molecular axis and induces a layer polarization along the bend direction. This in-layer-induced polarization can be reversed by the application of any external electric field. However, in 1997, Link *et al.* [10] demonstrated that the ground state structure of the smectic phase of compound 1,3-phenylene bis [4-(4-*n*-octylphenyliminomethyl)benzoate] is actually antiferroelectric and not ferroelectric as reported [9] earlier. Further, they found that, the molecules are tilted with respect to the layer normal in a plane normal to the polarization direction. The combination of polar order and tilt order gives the layer a chiral structure, although the molecules are achiral. The mesophases obtained from BC compounds are not completely miscible with any of the known mesophases of classical liquid crystals. Hence, in an International Workshop on “Banana-Shaped Liquid Crystals: Chirality by Achiral Molecules” held in Berlin in 1997, it was suggested to use the general symbol “B” for the mesophases exhibited by banana-shaped compounds. A total of seven phases were identified initially and assigned the symbol  $B_1, B_2, \dots, B_7$  [11]. Another phase was discovered later which was designated as  $B_8$  [12]. The letter B signifies the shape of the constituent molecules, viz.

banana, bent-core, bow, etc. and the suffix indicates the sequence of discovery of the mesophases.

This thesis contains seven chapters and the first chapter gives a brief description of the discovery and various other aspects of the mesophases of bent-core compounds. In the remaining six chapters the synthesis and mesomorphic properties of some novel bent-core compounds investigated by the author have been described. The important results obtained and presented in this thesis include the observation of a transition from  $\text{Col}_r\text{P}_{\text{AF}}$  phase to a  $\text{B}_{2x}$  phase, observation of a bistable linear electro-optical switching in the  $\text{B}_7'$  phase, observation of an odd-even effect in the nanoscopic director organization in the  $\text{B}_2$  phase as a function of the number of carbon atoms in the terminal chain, observation of a transition from the electro-optically non-switchable to a switchable  $\text{B}_7$  phase, observation of  $\text{SmCP}_A$  phase in five-ring bent-core compounds derived from 5-methoxyisophthalic acid and the first observation of a  $\text{Col}_{\text{ob}}\text{P}_F$  phase in mesogenic dimers composed of bent-core molecules with a flexible alkylene spacer.

In Chapter 1, a brief introduction to the discovery of bent-core mesogens and a detailed description of the well-known B-phases reported in the literature, structural models for some of the B-phases and the origin of chirality including the occurrence of ferro-/antiferro-electric mesophases from achiral molecules [10,11, 13-16] are given. In addition, a brief description of the structure-property relationships in bent-core compounds and the effect of lateral substituents on the mesophases are also included. A brief introduction to the mesogenic dimers composed of BC units is also provided.

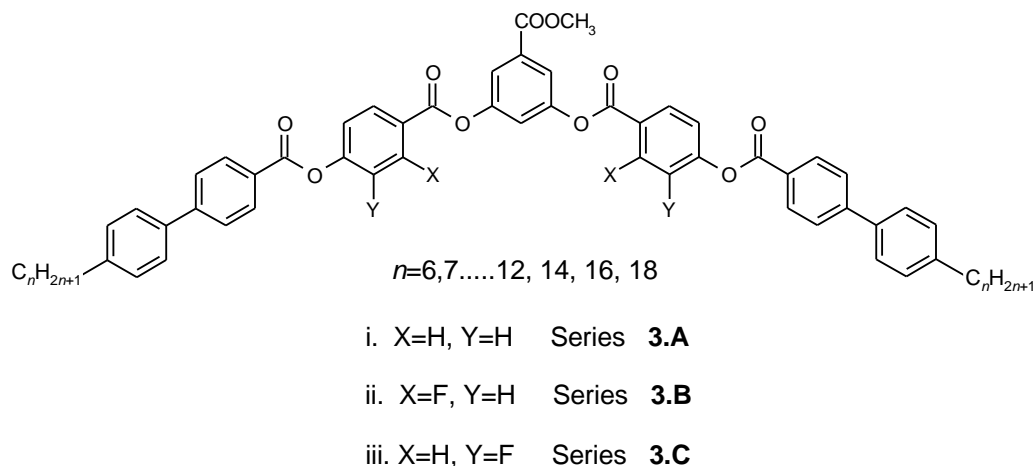
In Chapter 2, the synthesis and mesomorphic properties of two homologous series of compounds derived from 5-chlororesorcinol are described. The general molecular structure is shown below



The lateral substituents strongly influence the mesomorphic properties of the BC mesogens either by changing the packing of the molecules or by influencing the polar properties of the molecules. There are numerous studies on the effect of lateral substituents at different positions on the central phenyl ring as well as outer phenyl rings. These studies indicate that dipolar effects are more prominent than steric effects in determining the mesophase behaviour. However, the effect of a substituent at position 5 of the central phenyl ring is less studied. Until now, there is only one report [17] of seven-ring BC mesogens containing a substituent at the apex of the central phenyl ring. These are symmetrical ester compounds derived from 5-cyanoresorcinol, which exhibit interesting mesomorphic properties. In order to examine the effect of replacing the strongly polar cyano substituent (whose vector of the dipole moment is along the arrow axis of the BC molecule) by a chloro group with a weaker dipolar component, but whose contribution is along the same axis, two series of symmetrical bent-core compounds derived from 5-chlororesorcinol have been synthesized and their mesomorphic behaviour investigated.

The homologues of series **2.A** contain a fluoro substituent *ortho* to the ester carbonyl group connected to the central phenyl ring whereas those of series **2.B** contain fluorine at *meta* position. The lower homologues of both the series of compounds exhibit a columnar B<sub>1</sub> phase with a rectangular lattice. Interestingly, the B<sub>2x</sub> phase of higher homologues show helical patterns and exhibit a mixture of three different possible structures, two of which are chiral and the remaining one is racemic. A comparison of mesomorphic properties of these two series of compounds clearly reveals that *m*-fluoro substituted compounds (series **2.B**) are better in generating mesophases. Moreover, both the melting and clearing temperatures are lower for these compounds. A comparison of the mesomorphic properties of compounds of series **2.A** and **2.B**, with the analogous compounds derived from 5-cyanoresorcinol indicate that, replacement of cyano group by a chloro group results in reduction of melting and clearing temperatures. However, the type of the mesophases observed is unaffected.

Chapter 3 begins with a brief introduction to the effect of lateral substituents on the mesomorphic behaviour of bent-core compounds. In this chapter, synthesis and mesomorphic properties of three homologous series of compounds derived from methyl 3,5-dihydroxybenzoate have been described. The general structure of the compounds investigated is shown below.

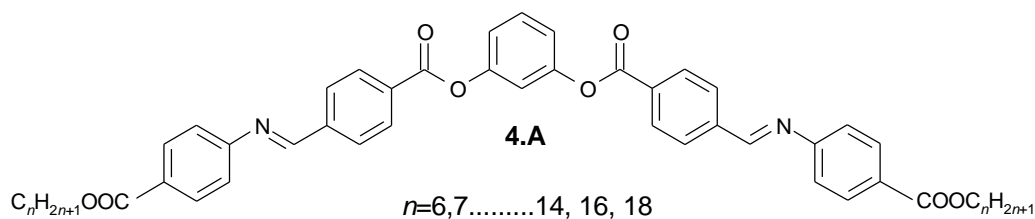


The compounds of series **3.A** do not contain any lateral substituent in the arms of the bent-core whereas compounds of series **3.B** and **3.C** contain a fluoro substituent in *ortho* and *meta* positions respectively, with respect to the ester carbonyl group of the middle phenyl ring. Three types of mesophases were observed in these three homologous series of compounds. The lower homologues show a  $B_6$  mesophase, middle homologues exhibit a  $Col_rP_{AF}$  phase and the higher homologues exhibit a  $B_{2x}$  phase. The substitution by fluorine results in a reduction of melting points as well as clearing temperatures. This effect is more pronounced in *meta* substituted compounds and a wider temperature range for the mesophases is observed. Interestingly, in one of the homologues (**3.B.7**) of series **3.B** a transition from  $Col_rP_{AF}$  to a  $B_{2x}$  phase occurs, which is the first observation of a transition from a switchable columnar phase to a switchable lamellar phase. The evidence for the occurrence of this transition is given by textural change, DSC thermogram and electro-optical studies. The compounds with fluoro substituent *meta* to the ester carbonyl group connecting the central phenyl ring show  $Col_rP_{AF}$  phase even for fairly long terminal chains ( $n=14$ ).

Electro-optical investigations indicate a polarization value of around  $500 \text{ nC cm}^{-2}$  for  $Col_rP_{AF}$  phase (compound **3.B.7**) and a very high polarization value of  $1130 \text{ nC cm}^{-2}$  (compound **3.B.9**) for the  $B_{2x}$  phase. The dc field experiments indicate a homochiral antiferroelectric structure for the  $B_{2x}$  phase.

A comparison of the mesomorphic behaviour of the compounds of series **3.B** and **3.C** with the analogous compounds derived from 5-chlororesorcinol (series **2.A** and **2.B**, described in Chapter 2) indicates the profound influence of the polar nature of the substituent on the mesomorphic behaviour of BC compounds. Replacement of a chloro group by a bulky methoxy carbonyl group at the apex of the central phenyl ring results in a antiferroelectrically switchable columnar phase. Further, both melting points and clearing temperatures are lowered substantially.

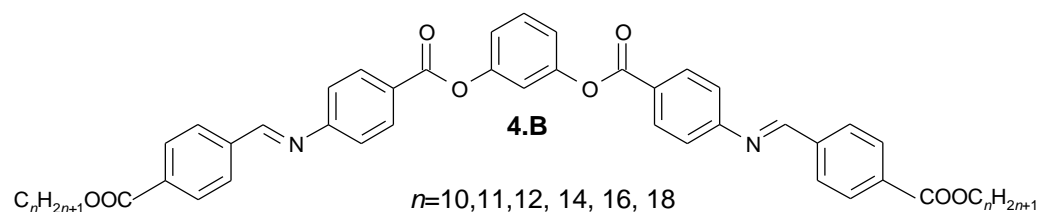
Chapter 4 begins with a brief introduction to SmC<sub>G</sub> phase [18]. This Chapter contains two parts. In the first part, the synthesis and mesomorphic properties of a homologous series of eleven five-ring symmetrical bent-core compounds, in which the terminal *n*-alkoxy linkages of the original bent-core mesogen forming a B<sub>2</sub> phase [10] are replaced by *n*-alkyl carboxylate groups, are described. This small difference induces significant changes in the phase behaviour. The general structure of the compounds investigated is shown below.



The lower homologues ( $n=6-11$ ) of the series show B<sub>2</sub> structures with an interesting odd-even effect concerning their local director tilt and polar arrangements. The odd-even effects were also observed in steady dielectric susceptibility and the value of the threshold voltage for polarization switching. This odd-even effect probably is due to steric (entropic) reasons, which are not suppressed by the relatively low polar interactions. Three of the middle homologues ( $n=12-14$ ) exhibit two mesophases. The higher temperature phase exhibits helical structures as well as other beautiful textures that are normally seen for a B<sub>7</sub> phase. This phase shows a bistable but linear electro-optical switching without any observable polarization peak. The mesophase has been designated as a B<sub>7</sub>' phase. On cooling, the mesophase shows a transition to the chiral antiferroelectric smectic phase at a lower temperature, which is designated as B<sub>2</sub>'. Two

theoretical models are analyzed for the B<sub>7</sub>' phase and it is shown that a local triclinic symmetry may be responsible for the unusual electro-optical switching. The higher homologues ( $n=16, 18$ ) exhibit only a B<sub>7</sub>' phase.

In the second part, the mesomorphic behaviour of a homologous series of compounds is investigated, in which the orientation of the azomethine linkage group in compounds discussed above is reversed. The general molecular structure of the compounds is shown below.

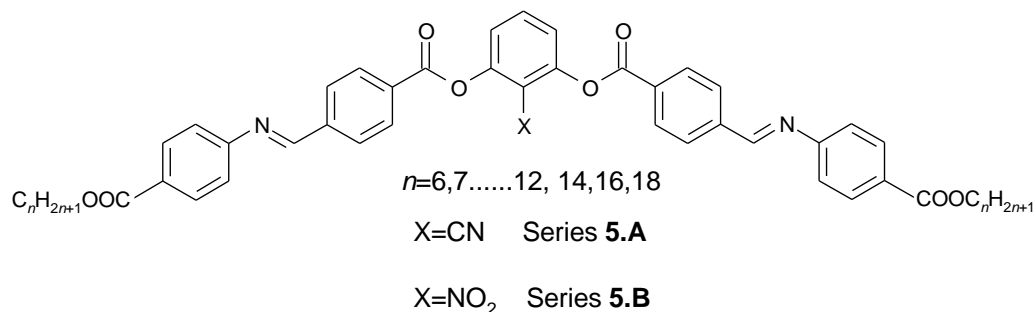


In this series, only six compounds were prepared and the lower homologues were not prepared because compound with *n*-decyl chain did not show any mesophase. The other five homologues exhibit a metastable mesophase whose optical textures are all similar. The phase exhibits chiral domains of opposite handedness on slow cooling from the isotropic phase. This has been identified as a SmCP<sub>A</sub> phase.

It should be pointed out here that the compounds of series **4.B** differ from those of series **4.A** only by the way in which the azomethine linking group is attached. The present study emphasizes the remarkable influence of the orientation of the linking group on the mesomorphic behaviour.

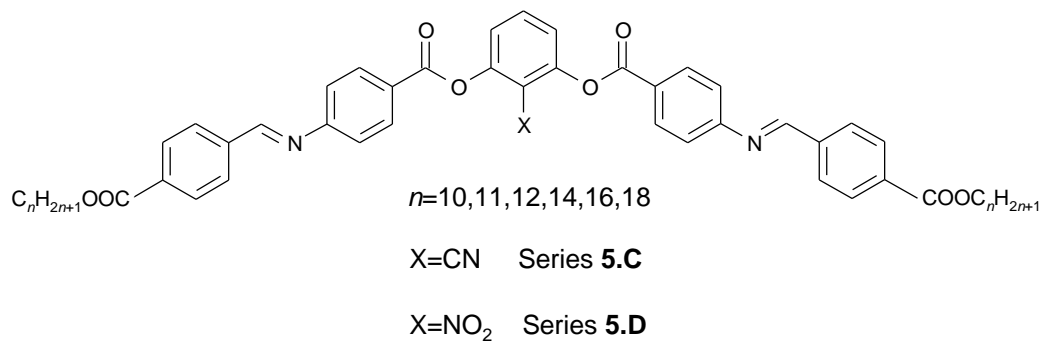
In Chapter 5, a brief introduction to the compounds exhibiting B<sub>7</sub> phase and the proposed structural models for this phase is given. Among all the mesophases exhibited by BC compounds, the B<sub>7</sub> phase exhibits the most beautiful and fascinating textures. A characteristic feature of the XRD pattern of this phase is the presence of a medium angle reflection in addition to several small angle reflections besides a diffuse wide-angle reflection [19]. In this chapter, the synthesis and liquid crystalline properties of four new homologous series of symmetrical five-ring bent-core compounds derived from 2-cyano- or 2-nitro-resorcinol having terminal *n*-alkyl carboxylate groups are described.

In the first part, compounds with general molecular structure shown below are investigated.



All these compounds exhibit a  $B_7$  phase, which shows ferroelectric switching characteristics. In addition, homologues of 2-cyano- substituted compounds display a transition from a switchable ( $B_{7FE}$ ) phase to a non-switchable ( $B_{7X}$ ) mesophase as the temperature is lowered. This is the first observation of dimorphism in BC compounds in which the higher temperature phase ( $B_{7FE}$ ) is electro-optically switchable and the lower temperature phase ( $B_{7X}$ ) is non-switchable, and the compounds are derived from 2-cyanoresorcinol. In addition, the  $B_7$  phase observed in compounds derived from 2-nitroresorcinol is monomorphic and responds to an applied electric field. This  $B_7$  phase and the higher temperature phase of the analogous cyano substituted compounds are found to be the same.

In the second part, the synthesis and mesomorphic properties of two homologous series of compounds having the general molecular structure shown below are described. The compounds of

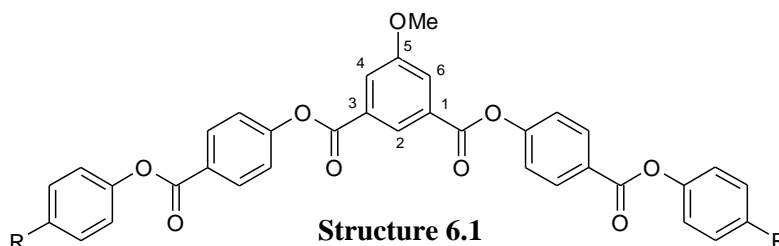




series **5.C** and **5.D** differ from the compounds of series **5.A** and **5.B** only in the orientation of the azomethine linking group. All the compounds of series **5.C** and **5.D** exhibit a non-switchable B<sub>7</sub> mesophase. Interestingly, the lower homologues of series **5.D** derived from 2-nitroresorcinol exhibit a texture which consists of chiral domains of opposite handedness. The mesophases exhibited by all these compounds show the medium angle reflection in the XRD pattern displayed by the original B<sub>7</sub> materials [19].

The influence of the orientation of linking groups on the phase behaviour of compounds derived from 2-cyano- and 2-nitro-resorcinol is examined by comparing the mesomorphic properties of compounds of series **5.A**, **5.B** with those of series **5.C** and **5.D**. Similarly, the influence of the type of terminal chain is also studied by comparing the mesomorphic properties of compounds of series **5.A** and **5.B** with the analogous compounds containing terminal *n*-alkoxy chains. The results are shown as bar diagrams.

In Chapter 6, the synthesis and mesomorphic properties of three series of compounds derived from 5-methoxyisophthalic acid are described. The compounds investigated have the general structure shown below.



R=OC<sub>n</sub>H<sub>2n+1</sub>,    *n*=8,9....12, 14, 16, 18    Series **6.A**

R=COOC<sub>n</sub>H<sub>2n+1</sub>,    *n*=10, 14, 18    Series **6.B**

R=OCOC<sub>n</sub>H<sub>2n+1</sub>,    *n*=10, 11, 13, 15, 17    Series **6.C**

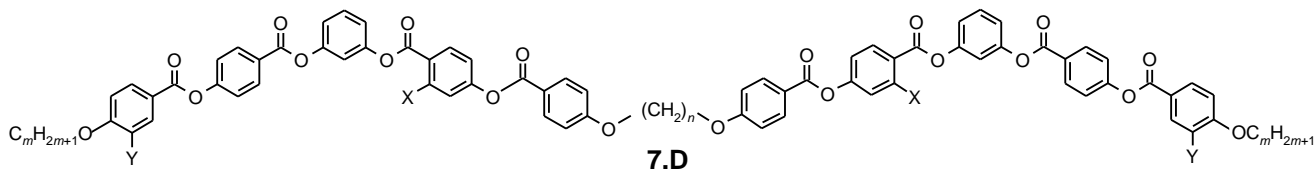
The studies on compounds derived from isophthalic acid are very limited, although they exhibit interesting phases and phase sequences. Nguyen *et al.* reported [20] several five-ring bent-core compounds derived from isophthalic acid and containing lateral substituents at positions 2 and 6 (positions shown in structure **6.1**) of the central ring and exhibiting interesting mesophases. However, so far there has been no report of a five-ring bent-core compound

containing a bulky substituent at position 5 and exhibiting a mesophase. The compounds presented in this chapter represent the first series of five-ring BC compounds containing a bulky substituent. These compounds are derived from 5-methoxyisophthalic acid and many of them exhibit an electro-optically switchable phase.

All the three series of compounds have similar molecular structure but differ in the way the terminal linking groups are attached. Compounds of series **6.A** with terminal *n*-alkoxy chains exhibit a polar smectic C phase with antiferroelectric properties (SmCP<sub>A</sub>). The replacement of terminal *n*-alkoxy chains by *n*-alkyl carboxylate groups resulted in elimination of SmCP<sub>A</sub> phase and a highly metastable SmA phase is induced. However, compounds containing terminal *n*-alkanoate groups also exhibit SmCP<sub>A</sub> phase. Interestingly, a polymorphism was observed for a homologue of this series with *n*=17. The investigations carried out in this chapter again emphasize the importance of the nature of the terminal-linking group in influencing the type of mesophase obtained.

Chapter 7 begins with a brief introduction to liquid crystal dimers. A variety of liquid crystalline dimers formed using both rod-like as well as disc-like units are quite well known [21]. However, mesogenic dimers made of BC units are relatively new and not investigated in detail. The first dimesogens in which two bent-core molecules are connected by flexible dimethylsiloxane units were also reported [22] a couple of years ago. Very recently, Kosata *et al.* reported [23] several liquid crystalline dimers composed of bent-core mesogenic units, which are terminally linked using three different types of spacers. However, they did not obtain a mesophase in dimer with an alkylene spacer. Interestingly, we were able to show that using the same basic structure but with suitable substituents, a switchable mesophase could be obtained.

In this chapter, the synthesis and mesomorphic properties of several novel symmetric dimers composed of BC molecules and linked by a flexible alkylene spacer and belonging to three different series are described. In order to study the structure-property relationships, the length of the alkylene spacer (*n*= 7-12 for *m*=14) as well as those of the terminal *n*-alkoxy chains (*m*=8-12, 14, 16, 18 for *n*=9 and 12) have been varied. The general structure of the dimers investigated is shown below.



X=H, Y=H,  $n=9$ ,  $m=14$

Dimer **7.D.1**

X=H, Y=H,  $n=12$ ,  $m=14$

Dimer **7.D.2**

X=F, Y=H,  $n=9$ ,  $m=14$

Dimer **7.D.3**

X=F, Y=H,  $n=12$ ,  $m=14$

Dimer **7.D.4**

X=H, Y=F,  $n=9$ ,  $m=14$

Dimer **7.D.5**

X=H, Y=F,  $n=12$ ,  $m=14$

Dimer **7.D.6**

X=F, Y=F,  $n=9$ ,  $m=14$

Dimer **7.D.7**

X=F, Y=F,  $n=12$ ,  $m=14$

Dimer **7.D.8**

X=F, Y=F,  $n=9$ ,  $m=8,9...12, 14, 16, 18$

Series **7.D.I**

X=F, Y=F,  $n=12$ ,  $m=8,9...12, 14, 16, 18$

Series **7.D.II**

X=F, Y=F,  $n=7-12$ ,  $m=14$

Series **7.D.III**

Dimers, which do not contain any lateral substituent in the bent-core exhibit a highly metastable phase. However, substitution by fluorine resulted in a thermodynamically stable enantiotropic phase. The dimers, which contain four fluoro substituents in the molecule, show wide thermal range for the mesophase. All the dimers investigated display the same type of mesophase, which has been characterized as a  $\text{Col}_{\text{ob}}\text{P}_{\text{F}}$  phase. However, in one dimer, a transition from  $\text{Col}_{\text{ob}}\text{P}_{\text{F}}$  phase to a metastable phase was observed. A structural model for the  $\text{Col}_{\text{ob}}\text{P}_{\text{F}}$  phase has been proposed, in which it is assumed that two BC units of a dimer are located at the opposite corners of the lattice. The investigations carried out on these dimers reveal that for a fixed spacer, the thermal range of the mesophase increases with increase in terminal chain length. Also, an odd-even effect is observed when the length of the flexible spacer is varied and it is observed that the dimers with even number of methylene units in the spacer have higher clearing temperatures than those with odd-number. The results also suggest that the parity of the spacer has no effect on the type of the mesophase observed at least in the dimers investigated.

The results presented in this thesis are reported in the following publications.

- [1] Banana-shaped mesogens: mesomorphic properties of seven-ring esters derived from 5-chlororesorcinol  
S. Umadevi and B. K. Sadashiva, *Liq. Cryst.*, **32**, 287 (2005).
- [2] New five-ring symmetrical bent-core mesogens exhibiting the fascinating B<sub>7</sub> phase  
S. Umadevi and B. K. Sadashiva, *Liq. Cryst.*, **32**, 1233 (2005).
- [3] Mesogenic dimers composed of bent-core molecules with flexible alkylene spacer  
S. Umadevi, B. K. Sadashiva, H. N. Shreenivasa Murthy and V. A. Raghunathan, *Soft Matter*, **2**, 210 (2006).
- [4] Bistable linear electro-optical switching in the B<sub>7</sub>' phase of novel bent-core molecules  
S. Umadevi, A. Jakli and B. K. Sadashiva, *Soft Matter*, **2**, 215 (2006).
- [5] The SmCP<sub>A</sub> phase in five-ring bent-core compounds derived from 5-methoxyisophthalic acid  
S. Umadevi, S. Radhika and B. K. Sadashiva, *Liq. Cryst.*, **33**, 139 (2006).
- [6] Odd – even effects in bent-core compounds containing terminal *n*-alkyl carboxylate groups  
S. Umadevi, A. Jakli and B. K. Sadashiva, *Soft Matter*, DOI: 10.1039/b605061a.
- [7] Novel five-ring bent-core compounds exhibiting a transition from the electro-optically non-switchable to a switchable B<sub>7</sub> phase  
S. Umadevi and B. K. Sadashiva, *Chem. Mater.*, (in press).

## **Papers under preparation**

- [1] Liquid crystalline properties and dependence of transition temperatures on the length of the flexible alkylene spacer of symmetric dimers composed of bent-core units  
S. Umadevi and B. K. Sadashiva
  
- [2] Polar columnar and lamellar mesophases in homologous bent-core compounds derived from methyl 3, 5-dihydroxybenzoate  
S. Umadevi and B. K. Sadashiva

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