

PREFACE

Liquid crystals may be broadly classified into two classes: (a) Thermotropic liquid crystals-which are obtained by the action of heat on certain pure organic compounds or their mixtures and (b) Lyotropic liquid crystals-which are formed by the action of a solvent, usually water on suitable substrates. Thermotropic liquid crystals may be further divided into three types on the basis of the shape of the constituent molecules. These are

- i) Calamitic liquid crystals-which are obtained from rod-like or lath-like shape of the molecules,
- ii) Discotic liquid crystals-which are formed from disk-like molecules and
- iii) Banana-shaped liquid crystals-whose constituent molecules have a bent-core.

The investigations carried out and described in this thesis are low molar mass thermotropic liquid crystalline compounds composed of bent-core molecules.

Compounds with non-linear molecular structure and exhibiting liquid crystalline properties were reported [1] long back but their phase structure could not be characterized. A reinvestigation on the synthesis and mesomorphic properties of such non-linear materials were carried out by Kuboshita *et al.* [2] in 1991. This work was further extended by Matsuzaki and Matsunaga [3] and in greater detail by Akutagawa *et al.* [4]. The real breakthrough came about in 1996, when Niori *et al.* [5] reported ferroelectric behaviour in a smectic phase formed by a bent-core (BC) achiral compound viz. 1,3-phenylene bis[4-(4-*n*-octylphenyliminomethyl)-benzoate]. This prompted several groups to synthesize such bent-core compounds and study their mesomorphic behaviour.

Interestingly, the ferroelectric behaviour observed in the mesophases of BC compounds was ascribed to C_{2v} symmetry which is due to the packing of such molecules into layers. Due to the intrinsic shape, the molecules adopt dense packing in the layers which align in the bend direction and this restricts the rotation of the molecules around the long-molecular axis and induces a layer polarization along the bend direction. This in-layer induced polarization could be reversed by the application of an external field. However, in 1997, Link *et al.* [6] demonstrated

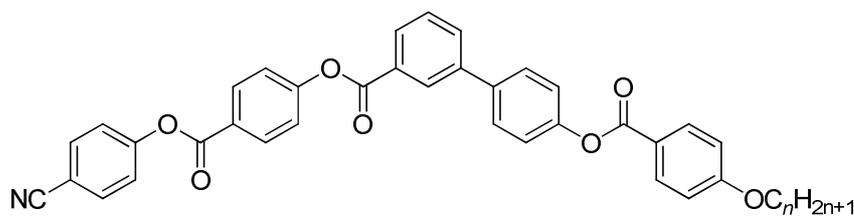
that the ground state structure of the smectic phase exhibited by 1,3-phenylene bis[4-(4-*n*-octylphenyliminomethyl)benzoate] is indeed antiferroelectric and not ferroelectric as reported [5] earlier. They also found that the molecules in the smectic phase are tilted with respect to the layer normal in a plane normal to the polarization direction. A combination of polar order and tilt order gives the layer a chiral structure, although the molecules are achiral. In addition, the mesophases obtained from several other BC compounds were not miscible with any of the known classical liquid crystals. Hence, an international workshop on “Banana-Shaped Liquid Crystal: Chirality by Achiral Molecules” was held in Berlin in 1997 to review the situation. It was suggested to use the symbol ‘B’ for the mesophases exhibited such banana-shaped or bent-core compounds. Initially, a total of seven mesophases were identified and assigned the symbols B₁, B₂,...B₇ [7]. Later, a new phase was discovered [8] and assigned the symbol B₈. It is of interest to note that the letter B signifies the shape of the constituent molecules, viz. banana, bow, boomerang etc. and the suffix indicates the sequence of the discovery of the mesophases.

This thesis contains eight chapters and the first chapter gives a brief introduction to calamitic liquid crystals and a description of bent-core liquid crystals in greater detail. The remaining seven chapters contain the investigations carried out on the synthesis and mesomorphic properties of 145 bent-core (BC) compounds and 30 zigzag-shaped (Z-shaped) compounds. Importantly, many new results have been obtained which include the occurrence of a transition between two polar partial bilayer orthogonal smectic phases, one of which is biaxial and the other is uniaxial, the first use of unsymmetrical 3,4-disubstituted biphenyl central unit which provided B_{7A} and B_{7'} phases, occurrence of a transition between SmC_sP_A and Col_{ob}P_F phases, the first observation of a transition between two apolar orthogonal mesophases as a result of change in chain conformation in symmetric five-ring bent-core dimers, occurrence of a transition between two antiferroelectric smectic C phases which have been designated as SmC_sP_A to SmC'_sP_A phases, occurrence of a dark conglomerate phase and finally, a new shape has been designed, viz. zigzag-shaped compounds exhibiting apolar columnar mesophases with rectangular and oblique lattices.

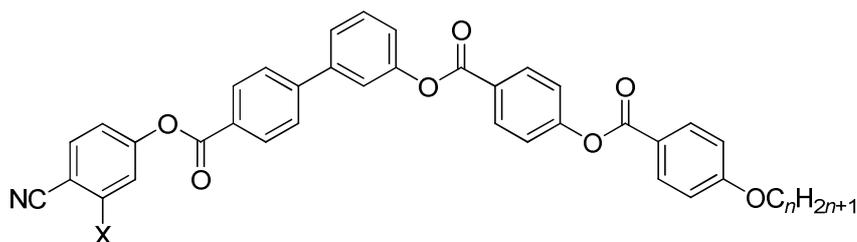
In chapter 1, a brief introduction to the discovery of bent-core liquid crystals and types of B-phases reported in the literature are described [5-13]. A description of calamitic phases formed by bent-core molecules [14-21] and a brief introduction to the mesogenic dimers

composed of BC units is also included [22-25]. In addition, a description of the structure-property relationships in bent-core compounds and the effect of lateral substituents on the mesophases are also included.

In chapter 2, the synthesis and characterization of two homologous series of unsymmetrical BC compounds containing a strongly polar cyano group at one terminal position while the other end is substituted by an *n*-alkoxy chain are described. In one of the series, the effect of a fluoro substituent *ortho* to the terminal cyano group is also examined. The unsymmetrical compounds described here have the general molecular structures shown below for series **2.A** and **2.B** respectively.



$n = 12, 13, 14, 15, 16, 18, 20$ Series **2.A**



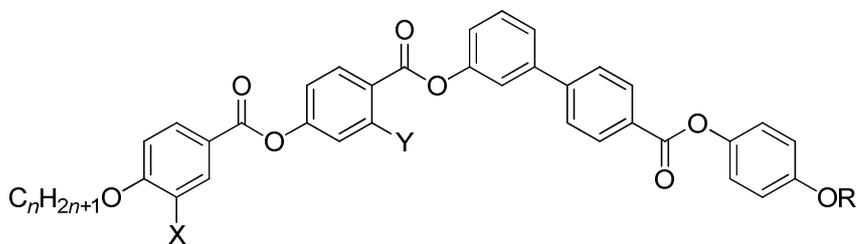
$X = H$ $n = 10, 11, 12, 13, 14, 15, 16, 18, 20$ Series **2.B**

$X = F$ $n = 16, 18, 20$ Series **2.B**

The compounds of series **2.A** are derived from 4-hydroxybiphenyl-3-carboxylic acid while those of series **2.B** are obtained from 3-hydroxybiphenyl-4-carboxylic acid. These represent the first examples of BC compounds derived from such moieties. While the biaxial

smectic A phase has been observed in both series of compounds, the physical properties are quite contrasting. In series **2.A**, both the uniaxial and biaxial phases are polar in nature and in series **2.B**, both these phases are apolar. The introduction of a fluorine substituent *ortho* to the highly polar terminal cyano group has the effect of inducing a non-polar uniaxial partial bilayer smectic A phase. The most interesting result has been the occurrence of a transition between two polar partial bilayer orthogonal smectic phases, one of which is biaxial and the other uniaxial. The dark texture of the polar uniaxial partial bilayer smectic phase shown by compounds **2.A.6** and **2.A.7** are interesting as they exhibit a polarization randomized inter layer structure.

In chapter **3**, the use of a new moiety viz. 3-hydroxybiphenyl 4-carboxylic acid has provided a number of compounds exhibiting the fascinating B₇ phase. In order to study the structure-property relationships, slight modification in the molecular structure has been made and thus four derivatives in each of the three parts of homologous series, **3.A**, **3.B** and **3.C** and a larger series **3.D** consisting of fourteen compounds have been synthesized. The synthesized and investigated compounds have the general structure shown below.

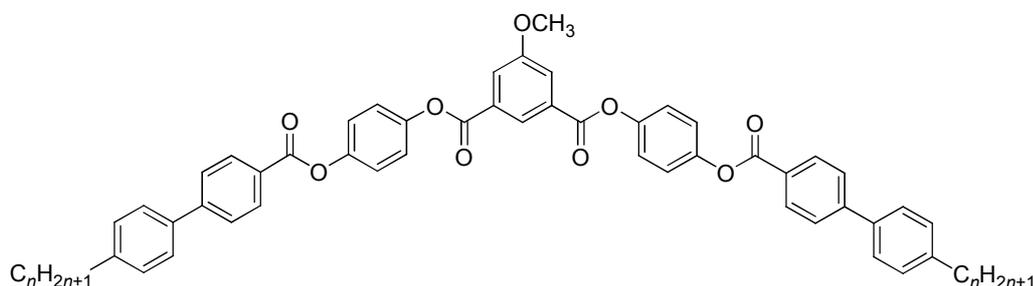


X = H, Y = H, R = -OC ₈ H ₁₇	n = 8, 10, 15, 18	Series 3.A
X = H, Y = H, R = -OCOC ₈ H ₁₇	n = 8, 10, 15, 18	Series 3.B
X = H, Y = H, R = -COOC ₈ H ₁₇	n = 8, 10, 15, 18	Series 3.C
X = F, Y = F, R = -OC ₈ H ₁₇	n = 5, 6, 7,..... 16, 18, 20	Series 3.D

Several compounds belonging to four different homologous series and derived from 3-hydroxybiphenyl-4-carboxylic acid have been synthesized and their mesomorphic properties

investigated. The compounds indicate that slight modification in the chemical structure has a bearing on the type of mesophase obtained. A non-switchable columnar phase with a rectangular lattice, a smectic C phase with antiferroelectric properties and showing helical textures and columnar phase with antiferroelectric properties with variants of fascinating optical textures have been obtained. Although, the symbol B_{7A} has been assigned to the mesophases of the higher homologues of series **3.D**, high resolution XRD data are necessary to conclusively establish their structures. These represent the first examples of B_{7A} phase obtained from unsymmetrical 3-hydroxybiphenyl-4-carboxylic acid moiety.

In chapter **4**, the synthesis and mesomorphic properties exhibited by ten compounds of a series of seven-ring BC compounds derived from 5-methoxyisophthalic acid are described. Mainly, the effect of the orientation of a ester linkage on the mesomorphic properties is examined. The symmetrical compounds investigated here have the general structure shown below.

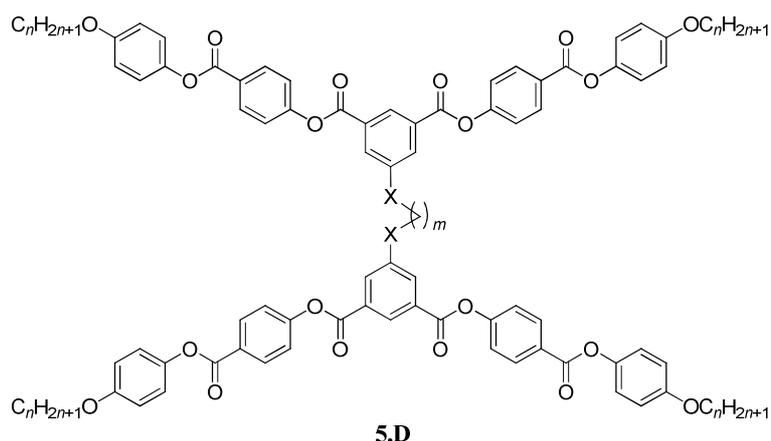


$n = 6, 7, 8, 9, 10, 11, 12, 14, 16, 18$ Series **4.A**

Four different types of mesophases were observed. While lower homologues **4.A.1** and **4.A.2** show an intercalated smectic (B_6) phase, middle homologues **4.A.3**, **4.A.4** and **4.A.5** exhibit a columnar phase with a rectangular lattice (Col_r) and both these phases do not switch electro-optically. Compound **4.A.6** shows a lamellar phase with antiferroelectric characteristics. Very interestingly, the higher homologues **4.A.7**, **4.A.8**, **4.A.9** and **4.A.10** show two mesophases

and both of them respond to an applied electric field. These mesophases have been characterized as $\text{Col}_{\text{ob}}\text{P}_F$ and SmC_sP_A phases and the transition between such phases are very rare.

In chapter 5, the design and synthesis of new type of dimers in which the individual monomers are connected at the apex positions via flexible alkylene spacers are described. We also assumed that a dimer of this type would be apolar as all the dipolar components of the individual monomeric units cancel with each other. With this in view, a new kind of symmetric five-ring BC dimers were synthesized using 5-hydroxyisophthalic acid as central unit. The synthesis and the mesomorphic properties of these new dimers in which the monomeric bent-core units are linked via an ether or an ester linkage are described. The general structure of this new type of bent-core dimers is shown in below.

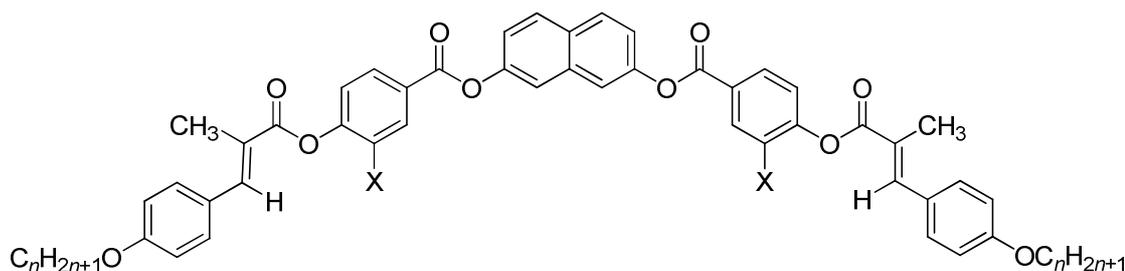


$\text{X} = \text{---O---}$	Series 5.D.I	$m = 5 - 12$	$n = 18$
	Series 5.D.II	$m = 9$	$n = 11, 12, \dots, 16, 18$
	Series 5.D.III	$m = 12$	$n = 11, 12, \dots, 16, 18$
$\text{X} = \text{---O---C(=O)---}$	Series 5.D.IV	$m = 6 - 12, 14$	$n = 18$
	Series 5.D.V	$m = 7$	$n = 10, 11, \dots, 16, 18$
	Series 5.D.VI	$m = 10$	$n = 10, 11, \dots, 16, 18$

In order to understand the structure-property relationships, a total of six different series of dimers using 5-hydroxyisophthalic acid central unit connected by two different linkages have been synthesized and investigated. In series, **5.D.I** to **5.D.III** and **5.D.IV** to **5.D.VI** the

monomeric units are connected by flexible alkylene spacers via ether and ester linkages respectively. The chemical structure has been characterized by a combination of spectroscopic techniques. The mesophases have been studied using polarizing optical microscopy, differential scanning calorimetry and X-ray diffraction measurements. The occurrence of the mesophase depends mainly on the terminal chain length and as a result series **5.D.I** and **5.D.IV** are dimesomorphic in nature and exhibit SmA and SmA' phases. The remaining series of dimers exhibit only SmA phase irrespective of the spacer and the terminal chain lengths. Interestingly, an odd-even effect is observed in the clearing temperatures as a function of terminal chain length for the ester linkage dimers containing a fixed odd spacer ($m = 7$). Very surprisingly, a phase transition between two orthogonal mesophases which are different only in their layer spacings has been observed. This has been attributed to conformational changes in the chains. Remarkably, the mesophases of all these dimers are stable upto room temperature. On the basis of our experiments, a model has been proposed for the packing of the dimeric molecules in the two orthogonal mesophases.

In chapter **6**, the synthesis of two new homologous series of symmetric BC compounds containing a chloro or a methyl lateral substituent are described and their mesomorphic properties investigated. The general structure of compounds investigated is shown below.

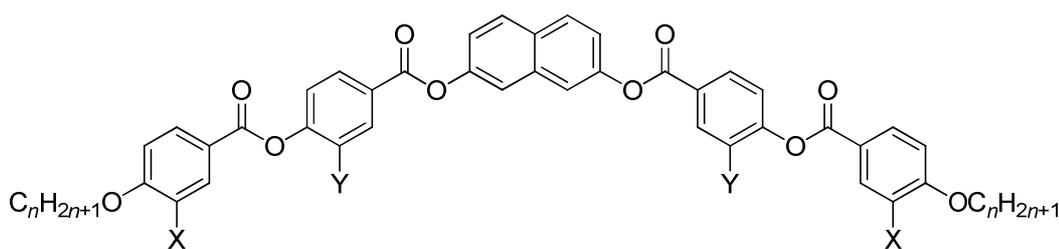


X = Cl	$n = 8, 9, 10, 11, 12, 13, 14, 15, 16, 18$	Series 6. A
X = CH ₃	$n = 5, 6, 7, 8, 9, 10, 12, 13, 14, 16$	Series 6. B

Two new series of bent-core compounds derived from 2,7-dihydroxynaphthalene containing a chloro or a methyl substituent on the middle phenyl rings in the side arms were

synthesized and the influence of these groups on the mesophases were investigated. All compounds exhibit a nematic phase. Interestingly, compounds of series **6.A** containing an electronegative chloro lateral substituent showed rich polymorphism and thus three different phase sequences such as $N \rightarrow Col_r$, $N \rightarrow SmCP_A$ and $N \rightarrow SmC_sP_A \rightarrow SmC'_sP_A$ phases were observed. Miscibility and XRD studies indicate that the two antiferroelectric mesophases are indeed lamellar and have been designated as SmC_sP_A and SmC'_sP_A . However, homologues of series **6.B** containing an electropositive methyl lateral substituent showed $N \rightarrow SmC$ and N phases. Although the size of chloro and methyl groups are comparable the dipolar nature is different. Thus, chloro lateral substituent stabilizes the nematic as well as B-phases whereas methyl substituent eliminates B-phases. Electrohydro-dynamic instabilities were observed in the nematic phase of compounds of series **6.B**.

In chapter 7, three new homologous series of BC compounds derived from 2,7-dihydroxynaphthalene have been synthesized and their mesomorphic properties investigated. Compounds belonging to series **7.A** and **7.B** containing chloro and methyl lateral substituents respectively in the terminal phenyl ring *ortho* to the *n*-alkoxy chain as well as the three homologues of series **7.C** which contain a lateral fluoro substituent in the middle phenyl ring are described. These compounds have been synthesized to understand the structure-property relationships. The general structure of compounds investigated is shown below.

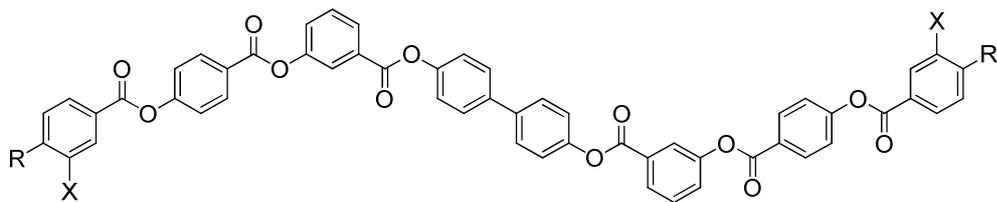


$X = Cl,$	$Y = H$	$n = 4, 6, 8, 9, 10, 11, 12, 13, 14, 15, 16, 18, 20$	Series 7.A
$X = CH_3,$	$Y = H$	$n = 6, 8, 9, 10, 11, 12, 13, 14, 15, 16, 18, 20$	Series 7.B
$X = CH_3,$	$Y = F$	$n = 8, 11, 18$	Series 7.C

These compounds exhibit three kinds of mesophases. Interestingly, compounds of series **7.A** containing a electronegative chloro substituent showed Col_r, SmCP_F and Col_{ob}P_x phases. Homologues of series **7.B** containing a electropositive methyl lateral substituent showed Col_r, DC and Col_{ob}P_x phases. Although the size of chloro and methyl groups are comparable, the dipolar nature is different. The introduction of a fluoro substituent in the middle phenyl ring of series **7.B** provided compounds of series **7.C**. As a result Col_{ob}P_x phase was eliminated and a polar dark conglomerate phase (SmCP_F) was induced in the higher homologues as well. The lower homologues show a Col_r phase similar to that obtained for compounds of series **7.A** and **7.B**.

In chapter **8**, a completely new shape of molecule has been designed and a total of eight different series/part of series of these zigzag-shaped (Z-shaped) compounds have been synthesized. The influence of a lateral fluoro substituent, replacing a biphenyl moiety with a phenyl benzoate unit in the central position of the molecule and replacing the terminal *n*-alkoxy chain by a *n*-alkyl chain, on the mesomorphic properties have all been examined. Thus, the structures of the zigzag-shaped compounds synthesized and investigated in this chapter are shown in general structure **8**.

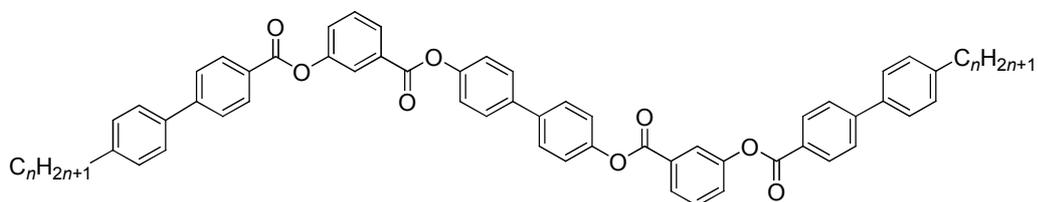
Several new series of symmetrical and unsymmetrical eight-ring zigzag-shaped compounds were designed and synthesized. All these compounds are derived from 3-hydroxybenzoic acid. In order to study the structure-property relationships, four series of compounds viz. **8.A**, **8.B**, **8.C** and **8.D** were synthesized and their mesomorphic properties investigated. The occurrence of the mesophase appears to depend mainly on the terminal chain length, and two different mesophases have been observed. The lower homologues exhibit a columnar phase with a rectangular lattice while the higher homologues exhibit a columnar phase with an oblique lattice and on the basis of experimental studies, these mesophases have been designated as Col_r and Col_{ob} phases respectively. These studies reveal that the mesophase gets stabilized in compounds of series **C** and interestingly the introduction of a fluoro substituent *ortho* to the terminal chain destabilizes the mesophase in contrast to that observed in polar BC compounds. To the best of our knowledge, these represent the first examples of zigzag-shaped compounds exhibiting a mesophase.



$R = OC_nH_{2n+1}$ $X = H$ $n = 7, 9, 10, 11, 12, 13, 14, 15, 16, 18, 20$ Series **8.A**

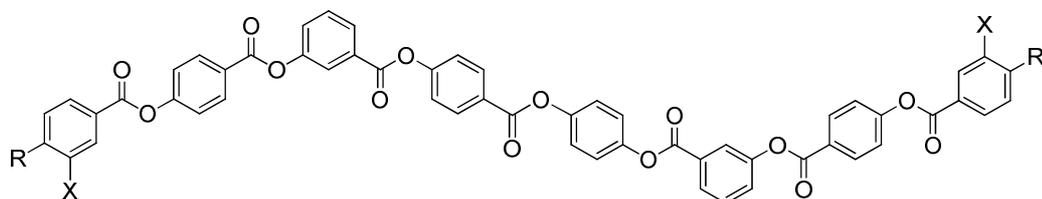
$R = OC_nH_{2n+1}$ $X = F$ $n = 18$ Series **8.A**

$R = C_nH_{2n+1}$ $X = H$ $n = 16$ Series **8.A**



$n = 12, 14, 16, 18$

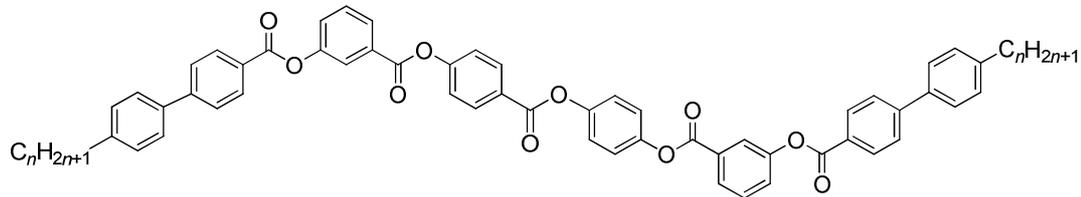
Series **8.B**



$R = OC_nH_{2n+1}$ $X = H$ $n = 7, 10, 11, 12, 13, 14, 16, 18, 20$ Series **8.C**

$R = OC_nH_{2n+1}$ $X = F$ $n = 16$ Series **8.C**

$R = C_nH_{2n+1}$ $X = H$ $n = 16$ Series **8.C**



$n = 12, 16$

Series **8.D**

General structure 8

The results presented in this thesis are reported in the following papers (published / to be published):

- [1] Occurrence of transition between lamellar antiferroelectric and columnar ferroelectric phases in achiral seven-ring bent-core compounds derived from 5-methoxyisophthalic acid
S. Radhika, B. K. Sadashiva and V. A. Raghunathan, *Ferroelectrics*, 2008, *364*, 20-32.

- [2] Occurrence of transition between two polar orthogonal smectic phases in a new homologous series of novel bent-core compounds
S. Radhika, B. K. Sadashiva and R. Pratibha, *Liquid Crystals*, 2010, *37*, 417-425.

- [3] Polar switching in the smectic- A_dP_A phase composed of asymmetric bent-core molecules
Lingfeng Guo, Surajit Dhara, B. K. Sadashiva, S. Radhika, R. Pratibha, Yoshio Shimbo, Fumito Araoka, Ken Ishikawa and Hideo Takezoe, *Physical Review E*, 2010, *81*, 011703-6.

- [4] Randomly polarised smectic A phase exhibited by bent-core molecules: experimental and theoretical studies
Meenal Gupta, Soma Datta, S. Radhika, B. K. Sadashiva and Arun Roy, *Soft Matter*, 2011, *7*, 4735-4741.

- [5] Strain glass analogue in a bent-core liquid crystal exhibiting the dark conglomerate phase
Arun Roy, Meenal Gupta, S. Radhika, B. K. Sadashiva and R. Pratibha, *Soft Matter*, 2012, *8*, 7207-7214.

- [6] Apolar novel mesogenic symmetric dimers composed of five-ring bent-core monomeric units
S. Radhika, B. K. Sadashiva and V. A. Raghunathan (Manuscript under preparation)

- [7] The influence of lateral substituents on the occurrence of transition between two polar smectic phases with antiferroelectric properties
S. Radhika, R. N. Keshava Murthy and B. K. Sadashiva (Manuscript under preparation)
- [8] Switchable B₇ phases in unsymmetrical five-ring bent-core compounds derived from 3-hydroxybiphenyl-4-carboxylic acid
S. Radhika and B. K. Sadashiva (Manuscript under preparation).
- [9] Occurrence of dark conglomerate phases in bent-core compounds derived from 2,7-dihydroxynaphthalene
S. Radhika and B. K. Sadashiva (Manuscript under preparation).
- [10] Novel zigzag-shaped compounds exhibiting apolar columnar mesophases with oblique and rectangular lattices
S. Radhika, M. Monika, B. K. Sadashiva and Arun Roy (Manuscript under preparation).

The present author was involved in other projects as well but the results obtained are not described in this thesis and published in the following journals:

- [11] Anticlinic smectic C phase in new and novel five-ring hockey stick-shaped compounds
S. Radhika, H. T. Srinivasa and B. K. Sadashiva, *Liquid Crystals*, 2011, 38, 785-792.
- [12] Structure-property correlation of a hockey stick-shaped compound exhibiting N-SmA-SmC_a phase transitions
P. Sathyanarayana, S. Radhika, B. K. Sadashiva and Surajit Dhara, *Soft Matter*, 2012, 8, 2322-2327.
- [13] Two distinct modulated layer structures of an asymmetric bent-shape smectic liquid crystal
C. Zhang, N. Diorio, S. Radhika, B. K. Sadashiva, S. N. Sprunt and A. Jákli, *Liquid Crystals*, 2012, 39, 1149-1157.

- [14] Achiral triclinic lamellar phases exhibited by bent-core hockey stick shaped molecules
R. Pratibha, Meenal Gupta, S. Radhika, B. K. Sadashiva and Arun Roy (Submitted).

References

- [1] D. Vorlander and A. Apel, *Ber. Dtsch. Chem. Ges.*, **65**, 1101 (1932).
- [2] M. Kuboshita, Y. Matsunaga and M. Matsuzaki, *Mol. Cryst. Liq. Cryst.*, **199**, 319 (1991).
- [3] H. Matsuzaki and Y. Matsunaga, *Liq. Cryst.*, **14**, 105 (1993).
- [4] T. Akutagawa, Y. Matsunaga and K. Yashubara, *Liq. Cryst.*, **17**, 659 (1994).
- [5] T. Niori, T. Sekine, J. Watanabe, T. Furukawa and H. Takezoe, *J. Mater. Chem.*, **6**, 1231 (1996).
- [6] D. R. Link, G. Natale, R. Shao, J. E. MacLennan, N. A. Clark, E. Korblova and D. M. Walba, *Science*, **278**, 1924 (1997).
- [7] G. Pelzl, S. Diele and W. Weissflog, *Adv. Mater.*, **11**, 707 (1999).
- [8] J. P. Bedel, J. C. Rouillon, J. P. Marcerou, M. Laguerre, H. T. Nguyen and M. F. Achard, *Liq. Cryst.*, **28**, 1285 (2001).
- [9] D. M. Walba, E. Korblova, R. Shao, J. E. MacLennan, D. R. Link, M. A. Glaser and N. A. Clark, *Science*, **288**, 2181 (2000).
- [10] D. A. Coleman, J. Fernsler, N. Chattham, M. Nakata, Y. Takanishi, E. Korblova, D. R. Link, R. -F. Shao, W. G. Jang, J. E. MacLennan, O. Mondainn-Monval, C. Boyer, W. Weissflog, G. Pelzl, L. -C. Chien, J. Zasadzinski, J. Watanabe, D. M. Walba, H. Takezoe and N. A. Clark, *Science*, **301**, 1204 (2003).
- [11] M. B. Ros, J. L. Serrano, M. Rosario de La Fuente and C. L. Folcia, *J. Mater. Chem.*, **15**, 5093 (2005).
- [12] R. Amaranatha Reddy and C. Tschierske, *J. Mater. Chem.*, **16**, 907 (2006).
- [13] H. Takezoe and Y. Takanishi, *Jpn. J. Appl. Phys.*, **45**, 597 (2006).
- [14] R. Pratibha, N. V. Madhusudana and B. K. Sadashiva, *Science*, **288**, 2184 (2000).
- [15] T. Hegmann, J. Kain, S. Diele, G. Pelzl and C. Tschierske, *Angew. Chem. Int. Ed.* **40**, 887 (2001).
- [16] B. K. Sadashiva, R. Amaranatha Reddy, R. Pratibha and N. V. Madhusudana, *Chem. Commun.*, 2140 (2001).

- [17] B. K. Sadashiva, R. Amaranatha Reddy, R. Pratibha and N. V. Madhusudana *J. Mater. Chem.*, **12**, 943 (2002).
- [18] R. Amaranatha Reddy and B. K. Sadashiva, *J. Mater. Chem.*, **14**, 310 (2004).
- [19] H. N. S. Murthy and B. K. Sadashiva, *Liq. Cryst.*, **31**, 567 (2004).
- [20] J. Mieczkowski, K. Gomola, J. Koseska, D. Pocięcha, J. Szydłowska and E. Gorecka, *J. Mater. Chem.* **13**, 2132 (2003).
- [21] K. Gomola, L. Guo, E. Gorecka, D. Pocięcha, J. Mieczkowski, K. Ishikawa and H. Takezoe, *Chem. Commun.*, 6592 (2009).
- [22] G. Dantlgraber, S. Diele and C. Tschierske, *Chem. Commun.*, 2768 (2002).
- [23] B. Kosata, G. M. Tamba, U. Baumeister, K. Pelz, S. Diele, G. Pelzl, G. Galli, S. Samaritani, E. V. Agina, N. I. Boiko, V. P. Shibaev and W. Weissflog, *Chem. Mater.*, **18**, 691 (2006).
- [24] S. Umadevi, B. K. Sadashiva, H. N. S. Murthy and V. A. Raghunathan, *Soft Matter*, **2**, 210 (2006).
- [25] S. Umadevi and B. K. Sadashiva, *Liq. Cryst.*, **34**, 673 (2007).