Synthesis and Characterisation of Mesophases Formed by Compounds Composed of Banana-Shaped Molecules

By

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Thesis submitted to the Jawaharlal Nehru University
for the award of the degree of

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Raman Research Institute
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CERTIFICATE

This is to certify that the thesis entitled ***Synthesis and Characterisation of Mesophases Formed by Compounds Composed of Banana-Shaped Molecules*** submitted by ***R. Amaranatha Reddy*** for the award of the degree of **DOCTOR OF PHILOSOPHY** of Jawaharlal Nehru University is his original work. This has not been published or submitted to any other University for any other degree or diploma.

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DECLARATION

I hereby declare that the work reported in this thesis is entirely original. This thesis is composed independently by me at the Raman Research Institute under the supervision of Prof. B. K. Sadashiva. I further declare that the subject matter presented in this thesis has not previously formed the basis for the award of any degree, diploma, membership, associateship, fellowship or any other similar title of any university or institution.

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List of abbreviations used in the text

Cr	crystalline phase
I	isotropic phase
N	nematic phase
N^*	cholesteric phase
B_1	rectangular columnar B-phase
$B_1^{\prime}$, B_{1X}	variants of B_1 phase
B_2	smectic antiferroelectric B-phase
$B_2^{\prime}$, $B_2^{\prime}$	variants of B_2 phase
B_2^*	smectic antiferroelectric chiral B_2 phase
B_3	crystalline B-phase
B_4	crystalline B-phase
B_5	smectic antiferroelectric B-phase with in-plane order
B_{5A}	antiferroelectric B_5 phase
B_{5F}	ferroelectric B_5 phase
B_6	smectic intercalated B-phase
B_7	two- or three-dimensional B-phase
B_{7bis}	bistable B_7 phase
B_8	bilayer B-phase
B_X	unidentified two- or three-dimensional B-phase
B_{X1}	novel smectic ferrolectric B-phase
B_{X2}	novel two-dimensional ferroelectric B-phase
B_{X3}	novel two-dimensional B-phase
B_{X4}	novel two-dimensional B-phase
B_{X5}	novel two-dimensional antiferroelectric B-phase
Col_r	columnar rectangular B-phase
Col_{rF}	columnar rectangular ferroelectric B-phase
Col_{hF}	columnar hexagonal ferroelectric B-phase
Col_{obF}	columnar oblique ferroelectric B-phase
Col_{obAF}	columnar oblique antiferroelectric B-phase
Col?	unidentified columnar B-phase
SmA	smectic A phase

SmA_c	interdigitated smectic A phase
SmA_d	partial bilayer uniaxial smectic A phase
$SmA_{db}P_A$	partial bilayer biaxial antiferroelectric smectic A phase
SmX	unidentified antiferroelectric smectic phase
SmC	smectic C phase
SmC_SP_A	synclinic smectic C - polar antiferroelectric
SmC_SP_F	synclinic smectic C - polar ferroelectric
SmC_AP_A	anticlinic smectic C - polar antiferroelectric
SmC_AP_F	anticlinic smectic C - polar ferroelectric
SmC^*	chiral ferroelectric smectic C phase
SmC^*_A	chiral antiferroelectric smectic C phase
SmC^*_α	chiral smectic C_{alpha} phase
SmC^*_γ	chiral ferrielectric smectic C phase
TGB_A	twist grain boundary smectic A phase
TGB_C	twist grain boundary smectic C phase
TGB_C*	twist grain boundary chiral smectic C phase
X_{AF}	unidentified columnar antiferroelectric phase
BP	blue phase
•	phase exists
–	phase does not exist
( )	monotropic transition
n	normal
IR	infrared
NMR	nuclear magnetic resonance
ppm	parts per million
s	singlet
d	doublet
dd	doublet of doublet
t	triplet
q	quartet
quin	quintet
m	multiplet
tlc	thin layer chromatography

DSC	differential scanning calorimeter
TMS	tetramethylsilane
$CDCl_3$	deuteriochloroform
CD_3COCD_3	deuterioacetone
DCC	N, N^{I}-dicyclohexylcarbodiimide
DMAP	4-(N, N-dimethylamino)pyridine
DEAD	diethylazodicarboxylate
MHPOBC	4-(1-methylheptyloxycarbonyl)phenyl-4^{I}-octyloxybiphenyl-4-carboxylate
TPP	triphenylphosphine
XRD	X-ray diffraction

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PREFACE

Liquid crystals represent a state intermediate between ordinary liquids and three-dimensional solids. These may be broadly classified into two types: (i) Thermotropic liquid crystals and (ii) Lyotropic liquid crystals. Thermotropic liquid crystals may be further divided into: (i) Calamitic liquid crystals, formed by rod-like molecules; (ii) Discotic liquid crystals, formed by disk-like molecules and (iii) Banana liquid crystals, formed by banana-shaped or bent-core molecules. The liquid crystalline phases are also called mesophases and a compound which exhibits a mesophase is referred to as a mesogen. The investigations carried out and described in this thesis are low molar mass thermotropic liquid crystalline compounds composed of bent-core molecules.

The discovery of ferroelectricity in liquid crystals has been attributed to the pioneering work of Meyer *et al.* [1], who showed that one of the requirements for this phenomenon to occur is compounds composed of enantiomerically rich molecules. The layer polarization in such materials can be stabilized 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^{I}-octyloxybiphenyl-4-carboxylate(MHPOBC). The structure of the antiferroelectric phase is similar to that of a ferroelectric phase except for the fact that the molecules tilt in opposite directions (opposite polarity) in adjacent layers. Later, they also found a few sub phases while conducting careful electro-optical switching characteristics for MHPOBC and they have been designated as SmC^{*}_{α} and SmC^{*}_{γ} etc. 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 the year 1977, Chandrasekhar *et al.* [4] discovered a new class of liquid crystals, in which compounds composed of disk-like molecules exhibit columnar mesophases. All these discoveries have stimulated the search for new materials and new mesophases.

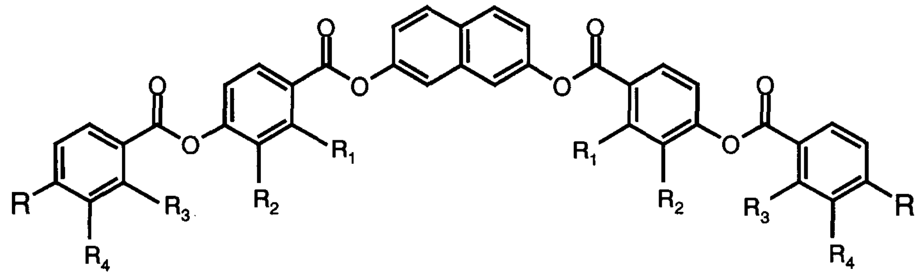
The credit for the synthesis of the first compound with non-linear molecular shape and exhibiting mesomorphic properties has been attributed to Vorlander and Apel[5]. However, there was no further activity of synthesis of such non-linear mesogenic compounds until 1990. In 1991, Kuboshita *et al.* [6] synthesized compounds derived from 1,2-dihydroxybenzene, 2,3-dihydroxynaphthalene and 1,2,3-trihydroxybenzene whose constituent molecules are non-linear and the mesophases obtained were nematic, smectic A and smectic B. In addition, Akutagawa *et al.* [7] reported the synthesis and mesomorphic properties of achiral non-linear mesogenic materials derived from resorcinol. They designated the mesophase obtained as a smectic C phase based on textural observations, enthalpy value, X-ray diffraction measurements and miscibility studies. No electro-optical switching measurements were carried out for these materials simply because the mesophase obtained was from achiral molecules.

However, till 1995 it was believed that the ferro- and / or antiferro-electric properties of mesophases could be obtained only from compounds composed of chiral molecules. The real breakthrough was made by Niori *et al.*[8] in 1996 who reported ferroelectric switching behaviour in compounds composed of achiral banana-shaped molecules, viz. 1,3-phenylene bis [4-(4-n-alkoxyphenyliminomethyl)benzoates]. The origin of ferroelectricity in these compounds was attributed to the efficient packing of bent-core (BC) molecules into smectic layers, which restrict the rotation around the long molecular axis and induces the layer polarization along the bent direction. This in-layer induced polarization can be reversed by the application of any external electric field. Further, the tilt of BC molecules w. r. t. the layer normal induces the layer chirality. The mesophases obtained from banana-shaped mesogens are not completely miscible with any of the known mesophases of classical liquid crystals. Hence a symbol **B** was accepted to be used to differentiate banana phases from other mesophases. With the passage of time, a few hundred such compounds with bent molecular shape have been synthesized and the mesophases exhibited by them investigated [9, 10, 11]. Atleast eight different B-phases have been reported and are designated as B_1, B_2,........,B_7, B_8. The letter **B** stands for banana- or bent- or bow-shaped mesogens, the suffix numbers of which indicate the order of discovery [10] of the different B-phases and has nothing to do with the phases themselves. However, the phases designated as B_3 and B_4 were later characterized as crystalline phases based on X-ray diffraction studies.

This thesis contains seven chapters and the first chapter gives a brief introduction to the subject matter described in the thesis. In the remaining six chapters the synthesis and mesomorphic properties of 323 new bent-core compounds are described. These investigations have resulted in some novel ferro- and antiferro-electric banana phases; new phase transitions and new phase sequences; biaxial smectic A liquid crystals in a single component system and a direct transition from a nematic phase to a polar biaxial smectic A phase for the first time.

Chapter-**1** begins with a brief description of some well known mesophases, such as nematic, smectic and ferroelectric phases in addition to antiferroelectric and twist grain boundary phases exhibited by rod-like molecules. The main topic of investigations carried out and described in this thesis is the occurrence of mesophases in compounds composed of achiral BC molecules, particularly the chiral and electro-optically switchable phases. Hence, a brief description of the proposed molecular models for the different B-phases reported in the literature are given. Though the origin of layer chirality, the occurrence of ferro- and / or antiferro-electric phases and the molecular structural requirements to obtain these phases have been reviewed [9, 10, 11], these aspects have been discussed in some detail. In addition, a brief description of the influence of the core, the terminal chain length and the lateral substituents is given.

In Chapter-**2**, the synthesis, characterization and the mesomorphic properties of about 85 symmetrically fluorinated bent-core esters derived from 2,7-dihydroxynaphthalene as the central angular unit are described. The general molecular structure indicating the different homologous series studied is shown below.



$R=C_nH_{2n+1}$ / OC_nH_{2n+1}

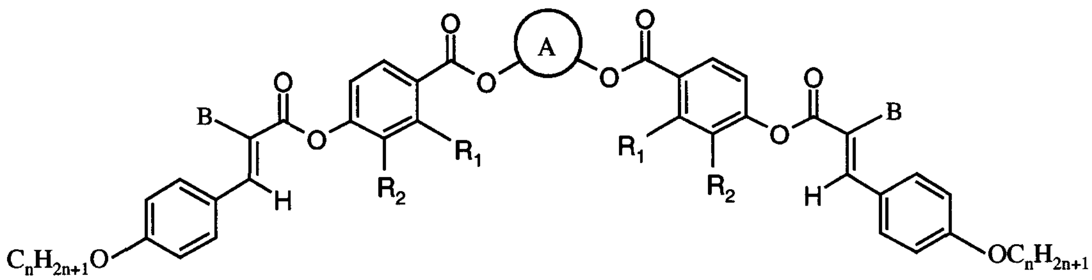
n=1,2,3.........12,14,16,18

R_1=H, R_2=H, R_3=H, R_4=H	Series-**I**	(n-alkyl)
R_1=F, R_2=H, R_3=H, R_4=H	Series-**II**	(n-alkyl)
R_1=H, R_2=F, R_3=H, R_4=H	Series-**III**	(n-alkyl)
R_1=H, R_2=H, R_3=H, R_4=H	Series-**IV**	(n-alkoxy)
R_1=F, R_2=H, R_3=H, R_4=H	Series-**V**	(n-alkoxy)
R_1=H, R_2=F, R_3=H, R_4=H	Series-**VI**	(n-alkoxy)
R_1=H, R_2=H, R_3=F, R_4=H	Series-**VII**	(n-alkoxy)
R_1=H, R_2=H, R_3=H, R_4=F	Series-**VIII**	(n-alkoxy)

A survey of the literature indicated that not many compounds with 2,7-dihydroxynaphthalene as the central unit and exhibiting B-phases are known. Also, there has not been any systematic evaluation of the influence of a lateral substituent on the liquid crystalline properties of compounds composed of banana-shaped molecules. It is for this reason that we decided to examine a system in detail. We chose a six-ring ester system as it does not contain the relatively unstable azomethine linking group. We have systematically substituted the phenyl rings of the arms of the bent-core molecules with fluorine and examined the mesomorphic properties. In any such study the starting point would be the unsubstituted parent compounds. The mesomorphic properties of fluorinated bent-core compounds have been compared with those of the unsubstituted parent compounds.

The homologues of series **I**, show B_1 and B_2 mesophases on ascending the homologous series while the fluorine substituted compounds of series **II** and **III** showed a nematic phase in addition. Interestingly, in the latter two cases, the mesophase range is increased (about three times) and also the melting as well as the clearing temperatures are reduced. These are compounds containing n-alkyl terminal chains. However, the n-alkoxy terminal chains stabilize the existing mesophases or induce new mesophases. The corresponding n-alkoxy chain containing compounds (series **IV**, **V**, **VI**) exhibit new phase transitions, which have not been reported so far. For example, the lower homologues of series **V** showed a direct transition from N to B_6 and N to B_1 phases and a new phase sequence; N to B_6 to B_1. In addition, a direct transition from SmA_C to B_6 is also observed which resulted in a new phase sequence; N to SmA to SmA_C to B_6. The higher homologues showed a chiral antiferroelectric B_2 (B_2^*) phase, which exists as chiral domains of opposite handedness as in the case of unsubstituted parent compounds (series **IV**). In series **VI**, compound with n-butyl chains showed a direct transition from SmA_C to B_1 phase and a new phase sequence; N to SmA to SmA_C to B_1. The middle homologues exhibit a transition from N to B_1 phase. The higher homologues exhibit a racemic B_2 phase in contrast to the parent compounds, which exhibit a chiral B_2 phase. The fluorine substitution on the outer phenyl ring, which is *ortho* to the n-alkoxy chains (series **VIII**), showed a very interesting phase behaviour. The lower homologues, n=4, 7 and 9 show a columnar B_1 phase while the middle homologues, n=10,11 and 12 show a novel smectic B_{X1} phase which exhibit ferroelectric switching behaviour. The higher homologues exhibit novel two-dimensional columnar phases with different lattice structures and all of these show ferroelectric switching behaviour. The novel columnar ferroelectric phases obtained show hexagonal, rectangular and oblique lattices on ascending the homologous series which have not been seen before. These are the first examples of a series of compounds exhibiting different mesophase structures and all of them show ferroelectric switching behaviour.

Chapter-3 begins with a brief account of the mesomorphic properties of five and six phenyl ring symmetrical esters. The influence of central angular unit derived from resorcinol has been compared with the mesophases of compounds obtained from 2,7-dihydroxynaphthalene central core. Also, the effect of ethenyl spacer in the arms of such compounds has been investigated. In all the series of fluorinated compounds derived from 2,7-dihydroxynaphthalene, a nematic phase is observed even for the higher homologues. However, the corresponding homologues derived from resorcinol do not show a nematic phase. This clearly demonstrates the influence of the central cores, which perhaps provide different bend angles. The general molecular structure of the compounds investigated is shown below.



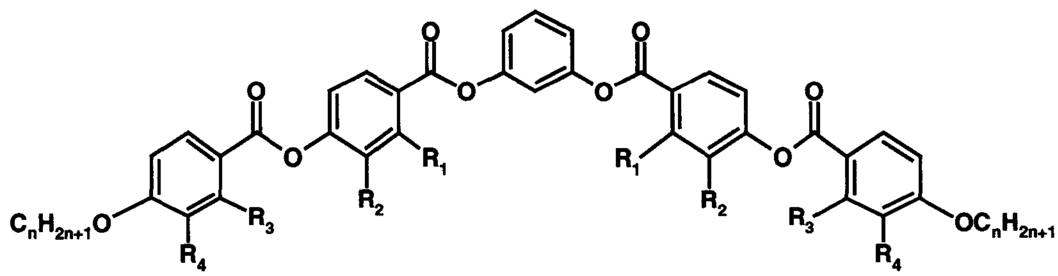
A= 2,7-Naphthylene, B=H; R_1=F, R_2=H	Series - **3.I**
A= 2,7-Naphthylene, B=CH_3; R_1=F, R_2=H	Series - **3.II**
A= 2,7-Naphthylene, B=H; R_1=H, R_2=F	Compound **3.C.1**
A= 2,7-Naphthylene, B=CH_3; R_1=H, R_2=F	Series - **3.III**
A= 2,7-Naphthylene, B=CH_3; R_1=H, R_2=H	Compound **3.E.1**
A= 1,3-Phenylene, B=H; R_1=F, R_2=H	Series - **3.IV**
A= 1,3-Phenylene, B=CH_3; R_1=F, R_2=H	Series - **3.V**

The non-fluorinated compound containing α-methylcinnamoyloxy unit in the arms of the bent-core molecule, is non-mesomorphic (compound **3.E.1**) while the corresponding fluorine substituted homologues (series **II** and **III**) show a direct transition from a nematic phase to an antiferroelectric B_2 phase. This is the first example of a compound exhibiting this phase transition. This is a good example to demonstrate that a fluorine substitution can induce nematic, polar and non-polar banana mesophases. The corresponding fluorinated cinnamoyloxy homologues show a direct transition from N to a non-polar mesophase with an oblique lattice. The lower homologues show a direct transition from N to B_6 and N to B_1 phases.

Interestingly, the mesophase obtained for higher homologues of series **IV**, shows an antiferroelectric switching behaviour. The XRD studies suggest the existence of an oblique lattice. The textural features obtained in this mesophase are completely different from the textures observed for the antiferroelectric B_7 phase. Hence this novel mesophase has been designated as B_{X5} (Col_{obAF}). The polarization value obtained is about 350 nC cm^{-2}.

In Chapter-**4**, a total of 109 achiral compounds belonging to twelve different homologous series shown below have been synthesized and the mesophases obtained are investigated. The influence of the position of the fluorine substituent on the nature of the mesophases obtained in these five-ring symmetrical esters has been investigated in detail. The homologues of series **II**, **IV** and **VI**, show B_6, B_1 and B_2 mesophases on increasing the chain length. However, in one series (series **III**), the mesomorphic properties are completely suppressed by the fluorine substitution. If a fluorine is substituted *meta* to the carbonyl group of the first phenyl moiety (series **III**), then irrespective of the position of the fluorine substituent on the terminal phenyl ring (series **VIII** and **IX**) of these five-ring esters, no mesophase has been observed. The most interesting result is the occurrence of two different mesophase structures (smectic and two-dimensional rectangular columnar) both of which are ferroelectric, when a fluorine is substituted *ortho* to the terminal n-alkoxy chain (series **V**). In contrast, the unsubstituted parent compounds show an antiferroelectric B_2 phase. Ferroelectricity in these two mesophases has been proved by very careful electro-optical studies and the bistable states for a two-dimensional ferroelectric phase have been shown for the first time.

By introducing a fluorine substituent on the middle phenyl ring (series **VII**), B_6 and B_1 phases are induced for the lower homologues and a two-dimensional rectangular columnar ferroelectric phase (B_{X2}) obtained for the higher homologues is completely eliminated, while retaining the smectic ferroelectric B_{X1} phase.

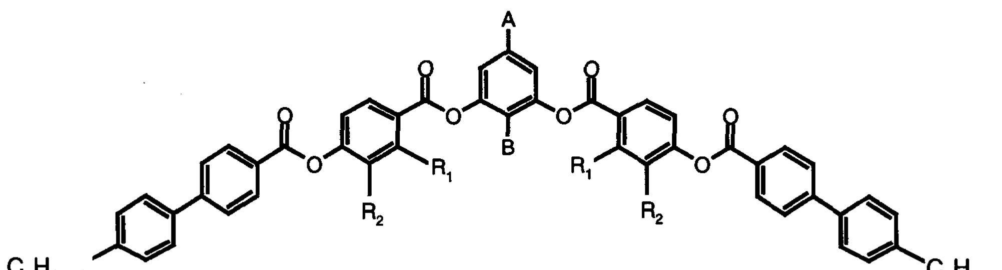


n=1,2,3,..........12,14,16,18,20

R_1=H, R_2=H, R_3=H, R_4=H	Series-**I**
R_1=F, R_2=H, R_3=H, R_4=H	Series-**II**
R_1=H, R_2=F, R_3=H, R_4=H	Series-**III**
R_1=H, R_2=H, R_3=F, R_4=H	Series-**IV**
R_1=H, R_2=H, R_3=H, R_4=F	Series-**V**
R_1=F, R_2=H, R_3=F, R_4=H	Series-**VI**
R_1=F, R_2=H, R_3=H, R_4=F	Series-**VII**
R_1=H, R_2=F, R_3=F, R_4=H	Series-**VIII**
R_1=H, R_2=F, R_3=H, R_4=F	Series-**IX**
R_1=H, R_2=Cl, R_3=H, R_4=H	Series-**XI**

Chapter-**5** begins with brief survey of the mesomorphic properties of compounds which show a B_7 mesophase and the elusive and novel SmC_G phase. The scientific investigations have been divided into two parts. Until now, there was no report of a bent-core compound derived from either 5-cyanoresorcinol or 2-cyanoresorcinol exhibiting mesophases. It is for this reason, that a number of bent-core compounds, using the above two central units have been synthesized and their mesomorphic properties investigated. In part-**I**, the synthesis and mesomorphic properties of two homologous series of seven-ring esters derived from 5-cyanoresorcinol are described. The lower homologues of both series of compounds show a columnar B_1 phase. The higher homologues exhibit a B_2-like mesophase with extraordinary textures and a complex electro-optical switching behaviour. Chiral domains of opposite handedness as also racemic domains are observed by the application of an electric field. The polarization value of this interesting antiferroelectric mesophase is about 885 nC cm^{-2}. The observation of helical structures and the spontaneously formed chiral domains in this mesophase point towards the ground state structure of the novel SmC_G phase.

In part-**II**, the synthesis and mesomorphic properties of two homologous series (**III** and **IV**) of seven-ring esters derived from 2-cyanoresorcinol are described. The lower homologues of both the series of compounds exhibit the columnar B_1 phase. The higher homologues show textural features, XRD patterns and electro-optical behaviour similar to those observed for the mesophase of 2-nitroresorcinol derivatives for which the symbol B_7 has been assigned [10]. In addition, the B_7 mesophase obtained in cyano substituted compounds is completely miscible with the B_7 mesophase obtained in nitro substituted compounds. Hence the mesophase obtained for the higher homologues of series **III** and **IV** is designated as B_7.

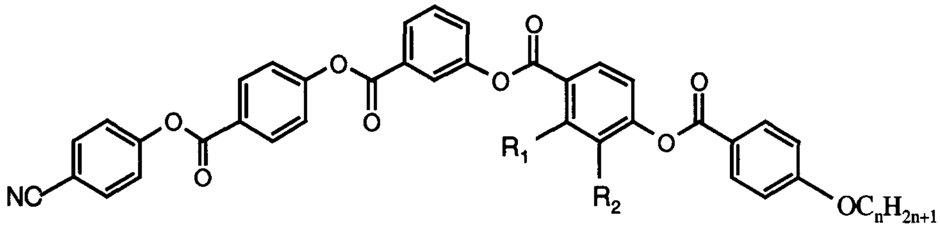


n=5, 6,......12, 14, 16, 18

A=CN, B=H;	R_1=F, R_2=H	Series-**I**	Part-**I**
A=CN, B=H;	R_1=H, R_2=F	Series-**II**	
A=H, B=CN;	R_1=F, R_2=H	Series-**III**	Part-**II**
A=H, B=CN;	R_1=H, R_2=F	Series-**IV**	

Chapter-**6** gives a brief introduction to the biaxial smectic A phase and its occurrence in mixtures [12, 13, 14]. It was our desire to obtain this mesophase in a single component system. We have designed and synthesized unsymmetrical compounds which have an n-alkoxy chain attached to only one of the arms of the bent-core, while the other arm ends with the highly polar cyano group. The general molecular structure is shown below.

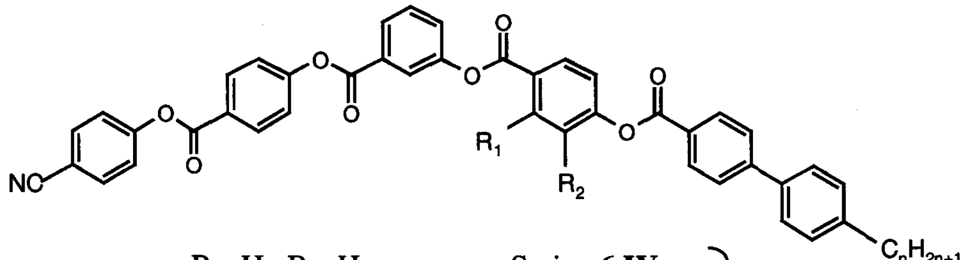
The higher homologues of series **I**, **II** and **III**, show both uniaxial and biaxial smectic A phases. The compounds of series **IV**, **V** and **VI**, exhibit uniaxial and biaxial smectic A phases in addition to a nematic phase. X-Ray studies suggest that these compounds exhibit a partial bilayer smectic A (SmA_d) phase in which the bent-cores of neighbouring molecules overlap in an antiparallel orientation. In addition, the lower temperature phase exhibits an antiferroelectric switching behaviour. Hence this mesophase has been designated as $SmA_{db}P_A$ (partial bilayer biaxial antiferroelectric smectic A) phase. This is the first example of a bent-



R_1=H, R_2=H Series-**6.I**

R_1=F, R_2=H Series-**6.II** Part-**I**

R_1=H, R_2=F Series-**6.III**



R_1=H, R_2=H Series-**6.IV**

R_1=F, R_2=H Series-**6.V** Part-**II**

R_1=H, R_2=F Series-**6.VI**

core compound exhibiting a partial bilayer structure. This indicates that each layer has a polar order of BC molecular pairs and the arrow-axis aligns parallel to the electric field such that the successive layers can have an antiferroelectric ordering. No optical switching could be observed under a polarizing microscope by the application of an electric field indicating that the molecular bow plane is coinciding the with the optical axes, suggesting an orthogonal arrangement of the BC molecules w.r.t the smectic layer planes. These experimental observations indicate that the lower temperature phase is a polar orthogonal smectic A_d phase. The calculated polarization value is about 120-150 nC cm^{-2}. Some of the compounds in series **IV**, **V**, and **VI** show a direct transition from a nematic phase to a polar orthogonal smectic A_d phase. These are the first examples to represent such a phase transition.

In Chapter-7, the mesomorphic properties of some bent-core esters containing a chiral group in the molecule are described. The chiral moiety has been located either in the rigid core part or on the terminal chain. The compounds containing a chiral moiety in the rigid core show blue phase, N^* and TGB_A phases. However, compounds with terminal chiral chains exhibit N^*, TGB_A, SmC^*, SmC^*_α, SmC^*_γ phases and an unknown columnar antiferroelectric phase. All the chiral compounds investigated are unsymmetrical bent-core esters.

Some of the results presented in this thesis are reported in the following publications.

1) Synthesis and mesomorphic properties of banana-shaped compounds derived from 2,7-dihydroxynaphthalene.
   R. Amaranatha Reddy and B. K. Sadashiva.
   Liquid Crystals, 2000, Vol. 27, No. 12, 1613-1623.

2) Banana-shaped mesogens: observation of a direct transition from the antiferroelectric B_2 to nematic phase.
   R. Amaranatha Reddy, B. K. Sadashiva and Surajit Dhara.
   Chemical Communications, 2001, 1972-1973.

3) Biaxial smectic A liquid crystal in a pure compound.
   B. K. Sadashiva, R. Amaranatha Reddy, R. Pratibha and N. V. Madhusudana.
   Chemical Communications, 2001, 2140-2141.

4) Biaxial smectic A phase in homologous series of compounds composed of highly polar unsymmetrically substituted bent-core molecules.
   B. K. Sadashiva, R. Amaranatha Reddy, R. Pratibha and N. V. Madhusudana.
   Journal of Materials Chemistry, 2002, 12, 943-950.

5) Helical superstructures in the mesophase of compounds derived from 2-cyanoresorcinol.
   R. Amaranatha Reddy and B. K. Sadashiva.
   Liquid Crystals, 2002, Vol. 29, No.10, 1365-1367.

6) Ferroelectric properties exhibited by mesophases of compounds composed of achiral banana-shaped molecules.
   R. Amaranatha Reddy and B. K. Sadashiva.
   Journal of Materials Chemistry, 2002, 12, 2627-2632.

7) Liquid crystals of compounds composed of banana-shaped molecules: Influence of a fluorine substituent. "Materials Research: Current Scenario and Future Projections", Ed: R. Chidambaram, Allied publishers 2003, pp. 157-169 (Invited article).
R. Amaranatha Reddy and B. K. Sadashiva.

8) Occurrence of B_7 mesophase in homologous series of seven-ring achiral compounds composed of banana-shaped molecules.
R. Amaranatha Reddy and B. K. Sadashiva.
Liquid Crystals, 2003, Vol. 30, No.3, 273-283.

9) Influence of fluorine substituent on the mesomorphic properties of five-ring ester banana-shaped molecules.
R. Amaranatha Reddy and B. K. Sadashiva.
(Liquid Crystals in the press).

The manuscripts of the following papers have been either submitted for publication or under preparation.

1) Direct transition from a nematic phase to a polar biaxial smectic A phase in homologous series of unsymmetrically substituted bent-core compounds.
R. Amaranatha Reddy and B. K. Sadashiva.

2) Unusual mesomorphic behaviour in bent-core compounds derived from 5-cyanoresorcinol - towards a SmC_G phase.
R. Amaranatha Reddy and B. K. Sadashiva.

3) Banana-shaped mesogens derived from 1,3-dihydroxybenzene and 2,7-dihydroxy-naphthalene: novel columnar phases with an oblique lattice.
R. Amaranatha Reddy, B. K. Sadashiva and V. A. Raghunathan.

4) Observation of novel ferroelectric columnar mesophases in fluorinated symmetrical bent-core compounds.
R. Amaranatha Reddy, V. A. Raghunathan and B. K. Sadashiva.

5) New phase sequences in banana-shaped mesogens: influence of fluorine substituent in 2,7-dihydroxynaphthalene system.
R. Amaranatha Reddy and B. K. Sadashiva.

6) Liquid crystalline properties of unsymmetrical bent-core compounds containing chiral moieties.

   R. Amaranatha Reddy and B. K. Sadashiva.

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