

*Synthesis of compounds composed of bent-core
molecules: characterization of mesophases and
some physical properties*

By

H N. Shreenivasa Murthy

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

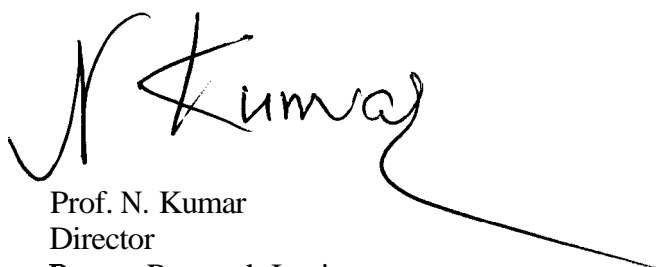
Doctor of Philosophy

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Bangalore – 560 080
India*

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CERTIFICATE

This is to certify that the thesis entitled "Synthesis of compounds composed of bent-core molecules: characterization of mesophases and some physical properties" submitted by H. N. Shreenivasa Murthy for the award of the degree of DOCTOR OF PHILOSOPHY of the Jawaharlal Nehru University is his original work. This has not been published or submitted to any other University for any other degree or diploma.



Prof. N. Kumar
Director
Raman Research Institute
Bangalore 560 080 INDIA



Prof. B. K. Sadashiva
(Thesis Supervisor)

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.



(Professor B. K. Sadashiva)

Liquid Crystal Laboratory
Raman Research Institute
Bangalore 560 080 - **INDIA**



(H. N. Shreenivasa Murthy)

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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 ₂	smectic antiferroelectric B-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	non-switchable, non-layered banana phase with helical superstructure
B _{7AF1}	novel two-or three- dimensional antiferroelectric B ₇ sub-phase 1
B _{7AF2}	novel two-or three- dimensional antiferroelectric B ₇ sub-phase 2
B _{7bis}	ferroelectric B ₇ phase
B ₈	bilayer B-phase
B _X	unidentified B-phase
B _Y	unidentified B-phase
B _Z	unidentified B-phase
SmA	smectic A phase
SmB	smectic B phase
SmA _d	partial bilayer uniaxial smectic A phase
SmA _d P _A	polar antiferroelectric partial bilayer biaxial smectic A phase
SmX	unidentified smectic phase
SmC	smectic C phase
SmCP _A	smectic C phase with antiferroelectric properties
SmC _S P _A	synclitic smectic C - polar antiferroelectric phase

SmC_SP_F	synclinic smectic C - polar ferroelectric phase
SmC_AP_A	anticlinic smectic C - polar antiferroelectric phase
SmC_AP_F	anticlinic smectic C - polar ferroelectric phase
SmC^*	chiral ferroelectric smectic C phase
SmC_A^*	chiral antiferroelectric smectic C phase
TGB_A	twist grain boundary smectic A phase
TGB_C	twist grain boundary smectic C phase
	phase exists
	phase does not exist
()	monotropic transition
a	compounds has a crystal-crystal transition and enthalpy is the sum of all such transitions
	compound exhibits textures of B_1 and B_2 phases simultaneously upon cooling the isotropic phase.
	compound exhibits a transition from B_1 to B_2 phase upon cooling the isotropic phase.
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 ₃ COCD ₃	deuterioacetone
DCC	N, N ¹ -dicyclohexylcarbodiimide
DMAP	4-(N,N-dimethylamino)pyridine
MHPOBC	4-(1-methylheptyloxycarbonyl)phenyl-4- <i>n</i> -octyloxybiphenyl-4-carboxylate
XRD	X-ray diffraction
ITO	indium tin oxide

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PREFACE

Liquid crystals may be broadly classified into two types; (i) Thermotropic liquid crystals and (ii) Lyotropic liquid crystals. Thermotropic liquid crystals which are formed by the action of heat on certain pure organic compounds or their mixtures, may be further divided into three categories viz. (i) Calamitic liquid crystals (ii) Discotic liquid crystals and (iii) Banana liquid crystals, depending on the shape of the constituent molecules. This thesis deals with the synthesis and characterization of low molar mass thermotropic liquid crystalline compounds composed of bent-core or banana-shaped molecules.

The credit for the discovery of ferroelectricity in liquid crystals has been attributed to Meyer *et al.* [1]. Ferroelectric liquid crystals exhibit a spontaneous helix and the macroscopic polarization averages to zero. On applying an external electric field, the helix can be unwound. In 1989, Chandani *et al.* [2] discovered the antiferroelectric phase in a compound viz. 4-(1-methylheptyloxycarbonyl)phenyl-4-*n*-octyloxybiphenyl-4-carboxylate (MHPOBC). The structure of the antiferroelectric phase can be considered as double twisted helicoidal structure formed by two identical ferroelectric SmC^* helices gearing into each other. Around the same time Goodby *et al.* [3] discovered a theoretically predicted defect stabilized twist grain boundary smectic phase in some phenyl propiolates. In 1977, a different class of thermotropic liquid crystals namely discotic liquid crystals formed by compounds whose constituent molecules are disk-like and exhibiting a columnar phase was discovered by Chandrasekhar *et al.* [4].

The credit for the synthesis of compounds with unconventional structure and exhibiting liquid crystalline properties goes back to early 20th century and is attributed to Vorlander and his group [5]. They explored the structure-property relationships by synthesizing various types of compounds including bent-core compounds. The study of the mesomorphic properties exhibited by bent-shaped compounds was renewed in 1991 by Kuboshita *et al.* [6] who synthesized dimers, derived from 1, 2-dihydroxybenzene and 2, 3-dihydroxynaphthalene. The mesophases obtained were characterized as N, SmA and SmB . However, in 1994 Akutagawa *et al.* [7] synthesized four homologous series of compounds derived from resorcinol. From the microscopic textural observations, enthalpy values, XRD and miscibility studies they concluded that the mesophases exhibited by these compounds as N and SmC . From XRD studies, they argued that the tails are nearly normal to the layers

whereas the cores are tilted by about 48° w.r.t. layer planes. No electro-optical experiments were carried out on the mesophases of these achiral compounds.

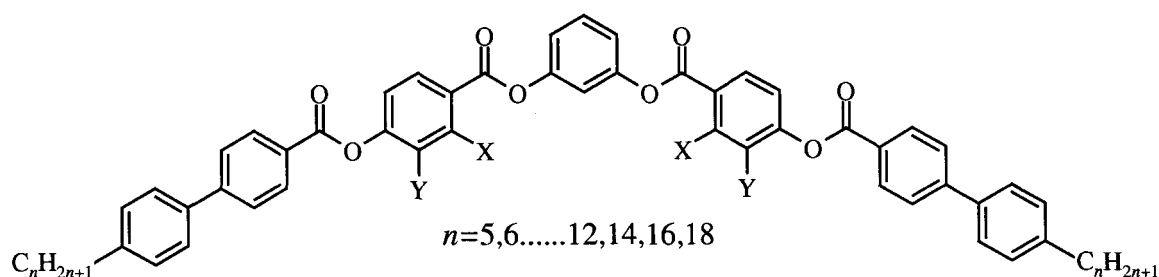
Ferro- and antiferro-electric properties in liquid crystals were limited to chiral compounds until 1996. However, the discovery of ferroelectric switching behaviour in achiral molecules by Niori *et al.* [8] in 1, 3-phenylene bis[4-(4-*n*-octylphenyliminomethyl)benzoate] led to a new sub-field of liquid crystals viz. banana liquid crystals. Although ferroelectric properties were reported for the mesophase of this compound composed of achiral banana-shaped molecules, it was shown to be actually antiferroelectric by the beautiful experiments of Link *et al.* [9]. The molecules in these LC materials are packed in a bent direction leading to a polar order. In addition, the molecules are tilted with respect to the layer normal thus generating the chiral layers. The molecules in adjacent layers are arranged in such a way that the bent directions oppose to avoid the macroscopic polarization. The antiferroelectric mesophases can be tilted (SmC_sP_A or SmC_AP_A) or orthogonal (SmAP_A). In the tilted smectic antiferroelectric arrangement the tilt sense in adjacent layers is either in the same direction which results in a racemic structure (SmC_sP_A) or in opposite directions which results in a chiral structure (SmC_AP_A). On application of an electric field, these antiferroelectric phases switch to a macroscopically chiral state. However, on switching off the field the dipoles relax to an antiferroelectric ground state. Towards the end of 1997, a workshop on Banana-Shaped Liquid Crystals: "Chirality by Achiral Molecules", was organized in Berlin to recommend a nomenclature for the different mesophases exhibited by such compounds. Since these mesophases were not miscible with any of the known thermotropic liquid crystalline phases, the symbol B was assigned to signify the shape of the molecules. Since seven different phases had been identified by then, they were designated $\text{B}_1, \text{B}_2, \dots, \text{B}_7$ [10]. Recently [12] another mesophase designated as B_8 has been added to the above list. However, the B_3 and B_4 phases were shown to have characteristics of crystals by careful XRD studies [10].

This thesis contains eight chapters and in the first chapter an introduction to some well-known liquid crystalline phases are given including the discovery and various other aspects of the mesophases of bent-core compounds. In the remaining seven chapters the investigations carried out on the synthesis and mesomorphic properties of 242 new bent-core compounds are described. The important results obtained and presented in this thesis include the effect of different lateral substituents on mesophases which proved that the dipolar effects are dominant over steric effects, the observation of novel antiferroelectric sub-phases below a

non-switchable **B**₇ phase, observation of filamentary growth patterns at the isotropic to an antiferroelectric smectic phase, observation of partial bilayer biaxial smectic A phase in a single component system, adequate proof for the occurrence of a **B**₁ to **B**₂ mesophase transition and the observation of a smectic ferroelectric phase and some novel columnar phases.

In Chapter 1, a brief description of some well-known mesophases of calamitic liquid crystals such as nematic, smectic A, smectic C, ferro-, antiferro-electric mesophases and TGB phases is given. Since this thesis describes the synthesis and mesomorphic properties of bent-core compounds, 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 [9-11] are given. In addition, a brief description of symmetry involved in BC molecules, 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 mesomorphic properties of six homologous series of compounds derived from resorcinol are described. These are seven-ring esters and are symmetrical about the central phenyl ring. The general molecular structure is shown below.



X= H,	Y= H	Series- 2.I
X= F,	Y= H	Series- 2.II
X= CH ₃ ,	Y= H	Series- 2.III
X= C ₂ H ₅ ,	Y= H	Series- 2.IV
X= H,	Y= F	Series- 2.V
X= H,	Y=OCH ₃	Series- 2.VI

A majority of the bent-core compounds reported in the literature are five-ring systems having lateral substituents in either the central phenyl ring or the outer phenyl rings. The number of compounds containing lateral substituents in the middle phenyl ring of the arms

are very few. Moreover, the thermal range of the mesophases exhibited by five-ring systems is rather short and hence a seven-ring system was chosen. The effect of various lateral substituents of different dimensions and polar properties were investigated systematically. For this purpose two kinds of lateral substituents were chosen; i) electron withdrawing substituents such as fluorine and ii) electron donating substituents such as methyl, ethyl and methoxy group. This kind of study enabled us to understand the structure-property relationships in bent-core compounds to some extent.

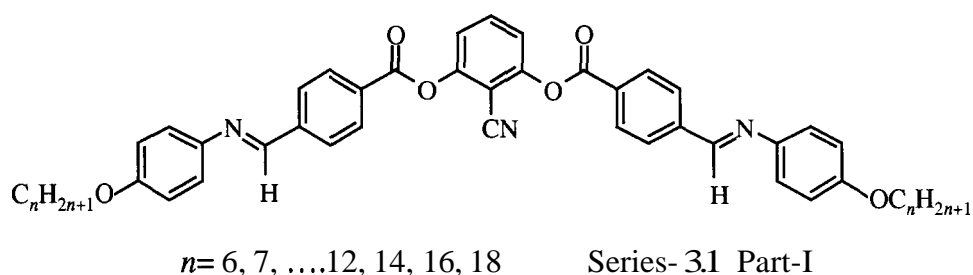
The homologues of series 2.1 are unsubstituted compounds having a large thermal range of the mesophase ($\approx 100^\circ\text{C}$) which enabled us to study the effect of lateral substituents of different dimensions. The compounds show \mathbf{B}_6 , \mathbf{B}_1 and \mathbf{B}_2 mesophases on ascending the homologous series. Interestingly compounds with a longer chain ($n=14, 16, 18$) show a \mathbf{B}_2 phase with chiral domains of opposite handedness. The compounds of series 2.11 with a fluorine substituent in the *ortho* position w.r.t the carbonyl group of the middle phenyl ring behave similarly but with a marginal reduction in the transition temperatures. The homologues with longer alkyl chain also showed a \mathbf{B}_2 phase with chiral domains. As a result of methyl substitution compounds of series **2.III** were obtained. The transition temperatures were reduced significantly in this series of compounds. The mesophase stability was greatly influenced by the bulkier substituents such as ethyl and methoxy groups in the middle phenyl ring (series **2.IV** and **2.VI**). The two-dimensional columnar \mathbf{B}_1 phase and lamellar \mathbf{B}_2 phase were affected significantly. The \mathbf{B}_1 phase was stabilized for longer alkyl chains (up to $n=12$) when fluorine was substituted such that its dipole vector was along the bend direction (series **2.V**).

A Comparison of the effect of substituents at *ortho* and *meta* positions w.r.t the carbonyl group of the middle phenyl ring shows that former compounds have a large thermal range of the mesophases. The substituent at *meta* position affects the mesophases drastically when compared to *ortho* substituted analogues.

However, the mesomorphic properties of chloro and methyl substituted compounds were different. Although the chloro and methyl groups have similar size, their effects on the mesophase in these bent-core compounds were different unlike in calamitic liquid crystals. Thus, dipolar effects appear to be more significant than steric effects in these seven-ring bent-core compounds.

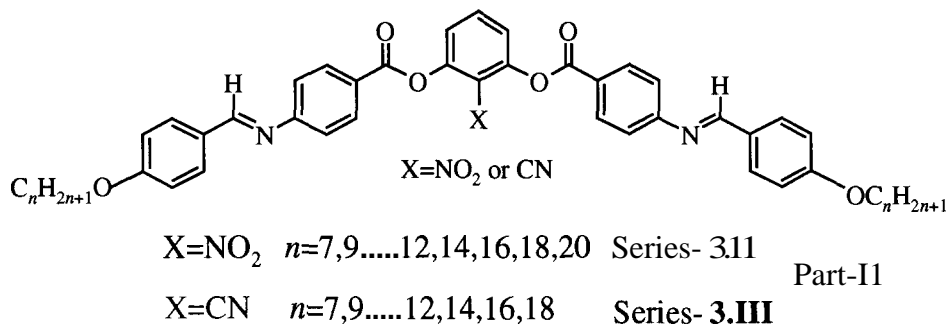
Chapter 3 begins with a brief introduction to compounds exhibiting the B_7 phase. One of the common features of a B_7 phase is the beautiful spiral optical textures that they exhibit. Such textural patterns have been observed in a number of different compounds but the XRD and electro-optical switching characteristics are different from what is observed in the standard compounds [13]. In spite of these differences the symbol B_7 was assigned to the mesophases.

Three homologous series of Schiff's base esters derived from either 2-cyano- or 2-nitro- resorcinol were investigated. In the first part, compounds with general molecular structure shown below were studied.



All the compounds are mesomorphic and show the fascinating B_7 phase. The optical textures, XRD pattern and the electro-optical behaviour were similar to the mesophase of standard B_7 compounds [13].

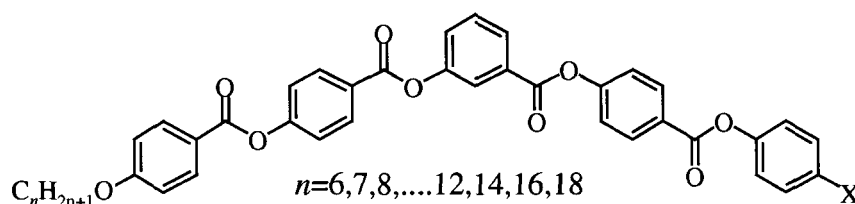
In the second part, two homologous series with the general structure shown below were investigated.



Most of the compounds of series 3.11 and 3.111 exhibit the fascinating B_7 mesophase. Some of the higher homologues of 2-nitro substituted compounds showed two additional novel antiferroelectric sub-phases, which have been assigned the symbols B_{7AF1} and B_{7AF2} . This is the first observation of a transition from a non-switchable, non-layered B_7 phase to an

antiferroelectric sub-phase. A comparison of the mesomorphic properties of the three homologous series (3.I-3.III) of compounds revealed that the 2-cyano substituted compounds are thermally more stable and are monomesomorphic, while some of the 2-nitro substituted compounds show polymorphism. The nitro and cyano substituents at acute angle induce a mesophase in these five-ring Schiff's base ester compounds. A comparison of the mesomorphic behavior of standard compounds showing the B₇ phase with those of series 3.11, and series 3.1 with series 3.III revealed that the orientation of the azomethine linkage has a strong influence on the mesomorphic behaviour.

In Chapter 4, a brief introduction to the filamentary growth patterns observed in the SmA and SmC phases of calamitic liquid crystals is given. The mesomorphic behaviour of three homologous series of compounds derived from 3-hydroxybenzoic acid has been investigated and the results are described in this chapter. These unsymmetrical bent-core compounds have only one terminal chain and the other terminal position is substituted by a fluoro, a chloro or a trifluoromethyl group. The general structure of the compounds investigated is shown below.



X= F, Series- 4.1

X= Cl, Series- 4.11

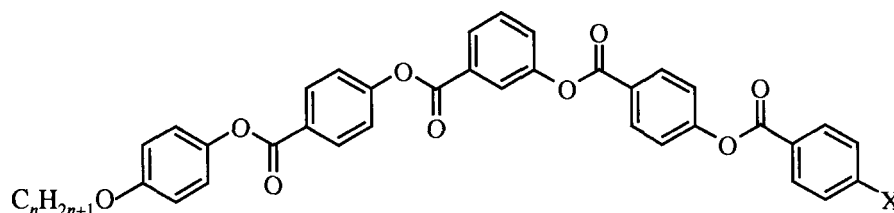
X= CF₃, Series- 4.111

The most interesting aspect is the observation of growth of filamentary textures when the isotropic liquids of compounds of series 4.11 were cooled. These filaments are short lived and collapse into a focal-conic texture. The stability of the filaments seems to increase with the increase in the terminal alkyl chain length. The compounds of series 4.111 do show filamentary textures but are very short lived. The mesophase exhibited by these compounds has been characterized as a SmCP_A phase based on XRD and electro-optical studies. The filamentary growth patterns have been attributed to the negative interfacial anisotropy. In these compounds the electronegative substituent will interact with the electropositive methyl

group of the n-alkoxy chain of molecules in adjacent layers there by stabilizing the antiferroelectric arrangement of the molecules. These represent the first example of bent-core compounds exhibiting a filamentary growth pattern at the isotropic-switchable mesophase transition.

Chapter 5 begins with a brief introduction to the theoretical prediction [14] as well as experimental observations of a biaxial smectic A phase in mixtures of compounds [15-17]. The first observation of a biaxial smectic A phase exhibited by bent-core compounds was reported from our laboratory [18-20].

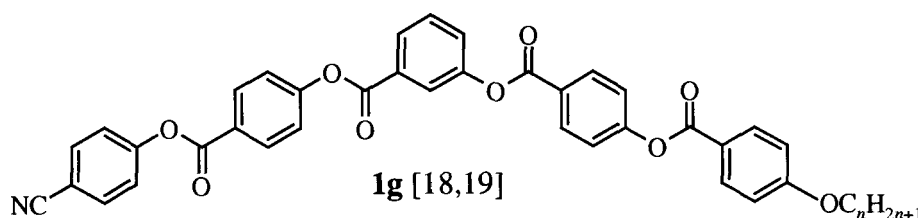
The investigated unsymmetrical compounds have an n-alkoxy chain at one end and the other end is substituted with a highly polar cyano or a nitro group. The general molecular structure of the compounds is shown below.



X= CN $n=8,10,12,14,16,18$ Series- **5.1**

X= NO₂ $n=8,10,12,14,16,18$ Series- **5.11**

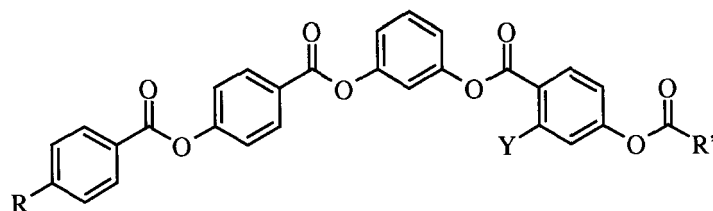
It was reported [18,19] that the homologous series of compounds **1g** showed both uniaxial and biaxial smectic A phases. The compounds of series **5.1** are isomeric with compounds of series **1g** in which the terminal n-alkoxy chain and the polar cyano group are interchanged. Interestingly, compounds of series **5.1** show only a uniaxial smectic A phase.



Some of the homologues of series **5.11** show both uniaxial and biaxial smectic A phases. XRD studies on both the mesophases suggest a partial bilayer smectic structure in which the molecules are arranged in an antiparallel arrangement. The electro-optical

experiments suggested that the lower temperature biaxial phase has an antiferroelectric arrangement. No optical switching was observed indicating an orthogonal arrangement of bent-core molecules in the mesophase. Based on these experimental observations, the smectic phases of compounds of series 5.1 and 5.11 have been designated as partial bilayer uniaxial smectic A (SmA_d) and polar partial bilayer biaxial smectic A (SmA_dP_A) phases.

Some unsymmetrical compounds derived from resorcinol having the general structure shown below were also investigated.

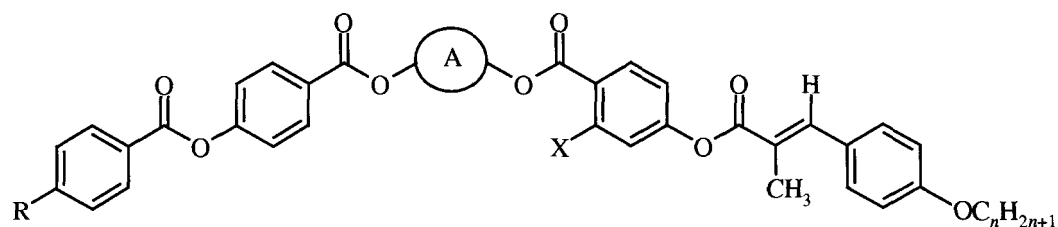


$R = n\text{-C}_{12}\text{H}_{25}\text{O} / n\text{-C}_{12}\text{H}_{25}$; $Y = \text{H} / \text{F}$;

$R' = \text{cyanophenyl} / \text{nitrophenyl} / \text{cyanobiphenyl}$

Interestingly, the analogous compounds of series 5.1 and series 5.11 obtained from resorcinol are non-mesomorphic. When the terminal cyanophenyl group was replaced by a cyanobiphenyl moiety the resulting compounds showed both uniaxial and biaxial smectic A phases. Thus, the polarity of the system plays an important role in stabilizing the biaxial smectic A phase.

In Chapter 6, synthesis the mesomorphic properties of fortyone unsymmetrical compounds containing 1, 3- phenylene or 2, 7-naphthylene as a central unit are described. These compounds have α -methylcinnamoyloxy bridging group in one of the arms. The general structure of the compounds is shown below.



$R = n\text{-C}_{12}\text{H}_{25}\text{O}$, $A = 1, 3\text{-Phenylene}$, $X = \text{H}$ Series- 6.1

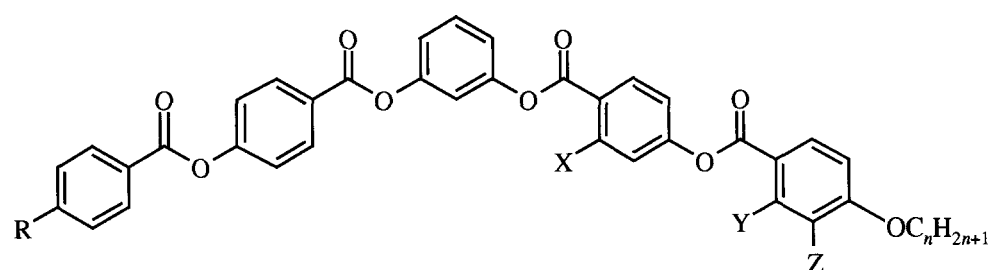
$R = n\text{-C}_{12}\text{H}_{25}\text{O}$, $A = 1, 3\text{-Phenylene}$, $X = \text{F}$ Series- 6.11

$R = n\text{-C}_{12}\text{H}_{25}$, $A = 1, 3\text{-Phenylene}$, $X = \text{F}$ Series- 6.111

$R = n\text{-C}_{12}\text{H}_{25}\text{O}$, $A = 2, 7\text{-Naphthylene}$, $X = \text{F}$ Series- **6.IV**

The compounds which have a 1, 3-phenylene central unit exhibit only B-phases whereas some compounds with 2, 7- naphthylene central unit show both nematic and B-phases. The nematic phase is dependent purely on the bend angle between the two arms of the molecules. The 1, 3-phenylene system with terminal n-alkyl chain yielded compounds with the lowest melting points reported so far, and these exhibit the B_2 phase. In one of the compounds of series 6.11, the B_1 and B_2 phases appeared simultaneously from the isotropic phase, which is rather unusual. The rarely observed transition from a nematic phase to an antiferroelectric B_2 phase and from a nematic phase to a two-dimensional rectangular columnar B_1 phase have been obtained in the 2, 7-naphthylene system.

The synthesis and mesomorphic properties of sixty unsymmetrical compounds derived from resorcinol are described in Chapter 7. These compounds represent six different homologous series and the general structure of the compounds is shown below.



	X=H,	Y=F,	Z=H	Series- 7.1
R = $n\text{-C}_{12}\text{H}_{25}\text{O}$	X=H,	Y=H,	Z=F	Series- 7.II
	X=F	Y=F,	Z=H	Series- 7.III
	X=F,	Y=H,	Z=F	Series- 7.IV
R = $n\text{-C}_{12}\text{H}_{25}$	X=F,	Y=F,	Z=H	Series- 7.V
	X=F,	Y=H,	Z=F	Series- 7.VI

In these unsymmetrical compounds, one terminal chain was fixed with a n-dodecyl-oxy or n-dodecyl chain and the other terminal chain length was varied.

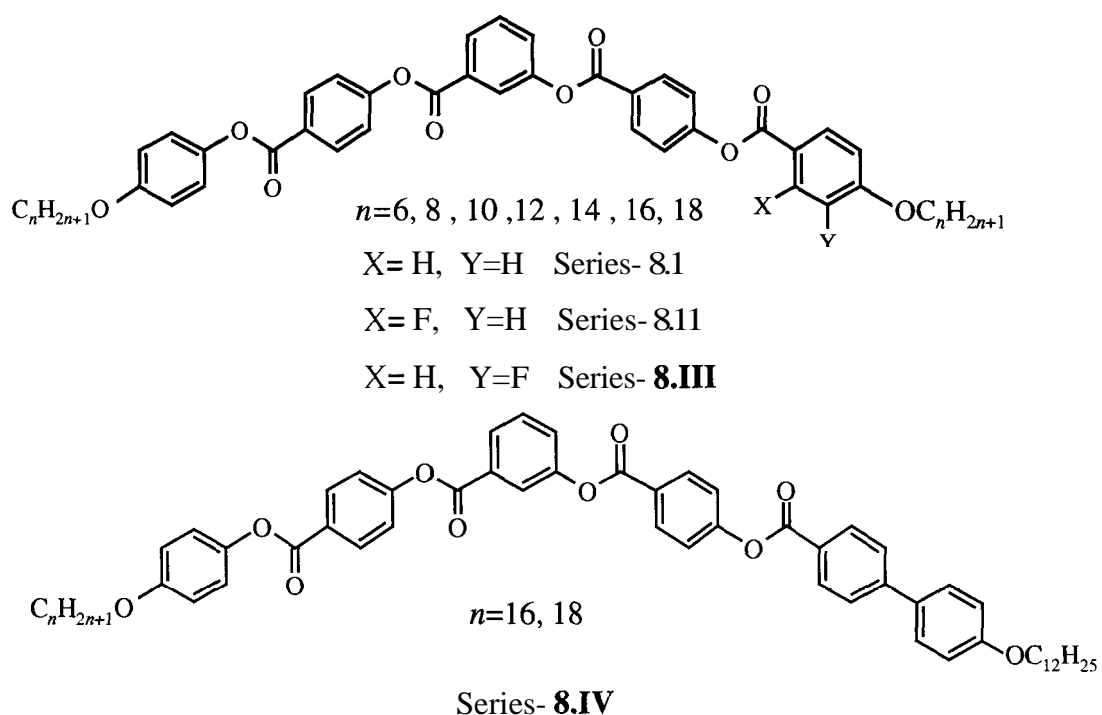
One of the compounds belonging to series 7.1 showed a transition from B_1 phase to B_2 phase. The evidence for this transition was provided both by textural change as well as on a DSC thermogram.

The unsymmetrical compounds (series 7.11) with only one fluorine substituent *ortho* to the n-alkoxy chain showed an antiferroelectric B_2 phase even for long chain lengths. This is in contrast to the symmetrical compounds (with two *ortho* fluorine substituents) which exhibit ferroelectric properties [21]. A Comparison of the d-spacings of the B_2 phase

exhibited by the homologues of these two series 7.1, and 7.11, which are isomeric indicated a conformational change of the molecules in the B_2 mesophase. The dc field experiments on the B_2 phase exhibited by compounds of series 7.1 showed unusual optical behaviour. The compounds of series 7.1 are low melting and the higher homologues show a large thermal range for the B_2 phase when compared to the analogous compounds of series 7.11. As a result of fluorine substitution at the *ortho* position w.r.t the carbonyl group in the middle phenyl ring of the arms of compounds of series 7.1 and 7.11, the homologous series 7.111 and **7.IV** were obtained. Surprisingly, fluorine substitution resulted in an increase of melting points and hence the thermal range of the mesophase was reduced. Compounds of series **7.IV** also showed an antiferroelectric mesophase, while the corresponding long chain symmetrical compounds showed a smectic ferroelectric mesophase. Thus, the position and the number of fluorine substituents play an important role in obtaining a ferro-/ antiferro-electric mesophase.

The introduction of *n*-alkyl chain (compounds of series 7.V and **7.VI**) resulted in a mesophase behaviour comparable to that of *n*-alkoxy counterparts but with a significant reduction in the transition temperatures.

In the chapter 8, the synthesis and mesomorphic properties of three homologous series of unsymmetrical compounds derived from 3-hydroxybenzoic acid are described. The general structure of the investigated compounds is shown below. In addition, two compounds of another series (**8.IV**) were also synthesized for comparison.



Compounds of series 8.1 with shorter alkyl chain ($n=6$) showed the B_1 phase and the middle homologues showed texture as well as XRD pattern different from the B_1 phase. However, compounds with longer alkyl chain showed a smectic ferroelectric mesophase. The compounds of homologous series 8.11 showed a mesophase behavior comparable to that of series 8.1 except for the compounds with longer alkyl chain, which showed anticlinic antiferroelectric B_2 phase. The compounds of series 8.111, which have a fluorine substituent *ortho* to the n-alkoxy chain, showed non-switchable columnar phases. Compounds of series **8.IV** showed smectic **A**, smectic **C** and smectic **X** phases. None of these phases responded to an applied electric field.

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

1. Effect of lateral substituents on the mesophases formed by some achiral **banana-shaped** molecules
B. K. Sadashiva, H. N. Shreenivasa Murthy, Surajit Dhara
Liquid Crystals, 2001, **28**, 483.
2. Banana-shaped mesogens: effect of lateral substituents on seven-ring esters containing a biphenyl moiety
H. N. Shreenivasa Murthy and B. K. Sadashiva
Liquid Crystals, 2002, **29**, 1223.
3. Banana-shaped mesogens: a new homologous series of compounds exhibiting the B_7 mesophase
H. N. Shreenivasa Murthy and B. K. Sadashiva
Liquid Crystals, 2003, **30**, 1051.
4. Observation of a transition from non-switchable B_7 mesophase to an antiferroelectric sub-phase in strongly polar bent-core compounds
H. N. Shreenivasa Murthy and B. K. Sadashiva
Journal of Materials Chemistry, 2003, **13**, 2863.

5. Observation of filamentary growth patterns at the isotropic-SmCP_A phase transition in new unsymmetrical compounds composed of bent-core molecules
H. N. Shreenivasa Murthy and B. K. Sadashiva
Liquid Crystals , 2004, **31**, 361.

6. A polar biaxial smectic A phase in new unsymmetrical compounds composed of bent-core molecules
H. N. Shreenivasa Murthy and B. K. Sadashiva
Liquid Crystals 2004, **31**, 567.

7. Synthesis and mesomorphic properties of unsymmetrical bent-core compounds containing 1, 3-phenylene or 2, 7-naphthylene as a central unit
H. N. Shreenivasa Murthy and B. K. Sadashiva
Liquid Crystals (in the press).

8. Influence of a fluorine substituent on the mesomorphic properties of unsymmetrical five-ring bent-core compounds
H. N. Shreenivasa Murthy and B. K. Sadashiva
Journal of Materials Chemistry (in the press).

9. Effect of fluorine as a lateral substituent in unsymmetrically substituted bent-core compounds derived from resorcinol
H. N. Shreenivasa Murthy and B. K. Sadashiva
(Submitted).

10. The mesomorphic properties of unsymmetrical compounds derived from 3- hydroxybenzoic acid
(Manuscript under preparation).

References

- [1] R. B. Meyer, L. Liebert, L. Strzelecki and P. Keller, *J. de Physique Letters*, 36, L-69, (1975).
- [2] A. D. L. Chandani, E. Gorecka, Y. Ouchi, H. Takezoe and A. Fukuda, *Jpn. J. Appl. Phys.*, 28, L1265, (1989).
- [3] J. W. Goodby, M. A. Waugh, S. M. Stein, E. Chin, R. Pindak and J. S. Patel, *Nature*, London, 337,449, (1989).
- [4] S. Chandrasekhar, B. K. Sadashiva and K. A. Suresh, *Pramana*, 9,471, (1977).
- [5] D. Vorlander and A. Apel, *Ber. Dtsch. Chem. Ges.*, 65, 1101, (1932).
- [6] M. Kuboshita, Y. Matsunaga and M. Matsuzaki, *Mol. Cryst. Liq. Cryst.*, 199, 319, (1991).
- [7] T. Akutagawa, Y. Matsunaga and K. Yashubara, *Liq. Cryst.*, 17,659, (1994).
- [8] T. Niori, T. Sekine, J. Watanabe, T. Furukawa and H. Takezoe, *J. Mater. Chem.*, 6, 1231, (1996).
- [9] D. R. Link, G. Natale, R. Shao, J. E. MacLennan, N. A. Clark, E. Korblova and D. M. Walba, *Science*, 278, 1924, (1997).
- [10] G. Pelzl, S. Diele, and W. Weissflog, *Adv. Mater.*, 11,707, (1999).
- [11] D. M. Walba, E. Korblova, R. Shao, J. E. MacLennan, D. R. Link, M. A. Glaser, N. A. Clark, *Science*, 288,2181, (2000).
- [12] J. P. Bedel, J. C. Rouillon, J. P. Marcerou, H. T. Nguyen and M. F. Achard, *Liq. Cryst.*, 28, 1285, (2001).
- [13] G. Pelzl, S. Diele, C. Lischka, I. Wirth and W. Weissflog, *Liq. Cryst.*, 26, 135, (1999).
- [14] H. R. Brand, P. E. Cladis and H. Pleiner, *Macromolecules*, 25,7223, (1992).
- [15] H. F. Leube and H. Finkelmann, *Makromol. Chem.*, 192, 1317, (1991).
- [16] R. Pratibha, N. V. Madhusudana and B. K. Sadashiva, *Science*, 288,2184, (2000).
- [17] T. Hegmann, J. Kain, S. Diele, G. Pelzl and C. Tschierske, *Angew. Chem. Znt. Ed.* 40, 887, (2001).
- [18] B. K. Sadashiva, R. Amaranatha Reddy, R. Prathiba and N. V. Madhusudana, *Chem. Commun.*, 2140, (2001).
- [19] B. K. Sadashiva, R. Amaranatha Reddy, R. Prathiba and N. V. Madhusudana *J. Mater. Chem.*, 12,943, (2002).
- [20] R. Amaranatha Reddy and B. K. Sadashiva, *J. Mater. Chem.*, 14,310, (2004).
- [21] R. Amaranatha Reddy and B. K. Sadashiva, *J. Mater. Chem.*, 12,2627, (2002).