Investigations on the Synthesis and Structure-Property Relationships of Novel Mesogenic Bent-Core Compounds

By

S. Radhika

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

Doctor of Philosophy



Raman Research Institute Bangalore – 560 080 India August 2012

CERTIFICATE

This is to certify that the thesis entitled "Investigations on the synthesis and structureproperty relationships of novel mesogenic bent-core compounds" submitted by Radhika S. for the award of the degree of **DOCTOR OF PHILOSOPHY** of the Jawaharlal Nehru University is her original work. This has not been published or submitted to any other University for any other degree or diploma.

Prof. B. K. Sadashiva (Thesis Supervisor) Dr. R. Pratibha (Thesis Co-supervisor)

Director Raman Research Institute Bangalore 560 080 - INDIA

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.

(Prof. B. K. Sadashiva) SCM Laboratory Raman Research Institute Bangalore 560 080 - INDIA (Dr. R. Pratibha) SCM Laboratory Raman Research Institute Bangalore 560 080 - INDIA (Radhika S.)

ACKNOWLEDGEMENTS

I wish to express my sincere gratitude to my supervisor Prof. B. K. Sadashiva for his valuable guidance and inspiration. There are no adequate words to describe the encouragement, support and freedom given by him for working in the laboratory during this time. I enjoyed working with him.

My special thanks are due to Dr. R. Pratibha for her kind gesture in accepting as my co-supervisor and her support during this period. I also thank for her keen interest in my work and useful discussions during the thesis work. I had nice time working with both of them.

I take this opportunity to thank Dr. Arun Roy for his useful suggestions and discussions regarding experiments. My sincere thanks to Prof. V. A. Raghunathan for his help in interpreting X-ray diffraction data, during which he taught me basics of X-ray analysis.

I wish to thank Prof. N. V. Madhusudana for his keen interest. I also thank Prof. N. Udayashankar for being part of my academic committee and his helpful suggestions.

It was my pleasure to have Dr. S. Umadevi as my friend and senior in the laboratory and I thank her for support and help given in the initial stages of my thesis work. I had wonderful time in RRI with her company. My thanks are due to Dr. R. Amaranatha Reddy and Dr. H. N. Shreenivasa Murthy whose research work provided me lot of inputs. I also thank Mr. Keshava Murthy, Dr. I. A. Khan, Mr. Aravind, Ms. Monika, Mrs. Vimala and Mr. Adithya for their kind co-operation and for providing me nice working environment in the laboratory during the course of my work.

I thank Mr. H. T. Srinivasa and Mr. Rame gowda for their help in chemistry lab in various ways. I also thank my colleagues in laboratory, Dr. Santanu, Dr. Hari, Dr. Satyam, Mrs. Lakshmi, Dr. Prajapati, Dr. Tandel, Mr. Swamy, Mr. Avinash, Mr. Velan, Mr. Shadakshari, Mr. Sagar, Mr. Jagadeesh, Mr. Marichandran, Mr. Suvratha and Dr. Mahesh for their friendship and support.

I sincerely thank Mrs. K. N. Vasudha for her constant help in recording IR, DSC, elemental analysis, X-ray for my samples and making cells. I also thank her for the pleasant friendship.

My sincere thanks to Mr. Ram, Mr. Mani and Mr. Dhason for their valuable helping hands. I also thank Prof. T. N. Ruckmongthan and Mr. A. R. Shashidara for allowing me to use their lab facility. Many thanks to Mr. Radhakrishna for his innumerable help throughout my stay in RRI. I also thank Mrs. Marisa, Mrs. Radha and Mr. Manjunath for their help. My thanks to Mr. Murali, Mr. Raja and Mrs. Sarojamma for their help.

It is my duty to express thanks to Prof. N. Jayaraman, Department of organic chemistry, IISc. The time which I spent in his lab laid a good platform for me to carry out my research work smoothly. I take this opportunity to thank my friends in IISc, Dr. O. Srinivas, Dr. T. Ramakrishna, Dr. Murthy, Dr. Somak, Dr. Jayamurugan, Dr. Vijayaganesh, Dr. Natarajan, Dr. Naresh, Dr. Kiran, Dr. Rajesh, Mr. Umesh, Mr. Rahul, Mr. Gour, Mrs. Arunima, Mr. Supriyo, Mr. Prabhat, Mr. Yesh pal, Dr. Chibber, Dr. Madan singh, Dr. Ramesh, Dr. Sivapriya, Dr. Vijay, Ms. Guna, Mrs. Raji, Dr. Nilesh, Dr. Gopi, Mr. Ganesh, Mr. Balaji, Dr. Saravanan, Dr. P. C. Ravikumar, Dr. Chandrakumar, Dr. Suresh and Dr. Radhika for their support, encouragement and help in various ways.

I thank NMR centre, Indian Institute of Science, Bangalore and Dr. D. Vijayaraghavan for recording ¹H NMR spectra.

I thank my seniors Dr. Brindaban, Dr. Manjula Devi, Dr. Alpana, Dr. Suresh, Dr. Bharat, Mrs. Mohanapriya, Dr. Sandeep, Dr. Nagaraj, Dr. Rakesh, Dr. Srikanth, Dr. Bibhu, Dr. Radhakrishnan, Mr. Arif, Mrs. Antara, Ms. Tripta, Mr. Jayakumar, Mr. Ravi, Mr. Arijith, Mr. Wasim, Mr. Yogesh, Dr. Meenal, Dr. Soma and Dr. Kavitha for their help and friendship.

I also thank my batch mates Mr. Deepak, Mr. Venkat, Dr. Anupam, Mr. Kshitij, Mr. Chaitra and juniors Ms. Seunghyun Lee, Ms. Anagha, Mrs. Anu, Mr. Madhukar, Mr. Santosh, Mr. Shabeeb, Mr. Tridib, Mr. Anirban, Mrs. Mamta, Mr. Nishant, Mr. Kanhaiya, Mr. Chandrakant, Mr. Jagadish, Mr. Mahavir, Ms. Renu, Mr. Giri, Mr. Rajib, Mr. Debasish, Mr. Samim, Mrs. Srividya, Mr. Senthil, Ms. Uma, Mr. Santosh, Mr. Prahlada, Ms. Varalakshmi, Ms. Swathi, Ms. Sreeja, Mrs. Deepa, Ms. Rashmi, Ms. Supreet, Mr. Arjun, Ms. Mitra and Mr. Prashant for their nice companionship.

I am grateful to Prof. H. Takezoe, Tokyo Institute of Technology, Tokyo, Japan, Dr. S. Dhara, University of Hyderabad, Hyderabad and Dr. A. Jákli, Kent State University, Kent, USA for their valuable collaboration.

I wish to thank director Prof. Ravi Subrahmanyan, all faculty members and administrative officer Mr. K. Krishnamaraju for their kind support and encouragement.

I sincerely acknowledge library staff, computer section staff, administrative staff, canteen staff, hostel cooks, clinic, security staff and transportation of RRI for their help in various ways.

My special thanks are due to my parents, my husband Dr. J. Nithyanandhan and other family members who gave their constant support and encouragement throughout this period.

Finally, I am grateful to the authorities of Raman Research Institute for providing me a research fellowship during the course of this work as well as for the book grant.

List of abbreviations and symbols used in the thesis

BC	bent-core
B ₁	columnar phase with a rectangular lattice
B ₂	tilted layered phase with polar properties
B_{2x}	variant of B ₇ phase
B_{2}', B_{2}''	variants of a B ₂ phase
B ₃	soft crystalline or hexatic mesophase
\mathbf{B}_4	soft crystalline mesophase with supramolecular chirality
B ₅	smectic monolayer phase with in-plane order
B _{5A}	antiferroelectric B ₅ phase
$\mathbf{B}_{5\mathrm{F}}$	ferroelectric B ₅ phase
B ₆	intercalated smectic B-phase
\mathbf{B}_7	non-switchable mesophase with a two-dimensional lattice
B ₇ ′	variant of a switchable B7 phase with a layered structure
\mathbf{B}_{7AF1}	novel antiferroelectric B7 sub-phase 1
B _{7AF2}	novel antiferroelectric B7 sub-phase 2
B _{7bis}	ferroelectric B ₇ phase
B _{7A}	antiferroelectric B7 phase
B_8	smectic bilayer phase with double tilted molecules
Cr	crystalline phase
Col_r	columnar phase with a rectangular lattice
$Col_r P_A$	polar columnar phase with a rectangular lattice and exhibiting
	antiferroelectric behaviour
$Col_{ob}P_A$	polar columnar phase with an oblique lattice showing antiferroelectric
	characteristics
$Col_{ob}P_{\rm F}$	polar columnar phase with an oblique lattice showing ferroelectric
	characteristics
$Col_{ob}P_x$	polar columnar phase with an oblique lattice
Col _{ob}	columnar phase with an oblique lattice
CDCl ₃	deuteriochloroform

CD ₃ COCD ₃	deuterioacetone
d	doublet
dd	doublet of doublet
dc	direct current
ac	alternating current
DCC	N,N'-dicyclohexylcarbodiimide
DMAP	4-(N,N-dimethylamino)pyridine
DMSO-d ₆	deuteriodimethyl sulfoxide
D_2O	deuterium oxide
DSC	differential scanning calorimeter
DC	dark conglomerate phase with smectic ordering
h	hour
Ι	isotropic phase
IR	infrared
ITO	indium tin oxide
m	multiplet
min	minutes
Ν	nematic phase
n	normal
NMR	nuclear magnetic resonance
ppm	parts per million
quin	quintet
SmA	smectic A phase
SmA'	variant of smectic A phase
SmA_d	partial bilayer uniaxial smectic A phase
$\mathrm{SmA}_{\mathrm{db}}$	partial bilayer biaxial smectic A phase
$SmA_{db}P_A$	partial bilayer biaxial antiferroelectric smectic A phase
$\mathrm{Sm}\mathrm{A}_{\mathrm{d}}\mathrm{P}_{\mathrm{R}}$	random polarized partial bilayer uniaxial smectic A phase
SmC	synclinic smectic C phase
SmC _a	anticlinic smectic C phase
SmCP _A	polar smectic C phase with antiferroelectric properties

- SmCP_F polar smectic C phase with ferroelectric properties
- SmC_sP_A polar smectic C phase with synclinic tilt in adjacent layers and antiferroelectric characteristics
- SmC'_sP_A variant of antiferroelectric smectic C phase with synclinic tilt in adjacent layers
- SmC_sP_F polar smectic C phase with synclinic tilt in adjacent layers and ferroelectric characteristics
- SmC_aP_A polar smectic C phase with anticlinic tilt in adjacent layers and antiferroelectric characteristics

SmC_aP_F polar smectic C phase with anticlinic tilt in adjacent layers and antiferroelectric characteristics

- s singlet
- t triplet
- TLC thin layer chromatography
- TMS tetramethylsilane
- XRD X-ray diffraction
- Z zigzag-shaped
- phase exists
- phase does not exist
- () monotropic transition
- * compound has a crystal-crystal transition and the enthalpy is the sum of all previous transitions
- mesophase observed only under microscope and not seen in DSC;
 enthalpy value could not be determined as the sample crystallizes
 immediately

CONTENTS

i-xiv

Chapter 1

Introduction

1

Chapter 2

	Synthesis and mesomorphic properties of	32
(i)	4-((4-Cyanophenoxy)carbonyl)phenyl-4'-(4-n-alkoxybenzoyloxy)-	
	biphenyl-3-carboxylates	
(ii)	4-Cyanophenyl-3'-(4-(4-n-alkoxybenzoyloxy)benzoyloxy)-	
	biphenyl-4-carboxylates	
(iii)	4-Cyano-3-fluorophenyl-3'-(4-(4-n-alkoxybenzoyloxy)benzoyloxy)-	
	biphenyl-4-carboxylates	

Chapter 3

	Synthesis and mesomorphic properties of	8
(i)	4-n-Octyloxyphenyl-3'-(4-(4-n-alkoxybenzoyloxy)benzoyloxy)-	
	biphenyl-4-carboxylates	
(ii)	$\label{eq:alpha} 4-n-Nonanoyloxyphenyl-3'-(4-(4-n-alkoxybenzoyloxy)benzoyloxy)-$	

biphenyl-4-carboxylates

81

- (iii) 4-*n*-Octyloxycarbonylphenyl-3'-(4-(4-*n*-alkoxybenzoyloxy)benzoyloxy)biphenyl-4-carboxylates
- (iv) 4-*n*-Octyloxyphenyl-3'-(2-fluoro-4-(3-fluoro-4-*n*-alkoxybenzoyloxy)benzoyloxy)biphenyl-4-carboxylates

Chapter 4

Synthesis and mesomorphic properties of	125

(i) 5-Methoxy bis(4-(4'-*n*-alkylbiphenylcarbonyloxy)phenylisophthalates)

Chapter 5

Synthesis and mesomorphic properties of	153
---	-----

(i) Apolar symmetric dimers composed of five-ring bent-core monomeric units separated by an alkylene spacer

Chapter 6

	Synthesis and mesomorphic properties of	217
(i)	2,7-Naphthylene bis(4-(E-4- <i>n</i> -alkoxy- α -methylcinnamoyloxy)-3-	
	chlorobenzoates)	
(ii)	2,7-Naphthylene bis(4-(E-4- <i>n</i> -alkoxy- α -methylcinnamoyloxy)-3-	
	methylbenzoates)	

Chapter 7

Synthesis and mesomorphic properties of

259

- (i) 2,7-Naphthylene bis(4-(4-*n*-alkoxy-3-chlorobenzoyloxy)benzoates)
- (ii) 2,7-Naphthylene bis(4-(4-*n*-alkoxy-3-methylbenzoyloxy)benzoates)
- (iii) 2,7-Naphthylene bis(4-(4-*n*-alkoxy-3-methylbenzoyloxy) 3-fluorobenzoates)

Chapter 8

	Synthesis and mesomorphic properties of	306
(i)	Biphenyl-4-4'-dilyl bis(3-(4-(4-n-alkoxy)benzoyloxy)benzoyloxy)-	
	benzoates	
(ii)	Biphenyl-4-4'-dilyl bis(3-(4-(4-n-octadecyloxy)-3-fluorobenzoyloxy)	
	benzoyloxy)benzoate	
(iii)	Biphenyl-4-4'-dilyl bis(3-(4-(4-n-hexadecyl)benzoyloxy)benzoyloxy)	
	benzoate	
(iv)	Biphenyl-4-4'-dilyl bis(3-(4-(4-n-alkylbiphenyl)carbonyloxy)benzoates	
(v)	4-(4-(3-(4-(4-n-Alkoxy)benzoyloxy)benzoyloxy)benzoyloxy)benzoyloxy)benzoyloxy)	
	phenyl 3-(4-(4-n-alkoxy)benzoyloxy)benzoyloxy)benzoates	
(vi)	4-((3-((4-(3-(4-(3-Fluoro-4- <i>n</i> -hexadecyloxybenzoyloxy)benzoyloxy)	
	benzoyloxy) benzoyloxy)phenoxy)carbonyl)phenoxy)carbonyl)phenyl	
	3-fluoro- 4- <i>n</i> -hexadecyloxybenzoate	
(vii)	4-(4-(3-(4-(4-n-Hexa decylbenzoyloxy)benzoyloxy)benzoyloxy)benzoyloxy)benzoyloxy)	
	phenyl 3-(4-(4-n-hexadecylbenzoyloxy)benzoyloxy)benzoate	
(viii)	3-((4-((4-(3-(-4'-n-Alkylbiphenylcarbonyloxy)benzoyloxy)phenoxy)	
	carbonyl)phenoxy)carbonyl)phenyl 4'-n-alkylbiphenyl-4-carboxylates	