SYNTHESIS AND LIQUID CRYSTALLINE PROPERTIES Of *SOME* HOMOLOGOUS SERIES Of OPTICALLY ACTIVE COMPOUNDS

A thesis submitted to the
Bangalore University for
the degree of

DOCTOR OF PHILOSOPHY

by

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December 1997

CERTIFZCATE

I certify that this thesis has been composed by Mr. N. KASTHURAIAH based on the investigations carried out by him at the Liquid Crystal Laboratory, Raman Research Institute, Bangalore - 560 080, under my supervision. The subject matter of this thesis has not previously formed the basis of the award of any Degree, Diploma, Associateship, Fellowship or any other similar title.

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DECLARATZON

I hereby declare that the entire work embodied in this thesis is the result of the investigations carried out by me independently in the Liquid Crystal Laboratory, Raman *Research Institute, Bangalore - 560 080, and that no part of it has been submitted for the award of any Degree, Diploma, Associateship or any other similar title.*

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TO

MY BELOVED PARENTS

KASTHURAIAH. N

Acknowledgements

I wish to express my deep sense of gratitude to Prof. B.K.Sadashiva for his able guidance and encouragement throughout this work.

I am very much thankful to my colleagues in the laboratory Mr. M.R.Subrahmanyam, Mr.P.N.Ramachandra and Mr. G.R.Seshadri, who helped in many ways and for their co-operation throughout the course of the present investigations.

My thanks are due to my friends Dr. Yuvraj sah, Dr. Gangadhar, Mr. Arun Roy and Mr. Gopala krishnan for their help and many useful discussions that I had with them. I also wish to thank my other friends in the Institute who made my stay enjoyable.

I thank Mr. K.Subramanya for microanalysis and for recording the various spectra, Mr. Radhakrishna for his help in official matters and to Dr. A.Ratnakar, Mrs. Girija and the library staff for helping me in various ways.

My thanks are also due to Mr. A.Dhason and Mr. Raju for their kind help.

I am grateful to Dr. H.T. Nguyen, CRPP, France, Dr. A.A. Khan, IICT, Hyderabad and Dr. Krishna Prasad and Geetha G. Nair who undertook various physical measurements.

I would like to express my gratefulness to my parents and other family members for their unstinted support to complete this work.

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

LIST OF ABBREVIATIONS

C	crystal
S	smectic
N	nematic
S_A	smectic **A**
S_C	smectic C
S_C^*	chiral smectic C
$S_{C_A^*}$	antiferroelectric smectic C
$S_{C_\gamma^*}$	ferrielectric smectic C
$S_{C_\alpha^*}$	chiral smectic C_α
$S_{C_X^*}$	chiral unidentified smectic C
TGB_A	twist grain boundary smectic **A**
N*	chiral nematic (cholesteric)
I	isotropic
•	phase exists
( )	brackets in tables indicate monotropic transition
†	enthalpy could not be measured
	phase does not exist
o	*ortho*
p	para
n	normal

IR	infrared
NMR	nuclear magnetic resonance
ppm	parts per million
s	singlet
d	doublet
dd	doublet of doublet
t	triplet
q	quartet
m	multiplet
tlc	thin layer chromatography
DSC	differential scanning calorimeter
TMS	tetramethylsilane
$CDCl_3$	deuterochloroform
DCC	N,N′-dicyclohexylcarbodiimide
DMAP	4-N,N′-dimethylaminopyridine
DEAD	diethylazodicarboxylate
DME	1,2-dimethoxyethane
MHPOBC	4-(1-methylheptyloxycarbonyl)phenyl-4′-octyloxybiphenyl-4-carboxylate

CONTENTS

PREFACE

Liquid crystals as the name implies are condensed phases in which the constituent molecules are neither randomly oriented nor packed with a high degree of three dimensional order as in a crystal; they have some properties of liquids but retain some of the characteristics of crystals as well. The liquid crystalline phases are also called mesophases, and a compound which exhibits a mesophase is referred to as a mesogen. Transitions to these intermediate states may be brought about by purely thermal process (thermotropic liquid crystals) or by the influence of solvents (lyotropic liquid crystals). Thermotropic liquid crystals can be further classified into two major classes: (a) calamitic liquid crystals, formed by the rod-like molecules and (b) discotic liquid crystals, formed by the disc-like molecules. The investigations carried out in this thesis deal with only thermotropic liquid crystals.

Thermotropic liquid crystals composed of rod-like molecules have been conveniently classified [1] into three categories, viz., nematic, smectic and cholesteric. Nematic liquid crystals are characterised by a long range orientational order of the molecules but no long range positional order. Smectic liquid crystals have a layered structure and thus have both orientational and positional ordering. Since different molecular arrangements are possible within the layers, various types of smectic liquid crystals have been observed.' Cholesteric mesophase is exhibited by compounds containing an optically active group. This phase is basically the same as the nematic except that the structure has a twist axis which is superimposed normal to the director or preferred molecular direction. If the smectic C phase is composed of optically active molecules it usually exhibits a helical macrostructure and the mesophase also exhibits optical activity. The helical structure is based on the rotation of the tilt direction of individual layers of the phase about an axis normal to the layer planes on passing from layer to layer. This phase exhibits ferroelectric property [3] under an electric field. In the absence of an electric field it is helielectric in nature.

In 1972 de Gennes [4] predicted that, at second order nematic to smectic A phase transition, a defect stabilised intermediate phase could occur when the liquid crystal was subjected to twist or bend distortions. de Genne's arguments were further developed by Renn and Lubensky[5] who suggested that such an intermediary phase could be formed at the cholesteric to smectic A transition and stabilised by screw dislocations. They called this phase the twist grain boundary smectic A (TGB_A) phase. Examples of this theoretically predicted phase was first discovered by Goodby *et al.*[6] in some phenyl propiolates. The structure of this phase is described in chapter 1.

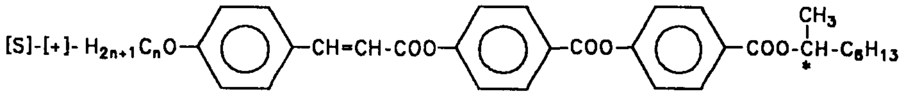
More recently Chandani *et al.*[7] have discovered an antiferroelectric phase ($S_{C_A}^*$) in MHPOBC. They also discovered a few sub-phases such as ferrielectric ($S_{C_\gamma}^*$)and chiral smectic C_α ($S_{C_\alpha}^*$) phases in the same compound. The structures of these phases are described in detail in chapter 1.

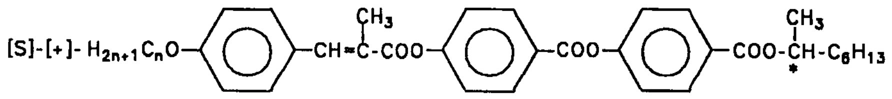
The object of this thesis has been to synthesise chiral compounds and examine the relationship between the molecular structure and the mesomorphic properties exhibited by them, the emphasis being on obtaining chiral smectic C (S_C^*), twist grain boundary smectic A

(TGB_A), antiferroelectric and its sub-phases, $S_{C_\gamma}^*$ and $S_{C_\alpha}^*$ phases with fairly large temperature ranges.

Chapter 1 begins with a general description of the molecular organisation in the different types of liquid crystals that are discussed in this thesis. Since the main emphasis of the present investigations has been on $S_{C_A}^*$, S_C^*, $S_{C_\gamma}^*$, $S_{C_\alpha}^*$ and TGB_A phases, the association of ferroelectricity in S_C^* phase and antiferroelectricity in $S_{C_A}^*$ phase have been discussed in detail. The occurrence of S_C^*, $S_{C_A}^*$ and TGB_A phases and the molecular structural requirements for these phases have been reviewed. The influence of the position and nature of chiral group on these phases has also been reviewed. Attempts to associate absolute configuration, helicity and the sign of polarisation with the structures of the compounds described in the literature have been included.

In chapter 2, a brief account of the mesomorphic properties of tri-esters containing three phenyl rings has been presented. The effect on mesomorphism by increasing a oxycarbonylphenyl group in the central part of the core has also been discussed. The following structurally related compounds were synthesised.

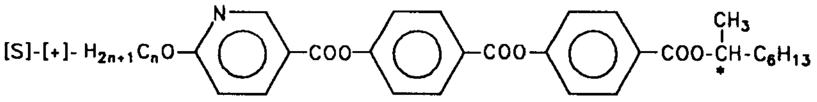


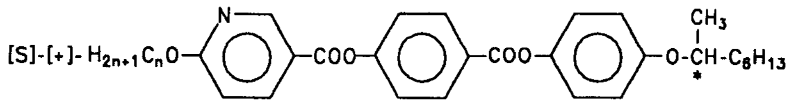


The mesomorphic behaviour of these compounds in relation to their structures has been discussed. In [S]-[+]-1-methylheptyl-4-[4′-(*trans*-4″-n-alkoxycinnamoyloxy)benzoyloxy]benzoates (X=H), in addition to S_A, S_C, $S_{C_\gamma^*}$ and $S_{C_\alpha^*}$ phases $S_{C_A^*}$ phase was also observed. The corresponding α-methyl substituted compounds ($X=CH_3$) did not exhibit $S_{C_A^*}$ phase and they do exhibit an unidentified $S_{C_X^*}$ phase. The n-decyloxy homologue of this series exhibits a direct transition from $S_{C_\alpha^*}$ phase to $S_{C_\gamma^*}$ phase. The melting and clearing temperatures of these compounds are relatively lower when compared with those of the unsubstituted compounds. The plots of transition temperatures ***versus*** the number of carbon atoms in the alkoxy chain show a smooth curve relationship. Spontaneous polarisation and optical tilt angle as a function of temperature for the n-decyloxy homologues of both series were measured.

In chapter **3**, a brief account of the mesomorphic properties of compounds containing a hetero atom (nitrogen) in aromatic ring have been presented. The occurrence of $S_{C_A^*}$ and its sub-phases by using this kind of compounds were established. The effect of this hetero atom on these phases has also been compared. The value for the spontaneous polarisation is expected to increase when a nitrogen atom is present in an aromatic ring. The effect of terminal bridging group between the core and chiral carbon on the occurrence of these phases were also examined. The following two series of compounds, viz., [S]-1-methylheptyl-4-[4′-(6″-n-alkoxypyridine-3-carbonyloxy)benzoyloxy]benzoates and [S]-4-(1-methylheptyloxy) phenyl-4′-(6″-n-alkoxypyridine-3-carbonyloxy)benzoates were synthesised for this purpose.

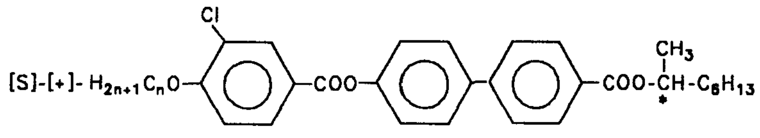
The structures of these compounds are shown below.





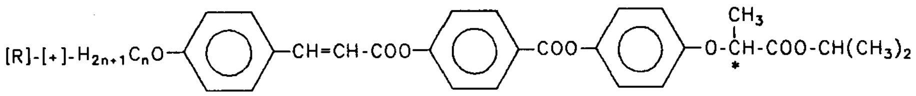
It was observed that when the terminal bridging group is an ester as in former series, exhibit $S_{C_A}^*$ and its sub-phases in addition to the S_A and S_C* phases while when it is a ether they exhibit only S_A and S_C* phases. The effect of nitrogen in these two series of compounds were compared with fluoro substituted compounds. The clearing temperatures of all the compounds synthesised and reported in this chapter were found to be less then 110.0°C. A binary phase diagram was constructed using MHPOBC and [S]-1-methylheptyl-4-[4′-(6″-n-decyloxy pyridine-3-carbonyloxy)benzoyloxy]benzoate. The continuous miscibility of all the phases in all compositions could be observed. The plot of transition temperatures against the number of carbon atoms in n-alkoxy chain shows a smooth curve relationship. Antiferroelectric and ferrielectric phases show a strong odd-even effect. Spontaneous polarisation, optical tilt angle and helical pitch for the [S]-4-(1-methylheptyloxy)phenyl-4′-(6″-n-decyloxypyridine-3-carbonyloxy)benzoate were measured. Similarly, spontaneous polarisation, optical tilt angle and dielectric constant for the [S]-1-methylheptyl-4-[4′-(6″-n-decyloxypyridine-3-carbonyloxy) benzoyloxy]benzoate were also measured.

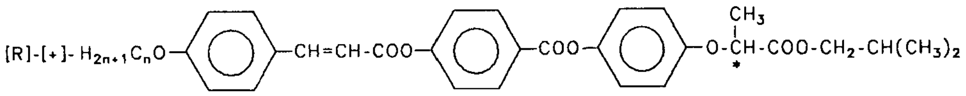
Chapter 4 begins with a survey of the compounds exhibiting TGB_A phase. A perusal of the literature indicated that the lateral chloro substituted mesogens are few in number when compared to the fluoro substituted ones. The occurrence of TGB$_A$ phase by lateral fluoro substituted compounds are numerous and there was no report of lateral chloro substituted compounds. We synthesised a homologous series having chloro substituent at a lateral position exhibiting TGB$_A$, S$_A$ and S$_C$* phases. The general structure of this series of compounds is shown below.

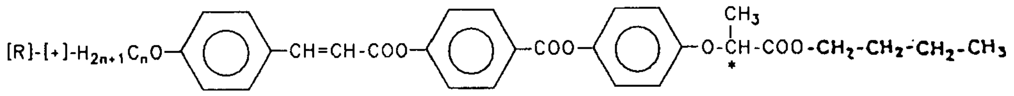


The TGB$_A$ to S$_A$ phase transition could not be observed in **DSC** thermogram but it could be easily observed under a optical microscope. The mesomorphic properties of these compounds were compared with those of the unsubstituted (parent) compounds. The unsubstituted compounds show $S_{C_A}^*$ and its sub-phases. The chloro substituted compounds do not exhibit these phases but they do exhibit a TGB$_A$ phase. **A** binary phase diagram containing the two enantiomers of the n-tetradecyloxy homologue was constructed. The clearing point rises as the optical purity of the binary mixture decreases. Two wing like regions of the TGB$_A$ phase appear between compositions of 0 and 5% wt./wt. of either **[R]** or **[S]** enantiomers. The clearing temperature of the racemate is slightly more than the pure enantiomers and exhibits only S$_A$ and S$_C$ phases.

In chapter 5 we report the effect of chirality on the occurrence of TGB$_A$ phase. It is known that chirality of the phase would be increased due to rotational damping of the motion of the chiral centre about the long axis of the molecules. Slaney ***et*** *al.*[8] have studied the effect of extending the terminal aliphatic chain on the peripheral side of the chiral centre. When the chiral centre is associated with a relatively short alkyl chain, it is able to move freely about the long axis of the molecules in the liquid crystalline state. As a result it did not show TGB$_A$ phase but showed cholesteric, S$_C$* and S$_A$ phases. When the chiral centre is associated with a branched alkyl chain, it exibits a TGB$_A$ phase at cholesteric to smectic **A** transition. In this chapter we have examined the effect of chiral carbon on the existence of S$_C$*and TGB$_A$ phases when it is relatively closer to the core. We also studied the effect of branching of the peripheral chain on the occurrence of TGB$_A$ phase. For this study, we have synthesised the compounds having the general structures shown below.

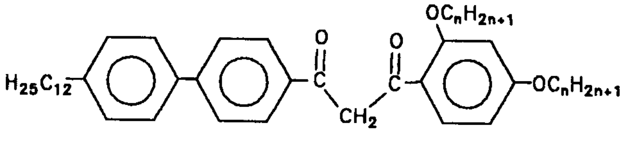


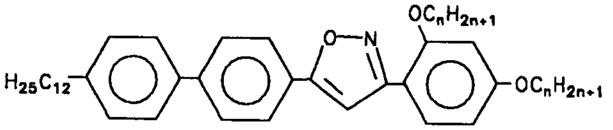




We observed that compounds where branched peripheral chain is closer to the chiral carbon exhibit short range (0.2°C) TGB$_A$ phase at **N*** to S$_A$ transition. When the branched alkyl chain is away from the chiral carbon or compounds having linear alkyl chain at the chiral centre exhibit stable S$_C$* phase in addition to N* and S$_A$ phases.

When the author started his research work, he undertook an ongoing project on the mesomorphic properties of substituted 1,3 diketones. The results of the investigations carried out on this project is presented in chapter 6. Though this does not form the main aim of the investigations described in this thesis, the same has been included. This chapter deals with lateral long alkoxy chain substituted 1,3-diketones and their isoxazole derivatives. The general structures of these compounds are shown below.





1,3-Diketones are prepared by using a Claisen condensation reaction between 4'-n-dodecylbiphenyl-4-yl-ketone and ethyl-2,4-dialkoxybenzoate in 1,2-dimethoxyethane. All the compounds synthesised were mesomorphic. Most of the compounds of 1,3-diketone series exhibit metastable mesophases. The odd homologues of this series are enantiotropic. The higher homologues are smectogens (S_A) and the lower homologues of this series are nematogenic. The plot of transition temperatures against the number of carbon atoms in n-alkoxy chains show a smooth curve relationship, but the melting points show the strong odd-even effect. Isoxazoles are obtained by treating the 1,3-diketones with hydroxylamine hydrochloride. These series of compounds exhibit thermally more stable nematic phase. Only the n-dodecyl homologue of this series shows stable nematic and metastable smectic **C** phases.

The phase transition from nematic to smectic C in this compound could not be seen in DSC thermogram but could be seen clearly under a microscope. A plot of transition temperatures against the number of carbon atoms in n-alkoxy chains of this series show a odd-even effect relationship.

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

[1] Ferroelectric and antiferroelectric liquid crystalline phases in some pyridine carboxylic acid derivatives (N. Kasthuraiah, B.K. Sadashiva, S. Krishna Prasad and Geetha G. Nair) - J. *Mater.* ***Chem.,*** 1619, **6(10)** (1996).

[2] Synthesis and mesomorphic properties of some esters of trans-p-n-alkoxycinnamic- and **trans-p-n-alkoxy-a-methylcinnamic** acids exhibiting ferroelectric and antiferroelectric phases (N. Kasthuraiah, B.K. Sadashiva, S. Krishna Prasad and Geetha G. Nair) - Liquid Crystals (in press).

[3] Twist grain boundary phases in some new cinnamic acid esters containing chiral isopropyl lactate group (N. Kasthuraiah and B.K. Sadashiva) - presented at the 5th International Conference on Ferroelectric Liquid crystals, 23-27th July 1995, Cambridge, UK.

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