SYNTHESIS AND LIQUID CRYSTALLINE BEHAVIOUR OF SOME CHIRAL AROMATIC COMPOUNDS

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By
B. SHIVKUMAR

Liquid Crystal Laboratory
RAMAN RESEARCH INSTITUTE
BANGALORE - 560 080 INDIA
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DECLARATION

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, and that no part of it has been submitted for the award of any Degree, Diploma, Associateship, Fellowship or any other similar title.

B. SHIVKUMAR

"CERTIFIED"

Professor N. V. MADHUSUDANA
HEAD
Liquid Crystal Laboratory
Raman Research Institute
BANGALORE 560080

CERTIFICATE

I certify that this thesis has been composed by Mr. B. Shivkumar based on investigations carried out by him at the Liquid Crystal Laboratory, Raman Research Institute, Bangalore, 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 other similar title.

Dr. B. K. SADASHIVA
Liquid Crystal Laboratory
Raman Research Institute
BANGALORE 560080

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LIST OF ABBREVIATIONS

C	crystal
S	smectic
N	nematic
I	isotropic
o	ortho
p	para
n	normal
br	broad
ppm	parts per million
s	singlet
d	doublet
dd	doublet of a doublet
t	triplet
q	quartet
m	multiplet
DMS.	dimethyl sulphate
DMSO	dimethyl sulphoxide
DCC	N,N-Dicyclohexylcarbodiimide
LAH	Lithium aluminium hydride

CONTENTS

PREFACE

Liquid crystals may be described as states of matter in which the degrees of molecular order lie intermediate between the three dimensional ordered crystalline state and the completely disordered isotropic liquid. Liquid crystals may be obtained by the action of heat on certain pure compounds or their mixtures and they may be formed by the effect of a solvent on suitable substrates. The former are called thermotropic liquid crystals and the latter lyotropic liquid crystals. The investigations carried out in this thesis deal with only thermotropic liquid crystals.

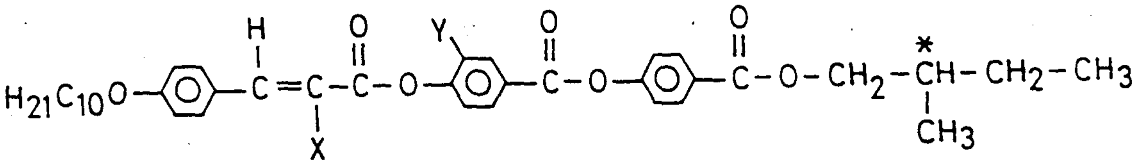
Thermotropic liquid crystals composed of lath-like molecules have been conveniently classified[1] into three categories, viz., nematic, smectic and cholesteric. Nematic liquid crystals are characterised by a long range orientational order of the molecules but no long range positional order. Smectic liquid 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.[2] Cholesteric mesophase is exhibited by compounds containing an optically active group. This phase is basically the same as the nematic type except that the structure has a screw axis which is superimposed normal to the director or preferred molecular direction.

Since the discovery of liquid crystals, it was believed that liquid crystalline phases could be obtained from compounds whose constituent molecules are rod-like. However, in 1977 Chandrasekhsr et al.[3] obtained mesophases from compounds composed of disc-like molecules. From optical and Xray studies they proposed a structure for the mesophase in which the discs are stacked one on top of the other aperiodically to form liquid like columns. Many new substances have since been prepared and these exhibit a number of mesophases.

The object of this thesis has been to synthesise and examine the relationship between the molecular structure of a compound and the mesomorphic properties exhibited by it; the emphasis being on obtaining chiral smectic C (S_{C^*}) phase at a relatively low temperature with a large value for the spontaneous polarisation.

Chapter I begins with a general description of the molecular organisation in the different types of liquid crystals. Since the main emphasis of the present investigations has been on S_{C^*} phase, the association of ferroelectricity in such a phase has been discussed in detail. The occurrence of S_{C^*} phase' and the structural requirements for it has been reviewed. An important parameter associated with ferroelectricity in liquid crystals is the value of spontaneous polarisation. The influence of chiral group on this parameter has been reviewed. Attempts to associate absolute configuration, helicity and the sign of polarisation with the structure of the compound described in the literature[4] have also been discussed.

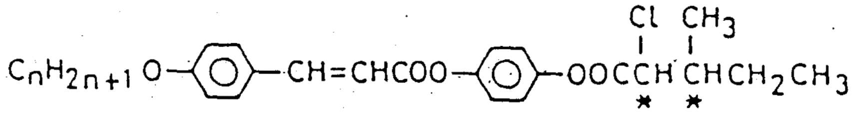
In Chapter II, a brief account of the mesomorphic properties of diesters containing two and three phenyl rings has been presented. 'The effect on mesomorphism by substituting a lateral chloro and a methyl group in the central phenyl ring has also been discussed. The following structurally related compounds were synthesised.



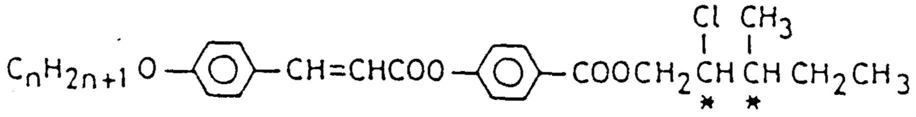
The mesomorphic behaviour of these compounds in relation to their structures has been discussed. In the case of [S]-2-methylbutyl 4-[4'-(4"- trans-n-decyloxycinnamoyloxy)benzoyloxy]benzoates (X=H; Y=H) and the corresponding chloro substituted compound (X=H; Y=Cl) in addition to chiral nematic (N*) and smectic A (S_A) phases, the S_{C*} phase was also observed. In the case of [S]-2-methylbutyl 4 - 4'-(4"-trans-n-decyloxy-a -methylcinnamoyloxy)benzoyloxy]benzoates ($X=CH_3$; Y=H), the chloro and methyl substi-tuted analogues the transition temperatures were found to be considerably lower. Also an S_{C*} and an S_A phases were observed for the compound in which the central phenyl ring was not substituted ($X=CH_3$; Y=H). As this compound exhibited the S_{C*} phase at a relatively low temperature a homologous series of the same was synthesised. The changes in the mesomorphic properties along this series have been described. The plot of transition temperatures versus the number of carbon atoms in the alkoxy chain shows a smooth curve relationship.

In Chapter III, a brief account of the mesomorphic properties of compounds containing optically active chloro alkyl groups have been presented. The emphasis has been on the following three optically active moieties,viz., [S]-2-chloro-3-methylbutanoyloxy, [S]-2-chloro-4-methylpentanoyloxy and [2S,3S]-2-chloro-3-methylpentanoyloxy groups. The value for spontaneous polarisation is expected to increase when a polar substituent is present on the chiral a carbon atom.[5] Hence the latter two of the above mentioned optically active groups were used in the synthesis of esters of 4-n-dodecyloxycinnamic- and 4-n-dodecyloxy-a-methylcinnamic acids. It was observed that the a-methyl group lowers the melting points and the thermal stabilities of the mesophases. Only an S_A phase was observed in these compounds. However, the esters of cinnamic acid exhibited enantiotropic S_A and S_{C^*} phases. Hence a homologous series of these compounds were synthesised.

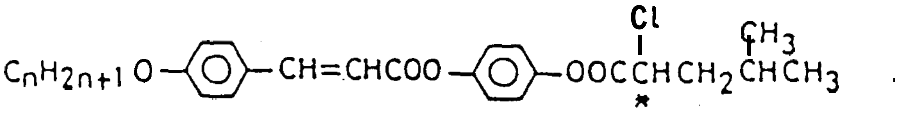
Series I


$C_nH_{2n+1}O-\bigcirc-CH=CHCOO-\bigcirc-OOC\underset{*}{\overset{Cl}{C}}H\underset{*}{\overset{CH_3}{C}}HCH_2CH_3$

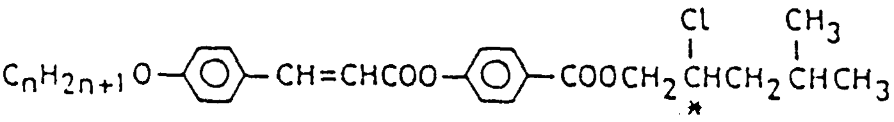
Series II


$C_nH_{2n+1}O-\bigcirc-CH=CHCOO-\bigcirc-COOCH_2\underset{*}{\overset{Cl}{C}}H\underset{*}{\overset{CH_3}{C}}HCH_2CH_3$

Sertes III

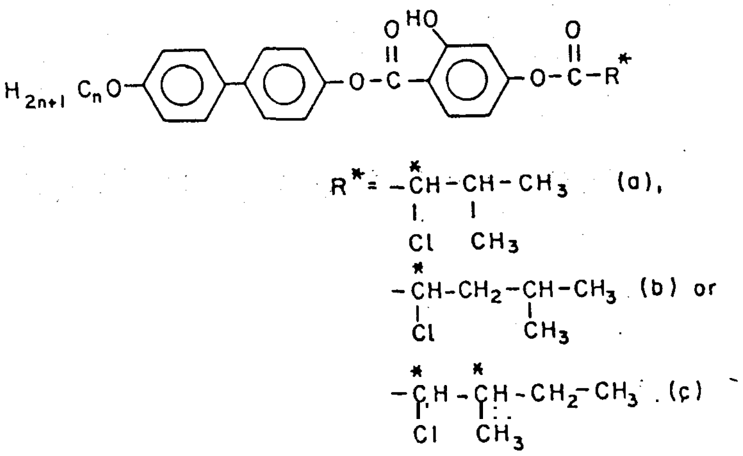

$C_nH_{2n+1}O-\bigcirc-CH=CHCOO-\bigcirc-OOC\underset{*}{\overset{Cl}{C}}HCH_2\overset{CH_3}{C}HCH_3$

Series IV


$C_nH_{2n+1}O-\bigcirc-CH=CHCOO-\bigcirc-COOCH_2\underset{*}{\overset{Cl}{C}}HCH_2\overset{CH_3}{C}HCH_3$

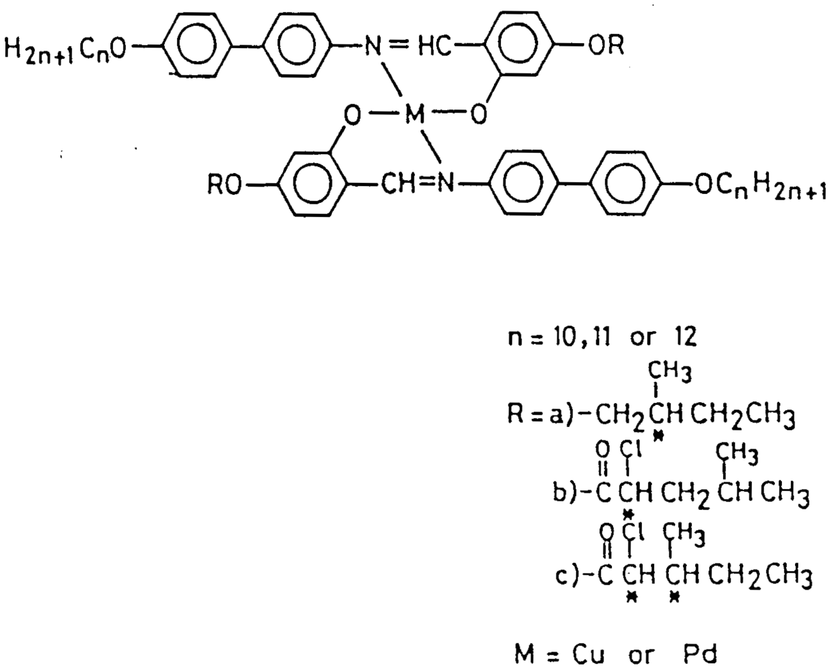
The lower homologues of the three series I, II and IV exhibited N* phase. In series II, N* phase was followed by a blue phase over a very short temperature range. Except the hexyloxy homologue of series II all the compounds exhibited the S_{C*} phase. The clearing temperatures of all the compounds synthesised and reported in this chapter were found to be less than 100°C. Spontaneous polarisation values of these compounds were measured by Prasad et al.[6] of our laboratory. The structural changes in these compounds and their effect on the thermal stabilities, the mesophase ranges and the associated spontaneous polarisation values have been discussed.

Chapter IV begins with a survey of the mesomorphic properties of aromatic compounds containing a hydroxyl group. A perusal of the literature indicated that the lateral hydroxy substituted mesogens are few in number when compared to the halogen substituted ones. However, in recent years more and more such compounds are being synthesised. The hydroxyl group, by participation in intramolecular hydrogen bonding is found to stabilise the smectic phases.[7] It can also enhance the lateral dipole moment of the compound which in turn can lead to higher values of spontaneous polarisation. The effect on mesomorphism of a laterally hydroxy substituted core in combination with an optically active moiety in which a chloro group is attached to the chiral carbon atom has been investigated. The optically active groups have been derived from [S]-2-chloro-3-methylbutanoic acid, [S]-2-chloro-4-methylpentanoic acid and [2S,3S]-2-chloro-3-methylpentanoic acid which were prepared from the corresponding optically active amino acids.



The higher homologues in all the three series exhibited an S_{C*} phase. The lower homologues of series (a) and (c) exhibited an N* phase. In series (c) a blue phase was also observed. The differences in the structure and their effects on mesomorphic properties have been discussed. The effect of introduction of a lateral hydroxyl group in a compound on mesomorphic properties has also been discussed.

It is only in the last decade or so that liquid crystalline compounds containing metal atoms have been investigated in greater detail. β-Diketones and salicylideneaniline derivatives are the most widely used ligands for preparing the metal chelates. In chapter V a survey of mesogenic properties exhibited by coordination compounds has been presented. The first transition metal complexes exhibiting a mesophase was reported by Giroud and Billard.[8] Paramagnetic nematic liquid crystals were reported by Chandrasekhar et al.[9] Complexes exhibiting S_C phase have also been reported.[10] Caruso et al.[11] have investigated copper(II) complexes using salicylidene aniline derivatives as ligands. Very recently Espinet et al.[12] have reported the first metallo-mesogen exhibiting an S_{C^*} phase. With a view to explore the possibility of obtaining a ferroelectric liquid crystalline phase in metal containing compounds a number of copper(II) and palladium(II) complexes have been synthesised.



n = 10,11 or 12

$R = a) -CH_2\overset{*}{C}H(CH_3)CH_2CH_3$

$b) -C(=O)\overset{*}{C}H(Cl)CH_2CH(CH_3)CH_3$

$c) -C(=O)\overset{*}{C}H(Cl)\overset{*}{C}H(CH_3)CH_2CH_3$

M = Cu or Pd

Lateral hydroxy substituted aromatic Schiff's bases have been used as ligands. The synthesis and the mesomorphic properties of these Schiff's bases and their complexes have been discussed in this chapter. It is observed that all the ligands exhibited smectic polymorphism. The S_{C^*} phase was observed to be the predominant phase in these Schiff's bases. All the complexes exhibited an S_A phase. Two of the copper(II) complexes with [S]-2-methylbutyl group (n=11 and 12) exhibited an enantiotropic S_{C*} phase. It is believed that these complexes synthesised by the author represent the first examples of paramagnetic ferroelectric liquid crystals. Complexes with [S]-2-chloro-4-methylpentanoyloxy group exhibited a monotropic S_{C*} phase. The palladium complexes exhibited only an S_A phase at high temperatures and no ferroelectric phase was observed.

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

1 Chiral smectic C phase exhibited by some 4-n-alkoxy- -methylcinnamates (B.Shivkumar, B.K.Sadashiva and B.R. Ratna) - FERROELECTRICS, 85, 461 (1988)

2 Ferroelectric liquid crystals derived from trans-p-n-alkoxycinnamic acid. (B. Shivkumar, B. K. Sadashiva, S. Krishna Prasad and S.M.Khened) - FERROELECTRICS, 114, 273 (1991)

3 Ferroelectric liquid crystals containing transition metals. (B.K. Sadashiva and B.Shivkumar) - Paper presented at the 13th International Liquid Crystal Conference, Vancouver, Canada,July 22-27,1990 (Abstract No.Fer.52-P-Tue).

The author has also collaborated in some other investigations, not described in this thesis, but reported in the following papers:-

1 Spontaneous polarisation and rotational viscosity measurements on ferroelectric liquid crystals derived from trans-p-n-alkoxycinnamic acids. (S.K.Prasad, S.M.Khened, S.Chandrasekhar, B.Shivkumar and B.K. Sadashiva) - MOLECULAR CRYSTALS & LIQUID CRYSTALS, 182B, 313 (1990)

2 Dielectric studies of Goldstone mode and soft mode in the vicinity of the A-C* transitions. (S.M.Khened, S.Krishna Prasad, B.Shivkumar and B.K. Sadashiva) - JOURNAL DE PHYSIQUE II, 1, 171 (1991).

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