# SYNTHESIS AND PROPERTIES OF SOME THERMOTROPIC LIQUID CRYSTALS

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BANGALORE UNIVERSITY
for the Degree of
DOCTOR OF PHILOSOPHY

by

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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 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.
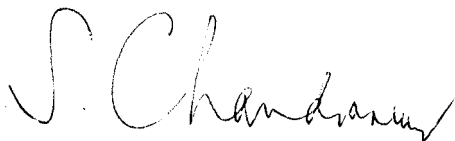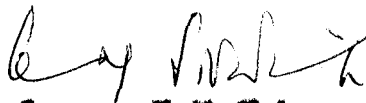
B. K. SADASHIVA

'CERTIFIED'

# CERTIFICATE

We certify that this thesis has been composed by Mr. B. K. Sadashiva based on investigations carried out by him at the Liquid Crystals Laboratory, Raman Research Institute, Bangalore, under our 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.

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# CONTENTS

# LIST OF ABBREVIATIONS

| | |
|---|---|
| K | crystal |
| S | smectic |
| N | nematic |
| I | isotropic |
| m | multiplet |
| q | quartet |
| t | triplet |
| d | doublet |
| s | singlet |
| ppm | parts per million |
| t.l.c. | thin layer chromatography |

# PREFACE

Liquid crystals are states of matter in which
the degrees of molecular order lie intermediate between
the crystalline solid and the isotropic liquid.  The
liquid crystalline phases are also called mesophases,
and a compound which exhibits a mesophase is referred
to as a mesogen.  Broadly speaking, liquid crystals may
be formed in two different ways: either by the action of
heat on pure compounds (or their mixtures), or by the
effect of a solvent;  the former are called thermotropic
liquid crystals and the latter lyotropic.  In the present
thesis, we shall be concerned only with thermotropic
liquid crystals, their synthesis and mesomorphic
properties.

Friedel[1] classified thermotropic liquid crystals
into three basic types, namely, nematic, cholesteric and
smectic.  Chapter I begins with a description of the
molecular organisation in these three types of liquid
crystals.  The relationship between chemical constitution
and liquid crystallinity, the variation of the mesomorphic
behaviour in a homologous series of compounds, the effect
of lateral and terminal substituents on the mesomorphic
properties are also discussed.  Mention is also made of

the applications of liquid crystals and the increasing importance of stable, low-melting mesogenic compounds of strong positive dielectric anisotropy.

The rest of the thesis deals with the new results obtained in the present investigations, viz., the synthesis and characterisation of nearly 100 new compounds belonging to five different homologous series, and new and more convenient procedures for the preparation of certain known compounds of technological importance. These studies have also led to some interesting new observations: (a) the first observation of the occurrence of the re-entrant nematic phase in pure compounds at atmospheric pressure, and (b) the discovery of thermotropic mesophases in pure compounds composed of disc-like molecules.

In chapter II, we describe the synthesis and properties of two new homologous series of compounds, (i) trans-p-n-alkoxy-α-methylcinnamic acids,
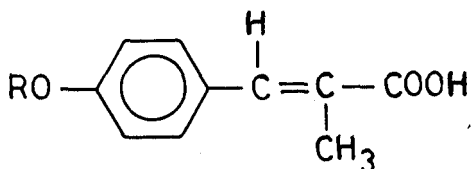
RO—⟨benzene ring⟩—C(H)=C(CH₃)—COOH          R = n-Alkyl

and (ii) p-cyanophenyl trans-p'-n-alkoxy-α-methylcinnamates
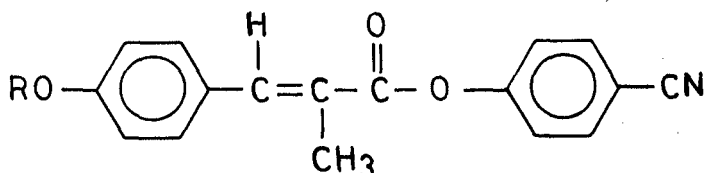
RO—⟨benzene ring⟩—C(H)=C(CH₃)—C(=O)—O—⟨benzene ring⟩—CN          R = n-Alkyl

Gray et al.[2] studied the mesomorphic behaviour of trans-
p-n-alkoxycinnamic acids.    These compounds have fairly
wide thermal ranges but rather high transition temperatures.
In order to study the effect of introducing an α-methyl
group into such a system we prepared a series of trans-
p-n-alkoxy-α-methylcinnamic acids and compared their
mesomorphic properties with those of the unsubstituted
parent compounds reported by Gray et al.  It was found
that the α-methyl group does not affect the thermal range
of the mesophase drastically but reduces the melting point
considerably.  We have attributed this to a thickening
effect[3] caused by a steric interaction of the α-methyl
group with the ortho ring protons.  The plot of the N-I
transition temperatures against the number of carbon atoms
in the alkoxy chain shows the familiar odd-even effect;
the plot for the even homologues lies on a smooth curve
above that for the odd homologues.  Further, because of
the increasing importance of compounds with low-melting
points and large positive dielectric anisotropy, another
homologous series of esters with these acids and 4-hydroxy-
benzonitrile was prepared.  The esters had fairly low
melting points but the thermal ranges were reduced to some
extent.  A comparison of the transition temperatures of
the above esters with those eight unsubstituted esters
reported by Titov et al.[4] reveals that the α-methyl group

plays an important role in understanding the reduction
in the transition temperatures. This has been discussed
taking into consideration the two possible conformations
that the ester molecule can adopt. The plot of the N-I
transition temperatures against the number of carbon atoms
in the alkoxy chain shows a different behaviour than those
that are commonly observed in homologous series of liquid
crystalline substances. A possible explanation for such
a behaviour has also been given in this chapter.

It was also observed that one of the homologues,
p-cyanophenyl trans-p'-n-decyloxy-α-methylcinnamate exhibits
a 're-entrant' nematic phase, i.e., on cooling the isotropic
liquid, the sequence of transition was as follows:

isotropic ──→ nematic ──→ smectic A ──→ nematic ──→ solid.

The lower temperature nematic phase, termed the 're-entrant'
nematic phase was observed by Cladis[5] either in mixtures or
in pure compounds at elevated pressures. Ours is the first
observation of a 're-entrant' nematic phase in a pure
compound at atmospheric pressure.

It is well known that most mesogens contain at least
two phenyl rings with suitable substituents in the para
positions. Dewar and Schroeder[6] and Dewar and Goldberg[7]
prepared a number of p-phenylene esters of hydroquinone
and p-substituted phenyl esters of terephthalic acid.

All these compounds are symmetrical in the sense that
they have identical wing groups, and they have high
transition temperatures.    Young and co-workers[8] and
Van Meter and Klandermann[9] obtained compounds which had
low transition temperatures by introducing dissymmetry
into such diesters.   Thus, they reported a number of
substituted phenyl 4-benzoyloxybenzoates I and II
respectively.



I
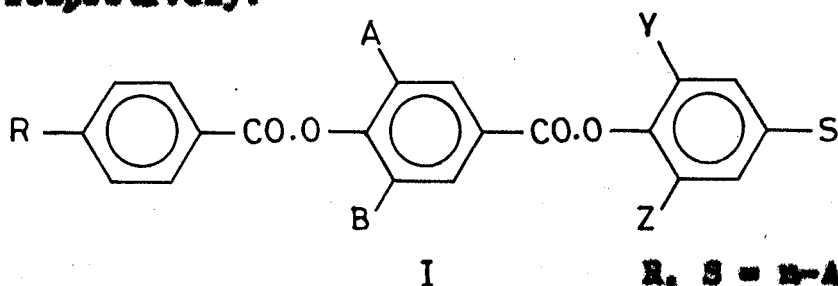
R, S = n-Alkyl or n-Alkoxy
A, B, Y, Z = H or $CH_3$

II
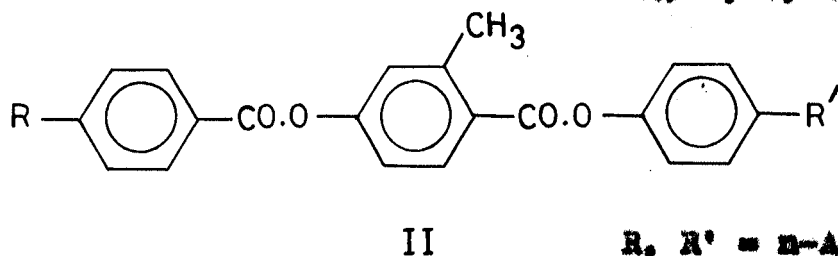
R, R' = n-Alkyl or n-Alkoxy
Y = H, $CH_3$

     Since the interest in the present study was to
prepare a homologous series of compounds with strong
positive dielectric anisotropy and wide nematic thermal
ranges, the phenyl 4-benzoyloxybenzoate system was chosen.
A terminal cyano group was incorporated so that the
resulting molecule would have a large positive dielectric

anisotropy. However, in esters which are already polar by virtue of the -CO-O- group, the position of the cyano group relative to the ester linkage is also important. It is known that the presence of the cyano group in the phenolic moiety will lead to much higher positive dielectric anisotropy. As the phenyl 4-benzoyloxybenzoate system has wide thermal range,[8,9] it can accommodate a lateral substituent. This would further contribute to the disymmetry of the molecule, which may lower the melting temperatures. As a consequence of these factors, a series of 4-cyanophenyl-3'-methyl-4'-(4"-n-alkylbenzoyloxy) benzoates, III, were synthesised and their mesomorphic properties are discussed in chapter III.



III                                    R = n-alkyl
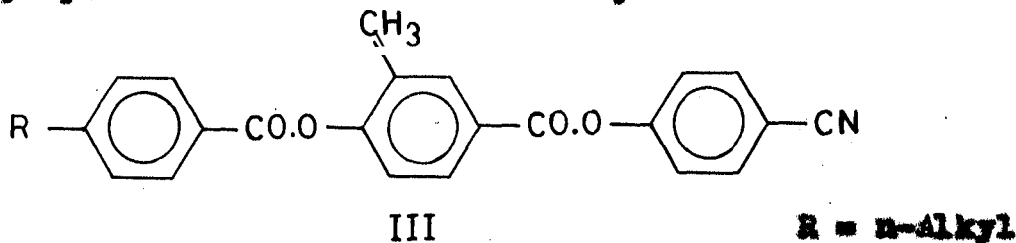
The plot of the N-I transition temperatures against the number of carbon atoms in the alkyl chain for this series follows the usual odd-even effect and those points lie on two smooth falling curves; the curve for the odd-homologues lies above that for the even homologues.

Two more instances of the occurrence of the re-entrant nematic phase in pure compounds were observed. The compounds were (i) 4-cyanophenyl-3'-methyl-4'-

(4"-n-undecylbenzoyloxy)benzoate, and (ii) 4-cyanophenyl-
3'-methyl-4'-(4"-n-dodecylbenzoyloxy)benzoate. These
two cases, along with the one mentioned in chapter II,
are the first observations of a re-entrant nematic phase
in pure compounds at atmospheric pressure.

In chapter IV, we discuss the mesomorphic behaviour
of two mow homologous series of 4-biphenylylbenzoates,
(i) 4-biphenylyl 4"-n-alkylbenzoates, IV and (if) 4-biphenylyl
4"-n-alkoxybenzoates, V.
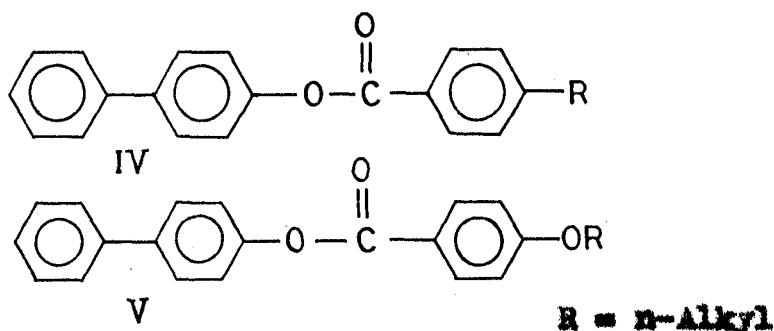


The biphenyl moiety is well suited to exhibiting liquid
crystalline properties because of its geometrical shape
and indeed a large number of compounds with biphenyl core
have been prepared and their mesomorphic properties
characterised. In most of these cases, both 4 and 4'
positions of the biphenyl molecule have been suitably
substituted and even small substituents in these positions
result in materials which show mesophases. In the present
study, we study the effect of having one of these two
positions free and suitably substituting the other position.

Series IV is compared with p-n-alkylbenzoic acids and a series of 4-p-n-alkylbenzylideneaminobiphenyls[10] and series V is compared with p-n-alkoxybenzoic acids and 4-p-n-alkoxybenzylideneaminobiphenyls[11] which are similar in structure except for the bridging groups. The meso-morphic properties of series IV and V are also compared and it was found that alkoxy substitution has higher thermal stability than alkyl substitution and that the former favours smectic mesophase formation. Plots of N-I transition temperatures against the number of carbon atoms in the terminal chains in both series give smooth curve relation-ships and also follow the usual odd-even effect. In an attempt to understand the substituent effect, various other groups such as chloro, bromo, nitro, cyano, etc., were incorporated into this system. The influence of these groups on the mesophase thermal stability have also been discussed.

The enthalpies and entropies of transition in both series of compounds have also been determined using a differential scanning calorimeter (DSC Model 2). The entropy of transition versus the number of carbon atoms in the terminal chain have been plotted for both series of compounds.

The observation of the twisted nematic effect, and

the recognition that it has very important applications
in display devices for watches, calculators, etc., prompted
the chemists to prepare compounds having large positive
dielectric anisotropy and showing the nematic phase at
or near room temperature. Gray and his co-workers[12]
prepared a series of stable room temperature nematic
liquid crystals with positive dielectric anisotropy.
These individually do not have enough mesophase range
for use in electro-optic devices of the twisted nematic
type. Later, they extended this work to prepare 4-n-alkyl-
4"-cyano-p-terphenyls.[13] Suitable mixtures of these
compounds with 4-n-alkyl-4'-cyanobiphenyls give ideal
temperature ranges for use in display devices. However,
the procedure of Gray et al. in preparing the intermediate
4-bromo-p-terphenyl in pure form presented some difficul-
ties. Since some of these compounds are of great commer-
cial importance, we developed a convenient procedure for
the preparation of both 4-n-alkyl-4'-cyanobiphenyls and
4-n-alkyl-4"-cyano-p-terphenyls. The detailed experi-
mental procedures form the contents of chapter V.

The last chapter (VI), deals with an entirely new
type of liquid crystal observed by us. Until this observa-
tion, all pure thermotropic mesogenic compounds were
elongated, had a rigid central core and normally had polar
end groups, as has been discussed in chapters II to V.

However, for a number of years, Chandrasekhar[14] was thinking about the possibility of flat, disc-like molecules showing mesophases. For the first time we succeeded in synthesizing a few disc-like molecules which exhibited mesomorphic behaviour. These belong to the class of benzene hexa-n-alkanoates.



R = n-Alkyl

We have also proposed a structure for the mesophase, based on optical and X-ray studies, in which the discs are stacked one on top of the other in columns that consti- tute a hexagonal arrangement, but the spacing between the discs in each column is irregular. It should, however, be mentioned that mesophases composed of large plate-like molecules are known[15] to occur at high temperatures during the carbonization of graphitizable substances, such as petroleum and coal-tar pitches, but these are rather complex materials and certainly cannot be regarded as

single component liquid crystalline systems.

Benzene hexa-n-hexanoate which does not exhibit
a mesophase in its pure form, does show a mesophase when
mixed with a small quantity of benzene. This is the first
observation of lyotropic mesomorphism in disc-like mole-
cules.

Some of the results discussed in this thesis have
been published in the following papers:

1    Mesomorphic properties of some biphenylylbenzoates
     (with G.S.R.Subba Rao), Current Science 44, 222 (1975).

2    Mesomorphic properties of some α-methylcinnamic acids
     and their esters, Molecular Crystals and Liquid
     Crystals 32, 205 (1976).

3    A convenient method for the preparation of 4-n-alkyl-
     4"-cyano-p-terphenyl (with G.S.R.Subba Rao), Molecular
     Crystals and Liquid Crystals 38, 703 (1977).

4    Liquid Crystals of disc-like molecules (with
     S. Chandrasekhar and K.A.Suresh) - Pramana 9, 471
     (1977).

5    Mesomorphic properties of a homologous series of
     substituted benzoyloxybenzoates, Molecular Crystals
     and Liquid Crystals 53, 253 (1979).

6       Diso-like mesogens (with S.Chandrasekhar, K.A.Suresh,
        N.V.Madhusudana, S.Kumar, R.Shashidhar and G.Venkatesh) -
        J. Physique 40, 03-121 (1979).

7       Biphenylylbenzoates: Synthesis and thermodynamic
        properties, Molecular Crystals and Liquid Crystals
        (in press).

8       Re-entrant nematic phase in pure compounds at atmospheric
        pressure (with N.V.Madhusudana and K.P.L.Moodithaya) -
        Current Science 48(14), 613 (1979).

        The present writer also collaborated in some other
investigations, not described here but reported in the
following papers:

9       Experimental studies of short range order in nematogens
        of strong positive dielectric anisotropy (with B.R.
        Ratna, M.S.Vijaya and R.Shashidhar) - Proc.Int.Liquid
        Crystals Conf., Bangalore 1973 - Pramana Supplement 1,
        p. 69.

10      Pressure induced mesomorphism (with S.Chandrasekhar,
        S. Ramaseshan, A.S.Reshamwala, R.Shashidhar and
        V. Surendranath), ibid., 117.

11      Miscibility studies of disc-like molecules (with
        J. Billard) - Pramana 13, 309 (1979).

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# CHAPTER I

## INTRODUCTION

### 1.1    Classification of thermotropic liquid crystals

As indicated in the preface, this thesis, except
for a brief reference to lyotropic mesomorphism in
chapter VI, mainly concerns with the study of thermotropic
liquid crystals, their structural classification and their
relationship to the chemical constitution of the molecule.

Friedel[1] classified thermotropic liquid crystals
broadly into three types: nematic, cholesteric and smectic.

(a) Nematic:  The nematic liquid crystal possesses a high
degree of long range orientational order, but no long range
positional order.   In other words it is somewhat similar to
the ordinary liquid except that the molecules are arranged
approximately parallel to one another. Because of the lack
of positional order of the molecules, the nematic phase is
quite fluid and the molecules can freely slide past one
another.  When a thin film of nematic is sandwiched between
two glass plates and examined through a polarising micro-
scope, one sees a complex optical pattern.   However, a
monodomain sample homogeneously aligned, i.e., the preferred
axis of orientation of the molecules lying unidirectionally

in a plane parallel to the glass surfaces, is optically
uniaxial, positive and strongly birefringent.  On the
other hand a homeotropically aligned sample, in which the
preferred axis is normal to the glass surfaces, appears
indistinguishable from the isotropic liquid when observed
normal to the glass plates between crossed polaroids
(except in the case of convergent light).  Some recent
X-ray studies[2,3] have indicated the presence of 'cybotactic'
clusters[4] in some nematics, the molecular centres within
each cybotactic cluster being arranged in layers.  The
molecular ordering in crystal, nematic and isotropic
phases is shown schematically in figure 1.1.

(b) <u>Cholesterics</u>:  The cholesteric liquid crystal is
essentially similar to the nematic phase except that the
molecules in this phase are optically active giving rise
to a helical structure (see fig. 1.2) with its screw axis
normal to the preferred direction of the molecules.  This
helicity imparts certain unique properties to the chole-
steric phase, viz., selective reflection of circularly
polarised light and a very high optical rotatory power,
about 1000 times greater than what is usually observed
for ordinary optically active substances.

(c) <u>Smectics</u>:  Smectic liquid crystals have a layered
structure, but different kinds of molecular arrangements
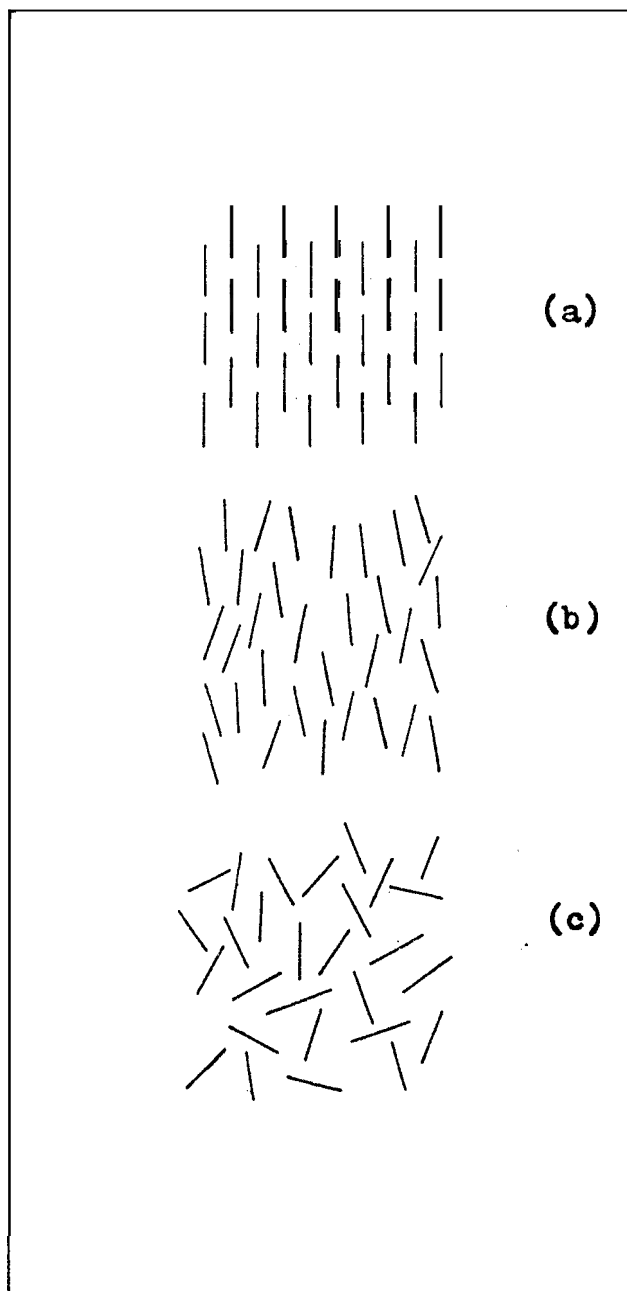
**(a)**

**(b)**

**(c)**

Figure 1.1

Schematic representation of molecular
ordering in (a) crystal (b) nematic, and
(c) isotropic phases,
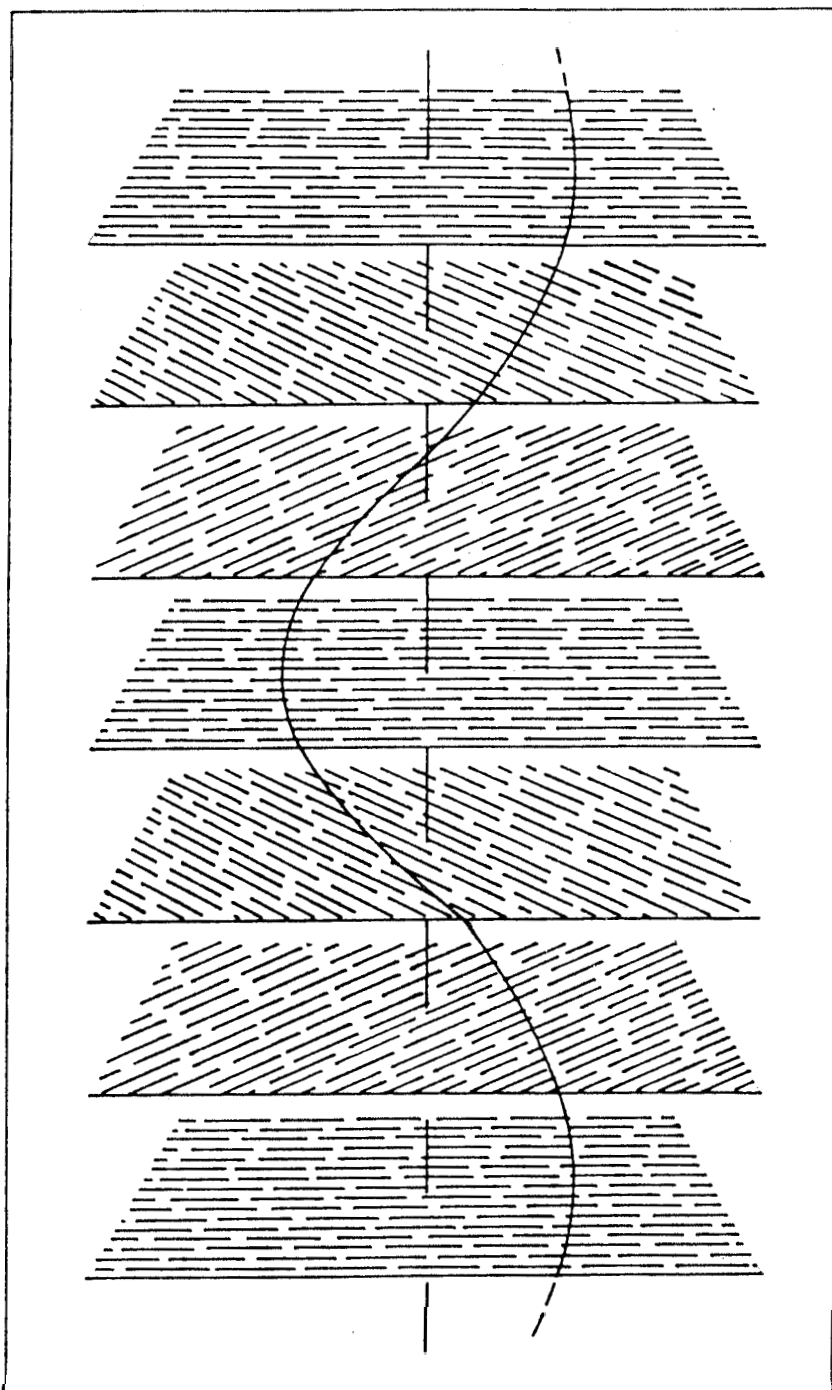
Figure **1.2**

Schematic representation of molecular ordering
in a cholesteric mesophase.

are possible within each layer. In smectic A (or $S_A$) phase the molecules are normal to the layer, but there is no regular arrangement of the molecular centres (Fig. 1.3a). The interlayer attractions are quite weak and thus the layers are able to slide over one another relatively easily. The $S_A$ phase therefore exhibits fluid properties but it is usually very much more viscous than the nematic. Optically $S_A$ phase is uniaxial positive and strongly birefringent. In the case of smectic B also the molecules are upright, but the centres of molecules in each layer are hexagonally close-packed. It is also uniaxial positive and strongly birefringent. Smectic C is similar to smectic B except that the molecules are tilted with respect to the layer normal (Fig. 1.3b). This phase is optically biaxial. At least five other smectic modifications have been identified[5,6] by miscibility, optical and X-ray studies, but at a molecular level their structures have not been fully understood, and even the nomenclature of these phases has not been unanimously agreed upon.

The code letters recommended recently by Goodby and Gray[7] for the different modifications of smectics is given in table 1.

(a)

(b)
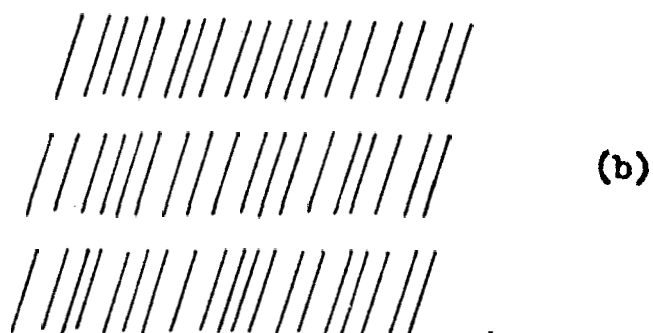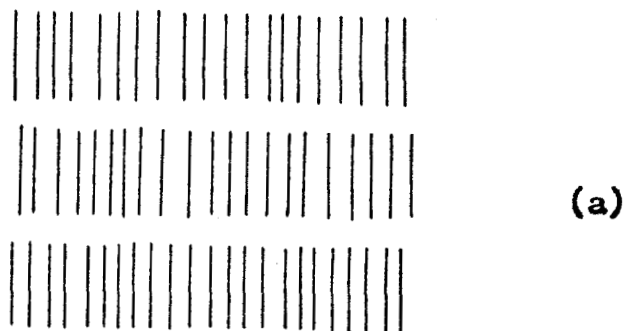
**Figure 1.3**

Schematic representation of molecular ordering
in (a) smectic A, (b) smectic C.

Table 1

Characteristics of the different types of smectic liquid crystals

| Packing arrangement | Molecular disposition | Code letters previously used | Recommended code letter | Textures exhibited by the phase |
|---|---|---|---|---|
| Random | Orthogonal | $S_A$ | $S_A$ | Focal conic (fan-shape, polygonal or batonnets). |
| Cubic | Micelles or rods | $S_D$ | $S_D$ | Homeotropic |
| Random | Tilted | $S_C$ | $S_C$ | Broken or striated fan-shape, schlieren |
| Pseudo-hexagonal | Tilted | $S_F$ | $S_F$ | Schlieren, broken or striated fan-shape |
| Hexagonally close-packed | Orthogonal | $S_B$[8], $S_{B_A}$ | $S_B$ | Mosaic, schlieren, fan-shape |
| Hexagonally close-packed | Tilted | $S_B$[8], $S_{B_C}$, $S_G$[9], $S_H$[10] | $S_H$ | Mosaic, broken fan-shape |
| Orthorhombic | Orthogonal | $S_E$, $S_{E_A}$ | $S_E$ | Mosaic |
| Orthorhombic | Tilted | $S_{E_C}$, $S_G$[8], $S_H$[9] | $S_G$ | Mosaic, broken fan-shape |

## 1.2 Identification of mesophases

Unless very special precautions are taken to give prior treatment to the glass surfaces, a film of liquid crystal contained between two glass surfaces forms a poly-domain sample and exhibits complex optical patterns when viewed through a polarising microscope. These patterns, known as 'optical textures', are useful in the optical identification of the different mesophases.[11] For instance, a nematic shows a characteristic threaded texture or schlieren texture while a cholesteric usually adopts a focal conic texture. The various kinds of textures that are normally exhibited by the different types of smectics are summarised in the last column of table 1.

## 1.3 Polymorphism in thermotropic liquid crystals

On the basis of the nomenclature recommended by Goodby and Gray, the sequence of transitions that occur (on cooling) in compounds which exhibit a number of meso-phases is given below along with examples.

(i) Terephthal-bis-4-n-butylaniline[12]

$$C_4H_9-\text{⬡}-N=CH-\text{⬡}-CH=N-\text{⬡}-C_4H_9$$

$$I \longrightarrow N \longrightarrow S_A \longrightarrow S_C \longrightarrow S_H \longrightarrow S_G$$
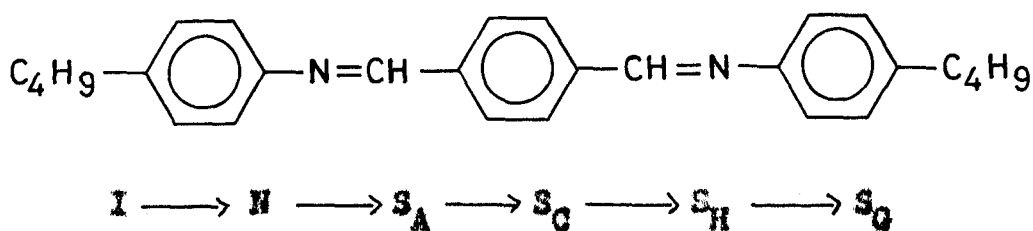
(11) Terephthal-bis-4-n-pentylaniline[12]



$$I \longrightarrow N \longrightarrow S_A \longrightarrow S_C \longrightarrow S_F \longrightarrow S_H \longrightarrow S_G$$
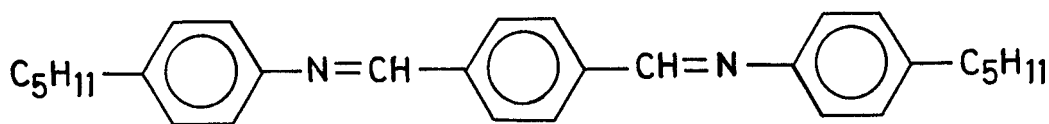
(iii) N-(4-n-heptyloxybenzylidene)-4'-n-pentylaniline[13]



$$I \longrightarrow N \longrightarrow S_A \longrightarrow S_C \longrightarrow S_B \longrightarrow S_H$$
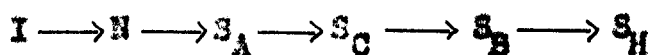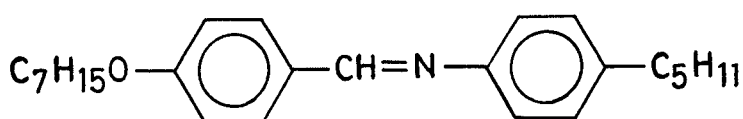
(iv)  2-(4-n-Pentylphenyl)-5-(4-n-pentyloxyphenyl)pyrimidine[6]



$$I \longrightarrow N \longrightarrow S_A \longrightarrow S_C \longrightarrow S_F \longrightarrow S_H$$
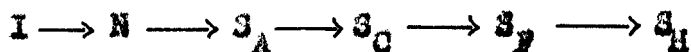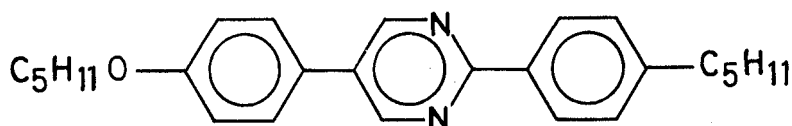
It should also be mentioned that the occurrence of a
second nematic phase, called 're-entrant nematic' was
observed recently in binary mixtures of cyano compounds
at atmospheric pressure[14] as well as *in* pure compounds at
high pressures.[15]  The sequence of transitions (on cooling)
in such cases is

$$I \longrightarrow N \longrightarrow S_A \longrightarrow \text{re-entrant } N$$

The existence of a re-entrant nematic phase in a pure
compound at atmospheric pressure has been observed for
the first time by the author. These findings will be
discussed in chapter III.

## 1.4    Mesomorphism and chemical constitution

It has been fairly well established that compounds
which exhibit thermotropic mesomorphism vary widely in
their chemical constitution, however retaining one funda-
mental feature, viz., their geometrical anisotropy.   In
other words, with the exception of one series of compounds
observed recently by us (chapter VI) all compounds that
show thermotropic mesomorphism have a lath-like shape.  It
must be stressed, however, that generalisation like longer
the molecule the more likely it is to show a mesophase
cannot be made.  There are other factors apart from geometry
of the molecule, which must be considered.  These are the
various intermolecular forces which play an important role
in the mesomorphic behaviour of a particular compound;

(a)    dipole-dipole interactions: the direct interaction
       between permanent dipoles in the molecules,

(b)    induced dipole interactions arising from the mutual
       polarisation of the molecules by their permanent
       dipole moments.

(c)    dispersion forces:  the attractions between instantaneous

dipoles produced by spontaneous oscillations
of the electron clouds of the molecules.

Therefore, we can say that compounds which are
elongated and contain polar and polarisable groups are
most likely to exhibit liquid crystalline behaviour.
However, if a substituent is present in a position which
broadens the molecule, then the thermal stability of the
mesophase will be affected to a large extent and the
compound sometimes may lose its liquid crystalline proper-
Woe.   More often the substituents are attached in terminal
positions.   The following are a few representative groups
which are used as terminal substituents:

$CH_3(CH_2)_n-$,   $CH_3(CH_2)_nO-$,   $CH_3(CH_2)_nCO-$, $CN$,

$NO_2$,   $Cl$,   $Br$   and   $F$.
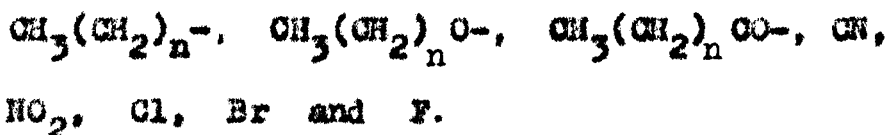
In addition to the anisotropy of the cohesive forces
between elongated molecules, the rigidity is an important
criterion for the formation of a mesophase.   The majority
of compounds that form liquid crystals on heating are
aromatic in character.   Aromatic nuclei are planar, rigid
and are polarisable.   Often suitable linkage groups are
attached between such nuclei.   Addition of substituents
mentioned in the previous paragraph in the para positions
of such a core generally leads to the formation of a

mesophase.   The linkage group itself must be rigid so
that the lath-like core of the molecule is retained.
Often the central group contains unsaturated bonds which
not only imposes rigidity but also increases the polarisa-
bility of the molecule.   Examples of central group are
$-CH=N-$,   $-N=N-$,   $-CH=CH-$,   $-C=C-$,   $-C-O-$, etc.   Although
the   $-C-O-$ group does not contain a double bond, the
steriochemistry of the unit retains the linearity of the
molecule.   Certain simple aliphatic open chain acids such
OR alkano 2,4-dienoic acid[16] (I) also exhibit a mesophase



I
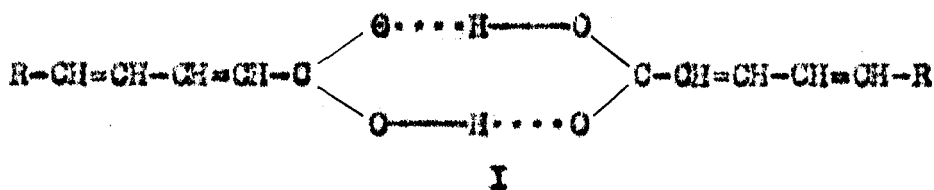
but these are rare.   However, alicyclic compounds which
are more rigid than aliphatic compounds, are potentially
more mesogenic.   Certain sterol derivatives with fused
alicyclic rings provide an important class of liquid
crystals, viz., the cholesteric type.[17,18,19]   Many hetero-
cyclic compounds exhibiting liquid crystalline properties
are also known.[20,21,22]

In the case of acids the central group involves
a ring formed by the dimerisation of carboxyl groups which
is due to intermolecular hydrogen bonding.   Because of the
elongated nature of such molecules, the acids exhibit

liquid orystalline properties, for example, para substi-
tuted benzoic and cinnamic acids of the type shown below.

$$n - C_3H_7O \text{---} \bigodot \text{---} C \begin{array}{c} O \cdots H \text{---} O \\ \\ O \text{---} H \cdots O \end{array} C \text{---} \bigodot \text{---} OC_3H_7 - n$$
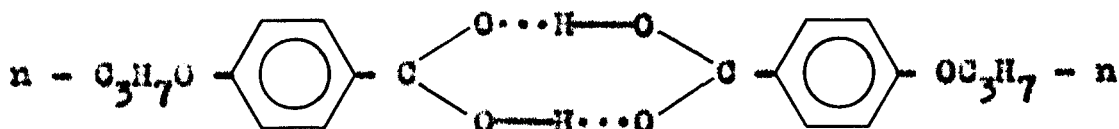
The melting point of compounds is the most unpredic-
table factor in connection with assessing the potentialities
of a new system to form liquid crystals.  Compounds with
strong intermolecular attractions in the crystal lattice
usually have high melting points irrespective of the mole-
cular weights.  As a result of this some compounds even-
though they possess other requisites of a potential mesogen,
do not exhibit a mesophase.  However, in some compounds a
monotropic mesophase may be observed if sufficient super-
cooling of the isotropic liquid occurs.  A delicate balance
between the molecular structure and the various attractive
forces is necessary for obtaining liquid crystal phases.

## 1.5   Effect of terminal and lateral substituents on liquid crystal behaviour

Replacement of a terminal hydrogen by a different

substituent generally enhances the potentiality of the
system to exhibit a mesophase and usually affects the
thermal stability of the parent system. In a majority
of the cases the substituted compounds have a higher
thermal stability. For example,

    <u>trans</u>-Cinnamic acid     K135I

    <u>trans</u>-<u>p</u>-Methoxycinnamic acid K175.5N190I.

In order to study the liquid crystalline behaviour
systematically, the general practice has been to prepare
a homologous series in which the terminal substituent such
as $CH_3(CH_2)_n-$ or $CH_3(CH_2)_nO-$ is lengthened by increasing
the number of methylene units successively. The plots of
the mesophase-isotropic liquid transition temperature
against the number of carbon atoms in the terminal chain
give smooth curve relationships and this is discussed in
the next section. A large number of such homologous series
of compounds have been reported in the literature and these
have been reviewed by Gray[23] in his excellent book. By
comparing the effects of a number of different terminal
substituents in the same molecular system, the relative
efficiency of a particular group in promoting liquid crystal
properties (both nematic and smectic) can be obtained.
After studying a large number of systems Gray[23] and Dave
and Dewar[24] have compiled terminal group efficiencies for

nematic, cholesteric and smectic phases. The terminal group efficiency of cholesteric and nematic phases are the same. The following average group efficiency has been proposed.[25]

Nematic group efficiency order:

$$Ph > CN > OMe > NO_2 > Cl > Br > NMe_2 > Me > F > H$$

Smectic group efficiency order:

$$Ph > Br > Cl > F > NMe_2 > Me > H > NO_2 > OMe > CN \quad .$$
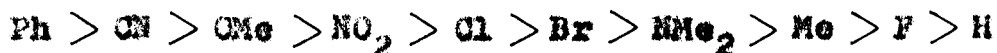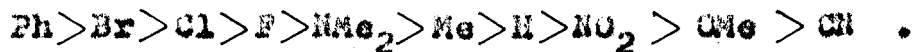
Although these orders may not strictly hold good for a given system, they will give a broad idea about the probability of obtaining a particular type of mesophase.

Usually, when substituents are introduced into positions along the sides of the elongated molecules, their breadths increase. The breadth of a molecule may be defined as the diameter of the smallest cylinder through which the molecule will pass, assuming that flexible parts such as alkyl chains do not interfere. The lateral substituent will have two opposing effects:

(a)   On account of broadening, the lateral separation of the elongated molecules increase, which leads to a decrease in the strength of the intermolecular lateral attractions. Both smectic and nematic thermal stabilities are affected as a result of this.

(b)     If the lateral substituent increases the
        polarity and molecular polarisability, it
        enhances the intermolecular cohesions.
        This increases the thermal stabilities of
        both nematic and smectic phases, especially
        that of the latter.

Experimental evidence[26] has shown that effect (a)
always predominates when the substituent increases the
molecular separation.  In certain cases such as 5-halogeno-
and 5-nitro-6-n-alkoxy-2 -naphthoic acids[27] the lateral
substituent may actually increase the thermal stability
of the mesophases.  In these compounds, the effective
breadth of the molecules is not altered and the dipolar
and polarisability effects mentioned above operate.  In
some other cases[28] a lateral substituent may sterically
affect the shape of the molecules.  For example, a 2- or
2'-substituent in a suitable biphenyl derivative may twist
the phenyl rings relative to each other about 1,1'-bond
so that there is a thickening of the molecules.  This
makes it difficult for the molecules to pack efficiently
in a parallel arrangement, thus weakening the lateral
intermolecular cohesions.  This results in a decreased
thermal stability of the liquid crystalline phases.


1.6   Mesomorphic behaviour in a homologous series
      When the liquid crystal transition temperatures are

plotted against the number of carbon atoms in the n-alkyl chain of the molecule, certain smooth curve relationships[23] are found for like transitions. However, the gradients of the curves may vary from series to series. We will present the results obtained on a few new homologous series of compounds in the subsequent chapters of this thesis. However, some of the salient features for a homologous series will be mentioned here. The N—I transition temperatures alternate and lie on two smooth curves, one for the odd homologues and the other for the even homologues. Usually, the first few homologues are purely nematic, the middle ones are both nematic and smectic and the higher homologues are purely smectic. It must again be mentioned that melting point trend in a homologous series is unpredictable and no generalisations can be made.

In a series which has a terminal n-alkyl chain, the $T_{N-I}$ for odd members have higher and those for even members lower values, as the series is ascended. In a n-alkoxy substituted series a reverse situation is observed. A common behaviour for the two separate curves for a series is that both either fall or rise initially and then level out, the alternation becoming less pronounced as the series is ascended. The falling types of curves are associated with the series whose members have relatively high N—I

temperatures. On the other hand curves which rise
initially and level out are associated with series whose
members have a relatively low N—I temperatures. Attempts
have been made[29,30] to explain the shapes of the N—I
curves by considering various factors such as anisotropy
of molecular polarisability, attractive dispersion forces
etc. But these arguments have not provided a complete
answer.

As a homologous series is ascended, the added
methylene unit enhances the later intermolecular attractions
which would increase the thermal stability of the smectic
phase. The usual trend is for the S—N temperature to
increase as the series is ascended. This has been observed
in a number of homologous series.[31,32,33] However, it must
be pointed out that in some cases the S—N transitions
are found to alternate in the series.[33,34,35] Suitable
explanations are yet to be given for these observed behaviour
of the S—N transitions. In majority of the cases, the
S—N curve merges with the N—I curve. In some cases,
the merging of S—N and N—I curves takes place only
after the S—N curve had reached a maximum and fallen again
slightly. S—I transitions closely resemble N—I transi-
tions in their temperature trends over homologous series.
Par a detailed description of the behaviour of various
liquid crystal transitions along a homologous series,

excellent reviews[23,25,36] are available.

## 1.7    Thermodynamic properties of liquid crystals

The identification and characterisation of phase
transitions is of general importance. A phase may be
defined as 'any homogeneous and physically distinct part
of a chemical system which is separated from other parts
of the system by definite boundary surfaces'.[37] Apart from
the temperatures of transition, many other physical proper-
ties such as the degree of order in a mesophase, the trends
in a homologous series of liquid crystals, can also be
determined from the thermodynamic data. The heat and
entropy of transition for homologous series of compounds
have also been measured. From the molar heats of transition
q, the entropy change of transition can be calculated using
the simple relationship $\Delta S = q/T$, where $T$ is the absolute
temperature. Since the heat of the melting transition is
very much larger than that of mesophase-isotropic transition,
these two have been sometimes referred to as the major and
minor calorimetric events respectively.

It was Arnold[38] who initiated the calorimetric study
of mesophases in a large number of compounds. He used the
classical adiabatic calorimetry for this purpose. However,
the majority of the thermodynamic data available now have
been determined from dynamic calorimetry. Differential

thermal analysis (DTA) and differential scanning calorimetry (DSC) methods have been applied for the determination of temperatures, heats of transition and heat capacities of various phases. Using DSC, one can get the information with a few milligrams of the sample quite rapidly. Transitions can be observed either on heating or cooling; temperatures can be measured to an accuracy of $\sim 0.1$ °C; transition energies can be determined to a fair degree of accuracy and a permanent recording is obtained showing the rate of transformation as a function of temperature. Moreover, solid phase polymorphism which is so common in mesophase forming materials, can also be detected and recorded. These transitions are sometimes difficult to detect optically. Finally, the absolute purities of the materials under investigation can be estimated. This is an important factor as the effect of purity[39,40] is quite considerable on the heat and temperatures of transition.

A large number of liquid crystal transitions have been detected and the available data gives a rough estimate of the probable heat of transition for a particular type of transition. In general, nematic and cholesteric mesophases exhibit small entropies of first order transition to the isotropic liquid. Smectic-isotropic liquid transition heats are five to ten times higher than those for N — I transitions. This indicates a higher molecular order in

the smectic phase compared to the nematic phase. Although the smectic-nematic transition involves a change from higher order to a lower order, a smectic A-nematic transition can be almost second order.[41] A smectic C-smectic A transition which involves a continuous change in the tilt angle has also bean found to be almost second order in character.[42] No generalisation can be made about the heats of solid-mesophase transition. This depends upon the packing of the molecules in the crystal lattice and moreover there can be solid-solid transitions. Therefore, no regular trend has been observed for this transition in a homologous series. We have found large heats for the mesophase-isotropic transition in disc-shaped molecules which will be discussed in chapter VI.

## 1.8    Applications of liquid crystals

Liquid crystals have been used in diverse fields such as various display systems, solvent for nuclear magnetic resonance speatrosoopy, stationary phases in gas-liquid chromatography, disposable thermometers, etc. However, since the discovery of the dynamic scattering effect by Heilmeier[43] in 1968, the majority of the applications of liquid crystals has been in the field of display technology. This has been possible because of the property of nematic liquid crystals to orient themselves in electric fields. The orientation of the molecules in the ON state depends

on whether their resultant dipole moment lies along the
major molecular axis (positive dielectric anisotropy) or
across the major molecular axis (negative dielectric
anisotropy). We will mention below the type of materials
needed for different types of display devices.

There are five important electro-optical effects
made use of in display technology and these will be very
briefly mentioned.

(i) Electrically controlled birefringence (ECB): For
this method, materials of either positive or negative
dielectric anisotropy may be used depending on whether
the molecules are aligned homogeneously or homeotropically.
In both cases the nematic phase should be of high resisti-
vity. The effect can be observed between crossed polarisers.

(ii) The dynamic scattering mode (DSM): For this effect
conducting nematic liquid crystals of negative dielectric
anisotropy are required. If the resistivity of the material
is high, then it can be suitably doped to achieve this
effect. DSM has certain disadvantages and therefore is
not widely used.

(iii) The twisted nematic (TN) effect: For this effect
nematic liquid crystals of high resistivity and high positive
dielectric anisotropy are required. Because of the

availability of excellent materials with suitable
characteristics this effect is very widely used, parti-
cularly for electronic watches and pocket calculators.

(iv)  The cholesteric memory effect:  For this, a
conducting cholesteric liquid crystal of negative dielec-
tric anisotropy is required.  Materials with high resisti-
vity can be suitably doped for conductivity.

(v)  The cholesteric-nematic phase change effect:  For
this effect, cholesteric liquid crystals of high resisti-
vity and high positive dielectric anisotropy are required.

A detailed description of these electro-optical
effects can be found in articles by Elliott,[44] Gray[45] and
in some books.[46,47]  Nematic and smectic liquid crystals
have been used by Kelker[48] in gas-liquid chromatography as
stationary phases, especially to separate geometrical isomers
and this technique has been reviewed by Schroeder.[49]  Smectic
liquid crystals have been used[50] in displays using infrared
laser addressing.  The unique colour displaying properties
of cholesteric liquid crystals which change with temperature,
have been detected by monitoring skin temperature using chole-
steric liquid crystals.  This is possible because of the fact
that the temperature of the skin in the vicinity of the
tumour is higher than in other parts.  The use of cholesteric
liquid crystals has also been reviewed by Gray.[51]

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