Synthesis, Characterization and Properties of some Chiral and Achiral Liquid Crystalline Molecules

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In
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By
NILESH KANTILAL PATEL

Department of Chemistry
Faculty of Science
The Maharaja Sayajirao University of Baroda
Vadodara 390 002
INDIA

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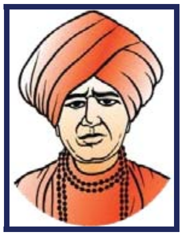

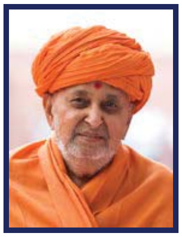

वक्रतुण्ड महाकाय सूर्यकोटिसमप्रभ ।
निर्विघ्नं कुरु मे देव सर्वकार्येषु सर्वदा ॥

Department of Chemistry
Centre of Advanced Studies in Chemistry
& DST-FIST sponsored Department
Faculty of Science, Vadodara 390 002
India Tel: +91-265-2795552

The Maharaja Sayajirao University of Baroda

CHL/

Date: 24/2/2014

CERTIFICATE

This is to certify that the thesis entitled **"Synthesis, Characterization and Properties of some Chiral and Achiral Liquid Crystalline Molecules"** submitted by **Mr. Nilesh Kantilal Patel,** for the award of the degree of **DOCTOR OF PHILOSOPHY in Chemistry** of The Maharaja Sayajirao University of Baroda, is his original research work and investigations carried out by him under my guidance and supervision in the Department of Chemistry, Faculty of Science, The Maharaja Sayajirao University of Baroda, Vadodara. The subject matter of this thesis has not been previously published or submitted to any other university for the award of any other degree, diploma, associateship, fellowship or any other similar title.

Prof. R. C. Tandel
Research Guide,
Formerly Associate Professor
Department of Chemistry, Faculty of Science,
The Maharaja Sayajirao University of Baroda,
Vadodara-390 002
Presently Professor
Applied Chemistry Department,
Faculty of Technology and Engineering,
The Maharaja Sayajirao University of Baroda,
Vadodara-390 001

24.02.14

Prof. N. D. Kulkarni
Head,
Department of Chemistry,
Faculty of Science,
The Maharaja Sayajirao University of Baroda,
Vadodara-390 002

Is Pyaar me Bewafai ka Dokha nahi hota,

Har Rishta itna Anokha nahi hota,

Fanaa kardo apni Zindagi,

Maa – Baap ke kadmon me kyun ki,

Yahi wo Pyaar hai jisme Dokha nahi hota . . .

Dedicated to

My beloved

Parents

DECLARATION

I hereby declare that the entire work embodied in this thesis entitled **"Synthesis, Characterization and Properties of some Chiral and Achiral Liquid Crystalline Molecules"** is the result of the experimental investigation carried out by me independently at Department of Chemistry, Faculty of Science, The Maharaja Sayajirao University of Baroda, Vadodara, under the guidance and supervision of Prof. R. C. Tandel. The work presented in this thesis has not been previously submitted and no part of this thesis work has formed the basis for the award of any other degree, diploma, fellowship, associateship or any other similar title.

24-2-14

Nilesh Kantilal Patel

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Nilesh Kantilal Patel

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List of abbreviations used in this Thesis

AC	Alternating Current
BP	Blue Phase
CLC	Cholesteric Liquid Crystal
Col_h	Columnar Hexagonal
Col_{ob}	Columnar Oblique
Col_r	Columnar Rectangular
CRT	Cathode Ray Tube
DCC	1,3-Dicyclohexylcarbodiimide
DCU	Dicyclohexylurea
DEAD	Diethylazodicarboxylate
DFT	Density Function Theory
DMAP	4-Dimethyl amino pyridine
DMF	N,N-Dimethyl formamide
DSC	Differential Scanning Calorimetry
EFIB	Electric Field-Induced Birefringence
EL	Electroluminescent
FLC	Ferroelectric Liquid Crystal
IR	Infra-red
Iso	Isotropic
ITO	Indium Tin Oxide
LC	Liquid Crystal
LCD	Liquid Crystal Display
MVA	Multi-domain Vertical Alignment
N	Nematic

N*	Chiral Nematic
NBS	N-Bromosuccinimide
N_D	Discotic Nematic
NLO	Non-Linear Optical
NMR	Nuclear Magnetic Resonance
PDLC	Polymer-Dispersed Liquid Crystal
PEM	Photo-Elastic Modulator
PL	Photoluminescent
POM	Polarized Optical Microscope
ppm	parts per million
P_s	Spontaneous Polarization
PSChLC	Polymer-Stabilized Cholesteric Liquid Crystal
p-TsOH	p-Toluenesulfonic acid
Sm	Smectic
SOR	Specific Optical Rotation
TBAF	t-Butyl Ammonium Fluoride
TBDPS	t-Butyldiphenylsilyl
T_g	Glass Transition Temperature
TGA	Thermo Gravimetric Analysis
TGB	Twist-Grain Boundary
TLC	Thin Layer Chromatography
TMS	Tetramethylsilane
TN	Twisted Nematic
$T_{N\text{-}I}$	Nematic Phase Stability
TTAB	Tetradecyl Trimethyl Ammonium Bromide

UTGB	Undulating Twist-Grain Boundary
UV	Ultraviolet
VA	Vertical Alignment

Chapter 1

INTRODUCTION

INTRODUCTION

1.1. Liquid Crystals

Liquid crystals are accepted as the fourth state of matter after solid, liquid and gas. The common states of matter, solid, liquid and gas differ mainly by the types of and degree of order present in the phase. These states of matter, however, are not sufficient to characterize the structures found in all systems. As most substances are heated, they go from a solid (usually crystalline, possessing high order) to an isotropic liquid (highly disordered). Some substances, however, exhibit intermediate states lacking some of the order found in solids, but possessing more order than found in liquids. These ordered fluids are called liquid crystals.

The term ‘liquid crystal’ (LC) is both intriguing and confusing; while it appears self-contradictory; the designation really is an attempt to describe a particular state of matter of great importance today, both scientifically and technologically. Thermodynamic phases of condensed matter with a degree of order intermediate between that of the crystalline solid and the simple liquid are called liquid crystals or mesophases (Figure 1). They occur as stable phases for many compounds; in fact one out of approximately two hundred synthesized organic compounds is a liquid crystalline material. The typical liquid crystal is highly anisotropic – in some cases simply an anisotropic liquid, in other cases solid-like in some directions.

The difference between crystals and liquids is that the molecules in a crystal are ordered whereas in a liquid they are not. The order in a crystal is usually both positional and orientational, in that the molecules are constrained both to occupy specific sites in a lattice and to point their molecular axes in specific directions. The molecules in liquids, on the other hand, diffuse randomly throughout the sample container with the molecular axes tumbling wildly. Interestingly enough, many phases with more order than present in liquids but less order than typical of crystals also exist in nature. These phases are grouped together and called liquid crystals, since they share properties normally associated with both liquids and crystals. The molecules in all liquid crystal phases diffuse about much like the molecules of a liquid, but they do so they maintain some degree of orientational order and sometimes some positional order also. The amount of order in a liquid crystal is quite small relative to a crystal. There is only a slight tendency for the molecules to point more in one direction than others or to spend more time in various positions than others.

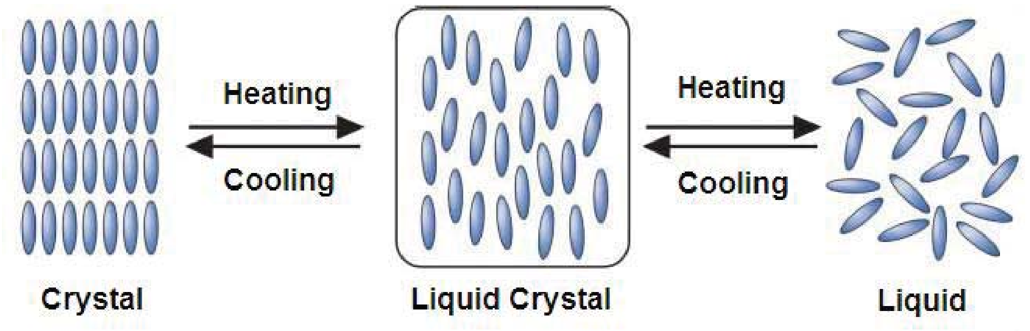


Figure 1. Basic structural difference among crystalline solid, liquid crystal and isotropic liquid.

1.2. Birefringence in Liquid Crystals

The speed that light propagates through isotropically structured transparent materials is determined by the refractive index, n. Light travels more slowly through high refractive index materials, whilst lower index materials permit light to travel more quickly. However, materials that consist of an anisotropic molecular structure will give rise to a correspondingly anisotropic refractive index. Light therefore travels at a different speed in one direction through these materials than it will in another. We call such materials birefringent. **Birefringence** or **Double Refraction** as it is also known occurs naturally in materials such as calcite, but is also a property of liquid crystals. More specifically, birefringent materials will have different refractive indices not only in different directions, but also for light of different polarizations. This is illustrated in the Figure 2a, where unpolarized light is used to view object through a birefringent crystal of calcite. The component of the light that is polarized in one direction is refracted through a different angle to the component of the light that is polarized in an orthogonal direction. This results in a double image of the object. These two rays of light are referred to as the 'ordinary ray' (which has been modulated by the ordinary refractive index, n_o) and the 'extraordinary ray' (which has been modulated by the extraordinary refractive index, n_e). The difference between ordinary and extraordinary refractive index (n_e - n_o) is called the birefringence.

The anisotropic molecular shape and alignment structure of nematic liquid crystals give them birefringence. The optic axis is determined by the director of the nematic (i.e.: in the direction of the long axis of the molecules). Consider two crossed polarizers. When an isotropic medium (like air) is between the polarizers, no light is permitted to pass through.

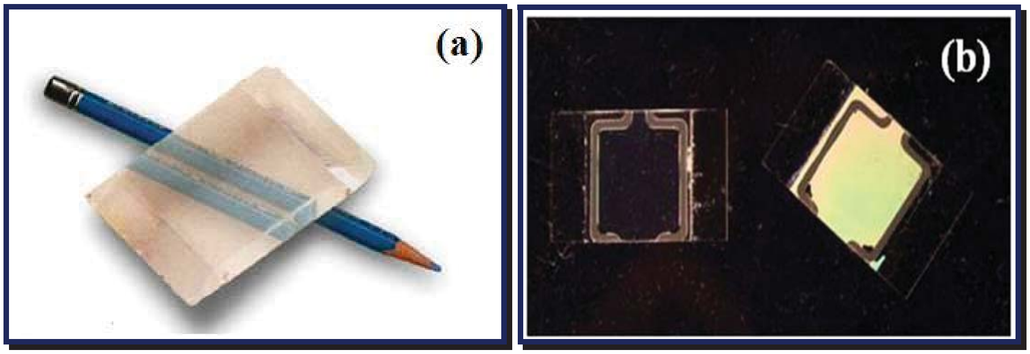


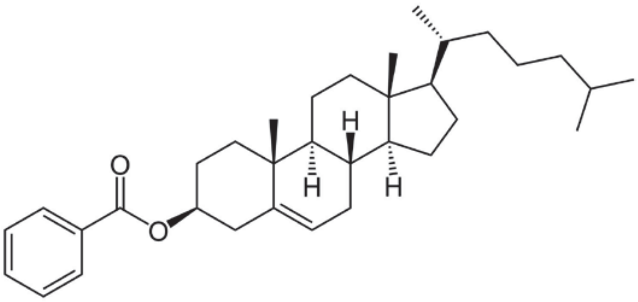
Figure 2. (a) Birefringence in a crystal of calcite; (b) Two identical nematic liquid crystal cells viewed between crossed polarizers.

However, consider now inserting a nematic liquid crystal cell between the crossed polarizers, its director aligned at an arbitrary angle to the 1st polarizer. Linearly polarized light emerging from the first polarizer can in general be considered to have two components of linear polarization: one aligned with the LC director, the other perpendicular to it. The birefringence of the LC will cause these two components of light to travel at different velocities, and therefore fall out of phase with each other. The result is that light emerging from the liquid crystal is elliptically polarized. This elliptically polarized light will be aligned with the 2nd polarizer twice every wave-cycle, and therefore some light is permitted to pass through, despite the two polarizers being crossed relative to each other. Liquid crystals therefore appear bright when viewed between crossed polarizers, except when the director of the LC is aligned either parallel or perpendicular to the incident polarization (Figure 2b).

1.3. Discovery and History of Liquid Crystals

During the middle of the nineteenth century, several people observing the covering of nerve fibers under a microscope noticed that they formed flexible and flowing shapes. Even more interesting was the fact that they produced unusual optical effects when polarized light was used. They were not able to explain the fluid properties typical of a liquid with the optical properties of certain solids. About this same time other workers were observing the crystallization of various substances. They noticed that some substances first changed to a non-crystalline form and then finally crystallized. Since impurities in a substance tend to produce a range of temperature over which both the liquid and solid phases coexist, it was not at all clear whether this was an effect due to impurities or something quite natural substances. They observed that in some cases the solid melted to form an opaque fluid and at a higher temperature the fluid turned clear. In one case, the investigators referred to the change at the higher temperature as a second melting point.

The discovery of liquid crystals is usually attributed to an Austrian botanist by the name of Friedrich Reinitzer. In 1888, he experimented with a substance Cholesteryl benzoate **1** and noted that it had two melting points [1].



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At 145.5 °C it melted from a solid to a cloudy liquid and at 178.5 °C it turned into a clear liquid. He also observed some unusual color behaviour upon cooling; first a pale blue color appeared as the clear liquid turned cloudy and second a bright blue-violet color was present as the cloudy liquid crystallized. Reinitzer sent samples of this substance to Otto Lehmann [2], a professor of natural philosophy (physics) in Germany. Lehman was one of the people studying the crystallization properties of various substances and Reinitzer wondered whether what he observed was related to what Lehmann was reporting. Lehmann had constructed a polarizing microscope with a stage on which he could precisely control the temperature of his samples. This instrument allowed him to observe the crystallization of his sample under controlled conditions. Lehmann observed Reinitzer's substance with his microscope and noted its similarity to some of his own samples. He first referred to them as soft crystals; later he used the term crystalline fluids. As he became more convinced that the opaque phase was a uniform phase of matter sharing properties both liquids and solids, he began to call them liquid crystals.

Shortly before 1960, interest in liquid crystals awakened in the United States, Great Britain, and the Soviet Union. An American chemist, Glenn Brown, published a lengthy review article on liquid crystals [3] and founded the Liquid Crystal Institute at Kent State University. George Gray, a British chemist, published a full-length book on liquid crystals, and I. G. Chistyakov started a group working on liquid crystals in Moscow. Research on liquid crystals also began in Germany and France. Progress was both swift and substantial.

Research on liquid crystals exploded during the 1970s and 1980s. In 1977, Chandrasekhar and his colleagues reported that not only rod-like i.e. calamitic molecules, but also compounds with disc-like molecular shape are able to form mesophases [4]. Currently more than 3000 discotic liquid crystals are known in the literature. The latest addition in the liquid crystal family is banana-shaped molecules in 1996 [5-11]. Typically their molecular structure can be regarded as being composed of three units; an angular central unit, two linear rigid cores and terminal chains. The discovery of ferroelectricity in non-chiral banana shaped molecules has led to a very intense research activity in the field. Several hundred bent molecular shape compounds have been synthesized so far. Bent shaped molecules provide access to mesophases with polar order and supramolecular chirality.

Scientifically, liquid crystals are an important phase for the investigation of cooperative phenomena, and liquid crystal synthesis is a field in its own right, especially in investigating structure-property relationships. Technologically, liquid crystals have become a part of our daily lives, first showing up in wristwatches and pocket calculators, but now being used for displays in all sorts of instrumentation, including portable computers and televisions. Their advantage was first their low power consumption and small size; now liquid crystal displays compete with other technologies for attractiveness, ease of viewing, cost, and durability.

1.4. Classification of Liquid Crystals

The classification of liquid crystals is shown in Figure 3. Liquid crystals can be classified in various ways. On the basis of molar mass of the constituent molecules one can categorize these materials in to low molar mass (monomeric, oligomeric etc.) and high molar mass (polymeric) liquid crystals; depending on how the liquid crystalline phase has been obtained whether by adding solvent (lyotropic) or by varying the temperature (thermotropic); depending the nature of the constituent molecules (organic, inorganic and organometallic); depending on the geometrical shape of the molecules (rod-like , disc-like, bent core); depending on the arrangement of the molecules in the liquid crystalline phase (nematic, smectic, columnar, helical, B phases etc).

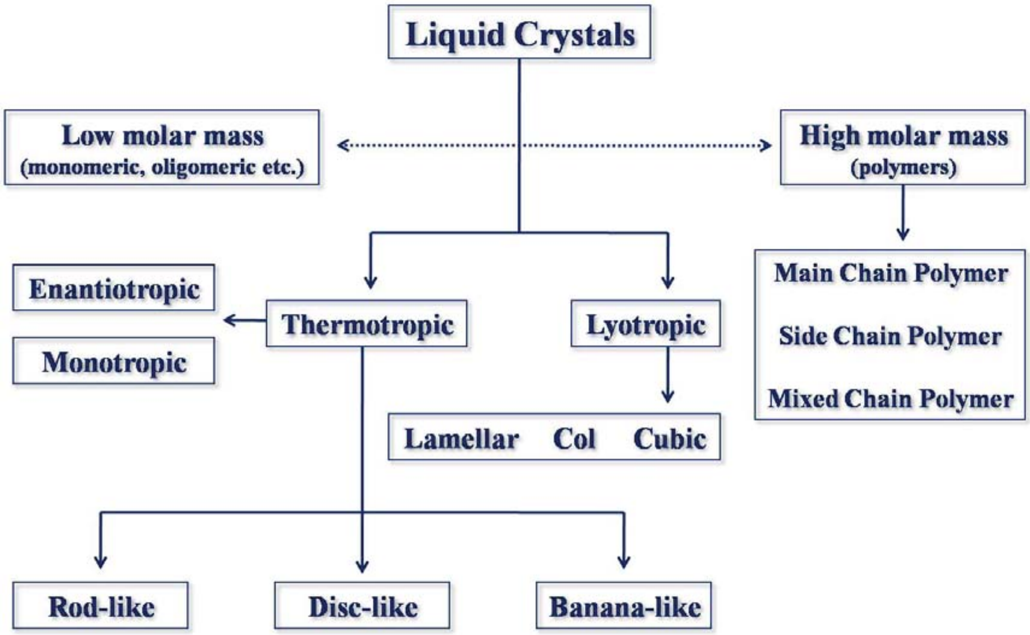


Figure 3. Classification of liquid crystals.

However, the most widely used classification of liquid crystals is into two major categories;

(a) Thermotropic liquid crystals (mesophase formation is temperature dependent), and

(b) Lyotropic liquid crystals (mesophase formation is solvent and concentration dependent).

If a compound displays both thermotropic and lyotropic liquid crystalline phases then it is called *Amphotropic* liquid crystal. Since this thesis deals with **thermotropic liquid crystals,** a very brief introduction of the lyotropic liquid crystals has been given below owing to their biological significance and they play an important role in living systems [12].

1.4.1. Lyotropic Liquid Crystals

A liquid crystalline material is called **lyotropic** if phases having long-ranged orientational order are induced by the addition of a solvent. Historically the term was used to describe materials composed of amphiphilic molecules. Such molecules are characterized by two distinct parts of contrasting character, a hydrophilic polar "head" and a hydrophobic non-polar "tail". Typical hydrophobic groups are saturated or unsaturated hydrocarbon chains. Examples of amphiphilic compounds are the salts of fatty acids, phospholipids. Many simple amphiphiles are used as detergents. Mesophase formation in lyotropic liquid crystals is controlled by concentration and/or temperature. Just as there are many different types of structural modifications for thermotropic liquid crystals, there are several different types of lyotropic liquid crystal phase structures. Each of these different types has a different extent of molecular ordering within the solvent matrix. Three different classes of lyotropic liquid crystal phase structures are widely recognized. These are the cubic, the hexagonal columnar and the lamellar phases (Figure 4), and their structures have each been classified by X-ray diffraction techniques.

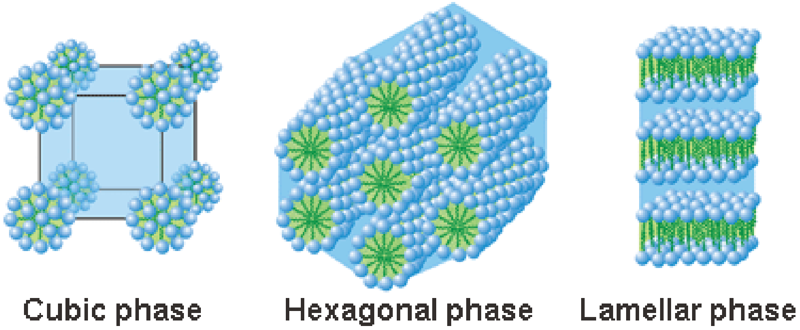


Figure 4. Lyotropic liquid crystalline phases.

1.4.2. Thermotropic Liquid Crystals

Thermotropic liquid crystals are those that occur in a certain range of temperature (Figure 5). If the temperature rise is too high, thermal motion will destroy the delicate and balance ordering of molecules, forcing the material to go into a usual isotropic liquid phase. At too low temperature, most mesomorphic materials will form a conventional crystal [13, 14].

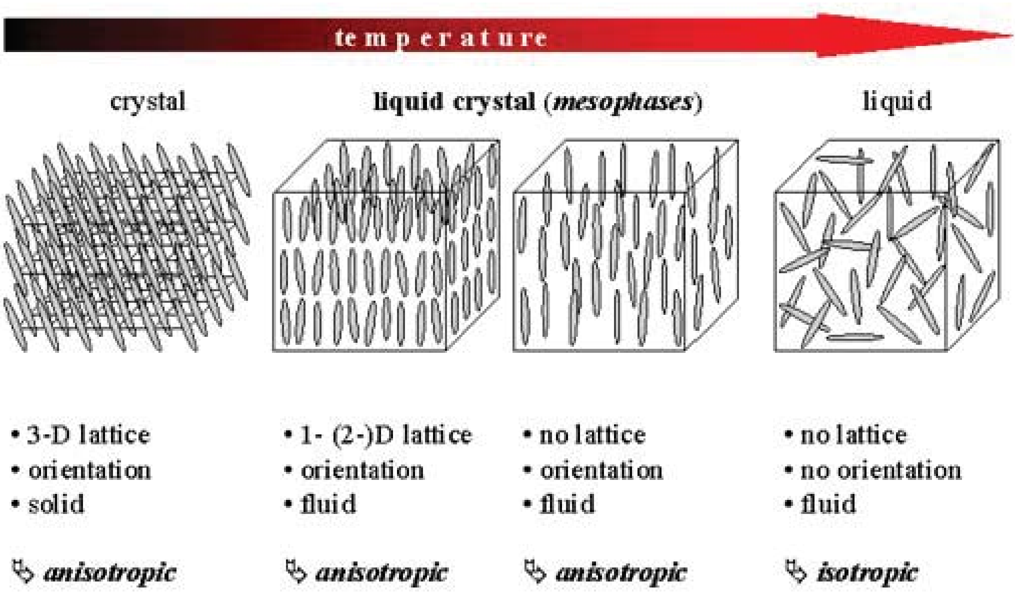


Figure 5. Intermediate liquid crystalline state between solid and liquid.

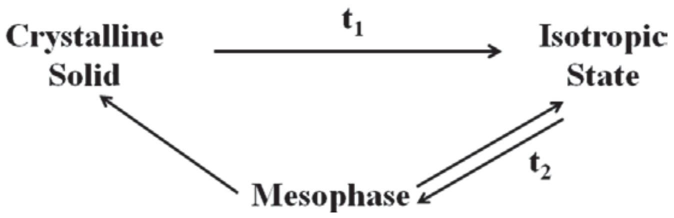
Many thermotropic LCs exhibit a range of phases as temperature is varied. The mesophase can be achieved either by heating a crystalline solid or by cooling an isotropic liquid. The temperature on heating at which the state of matter changes from that of a solid to that of a liquid crystal is called the ***melting point.*** For the liquid crystal-isotropic liquid transition the respective temperature is referred to as the ***clearing point.*** However there are some molecules which are liquid crystalline at room temperature. For these type of molecules only clearing point is observed. Some molecules have more than one type of crystalline or liquid crystalline arrangements. Crystal-to-crystal, crystal-to-mesophase and/or mesophase-to-mesophase transitions can be noticed in these systems depending on various interactions.

Enantiotropic Liquid Crystals

When thermodynamically stable mesophases are detect both on heating and on cooling then the phases are termed as *enantiotropic*. The transitions t_1 and t_2 take place at sharp definite temperatures and are precisely reversible. The schematic representation for enantiotropic mesophase is as under:

Monotropic Liquid Crystals

In some instances, a solid melts to an isotropic liquid at temperature t_1, on cooling the temperature may fall considerably below t_1 and mesophase may appear at temperature t_2 before the crystallization occurs. This type of mesomorphic state where, t_2 is at lower temperature than t_1 and is observed only on cooling is known as *monotropic* mesophase. The schematic representation for monotropic mesophase is as under:



Polymorphism

Many mesomorphic substances which have been studied are either of exclusively smectic structure or of exclusively nematic structure, but some can exist as both types of structures, smectic followed by nematic, and in these cases there are always definite transition temperatures defining the stability of different phases, which are completely reproducible. A few substances have been found to possess more than one smectic phase and here also the temperature range of stability of the different phases are sharply defined. This is known as *polymorphism*.

$$\text{Crystalline Solid} \overset{t_1}{\rightleftarrows} \text{Smectic I} \overset{t_2}{\rightleftarrows} \text{Smectic II} \overset{t_3}{\rightleftarrows} \text{Nematic or Cholesteric} \overset{t_4}{\rightleftarrows} \text{Isotropic Liquid}$$

On the basis of molecular shape of mesogens, thermotropic liquid crystals are classified into three main groups:

1. Calamitic (rod-like)
2. Discotic (disc-like)
3. Bent core (banana-like)

1.4.2.1. Calamitic Liquid Crystals

The most common type of molecules that forms liquid crystal phases is a rod-shaped molecule in which one molecular axis is much longer than the other two. Such compounds are called calamitic liquid crystals. The molecular length (l) is significantly greater than the molecular breadth (b) as depicted in Figure 6.

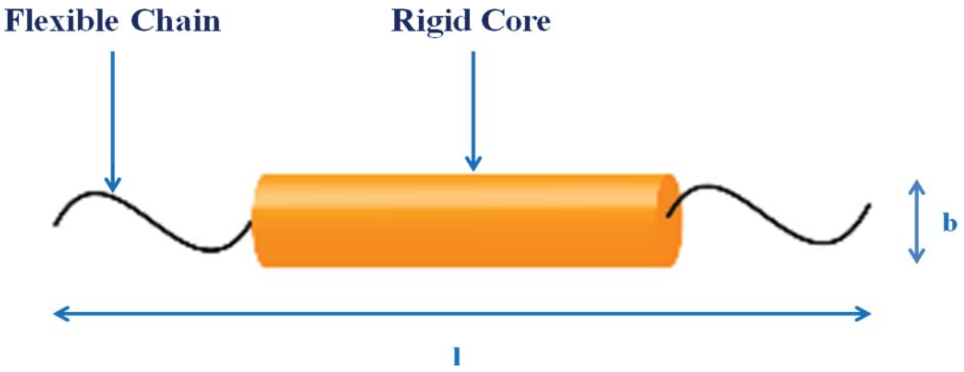


Figure 6. Representation of a calamitic liquid crystal where length (l) >> breadth (b).

In calamitic liquid crystal, the molecule is fairly rigid for a least some portion of its length, since it must maintain an elongated shape in order to produce interactions that favor alignment. Most of the calamitic liquid crystals consist of two or more ring structures, linked together directly or via rigid linking groups, plus hydrocarbon chains at each end. Figure 7 shows a general structural template that can be used to describe calamitic liquid crystalline compounds, including those that exhibit the nematic phase and smectic phases. A and B represents the rigid core units;

Y represents linking group; R and R’ represents the terminal chains linked to the rigid core through groups X and Z; M and N represents the lateral substituents (Table 1). Lateral substituents M and N are used to modify the mesophase morphology and the physical properties of LCs to generate enhanced properties for application purpose. Certain rigidity is required to provide the anisotropic molecular structure; these rigid cores are often aromatic as well as alicyclic ring systems. The rings can be directly linked or they may be joined by a linking group Y which maintains the linearity and polarizability anisotropy of the core. The flexible terminals R and R’ are required to ensure reasonably low melting points and to stabilize the molecular alignment within the mesophase structure.

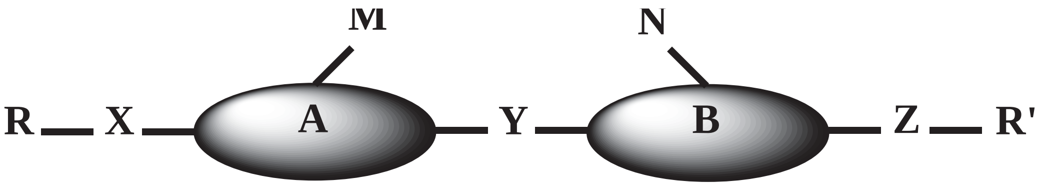


Figure 7. General structural template for calamitic liquid crystals.

Table 1. Different substituents for calamitic liquid crystals.

A and B (Rigid Core)	**Y (Linking Group)**	**R and R’ (Flexible Chain)**	**M and N (Lateral Substituents)**
1,4-Phenyl	-COO-	Alkyl chains	F/Cl/Br/I
2,5-Pyrimidinyl	—C≡C—	Alkoxy chains	CN
2,6-Naphtyl	$-CH_2-CH_2-$	CN	CH_3
1,4-Biphenyl	-CH=CH-	F/Cl/Br/I	NO_2
1,4-Cyclohexyl	$-(CH=CH)_n-$	NCS	
1,4-Cyclopentyl	-N=N-	NO_2	
	-CH=CH-COO-	CH_3	
	-CH=N-	CF_3	
	$-O-CH_2-CH_2-O-$		
	-COS-		

Depending on the arrangement of the mesogens in different mesophases, calamitic liquid crystals can be further classified into two types.

(a) Nematic Phase and

(b) Smectic Phase

1.4.2.1.1. Nematic Phase

The word nematic is derived from the Greek word *nema* meaning thread-like and has a special meaning in that many nematic phases have a characteristic threaded appearance when examined in polarized light under the microscope. Compared to smectic phases, nematic phase is less ordered as there is no layer arrangement. The term originates from the thread-like topological defects observed in nematics, which are formally called disclinations. Nematics also exhibit so-called "hedgehog" topological defects.

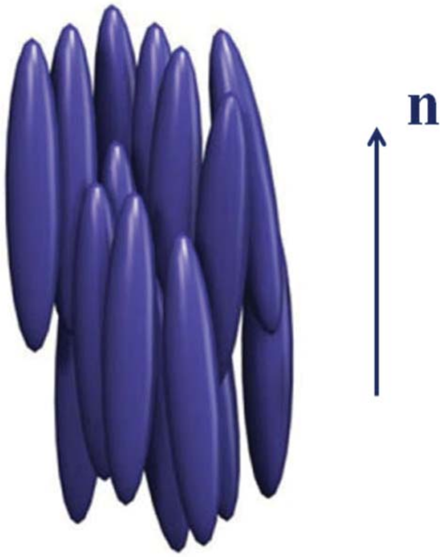


Figure 8. Orientation of molecules in Nematic Phase.

The nematic phase has no positional order, but has orientational order. They self-align to have long-range directional order with their long axes roughly parallel. Thus, the molecules are free to flow and their center of mass positions are randomly distributed as in a liquid, but still maintain their long-rang directional order. For an isotropic liquid, averaging molecular orientations gives no result, since there are as many molecules lying along one axis as another. In the nematic phase, averaging molecular orientations gives a definite preferred direction, which is referred to as the director (n). A simplified picture of the relative arrangement of the molecules in the nematic phase is shown in Figure 8. Nematics have fluidity similar to that of isotropic liquids but they can be easily aligned by an external magnetic or electric field. Aligned nematics have the optical properties of uniaxial crystals and this makes them extremely useful in liquid crystal displays (LCD) [13].

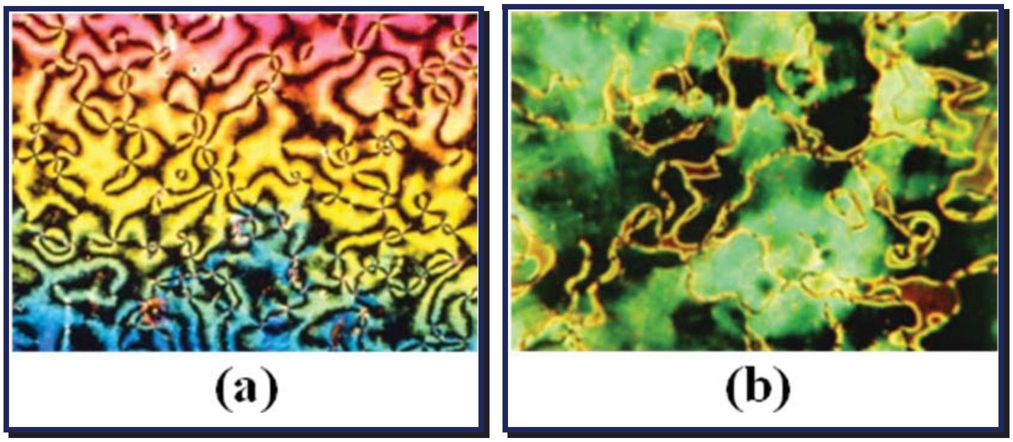

(a)
(b)

Figure 9. (a) Schlieren texture of nematic phase; (b) Nematic thread-like texture.

When viewed between crossed polarizers in polarizing microscope, thin films of liquid crystals exhibit ***Schlieren textures,*** as seen in the polarized optical microphotograph (Figure 9a). The black brushes are regions where the director is either parallel or perpendicular to the plane of polarization of the incident radiation, and the brushes meets at the disclinations. Figure 9b represents the thread-like texture of nematic liquid crystals.

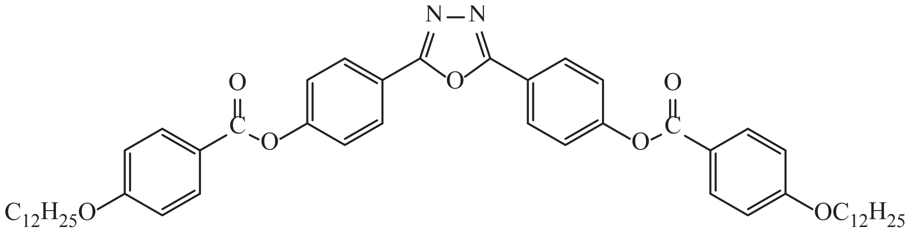
Biaxial Nematic

A **biaxial nematic** is a spatially homogeneous liquid crystal with three distinct optical axes. This is to be contrasted to a simple nematic, which has a single preferred axis, around which the system is rotationally symmetric. The symmetry group of a biaxial nematic is D_{2h} i.e. that of a rectangular right parallelepiped, having three orthogonal C_2 axes and three orthogonal mirror planes. In a frame co-aligned with optical axes the second rank order parameter tensor of a biaxial nematic has the form

$$Q = \begin{pmatrix} -\frac{1}{2}S + T & 0 & 0 \\ 0 & -\frac{1}{2}S - T & 0 \\ 0 & 0 & S \end{pmatrix}$$

Where S is the standard nematic scalar order parameter and T is a measure of the biaxiality.

The first report of a thermotropic biaxial nematic appeared in 2004 [15, 16] based on a boomerang shaped oxadiazole **bent-core mesogen**. The biaxial nematic phase for this particular compound only occurs at temperatures around 200 °C and is preceded by as yet unidentified smectic phases. It is also found that this material can segregate into chiral domains of opposite handedness [17]. For this to happen, the boomerang shaped molecules adopt a helical superstructure.



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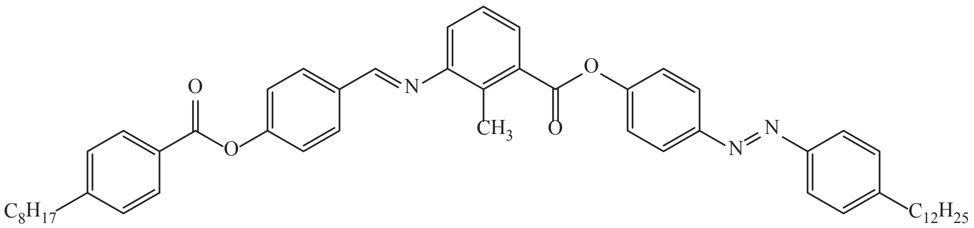
In one azo bent-core mesogen a thermal transition is found from a uniaxial N_u to a biaxial nematic N_b mesophase [16] as predicted by theory and simulation [18]. This transition is observed on heating from the N_u phase with Polarizing optical microscopy as a change in Schlieren texture and increased light transmittance and from X-ray diffraction as the splitting of the nematic reflection. The transition is a second order transition with low energy content and therefore not observed in Differential Scanning Calorimetry (DSC). The positional order parameters for the uniaxial nematic phase is 0.75 to 1.5 times the mesogen length and for the biaxial nematic phase 2 to 3.3 times the mesogen length.

Another strategy towards biaxial nematics is the use of mixtures of classical rod-like mesogens and disc-like discotic mesogens. The biaxial nematic phase is expected to be located below the minimum in the rod-disc phase diagram. In one study [19] a miscible system of rods and disks is actually found although the biaxial nematic phase remains elusive.



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1.4.2.1.2. Chiral Nematic (N*) Phase

The *Chiral Nematic* (or Cholesteric) liquid crystal phase is typically composed of nematic mesogenic molecules containing a chiral center which produces intermolecular forces that favor alignment between molecules at a slight angle to one another. This leads to the formation of a structure which can be visualized as a stack of very thin 2-D nematic-like layers with the director in each layer twisted with respect to those above and below. In this structure, the directors actually form in a continuous helical pattern about the layer normal as illustrated by the arrow in the following Figure 10 and animation. The arrow in the animation represents director orientation in the succession of layers along the stack.

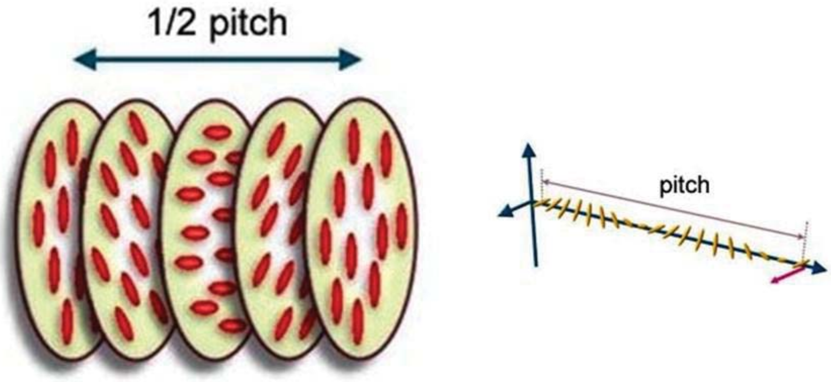


Figure 10. Schematic representation of the Chiral Nematic Phase.

The molecules shown are merely representations of the many chiral nematic mesogens lying in the slabs of infinitesimal thickness with a distribution of orientation around the director. This is not to be confused with the planar arrangement found in smectic mesophases.

An important characteristic of the chiral nematic mesophase is the ***pitch.*** The pitch ‘p’ is defined as the distance it takes for the director to rotate one full turn in the helix as illustrated in the above animation. A byproduct of the helical structure of the chiral nematic phase is its ability to selectively reflect light of wavelengths equal to the pitch length, so that a color will be reflected when the pitch is equal to the corresponding wavelength of light in the visible spectrum. The effect is based on the temperature dependence of the gradual change in director orientation between successive layers (illustrated above), which modifies the pitch length resulting in an alteration of the wavelength of reflected light according to the temperature. The angle at which the director changes can be made larger, and thus tighten the pitch, by increasing the temperature of the molecules, hence giving them more thermal energy. Similarly, decreasing the temperature of the molecules increases the pitch length of the chiral nematic liquid crystal. This makes it possible to build a liquid crystal thermometer that displays the temperature of its environment by the reflected color. Mixtures of various types of these liquid crystals are often used to create sensors with a wide variety of responses to temperature change. Such sensors are used for thermometers often in the form of heat sensitive films to detect flaws in circuit board connections, fluid flow patterns, condition of batteries, the presence of radiation, or in novelties such as "mood" rings. The following Figure 11 represents the different textures of the N* phase observed under Polarized Optical Microscope (POM).

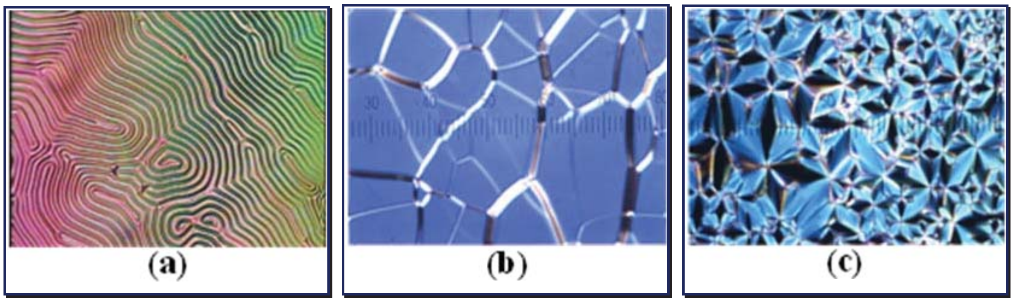


Figure 11. (a) Cholesteric fingerprint texture. The line pattern is due to the helical structure of the cholesteric phase, with the helical axis in the plane of the substrate; (b) Cholesteric ‘oily-streaks’ (Grandjean) texture except for the so called oily-streaks defects, the helical axis of the cholesteric phase is oriented perpendicular to the substrate plane; (c) Cholesteric fan-like texture. The fans are the back of focal-conic domains. A very similar texture, though not as smooth in appearance is often also observed for the smectic A phase.

1.4.2.1.3. Smectic Phase

The word smectic is derived from the Greek word meaning soap-like and has no specific significance. It was first used for ammonium oleate a soap-salt, it being the first smectic substance known. The mesophase is turbid and viscous forming greasy droplets. Smectic mesophases has a stratified structure; the long molecules are arranged side by side, parallel to one another and in series of layers, with their long axes approximately normal to the plane of layers. Though the smectic phase is a highly ordered phase, the spacing of the molecules within each layer is, however, not uniform as it would be in a true crystal. The fluidity of the phase is attributed to the fact that the layers can glide over one another in hundred like individual units in pack of cards as illustrated in Figure 12.

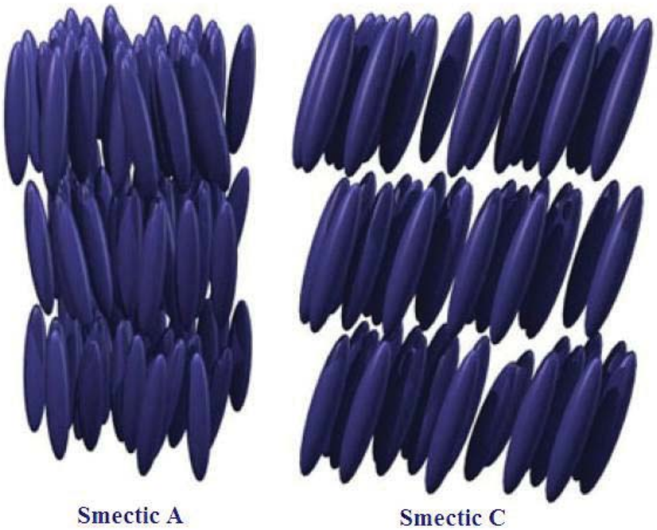


Figure 12. Schematic of alignment in the smectic phases; the smectic A (SmA) phase has molecules organized into layers; in the smectic C (SmC) phase, the molecules are tilted inside the layers.

From the structural point of view, the smectic liquid crystals have layered structured with a well-defined interlayer spacing, which can be measured by X-ray diffraction. Smectics are thus more ordered than nematics. A number of different classes of smectic liquid crystals are known which differ from each other in the way of layer formation namely SmA, SmB, SmC, SmF, SmI, etc. However, the best understood smectic phases are SmA and SmC (Figure 13). In **Smectic A,** the molecules are upright in each layer with their centers irregularly spaced in a liquid like fashion. The thickness of each layer is of the order of the length of free molecules. The lateral forces between the molecules are strong as compared with interlayer attraction. As a consequence, the layers are able to slide over one another relatively easily. Thus this phase has fluid properties, though it is usually much more viscous than nematic liquid crystal. The system is optically uniaxial.

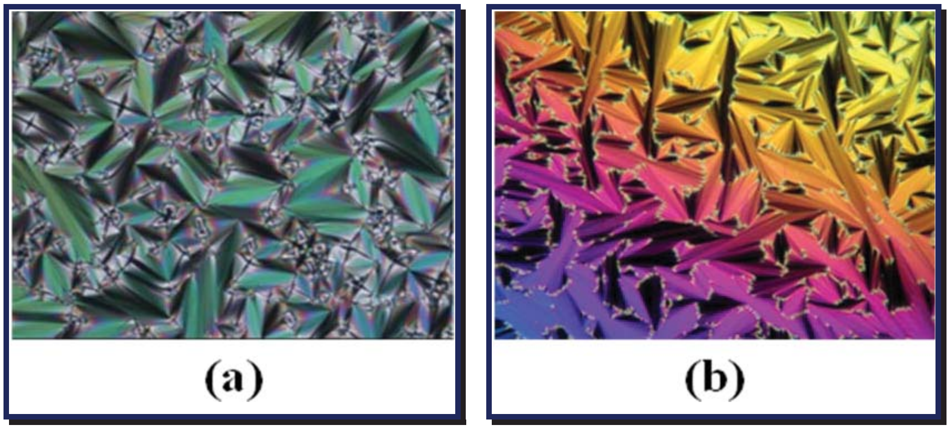


Figure 13. (a) Smectic A phase texture; (b) Smectic C phase texture

Smectic C is tilted form of smectic A. The molecules are inclined with respect to the layers. This phase is optically biaxial. Tilted smectic mesophases formed by chiral compounds or containing chiral mixtures are designated by superscript * namely SmC*, SmF*, etc.

Twist-Grain Boundary (TGB) Phase

More recently, a frustrated smectic liquid crystal phase has been predicted [20, 21] and discovered [22, 23] that occurs above the temperature of the normal smectic phases in some chiral materials; this phase is called the **Twist-Grain Boundary Phase (TGBA*).** This frustrated phase structure is based on the SmA phase (non-helical), but the strong chirality favors the formations of a helical structure which appears in the TGBA* phase. The TGBA* phase structure consists of blocks of SmA phase that are broken by screw dislocations which abruptly twist the molecular director of the next block through a small angle; this twisting continues through the phase to describe a helix. Accordingly, most of the microscopic phase structure consists of SmA, but as the screw dislocation begins the phase structure becomes SmC, and right in the centre of the screw dislocation a nematic phase structure exists. The screw dislocation is also helical and so the TGBA* phase has a double helix structure.

1.4.2.1.4. Smectic C* Phase

The chiral smectic C phase is the chiral analogue of the SmA phase. The structure of the SmC phase is lamellar and the molecules within the layers are tilted. When the molecules of the SmC phase are chiral, the phase structure is basically the same except that the molecular chirality causes a slight and gradual change in the direction of the molecular tilt (there is no change in the tilt angle with respect to the layer normal). This change in tilt direction from layer to layer gradually describes a helix (Figure 14).

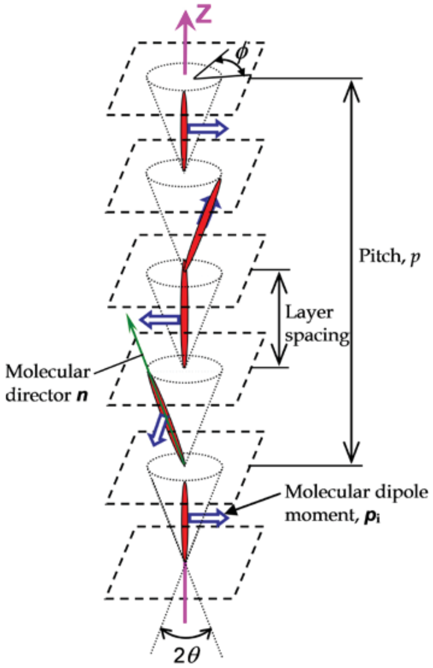


Figure 14. Helielectric structure of smectic C* liquid crystal.

When the tilted molecules of the SmC phase are chiral, the symmetry of a unit cell is reduced to solely a two-fold axis of rotation. Even though the molecules are undergoing rapid reorientational motion, the overall result of this drastic reduction of symmetry is to create an in-equivalence in the dipole moment along the C_2 axis. Such dipole in-equivalence generates a spontaneous polarization (P_s) along the C_2 axis, the direction of which changes with the changing tilt direction of the helix. Accordingly, P_s is reduced to zero throughout a bulk sample, hence the SmC* phase is truly defined as helielectric. However, a single layer of the chiral smectic C phase is ferroelectric and so by unwinding the helix a true ferroelectric phase is generated [24].

1.4.2.1.5. Ferro- antiferro- and ferrielectric chiral smectic C Phases

All the smectic phases with tilted structure exhibit ferroelectric properties. Due to their low symmetry they are able to exhibit spontaneous polarization and piezoelectric properties and are known as **ferroelectric liquid crystals.** It is well established that any tilted smectic phase derived from chiral molecules should possess a permanent electric polarization ***P*** which is oriented perpendicular to the director ***n*** and parallel to the smectic layer plane. The presence of permanent dipoles fundamentally alters the nature of the interactions between the molecules themselves and with any cell wall or applied electric field. The ferroelectric SmC* phase (Figure 15) has become very important for its fast electronic switching of the twist of the layers with respect to tilt direction. The optical activity in this phase arises as a result of molecular asymmetry. A macroscopic helical arrangement of molecules occurs as a result of precession of the molecular tilt about an axis perpendicular to the layer planes. The tilt direction is rotated through an angle upon moving from one layer to the next. As the rotation is in a constant direction, a helix is formed which is either left- or right-handed. The helical twist sense is determined by the nature and position of the chiral centre with respect to the central core of other mesogenic material.

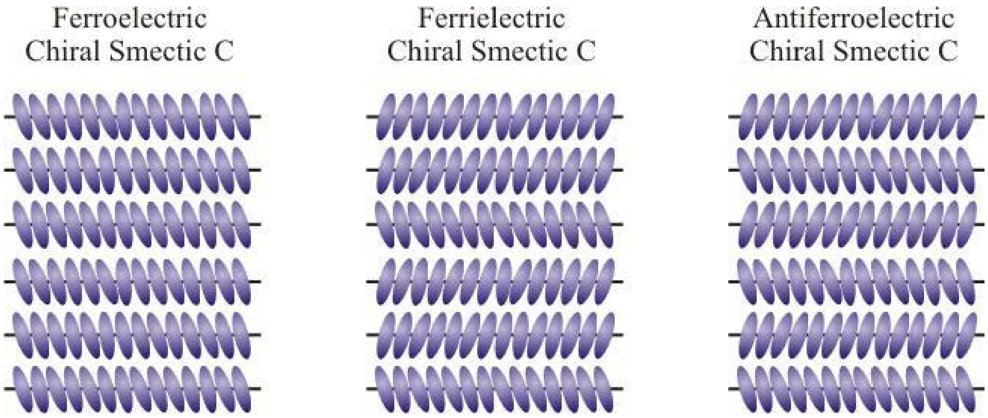


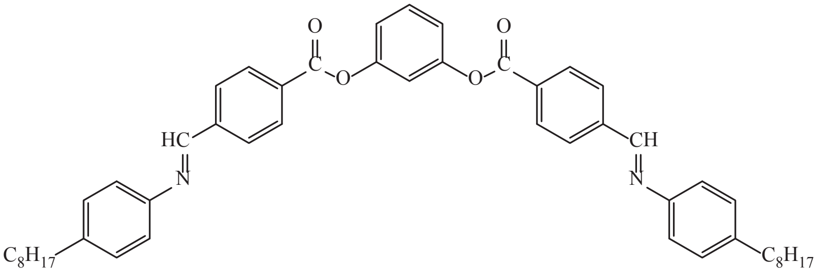
Figure 15. The arrangement of molecules in ferro- ferri- and antiferroelectric chiral smectic C phases.

Two new associated phenomena [25-27] are known as **antiferroelectric** and **ferrielectric phases** (Figure 15). In an antiferroelectric SmC* phase the molecular layers are arranged in such a way that the polarization directions in subsequent layers point in opposite directions which result in an average of the spontaneous polarization equal to zero. This structure is evidenced by the fact that when a strong electric field is applied to this phase, the layer ordering is perturbed and the phase returns to a normal ferroelectric phase. In the switching of antiferroelectric phases three states are produced: one antiferroelectric and two ferroelectric. This tristable switching occurs at a defined electric field and thus the presence of a sharp switching threshold may be useful in display applications which require multiplexing with grey scales. The structure of ferroelectric SmC* is repeated every 360° rotation of the helix, whereas the helical structure of the antiferroelectric phase repeats every 180° rotation. The phase, therefore, appears to have a relatively short pitch and the pitch appears to change quite significantly as the temperature is changed.

In a ferrielectric smectic phase, the layers are stacked in such a way that there is a net overall spontaneous polarization. The number of layers of opposite polarization is not equal. There could be, for example, twice as many layers where the polarization direction is opposite to that of the other layer type. It also has been suggested that the stacking of the layers has two interpenetrating sub lattices. There will be alternating layer structures, i.e., two layers tilted to the right and one to the left, with this arrangement repeating itself through the bulk of the phase. Thus, the ferroelectric phase will have a measurable polarization.

1.4.2.2. Banana Liquid Crystals

Banana liquid crystals represent a new sub-field of liquid crystals. Banana liquid crystals were synthesized by Vorländer in 1929 [28]. But, they were not recognized as interesting materials for a long time. In 1993, Matsunaga *et al.* [29] synthesized the banana liquid crystals but reported only the mesomorphic properties. At the same time, Cladis and Brand [30] displayed the model structure of SmCP, which has C_{2v} symmetry and is similar to the B_2 phase realized in banana-shaped mesogens. The real breakthrough came from Niori *et al.* [5] who reported ferroelectric properties in the achiral compound **4** namely 1,3-phenylene bis[4-(4-n-octyliminomethyl)benzoate].



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Thus, the observation of switchable mesophases from achiral molecules opened a new sub-field of thermotropic liquid crystals. Their results can be summarized as follows:

1. The ferroelectricity in achiral compounds can be ascribed to C_{2v} symmetry of the molecular packing.
2. Because of their shape, these compounds form a peculiar smectic phase in which the molecules are closely packed along the bend direction. Due to this, there exists a P_s along the bend direction. This polarization direction can be reversed by applying an electric field.
3. The observation of a single current peak in the triangular wave electric field experiment point towards a ferroelectric ordering of the molecules in the ground state.
4. X-ray diffraction studies on this compound showed SmA type arrangement of the molecules within the layers.

In the year 1997, an International Workshop on Banana-shaped mesogens: “Chirality by Achiral Molecules”, was organized in Berlin to recommend a nomenclature for the different mesophases exhibited by banana-shaped 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. Seven mesophases were identified and assigned the symbols $\mathbf{B_1}$ to the most recent $\mathbf{B_8}$**.** The suffixes indicate the chronological order of the discovery of the mesophases. The three vectors (1) layer normal, (2) tilt direction and (3) polar axis (kink direction) make-up an orthogonal system which may be left or right handed. Right and left handed systems are mirror images of one another and hence chiral (Figure 16). If there is a dipole moment associated with the kink this axis becomes the polar axis which is responsible for ferroelectricity. Macroscopic samples are achiral. If chirality alters from layer to layer in a sample, it is called racemic. If there are macroscopic domains with homogeneous chirality, the sample is homochiral.

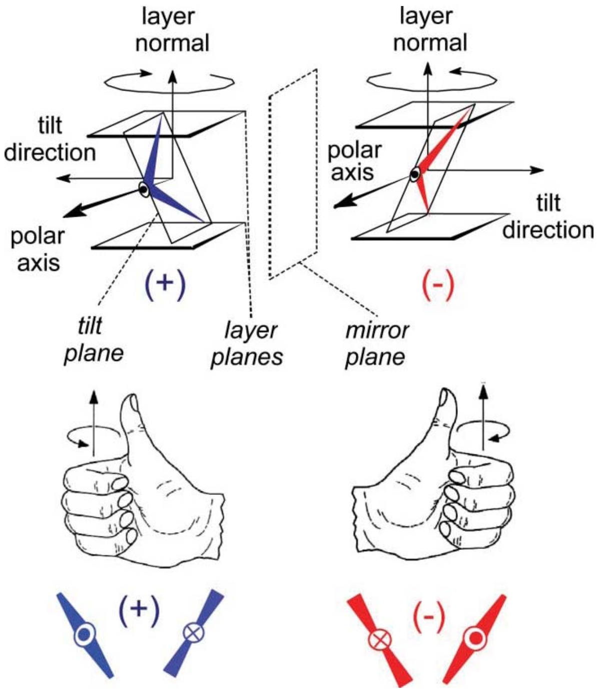
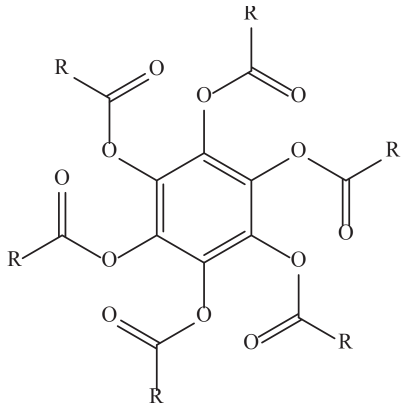


Figure 16. Origin of the superstructural chirality within the smectic phases of banana liquid crystals (Reproduced from R. A. Reddy and C. Tschierske, *J. Mater. Chem.*, **16**(10), 907-961, 2006).

1.4.2.3. Discotic Liquid Crystals

Disc-shaped mesogens are called Discotic liquid crystals [31-33]. Mesomorphism in discotic materials was first reported in 1977 by S. Chandrasekhar [4]. He reported that what is probably the first observation of thermotropic mesomorphism in pure, single-component systems of relatively simple plate-like or more appropriately disk-like, molecules. They synthesized a number of benzene hexa-*n*-alkanoates (**5**) and from thermodynamic, optical and X-ray studies, it was established that these materials form a new class of liquid crystals in which molecules are stacked one on the top of other in columns that constitute a hexagonal arrangement. This opened a whole new field of fascinating liquid crystal research.



R = n-C_4H_9 to C_9H_{19}

5

The simplest, least-ordered mesophase formed by disc-like molecules is the **nematic (N_D) phase,** which is characterized by the presence of orientational but not positional order: the axes of the discs all point in more or less the same direction, but their positions are randomized (Figure 17). This is directly analogous to the nematic phase of rod-like molecules but, in terms of the more ordered liquid crystal phases, discogens are different. Whereas the rod-like molecules give rise to smectic phases (molecular orientational order together with positional ordering in one dimension), the disc-like molecules give rise to **columnar phases** (molecular orientational order together with positional ordering in two dimensions). In these **columnar phases,** the molecules are stacked on top of one another like a pile of pennies. The columns are then arranged on a regular two-dimensional lattice. Like their smectic counterparts, they show rich poly-mesomorphism. They are classified primarily in terms of their symmetry. Columns stacked on a regular hexagonal lattice are called **Col_h**; on a rectangular lattice, **Col_r**; an oblique lattice, **Col_{ob}**; etc. (Figure 17). Sometimes these groups are sub-divided according to the orientation of the discs with respect to the columnar axis and/or the degree of ordering within the column, although division by 'degree of order' tends to be somewhat subjective. There is usually short-range positional order of the discs along the length of the columns but there is never any correlation of the positions of the discs between columns.

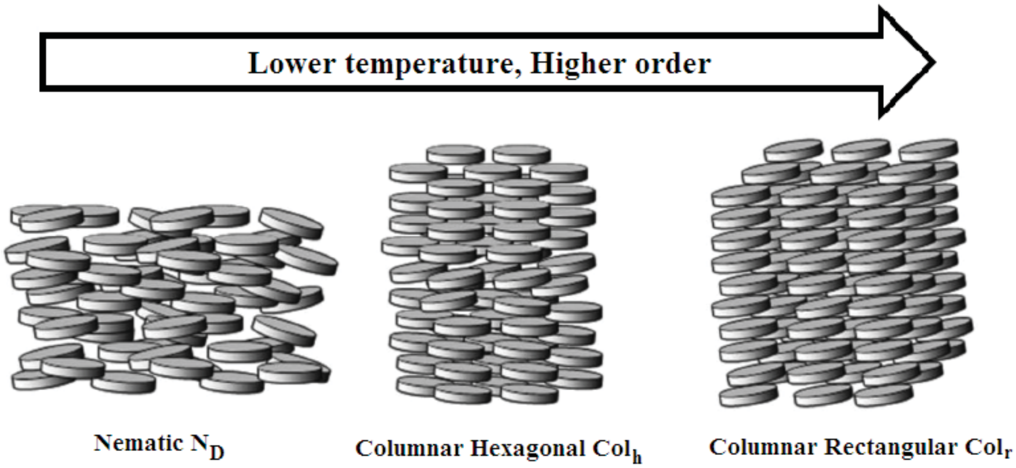


Figure 17. Most common discotic liquid crystal phases.

1.5. Effect of Chemical Constitution on Mesomorphism

There is a close relationship between the molecular structure and the mesomorphism of a compound. However, a characteristic structure of a molecule that will show the mesomorphic state cannot be easily defined. Organic compounds are the ones known to exhibit the liquid crystalline state. Mesomorphism is found in aromatic as well as in aliphatic compounds. An example of a simple aliphatic compound showing liquid crystallinity is 2,4-nonadienoic acid while the simplest aromatic compounds are p-propoxy benzoic acid, p-butyl benzoic acid, p-azoxy anisole, p-methoxy cinnamic acid etc. The existence of mesomorphic states may be explained by considering the molecular structure of compounds showing liquid crystalline behaviour.

It is known that the anisotropic shape and the resulting anisotropic forces of a rod-shaped molecule can give rise to the formation of the liquid crystal phases [34-37]. The requirement that the molecule of a nematogen possesses a fairly rigid core structure, usually with terminal substituents associated with it. Chemists [13, 34, 35] have been trying to understand the factors, which relate molecular structure to liquid crystal properties. For certain properties like liquid crystal transition temperatures this has been reasonably successful, but for others such as elastic constants and molecular dynamics, there is still much work to be done. A general structural template for calamitic liquid crystals is shown in Figure 7.

1.5.1. Effect of the Core

The core is usually defined as the rigid unit which is constructed from linearly linked ring units; often defined to include any linking groups and any lateral substituents that are connected to the rings. Calamitic liquid crystals usually possess 1,4-phenyl aromatic rings (Figure 18) but 2,5-pyrimidine and 2,6-naphthalene are also common.

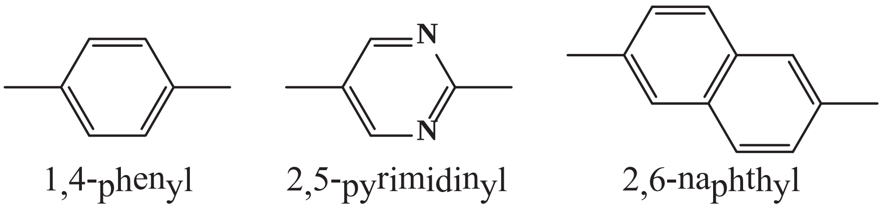
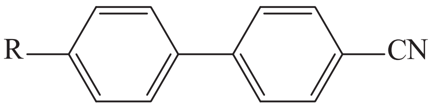

1,4-phenyl 2,5-pyrimidinyl 2,6-naphthyl

Figure 18. Selected aromatic core units.

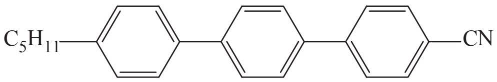
The aromatic core in conjugation with a terminal cyano group confers a positive dielectric anisotropy and a reasonably high optical anisotropy (birefringence). They have a reasonably low viscosity and more importantly, they are chemically and photochemically stable. These materials are still successfully used in simple watch and calculator type twisted nematic display devices. The 4,4'-disubstituted biphenyl core is used here. This core provides high nematic phase stability (T_{N-I}) values due to the anti-parallel correlations that exist and in effect enhance the true molecular length. The alkylcyanobiphenyls **(6)** were the first commercially viable nematic liquid crystals for use in display devices. The compounds have low melting points with high T_{N-I} values.



R = n-C_nH_{2n+1}; where, n = 1 to 10.

6

Adding another aromatic ring i.e. three ring systems extends the linear core and gives a much higher length to breadth ratio and increased polarizability anisotropy, which results in a large increase in the $T_{N\text{-}I}$ (compound **7**). This compound is used in commercial nematic mixtures of biphenyls to extend $T_{N\text{-}I}$. The three ring system compound **8** also possesses the strong smectic phase stability [13].



Cr 130.0 N 239.0 Iso

7

Cr 192.0 SmA 213.0 Iso

8

1.5.2. Effect of Linking Groups

Linking groups are the structural units that connect one part of a core to another for the formation of liquid crystalline molecules (Figure 19).

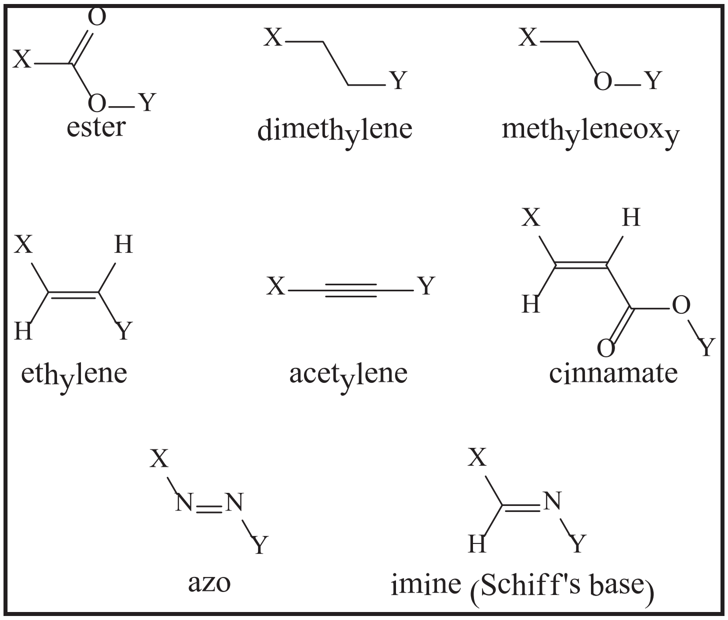
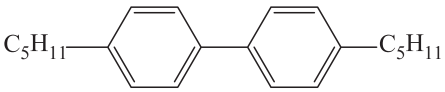


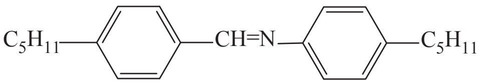
Figure 19. Selected linking groups in liquid crystals.

Linking groups maintains the linearity of the core and are compatible with the rest of the structure. They are used to extend the length and polarizability anisotropy of the molecular core in order to enhance the liquid crystal phase stability by more than any increase in melting point, producing wider liquid crystal phase ranges. Where the parent compounds exhibit smectic phases (e.g., compound **9**) the linked materials (compounds **10** and **11**) tend to exhibit the nematic phase.



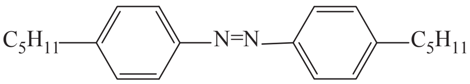
Cr 26.0 Sm 47.6 Sm 52.2 Iso

9



Cr 34.5 (SmB 32.0) N 43.7 Iso

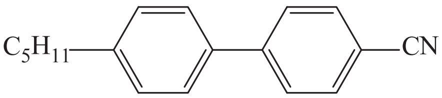
10



Cr 49.5 (N 38.0) Iso

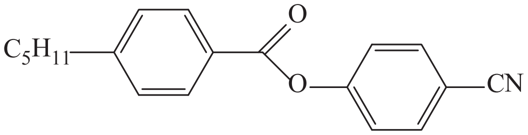
11

The ester -COO- unit is the most commonly used linking group in liquid crystals because it is relatively stable, easily synthesized and can provide useful liquid crystals with low melting points. It is a planar linking group with a degree of polarizability due to the π-electrons associated with the carbonyl group but the ester linkage is not a completely conjugative unit. Accordingly, the ester linkage can be used to link two aromatic units or an alicyclic unit to an aromatic unit and hence the ester is a versatile linking unit capable of being used in a wide range of different molecular circumstances. In comparison with the directly linked analogue **12,** the ester unit in compound **13** has clearly enhanced the $T_{N\text{-}I}$ but the melting point has risen by more, resulting in just a monotropic nematogen.



Cr 24.0 N 35.0 Iso

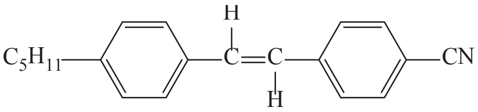
12



Cr 64.5 (N 55.5) Iso

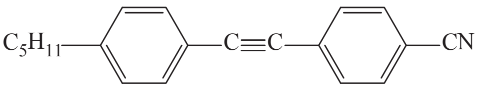
13

The ethylene linkage in compound **14** is a fully conjugative linking group that enhances the longitudinal polarizability and extends the molecular length while maintaining linearity; accordingly the $T_{N\text{-}I}$ value is very high. The acetylene linkage, illustrated in compound **15** maintains the rigidity, linearity and the polarizability of the core and extends the molecular length. Although the $T_{N\text{-}I}$ value of **15** is much higher than the parent cyanobiphenyl (**12**), it is still lower than the **14** because the conjugativity of the linkage is less effective and the polarizability is lower.



Cr 55.1 N 101.0 Iso

14



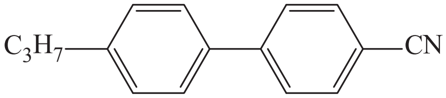
Cr 79.5 (N 70.5) Iso

15

1.5.3. Effect of Terminal Substituents

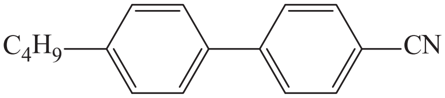
Most of the liquid crystal molecules contain at least one terminal alkyl/alkoxy chain. These chains are responsible for stabilizing the molecular orientations necessary for liquid crystal phase generation. Polar groups enable considerable and significant intermolecular forces of attraction which serve to stabilize molecular orientation. The choice of terminal moieties is crucial in the generation of a specific type of liquid crystal phase. The theories of Maier and Saupe [36] suggest, that the nematic-isotropic transition temperature of the compound is related to the molecular polarizability of the molecule, which is invariably related to the terminal group and its influence on the conjugation within the molecule.

The melting points are considerably reduced by increasing chain length because of increased flexibility, but when very long, the excessive van der Waals intermolecular forces of attraction increase melting points; so a compromise of chain length is required for a low melting point. The $T_{N\text{-}I}$ value decreases with increasing chain length but does begin to increase with the very long terminal chains of compounds. However, in the trend of $T_{N\text{-}I}$ value, the odd-member chains generate higher TN-I values than the even-member chains. This effect is called **odd-even effect.** This can be explained by the fact that the extra carbon which makes the chain even does so by generating a derivation from the linear structure of more favorable all-*trans* conformation of the chain illustrated by compounds **16** and **17.**



Cr 66.0 (N 25.5) Iso

16



Cr 48.0 (N 16.5) Iso

17

As the length of the terminal chain increases, the smectic tendency increases and eventually eliminates the nematic phase. This is because the long chains become attracted and intertwined, which facilitates the lamellar packing required for smectic phase generation.

Branching the alkyl chain, has a significant effect on the liquid crystal phase behaviour of a material. Chain-branching enables chirality to be introduced into a molecule which is of a special significance. The branching in a terminal chain causes a disruption in the molecular packing which often reduces melting points and invariably reduces the liquid crystal phase stability. Where the branch is close to the core, the disruption is considerably enhanced which results in a low melting point.

The terminal group efficiency orders for the Nematic phase [34] could be represented as:

$$\mathrm{Ph > NHCOCH_3 > CN > OCH_3 > NO_2 > Cl > Br > N(CH_3)_2 > CH_3 > F > H}$$

In Smectic phases lateral attractions are important, thus the group efficiency order is different from that of the Nematic phase. For SmA phases, the order is often reported as [34]:

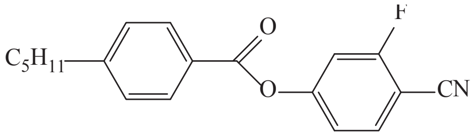
$$\mathrm{Ph > Br > Cl > F > N(CH_3) > CH_3 > H > OCH_3 > CN}$$

1.5.4. Effect of Lateral Substituents

A lateral substituent is one that is attached off the linear axis of the molecule, usually on the side of an aromatic core. However, lateral substituents have also been incorporated into alicyclic moieties. Many materials have been synthesized with lateral fluoro substituents and lateral cyano groups on a cyclohexane ring. A wide range of different lateral substituents have been incorporated into many different liquid crystal systems, these includes F, Cl, CN, NO_2, CH_3, CF_3.

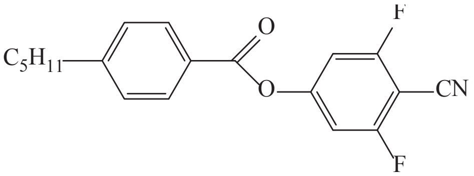
Lateral substituent is important in both nematic systems and smectic systems; however, because of the particular disruption to the lamellar packing, necessary for smectic phases, lateral substitution nearly always reduces smectic phase stability more than nematic phase stability. However, the depression of smectic phase stability by a lateral substituent can be partially countered if polar lateral substituent is used. Lamellar packing is disrupted by increased size but enhanced by increased polarity.

The most commonly used lateral substituent is the fluoro substituent. The fluoro substituent is very small in size. A lateral fluoro substituent exerts a steric effect. Additionally, the fluoro substituent is of high polarity. This unique combination of steric and polarity effects enables some significant tailoring of physical properties without too much disruption to the liquid crystal phase stability. Lateral fluoro substitution is very important in nematic mixtures and in ferroelectric host mixtures because of the improved physical properties for display device applications. The chloro substituent actually generates a greater dipole than the fluoro substituent because of the longer bond to carbon; however, the greater size of the chloro substituent renders it of little use as lateral substituent in liquid crystalline compounds due to low liquid crystal phase stability and high viscosity. When compared with compound **13,** the lateral fluoro substituent of compound **18** causes a fall in the melting point and a similar reduction in the T_{N-I} is seen. The introduction of a second fluoro substituent (compound **19**) further reduces the T_{N-I} value but the melting point is little changed.



Cr 30.5 (N 24.5) Iso

18



Cr 29.5 (N -8.0) Iso

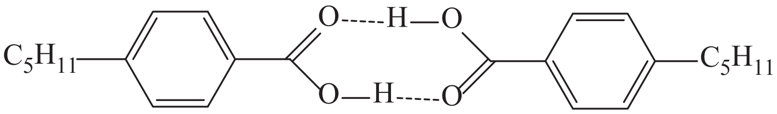
19

Lateral fluoro substitution has been widely used to generate materials that exhibit the SmC phase and can be used as ferroelectric host materials. A lateral fluoro substituent will provide a lateral dipole that can cause molecular tilting. Compounds that have a high smectic, but not necessarily tilted, character make ideal candidates for fluoro substitution. The fluoro substituent considerably reduces the smectic character, but the remaining smectic character is often of the tilted variety. Moreover, a lateral fluoro substituent is commonly used to convert highly smectic materials into pure nematogens with low melting points.

Lateral substitution has also been used in alicyclic systems where the lateral substituent is located at the axial position of the terminal chain location. Alkyl chains as lateral groups have also been included in the liquid crystalline systems.

1.5.5. Effect of Hydrogen Bonding

Hydrogen bonding is one of the most important interactions in nature. It plays a significant role in molecular recognition and self-assembly [37]. The first compounds found to exhibit liquid crystalline behaviour due to hydrogen bond formation were 4-substituted benzoic acids themselves discovered by Jones and coworkers [38, 39]. These compounds dimerize through intermolecular hydrogen bonding leading to a lengthening of the rigid-rod moiety, which in turn induces liquid crystallinity. The intermolecular hydrogen bonding of these compounds is represented as follow:



Cr 88.0 N 126.5 Iso

20

After the work of Jones, Kato and Frechet enlarged the hydrogen-bonded liquid-crystal systems by assembling 4-alkoxybenzoic acids with pyridine derivatives, which led to increased interests in the study of hydrogen-bonded liquid crystals [40]. Since then, a large number of hydrogen-bonded mesogenic materials have been synthesized and their properties have been thoroughly investigated [41-48].

1.6. Identification of Liquid Crystal Phases

Among all the liquid crystalline phases, some mesophases are of particular importance because of their technological applications. It is therefore important to be able to identify the types of liquid crystal phases that are exhibited by a compound or a mixture of compounds. Following major methods are employed to identify and characterize the liquid crystal phases.

Optical Polarizing Microscopy

The most widely used technique of liquid crystal phase identification is optical polarizing microscopy. This technique reveals that each different liquid crystal phase has a distinct optical texture. However, the identification of liquid crystal phases through optical polarizing microscopy is often difficult and requires a lot of experience.

Differential Scanning Calorimetry (DSC)

DSC is always employed as a complementary tool to optical microscopy and reveals the presence of mesophases and liquid crystal phases by detecting the enthalpy change that is associated with a phase transition. However, this technique cannot identify the type of liquid crystal phase, but the level of enthalpy change does give some information about the degree of molecular ordering within a mesophase.

X-ray Analysis

The ultimate technique for the identification and classification of mesophases is X-ray analysis. X-ray analysis of a liquid crystal will map the positions of the molecules within the phase and hence determine the phase structure and classification to which the particular phase belongs. However, to maximize information, aligned samples are needed.

Miscibility Studies

Liquid crystal phases present in novel compounds can be identified and classified by miscibility studies. The material with unknown mesophases is mixed with a known material that possesses mesophases that have already been identified (ultimately by X-ray analysis). If a particular mesophase of the unknown material is completely miscible with a known mesophase of the known material, then it can be concluded that the two phases of each compound are identical and belong to the same miscibility group.

Other Techniques

Other techniques used to identify the structure of mesophases and liquid crystalline mesophases includes:

- **Neutron Scattering Studies:** This technique is usually of partially deuteriated samples
- **Nuclear Magnetic Resonance (NMR) studies:** This study is particularly useful for analyzing lyotropic liquid crystal phases.

1.7. Applications of Liquid Crystals

Liquid Crystal Displays (LCDs)

The most common application of liquid crystal technology is LCDs. This field has grown into a multi-billion dollar industry and many significant scientific and engineering discoveries have been made. A LCD differs fundamentally from an electronic display device such as a cathode ray tube (CRT), in that the LCD generates no light of its own but it scatters light. A LCD offers two advantages over other display devices:

(a) It reflects light instead of generating it; thus it can be viewed under a wide range of light conditions including direct sunlight or a flood light, and
(b) It does not emit light and therefore draws much less power than light emitting diodes and is less expensive.

LCD devices consisting of digital readouts are used in watches, calculators, outdoor electronic advertising, mobile phones, LCD projectors, flat TV screens and several other instruments. Some liquid crystal substances could be useful in the computer industry, for making new computer elements with high memory capacity.

There are many types of liquid crystal displays, each with unique properties. The most common LCD that is used for everyday items like watches and calculators is called the **twisted nematic** (TN) display. The TN display is based on the precisely controlled realignment of liquid crystal molecules between different ordered molecular configurations under the action of an applied electric field. This is achieved with little power consumption and at low operating voltages. Figure 20 illustrates the OFF and the ON-state of a single picture element (pixel) of a TN-LCD operating in the normally white mode, i.e., a mode in which light is transmitted when no electrical field is applied to the liquid crystal.

In the OFF state, i.e., when no electrical field is applied, a twisted configuration (i.e. helical structure or helix) of nematic liquid crystal molecules is formed between two glass plates, G in the Figure 20, which are separated by several spacers and coated with transparent electrodes, E_1 and E_2. The electrodes themselves are coated with alignment layers that precisely twist the liquid crystal by 90° when no external field is present (Figure 20a). If a light source with the proper polarization of about half, shines on the front of the LCD, the light will pass through the first polarizer, P_2 and then into the liquid crystal, where it is rotated by the helical structure. The light is then properly polarized to pass through the second polarizer, P_1, set at 90° to the first. The light then passes through the back of the cell and the image, I, appears transparent.

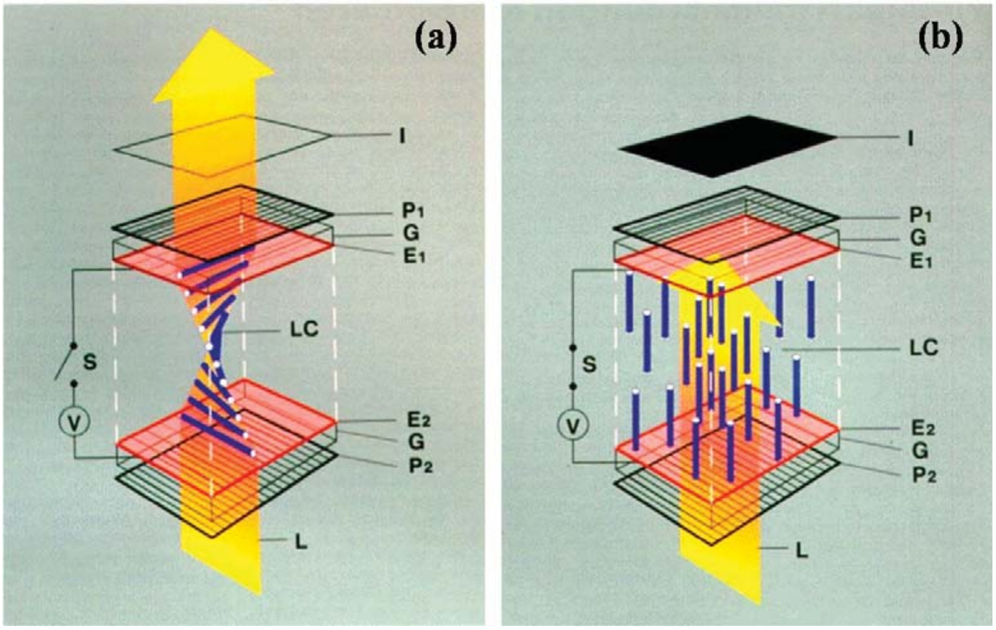


Figure 20. Operating principle of the twisted-nematic LCD; (a) off-state; (b) on-state

In the ON state, i.e., when a field is applied between the two electrodes, the crystal re-aligns itself with the external field (Figure 20b). This breaks the careful twist in the crystal and fails to re-orient the polarized light passing through the crystal. In this case the light is blocked by the rear polarizer, P_1, and the image, I, appears opaque. The amount of opacity can be controlled by varying the voltage. At voltages near the threshold, only some of the crystals will re-align, and the display will be partially transparent. As the voltage is increased, more of the crystals will re-align until it becomes completely switched. A voltage of about 1 V is required to make the crystal align itself with the field, and no current passes through the crystal itself. Thus the electrical power required for that action is very low.

To display information with a twisted nematic liquid crystal, the transparent electrodes are structured by photo-lithography to form a matrix or other pattern of electrodes. Only one of the electrodes has to be patterned in this way, the other can remain continuous (common electrode). For low information content numerical and alpha-numerical TN-LCDs, like digital watches or calculators, segmented electrodes are sufficient. If more complex data or graphics information have to be displayed, a matrix arrangement of electrodes is used. Obviously, the voltage controlled addressing of matrix displays, such as in LCD-screens for computer monitors or flat television screens, is more complex than with segmented electrodes. These matrix LCDs necessitate integration of additional non-linear electronic elements into each picture element of the display in order to allow the addressing of individual picture elements without crosstalk (unintended activation of non-addressed pixels).

Temperature Sensors

Liquid crystals have found a number of applications as temperature sensors. The most common device is based on the selective reflection of light by chiral nematic liquid crystals. A chiral nematic material under incident white light reflects light with a wave length determined by the pitch of the chiral nematic and the angle of viewing. Thus some chiral nematic liquid crystals appear highly colored in white light. Since the pitch of a chiral nematic is temperature dependent, the color observed changes as the temperature changes. Thus the color of the display can be used to determine the temperature. Proper use of various mixtures allows the production of temperature sensors with a wide variety of responses. All that is necessary to produce extremely sensitive temperature sensors is to mix together the proper compounds so that the smectic-chiral nematic phase transition occurs at the appropriate temperature.

Such devices have found use in a wide variety of applications. These include fever thermometers, hot warning indicators, monitoring devices for the packaging of chilled food, battery testers as well as novelties such as ‘stress’ and ‘mood’ sensors (Figure 21), and color changing jewellery, clothing, decorative wall coverings and tiles. Such a device has also been used in medical thermography, in which application of a color sensitive device to a part of the body produces a visual image of the temperature variations of the skin, thus providing an aid for the diagnosis of circulation problems and cancerous growths.

Figure 21. Heart mood ring and color codes.

Optical Imaging

An application of liquid crystals that is only now being explored is optical imaging and recording. In this technology, a liquid crystal cell is placed between two layers of photoconductor. Light is applied to the photoconductor, which increases the material's conductivity. This causes an electric field to develop in the liquid crystal corresponding to the intensity of the light. The electric pattern can be transmitted by an electrode, which enables the image to be recorded. This technology is still being developed and is one of the most promising areas of liquid crystal research.

Medical Applications

Liquid crystals can be used as a safe and effective means for evaluation of complex pain states associated with arthritis, soft tissue injuries and back-pain diseases. It facilitates identification of the damage to the nervous system. In case of nerve injuries, a temperature increase is observed in the area of the nerve distribution, which becomes colder during later stages of the injury. The area of this abnormality (temperature variation) remains confined to the area of the distribution of the injured nerve. The skin temperature changes can be measured by using liquid crystals, leading to the greater depth of understanding of the scientific basis behind skin temperature changes. Usually, the test using liquid crystals is carried out in a room kept at constant temperature. The patient's back or extremities to be examined are kept in contact with liquid crystal sheets. The liquid crystal sheets are allowed to equilibrate with the body temperature for 10-15 minutes. The color pattern of liquid crystal sheet indicates the temperature pattern over the skin.

Liquid crystalline materials can be used as a vehicle for controlled drug delivery system [49, 50]. In Gynecology, where there is a possibility that a cesarean section may be necessary, liquid crystals can be used to locate the placenta, thus avoiding the need for an X-ray. In Psychology, cholesteric liquid crystals could be used as lie-detectors.

Liquid Crystals in Cosmetics [51]

A large part of cosmetic products are made in the form of emulsions, a form that allows the simultaneous use of lipophilic and hydrophilic ingredients in the required dosages. A product in the form of an emulsion also has the advantage of having the most convenient appearance and texture that also facilitates its application. They can be formulated to be liquid, milk type emulsions of variable consistency, creams, or even super liquid spray able emulsions. Finally, we should also consider the fact that an emulsion is the best carrier for active ingredients and functional substances. Liquid crystals provide the following advantages to emulsion.

1. **Stability:** Emulsion stability of the multilayers around the oil droplets act as a barrier to coalescence. If oil droplets coalesce emulsion breaks. This barrier for coalescence acts as increased stability property of the emulsion.
2. **Prolonged hydration:** Lamellar liquid crystalline and gel network contain water layer, which shows that 50% of the water of oil in water (o/w) emulsion can be bound to such structures. Such water is less prone to evaporation when applied to the skin and permits a long lasting moisturisation / hydrating effect, necessary for drug entry.
3. **Controlled drug delivery:** Liquid crystals prevent the fast release of the drug dissolved in the oil phase of an emulsion. This is attributed to the lamellar liquid crystalline multilayer, which reduces the interfacial transport of a drug dissolved within the oil droplets. Microscopic observation under polarized light shows the exceptional thickness of liquid crystalline lamellar layer around the oil droplets.

Polymer-Dispersed Liquid Crystals (PDLCs)

Polymer-dispersed liquid crystals (PDLCs) are a relatively new class of materials that hold promise for many applications ranging from switchable windows to projection displays. These materials are simply a combined application of polymers and liquid crystals. These materials are the focus of extensive research in the display industry. PDLCs consist of liquid crystal droplets that are dispersed in a solid polymer matrix. The resulting material is a sort of "swiss cheese" polymer with liquid crystal droplets filling in the holes. These tiny droplets (a few microns across for practical applications) are responsible for the unique behavior of the material. By changing the orientation of the liquid crystal molecules with an electric field, it is possible to vary the intensity of transmitted light.

Polymer-dispersed liquid crystals hold potential for a variety of electro-optic applications ranging from displays to light shutters. Below, we illustrate their applications as electro-optic light shutters in the construction of privacy windows. PDLC windows are based on the ability of the nematic director of the liquid crystal droplets to align under an electric field. In a typical application, a thin PDLC film (about 25 microns thick) is deposited between clear plastic covers. The plastic substrates are coated with a very thin layer of a conducting material known as indium tin oxide (ITO). The following diagram (Figure 22) shows a simple PDLC cell.

Transmission of light through a PDLC window depends primarily on scattering which in turn depends on the difference in refractive index between droplets and their environment. In the case of high droplet density, the environment consists mainly of other droplets, which makes the relative orientation of their directors an important factor. The droplets are anisotropic with the index of refraction parallel to the director different from that perpendicular to it.

In the field OFF, the random array of droplet orientation provides significant differences in indices and hence strong scattering. In this state, the cell appears opaque. When a voltage is applied, however, the director of the individual droplets aligns with the field. There is now little difference in refractive index for neighboring droplets, and the cell appears transparent.

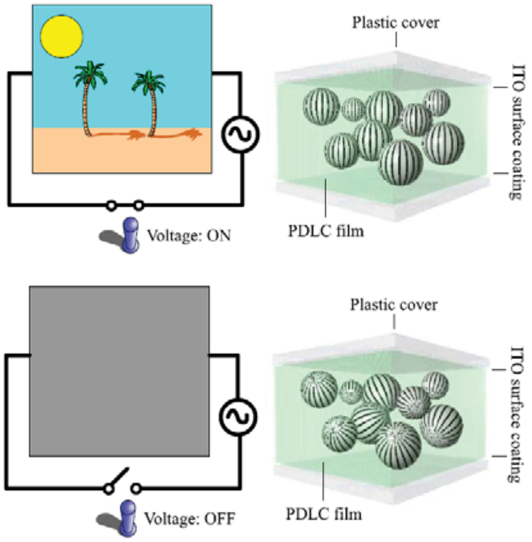


Figure 22. A simple PDLC Cell.

Other Applications of Liquid Crystals

- **Polymer Liquid Crystals** can be processed into high-strength fibers. The spontaneous orientational order of main chain polymer liquid crystals can be ‘frozen in’ during the fabrication process, yielding much stronger fibers than if the polymer chains remained unorientated. The best-known example is Kevlar, a polyamide.
- Liquid crystals can be used in chromatographic applications, where they create an anisotropic medium that promotes the separation of similar compounds.
- Various kinds of optical switches can also be designed using liquid crystal devices.
- Liquid crystals can be used as anisotropic solvents for certain spectrographic applications. In NMR spectroscopy, the NMR spectra of compounds dissolved in a nematic liquid crystal allow the anisotropic dipolar and quadrupolar splitting and anisotropic chemical shifts to be measured.
- The sensitivity of cholesteric liquid crystals to react to pressure as well as temperature by color changes is used to make some very interesting publicity materials and toys.
- Cholesteric liquid crystals can be used as an analytical tool to detect the presence of very small amount of gases or vapors by color changes to the extent of about 1 ppm.

1.8. References

[1] F. Reinitzer, *Wiener Monatsh. Chem.*, **9**, 421–441, 1888.

[2] O. Lehmann, *Z. Phys. Chem.*, **4**, 462–472, 1889.

[3] G. H. Brown, *Anal. Chem.*, **41**(13), 26A-39A, 1969.

[4] S. Chandrasekhar, B. K. Sadashiva and K. A. Suresh, *Pramana*, **9**(5), 471-480, 1977.

[5] T. Niori, T. Sekine, J. Watanabe, T. Furukawa and H. Takezoe, *J. Mater. Chem.*, **6**(7), 1231-1233, 1996.

[6] G. Pelzl, S. Diele and W. Weissflog, *Adv. Mater*., **11**(9), 707-724, 1999.

[7] C. Tschierske and G. Dantlgraber, *Pramana*, **61**(2), 455-481, 2003.

[8] M. B. Ros, J. L. Serrano, M. R. de la Fuente and C. L. Folcia, *J. Mater. Chem.*, **15**(48), 5093-5098, 2005.

[9] R. A. Reddy and C. Tschierske, *J. Mater. Chem.*, **16**(10), 907-961, 2006.

[10] H. Takezoe and Y. Takanishi, *Jpn. J. Appl. Phys*., **45**(2A), 597-625, 2006.

[11] J. Etxebarria and M. B. Ros, *J. Mater. Chem*., **18**(25), 2919-2926, 2008.

[12] I. Koltover, T. Salditt, J. O. Radler and C. R. Safinya, *Science*, **281**, 78-81, 1998.

[13] P. J. Collings and M. Hird, *Introduction to Liquid Crystals Chemistry and Physics*, Taylor and Francis, London, 1997.

[14] S. Chandrasekhar, *Liquid Crystals*, Cambridge University Press, Cambridge, 1992.

[15] L. A. Madsen, T. J. Dingemans, M. Nakata and E. T. Samulski, *Phys. Rev. Lett.*, **92**(14), 145505/1-145505/4, 2004.

[16] V. Prasad, S. -W. Kang, K. A. Suresh, L. Joshi, Q. Wang and S. Kumar, *J. Am. Chem. Soc.*, **127**(49), 17224-17227, 2005.

[17] V. Görtz and J. W. Goodby, *Chem. Commun.*, (26), 3262-3264, 2005.

[18] M. A. Bates and G. R. Luckhurst, *Phys. Rev. E.*, **72**(5-1), 051702/1-051702/15, 2005.

[19] D. Apreutesei and G. H. Mehl, *Chem. Commun.*, (6), 609-611, 2006.

[20] P. G. de Gennes, *Sol. State. Commun.*, **10**, 753-756, 1972.

[21] S. R. Renn and T. C. Lubensky, *Phys. Rev. A.*, **38**(4), 2132-2147, 1988.

[22] J. W. Goodby, M. A. Waugh, S. M. Stein, E. Chin, R. Pindak and J. S. Patel, *Nature*, **337**, 449-452, 1989.

[23] J. W. Goodby, M. A. Waugh, S. M. Stein, E. Chin, R. Pindak and J. S. Patel, *J. Am. Chem. Soc.*, **111**(21), 8119-8125, 1989.

[24] (a) S. T. Lagerwall, *Ferroelectric and Antiferroelectric Liquid Crystals*, Wiley-VCH, Weinheim, 1999; (b) P. F. Lagerwall and F. Giesselmann, *ChemPhyChem*, **7**(1), 20-45, 2006.

[25] A. D. L. Chandani, Y. Ouchi, H. Takezoe, A. Fukuda, K. Terashima, K. Furukawa and A. Kishi, *Jpn. J. Appl. Phys. Lett.*, **28**(7), 1261-1264, 1989.

[26] E. Gorecka, A. D. L. Chandani, Y. Ouchi, H. Takezoe and A. Fukuda, *Jpn. J. Appl. Phys.*, **29**(1), 131-137, 1990.

[27] S. Inui, S. Kawano, M. Saito, H. Iwana, Y. Takanishi, K. Hiraoka, Y. Ouchi, H. Takezoe and A. Fukuda, *Jpn. J. Appl. Phys. Lett.*, **29**(6), 987-990, 1990.

[28] D. Vorländer, *Ber. Dtsch. Chem. Ges.*, **62**(10), 2831-2835, 1929.

[29] Y. Matsunaga and S. Miyamoto, *Mol. Cryst. Liq. Cryst.*, **237**, 311-317, 1993.

[30] P. E. Cladis and H. R. Brand, *Liq. Cryst.*, **14**(5), 1327-1349, 1993.

[31] S. Kumar, *Chemistry of Discotic Liquid Crystals: From Monomer to Polymer*, CRC Press, Boca Raton, 2011.

[32] X. Feng, W. Pisula and K. Müllen, *Pure Appl. Chem.*, **81**(12), 2203-2224, 2009.

[33] R. J. Bushby and O. R. Lozman, *Curr. Op. Coll. Interfacial Sci.*, **7**, 343-354, 2002.

[34] B. Bahadur, *Liquid Crystals Applications and Uses*, World Scientific, Singapore, 1990.

[35] G. W. Gray, *Molecular Structure and the Properties of Liquid Crystals*, Academic Press, London, 1962.

[36] W. Maier and A. Saupe, *Z. Naturforsch*, **15a**, 287-292, 1960.

[37] J. M. Lehn, *Angew. Chem. Int. Ed.*, **27**(1), 89-112, 1988.

[38] A. E. Bradfield and B. Jones, *J. Chem. Soc.*, 2660-2661, 1929.

[39] G. W. Gray and B. Jones, *J. Chem. Soc.*, 4179-4180, 1953.

[40] T. Kato and J. M. Frechet, *J. Am. Chem. Soc.*, **111**(22), 8533-8534, 1989.

[41] C. M. Paleos and D. Tsiourvas, *Liq. Cryst.*, **28**(8), 1127-1161, 2001.

[42] B. Gundogan and K. Binnemans, *Liq. Cryst.*, **27**(6), 851-858, 2000.

[43] H.-C. Lin, C.-W. Ko, K. Guo and T.-W. Cheng, *Liq. Cryst.*, **26**(4), 613-618, 1999.

[44] X. Song, J. Li, G. Liu, S. Zhang, C. Ye and E. Chen, *Liq. Cryst.*, **29**(12), 1533-1537, 2002.

[45] X. Song, J. Li and S. Zhang, *Liq. Cryst.*, **30**(9), 1123-1128, 2003.

[46] X. Y. Xu, B. Y. Zhang, L. X. Wang and W. M. Gu, *Liq. Cryst.*, **36**(12), 1365-1372, 2009.

[47] T. Kato and J. M. J. Fréchet, *Liq. Cryst.*, **33**(11-12), 1429-1433, 2006.

[48] K. Sakajiri, H. Yoshida, K. Moriya and S. Kutsumizu, *Chem. Lett.*, **38**(11), 1066-1067, 2009.

[49] R. K. Thapa, R. Baskaran, T. Madheswaran, J. O. Kim, C. S. Yong and B. K. Yoo, *J. Dispersion Sci. Technol.*, **34**(1), 72-77, 2013.

[50] Y. -C. Xu and C. -M. Dong, *J. Polym. Sci., Part A: Polym. Chem.*, **50**(6), 1216-1225, 2012.

[51] I. Tadwee, S. Shahi, V. Ramteke and I. Syed, *Int. J. Pharm. Res. Allied Sci.*, **1**(2), 6-11, 2012.

Chapter 2

LIQUID CRYSTALLINE 1,3,4-THIADIAZOLE DERIVATIVES

LIQUID CRYSTALLINE 1,3,4-THIADIAZOLE DERIVATIVES

2.1. Introduction

Heterocycles are of great importance as core units in liquid crystals due to their ability to impart lateral and / or longitudinal dipoles combined with changes in the molecular shape. These materials hold great potential for use in spatial light modulation [1], all-optical signal processing, optical information storage [2], organic thin-film transistors [3, 4], fast switching ferroelectric materials [5], fluorescent probes for the detection and analysis of biomolecules [6] *etc*. Also, some of these materials have been patented in agricultural field as herbicides, fungicides and bactericides [7-9]. The majority of low molar mass calamitic mesogenic systems in the literature contain linear cores based on the 1,4-disubstituted phenyl ring [10-13]. Heterocyclic cores impart unique physical properties as their slightly bent structure leads to features including a reduced packing ability generally giving rise to lower melting points than their phenyl counterparts, a medium to strong lateral dipole, high anisotropy of the polarizability, low viscosity *etc*. Materials containing 1,3,4-thiadiazole core units have significant lateral dipole moments (Figure 1). It imparts a large lateral dipole from S to the centre of the N-N bond (3.0 D) [14]. This help to contribute to physical parameters such as increased dielectric anisotropy and dielectric biaxiality. The latter property allows for AC field stabilization, a feature that is currently essential for ferroelectric device operation [15, 16].

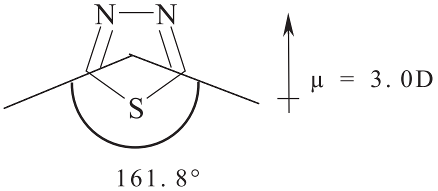


Figure 1. Bond angle and dipole moment of 1,3,4-thiadiazole.

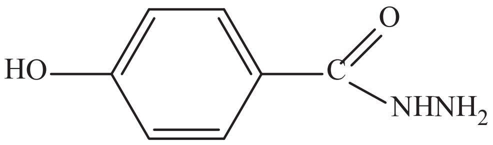
Ferroelectric liquid crystal devices use materials in the SmC* phase which is a tilted smectic with a P_s that may be reoriented upon application of an external electric field [17]. The constituent chiral molecules are tilted within diffuse layers where the tilt angle θ is temperature dependent, generally having an inverse relationship with temperature. Upon passing from layer to layer the director (direction of orientation of the long molecular axes) is seen to rotate in either a clockwise or counter-clockwise fashion [determined by the absolute configuration of the constituent molecules and the proximity of the stereo center to the rigid molecular core (ignoring axial chirality)] to generate a macroscopic helical structure where the helical axis is normal to the layer plane. The local layer symmetry is C_2 and there is a time-dependent alignment of the molecular dipoles along the C_2 axis, leading to a P_s along this axis, which is parallel to the layer planes and perpendicular to the tilt direction [17]. This structure is therefore helielectric and can be made truly ferroelectric by the application of an external electric field which unwinds the helix. Reversal of the field will see the molecules rotate through an angle equal to 2θ, and it is this reorientational effect that is the basis of the ferroelectric display. When a ferroelectric device is fabricated, the liquid crystal is introduced into a thin cell (the cell thickness is smaller than the helical pitch of the material being introduced so as to suppress helix formation) using a vacuum. The liquid crystal itself is usually heated into the SmA phase (SmA, an orthogonal smectic phase that is the most fluid of all the smectic variants) to allow for good alignment. The cell is then cooled and the material enters the SmC* phase where the molecules tilt and the tilt is accompanied by a volume contraction. In response, the layers are seen to buckle in order to fill the space created which results in the formation of chevron domains [18]. The molecules have a small pre-tilt at the surface of the cell (due to boundary conditions) and the layers may tilt in the same sense as the pre-tilt (C_1 chevron domain) or with the opposite sense (C_2 chevron domain) [16]. At the interface where the two domains meet within the cell, a defect forms that is observed as a zig-zag. This results in a serious loss of contrast and effectively renders the display as useless.

Technological advances in display engineering have allowed the construction of displays solely consisting of C_2 chevron domains. However, the one drawback with this type of display is found upon removal of the external electric field. Instead of the molecules remaining in the desired position, there is a slight molecular relaxation that results in a reduction of contrast. To counteract this, an AC field is applied to maintain the desired orientation of the molecules that requires a high dielectric biaxiality (related to the magnitude of the transverse dipole moment). Clearly, heterocyclic materials can be synthesized that have high dielectric biaxiality built into the compact core unit. In phenyl-based materials lateral substituents are required to impart high dielectric biaxiality but the addition of any increased molecular breadth results in a lowering of the mesophase (intermediate phase) thermal stability and an increase in the viscosity.

Sulfur-based heterocycles are also being used to elucidate the structures of complex mesophases such as the smectic C variants. Resonant X-ray scattering has been used to probe the molecular ordering through scattering near the sulfur K edge and this has provided detailed and unambiguous proof of the repeat structure of the ferrielectric variants [19]. Five-membered heterocycles have potential promise for flexo-electric applications such as found in bistable nematic displays. A number of such compounds [20] have already been evaluated for such applications, and other bent heterocycles may have equal promise. Vertical alignment (VA) displays operating with very short switching times and viewing angles of up to 170° require molecules with negative dielectric anisotropy. Once again the in-built lateral dipole of the five-membered heterocycles holds potential for such applications. The multi-domain vertical alignment method (MVA) is of particular importance having being commercialized in late 1997.

1,3,4-Thiadiazoles are relatively common in the literature although the variety of structural modifications that have been studied are actually very limited. The majority of systems have the 1,3,4-thiadiazole core substituted at the 2 and 5-positions by aryl units or a combination of aryl and alkyl / cyclo alkyl units [21-26]. These materials are constructed through sulfurization and cyclization of appropriate diacylhydrazines [27-30].

The 1,3,4-thiadiazole core has provided interest in second order nonlinear optical (NLO) applications where bulky donor-acceptor lateral substituents are undesirable. In 1995, Loos-Wildenauer *et al.* reported the synthesis of a ferroelectric 1,3,4-thiadiazole with enhanced NLO activity and a chiral thio alkyl substituent at the 2-position of the thiadiazole ring [31]. Synthesis of the heterocycle began with the reaction of 4-hydroxybenzohydrazide **1** with carbon disulfide and potassium hydroxide to give the di-potassium salt of aroyldithiocarbazate [32]. Acidification of freshly prepared aroyldithiocarbazate at 0 to -5 °C and concomitant cyclization gave 1,3,4-thiadiazolin-2-thione. The maintenance of temperatures below 10 °C is important if significant disulfide formation (RNHCSSSSCNHR, a thiuram disulfide) is to be avoided [32]. The thione is the most stable tautomeric form and direct alkylation of the thione is not possible. Formation of the thiadiazole disulfide and protection of the phenolic -OH group provides a useful etherification precursor.



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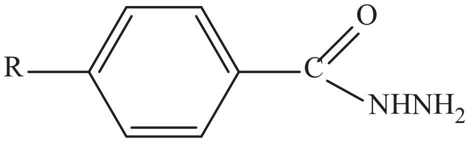
The vast majority of ferroelectric LCs is chiral as a result of the incorporation of a stereo center. Tschierske *et al.* have synthesized a number of 1,3,4-thiadiazole mesogens that are axially chiral by virtue of the incorporation of a chiral allene group [21, 28, 33]. Propargylic alcohol was protected as its *t*-butyldiphenylsilyl (TBDPS) ether before being deprotonated, and the resulting lithium salt reacted with octanal to give racemic alcohol. Dess-Martin periodinane [34] was used to oxidize the alcohol to afford ketone before the ketone was subjected to asymmetric reduction using (R)-Alpine-Borane [35]. Alcohol was then converted into its mesylate followed by substitution by hydrazine and oxidation with DEAD. The oxidation is followed by a 1,5-sigmatropic shift of hydrogen and loss of nitrogen gas. This reaction is stereo-specific and the enantiomeric excess of the product allene is therefore determined by the level of enantio-selectivity in the asymmetric reduction of ketone to give alcohol. Finally, the TBDPS group was removed using tert-butyl ammonium fluoride (TBAF) before the resulting alcohol was etherified under Mitsunobu conditions to give the desired axially chiral allene.

Liquid crystalline thiadiazoles that contain a linking group between the thiadiazole ring and another aryl group constitute a relatively new class of mesogen. A significant portion of literature in this area has come from Parra *et al.*, where Parra's syntheses are centered on 2-amino-1,3,4-thiadiazole building blocks. The amine moiety on the thiadiazole has been transformed into amide [36, 37], imine [38-43] and azo [44, 45] linking groups. Hydrazide **2** was reacted with ammonium thiocyanate in a mixture of concentrated hydrochloric acid and ethanol to give

Thiosemicarbazide. The Thiosemicarbazide then underwent cyclization and concomitant dehydration upon reaction with acetyl chloride. The resulting thiadiazole was subjected to acidic hydrolysis to give the key amino-thiadiazole **3**. Heating this compound **3** with substituted aromatic aldehydes at 140 °C gave imines. The imines display the nematic phase with a broad underlying smectic C phase. Similar chiral materials were constructed to afford ferroelectric materials [43].



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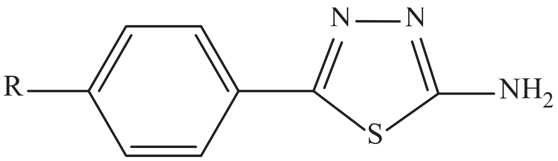

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Electro-optic switching was attempted to evaluate their potential for device use, but upon application of an external electric field the molecules were observed to decompose. Reaction of compound **3** with acid chloride of 4-*n*-octyloxy benzoic acid gave different amides. Introduction of the amide linkage gave rise to high melting points (all melting points were greater than 195 °C) due to strong intermolecular hydrogen bonding.

Azo compounds were prepared by diazotizing compound **3** in a mixture of 85 % phosphoric acid and nitric acid, followed by addition of decyloxy benzene. The azo compounds again possessed the smectic C phase although this time the linkage is unstable and is subject to photochemical isomerization. Parra’s work has demonstrated the power of the thiadiazole ring in supporting tilted phase behavior.

Lai *et al.* have used similar chemistry in the investigation of complexes of similar azo compounds with a terminal thiadiazole ring with *m*-alkoxybenzoic acids [46]. Xu *et al.* have utilized a different ring closure approach [47] whereby an appropriate thiosemicarbazone was chosen as the key precursor. 4-*n*-alkoxy aldehydes are treated with thiosemicarbazide in ethanol to give thiosemicarbazone. Cyclization was then effected using iron(III) chloride and hydrochloric acid before neutralizing the obtained hydrochloride salt. The resulting 2-amino-1,3,4,-thiadiazole was reacted with 4-pyridinecarboxaldehyde to give the targeted Schiff's bases.

In 2004 the Seed group initiated a program of study that centered on the synthesis of thiadiazole carboxylate esters. These linking groups have been demonstrated as excellent supporters of tilted phase morphology in phenyl based systems. In addition, there are no problems with photochemical instability or high melting points and this makes them ideal candidates for ferroelectric applications. However, synthesis of these units is far from trivial and there is a notable absence of such synthetic methodology in the general organic literature. Seed's group used a novel ring-closure methodology using Lawesson's reagent to achieve the desired targeted ester linked ferroelectric 1,3,4-thiadiazoles [48].

The work of Sato [49] describes the preparation of new semi rigid polyesters composed of a quinque phenyl analogue containing 1,3,4-thiadiazole with a central 1,3-phenylene unit and aliphatic chains, by the high temperature solution polycondensation of the dimethyl ester monomer with aliphatic diols. The LC and light-emitting properties of these polymers are also described. The polyesters not only form thermotropic mesomorphic phases, but also show photoluminescent (PL) properties, and may be considered as candidate organic materials for electroluminescent (EL) devices. The author have also described the PL properties of phenylstilbene analogue of 1,3,4-thiadiazole [50].

In 2008, M. Parra *et al.* [51] have reported new chiral amides and new chiral azo compounds incorporating the thiadiazole in the rigid core. Amides were obtained by reaction of the 5-(4-*n*-alkoxy)phenyl-2-amino-1,3,4-thiadiazole with the corresponding chiral benzoic acid chloride. The azo compounds were synthesized by reaction of the 5-(4-*n*-decyloxy)phenyl-2-amino-1,3,4-thiadiazole with the corresponding chiral alkoxybenzene. The alcohols chosen as chiral precursors were (2S, 3S)-2-chloro-3-methylpentanol and (R)-2-octanol. The chiral alcohol (2S, 3S)-2-chloro-3-methylpentanol was obtained by diazotization of (S)-isoleucine with sodium nitrite and HCl followed by reduction of the acid group with $LiAlH_4$. The synthesis of the chiral 4-alkoxybenzoic acid chlorides was achieved by the Mitsunobu reaction starting from methyl 4-hydroxybenzoate and the corresponding chiral alcohol, (R)-2-octanol or (2S, 3S)-2-chloro-3-methylpentanol. The resulting esters were saponified, followed by reaction with thionyl chloride. The Mitsunobu reaction between phenol and (R)-2-octanol or (2S, 3S)-2-chloro-3-methylpentanol yielded the chiral ethers. For amides the layered smectic order is more favored than for azo compounds; this is fully compatible with a molecular arrangement resulting from intermolecular hydrogen bonding, which is a powerful tool for stabilizing and inducing mesophases, even in compounds in which the structure largely deviates from that of the classical calamitic liquid crystals. The author have also reported novel liquid crystalline materials based on amino-thiadiazoles [52], specifically 5-(di-, and / or tri-*n*-alkoxy)phenyl-2-amino-1,3,4-thiadiazoles and 5-(di-, and / or tri-*n*-alkoxy)phenyl-2-(4-amino)phenyl-1,3,4-thiadiazoles. These amino-thiadiazoles display columnar LC behaviour, which can be attributed both to the presence of two and / or three lateral alkoxy chains and the intermolecular hydrogen bonding, which in turn stabilize supramolecular structures in a columnar order. The prepared compounds are the first amino-thiadiazole derivatives exhibiting columnar liquid crystalline behaviour. Special attention was paid to the columnar phase behaviour, the effect of the number of the terminal alkoxy chains on the phase behaviour and the length of the rigid core. The amino-1,3,4- thiadiazole derivatives were synthesized starting with the alkylation of methyl 3,4-dihydroxy and / or 3,4,5-trihydroxybenzoate with 1-bromoalkane under basic conditions yielding the corresponding methyl 3,4-*n*-dialkoxy- and 3,4,5-*n*-trialkoxybenzoate followed by condensation with hydrazine hydrate, yielding the corresponding hydrazides; these were reacted with ammonium thiocyanate in concentrated HCl leading to the formation of the 3,4-*n*-dialkoxybenzoyl- and 3,4,5-*n*-trialkoxybenzoylthiosemicarbazides which on dehydration with acetyl chloride followed by hydrolysis of the acetamide compound gives the required amino-1,3,4-thiadiazoles. The nitro-phenyl-1,3,4-thiadiazole derivatives and amino-phenyl-1,3,4-thiadiazole derivatives were synthesized starting with the condensation of hydrazides with 4-nitrobenzoyl chloride leading to the formation of the diacylhydrazines which, by reaction with Lawesson's reagent, led to the formation of nitro-phenyl-1,3,4- thiadiazoles. Reduction of the nitro group with $SnCl_2$ gives the amino-phenyl-1,3,4-thiadiazole derivatives. These compounds opened an interesting possibility for the design of polycatenar amides and / or Schiff's bases, because the amino-thiadiazole derivatives are the precursors in the synthesis of these compounds, which might exhibit interesting columnar mesomorphic behaviour. Secondly, the amino-thiadiazoles also can be used as precursors in the synthesis of columnar tris-amides and / or tris-amines based on threefold symmetric discoid ('starburst') tris-thiadiazole derivatives with benzene and / or triazine cores.

1,3,4-thiadiazole-based compounds synthesized by microwave irradiation were relatively scarce, and few of them are mesogenic compounds [53]. Han *et al.* [54] have synthesized a series of 2-(4-alkoxyphenyl)-5-*p*-tolyl-1,3,4-thiadiazoles in high yields under microwave irradiation and solvent-free conditions. All of these compounds have the same 2,5-diphenyl-1,3,4-thiadiazole unit connected with an alkoxy chain and a terminal methyl group. The mesogenic 1,3,4-thiadiazole derivatives with the terminal methyl group often exhibit richer mesophases and wider mesomorphic temperature ranges than the analogues with other groups [55]. Furthermore, compounds with end methyl group can be structurally modified easily to prepare various liquid crystal materials. All of these compounds exhibited stable liquid crystal behaviour in a wide temperature range. The lower homologue is also mesogenic with the shortest alkyl (-CH_3) and alkoxy (-OCH_3) chains. In addition, authors have also reported the liquid crystalline behaviors of a heterocyclic compounds containing 1,3,4-thiadiazole with furan and thiophene rings [56]. The relationship between the structures and properties shows that the linear molecules fascinate to form stable mesophases with wide mesomorphic temperature ranges, while the bent-shaped molecules result in the disappearance of mesomorphic properties in all of the compounds containing a central furan ring. The tendency to form mesophases follows the sequence:

1,4-disustituted benzene > 2,5-disubstituted thiophene > 2,5-disustituted furan and 1,3,4-thiadiazole.

Microwave-assisted synthesis and biological activity of 3-alkyl / aryl-6-(1-chloro-3,4-dihydronaphth-2-yl)-5,6-dihydro-s-triazolo [3,4-*b*] thiadiazoles was reported by Kamotra *et al.* [57]. The synthesis followed by condensation of 5-alkyl / aryl-4-amino-3-mercapto-1,2,4-triazoles with 1-chloro-2-formyl-3,4-dihydronaphthalene in presence of catalytic amount of *p*-TsOH under microwave irradiation using 1.0 ml of

DMF as energy transfer medium as well as homogenizer or by stirring at 70-80 °C using DMF as solvent. All the reactions were repeated using the conventional mode of heating at the same final temperatures and reaction times as in the case of microwave irradiation experiments. In all cases using the conventional mode, no reaction or trace of the product was detected as determined by thin layer chromatography (TLC).

Seltmann and Lehmann [58] have described a series of symmetrical and non-symmetrical V-shaped nematic mesogens containing a 1,3,4-thiadiazole bending-unit. They have studied the effect of a variety of substituents on the terminal alkyl chains, including -F, -CH_3 or ester groups, and their influence on mesomorphic behaviour. Terminal ester groups significantly lower the transition temperatures in comparison with derivatives containing unsubstituted terminal alkyl chains. Fluorine substituents increases melting and clearing temperatures, whereas mesogens containing methyl groups exhibit much lower clearing transitions than the parent mesogens. Combining -F and -CH_3 substituents in the same compound, results in greatly increased melting temperatures, probably due to additional donor-acceptor interactions within the crystal. On the other hand, a remarkable decrease in melting temperature, by 20 °C, at the same time maintaining the clearing temperature, has been achieved by introducing two chains of different length within one mesogen. An example of a mesogen containing four dissimilar chains did not show any further improvement in the stability of the mesophase. Presumably the choice of chain length will be a crucial factor in future examples of molecular engineering. Investigations using POM and DSC revealed the uniaxial nematic nature of the liquid crystalline phases in the enantiotropic interval of the LC phases. However, X-ray studies indicated that these uniaxial phases consisted of small biaxial domains.

Gallardo and co-workers [59] have synthesized a series of symmetrical and unsymmetrical fluorescent LC compounds containing the 2,1,3-benzothiadiazole chromophore as the central core substituted with 1,2,4-oxadiazole, 1,2,3-triazole and 1,2-isoxazole heterocycles. They have evaluated the influence of the structure on the thermal and optical properties; the designed compounds possess different degrees of curvatures due to different inherent bent angles of the N-heterocyclic substituents. In the unsymmetrical series, the C–C triple bond was used to extend the π-conjugated system. They have also reported the synthetic pathway for the synthesis of a novel series of liquid crystals 2,6-disubstituted imidazo [2,1-*b*]-1,3,4-thiadiazoles [60].

These fused heterocyclic compounds were prepared through cyclo-dehydration on heating between different combinations of 5-substituted-1,3,4-thiadiazole-2-amino derivatives and α-bromo arylketones. The derivatives of 2-amino-1,3,4-thiadiazole were obtained from the condensation reaction between thiosemicarbazide and aryl / alkyl nitriles with good yields. The α-bromination of arylketones was carried out using N-bromosuccinimide (NBS) as a source of electrophilic bromine, also with good yields. They showed that the liquid crystal behaviour of the final compounds was dependent on the number of chains. Mesomorphism was not observed for compounds without aliphatic chains, with more than two aliphatic chains or when the aliphatic chains are methoxy groups. Banu and co-workers have also synthesized fused heterocycles namely 2-(Fluorobenzyl)-6-(4-nitrophenyl) imidazo[2,1-*b*] [1,3,4] thiadiazole [61] and 2-(4-Fluorobenzyl)-6-Phenylimidazo-[2,1-*b*][1,3,4] Thiadiazole-5-Carbaldehyde [62] and discussed their crystal structures. 2-(Fluorobenzyl)-6-(4-nitrophenyl) imidazo[2,1-*b*] [1,3,4]thiadiazole could be screened for its pharmacological activities and to carry out its crystallographic structure elucidation. The compound will be a good intermediate to synthesize various candidate compounds for pharmacological testing. This compound was prepared by the reaction of 2-amino-(4-fluorobenzyl)-1,3,4-thiadiazole and nitro phenacyl bromide in boiling ethanol affording the 2-amino-(4-fluorobenzyl)-6-(4-nitrophenyl)-imidazo[2,1-b] [1,3,4]thiadiazole as hydrobromide salt, which was neutralized by sodium carbonate solution to get the free base. It is well established that this reaction proceeds via the intermediate iminothiadiazole, which under reflux temperature spontaneously undergoes dehydrocyclization to form the desired fused heterocycle [63]. 2-(4-Fluorobenzyl)-6-Phenylimidazo-[2,1-*b*][1,3,4]Thiadiazole-5-Carbaldehyde was also prepared by similar methodology. The reaction of 2-amino-5-(4-fluorobenzyl)-1,3,4-thiadiazole and phenacyl bromide in boiling ethanol afforded the 2-(4-fluorobenzyl)-6-phenylimidazo[2,1-b][1,3,4]thiadiazole as hydrobromide salt, which was neutralized by sodium carbonate solution to get the free base. It was subjected to Vilsmeier-Haack reaction to yield 2-(4-fluorobenzyl)-6-phenylimidazo [2,1-b][1,3,4]thiadiazole-5-carbaldehyde. Kolavi *et al.* [64] have developed a method for imidazo [2,1-b] [1,3,4]thiadiazole fused pyradizinones. A pyridazine nucleus has been incorporated in the system under Vilsmeier-Haack reaction condition. Although the Vilsmeier-Haack reaction has mainly been employed in the synthesis of aldehydes, authors applied this reaction to the synthesis of this system by trapping the intermediate by intramolecular nucleophilic attack.

Tomma *et al.* have studied the liquid crystalline schiff's bases containing both thiadiazole and trizole units in the same molecule [65]. The presence of more polarized nitrogen atoms on the both heterocyclic rings might be responsible for the formation of mesomorphic properties over other molecules containing only one heterocyclic ring. Also, It was found that the conformational molecular structure play an important role in the stability and formation of these mesophases.

1,3,4-Thiadiazoles have also been noted to be exceptionally good promoters of the SmC phase [33, 66, 67]. Seed group [68] have identified 1,3,4-thiadiazole-2-carboxylates as worthy targets with potentially low viscosities, high dielectric biaxialities due to the large heterocyclic dipole of 3.0 D [14], and more linear structures than other common five-membered heterocycles thus leading to higher mesophase thermal stabilities. This 1,3,4-thiadiazole-2-carboxylate esters would allow to assess the feasibility of this new core as a promoter of SmC phase behavior and the group has fully optimized the synthetic methodology that was used to prepare this new class of materials. Chemo-selective ring-closing methodology was used to synthesize these liquid crystals. These novel materials possess remarkably high mesophase thermal stabilities that, surprisingly, exceed those of the analogous phenyl derivatives. The materials have proven to be both thermally and photochemically stable.

Some new 2,5-disubstituted 1,3,4-thiadiazole derivatives show antituberculosis activity [69]. These compounds were screened against *Mycobacterium tuberculosis* H37Rv using the BACTEC 460 radiometric system. Among the tested compounds, 2-phenylamino-5-(4-fluorophenyl)-1,3,4-thiadiazole showed the highest inhibitory activity. In synthesizing these compounds, 4-substituted benzoic acid hydrazides being the starting materials were prepared by etherification of 4-substituted benzoyl chloride with phenol in sodium hydroxide, followed by refluxing with hydrazine hydrate in dry methanol. After treatment with different arylisothiocyanates in ethanol or acetonitrile, corresponding hydrazide compounds gave the thiosemicarbazides, which were cyclized into the thiadiazoles as the result of a ring closure reaction with concentrated sulfuric acid at room temperature.

Pati *et al.* have constructed macrocyclic compounds by incorporating a 2,5-thiadiazolo subunit into crown ether framework through carbon-oxygen linkages by the reaction of 2,5-dichloro-1,3,4-thiadiazole with polyethylene glycols [70]. These compounds have been shown to possess unique chemical and biological properties. The quaternization studies of a few macrocycles with methyl iodide at elevated temperature furnished a di-keto derivative through a facile Hilbert–Johnson reaction.

Sato and co-workers have evaluated the effect of monomer structures on the liquid crystalline and optical properties of hyper-branched polymers composed of an internal 2,5-diphenyl-1,3,4-thiadiazole as a mesogen [71]. Among them, polymers with short aliphatic spacers between the central site of monomers and the 2,5-diphenyl-1,3,4-thiadiazole unit formed thermotropic smectic phases independent of the feed mole ratios. In polymers having long aliphatic spacer and benzene ring, only one polymer prepared in the highest feed mole ratio formed the LC phase, probably due to steric hindrance. The UV-vis absorption and PL spectra of hyper-branched polymers in solution showed peak maxima at the same wavelengths independent of the feed mole ratios of the monomer structures.

Yarovenko *et al.* have developed a method for obtaining derivatives of 4,5-dihydro-1,3,4-thiadiazole-2-carboxamide by acylation of hydrazones of oxamic acid thiohydrazides [72]. Oxidation of the dihydro-thiadiazole ring of the indicated products by hydrogen peroxide leads to formation of 2-carbamoyl-4,5-dihydro-1,3,4-thiadiazole 1-oxides.

In this chapter, we describe the synthesis and mesomorphic properties of homologous series of schiff's bases derived from substituted 2-amino 1,3,4-thiadiazoles. The growing scientific interest in the synthesis of 1,3,4-thiadiazole-based liquid crystals and also the interesting properties of 1,3,4-thiadiazole-based derivatives has prompted us to synthesize a series of 2-amino 1,3,4-thiadiazole based liquid crystals in this class of materials. We have study their structure-property relationship. We have evaluated the effect of lateral substitution and bent core on mesomorphism of the series. We have also evaluated the photoluminescent properties of the compounds of the series.

2.2. Experimental

2.2.1. Instrumentation

The synthetic route adopted for the series of mesogens is given in Figure 2. The structures of the compounds were determined by using standard spectroscopic methods. IR spectra were determined for KBr pellets, using a Shimadzu make spectrophotometer. ^1H NMR spectra were obtained with a Bruker 400 MHz instrument using tetramethylsilane (TMS) as internal reference standard. Liquid crystalline properties were determined using Leica DM 2500P polarizing optical microscope provided with a Linkam heating stage. The transition temperatures and enthalpies were investigated by Differential Scanning Calorimetry (DSC) using a PerkinElmer Thermal Analyser with a heating and cooling rate of 10 °C min^{-1}. The instrument was calibrated using indium as a standard. UV-visible spectra were recorded on Perkin Elmer LAMDA 35 spectrophotometer. Fluorescence properties were determined using JASCO FP 6300 fluorescence spectrophotometer.

2.2.2. Synthesis and Characterization

2.2.2.1. 4-(4’-*n*-Alkoxybenzoyloxy)-3-methoxy benzaldehydes (2)

4-*n*-Alkoxybenzoic acids and 4-*n*-alkoxybenzoyl chlorides were synthesized by the modified method of Dave and Vora [73]. A mixture of 4-hydroxybenzoic acid (0.1 mol), an appropriate *n*-alkyl iodide or bromide (0.12 mol), potassium hydroxide (0.25 mol) and ethanol (50 ml) were refluxed for 4-5 hrs. 10 % aqueous KOH solution (25 ml) was added and reflux was continued for 2 hrs to hydrolyze any ester formed. After being cooled, the mixture was poured into a stirred mixture of concentrated hydrochloric acid (25 ml) and ice cold water (50 ml). The product was then filtered off, washed with water, dried and recrystallised from ethanol until constant melting points were obtained. Purity of the compounds were checked by TLC and characterized by spectral data. The transition temperatures are in good accordance with the literature [73]. The acids were converted into their acid chlorides by treating the corresponding 4-*n*-alkoxybenzoic acid with excess of thionyl chloride by heating on water bath till evolution of hydrochloric acid ceased. The excess of thionyl chloride was distilled off. The crude product was used immediately in the next reaction without further purification.

4-(4’-*n*-Alkoxybenzoyloxy)-3-methoxy benzaldehydes were synthesized according to reference [74]. 4-Hydroxy-3-methoxy benzaldehyde (0.01 mol) was dissolved in dry pyridine (10 ml) and was added slowly with stirring to cold 4-*n*-alkoxybenzoyl chloride (0.01 mol). The mixture was heated on a water-bath for an hour and was allowed to stand overnight. It was acidified with cold 1:1 hydrochloric acid, filtered and the precipitates were washed with cold dilute sodium hydroxide solution, followed by cold water. The esters were crystallized several times from ethanol until constant melting points were obtained. The melting points agree well with the reported value [74].

2.2.2.2. Methyl p-*n*-Decyloxybenzoate (3) [75]

Methyl p-hydroxybenzoate (0.01 mol), an appropriate *n*-alkyl iodide or bromide (0.012 mol), potassium carbonate (0.07 mol) and dimethyl formamide (15 ml) were mixed and heated on a steam bath for 20 hrs. The reaction mixture was decomposed on crushed ice. The product was filtered, washed with water and crystallized from ethanol. Melting point: 49 °C.

2.2.2.3. p-*n*-Decyloxyphenylhydrazide (4) [38]

A solution of methyl p-*n*-Decyloxybenzoate (0.18 mol) and excess of a solution of hydrazine hydrate (80%) in 20 ml of ethanol was heated to reflux during 8 hrs. The mixture was then cooled to room temperature, and the solid obtained was filtered, washed with water and recrystallised from ethanol. Melting point: 93 °C.

2.2.2.4. p-*n*-Decyloxybenzoylthiosemicarbazide (5) [38]

p-*n*-Decyloxyphenylhydrazide (0.14 mol) was suspended in alcoholic hydrogen chloride solution (12 ml) and evaporated under reduced pressure, the residue dried by evaporation of alcohol and heated under reflux for 18 hrs with a solution of dry ammonium thiocyanate (0.15 mol) in absolute ethanol. The solid was filtered, washed several times with water and recrystallised from ethanol. Melting point: 196 °C.

2.2.2.5. 5-(p-*n*-Decyloxy)-phenyl-2-amino-1,3,4-thiadiazole (6) [40]

Thiosemicarbazide **5** (24 g, 0.08 mol) and acetyl chloride (250 ml) were mixed ice-cold and afterwards cautiously heated under reflux. After the vigorous reaction subsided, heating was continued for 15 min, and water was added (200 ml). The solid separated was filtered, washed with water (3 times) and recrystallised from 2-ethoxyethanol, yielding the acetamido compound. This compound (10 g, 0.031 mol) was mixed with concentrated hydrochloric acid (52 ml) and 2-ethoxyethanol (200 ml) and was then heated under reflux for 18 hrs. The solvent was distilled under reduced pressure and the residue poured into concentrated sodium hydroxide solution (80 ml). The resulting solid was filtered, washed several times with water and recrystallised from ethanol-water mixture. Melting point: 164 °C.

2.2.2.6. 5-(p-*n*-Decyloxy) phenyl-2-(4-(4’-*n*-alkoxy-benzoyloxy)-3-methoxy) benzylideneamino-1,3,4-thiadiazoles (Series: I) [38]

A mixture of compound **6** (0.002 mol), compound **2** (0.004 mol), glacial acetic acid (2-3 drops) and ethanol (20 ml) was refluxed for 18 hrs. The solvent was distilled under reduced pressure and the residue crystallized from ethanol till constant transition temperatures obtained, giving yellow crystals. Yield: 65-70 %.

***n*-Pentyloxy derivative:** IR (KBr) cm^{-1}: 3078 aromatic C-H stretch, 2955, 2920, 2870, 2850 aliphatic C-H stretch, 1735 >C=O stretch, 1620, 1502, 1446 ring breathing vibrations, 1606 C=N stretch, 1251 C-O stretch, 1157 C-N stretch, 720 CH_2 rocking (Figure 3).

^{1}H NMR ($CDCl_3$, δ, ppm): 0.87-0.90 (t, 3H, CH_3), 0.93-0.97 (m, 3H, CH_3), 1.28-1.49 (m, 18H, $9CH_2$), 1.78-1.87 (m, 4H, $2CH_2$), 3.92 (s, 3H, OCH_3), 4.01-4.03 (t, 2H, OCH_2), 4.04-4.07 (t, 2H, OCH_2), 6.97 (d, 2H, Ar-CH), 6.99 (d, 2H, Ar-CH), 7.29-7.31 (d, 1H, Ar-CH), 7.48-7.50 (dd, 1H, Ar-CH), 7.80-7.81 (d, 1H, Ar-CH), 7.90-7.92 (d, 2H, Ar-CH), 8.14-8.16 (d, 2H, Ar-CH), 8.91 (s, 1H, N=CH) (Figure 4).

^{13}C NMR ($CDCl_3$, δ, ppm): 165.41 carbonyl C, 149.07 imine C, 162, 141.31, 139.71, 135.31, 130.92, 130.84, 127.02, 125.21, 122.78, 119.80, 119.25, 113.71, 112.17 aromatic C, 69.02, 56.74, 56.19, 56.13, 28.03, 24.32, 23.86, 22.82, 22.57, 21.09, 19.40, 18.74, 13.99, 11.88 aliphatic C (Figure 5).

***n*-Hexyloxy derivative:** IR and ^{1}H NMR spectra are given in Figure 6 and 7, respectively.

***n*-Tetradecyloxy derivative:** IR, ^{1}H NMR and Mass spectra are given in Figure 8, 9 and 10, respectively.

2.2.3. Determination of transition temperatures with the help of a polarizing optical microscope

To determine the transition temperatures the Leica DM 2500P polarizing optical microscope equipped with a Linkam heating stage was used.

To determine the various transitions, a glass slide with a thin coating of material, covered with a glass cover slip, was observed under microscope. The slide was kept on the hot stage and the temperature was raised rapidly to find the approximate transition temperatures. The observations were repeated and the rate of heating was regulated to slowly near the transition, to determine the transition temperatures more precisely.

The heating device was standardized and its accuracy was checked by determining the transition temperatures of the known compounds, such as 4-*n*-alkoxy benzoic acids.

The members of the homologous series **I,** 5-(p-*n*-Decyloxy) phenyl-2-(4-(4'-*n*-alkoxy-benzoyloxy)-3-methoxy)benzylideneamino-1,3,4-thiadiazoles exhibit enantio-tropic mesomorphic states. The methyl to *n*-hexyl derivatives exhibit only the Nematic phase; the higher members, starting with the *n*-heptyl derivative, show both Smectic as well as Nematic phases. The smectic phase shows smectic C type phase which was characterized by the formation of a typical broken focal conic texture. SmC phase also can be further confirmed by mixing with known SmC compound. The nematic phase showed a characteristic thread-like texture or schlieren texture under microscope.

2.2.4. Differential Scanning Calorimetry studies

The transition temperatures and enthalpies were investigated by Differential Scanning Calorimetry (DSC) using a PerkinElmer Thermal Analyser with a heating and cooling rate of 10 °C min^{-1}. The instrument was calibrated using indium as a standard. The phase transition temperatures observed through polarizing optical microscope were found to be in reasonable agreement with the corresponding DSC thermograms. The thermograms and related discussions are given in the Results and Discussion section for the series **I** compounds.

2.3. Results and Discussion

The Schiff's bases were synthesized by condensation of 5-(p-*n*-decyloxy)-phenyl-2-amino-1,3,4-thiadiazole with the appropriate 4-(4'-*n*-Alkoxybenzoyloxy)-3-methoxy benzaldehydes. The synthetic route adopted for the synthesis of these mesogens is given in Figure 2.

All the members of the series 4-(4'-*n*-Alkoxybenzoyloxy)-3-methoxy benzaldehydes are non-mesogenic in nature. This is quite an interesting phenomenon as similar homologous series 4-(4'-*n*-Alkoxybenzoyloxy) benzaldehydes [76], without lateral methoxy group, is mesogenic in nature. If we consider the possibility of a dimer in the present series, due to intermolecular hydrogen bonding, trans-methoxy group should not eliminate mesomorphism. This may be attributed to the fact, that the length-to-breadth ratio is considerably reduced in the present series; moreover the hydrogen bonding would be very weak.

All the compounds of the series **I** show mesomorphic properties and all are enantiotropic in nature. The lower members starting with methyl to *n*-hexyl derivatives exhibit only the Nematic phase; while the higher member homologues starting with the *n*-heptyl derivative show both Smectic and Nematic phases and persists upto the last member of the series. The transition temperatures are recorded in Table 1.

The mesophases exhibited by this series were identified according to their optical textures. These textures were observed by polarizing optical microscopy. The smectic and nematic phases were determined from textural observations by thermal microscopy under a polarizing microscope using heating and cooling cycles. The smectic phase is of smectic C type with characteristic broken focal conic or broken fan shape texture. Smectic C phase also can be further confirmed by mixing with known SmC compound. The nematic phase shows its schlieren texture or thread-like texture pattern. Phase transition temperatures observed through thermal microscopy were found to be in reasonable agreement with the corresponding DSC thermograms. Optical textures are shown in Figures 21-24 (section 2.3.2).

A graphical representation of the mesomorphic behaviour as a function of the number (n) of carbon atoms in the alkoxy chain is given in Figure 11. This exhibits falling tendency for the nematic-isotropic transition temperature while the smectic-nematic transition temperature shows rising tendency with the increasing terminal chain length. With increase in the terminal chain length, Series **I** compounds shows characteristic tendency of decreasing in the nematic-isotropic transition temperature and also it shows commencement of smectic phase from middle member homologues. This particular trend is expected in such a mesogenic system [77, 78].

The molecules, forming liquid crystals, generally possess the basic skeleton of relatively rigid aromatic or alicyclic rings with alkoxy or alkyl chains attached to one or both the ends. Within the isotropic or nematic phases, different regions of each molecule are continuously in contact with parts of neighbouring molecules. The energy of the system depends on different conformations of molecules, Van der Waals dispersive forces between the neighbouring molecules and on steric repulsions between different molecules [79]. For the mesogenic homologous series, Gray [80, 81] has successfully used the concepts of molecular arrangement and complex molecular interactions with lateral and terminal attractions between neighbouring molecules. These ordering forces, which are strongly dependent on molecular separations, have to compete with disordering thermal fluctuations.

Due to the presence of balancing lateral and terminal cohesions and long lath-like molecules, mesogenic compounds melt in stages. They pass through one or more ordered intermediate stages before changing to isotropic liquid phase. The molecular layer structure of the smectic phase occurs in temperature regions where lateral attractions dominate, while the parallel molecular arrangement of nematic phase occurs in a temperature interval with predominant terminal attractions. Thus at the crystal-smectic transition, the primary terminal cohesions of the molecules are overcome and at the smectic-nematic or smectic-chiral nematic change, the strong lateral attractions are overcome, and a nematic or chiral nematic mesophase is formed. The molecules, either in the nematic or in the chiral nematic mesophase are maintained by residual lateral and terminal cohesions. On further heating all the Van der Waals forces are again broken down and the molecules pass into randomly arranged isotropic liquid state. These changes can be represented schematically as shown in the Figure 12.

In a mesomorphic homologous series, usually the mesomorphic-isotropic transition temperatures change in a regular manner. The increment of each methylene unit brings about regular changes in the transition temperatures of the series. Gray [82] has explained this behaviour by taking into consideration the chain-length of terminal alkyl or alkoxy group. As the alkoxy or alkyl chain is lengthened, the separation of the aromatic centres, which are highly polarisable and have permanent dipolar substituents, is increased; consequently there should be a decrease in the strength of the terminal intermolecular cohesions. However, Gray [82] and Maier and Baumgartner [83] have suggested that the addition of each methylene unit simultaneously increases the overall polarizability of the molecules and the lateral intermolecular attractions. In series **I,** the lower homologues are purely nematic. In the lower homologues the separation of the aromatic nuclei is at a minimum and the terminal cohesions are strongest which results into the purely nematogens. As we ascend the series, smectic phase commences from the middle members of the series, because as the terminal chain length increases, the lateral cohesive forces are also increased and the molecules align themselves in the layered structure before passing to nematic phase. Hence with increase in the terminal chain length, smectogenic character should predominate at the expense of nematic phase stability. At this stage, the terminal intermolecular attractions are inadequate to maintain the parallel molecular orientation, required for the nematic mesophase. This is the general pattern observed for a normal nematogenic homologous series.

The alternations of nematic-isotropic transitions have been discussed by Gray [80]. He has tried to explain such behaviour for nematic-isotropic transitions in terms of the conformation of the alkyl chain. He has considered the Zig-Zag conformation for the alkyl chain, an evidenced from the X-ray studies of crystalline state of some liquid crystalline compounds.

The increase in chain-length will have the following effects and the nematic-isotropic transition temperatures will be determined by those effects which predominate:

1. The longer molecules will be rotated less readily out of the ordered state.
2. The overall polarizability increases with each added methylene unit.
3. The frequency with which readily polarizable aromatic parts of the molecules lie next to one another in the fluid nematic melt will decrease i.e., the residual lateral attractions will tend to decrease.
4. Each methylene unit forces apart polarizable centers in the molecules and decreases the residual terminal attractions.

Effect (1) and (2) would increase the nematic-isotropic transition temperatures and (3) and (4) would decrease the nematic-isotropic temperatures. Thus rising transition lines are obtained where the effects (1) and (2) predominate and vice versa. Keeping this in view, the rising mesomorphic-isotropic transition lines are found in the series whose transition temperatures are low and the residual attraction are weak. Gray has explained the alternation of nematic-isotropic transition temperatures by a diagrammatic representation of the possible relative orientations of terminal methyl groups in an end-to-end packing of the molecules of *n*-alkyl aryl ethers, such as p-*n*-alkoxybenzoic acids. For short alkyl chains, if the chain extends strictly along its own axis (dotted line as shown in Figure 13), then the terminal methyl groups present different faces to one another or to other end groups in the molecules depending on whether the chain is even or odd. The different resultant attractive forces could affect the energy of the system and account for an alternation of the transition temperatures.

With the higher homologues the alkyl chain may be forced (curved line as shown in Figure 13) into line with the main axis defined by the more rigid aromatic parts. Gradually the end groups' contact would become the same in nature for odd and even carbon chains, and can explain the petering out of the alternation as the series is ascended.

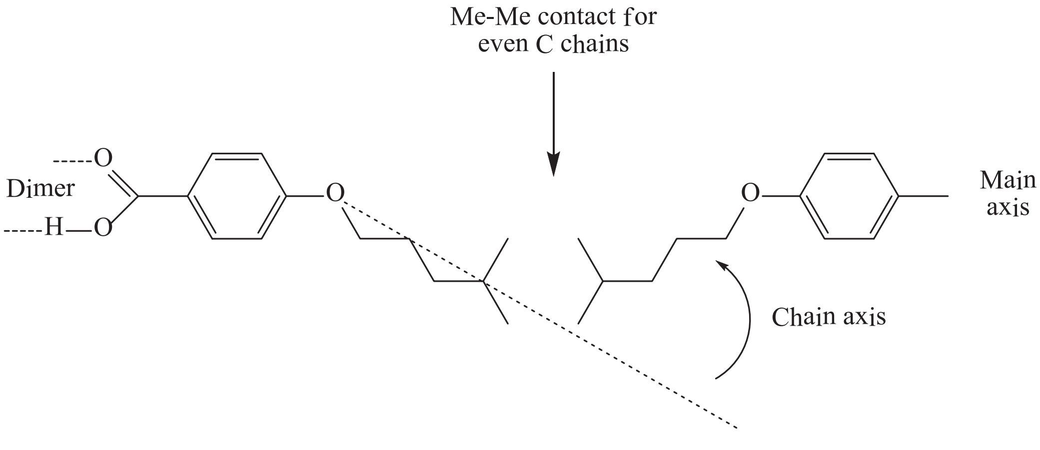


Figure 13. Schematic representation of the possible relative orientations of terminal methyl groups in an end-to-end packing of the molecules of *n*-alkyl aryl ethers.

Maier [84] and Maier and Baumgartner [83] have also tried to explain the alternation effect on the basis of their study of the dipole moment and dielectric anisotropies of a nematogenic homologous series. Marčelja's theory [79] explains the odd-even effect in isotropic-nematic transition temperatures and entropies. From the geometry of p,p'-di-*n*-alkoxy azoxybenzenes, they have shown that the addition of carbon atom C_2, increases the anisotropy of the molecule and helps the ordering process; subsequent addition of atom C_3 hinders the ordering, atom C_4 helps again, and so on. As the chains become longer, their flexibility makes the effect progressively smaller until for long end chains, it becomes unnoticeable. Pines *et al.* [85] have measured the order parameters in a series of nematic liquid crystals p-alkoxy azoxybenzenes by ^{13}C NMR. The ordering exhibits an odd-even alteration along the series. They conclude that the benzene rings rotate or flip about the para axes, at a rate greater than 1 kHz for the whole series, throughout the nematic range. De Jeu and Van der Veen [86] have reviewed some experimental results on the variation of the nematic-isotropic transition temperatures T_{N-I} and evaluated molecular structure with the aid of expressions for T_{N-I} from molecular statistical theories.

There is a close relationship between liquid crystalline properties and molecular constitution of organic compounds, hence the thermal stability; a measure of liquid crystalline properties can be correlated with the molecular constitution of the compounds. The average thermal stabilities of different mesogenic homologous series are compared and recorded in Table 2.

Table 2. Average thermal stabilities (°C) of series I, A, B and C compounds.

Series	I	A	B	C
N-Iso or Sm-N	209.5 (C_5-C_{10})	213.5 (C_5-C_6)	205.7 (C_5-C_{10})	176.6 (C_5-C_{10})
N-Sm / Sm-N or Sm-Iso	152.3 (C_7-C_{10})	213.0 (C_7-C_8)	170.0 (C_7-C_{10})	147.6 (C_7-C_{10})

Comparison of molecular structure of present series **I** with reported Series:

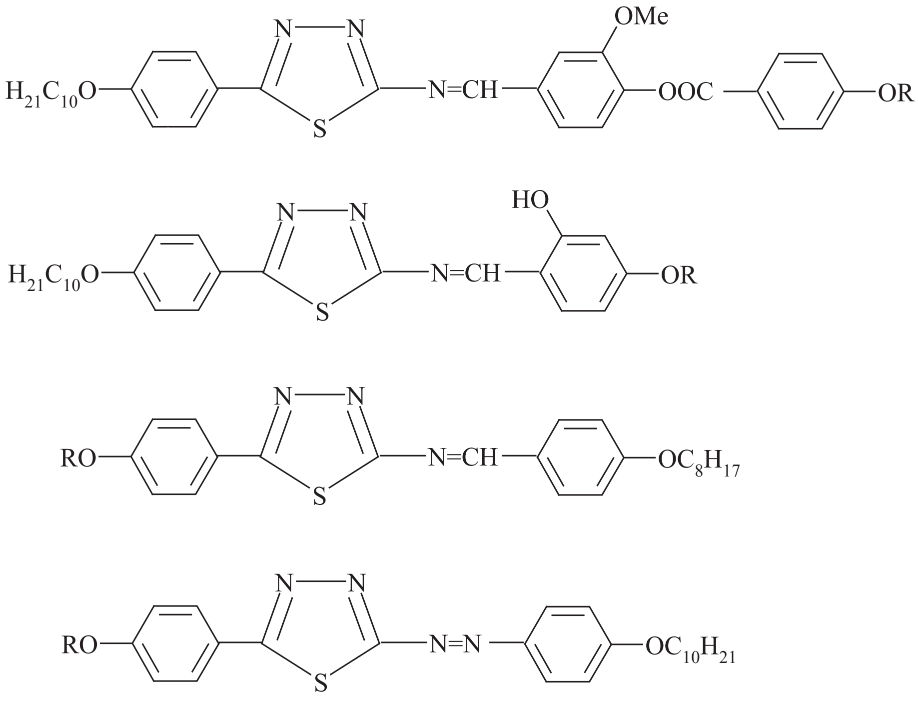
(1) 5-(4-*n*-Decyloxy)-phenyl-2-[4-(4’-*n*-alkoxy-benzoyloxy)-3-methoxy]-benzylideneamino-1,3,4-thiadiazoles; **Series: I**

(2) 5-(4-*n*-Decyloxy)-phenyl-2-(2-hydroxy-4-*n*-alkoxy)-benzylideneamino-1,3,4-thiadiazoles; **Series: A** [40]

(3) 5-(4-*n*-Alkoxy)-phenyl-2-(4-*n*-octyloxy) benzylidene-1,3,4-thiadiazoles; **Series B** [45]

(4) 5-(4-*n*-Alkoxy)-phenyl-2-(4-*n*-decyloxy) phenyl azo-1,3,4-thiadiazoles; **Series C** [45]

The geometry of these series is given in Figure 14.



(I)

(A)

(B)

(C)

Figure 14. Comparative geometry of series I, A, B, and C compounds.

The molecules of series **I** have *n*-decyloxy phenyl 1,3,4-thiadiazole moiety linked with substituted benzaldehydes forming a schiff’s base linkage. Series **A** has only one phenyl ring on the end with lateral hydroxy group adjacent to schiff’s base linkage. Molecules of series **I** have *n*-alkoxy phenyl ester linkage attached to substituted benzaldehydes forming a schiff's base linkage and a lateral methoxy group adjacent to an ester linkage (Figure 14). Molecules of series **I** therefore are longer by one phenyl ring and an ester linkage compared to molecules of series **A.** The lateral hydroxy group in series **A** will form strong intramolecular hydrogen bonding with Schiff's base linkage. Against that lateral methoxy group in series **I** will increase the breadth of the molecules of the series over and above non-linearity of 2,5-disubstituted 1,3,4-thiadiazole moiety. This possibly is the reason that the average nematic thermal stabilities of series **I** and series **A** are almost same. The role of lateral methoxy group of series **I** would be more deterrent for the smectic phase, where close packing is required. This is reflected lower average smectic-isotropic thermal stabilities of series **I** even though it is longer and more polarizable compare to series **A.**

In the case of molecules of series **B,** terminal groups are on opposite end compared to that of series **I** and they do not possess any lateral substituent. Based on previous discussion, the average N-Iso thermal stability is almost equal in both the series. Smectic thermal stabilities of series **B** is higher than those of series **I,** but the increase in smectic thermal stability is much less compared to that of series **A.** This is again attributed to the close packing of molecules of series **A** and increase polarizability due to hydrogen bonding.

The molecules of series **I** and **C** not only differ in terminal substituents but also in one of the central linkages which is an azomethine in series **I,** and an azo linkage in series **C.** It has been already indicated in the introduction [21] that 2,5-disubstituted linkage in 1,3,4-thiadiazole increases non-linearity of the molecules. The azo linkage is also known to increase further this non-linearity of the molecule which affects nematic as well as smectic thermal stabilities which is the case (Table 2).

The transition temperatures identified under POM were confirmed with DSC study. The representative DSC thermograms of *n*-pentyloxy, *n*-hexyloxy, *n*-heptyloxy and *n*-tetradecyloxy derivatives are shown in Figures 15 to 18, respectively. The DSC data are recorded in Table 3. For all the compounds shown as in Table 3, for the first transition of crystal-nematic / smectic C, enthalpy changes are reasonably expected for these transitions. In contrast, the enthalpy changes for nematic-isotropic transition are lower than the expected. Again this is certainly expected for these types of mesogens [87]. Imrie [87] have synthesized the homologous series α,ω-bis(2,4-

dimethylanilinebenzylidine-4’-oxy)alkanes and α-(4-cyanobiphenyl-4’-oxy)-ω-(2,4-dimethylanilinebenzylidine-4’-oxy)alkanes and studied their liquid crystalline properties. He has compared transitional properties of these compounds with those of the analogous compounds not possessing the 2-methyl substituent. The results indicated that the lateral substitution results in a large decrease in the nematic-isotropic transition temperatures. In contrast, the reduction in the entropy change associated with the nematic-isotropic transition is only slight. In our compounds, methoxy group is lateral substitution which results in a decrease in the nematic-isotropic transition.

Table 3. Differential Scanning Calorimetry (DSC) data.

Homologue (Table 1)	Heating rate (°C min^{-1})	Transition	ΔH (kJ $mole^{-1}$)
5	10	Cr-N	41.34
		N-I	1.37
6	10	Cr-N	43.82
		N-I	1.19
7	10	Cr-SmC	37.49
		SmC-N	1.12
		N-I	1.36
14	10	Cr-SmC	45.78
		SmC-N	3.04
		N-I	1.28

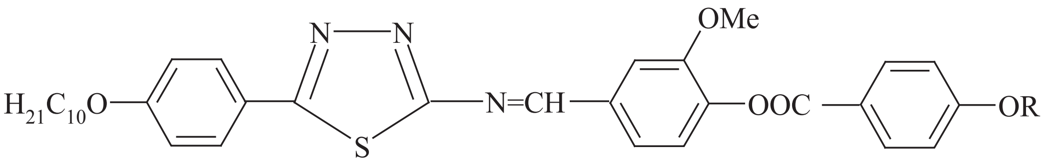
Although an additional factor of molecular shape is also responsible for such change which impart bending in the system. This may also be attributed to the increased molecular biaxiality arising from this thiadiazole core [88, 89]. Imrie and co-workers [88] have synthesized liquid crystal dimers containing two mesogenic units separated by a flexible spacer. One of the main characteristics of this class of materials is the pronounced alternation of the transitional properties on varying the number of methylene groups in the spacer. For example, both the nematic-isotropic transition temperature, T_{N-I}, and the associated entropy change, $\Delta S_{N-I} / R$, depend critically on the length and parity of the spacer. The alternation in T_{N-I} is attenuated as the length of the spacer is increased, unlike that exhibited by $\Delta S_{N-I} / R$ which remains essentially unaffected. These characteristic differences in behaviour between odd- and even-membered dimers are most often attributed to the dependence of the molecular shape on the parity of the spacer when considered in the all-*trans*-conformation. Thus, in an even-membered the mesogenic dimer the mesogenic groups are anti parallel, whereas an odd-membered dimer they are inclined. The more linear structure of the even-membered dimers is then considered to be more compatible with the molecular organization found in the nematic phase resulting in, for example, higher values of $\Delta S_{N-I} / R$ than found for odd-members.

Luckhurst and his co-workers have suggested that the differences in the transitional behaviour of ether and methylene-linked dimers arise from differences in molecular geometry and, specifically, from the bond angle between the *para*-axis of the mesogen and the first bond in the spacer [90, 91]. In a more transparent model developed by Luckhurst and co-workers, to understand how geometrical factors influence the transitional properties of dimers, the dimers can adopt just two conformations, one linear and one bent [92, 93]. This approach makes the intriguing prediction that systems containing high concentrations of bent conformers in the isotropic phase should exhibit a nematic-nematic transition. The nematic-isotropic entropy exhibited by 1,5-bis(4-cyano-biphenyl-4’-yl)pentane is very small suggesting that the transition is approaching second order in nature [94]. Theory suggests that following such a second order transition a biaxial nematic phase should be observed. The possibility of small nematic-isotropic transition is observed for this type of thiadiazole containing compounds.

For smectic C-nematic transition it is interesting to note that the smectic C-nematic transitional enthalpy change for homologue 7 is 1.12 kJ mole^{-1} which is much lower than the transitional enthalpy change for homologue 14. The transitional enthalpy change for homologue 14 is 3.04 kJ mole^{-1}. This is expected as per McMillan theory [95]. This theory predicts that as the nematic phase length decreases, the enthalpy changes associated with the smectic-nematic transition increases. It is possible that in this instance the packing efficiency of molecules is higher for homologue 14 than for homologue 7.

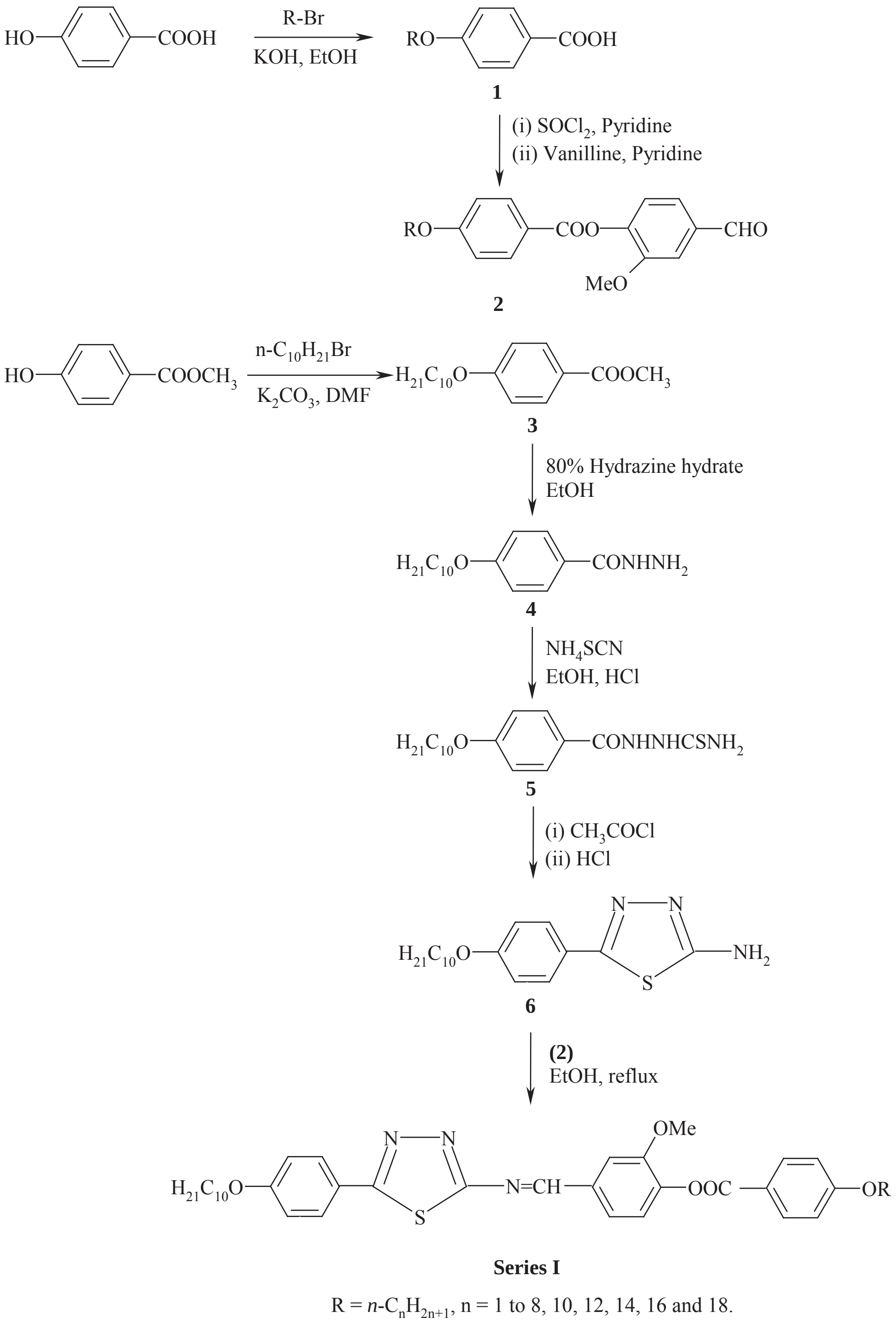
Forgoing discussion indicated that in a non-linear molecule, lateral substituent or non-linear central linkage can adversely affect mesomorphic properties of the system. The study has provided host of compounds which absorb UV radiation and also are fluorescent in nature (section 2.3.1). The study of their application aspect would be quite interesting.

Table 1. Transition temperatures of 5-(p-*n*-Decyloxy) phenyl-2-(4-(4'-*n*-alkoxy-benzoyloxy)-3-methoxy) benzylideneamino-1,3,4-thiadiazoles **(Series I).**



Sr. No.	R = *n*-alkyl group	Transition temperatures (°C)						
		Cr		SmC		N		I
1	Methyl	•	-	-	101.5	•	224.9	•
2	Ethyl	•	-	-	107.4	•	230.6	•
3	Propyl	•	-	-	132.6	•	228.0	•
4	Butyl	•	-	-	135.2	•	220.2	•
5	Pentyl	•	-	-	134.9	•	220.6	•
6	Hexyl	•	-	-	135.2	•	213.7	•
7	Heptyl	•	130.5	•	140.0	•	207.8	•
8	Octyl	•	134.3	•	155.0	•	207.5	•
9	Decyl	•	129.4	•	167.2	•	198.0	•
10	Dodecyl	•	123.5	•	168.4	•	189.2	•
11	Tetradecyl	•	125.8	•	175.2	•	185.8	•
12	Hexadecyl	•	123.8	•	179.9	•	185.6	•
13	Octadecyl	•	115.2	•	174.6	•	178.6	•

Cr = crystal, SmC = smectic C, N = nematic, I = isotropic.



R = n-C_nH_{2n+1}, n = 1 to 8, 10, 12, 14, 16 and 18.

Figure 2. Synthetic route to series I.

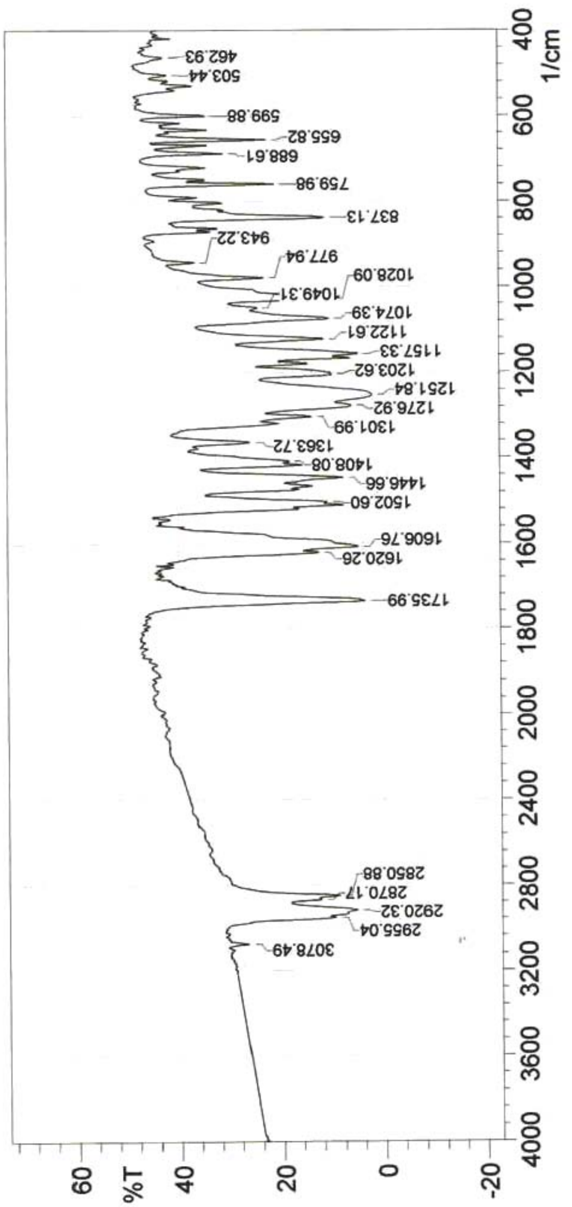


Figure 3. Representative IR spectra of *n*-pentyl derivative.

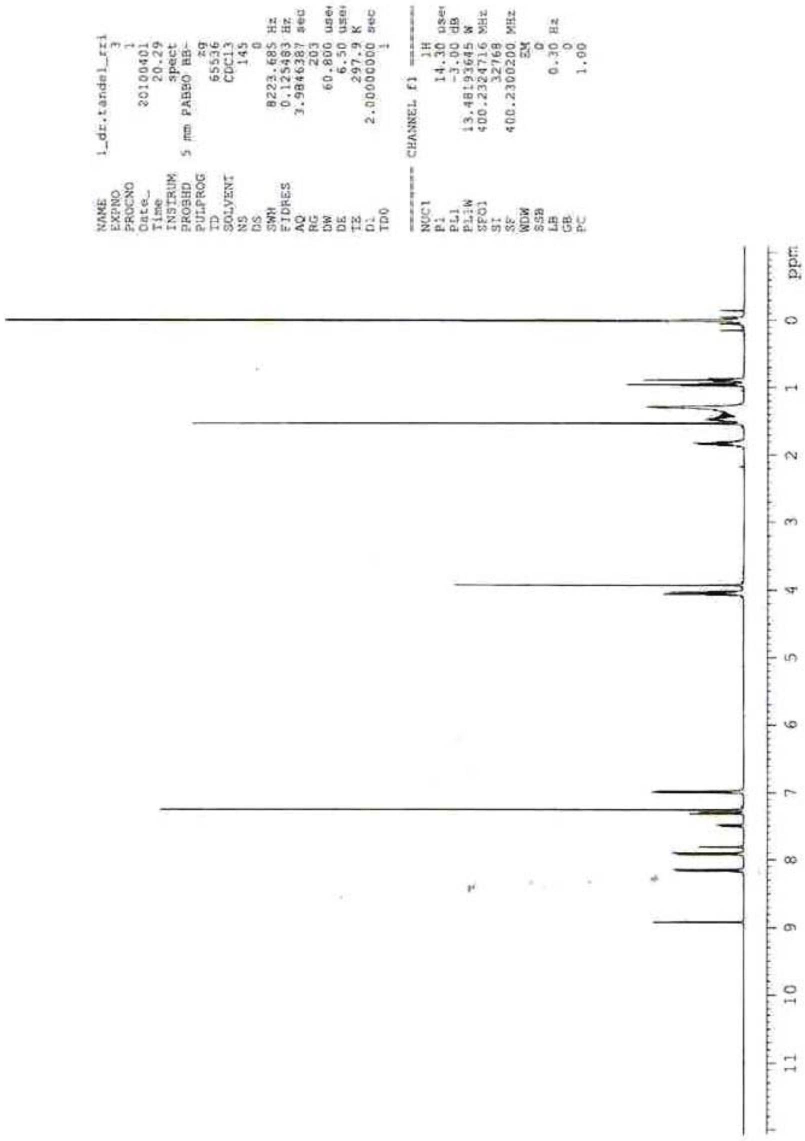
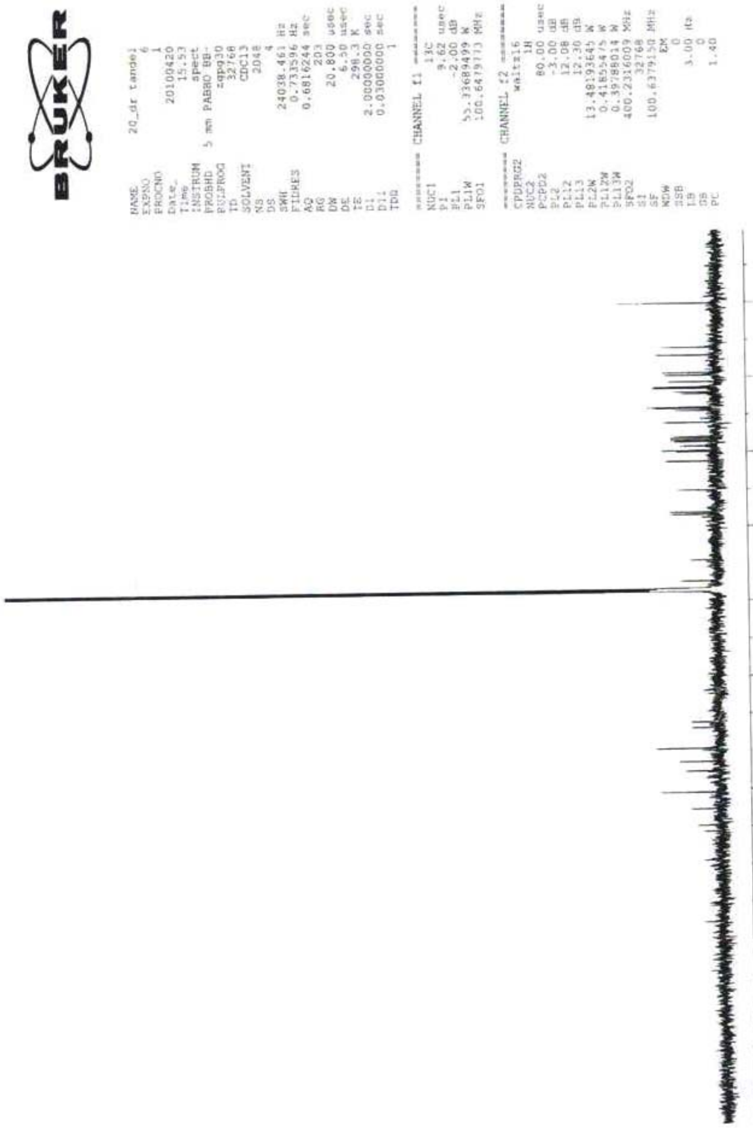


Figure 4. ^{1}H NMR spectra of *n*-pentyl derivative.



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PROCNO                   1
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Time                 15.53
INSTRUM              spect
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PULPROG            zgpg30
TD                   32768
SOLVENT              CDCl3
NS                    2048
DS                       4
SWH              24038.461 Hz
FIDRES            0.733596 Hz
AQ               0.6816244 sec
RG                     203
DW                  20.800 usec
DE                    6.50 usec
TE                   298.3 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    9.62 usec
PL1                  -2.00 dB
PL1W           55.33689499 W
SFO1          100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                  -3.00 dB
PL12                 12.08 dB
PL13                 12.30 dB
PL2W           13.48193645 W
PL12W           0.41855475 W
PL13W           0.39788014 W
SFO2          400.2316009 MHz
SI                   32768
SF            100.6379150 MHz
WDW                     EM
SSB                      0
LB                    3.00 Hz
GB                       0
PC                    1.40
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Figure 5. ${}^{13}C$ NMR spectra of *n*-pentyl derivative.

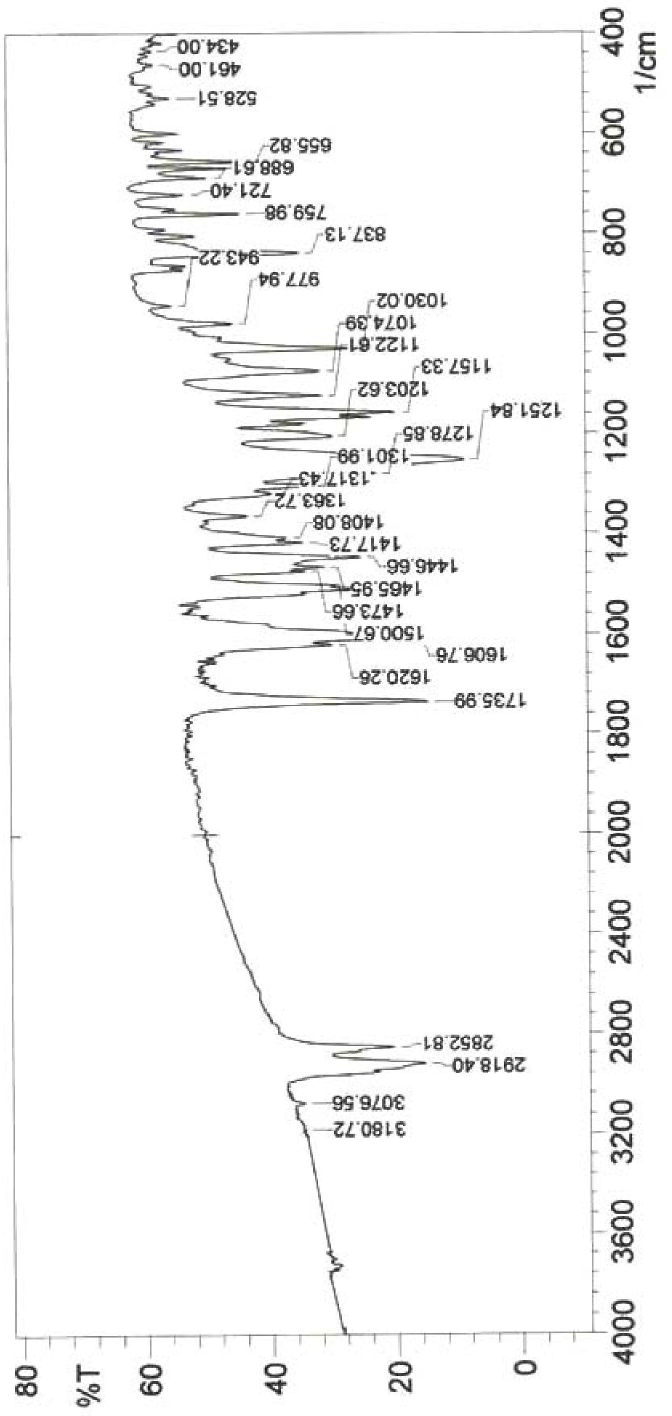


Figure 6. Representative IR spectra of *n*-hexyl derivative.

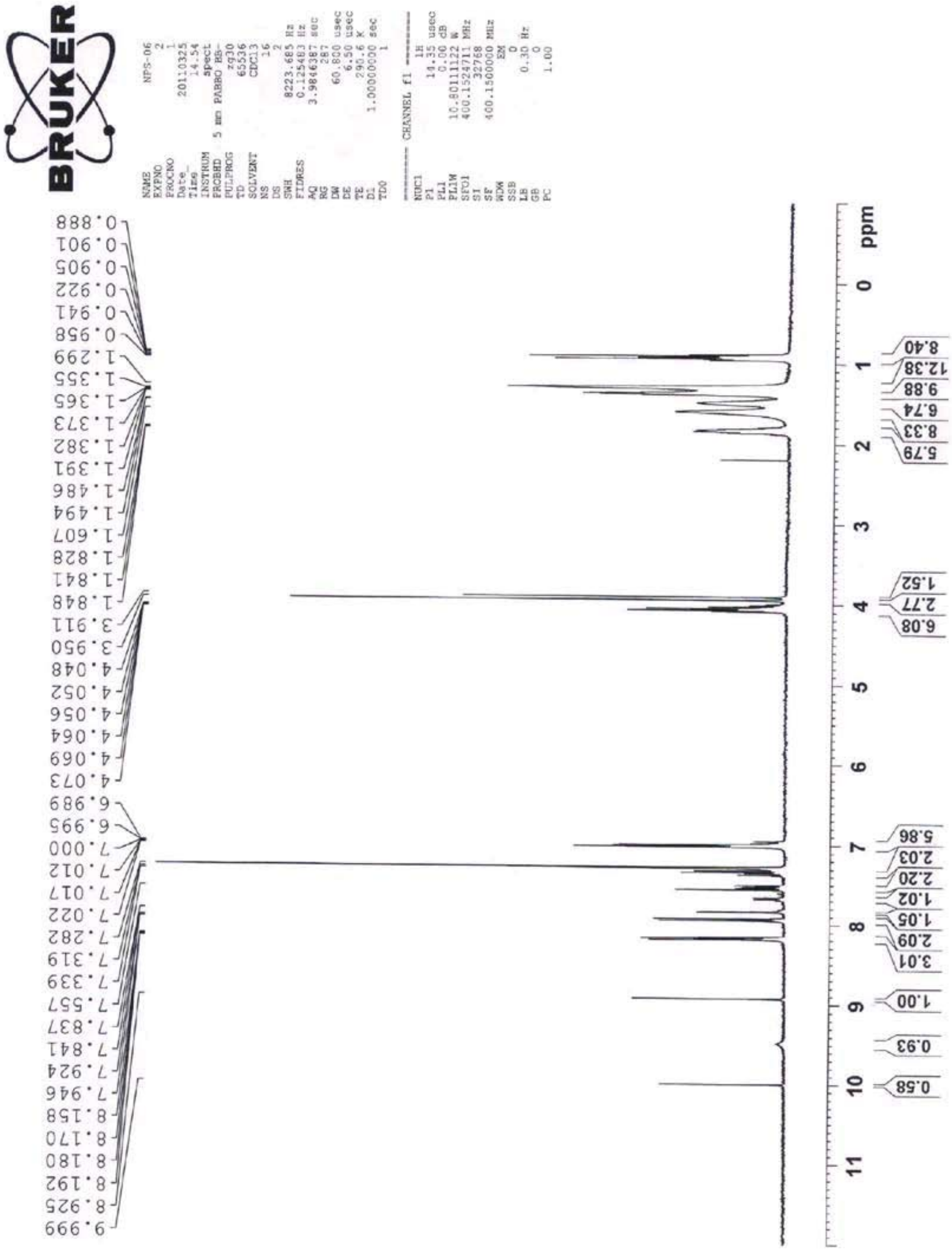


Figure 7. ^{1}H NMR spectra of *n*-hexyl derivative.

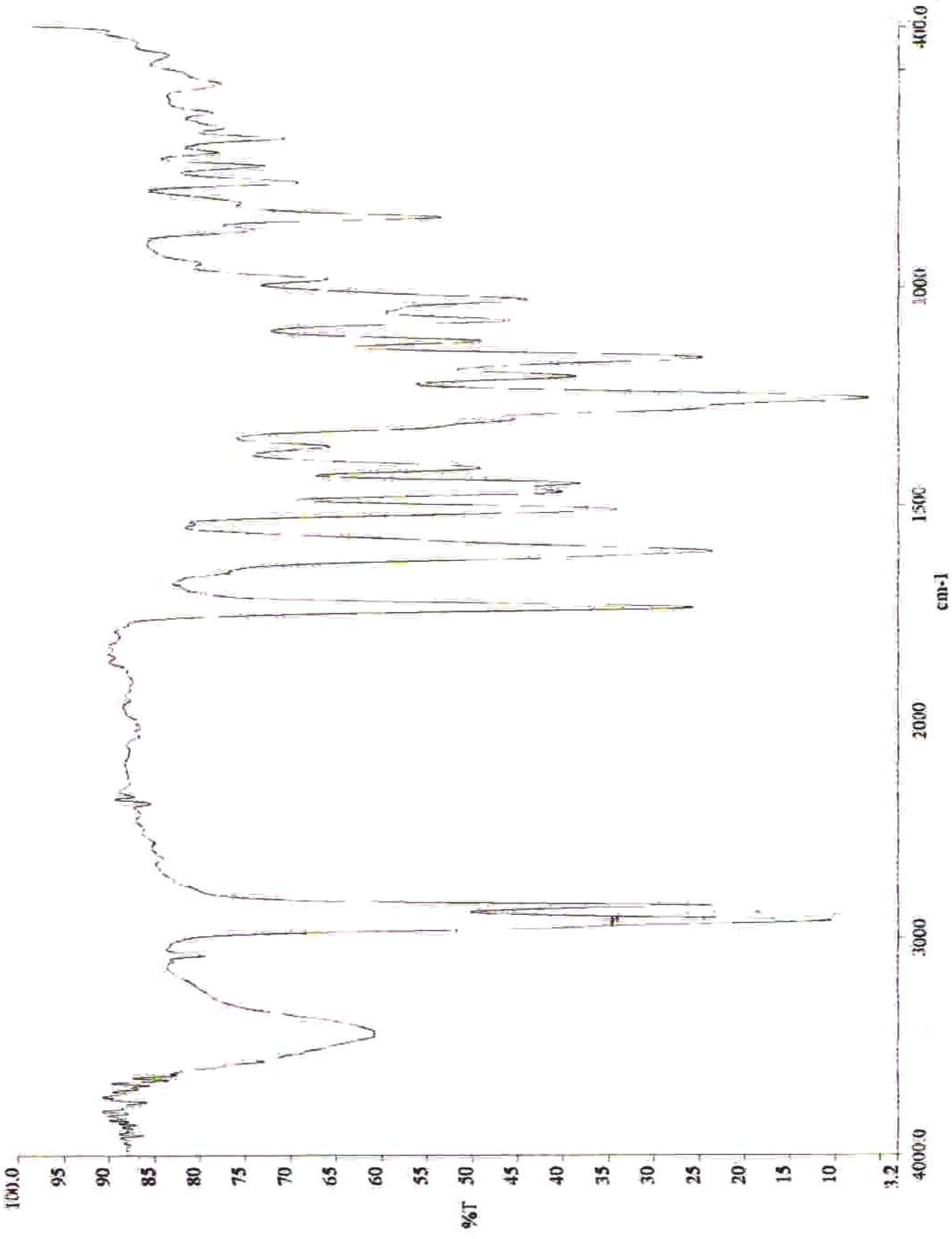


Figure 8. Representative IR spectra of *n*-tetradecyl derivative.

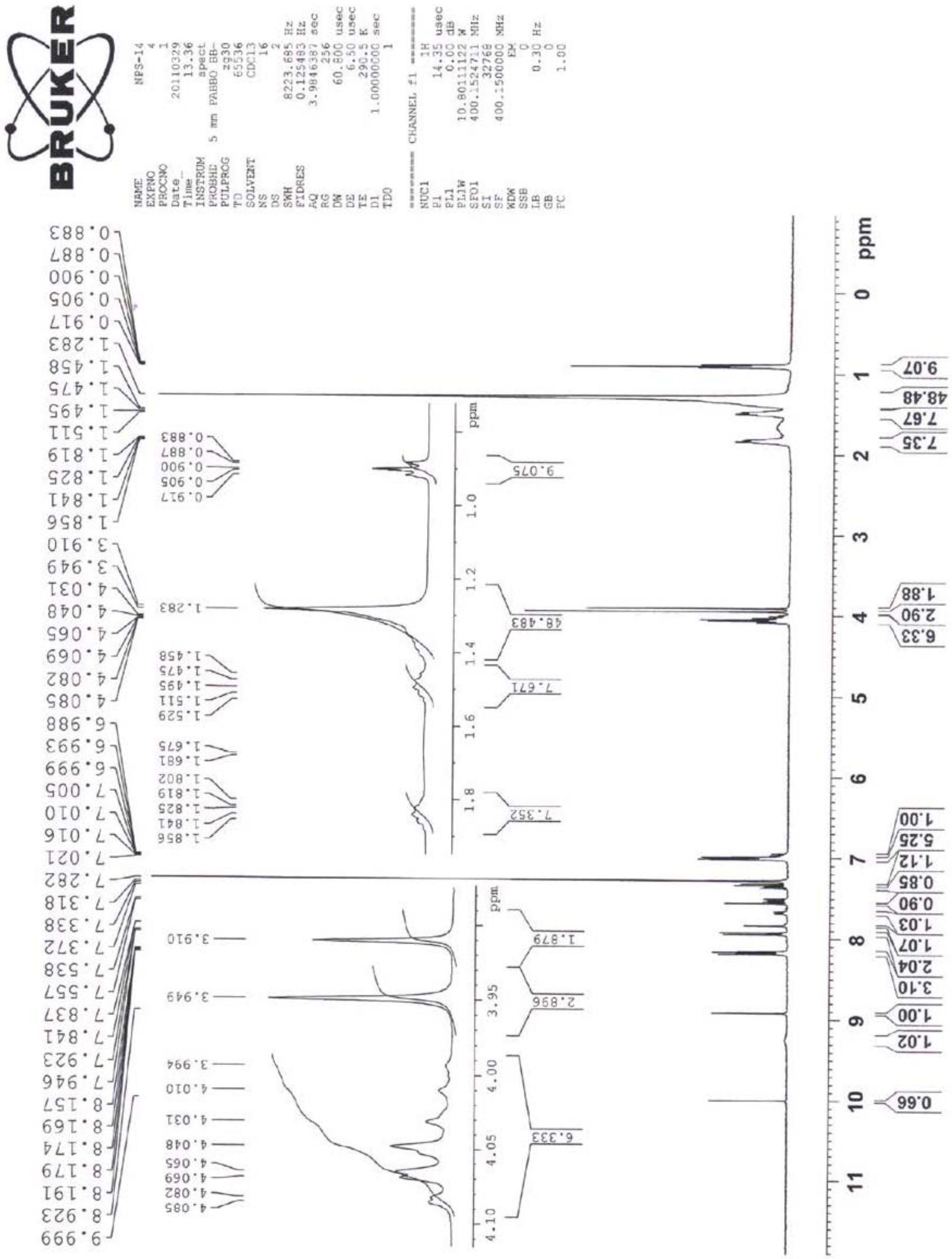


Figure 9. ^{1}H NMR spectra of *n*-tetradecyl derivative.

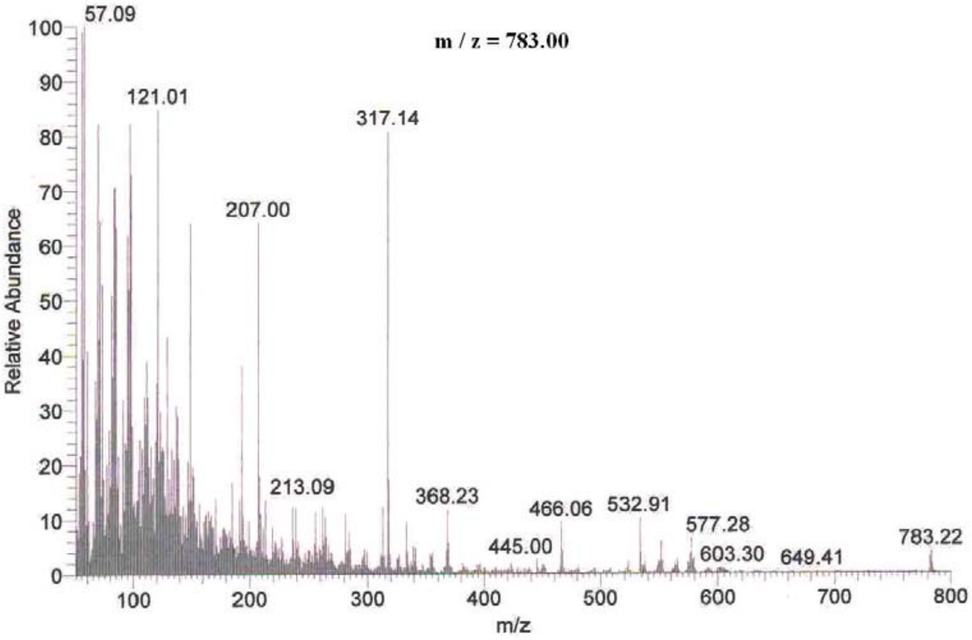


Figure 10. Mass spectra of *n*-tetradecyl derivative.

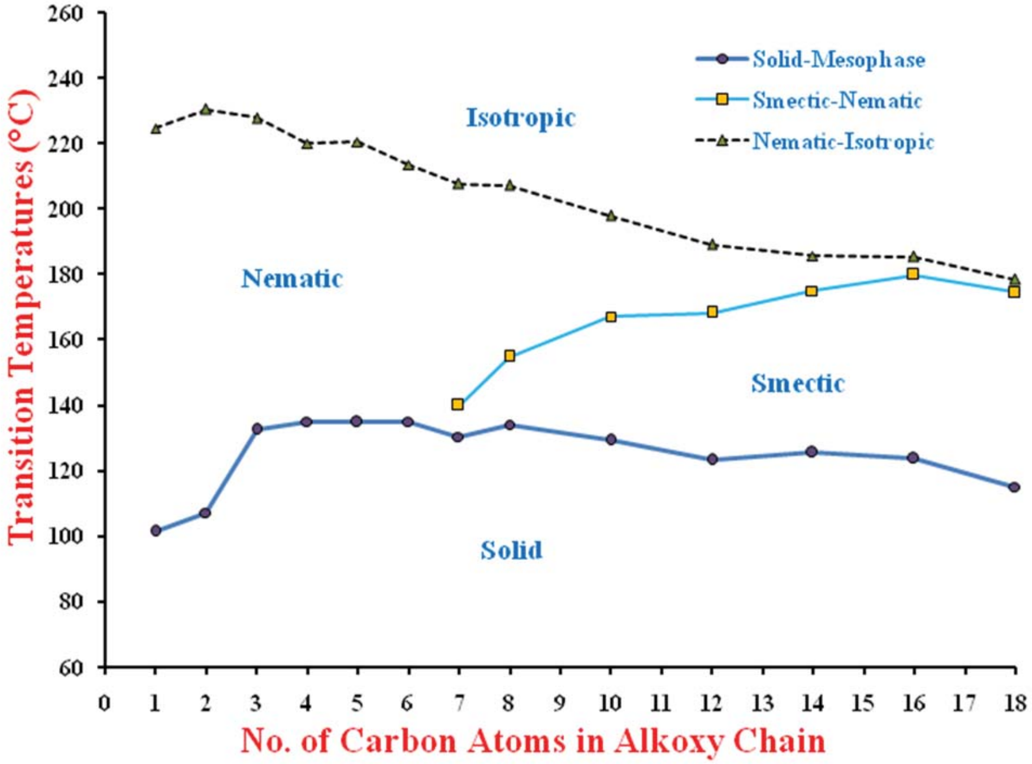


Figure 11. Plot of Transition temperatures (°C) versus number of carbon atoms in the alkoxy chain.

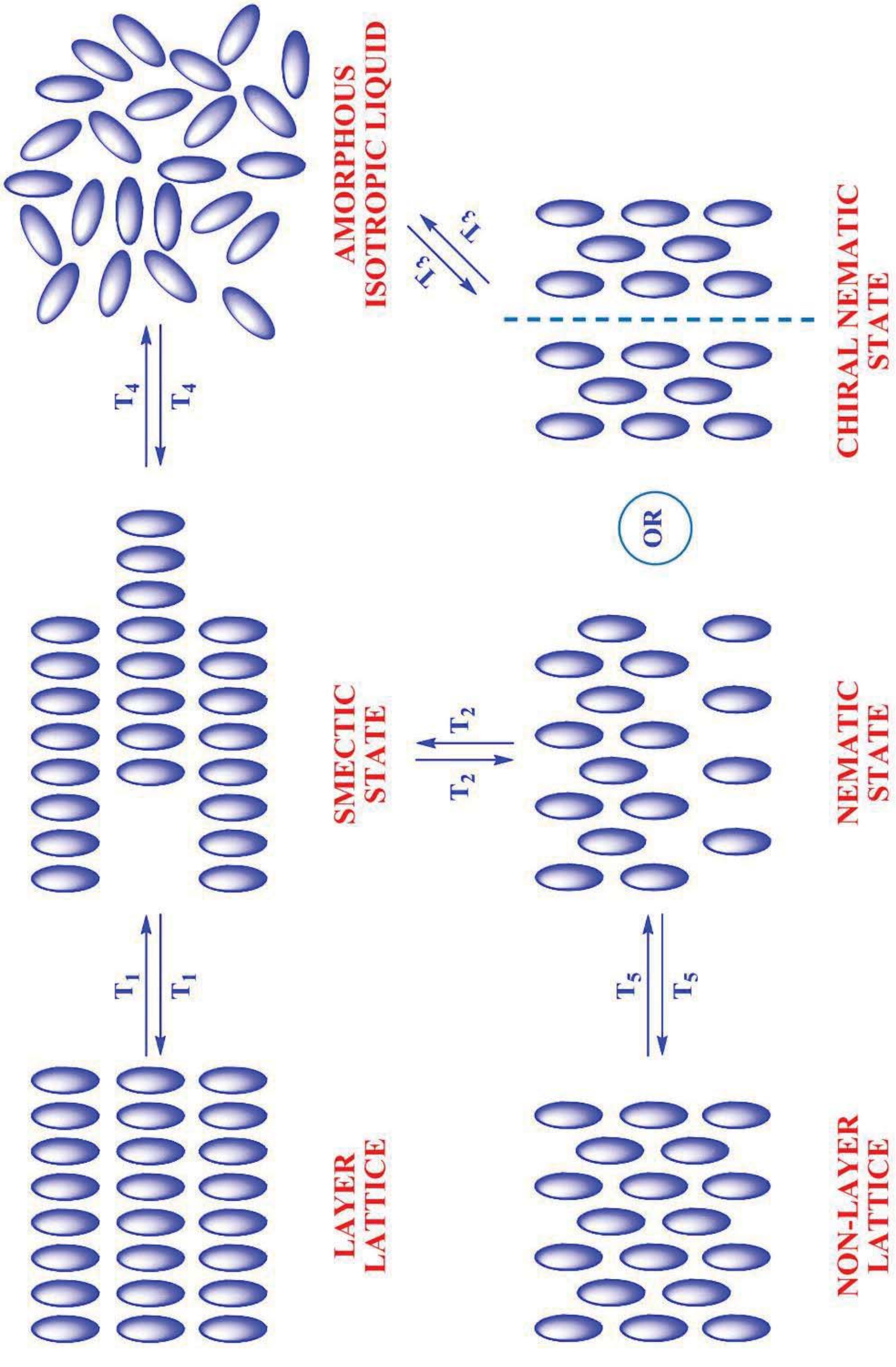


Figure 12. Arrangement of lath-like molecules in various states of matter.

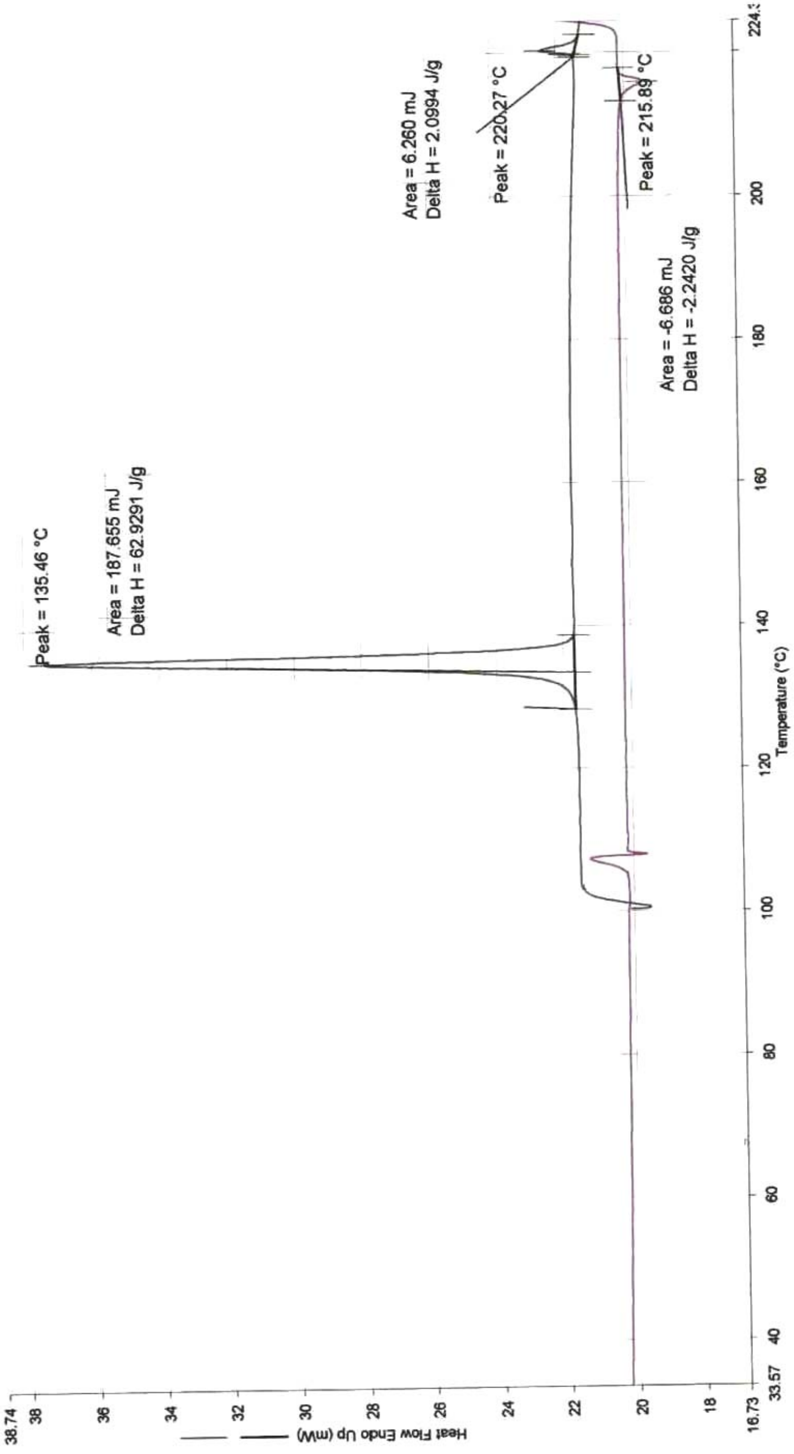


Figure 15. Representative DSC thermograms of *n*-pentyloxy derivative at heating rate of 10 °C min^{-1}.

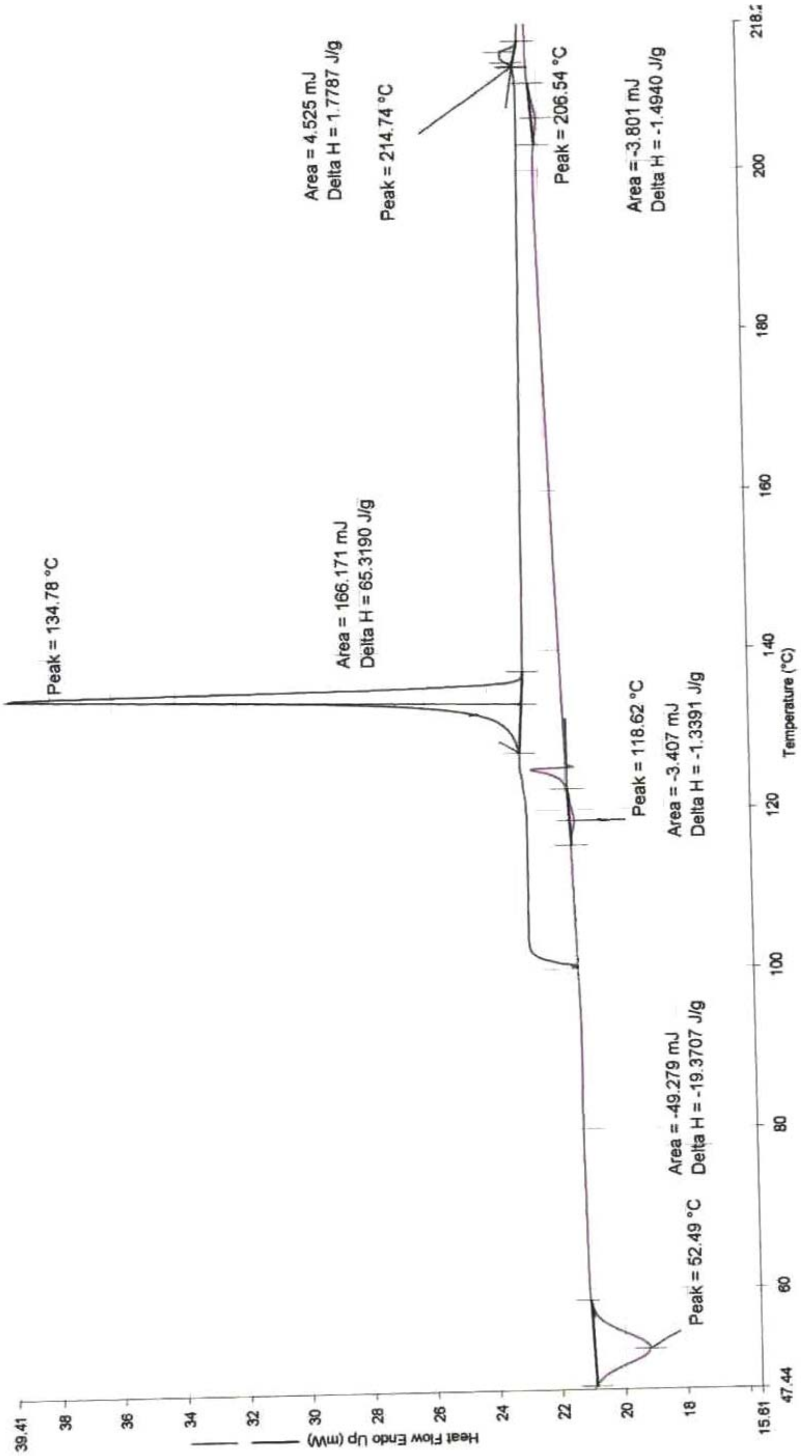


Figure 16. Representative DSC thermograms of *n*-hexyloxy derivative at heating rate of 10 °C min^{-1}.

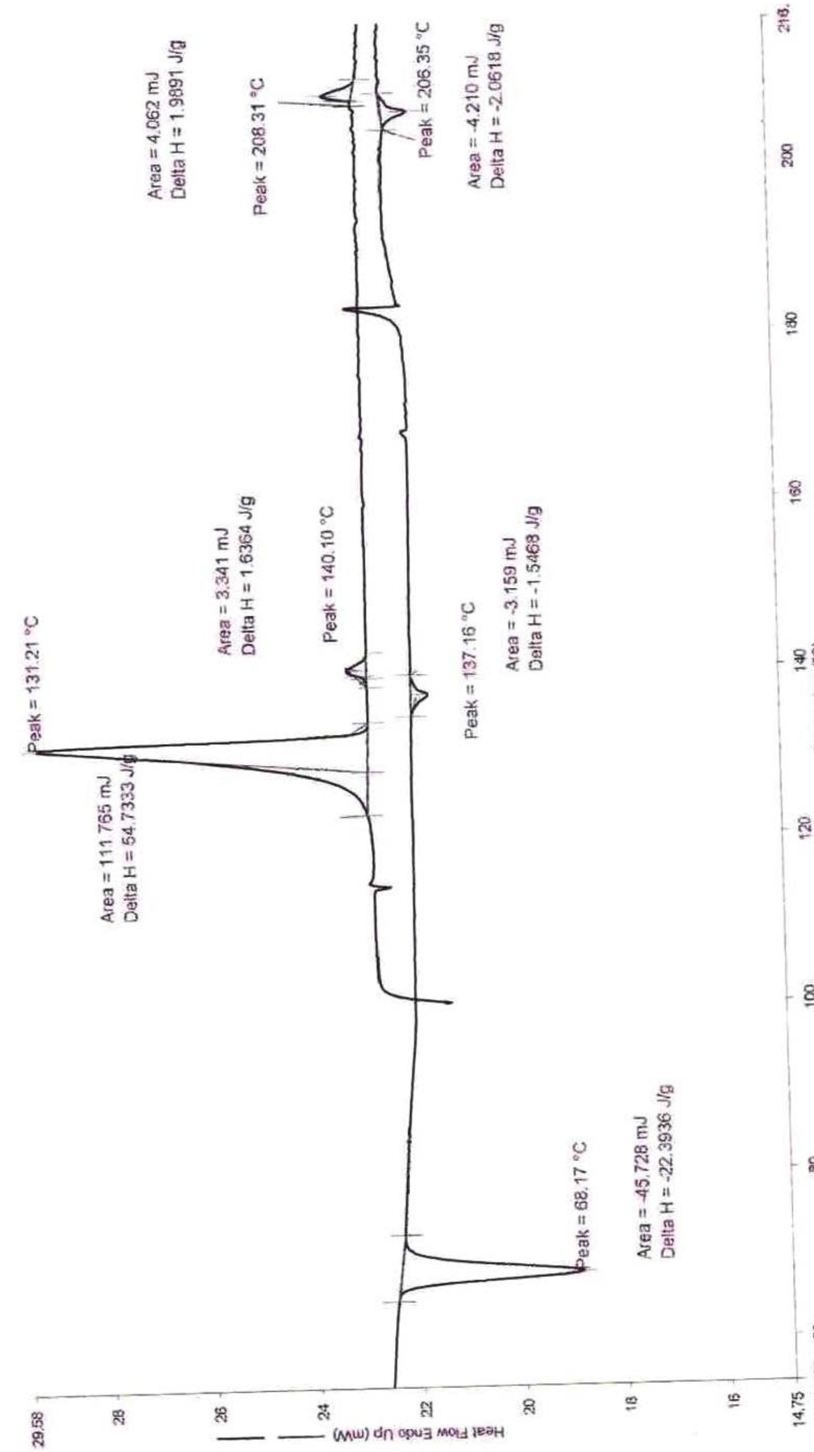


Figure 17. Representative DSC thermograms of *n*-heptyloxy derivative at heating rate of 10 °C min^{-1}.

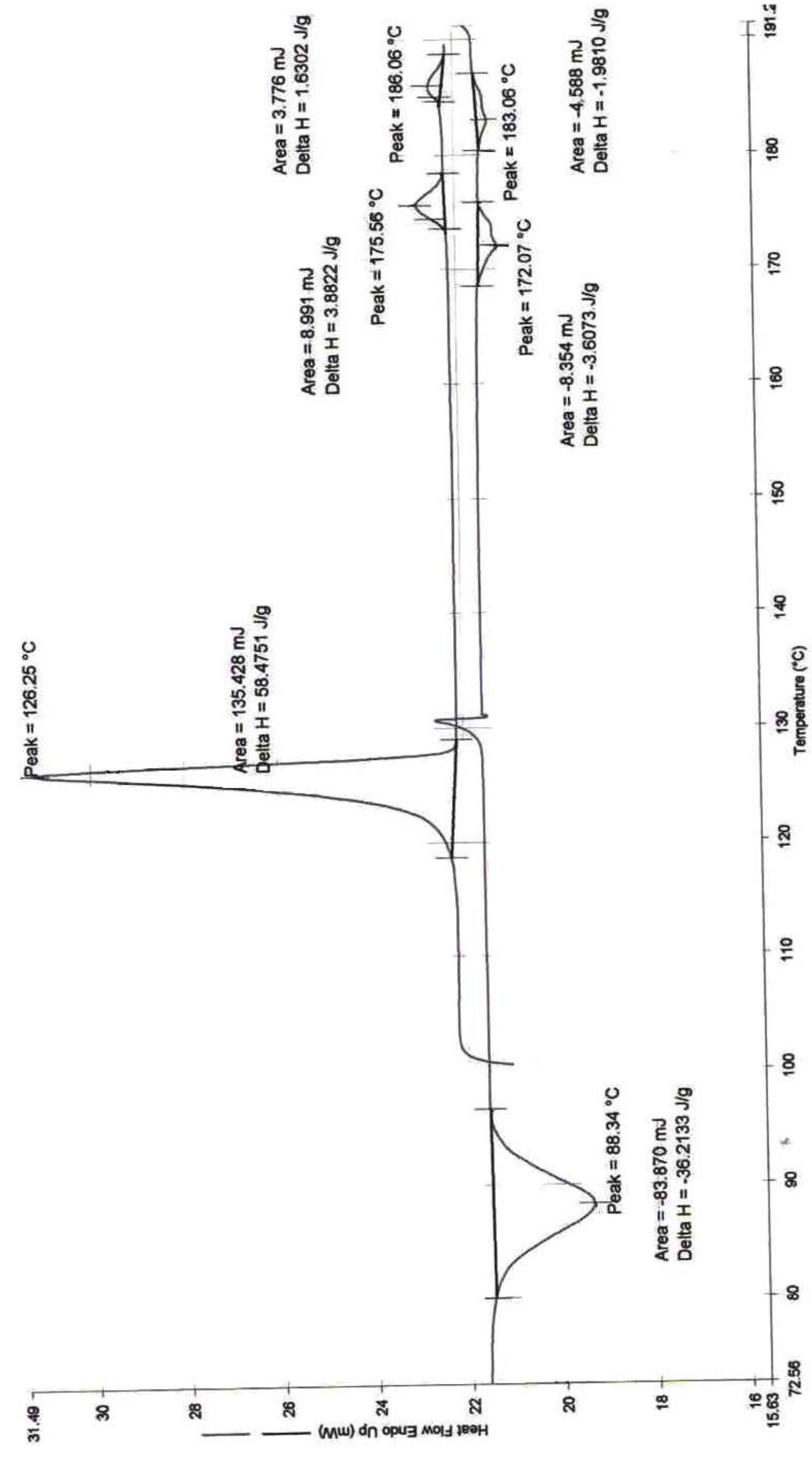


Figure 18. Representative DSC thermograms of *n*-tetradecyloxy derivative at heating rate of 10 °C min^{-1}.

2.3.1. Optical properties

1,3,4-Thiadiazoles have been investigated as an excellent candidate for light-emitting materials due to their photophysical and fluorescent properties. We were interested in studying some optical properties of our synthesized compounds. Hence, the UV-vis and fluorescence spectra were recorded. The UV-vis absorption and fluorescence spectra of *n*-hexyl and *n*-tetradecyl derivatives in $CHCl_3$ solution are shown in Figures 19 and 20, respectively. For *n*-hexyl derivative, in absorbance spectra, the λ_{max} occurred at 357 nm and the fluorescent emission peak is observed at 375 nm. For *n*-tetradecyl derivative, in absorbance spectra, the λ_{max} occurred at 307 nm and the fluorescent emission peak is observed at 375 nm.

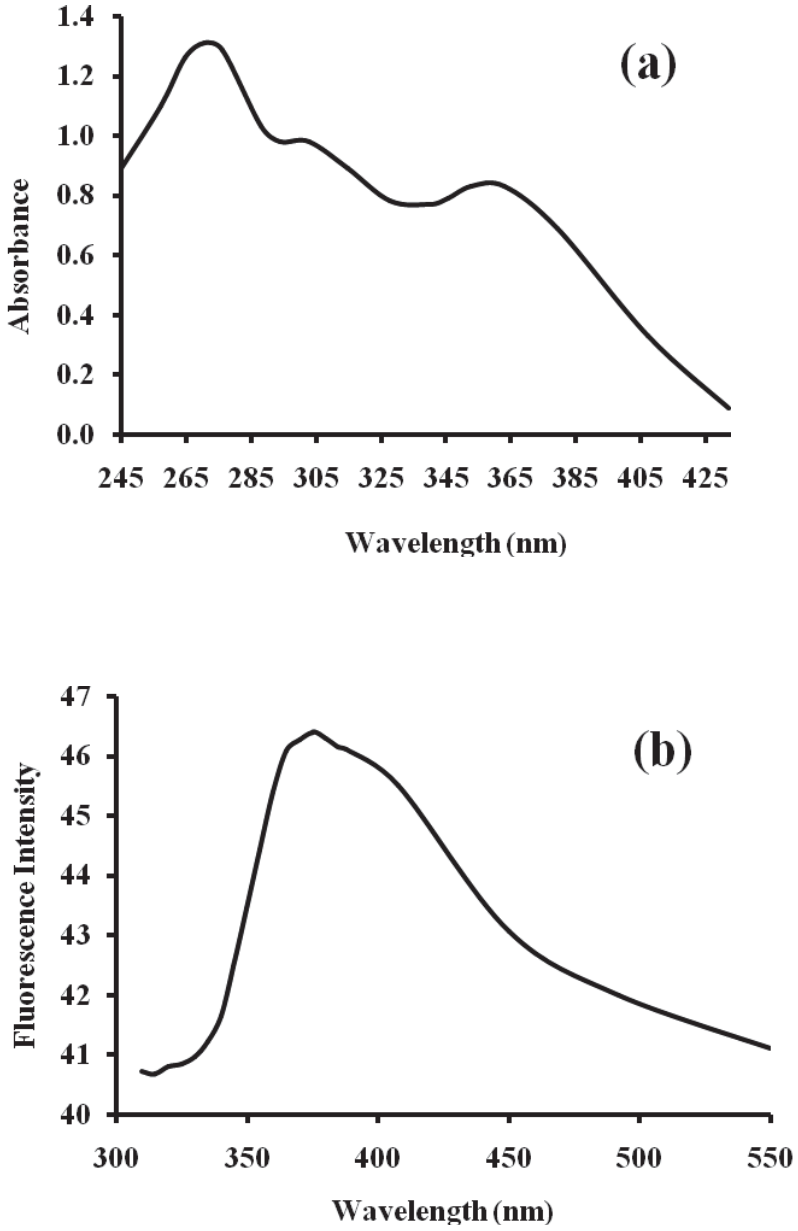


Figure 19. (a) UV-vis absorption spectra and (b) Fluorescence spectra of *n*-hexyl derivative in $CHCl_3$.

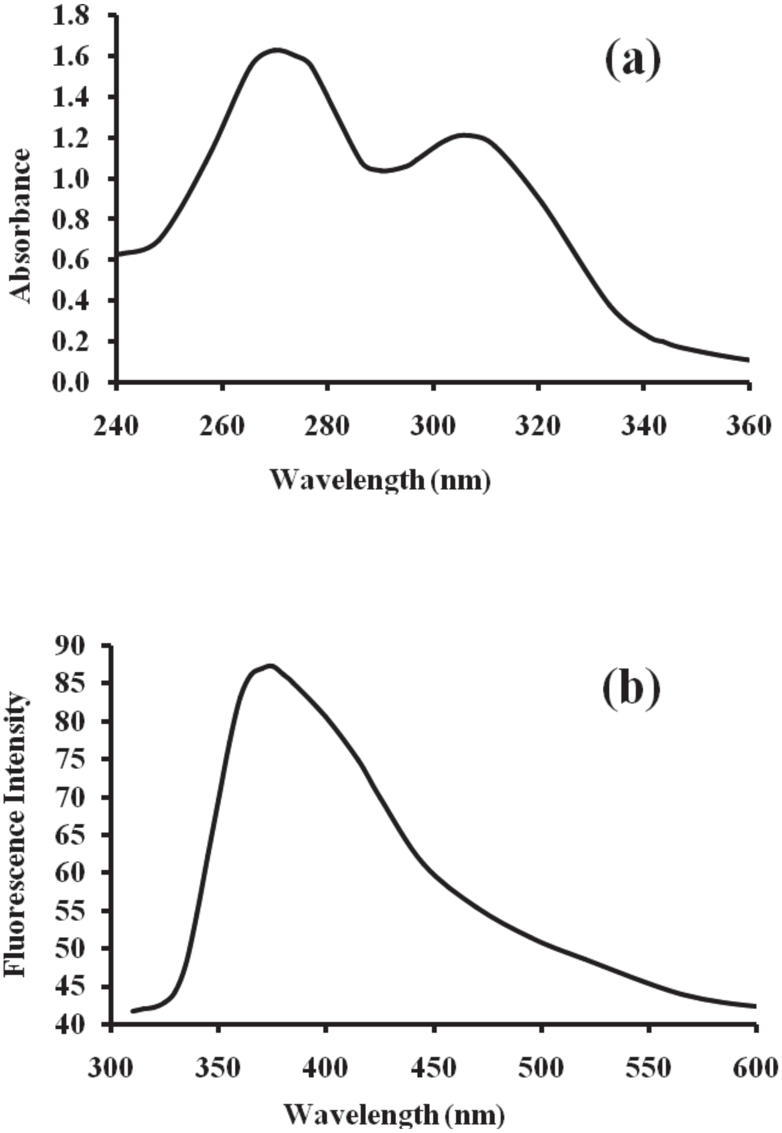


Figure 20. (a) UV-vis absorption spectra and (b) Fluorescence spectra of *n*-tetradecyl derivative in $CHCl_3$.

2.3.2. Optical textures

The most widely used technique of liquid crystal phase identification is optical polarizing microscopy. This technique reveals that each different liquid crystal phase has a distinct optical texture. However, the identification of liquid crystal phases through optical polarizing microscopy is often difficult and requires a lot of experience. Optical polarizing microscopy enables the identification of the type of liquid crystal and other mesophases from the optical texture that is generated. The identification of mesophases through optical polarizing microscopy usually involves the magnified view of a thin sample of a mesogenic material sandwiched between a glass microscope slide and a glass cover-slip. The microscope slide of material is usually placed in a stage between polarisers which are crossed at 90° to each other.

All the compounds of the series **I** show mesomorphic properties and all are enantiotropic in nature. The lower members starting with methyl to *n*-hexyl derivatives exhibit only the Nematic phase; while the higher member homologues starting with the *n*-heptyl derivative show both Smectic and Nematic phases and persists upto the last member of the series. The smectic and nematic phases were determined from optical texture observations under both heating and cooling cycles. The smectic phase is of smectic C type with characteristic broken focal conic or broken fan shape texture. Optical textures of some of the compounds of the series **I** are shown in Figures 21-24.

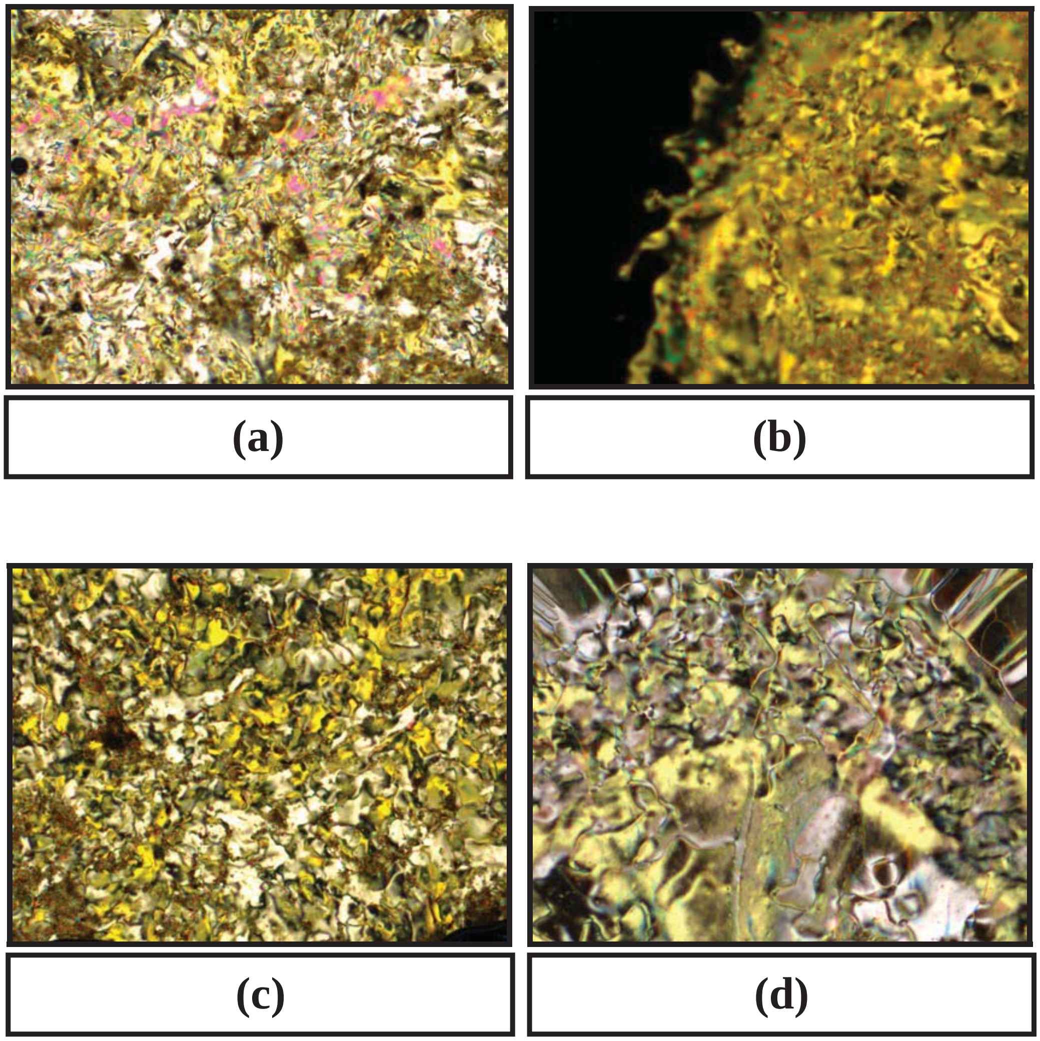


Figure 21. Polarised optical microphotographs of *n*-hexyl derivative. (a) Nematic-schlieren texture observed at 149.3 °C on heating, (b) Nematic to isotropic phase transition observed at 210.5 °C on heating, (c) Nematic-schlieren texture observed at 166.0 °C on cooling and (d) Nematic phase observed at 108.6 °C on cooling.

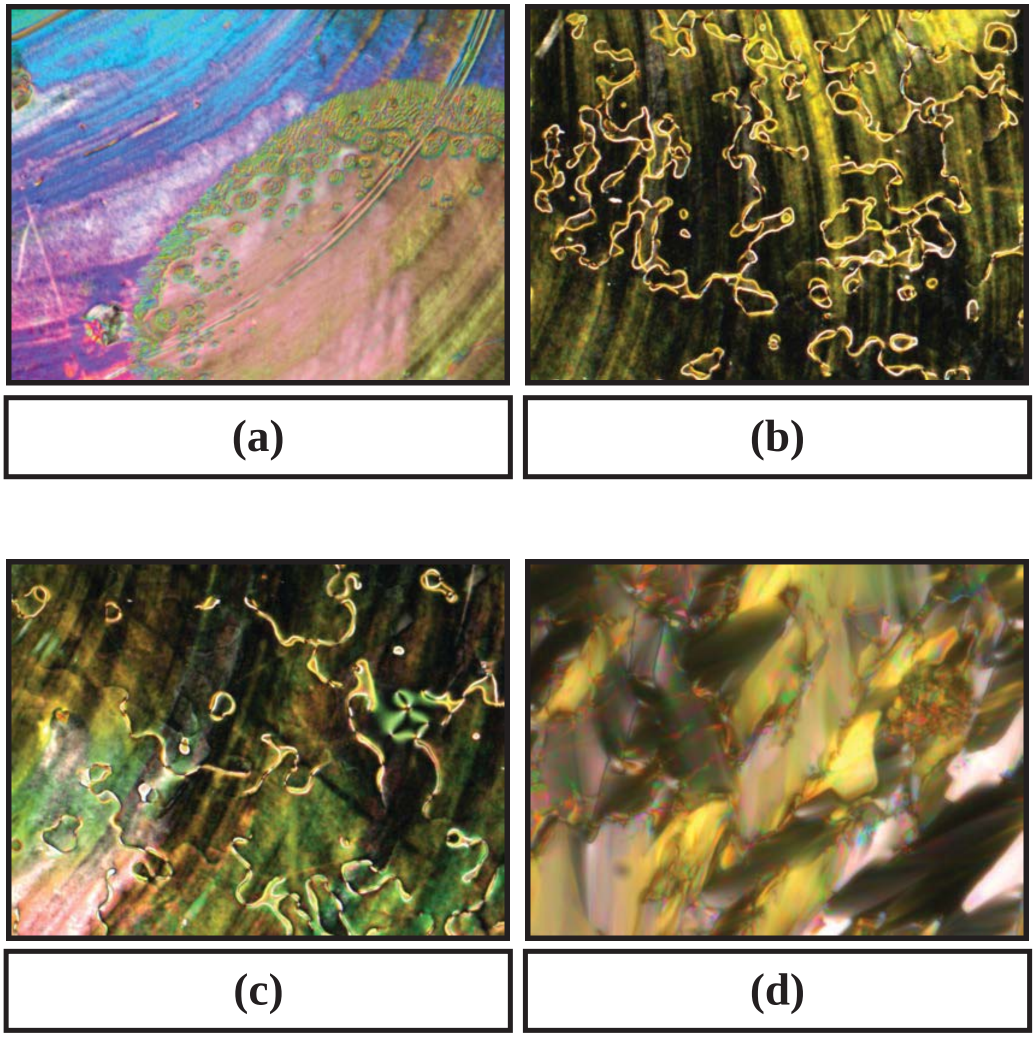


Figure 22. Polarised optical microphotographs of *n*-octyl derivative. (a) SmC to nematic phase transition observed at 153.5 °C on heating, (b) Nematic-thread like texture observed at 177.0 °C on cooling, (c) Nematic-thread like texture observed at 192.0 °C on heating and (d) SmC-broken focal conic texture observed at 146.0 °C on heating.

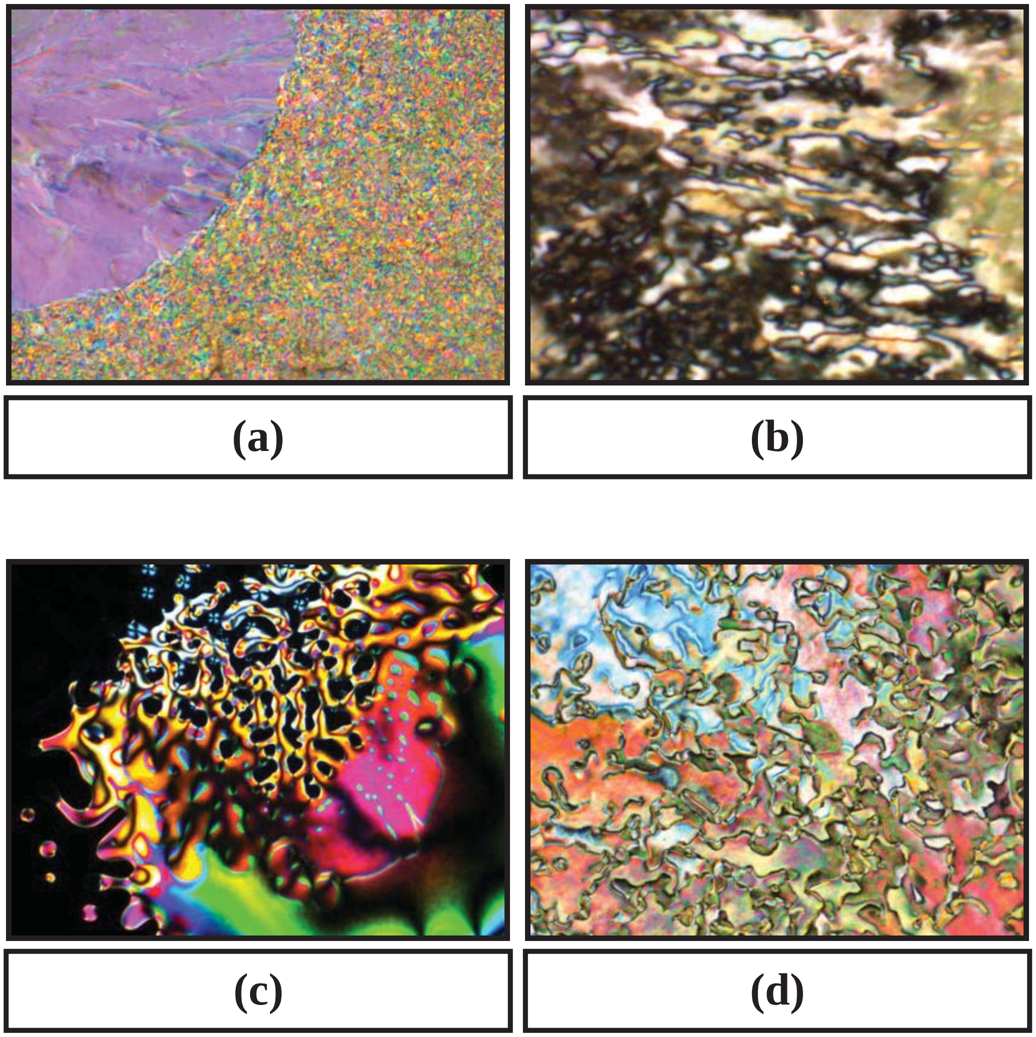


Figure 23. Polarised optical microphotographs of *n*-decyl derivative. (a) Appearance of SmC phase from solid observed at 126.5 °C on heating, (b) Nematic-thread like texture observed at 190.6 °C on heating, (c) Nematic to isotropic phase change observed at 195.4 °C on heating and (d) Nematic-thread like texture observed at 194.0 °C on cooling.

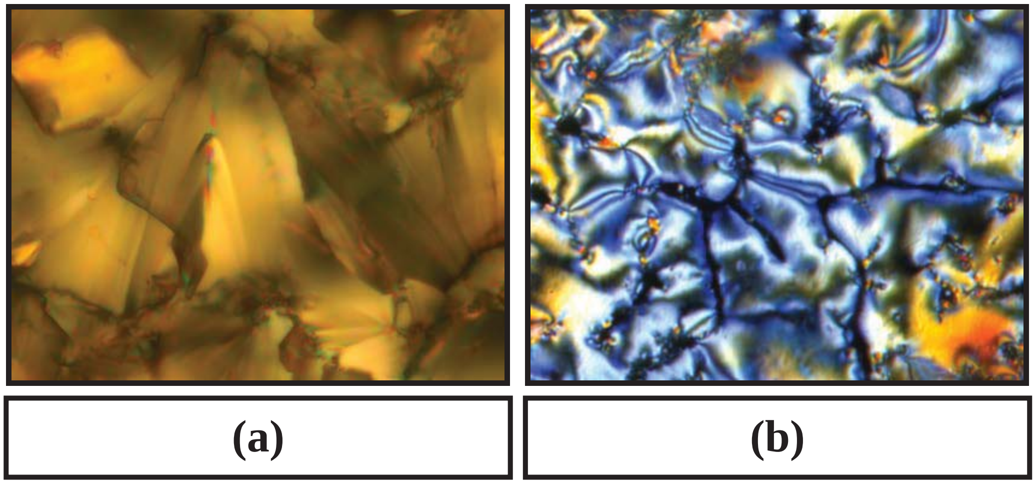


Figure 24. Polarised optical microphotographs of *n*-tetradecyl derivative. (a) SmC-broken focal conic texture observed at 138.6 °C on heating and (b) Nematic-schlieren texture observed at 179.0 °C on heating.

2.4. References

[1] P. Bäuerle, *Oligothiophenes*, Wiley-VCH, Weinheim, 1998.

[2] H. Zhang, S. Shiino, A. Shishido, A. Kanazawa, O. Tsutsumi, T. Shiono and T. Ikeda, *Adv. Mater.*, **12**(18), 1336-1339, 2000.

[3] M. O'Neill and S. M. Kelly, *Adv. Mater.*, **15**(14), 1135-1146, 2003.

[4] Y. S. Park, D. Kim, H. Lee and B. Moon, *Org. Lett.*, **8**(21), 4699-4702, 2006.

[5] T. Geelhaar, *Ferroelectrics*, **85**(1), 329-349, 1988.

[6] G. Barbarella, M. Zambianchi, O. Pudova, V. Paladini, A. Ventola, F. Cipriani, G. Gigli, R. Cingolani and G. Citro, *J. Am. Chem. Soc.*, **123**(47), 11600-11607, 2001.

[7] A. Mohd and S. Kumar, *Eur. J. Med. Chem.*, **39**, 535-545, 2004.

[8] N. D. Hatice, D. Arzu, R. Sevim, G. Sener, K. U. Meral and G. Dumrul, *Bioorg. Med. Chem.*, **10**, 2893-2898, 2002.

[9] F. Alireza, M. Shahla, K. Zahra and R. Afsaneh, *Eur. J. Med. Chem.*, **38**, 851-854, 2003.

[10] R. Nandi, H. K. Singh, S. K. Singh, B. Singh and R. K. Singh, *Liq. Cryst.*, **40**(7), 884-899, 2013.

[11] M. Hird, *Chem. Soc. Rev.*, **36**, 2070-2095, 2007.

[12] M. Z. A. Rahman, A. A. Salisu, S. Silong, M. R. Lutfor and M. B. A. Ayub, *Asian J. Appl. Sci.*, **2**(2), 177-183, 2009.

[13] A. A. Salisu, M. Z. A. Rahman, S. Silong, M. R. Lutfor and M. B. Ahmad, *Liq. Cryst.*, **38**(4), 423-431, 2011.

[14] G. I. Kornis, *Comprehensive Heterocyclic Chemistry*, Elsevier Science, Oxford, 1996.

[15] S. T. Lagerwall, *Ferroelectric and Antiferroelectric Liquid Crystals*, Wiley-VCH, Weinheim, 1999.

[16] J. C. Jones, M. J. Towler and J. R. Hughes, *Displays*, **14**(2), 86-93, 1993.

[17] J. W. Goodby, *Properties and Structures of Ferroelectric Liquid Crystals*, Gordon and Breach Publishers, Philadelphia, 1991.

[18] T. P. Rieker, N. A. Clark, G. S. Smith, D. S. Parmar, E. B. Sirota and C. R. Safinya, *Phys. Rev. Lett.*, **59**(23), 2658-2661, 1987.

[19] P. Mach, R. Pindak, A. -M. Levelut, P. Barois, H. T. Nguyen, C. C. Huang and L. Furenlid, *Phys. Rev. Lett.*, **81**(5), 1015-1018, 1998.

[20] N. L. Campbell, W. L. Duffy, G. I. Thomas, J. H. Wild, S. M. Kelly, K. Bartle, M. O'Neill, V. Minter and R. P. Tuffin, *J. Mater. Chem.*, **12**(9), 2706-2721, 2002.

[21] R. Lunkwitz, C. Tschierske, A. Langhoff, F. Gieβelmann and P. Zugenmaier, *J. Mater. Chem.*, **7**(9), 1713-1721, 1997.

[22] C. Tschierske, H. Zaschke, H. Kresse, A. Mädieke, D. Demus, D. Girdziunaite and G. Y. Bak, *Mol. Cryst. Liq. Cryst.*, **191**(1), 223-230, 1990.

[23] S. Sugita, S. Toda, T. Yamashita and T. Teraji, *Bull. Chem. Soc. Jpn.*, **66**(2), 568-572, 1993.

[24] S. -I. Sugita, S. Toda and T. Teraji, *Mol. Cryst. Liq. Cryst.*, **237**(1), 33-38, 1993.

[25] W. Schäfer, U. Rosenfeld, H. Zaschke, H. Stellin and H. Kresse, *J. Prakt. Chem.*, **331**(4), 631-636, 1989.

[26] K. Dimitrowa, J. Hauschild, H. Zaschke and H. Schubert, *J. Prakt. Chem.*, **322**(6), 933-944, 1980.

[27] S. -I. Sugita, S. Toda, T. Teraji, A. Murayama and M. Ishikawa, *Mol. Cryst. Liq. Cryst.*, **226**(1), 7-12, 1993.

[28] J. Stichler-Bonaparte, H. Kruth, R. Lunkwitz and C. Tschierske, *Leibigs. Ann.*, (9), 1375-1379, 1996.

[29] C. Tschierske and D. Girdziunaite, *J. Prakt. Chem.*, **333**(9), 135-137, 1991.

[30] B. Neumann, C. Sauer, S. Diele and C. Tschierske, *J. Mater. Chem.*, **6**(7), 1087-1098, 1996.

[31] M. Loos-Wildenauer, S. Kunz, I. G. Voigt-Martin, A. Yakimanski, E. Wischerhoff, R. Zentel, C. Tschierske and M. Muller, *Adv. Mater.*, **7**(2), 170-173, 1995.

[32] M. Baron and C. V. Wilson, *J. Org. Chem.*, **23**, 1021-1023, 1958.

[33] K. Zab, H. Kruth and C. Tschierske, *Chem. Commun.*, (8), 977-978, 1996.

[34] D. B. Dess and J. C. Martin, *J. Am. Chem. Soc.*, **113**(19), 7277-7287, 1991.

[35] M. M. Midland, A. Tramontano, A. Kazubski, R. S. Graham, D. J. S. Tsai and D. B. Cardin, Tetrahedron, **40**(8), 1371-1380, 1984.

[36] M. Parra, J. Belmar, H. Zunza, C. Zuñiga, S. Villouta and R. Martinez, *Bol. Soc. Chil. Quim.*, **38**(4), 325-330, 1993.

[37] M. Parra, J. Alderete, C. Zúñiga and S. Hernández, *Liq. Cryst.*, **29**(5), 647-652, 2002.

[38] M. Parra, J. Belmar, H. Zunza, C. Zúñiga, S. Villouta and R. Martinez, *J. Prakt. Chem.*, **337**(1), 325-327, 1995.

[39] M. Parra, J. Belmar, S. Villouta, R. Martinez, C. Zúñiga and H. Zunza, *Bol. Soc. Chil. Quim.*, **40**(2), 175-182, 1995.

[40] M. Parra, S. Hernández, J. Alderete and C. Zúñiga, *Liq. Cryst.*, **27**(8), 995-1000, 2000.

[41] M. Parra, J. Vergara, J. Alderete and C. Zuniga, *Liq. Cryst.*, **31**(11), 1531-1537, 2004.

[42] M. Parra, J. Vergara, C. Zúñiga, E. Soto, T. Sierra and J. Serrano, *Liq. Cryst.*, **32**(4), 457-462, 2005.

[43] M. Parra, J. Vergara, P. Hidalgo, J. Barberá and T. Sierra, *Liq. Cryst.*, **33**(6), 739-745, 2006.

[44] M. Parra, S. Villouta, V. Vera, J. Belmar, C. Zúñiga and H. Zunza, *Z Naturforsch B: Chem. Sci.*, **52**(12), 1533-1538, 1997.

[45] M. Parra, J. Alderete, C. Zúñiga, H. Gallardo, P. Hidalgo, J. Vergara and S. Hernández, *Liq. Cryst.*, **28**(11), 1659-1666, 2001.

[46] L. -L. Lai and E. Wang, *Helv. Chim. Acta.*, **84**(12), 3581-3587, 2001.

[47] Y. Xu, Z. -G. Zhu and Z. Xu, *Chin. J. Chem.*, **19**(9), 870-876, 2001.

[48] P. Bradley, P. Sampson and A. J. Seed, *Liq. Cryst. Today.*, **14**(1), 15-18, 2005.

[49] M. Sato and Y. Kitani, *Liq. Cryst.*, **30**(9), 1109-1114, 2003.

[50] M. Sato and R. Ohta, *Liq. Cryst.*, **34**(3), 295-303, 2007.

[51] M. L. Parra, C. G. Saavedra, P. I. Hidalgo and E. Y. Elgueta, *Liq. Cryst.*, **35**(1), 55-64, 2008.

[52] M. L. Parra, E. Y. Elgueta, J. A. Ulloa, J. M. Vergara and A. I. Sanchez, *Liq. Cryst.*, **39**(8), 917-925, 2012.

[53] H. Huang, H. Yu, P. Chen and J. Han, *Chin. J. Org. Chem.*, **24**, 502-505, 2004.

[54] J. Han, X. Chang, X. Wang, L. Zhu, M. Pang and J. Meng, *Liq. Cryst.*, **36**(2), 157-163, 2009.

[55] J. Han, J. -Y. Wang, F. -Y. Zhang, L. -R. Zhu, M. -L. Pang and J. -B. Meng, *Liq. Cryst.*, **35**(10), 1205-1214, 2008.

[56] J. Han, F. -Y. Zhang, J. -Y. Wang, Y. -M. Wang, M. -L. Pang and J. -B. Meng, *Liq. Cryst.*, **36**(8), 825-833, 2009.

[57] P. Kamotra, A. K. Gupta, R. Gupta, P. Somal and S. Singh, *Indian J. Chem. Sect. B: Org. Chem. Incl. Med. Chem.*, **46B**(6), 980-984, 2007.

[58] J. Seltmann and M. Lehmann, *Liq. Cryst.*, **38**(4), 407-422, 2011.

[59] H. Gallardo, G. Conte, P. A. Tuzimoto, B. Behramand, F. Molin, J. Eccher and I. H. Bechtold, *Liq. Cryst.*, **39**(9), 1099-1111, 2012.

[60] H. Gallardo, D. M. P. de O. Santos, G. F. Caramori, F. Molin and I. H. Bechtold, *Liq. Cryst.*, **40**(5), 570-580, 2013.

[61] A. Banu, R. S. Lamani, I. M. Khazi and N. S. Begum, *Mol. Cryst. Liq. Cryst.*, **533**, 162-171, 2010.

[62] A. Banu, R. S. Lamani, I. M. Khazi and N. S. Begum, *Mol. Cryst. Liq. Cryst.*, **533**, 141-151, 2010.

[63] A. K. Gadad, C. S. Mahajanshetti, S. Nimbalkar and A. Raichurkar, *Eur. J. Med. Chem.*, **35**(9), 853-857, 2000.

[64] G. Kolavi, V. Hegde and I. A. Khazi, *Synth. Commun.*, **36**(13), 1837-1843, 2006.

[65] J. H. Tomma, I. H. Rou’il and A. H. Al-Dujaili, *Mol. Cryst. Liq. Cryst.*, **501**, 3-19, 2009.

[66] D. Joachimi, C. Tschierske, A. Öhlmann and W. Rettig, *J. Mater. Chem.*, **4**(7), 1021-1027, 1994.

[67] C. Tschierske, D. Joachimi, H. Zaschke, H. Kresse, B. Linström, G. Pelzl, D. Demus and G. Y. Bak, *Mol. Cryst. Liq. Cryst.*, **191**, 231-236, 1990.

[68] B. Sybo, P. Bradley, A. Grubb, S. Miller, K. J. W. Proctor, L. Clowes, M. R. Lawrie, P. Sampson and A. J. Seed, *J. Mater. Chem.*, **17**(32), 3406-3411, 2007.

[69] E. E. Oruç , S. Rollas, F. Kandemirali, N. Shvets and A. S. Dimoglo, *J. Med. Chem.*, **47**(27), 6760-6767, 2004.

[70] A. Pati, M. Patra and R. K. Behera, *Synth. Commun.*, **36**(12), 1801-1808, 2006.

[71] M. Sato, Y. Matsuoka and I. Yamaguchi, *Liq. Cryst.*, **39**(9), 1071-1081, 2012.

[72] V. N. Yarovenko, A. V. Shirokov, I. V. Zavarzin, O. N. Krupinova, A. V. Ignatenko and M. M. Krayushkin, *Chem. Heterocycl. Compd.*, **39**(12), 1633-1638, 2003.

[73] J. S. Dave and R. A. Vora, *Liquid Crystals and Ordered Fluids*, **4**, 477-487, 1970.

[74] R. Gupta, *Synthesis of potential mesogens and study of their mesogenic properties*, Ph.D. Thesis, The M. S. University of Baroda, Vadodara, 1980.

[75] R. A. Parker, T. Kariya, J. M. Grisar and V. Petrow, *J. Med. Chem.*, **20**(6), 781-791, 1977.

[76] J. S. Dave and G. Kurian, *J. Phys. (Paris, Colloq.*, **36**(C1), 403-408, 1975.

[77] C. T. Imrie, *Liq. Cryst.*, **6**(1), 1-10, 1989.

[78] R. W. Date, C. T. Imrie, R. Luckhurst and J. M. Seddon, *Liq. Cryst.*, **12**(2), 203-238, 1992.

[79] S. Marčelja, *J. Chem. Phys.*, **60**(9), 3599-3604, 1974.

[80] G. W. Gray, *Mol. Cryst.*, **1**(2), 333-349, 1966.

[81] G. W. Gray, *Mol. Cryst.*, **7**, 127-151, 1969.

[82] G. W. Gray, *Molecular Structure and the Properties of Liquid Crystals*, Academic Press, London, 1962.

[83] W. Maier and G. Baumgartner, *Z. Naturforsch*, **7**(a), 172, 1952.

[84] W. Maier, *Z. Naturforsch*, **2**(a), 458-464, 1947.

[85] A. Pines, D. J. Ruben and S. Allison, *Phys. Rev. Lett.*, **33**(17), 1002-1005, 1974.

[86] W. H. De Jeu and J. van der Veen, *Mol. Cryst. Liq. Cryst.*, **40**, 1-17, 1977.

[87] C. T. Imrie, *Liq. Cryst.*, **6**(4), 391-396, 1989.

[88] P. A. Henderson, O. Niemeyer and C. T. Imrie, *Liq. Cryst.*, **28**(3), 463-472, 2001.

[89] G. -Y. Yeap, T. –C. Hng, S. –Y. Yeap, E. Gorecka, M. M. Ito, K. Ueno, M. Okamoto, W. A. K. Mahmood and C. T. Imrie, *Liq. Cryst.*, **36**(12), 1431-1441, 2009.

[90] A. P. J. Emerson and G. R. Luckhurst, *Liq. Cryst.*, **10**(6), 861-868, 1991.

[91] A. P. J. Ferrarini and G. R. Luckhurst, *J. Chem. Phys.*, 100(2), 1460-1469, 1994.

[92] A. Ferrarini, G. R. Luckhurst, P. L. Nordio and S. J. Roskilly, *Chem. Phys. Lett.*, **214**(3-4), 409-417, 1993.

[93] A. Ferrarini, G. R. Luckhurst, P. L. Nordio and S. J. Roskilly, *Liq. Cryst.*, **21**(3), 373-382, 1996.

[94] P. J. Barnes, A. G. Douglass, S. K. Heeks and G. R. Luckhurst, *Liq. Cryst.*, **13**(4), 603-613, 1993.

[95] W. L. McMillan, *Phys. Rev. A.*, **4**(3), 1238-1246, 1971.

Chapter 3

LIQUID CRYSTALLINE CHOLESTEROL DERIVATIVES

LIQUID CRYSTALLINE CHOLESTEROL DERIVATIVES

3.1. Introduction

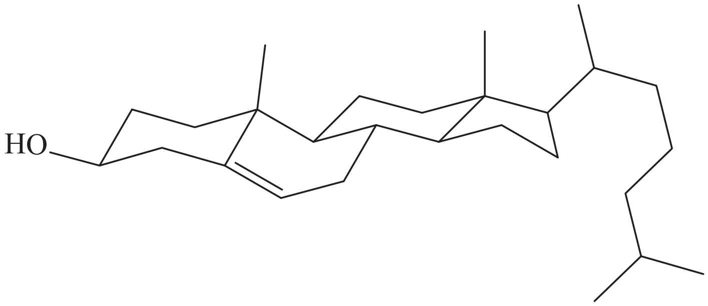
Cholesterol-based liquid crystals have attracted attention from more and more researchers over the last decade. This growing interest in the cholesterol-based liquid crystals is due its abundant in nature and also it is a commercially available chiral compound. The first reported example of a thermotropic liquid crystal, cholesteryl benzoate occupies a unique place in the history of liquid crystals [1] and since its discovery over 100 years ago, more than 3000 cholesterol derivatives have been reported [2]. Cholesterol-based compounds have many unique optical properties, such as selective reflection, circular dichroism, electro-optical and magneto-optical effects; they could be applied to optical storage, optical switching, nonlinear optics and liquid crystal display devices [3-5].

Cholesterol itself does not form a liquid crystalline state but nearly all the compounds derived from it exhibit the properties of the cholesteric mesophase (historically, the chiral nematic N* phase was called the cholesteric mesophase). The basic units in nearly all cholesteric liquid crystal (CLC) formulations are molecules of cholesterol, or steroids with closely related structures such as betasitosterol, cholestanol and stignasterol, in which the hydroxyl group at the 3-position has been replaced by an ester, carbonate, or halo group [6]. The primary factor in forming a chiral nematic mesophase is the shape of the cholesterol molecule (compound **1**). As can be seen it is quite broad but elongated, and so satisfies the basic requirement of a "rod like" nature necessary for mesomorphic compound. More important though are two other factors:

(a) The molecule is slightly non-planar. The skeleton of the molecule is four rings of carbon atoms fused together to form a shape which zig-zag slightly in and out of the plane of the paper. Attached to this skeleton are groups which stick up out of the plane.

(b) The shape of the molecule is not symmetrical; in no way can it be superimposed on its mirror image.

In a CLC the molecules tend firstly because of their elongation to align themselves parallel to each other. Once one layer of parallel alignment has formed then, because of the slight non-polarity of the molecules in this layer, the next layer of molecules will be skewed slightly to allow it to "sit" better on the layer underneath. Since the molecules in the layers are asymmetric it can be postulated that the skewing will always occur for layer after layer in the same direction, either to the left or the right, to form the corresponding left or right handed helix.



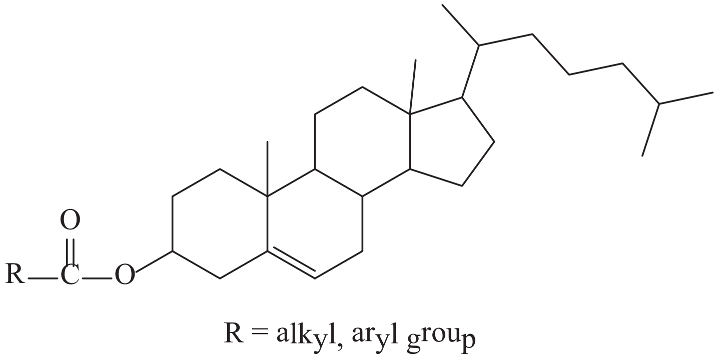
1

Variations in the substituent group at the 3-position of the cholesterol ring system will have a strong effect on the cohesive forces which determine the properties of the helix as follows:

(a) By affecting the degree of non-planarity and thus the closeness with which the molecular "layers" approach parallel alignment to each other and also the amount of skewing between layers.

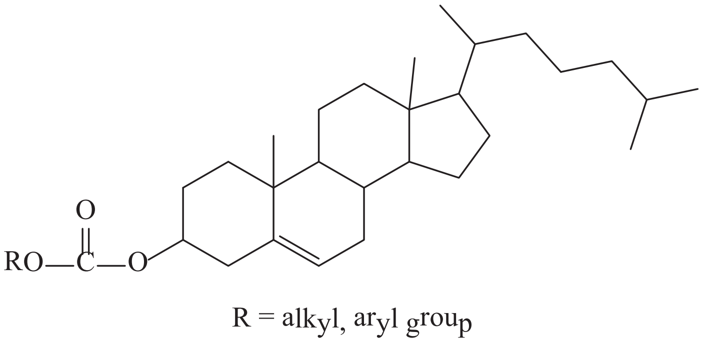
(b) By Polar (electric charge) effects altering the electrostatic attractive and repulsive forces between molecules.

Gray [7] has studied the transition temperatures and colours shown in the N* mesophase for a series of alkyl esters of cholesterol (compound **2**). The lower alkyl esters are monomorphic, with the formate and acetate behaving monotropically and the propionate to hexanoate behaving enantiotropically. From the heptylate onwards, dimorphism is observed and a variety of monotropic and enantiotropic behaviour exists. For the longer chain alkyl esters, the gently dropping curve for N*-Iso transition temperature is approached by the curve for the Sm-N* transition temperature to create a narrower and narrower temperature range for the N* mesophase. Gray [8] noted the visible colour scattered by the ester in the N* mesophase does not always span the entire spectrum from red to violet. For example cholesteryl formate and acetate reflect only in the red to orange region. But as alkyl chain length increases then scattering shifts towards shorter wavelengths so that for the long chain alkyl esters it is entirely in the blue or violet region. However for the nonanoate and decanoate esters the colour spectrum spans from red to violet.



2

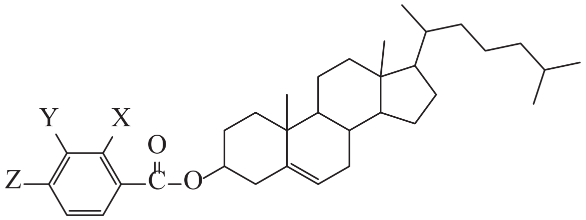
Daumer [9] and Elser [10] have described the properties of the series of *n*-alkyl carbonates for R = 1 to 22 Carbon (compound **3**) (Methyl to docosyl cholesteryl carbonates). As for the cholesteryl alkyl esters, the N*-Iso transition temperature drops with increasing alkyl chain length. Sm-N* dimorphism exists for cholesteryl oleyl carbonate, but it was not observed by Elser for the series (5 to 22 Carbon) of *n*-alkyl carbonates he studied, where the N* mesophase solidifies directly to the crystalline solid. The temperature at which the monotropic N* mesophase solidifies on cooling rises from 33 °C for the heptyl carbonate to 60 °C for the docosyl carbonate. Thus the temperature range over which the N* mesophase exists narrows with increasing alkyl chain length, as the cholesteryl alkyl esters.



3

The cholesterol esters, carbonates and halides are not usually used by themselves in CLC applications as often the temperature range for the cholesteric mesophase or other properties of the pure compound do not fit the requirements of the application. However, by mixing cholesterol derivatives, the properties of the eventual CLC system can be tailored to meet a wide range of requirements.

Study of the effect of the molecular structure of esters of cholesterol and aromatic acids on their mesomorphic properties is being given consideration. These data are summarized in the works of Dave and Vora [11] describing stereo-regular substituents in different positions of the phenyl radical (**4**).



(a) X = Cl, Br, I, CH_3, NO_2; Y, Z = H.
(b) Y = Cl, Br, I, CH_3, NO_2; X, Z = H.
(c) Z = Cl, Br, I, CH_3, NO_2, C_6H_5; Y, X = H.

4

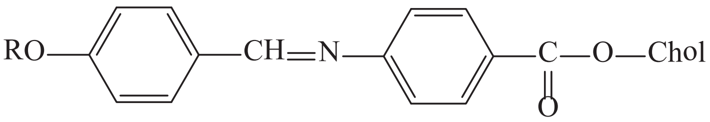
It would found that *o*- and *p*- derivatives show enantiotropic N* mesophase, while *m*- derivatives show monotropic mesophase. *n*-Substitution results in the increase of the temperature of isotropic transition as compared with unsubstituted cholesteryl benzoate, whereas the substitution in *o*- and *m*- position results in its decrease. Higher temperatures of transitions into isotropic liquid and enantiotropic mesomorphism of *p*-substituted cholesteryl alkanoates are explained by the linearity of the molecules and by the presence of a polar substituent at their terminal. According to their effect on the mesomorphic characteristics, the substituents form the following series:

$$C_6H_5 > CH_3O > NO_2 > Br > Cl > I > CH_3 > H$$

In the case of *m*-substituted derivatives, the substituent reduces the anisotropy of the molecules which impedes, as the authors suggests, their layer packing within the crystalline lattice and the compound melts directly into the isotropic liquid. Upon cooling the possibility appears of the mutual orientation of the molecules to give the monotropic phase. Cholesteryl-*m*-nitrobenzote forming enantiotropic N* mesophase is the exception. The increase of thermal stability and the appearance of the enantiotropic mesophase in this case are due to the high polarity of the nitro-group. The decrease of the temperatures of the phase transitions for *o*-substituted cholesteryl benzoates is connected, as in the case of *m*-substituted ones, with the increase of the molecular width.

Dave and Vora have also described the homologous series of cholesteryl *p*-*n*-alkoxybenzoates [12]. In this work synthesis is described as well as the methods for the compound purification, determination of the phase transition temperatures by polarizing microscopy. The dependences of the phase transition temperatures on the length of the *n*-alkyl radical are summarized in the work. It was noted that for all the compounds described, enantiotropic mesophase is characteristic and beginning from the seventh member of the homologous series, in addition to the N* mesophase, smectic mesophase is also observed. The authors draw an analogy of the studied series with the cholesteryl alkanoates. The appearance of the smectic mesophase of cholesteryl benzoates with the long hydrocarbon chain in the 3β-position of cholesterol is due to the increase of the side and the weakening of the terminal intermolecular interactions.

Mesogenic properties of *p*-*n*-alkoxybenzylidene-*p*-benzoates of cholesterol (**5**) were also studied by Dave and Kurian [13]. Synthesized cholesterol derivatives possess high temperature N* phase; at the transition to the isotropic liquid, the above compounds decompose. Homologues with *n* = 1-6 are characterized by enantiotropic N* phase. Beginning from seventh homologue smectic phases are observed.



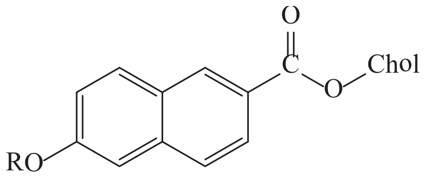
$R = C_nH_{2n+1}$

n = 1-10, 12, 16, 18.

Chol = Cholesteryl group

5

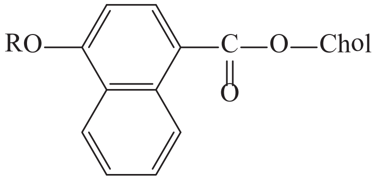
Dave and Kurian [14] have also described the synthesis and properties of cholesteryl 6-*n*-alkoxy-2-naphthanoates (**6**). Compounds of this homologous series are obtained by means of condensation of 6-*n*-alkoxy-2-naphthoic acids chlorides with cholesterol in the presence of dimethylaniline at 150 °C. All the mentioned esters possess enantiotropic N* mesomorphism; beginning from the 5th homologue, the smectic phase appears. They have also reported the synthesis of cholesteryl 4-*n*-alkoxy-1-naphthanoate (**7**) [15]. Within this series, mesophase is less thermostable. It should be noted that, although the presence of condensed benzene rings in the acyl radical increases molecular polarizability, the degradation of the mesomorphic characteristics of these compounds is due to the decrease of their geometric anisotropy owing to 1,4-substitution in the naphthalene fragment. In continuation of this work, the synthesis of cholesteryl 4-*n*-alkoxy-1-naphthylidene-*n*-aminobenzoates (**8**) was carried out [15]. All the members of this homologous series possess enantiotropic N* phase with a wide temperature range of existence. The 12th homologue forms monotropic smectic phase which is transformed into enantiotropic one for the subsequent homologues.



$R = C_nH_{2n+1}$
n = 1-10, 12, 16, 18.

Chol = Cholesteryl group

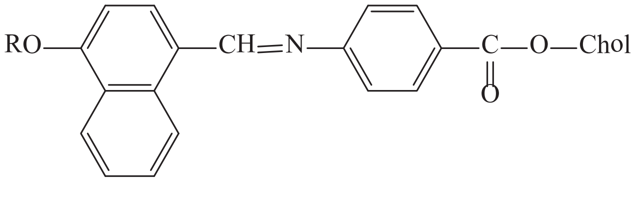
6



$R = C_nH_{2n+1}$
n = 1-10, 12, 16, 18.

Chol = Cholesteryl group

7



$R = C_nH_{2n+1}$
n = 1-10, 12, 16, 18.

Chol = Cholesteryl group

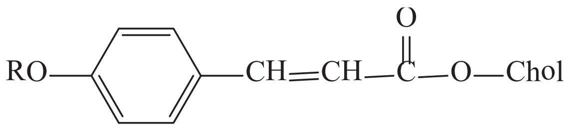
8

The presence of multiple bonds within an acyl fragment of the cholesteryl ester molecule changes considerably the mesomorphic properties. Conjugation of the double bond with the carbonyl group results in the increase of the phase transition temperatures. The increase of the number of conjugated double bonds results in the intensification of this effect. The configuration of the substituents relative to the double bond is also of importance. The phase transition temperatures of cis-isomers are usually lower than those of the corresponding trans-forms.

The literature data on the esters of cholesterol and unsaturated acids of the aliphatic series are not as numerous as those on similar compounds of the aromatic series. In the work of Dave et al. [16], the synthesis and phase transitions of a series of trans-*p*-*n*-alkoxycinnamates of cholesterol (**9**) are described. The authors draw an analogy with the saturated cholesteryl-alkanoates. The transition temperatures to the isotropic liquid of the above compounds are higher than those of their analogues of the saturated series. The first nine members of the series form enantiotropic N* mesophase, while higher homologues show polymorphism forming smectic and N* phases. Investigations using polarizing microscopy have shown selective reflection of light.

For the transition temperature of N* mesophase to the isotropic liquid, an odd-even effect is observed which consists of the fact that esters with an even number of carbon atoms in the side chain transform to the isotropic state at the higher temperature. Changes in mesomorphic characteristics of the homologue series as compared with that of the alkoxybenzoates are explained by the presence of the phenyl fragment and the conjugated double bond which contribute to the geometric anisotropy and the increase of molecular polarizability. The authors suggest that the high polarizability of the molecules increases the transition temperature to the isotropic liquid while the broadening of a molecule owing to the double bond reduces the energy of intermolecular interaction, and hence the smectic phase in the homologue series of cholesteryl alkoxycinnamates appears much later than in the case of cholesteryl alkoxybenzoates.

Thus, literature data on the synthesis and study of the mesomorphic properties of the cholesteryl esters containing unsaturated fragment are not sufficient, and the effect of the molecular structure of these compounds on their mesogenic ability is not elucidated. As for the stereochemical aspects of this problem they have been even less studied.



R = C_nH_{2n+1}
n = 1-10, 12, 17, 18.

Chol = Cholesteryl group

9

Cha *et al.* [17] have prepared new non-symmetric dimesogens consisting of a cholesteryl moiety and an aromatic mesogenic unit interconnected through a penta methylene spacer. The aromatic units consist of two phenyl rings linked by carboxy, oxycarbonyl, ethylene, ethynylene, azo or Schiff's base groups. From a structural point of view, these systems are interesting since several smectic structures are obtained depending on the molecular parameters. Several kinds of smectic packings are observed depending on the nature of the linking group and an attempt to understand the origin of the different phase structures at a molecular level is made. Authors have also described the molecular structure liquid crystal-property relationships for dimesogenic compounds.

The phase behaviour of 3β-cholesteryl 9,10-anthraquinone-2-carboxylate and 3βb-cholesteryl 9,10-dimethoxyanthracene-2-carboxylate has been investigated by Ostuni and Weiss [18] as a neat as well as mixtures by a variety of techniques. Both molecules form thermotropic N* phases. UV-Vis absorption spectra of mixtures provide strong evidence for the formation of charge-transfer complexes in the solid state. X-ray powder diffraction patterns confirm that 3β-cholesteryl 9,10-anthraquinone-2-carboxylate forms different crystalline phases upon being cooled from the mesophase and by recrystallization from solvents. The equal mixture can be supercooled to a glass from its N* phase. Some of the phase behaviour of these mixtures is explained with a model that includes selective crystallization of the two components into eutectics from supercooled liquid crystalline matrices. Charge-transfer interactions between the electron-poor anthraquinone and electron-rich 9,10-

dimethoxyanthracene groups (both of which are quite polarizable) lead to stabilized N* phases whose properties are very different from those of either neat component.

Large portion of literature related to the synthesis and mesomorphic properties of cholesterol-based liquid crystals is available from the work of Yelamaggad and co-workers. Authors have investigated liquid crystalline properties of chiral non-symmetric dimeric liquid crystals consisting of a cholesteryl ester moiety as chiral entity and a biphenyl aromatic core, interconnected through *n*-butyl or *n*-pentyl parity alkylene spacers [19]. All the dimers exhibit enantiotropic mesophases. The first member of the dimers having the C_4 central spacer exhibit only the N* mesophase, while the higher homologues also show SmA and TGB mesophases. The dimers of the other series containing the C_5 central spacer also have stable SmA, TGB and N* mesophases, except for the first which does not show the TGB phase. Both series of compounds show a weak odd-even effect with terminal alkyl chain substitution, while the spacer length has a marked influence on the phase transition temperatures. Both the spacer and terminal chain lengths have been varied with a view to stabilizing different smectic mesophases and understanding structure-property relationships.

A series of unsymmetric dimers consisting of a diphenylacetylene moiety having an alkyl chain and a cholesteryl ester unit joined through a paraffinic spacer have also been synthesized and their liquid crystalline properties were evaluated [20]. The lengths of the central methylene spacer as well as that of the alkyl chain have been varied to establish the structure-property relationships. All the dimers exhibit SmA, TGB and N* phases with the exception of one of the dimers for which only the N* phase was observed. Some differences in the mesomorphic properties of the unsymmetric dimers containing odd or even parity methylene spacers have been observed. The majority of dimers having an even parity paraffinic spacer shows a blue phase (BP) while the dimers with odd parity spacers exhibit the SmC* phase.

Yelamaggad and Mathew [21] have synthesized unsymmetrical dimers possessing a cholesteryl ester moiety and a difluoro-substituted biphenyl core and studied their mesomorphic behaviour. These dimers consisting of a cholesteryl ester moiety, covalently linked to either a 4’-(2,3-difluoro-4-*n*-octyloxy)biphenyloxy or a 4’-(2,3-difluoro-4-*n*-decyloxy)biphenyloxy through odd–even parity paraffinic central spacers. Except for one, all the dimers exhibit enantiotropic SmA, twist grain boundary and chiral nematic mesophases. Five of the eight unsymmetrical dimers synthesized show a chiral smectic C phase. Interestingly in some of the compounds the SmC* exists over a wide temperature range including room temperature. Among the eight compounds, a dimer having a C_7 central paraffinic spacer and a C_8 alkoxy terminal chain shows an enantiotropic twist grain boundary with SmC* blocks (TGBC*) phase. It appears that the variation in the length of the spacer has a remarkable influence on the phase transition temperatures as well as on the mesomorphic behaviour. These dimers stabilize the SmC* phase that can be used in ferroelectric liquid crystal (FLC) device applications, either as a single chiral component or as a chiral dopant to an achiral SmC host to form a mixture. These molecular assemblies may help in giving a better understanding of the underlying relation between molecular structure and mesomorphic behaviour, and may serve as cheap material for FLC device technology.

Chirality in functional molecular materials is a powerful tool for inducing properties and molecular organizations absent in non-chiral materials. This is particularly true in mesogenic materials. For instance, the TGB phase is a type of frustrated phase with absorbing physical and structural features, which are found exclusively in optically active systems. Yelamaggad and co-workers have studied thermodynamic, optical and dielectric properties of the TGB phases of the homologous series of 4-*n*-alkyloxy-4'-(cholesteryloxycarbonyl-1-butyloxy) chalcone [22] having wide temperature ranges of two TGB phases, namely TGBA and TGBC*. The experimental dielectric spectra display two feeble collective relaxation modes for the planar oriented sample. One mode, which exists in the MHz region, has behaviour similar to that of the soft mode due to amplitude fluctuations. The second mode exists in the low-frequency region and appears due to phase fluctuations. Various electrical parameters have been determined for the two TGB phases of the above-mentioned compounds. This study reports the temperature and frequency dependence of the dielectric properties of the above-mentioned compounds.

Yelamaggad *et al.* have also reported binary mixtures of Cholesteryl 5-(4-((4-hexylphenylimino)methyl)-3-hydroxylphenoxy)pentanoate and *n*-butyloxy benzylidene-*p*-pentylaniline and studied their phase behaviors [23]. The mixtures of lower concentrations of second component exhibit N*-SmA-SmG phases sequentially when they are cooled from isotropic phase. The molecules in SmG phase are packed in layers and within the layers molecules have their long axes tilted with respect to the layer planes. The studies of these mixtures with concentrations from 30 to 69 % are of very interesting because of the fact that these mixtures exhibit SmA phase followed by SmC* and SmG phases. The samples of this intermediate concentrations exhibits SmA - SmC* - SmG - SmB - Crystal phases on cooling from isotropic melt. The mixtures with higher concentrations show BP (Blue Phase) - N* - TGBA - TGBC - TGBC* - UTGBC* phases, sequentially.

Cholesterol-based dimers are generally pure and reasonably stable. Indeed, such dimers are generally purified by repeated column chromatography and/or recrystallisation techniques; perhaps during this process the fine impurities are eliminated effectively. In order to demonstrate experimentally that dimers containing a cholesteryl segment are relatively free from impurities, Yelamaggad have been developing single crystals and subjecting compounds to X-ray diffraction analysis. Suitable single crystals of synthesized compounds were grown in a mixture of different solvents in different ratio [24-27].

Several trimers consisting of benzalazine as a central mesogenic segment, connected linearly on both the terminals with the cholesteryl ester moieties through either even–even or odd–odd alkylene spacers, have also been synthesized and investigated for their liquid crystalline properties [28]. All the members exhibited an enantiotropic N* mesophase with a characteristic oily streak texture when the sample was placed on an untreated glass plate. Interestingly, among the trimers consisting of odd-odd alkylene spacers, one of the trimer having C_5 parity exhibits a TGBC* phase, indicating that the length of the two central paraffinic spacers are critical in order to stabilize the TGBC* phase.

Yelamaggad and co-workers have first reported chiral organometallic trimers [29] having bis[(4-phenyl)ethynyl]mercury as the central core connected on either side to cholesteryl ester moieties through either even–even or odd–odd central alkylene spacers. All organo-mercury trimers exhibit N* phase. It is surprising to note that the intermediate cholesteryl ω-[(4-trimethylsilylethynyl)phenoxy]alkanoates are non-mesomorphic, though they contain cholesterol as a chiral moiety which is itself a pro-mesogenic structure. This behaviour could be attributed to the presence of the bulky terminal trimethylsilyl group in the molecule. The corresponding free phenyl acetylenes, namely the cholesteryl ω-(4-ethynylphenoxy)alkanoates show an enantiotropic N* mesophase. In these compounds, the cholesterol moiety and the phenylacetylene core are linked to the alkylene spacer via a carbonyl group and an ether linkage respectively.

The first examples of monodisperse liquid crystalline pentamers have been reported by the Yelamaggad's group [30]. The pentamers composed of five mesogenic segments interlinked through four flexible spacers varying in their length and parity. The design is considered to provide functional diversity and maximize the probability of mesophase formation. The pentamers comprise tolane, biphenyl, azobenzene, cholesterol and naphthalene entities. These monodispersive supermolecules have been evidenced to self-assemble into monolayered or intercalated phases, which appear to be rather new smectic modifications given the fact they possess unique textural pattern. Besides this, they possess electrochemical activity. Indubitably, this approach offers a unique way to design a multifunctional material which can bridge the gap between low molar mass and polymeric LCs, with enhanced functional capability and ease of processability.

Majumdar *et al.* have reported cholesterol based unsymmetrical dimers [31]. All the dimers possess a cholesterol unit connected with a 4-alkoxy-5-phenylthiphene unit through Schiff's base linkage. All the dimers exhibit mesomorphism. The dimers with long alkyl spacers exhibit only the N* phase, while some of the dimers with short alkyl spacers exhibit a variety of phase sequences which includes SmA, SmC*, N* and TGB phases. The author has also achieved the unsymmetrical cholesterol and benzoxazole-based liquid crystalline dimers by connecting the 2-phenyl substituted benzoxazole unit to a cholesterol unit having an alkyl spacer through an imine linkage [32]. Such a molecular design favors the formation of an amorphous BP over a reasonable thermal range.

In continuation of the effort to synthesize different cholesterol-based liquid crystalline compounds, Majumdar have also synthesized series of cholesterol-based liquid crystalline tetramers [33] that look like a combination of two non-symmetric dimers separated by a flexible central spacer. Tetramers exhibit the N* phase in addition to the SmA phase.

Majumdar have also reported an oxadiazole-based schiff's base dimers [34] and trimers having cholesterol and ferrocene unit at the two terminal ends [35]. In oxadiazole-based dimers, 1,3,4-oxadiazole and cholesteryl units are linked *via* a flexible imine linkage. All the compounds exhibited enantiotropic liquid crystalline behaviour. Most of them showed the SmC* - SmA - N* - BP phase sequence. The clearing enthalpies observed were small for dimers probably due to the biaxial nature of these molecules. With increasing the alkyl chain length, these compounds showed reduced clearing temperatures in addition to the range of the N* phase. The occurrence of blue phase over a reasonable thermal range is interesting. A large negative thermal expansion is observed in the SmA phase although the layer shrinkage is quite large in the SmC* phase. Oxadiazole-based liquid crystalline trimers contain a cholesterol and ferrocene units at the two terminal ends of the molecules. The study follows with varied lengths of the alkyl spacer connecting the cholesterol and oxadiazole unit and also of the alkyl spacer connecting ferrocene and aromatic core. All the trimers are liquid crystalline in nature and exhibit either TGBC* - N* - BP* or TGBC* - N* phase sequence. These trimers exhibit the TGBC* phase over a remarkably wide thermal range in both the heating and cooling cycles. The main feature of this study is the first observation of an unusually large temperature range for the TGBC* phase in a chiral unsymmetrical metallomesogen.

Influence of spacer and terminal group lengths on the smectic phase ordering of cholesterol-containing dimer liquid crystals have been investigated by Marcelis and co-workers [36, 37]. They have studied the smectic properties of series of dimers containing cholesterol and biphenylyl groups. Compounds containing the strongly dipolar cyanobiphenylyl group exhibit a smectic layer spacing that is about 1.7 times the length of the molecule. Series of alkoxybiphenylyl containing dimers exhibit two other smectic modifications. For short spacers, smectic layer spacing is observed that is about the same length as the molecule and for long spacers the smectic layer spacing is about half the length of the molecule. In the latter cases the entropy changes at the SmA-N* transition is clearly larger than for the compounds with the other smectic modifications. One or two compounds in each alkoxybiphenylyl-containing series that have similar spacer length and terminal group length and have an odd number of flexible units in the spacer, exhibit only a chiral nematic phase, and no smectic phase.

Mallia *et al.* [38] have prepared mesogenic systems with cholesterol linked supramolecular mesogens. This system can exhibit marked changes in pitch and wavelength of selective reflection on irradiation. The study aimed to synthesize supramolecular mesogens with cholest-5-en-3-ol-(3β)[4-phenyl-pyridylazo]carbonate as hydrogen bond acceptor and different 4-*n*-alkyloxy benzoic acids as hydrogen bond donors and studied their liquid crystalline properties and photoisomerization. The presence of the azo-moiety can impart photo switching properties to these materials, since irradiation can lead to photoisomerization of the azo moiety from the *trans*- to the *cis*-form. All the supramolecular assemblies built from 1 : 1 molar ratios of the hydrogen bond donor and acceptor moieties exhibit well defined SmA liquid crystal phases on heating and cooling cycles. The SmA phases exhibited by the complexes are not observed for the individual components.

Hydrogen bonding is a powerful tool for assembling molecules and building new liquid crystalline structures. In the study of Lee [39], non-symmetric dimesogens were prepared by intermolecular hydrogen bonding between rationally designed H-bond donor 3-cholesteryloxycarbonylpentanoic acid and acceptor 4-(pyridine-4-ylmethyleneimino)phenyl 4-alkoxybenzoate moieties. N* and Sm phases were observed for these mesogens. As for the covalently linked dimesogens, several types of smectic periodicities occur for these H-bonded cholesteryl compounds depending on the molecular parameters. Specifically they form smectic phases with different types of lamellar packing and depending on the molecular parameters, the layer spacing can be smaller than one half the molecular length or, alternatively, larger than the molecular length. More unusually, between these two extremes, anomalies of periodicity are revealed through the occurrence of two-dimensional modulated phases. Proton donors and proton acceptors, which themselves exhibit liquid crystalline phases, were selected to obtain smectic phases for the complexes induced by hydrogen bonding.

Felekis *et al.* [40] have functionalized diaminobutane poly(propyleneimine) dendrimers by the introduction of pyridyl moieties at their primary amino groups through their interaction with 3-pyridyl isothiocyanate. These pyridylated diaminobutane poly (propyleneimine) dendrimers were subsequently mixed with 3-cholesteryloxycarbonylpropanoic acid to form the corresponding hydrogen-bonded supramolecular complexes by their interaction. The materials obtained exhibit SmA phases over a relatively broad temperature range from about 60 °C to 140 °C. Within the smectic layer the cholesteryl moieties are almost orthogonal above and below to the dendrimeric portion of the molecule. On cooling, the materials form liquid crystalline glasses which retain the structural characteristics of the SmA phase. These dendrimers are capable of forming supramolecular hydrogen-bonded complexes by their interaction with 3-cholesteryloxycarbonylpropanoic acid.

He *et al.* [41] have also study the optical behaviour of hydrogen-bonded liquid crystals based on a chiral pyridine derivative. They have synthesized cholesteryl-containing supramolecular hydrogen-bonded liquid crystal complexes with different number of fluoro-substituent. Cholesteryl isonicotinate as proton acceptor and 4-*n*-alkoxybenzoic acids with or without fluoro-substituent as proton donor had been mixed in tetrahydrofuran to obtain H-bonded LC complexes. The effect of lateral substitution and the length of terminal chain in the H-bonded precursors on the formation of the supramolecular complexes had been examined. It was found that the introduction of fluoro substituent on the induced mesogens could widen the molecular width and thus reduce the molecular aspect ratio of the complexes; therefore it could lead to compress the formation of the LCs. However, the fluoro substituent played a positive role in enhancing the intermolecular interactions and stabilizing the H-bond structure of the complexes. On increasing the spacer length, the clear point and the thermal range of induced mesophase-like N* phase decreased, and an induced chiral smectic phase began to appear in some complexes with long terminal tails.

Recently, Tamaoki and co-workers [42] have investigated 4-[6-((cholesteryloxy) carbonyl)oxy hexyloxy] benzoic acid as a novel supramolecular hydrogen-bonded cholesteric mesogen exhibiting macromolecular behaviour. All the compounds exhibited Sm and N* mesophases. The results of these study led to the conclusion that the formation of identical dimers by intermolecular hydrogen-bonding of the terminal carboxylic acids accompanying the lateral packing of the rigid cores, built a trimeric arrangement and this was responsible for the macromolecular behaviour of this cholesteryl derivative, despite its relatively simple structure and low molecular weight. The films prepared could be made to reflect colours selectively throughout the entire visible region by changing the evaporation temperature. Subsequent rapid cooling of these samples resulted in glassy cholesteric films which were capable of preserving the colours at room temperature for several weeks. The colours were even stable at temperatures above the glass transition temperature (T_g), since the smectic phase is by nature solid-like.

Meng *et al.* have prepared a novel ionic low molar mass liquid crystal bearing a sulphonate group in the mesogenic core, potassium 2-allyloxy-5-

cholesteryloxycarbonyl benzene sulphonate [43]. The morphology of this ionic liquid crystal indicated a slant array of ionic mesogenic units under a static electric field. One of the most obvious advantages of liquid crystalline systems bearing ionic mesogens is their polar structure, which would be sensitive towards both electric and magnetic fields, leading to the feasibility of applications in electro-optic displays. In these systems, the mesogens lead to mesomorphic orientational ordering, with strong orienting forces due to ions in electric fields. Dielectric constant measurements exhibited negative dielectric anisotropy with a maximum $\Delta\varepsilon$ of -43.0D at 210 °C. The ionic liquid crystal was with the help of an oriented sample under a static electric field to determine its morphology under this field. Ions exist in abundance in the mesophase, tending to move under the influence of the electric field.

The introduction of a ferrocene unit to a liquid crystal system may contribute active redox properties and planar chirality of 1,3-asymmetrically substituted derivatives. Taking into account the advantages brought by the presence of chirality, ferrocene and azo units, these structures could be good precursors in obtaining materials capable of responding to magnetic and electric fields or to UV light exposure. For this purpose, different kinds of cholesteryl-containing ferrocene derivatives were synthesized by Apreutesei [44] where ferrocenyl and cholesteryl units were being connected by a rigid aromatic group or *via* a flexible spacer. All derivatives exhibit liquid crystalline properties with a N* phase as the highest stable mesophases.

Liquid crystalline properties of a series of dimesogenic compounds containing the cholesteryl ester unit and a phenyl benzoate group are reported by Wu [45]. The two mesogenic units of these compounds are linked through dicarboxylic ester bonds, with alkylene spacer lengths of 2, 4, 6 and 8 methylene units. The results show that this series of compounds are cholesteric liquid crystals over a wide range, both during heating and cooling, and they exhibit iridescent colours in the liquid crystalline state. Wu have also synthesized series of symmetric liquid crystal tetramers involving cholesteryl-based mesogenic units and Schiff's base moiety [46]. The target compounds were obtained by the reaction of 4-(ω-cholesteryloxycarbonylalkonoyloxy) benzaldehyde with compound 1,4-bis (aminophenyl-1-oxy) butane. The length of the outer two spacers is varied from 2 to 8 even-numbered methylene units, while the central spacer is held at 4 methylene units.

All of these liquid crystal tetramers showed only one N* mesophase on a very large temperature domain (~100 °C), and the clearing temperature above 250 °C.

Yang and co-workers have described the synthesis of cholesteryl compounds of different functionality [47]. A series of polymer-stabilized cholesteric liquid crystal (PSChLC) cells are prepared by photo-polymerisation of a CLC mixture containing a non-reactive liquid crystal, a nematic diacrylate and the cholesteryl compounds. The effect of cholesteryl compound functionality on the morphology and the reflectance properties of PSChLC cells are evaluated, as are parameters such as the polymerisation temperature. The results indicate that the higher functional cholesteryl compound is more effective for broadening the reflection band of the CLC composites, which is speculated to be a result of the pitch differences in the local network environment. Zhang *et al.* have fabricated PSChCLs by UV induced polymerization of photo polymerisable acrylate monomers mixed in a CLC [48, 49]. A polymer network with a concentration gradient, which was induced by UV light absorption of dye along the propagation direction, was formed. A hydrogen bond, arising between the polymer network with a concentration gradient containing carboxyl as proton donors and chiral dopant as proton acceptors, induced a pitch gradient in PSChLC and then, as a consequence, broadband reflection. The broadband reflection is associated with the concentration and the composition of photopolymerisable acrylate monomers, the concentration of chiral dopant and the polymerisation temperature.

Jeon and co-workers [50] have reported the synthesis of series of non-symmetric liquid crystal dimers having cholesteryl and 4-trans-(4-*n*-alkylcyclohexyl) phenoxy groups by condensation of cholesteryl ω-bromoalkanoates with appropriate 4-trans-(4-*n*-alkylcyclohexyl)phenols. Dimers with a shorter terminal alkyl chain and longer spacer tend to exhibit only the N* mesophase. Some dimers exhibit a wide temperature range for the N* phase. These dimers are promising candidates for applications in liquid crystalline displays and electro-optical devices.

Imrie and co-workers have designed cholesteryl-based trimers [51] and tetramers [52] and established that the formation of smectic phases is strongly dependent on the length and parity of the flexible spacers due to packing constraints, while the driving force for the phase formation is attributed to the specific electrostatic interactions between electron rich and electron deficient segments of the molecules. Trimers consist of molecules containing a cholesteryl-based group, a 4-methoxy azobenzene unit and a central benzylidene aniline group, interconnected in a linear fashion *via* two flexible spacers. The length of the spacer connecting the 4-methoxy azobenzene moiety to the benzylidene aniline group is held constant at either five or six methylene units while the length of the second spacer is varied. All trimers exhibited an enantiotropic N* phase. In tetramers, the outer two mesogenic groups are cholesteryl-based while the inner two are schiff's bases. All tetramers exhibit an enantiotropic N* phase. Imrie have also synthesized chiral liquid crystalline dimers with cholesteryl unit [53, 54]. Non-symmetric liquid crystal dimers [53] consisting of a cholesteryl-based unit and either 4-methoxybiphenyl, 4-cyanobiphenyl or (S)-2-methylbutyl 4'-oxybiphenyl-4-carboxylate are described. The symmetric dimers exhibit only chiral nematic or nematic phase behaviour. By contrast, members of the non-symmetric dimer series containing either 4-cyanobiphenyl or (S)-2-methylbutyl 4'-oxybiphenyl-4-carboxylate groups exhibit smectic behaviour. The former series show an interdigitated smectic A phase while for the latter the structure of smectic A phase depends on the length of the flexible spacer. Specifically, for short spacer lengths a monolayer arrangement is seen while for long spacers an intercalated smectic A phase is formed. For an intermediate spacer length, the small-angle X-ray scattering pattern for the intercalated smectic A phase reveals short-range incommensurate structural fluctuations associated with the monolayer smectic A phase. The driving force for the formation of the intercalated phase may be an electrostatic interaction between the electron rich carbonyl linking group attached to the cholesteryl unit and the electron deficient aromatic unit while the monolayer arrangement may be stabilized by the van der Waals interactions between the cholesteryl unit and the alkyl chains. The bis(ω-(cholesteryloxycarbonyl)alkyl) disulfides contain a sulfur−sulfur link in the flexible spacer [54]. All dimers exhibit a chiral nematic phase and for the longest three members a smectic A phase was also observed. The smectic A phase is proposed to consist of an intercalated arrangement of the dimers which is driven by the mismatch in cross-sectional areas of the cholesteryl-based groups and alkyl chains.

New Cholesteric monomers and their corresponding smectic polysiloxanes based on Cholesteryl groups were important for the structure-property relationships of new chiral monomers and polymers [55, 56]. These materials are also useful to obtain piezoelectric LC networks by reaction of these monomers with a nematic cross linking agent. All of the elastomers also displayed very good thermal stability.

Yang *et al.* [57] studied the influence of linkage and terminal group on the liquid crystalline and helical twisting behaviours of cholesteryl esters. The insertion of a 4-phenoxyl and a 4-biphenylyloxy group in the ester can increase the molecular length, broaden the whole mesophase width and heighten the clearing temperature. They have also synthesized the cyclic siloxane tetramers containing cyclotetrasiloxane, cholestryl-4-allyloxy-benzoate and biphenyl-4-yl 4-allyloxy benzoate, and the effects of the cholesteryl-based mesogenic units on liquid crystalline and thermo-optical properties were studied [58]. The presence of a cholesteric mesogen was observed to widen the mesogenic temperature range and tended to induce SmA phases in the tetramers containing a higher mole fraction of cholestryl-4-allyloxy-benzoate. The selective reflection of cholesteric tetramers shifted to shorter wavelengths with increasing cholesteryl-4-allyloxy-benzoate and temperature. Blue phases can be easily observed for those tetramers containing more than 50 mol% cholesteric mesogen. The shorter pitch sample showed the wider blue phases range. The author has also studied on concept of intramolecular chiral conflict between the (R)-1,1'-binaphthyl and cholesteryl ester moieties [59].

Cholesterol-based chiral unsymmetrical dimeric liquid crystals consisting of a cholesterol moiety as chiral entity and a substituted salicylidene imine core with the substituent being butyl or fluoro or chloro group interconnected through an even methylene spacer have been synthesized by Sarkar *et al.* [60]. The butyl homologue exhibited N* phase only, the fluoro- and chloro-substituted compound exhibited frustrated blue phases, N* phase and SmC* or TGB phases. The occurrence of a fluid frustrated phase, the BP, in particular, observed in compounds with a polar moiety and bent optimised conformation by density functional theory (DFT) study, indicates the importance of polar structures and bent shape of the compounds.

Recently, Tandel and Vora have reported a series of mesogens having a cholesteryl moiety condensed with 4-(4'-*n*-alkoxy benzoyl) amido benzoyl chlorides [61]. The methyl to *n*-hexyl derivatives exhibits only N* mesophases. The *n*-heptyl to *n*-dodecyl derivatives exhibits SmC and N* phases. The *n*-tetradecyl to *n*-octadecyl derivatives exhibit SmC, SmA and N* phases. Kurian *et al.* have reported schiff's bases by condensing *p*-aminobenzoate of cholesterol with *p*-*n*-alkoxybenzaldehydes and studied their mesomorphic behaviour [62]. The first six members show N* phase while rest are polymesomorphic showing Sm and N* phase. Vora and Teckchandani have reported dicholesteryl imide esters and carbamates with flexible spacers [63]. Dicholesteryl esters exhibit N* phases of high thermal stabilities. Dicholesteryl carbamates with C_8 chain length exhibits N* phase which on cooling also give monotropic Sm phase. Cholesteryl derivatives with amide linkages are rare. Sun et al. [64] have also reported troponoid esters and amides connected with cholest-5-ene-3β-carboxylic acid moiety. 5-Alkoxytroponyl esters and amides with a long alkoxy group exhibited a TGBA* phase as well as N* and SmA* phases. The corresponding benzenoid esters exhibited SmA* and blue phases and the benzenoid amides only a SmA* phase.

In this chapter, we have attempted to view the effect of non-mesogenic lateral methoxy cinnamic acids on cholesterol-based unit. The growing scientific interest in the synthesis of cholesterol-based chiral liquid crystals has prompted us to synthesize a series of cholesterol-based chiral liquid crystals in this class of materials. We have synthesized a series of novel mesogenic compounds in which the cholesterol-based unit is connected to the 4-*n*-alkoxy-3-methoxycinnamic acids *via* an amide linkage and have investigated their liquid crystalline behaviour. We have studied their structure-property relationship. We have also investigated the optical properties of the compounds of the series.

3.2. Experimental

3.2.1. Instrumentation

The synthetic route adopted for the series of mesogens is given in the Figure 1. All synthesized compounds were purified by column chromatography on silica gel (60-120 mesh). The purity of the samples was checked by thin-layer chromatography. The chemical structures of the compounds were determined by standard spectroscopic methods. IR spectra were determined for KBr pellets, using a Perkin Elmer-RX1 spectrophotometer. ^{1}H NMR spectra was recorded on a Bruker 400 MHz spectrometer using tetramethylsilane (TMS) as internal reference standard. Liquid crystalline properties were investigated using Leica DM 2500P polarizing optical microscope provided with a Linkam heating stage. The transition temperatures were confirmed by Differential Scanning Calorimeter on Mettler Toledo – DSC 822 system which was calibrated using indium as a standard. Optical rotation data were measured with a JASCO P-2000 polarimeter, using chloroform as a solvent.

3.2.2. Synthesis and Characterization

3.2.2.1. *p*-Nitrobenzoate of cholesterol (2) [65, 66]

Cholesterol (5.0 g, 0.013 mol) and *p*-nitrobenzoyl chloride [62] (2.4 g, 0.013 mol) were mixed with dry pyridine (10 ml) in a conical flask and slowly heated to boiling. The solution was allowed to cool and the separated cholesteryl *p*-nitrobenzoate was washed with a little alcohol to remove the pyridine. The crude product was dissolved in chloroform and filtered. On addition of acetone to the filtrate, cholesteryl *p*-nitrobenzoate precipitated. It was then recrystallised from ethyl methyl ketone yielding white plates. The percentage yield of the product is 60%. Melting point 191.5 °C.

3.2.2.2. *p*-Aminobenzoate of cholesterol (3) [65, 66]

p-Nitrobenzoate of cholesterol (3 g, 0.0056 mol) and glacial acetic acid (14 ml) were taken in a 150 ml round bottom flask fitted with a water condenser. The mixture was heated to boiling and iron powder (1.7 g, 100 mesh) was added portion-wise. After refluxing for three hours the mixture was cooled and filtered. The solid mass obtained was washed with 1 N hydrochloric acid until the washings were colourless. It was then washed with water until the washings were neutral to litmus. The crude product was dried and purified by column chromatography on silica gel with mixture of ethyl acetate and petroleum ether (10:90) as an eluent. The percentage yield of the product is 55%. Melting point 237.0 °C.

3.2.2.3. Trans-4-*n*-alkoxy-3-methoxycinnamic acids (5)

A mixture of 4-hydroxy-3-methoxycinnamic acid [67, 68] (4.85 g, 0.025 mol), alkyl iodide or bromide (0.03 mol), potassium hydroxide (3.5 g, 0.062 mol) and ethanol (50 ml) were refluxed for 4-5 hr. After being cooled, the mixture was poured into a stirred mixture of concentrated hydrochloric acid (25 ml) and ice cold water (50 ml). The product was then filtered off, washed with water, dried and recrystallised from ethanol until constant melting points were obtained. Purity of the compounds were checked by TLC and characterized by spectral data. The melting points are summarized in Table 1.

***n*-Butoxy derivative:** IR (KBr): 2594-2956 cm^{-1} -O-H stretch broad band superimposed upon C-H stretch, 2880, 2827 cm^{-1} aromatic –C-H stretch, 1683 cm^{-1} >C=O stretch, 1260 cm^{-1} C-O stretch, 979 cm^{-1} strong =C-H bending (Figure 2).

^{1}H NMR ($CDCl_3$, δ, ppm): 0.98-1.02 (t, 3H, CH_3), 1.49-1.55 (m, 2H, CH_2), 1.83-1.88 (m, 2H, CH_2), 3.92 (s, 3H, OCH_3), 4.06-4.10 (t, 2H, OCH_2), 6.31-6.35 (d, 1H, =CH-), 6.88-6.90 (d, 1H, Ar-CH), 7.09-7.10 (d, 1H, Ar-CH), 7.12-7.14 (dd, 1H, Ar-CH), 7.73-7.77 (d, 1H, -CH=) (Figure 3).

Mass spectra are given in Figure 4.

3.2.2.4. Trans-4-*n*-alkoxy-3-methoxycinnamoyl chlorides (6)

The acids were converted into their acid chlorides by treating them with thionyl chloride on water bath till evolution of hydrochloric acid ceased. The excess of thionyl chloride was distilled off. The crude product was used immediately in the next reaction without further purification.

3.2.2.5. Cholesteryl 4-(4’-*n*-alkoxy-3’-methoxycinnamoyl) amido benzoates (Series: I)

The respective 4-*n*-alkoxy-3-methoxycinnamoyl chloride (0.01 mol) was dissolved in about 5 ml of dry pyridine. The solution of compound **3** (0.01 mol) in 10 ml of dry pyridine was added slowly to a cold solution of the above acid chloride. The mixture was heated on a water bath for about half an hour and was allowed to stand overnight. It was acidified with cold 1:1 hydrochloric acid. Precipitates were filtered and washed with water followed by dilute sodium hydroxide solution and water. The residue was purified by column chromatography on silica gel with mixture of ethyl acetate and petroleum ether (10:90) as an eluent.

***n*-Butoxy derivative:** IR (KBr): 3405, 1599 cm^{-1} –NH stretching and bending, 2935 cm^{-1} =C–H stretching of –CH=CH–, 1710 cm^{-1} >C=O stretching of ester, 1664 cm^{-1} >C=O stretching of amide, 1407 cm^{-1} –C–C– (skeletal) stretching of benzene ring, 1374, 1278, 1174, 1114 cm^{-1} –C–O– stretching of –C–O–Ar, 851, 768 cm^{-1} Ar–H bending in *p*-substituted benzene ring (Figure 5).

^{1}H NMR (CDCl$_3$, δ, ppm): 0.70-2.49 (m, 43H of cholesterol as well as 7H of propyl group, aliphatic), 3.93 (s, 3H, OCH$_3$), 4.12-4.13 (t, 2H, OCH$_2$), 4.85 (m, 1H, aliphatic), 5.45 (m, 1H, aliphatic), 6.93-6.95 (d, 1H, =CH-), 7.22-7.25 (d, 1H, Ar-CH), 7.44-7.47 (dd, 1H, Ar-CH), 7.73-7.75 (d, 2H, Ar-CH), 7.79-7.81 (d, 1H, -CH=), 8.07-8.09 (d, 2H, Ar-CH), 8.07-8.09 (d, 1H, Ar-CH), 8.66 (s, 1H, -CONH-) (Figure 6).

***n*-Octyloxy derivative:** IR and ^{1}H NMR spectra are given in Figure 7 and 8, respectively.

3.2.3. Determination of transition temperatures with the help of a polarizing optical microscope

To determine the transition temperatures the Leica DM 2500P polarizing optical microscope equipped with a Linkam heating stage was used.

To determine the various transitions, a glass slide with a thin coating of material, covered with a glass cover slip, was observed under microscope. The slide was kept on the hot stage and the temperature was raised rapidly to find the approximate transition temperatures. The observations were repeated and the rate of heating was regulated to slowly near the transition, to determine the transition temperatures more precisely.

The heating device was standardized and its accuracy was checked by determining the transition temperatures of the known compounds, such as 4-*n*-alkoxy benzoic acids.

The members of the homologous series **I,** Cholesteryl 4-(4'-*n*-alkoxy-3'-methoxycinnamoyl) amido benzoates exhibit enantiotropic mesomorphic states. All derivatives starting from methyl to *n*-octadecyl derivatives exhibit chiral nematic phases. The N* phase shows typical oily streak texture under microscope. Colour of the texture is attributed to the high birefringence. Network-like defect lines are the lines of oily streak.

3.2.4. Differential Scanning Calorimetry studies

The transition temperatures and enthalpies were investigated by Differential Scanning Calorimetry (DSC) using a PerkinElmer Thermal Analyser with a heating and cooling rate of 10 °C min^{-1}. The instrument was calibrated using indium as a standard. The phase transition temperatures observed through polarizing optical microscope were found to be in reasonable agreement with the corresponding DSC thermograms. The thermograms and related discussions are given in the Results and Discussion section for the series **I** compounds.

3.3. Results and Discussion

Thirteen homologues were synthesized by condensation of appropriate 4-*n*-alkoxy-3-methoxy cinnamoyl chlorides with *p*-aminobenzoate of cholesterol. The synthetic route adopted for the synthesis of this series **I** is given in Figure 1.

All the members of the series 4-*n*-alkoxy-3-methoxy cinnamic acids are non-mesogenic in nature. This behaviour is attributed to the presence of bulky lateral methoxy group. Lateral methoxy group hinders the packing of the molecules required for the mesomorphism. Cholesteryl-*p*-aminobenzoate itself is mesomorphic. All cholesteryl 4-(4’-*n*-alkoxy-3’-methoxycinnamoyl) amido benzoates are mesogenic in nature and shows enantiotropic chiral nematic mesophases. The chiral nematic mesophase observed from very first member of the series and persists up to the last member of the series investigated. This common behaviour of the cholesteryl compounds can be attributed to the flat and broad cholesteryl moiety of these compounds. The transition temperatures are summarized in Table 2.

The mesophases exhibited by this series were identified according to their optical textures. These textures were observed by polarizing optical microscopy. The N* phases were determined from textural observations by thermal microscopy under a polarizing microscope using heating and cooling cycles. It shows typical oily streak texture pattern. Phase transition temperatures observed through thermal microscopy were found to be in reasonable agreement with the corresponding DSC thermograms. Optical textures are shown in Figures 14-18 (section 3.3.2).

A graphical representation of the mesomorphic behaviour as a function of the number (n) of carbon atoms in the alkoxy chain is given in Figure 9. This exhibits falling tendency for the chiral nematic-isotropic transition temperature. Also, this chiral nematic-isotropic transition temperature curve exhibits odd-even effect. The odd-even effect in the molecules, forming liquid crystals, generally possesses the basic skeleton of relatively rigid aromatic or alicyclic rings with alkoxy or alkyl chain attached to one or both the end. It is worth noting that N* phase persist up to the last member of the series **I.** This was attributed to the effect of broad cholesteryl moiety, which outweighs polarizability effect of higher alkyl chain in the system. It needs strong polar group or a central linkage like carbamates to eliminate N* phase from the higher homologues [69]. The carbamate linkage will impart higher polarizability as well as more flexibility to the system compared to the –CH=CH–CONH– linkage.

Both these factors act opposite to each other in strengthening of N* phase. Higher polarizability enhances mesophase thermal stability and increased flexibility decreases mesophase thermal stability. The net effect is that carbamate linkage adversely affects the N* thermal stability compared to the –CH=CH–CONH– linkage as observed in the present series.

Mesomorphic-Isotropic transition temperatures generally change regularly in a mesomorphic homologous series. In the case of mesomorphic compounds, the melting process occurs in stages. The mesomorphic compound on heating passes through thermal agitations giving rise to the isotropic liquid. When a poly-mesomorphic compound is heated, at the solid-Sm transition, the primary terminal cohesions between the ends of the molecules are overcome. As the temperature of the Sm mesophase is raised further, the thermal vibrations eventually become great enough to overcome the strong lateral intermolecular attractions and the molecules are no longer maintained in their layer arrangement. Consequently the Sm-N or Sm-N* change takes place and the molecules are arranged in a parallel orientation but not in strata. Thus the N or N* mesophase is formed. The parallel arrangement of the molecules in the N or N* melt is maintained by the residual lateral and terminal cohesions, the weaker of these two determining the N-Iso and N*-Iso transition temperatures. On further heating, the molecules pass to a disordered isotropic liquid state.

In a homologous series exhibiting mesomorphism, as we ascend the series the increment of each methylene group brings about regular changes in the transition temperatures for the series. Gray [8] has tried to explain this behaviour of homologous series. As the methylene chain is lengthened, the separation of the aromatic centres, which are highly polarizable and which carry permanently dipolar substituents, is increased; consequently there should be a decrease in the strength of the terminal intermolecular cohesions. However, Gray [8] and Maier and Baumgartner [70] have suggested that the addition of each methylene group simultaneously increases the overall polarizability of the molecules and so the lateral intermolecular attractions may also increase with the growing chain length. In this way the behaviour of the homologous series can be explained.

In the present series **I,** all the members show enantiotropic N* mesophases. This is attributed to the relatively strong terminal cohesive forces acting in this system. Though the first mesomorphic substance reported was a cholesterol derivative

[1], the effect of chemical constitution on this mesophase has not been studied in detail. There is a close relationship between liquid crystalline properties and molecular constitution of organic compounds, hence the thermal stability; a measure of liquid crystalline properties can be correlated with the molecular constitution of the compounds. The average thermal stabilities of different mesogenic homologous series are compared and recorded in Table 3.

Table 3. Average thermal stabilities (°C) of series I, A, B and C compounds.

Series	I	A	B	C
N* / Sm - Iso (C_1-C_{18})	282.65	313.23	307.42	172.08
Commencement of Sm mesophase	-	C_7	C_7	C_1

Comparison of molecular structure of present series **I** with reported Series:

(1) Cholesteryl 4-(4’-*n*-alkoxy-3’-methoxycinnamoyl) amido benzoates; **Series: I**
(2) Cholesteryl 4-(4’-*n*-alkoxy benzoyl) amido benzoates; **Series: A** [61]
(3) Cholesteryl 4-*n*-alkoxybenzylidene-4’-amino benzoates; **Series B** [62]
(4) Cholesteryl 4-*n*-alkoxy phenyl carbamates; **Series C** [63]

The geometry of these series is given in Figure 10. The average chiral nematic thermal stabilities of series **I** is slightly lower than those of series **A.** Molecules of series **I** differ from series **A** by the central linkage between two phenyl groups. Additionally, molecules of series **I** have lateral methoxy group in the terminal phenyl ring. The central linkage of series **I** i.e. –CH=CH–CONH– linkage is longer and more polarisable compare to central amide linkage of series **A.** One would expect that the linkage would enhance chiral nematic thermal stabilities of series **I.** However, the presence of lateral methoxy group at the terminal phenyl ring acts as a deterrent to the chiral nematic thermal stabilities. Hence the N*-Iso thermal stabilities are lower than those of series **A.**

The same situation is observed when molecules of series **I** is compared with that of series **B.** Molecules of series I also differ from series **B** by central linkage as well as lateral substitution. Series **B** have –CH=N– and series **I** have additional lateral methoxy group in the terminal phenyl ring. The average thermal stabilities of series **I** are lower by ~ 25 °C than those of series **B.**

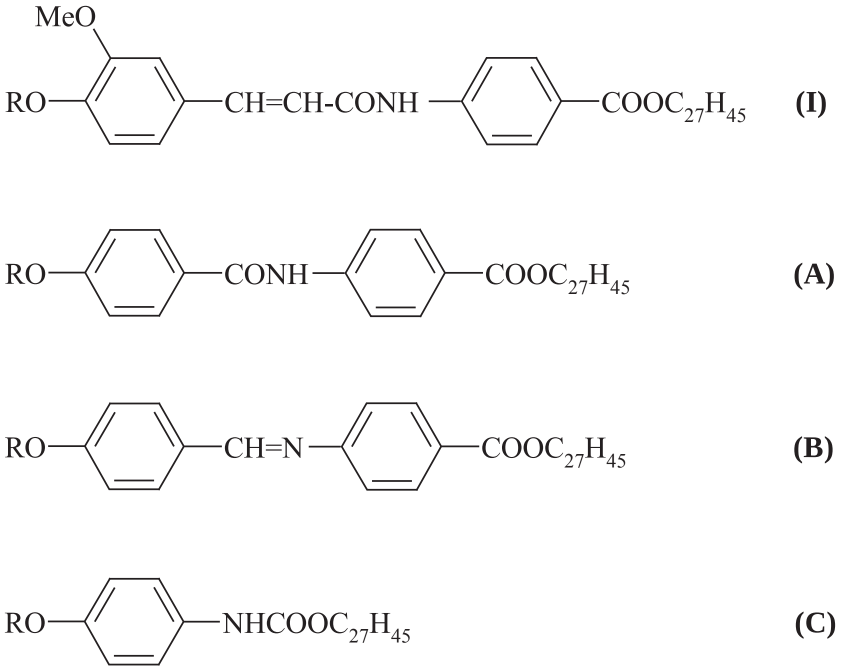


Figure 10. Comparative geometry of series I, A, B, and C compounds.

The molecules of series C have only one phenyl ring attached to cholesterol via urethane linkage, compared to two phenyl rings of series **I.** The N* thermal stabilities of series **C** are much lower compared to those of series **I.** This is understandable as molecules of series **C** have one phenyl ring and a central linkage less compared to molecules of series **I.** However, smectogenic tendencies of series **C** are very high due to the presence of carbamate linkage. It is worth noting that N* mesophase persists up to the last member of the series **I** as observed in series **A** and series **B.** This was attributed to the effect of broad cholesteryl moiety, which outweighs polarizability effect of higher alkyl chain in the system. It needs strong polar group or a central linkage like carbamates present as in series **C** to eliminate N* mesophase from the mesogenic system from the higher homologues (C_5 onwards). This is observed in normal nematogenic systems of rod-like molecules.

The preparation and characterization of supramolecular liquid crystals, obtained through hydrogen-bonding interactions of complementary molecules, has been extensively studied in the last 10 years. For the formation of liquid crystalline materials through hydrogen-bonding interactions, complementarity of the interacting components coupled with the direction ability of hydrogen bonds are the main (but not the sole) factors contributing to the exhibition of liquid crystallinity. The appropriate shape and stability of the hydrogen-bonded structures are also required.

The central theme of hydrogen-bonded liquid crystals is the development of new complementary component or the use of existing ones for the formation of supramolecular structures, which are then characterized as far as their liquid crystalline properties are concerned. In parallel, some investigations have been conducted concerning the theoretical aspects and practical applications of hydrogen-bonded liquid crystals. Thus a mean-field theory of liquid crystalline ordering for hydrogen-bonded liquid crystals was proposed by Veytsman [71], according to which, hydrogen bonds with a proper geometry enhance nematic ordering. The behaviour of the system proves to be completely different when the molecules form dimers or hydrogen-bonded polymers. In the area of applications of hydrogen-bonded liquid crystals in electro-optic devices, both smectogenic and nematogenic structures have been employed. Thus, room temperature hydrogen-bonded liquid crystals derived from 4-alkoxybenzoic acid derivatives and alkyl pyridines align in twisted nematic cells and show electro-optic effects [72]. Furthermore, mixtures of hydrogen-bonded structures with conventional liquid crystal materials were prepared [73] leading to various types of mesomorphic behaviour.

The first hydrogen-bonded complexes exhibiting liquid crystalline behaviour resulted from the dimerization of aromatic carboxylic acid [8]. Lengthening of the rigid-rod segment occurs, inducing in this way liquid crystalline behaviour. Trans-*p*-methoxy- and trans-*p*-ethoxy-cinnamic acids [8] and their higher homologues [74], as well as the *p*-*n*-alkoxybenzoic acids, exhibited liquid crystalline phases as reported by Gray and Jones [8, 75] more than 50 years ago.

Cholesterol-based liquid crystals were also prepared [76] by hydrogen bonding interaction of 3-cholesteryl-oxycarbonylpropanoic acid with 4-(4-alkoxybenzoyl-oxy)-4'-stilbazoles and *N*-(4-pyridylmethylidene)anilines affording complexes. In addition to unidentified Sm phases, SmA, SmC and N phases were observed. It was found from the study that the phase transition temperatures were higher than those for the analogous of hydrogen-bonded complexes.

In 2001, Lee *et al.* [77] have designed dimesogenic compounds through H-bonding in order to compare the smectic periodicities of these H-bonded materials with those of the corresponding chemically bonded dimesogens. The mesogenic 1:1 complexes were prepared from an equimolar mixture of 3-cholesteryloxy carbonyl pentanoic acid as proton donor and 4-(pyridine-4-ylmethyleneimino) phenyl 4-alkoxy-benzoate as proton acceptor. The study demonstrated that the H-bonded dimesogens behave as single components with properties comparable to those of covalently linked dimesogens. Also, the use of non-stochiometric mixtures provides another degree of freedom for fine-tuning the mesomorphic and structural properties.

Supramolecular H-bonded assemblies containing cholesterol and azobenzene linked moieties were prepared by Mallia and Das [78] from cholest-5-en-3-ol-(3β)[4-phenyl-pyridylazo]carbonate as hydrogen bond acceptor and different 4-*n*-alkyloxybenzoic acids as hydrogen bond donors. The presence of the azo moiety can impart photo-switching properties to these materials, since irradiation can lead to photo isomerization of the azo moiety from the *trans*- to the *cis*-form.

Recently, Paleos and co-workers [79] have introduced external pyridyl moieties at the external primary amino groups of diaminobutane poly(propyleneimine) dendrimers and subsequently interacted *via* H-bonding with 3-cholesteryloxy carbonyl propanoic acid. The materials obtained exhibit SmA phases over a relatively broad temperature range from about 60 °C to 140 °C.

There are however relatively few reports in the area of cholesterol linked supramolecular mesogens and to our knowledge no amide-linked cholesterol systems have been prepared. In the present study we have incorporated an amide linkage in the side chain of cholesteryl derivatives. The side chain also incorporates methoxy group as lateral substituent. It is known that the high anisotropy, linearity and intermolecular hydrogen bonding confer rich mesogenic properties on the system (Figure 11). In this present chiral nematogenic series one would have expected exhibition of smectic phase. It seems lateral methoxy group has exhibited breadth increasing effect to the molecules which has a hindered close packing of the molecules of smectic phase. The amide linkage is capable of giving supramolecular structure in mesomorphic state as well as in crystalline state [80]. This supramolecular self-assembly of molecules occurs as a result of hydrogen-bonding (confirmed by IR band at ~3400 cm^{-1} for N-H stretching) and packing of the mesogenic cores. In this way a hydrogen-bonded network is created and the compound exhibits macromolecular behaviour. Figure 11 represents the probable packing of the molecular orientation model with intermolecular hydrogen-bonding. The helical structure is formed by the propagation of this ordering.

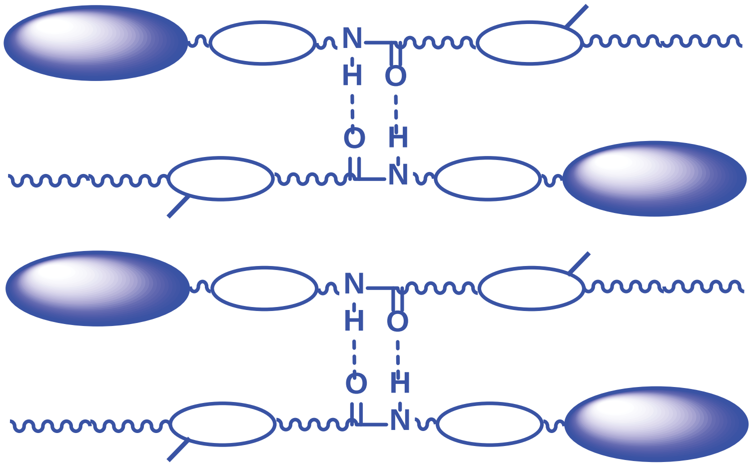


Figure 11. Schematic of probable packing of molecules with intermolecular hydrogen-bonding.

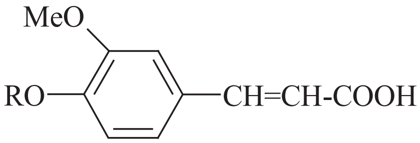
The transition temperatures identified under POM were confirmed with DSC study. The representative DSC thermograms of *n*-butoxy and *n*-octyloxy derivatives are shown in Figure 12 and 13, respectively. The DSC data are recorded in Table 4. Both members are showing endothermic peaks as well as exothermic peaks on heating and cooling respectively. It should be noted that the enthalpy change associated with N*-isotropic transitions are very small. This would be expected as the molecules has greater biaxiality than the individual non-hydrogen bonded molecules. This may be attributed to the increased molecular biaxiality arising from the rather bulky cholesteryl unit [53, 81]. Also, the presence of lateral methoxy group serves to increase the molecular biaxiality which results into decrease in the clearing enthalpy [82].

Table 4. Differential Scanning Calorimetry (DSC) data.

Sr. No.	R-*n*-alkyl group	Transition	Peak temperatures (microscopic reading)	ΔH kJ/mole	ΔS kJ/mole.°K^{-1}
1	Butyl	Cr-N*	192.0 (194.18)	21.98	0.0470
		N*-I	318.0		
2	Octyl	Cr-N*	164.5 (163.77)	25.03	0.0572
		N*-I	305.6		

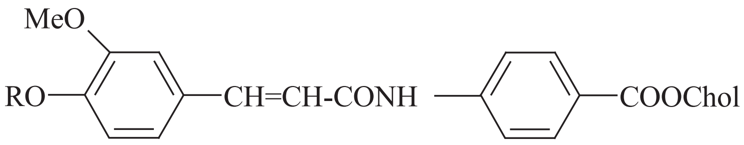
The compounds of the present series exhibit iridescent colours in the plane texture. In such a molecular system, lateral substituent or amide linkage can adversely affect mesomorphic properties of the system. High anisotropy, linearity and intermolecular hydrogen bonding confer rich mesomorphic properties on the system. Intermolecular hydrogen bonding arising from amide linkage can lead to supramolecular motifs. Several of these compounds are potentially useful thermo-chromic materials for higher temperatures as their solid to N* range covers 170 °C to 300 °C.

Table 1. Melting points (°C) of trans-4'-*n*-alkoxy-3'-methoxycinnamic acid. (**5**)



Sr. No.	R = *n*-alkyl group	Melting points (°C)
1	Methyl	181.0
2	Ethyl	178.0
3	Propyl	163.0
4	Butyl	149.0
5	Pentyl	132.0
6	Hexyl	125.0
7	Heptyl	120.0
8	Octyl	105.0
9	Decyl	103.0
10	Dodecyl	104.0
11	Tetradecyl	105.0
12	Hexadecyl	107.0
13	Octadecyl	107.0

Table 2. Transition temperatures of Cholesteryl 4-(4’-*n*-alkoxy-3’-methoxycinnamoyl) amido benzoates **(Series I).**

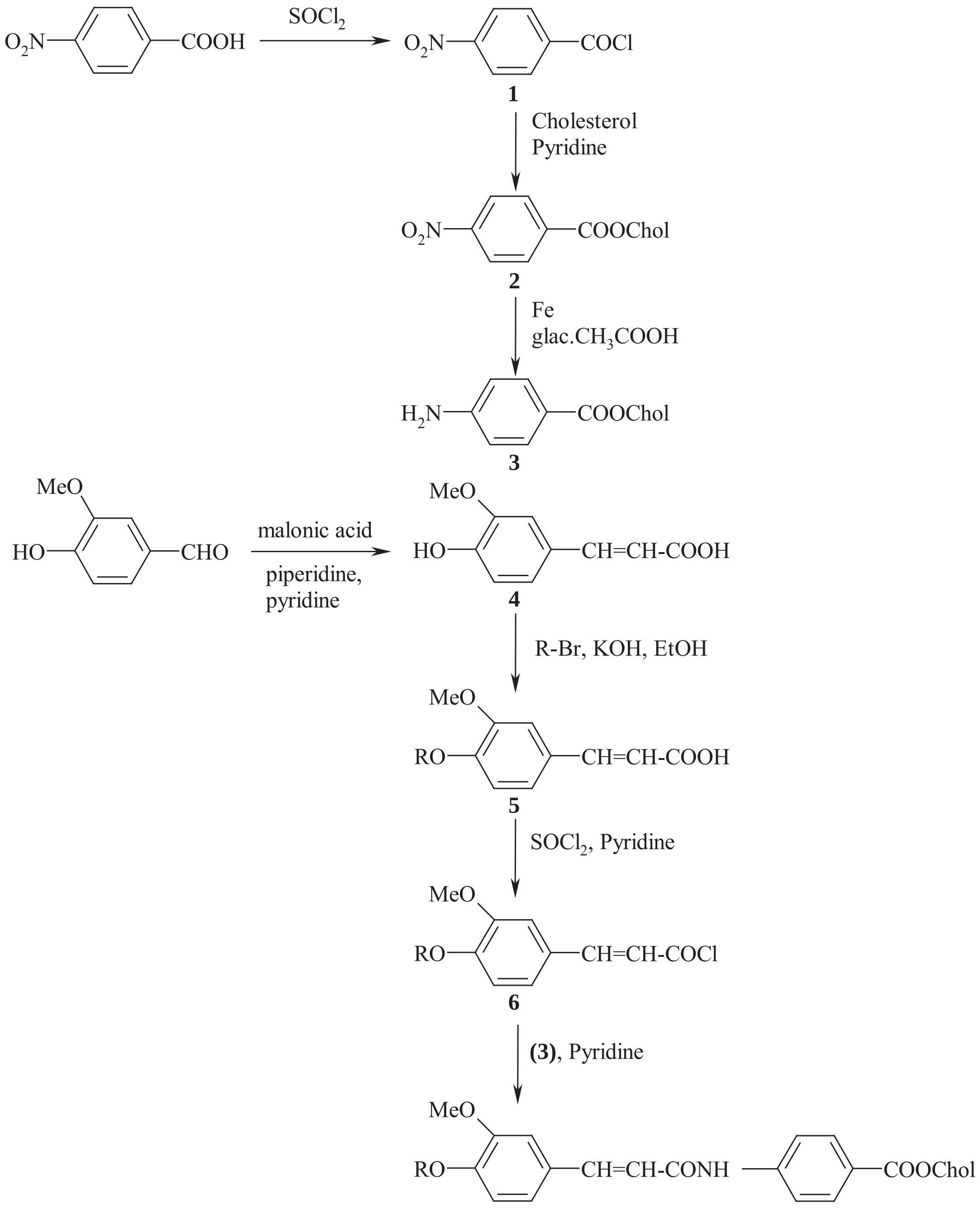


Sr. No.	R = *n*-alkyl group	Transition temperatures (°C)				
		Cr		N*		I
1	Methyl	•	211.0	•	280.8	•
2	Ethyl	•	172.3	•	304.0(d)	•
3	Propyl	•	170.0	•	300.0	•
4	Butyl	•	192.0 (194.18)	•	318.0(d)	•
5	Pentyl	•	194.0	•	292.0	•
6	Hexyl	•	187.0	•	321.0(d)	•
7	Heptyl	•	187.0	•	263.0	•
8	Octyl	•	164.5 (163.77)	•	305.6(d)	•
9	Decyl	•	172.8	•	275.8	•
10	Dodecyl	•	194.0	•	266.3	•
11	Tetradecyl	•	181.4	•	257.5	•
12	Hexadecyl	•	171.6	•	247.9	•
13	Octadecyl	•	170.0	•	242.5	•

Cr = crystal, N* = nematic, I = isotropic.

( ) indicates DSC transition temperatures on heating.

(d) indicates decomposition.



Series I

R = n-C_nH_{2n+1}, n = 1 to 8, 10, 12, 14, 16 and 18; Chol = Cholesteryl group.

Figure 1. Synthetic route to series I.

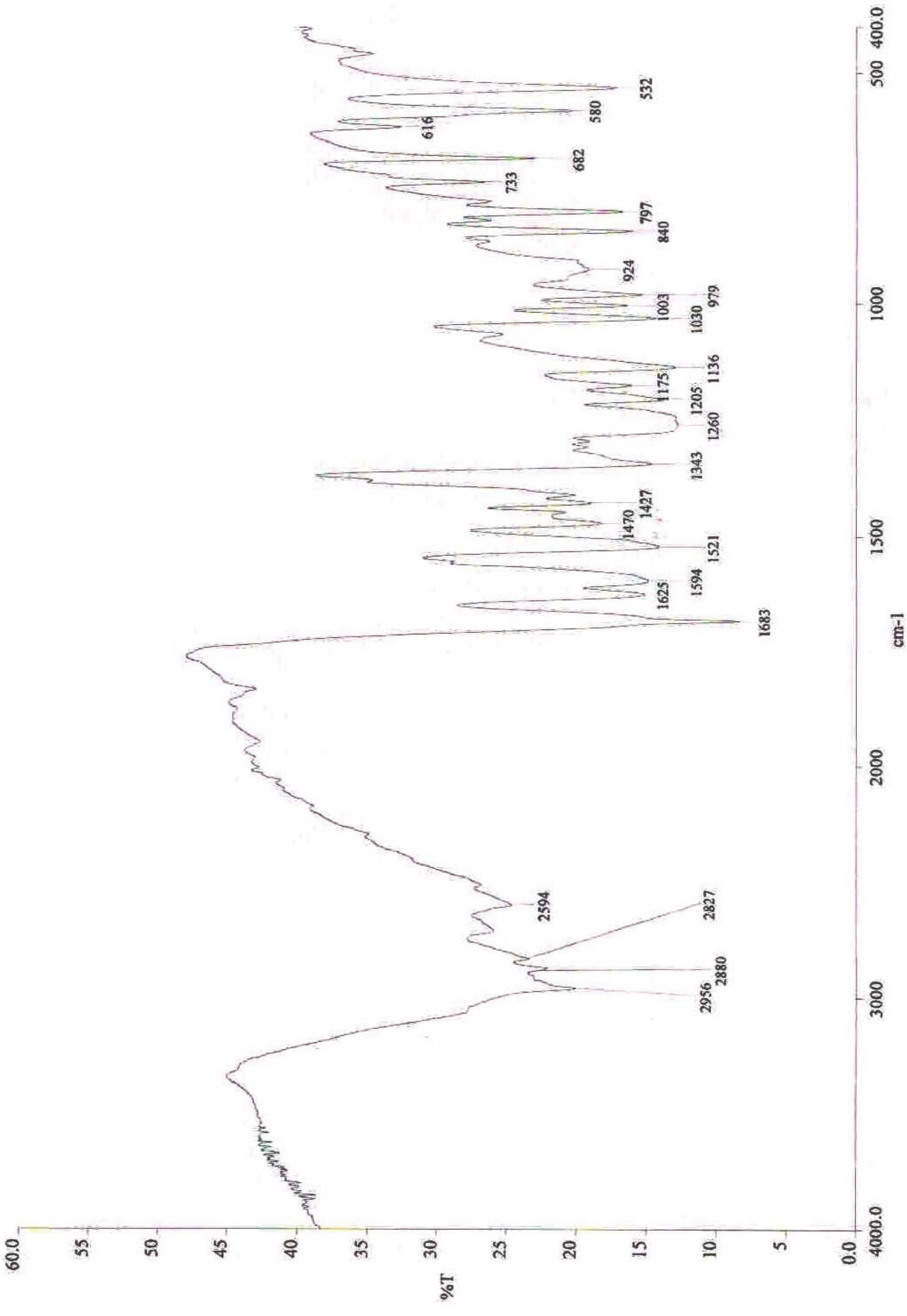


Figure 2. Representative IR spectra of 4-*n*-butoxy-3-methoxy cinnamic acid.

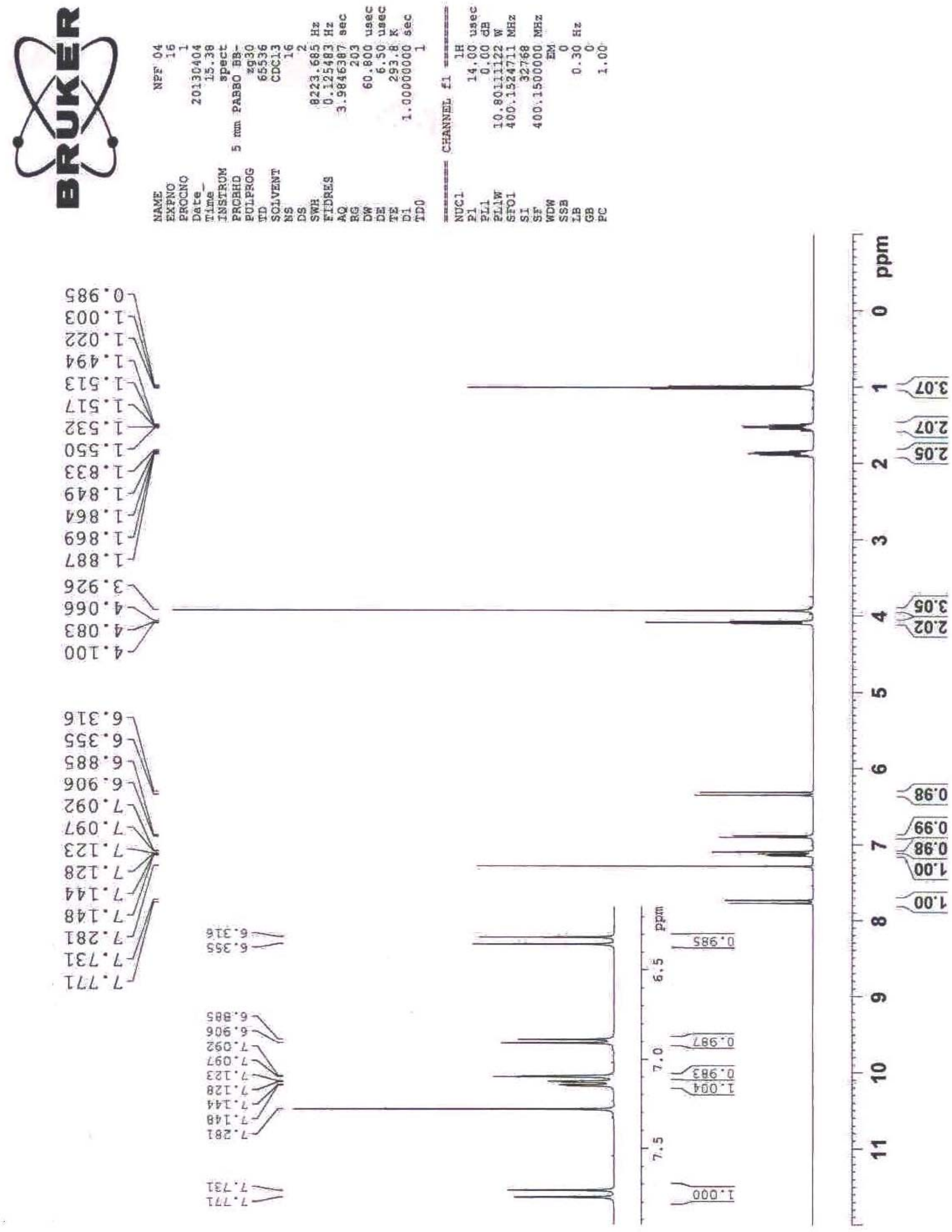


Figure 3. ^{1}H NMR spectra of 4-*n*-butoxy-3-methoxy cinnamic acid.

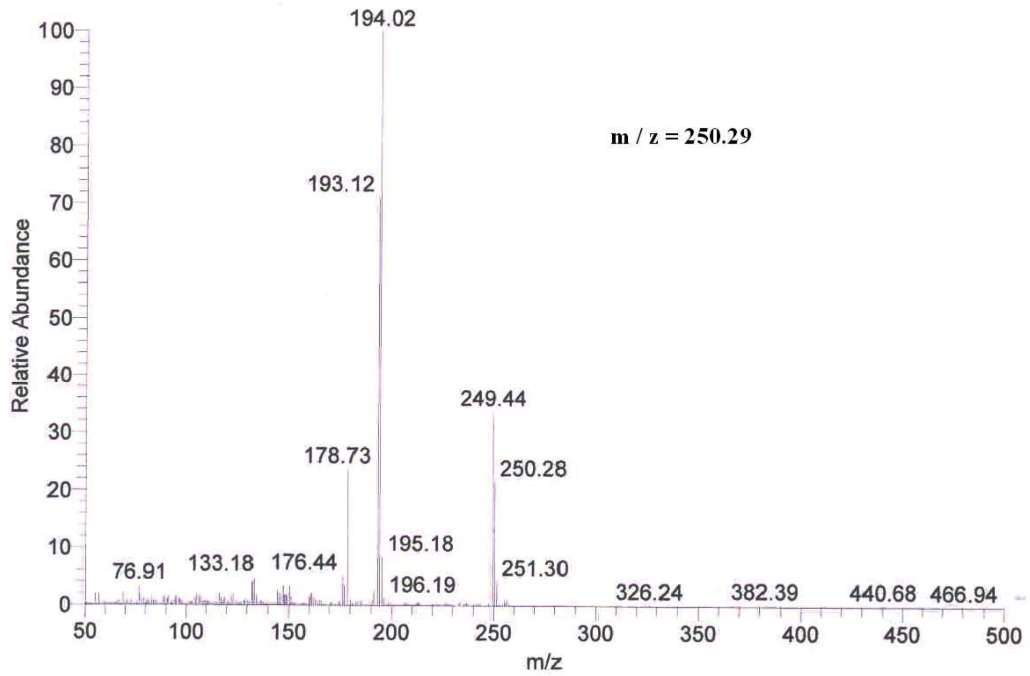


Figure 4. Mass spectra of 4-*n*-butoxy-3-methoxy cinnamic acid.

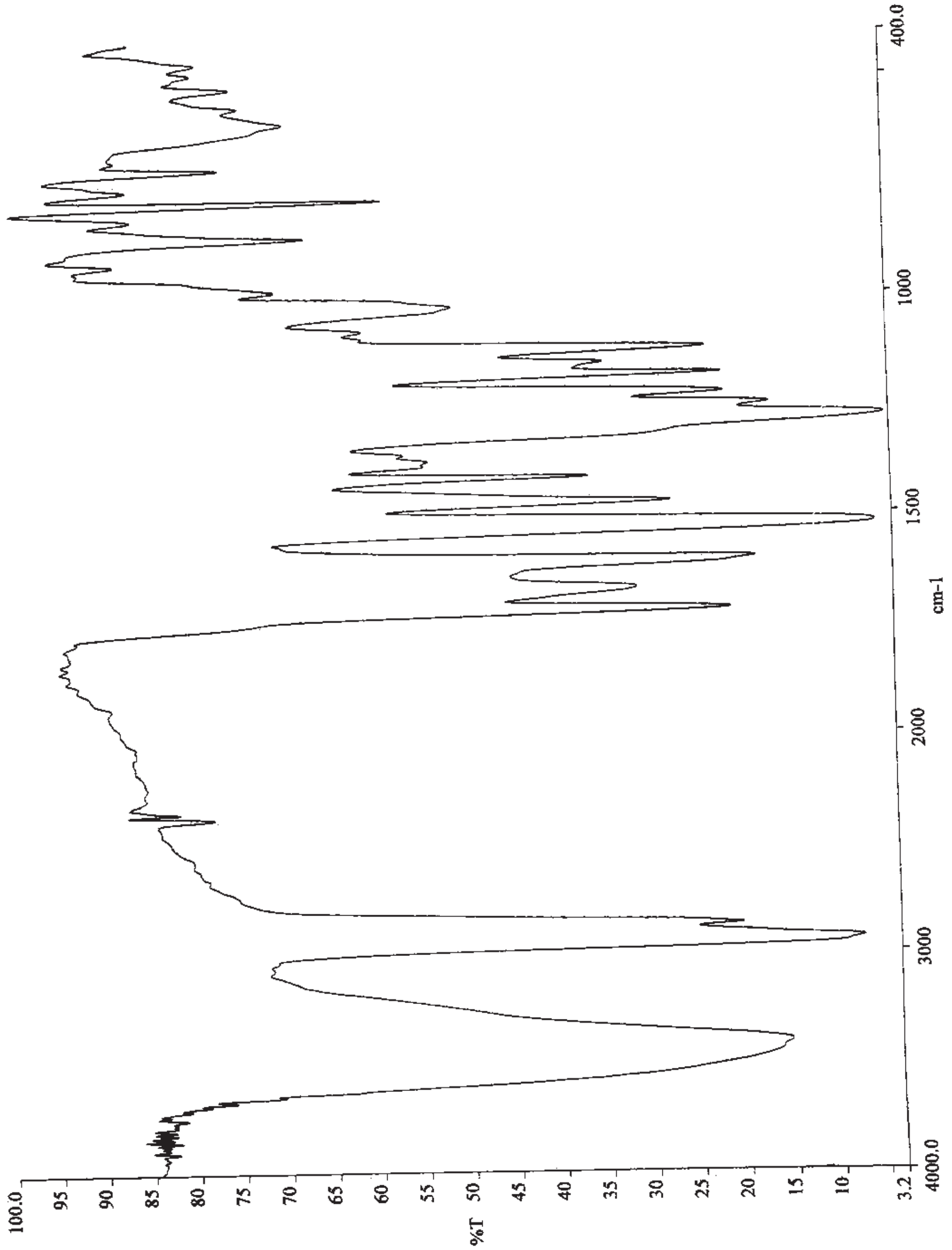


Figure 5. Representative IR spectra of Cholesteryl 4-(4’-*n*-butoxy-3’-methoxycinnamoyl) amido benzoate.

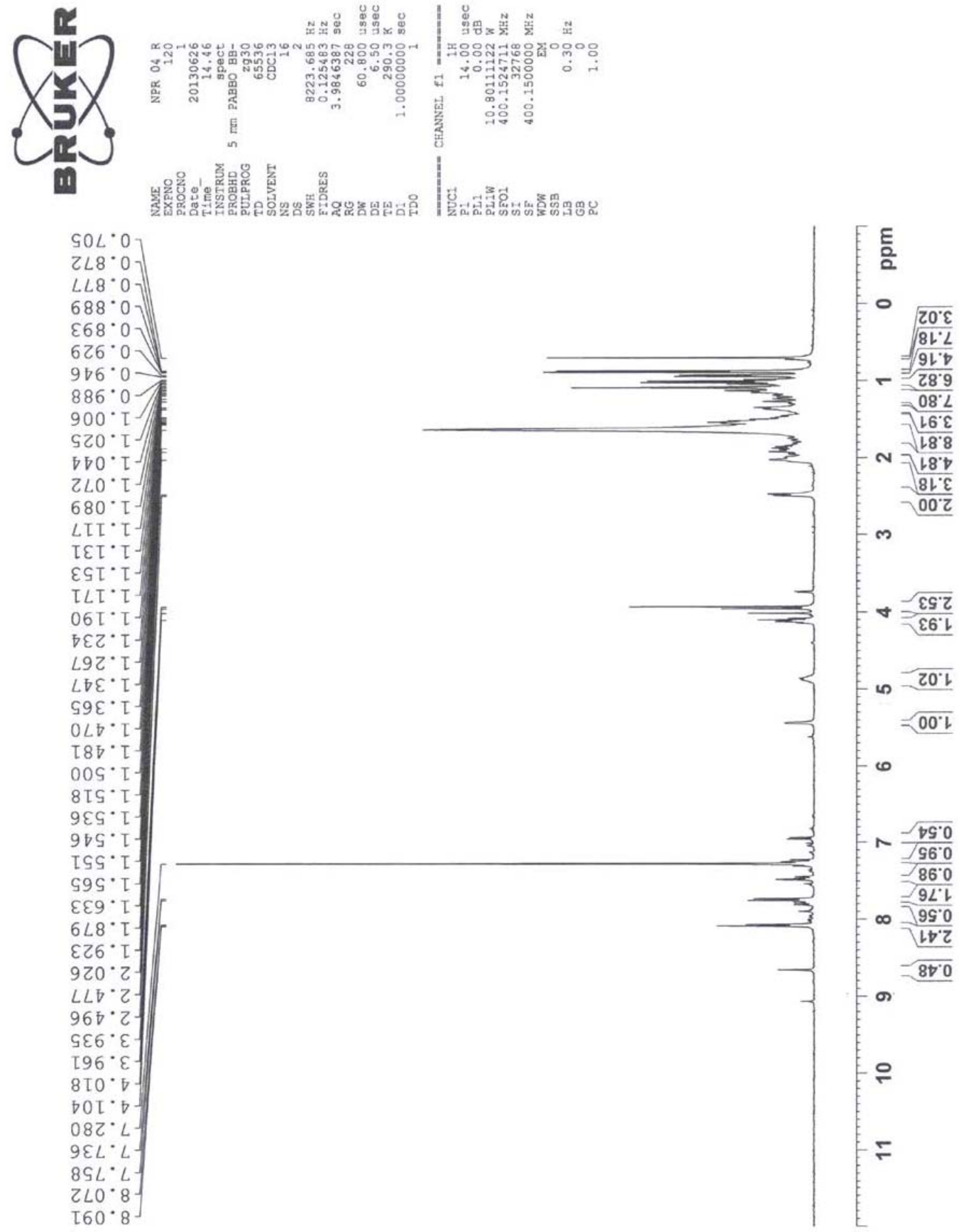


Figure 6. ^{1}H NMR spectra of Cholesteryl 4-(4’-*n*-butoxy-3’-methoxycinnamoyl) amido benzoate.

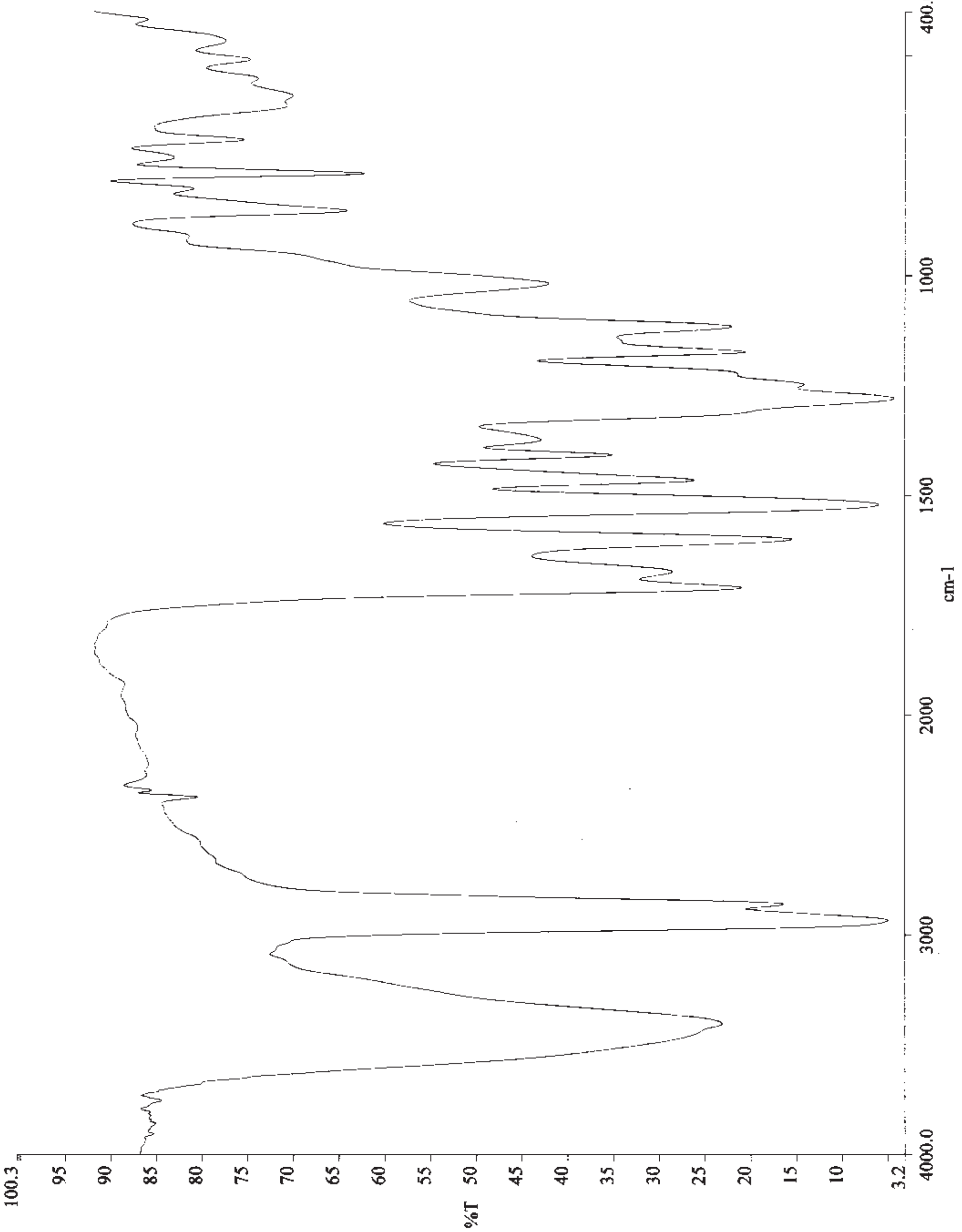


Figure 7. Representative IR spectra of Cholesteryl 4-(4’-*n*-octyloxy-3’-methoxycinnamoyl) amido benzoate.

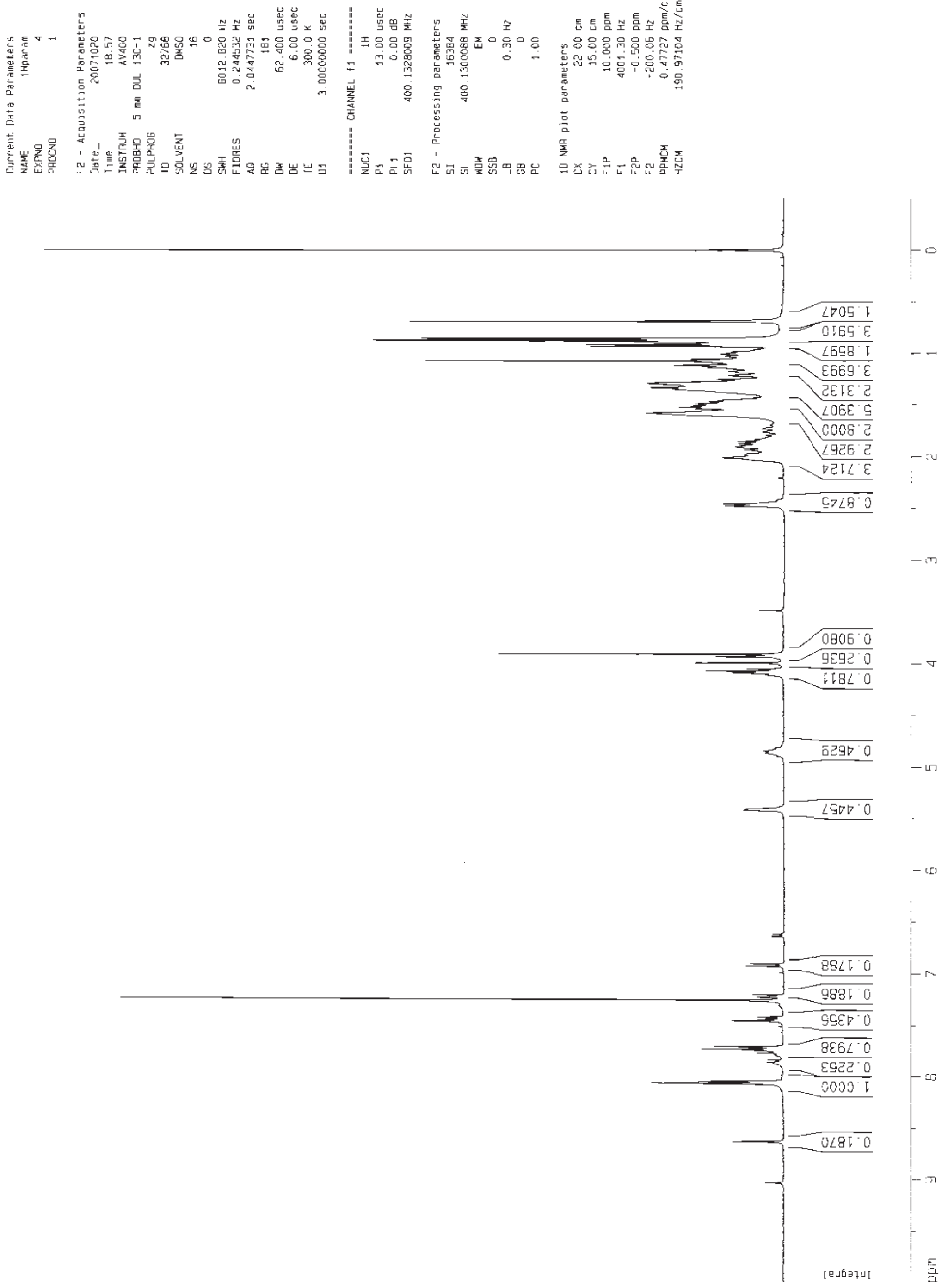


Figure 8. ^{1}H NMR spectra of Cholesteryl 4-(4’-*n*-octyloxy-3’-methoxycinnamoyl) amido benzoate.

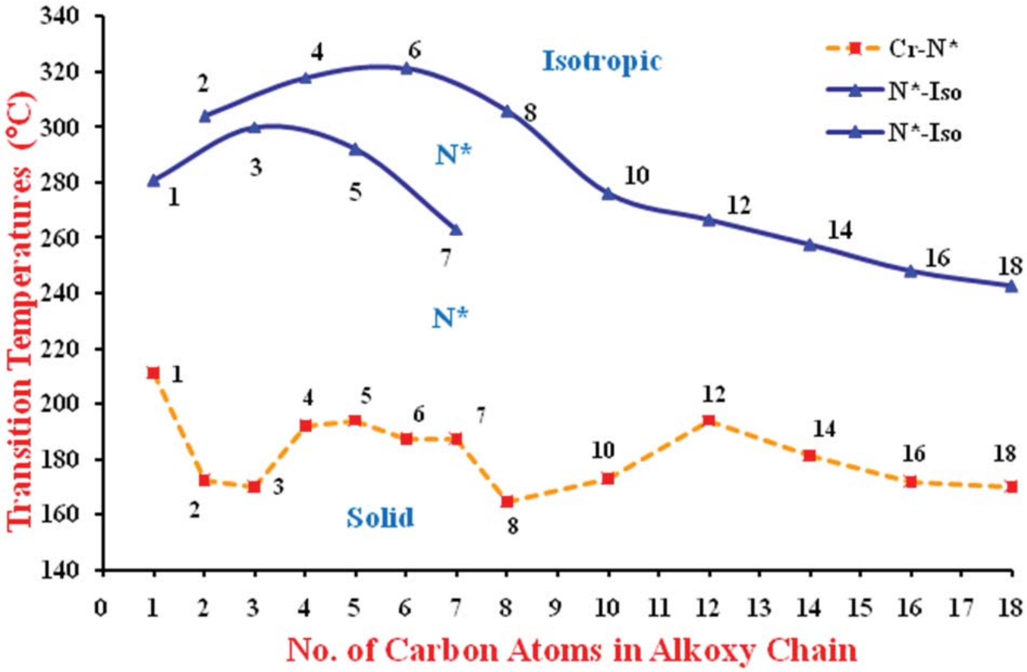


Figure 9. Plot of Transition temperatures (°C) versus number of carbon atoms in the alkoxy chain.

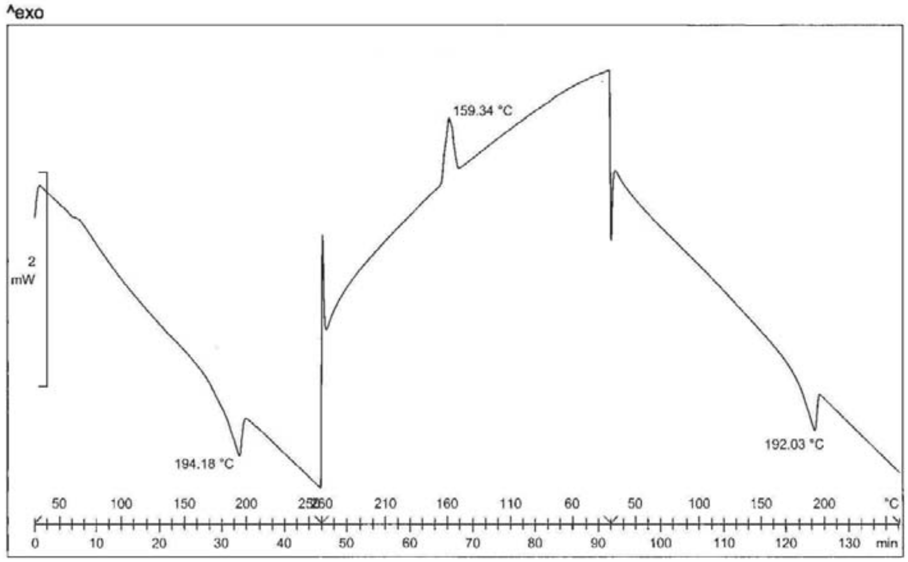


Figure 12. Representative DSC thermograms of *n*-butyloxy derivative at heating rate of 10 °C min^{-1}.

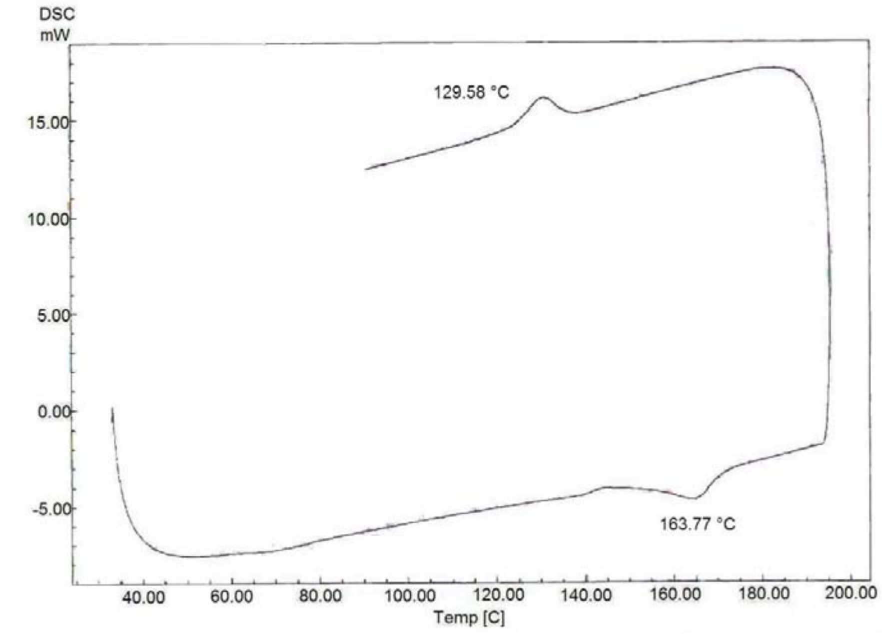


Figure 13. Representative DSC thermograms of *n*-octyloxy derivative at heating rate of 10 °C min^{-1}.

3.3.1. Optical properties

The Specific Optical Rotation (SOR) [α] of a chemical compound is defined as the observed angle of optical rotation α when plane-polarized light is passed through a sample with a path length of 1 decimeter and a sample concentration of 1 gram per 1 millilitre. It is the main property used to quantify the chirality of a molecular species. The SOR of a pure material is an intrinsic property of that material at a given wavelength and temperature. Values should always be accompanied by the temperature at which the measurement was performed and the solvent in which the material was dissolved. We have investigated these cholesteryl derivatives for SOR. The SOR values obtained are recorded as shown below:

Specific Optical Rotation:

$[\alpha]^{30}_{D} = +18.1$ ° ($c = 1.00$, $CHCl_3$) (*n*-pentyloxy derivative)

$[\alpha]^{30}_{D} = +17.7$ ° ($c = 1.00$, $CHCl_3$) (*n*-hexyloxy derivative)

3.3.2. Optical textures

The most widely used technique of liquid crystal phase identification is optical polarizing microscopy. This technique reveals that each different liquid crystal phase has a distinct optical texture. However, the identification of liquid crystal phases through optical polarizing microscopy is often difficult and requires a lot of experience. Optical polarizing microscopy enables the identification of the type of liquid crystal and other mesophases from the optical texture that is generated. The identification of mesophases through optical polarizing microscopy usually involves the magnified view of a thin sample of a mesogenic material sandwiched between a glass microscope slide and a glass cover-slip. The microscope slide of material is usually placed in a stage between polarisers which are crossed at 90° to each other.

All the compounds of the series **I** show mesomorphic properties and all are enantiotropic in nature. All the members starting with methyl derivative exhibit chiral nematic phase and persists upto the last member *n*-octadecyl derivative. The phase was determined from optical texture observations under both heating and cooling cycles and shows typical characteristic oily streak texture pattern of N* phase. Colour of the texture is attributed to the high birefringence. Network-like detect lines are the lines of oily streak. Optical textures of some of the compounds of the series **I** are shown in Figures 14-18.

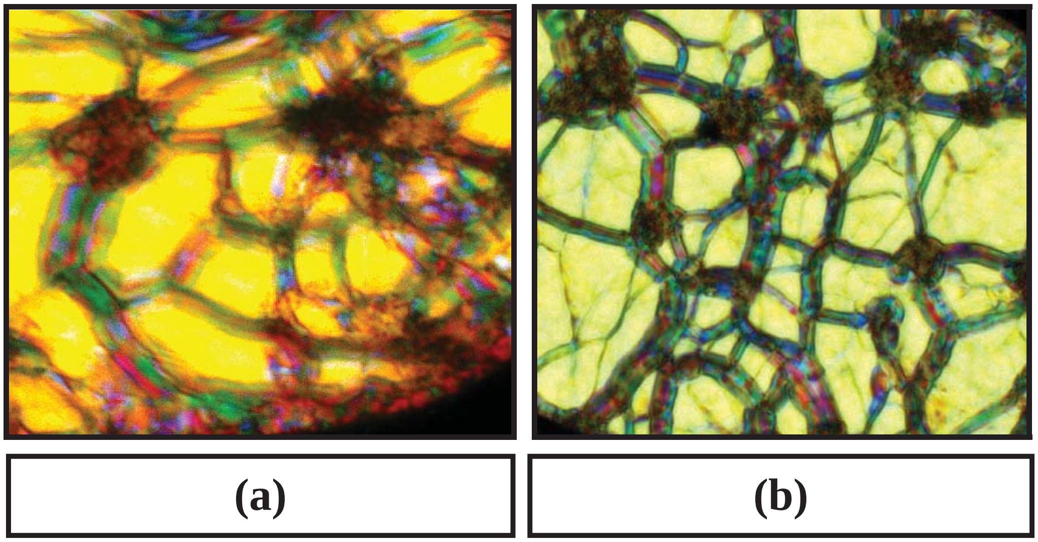
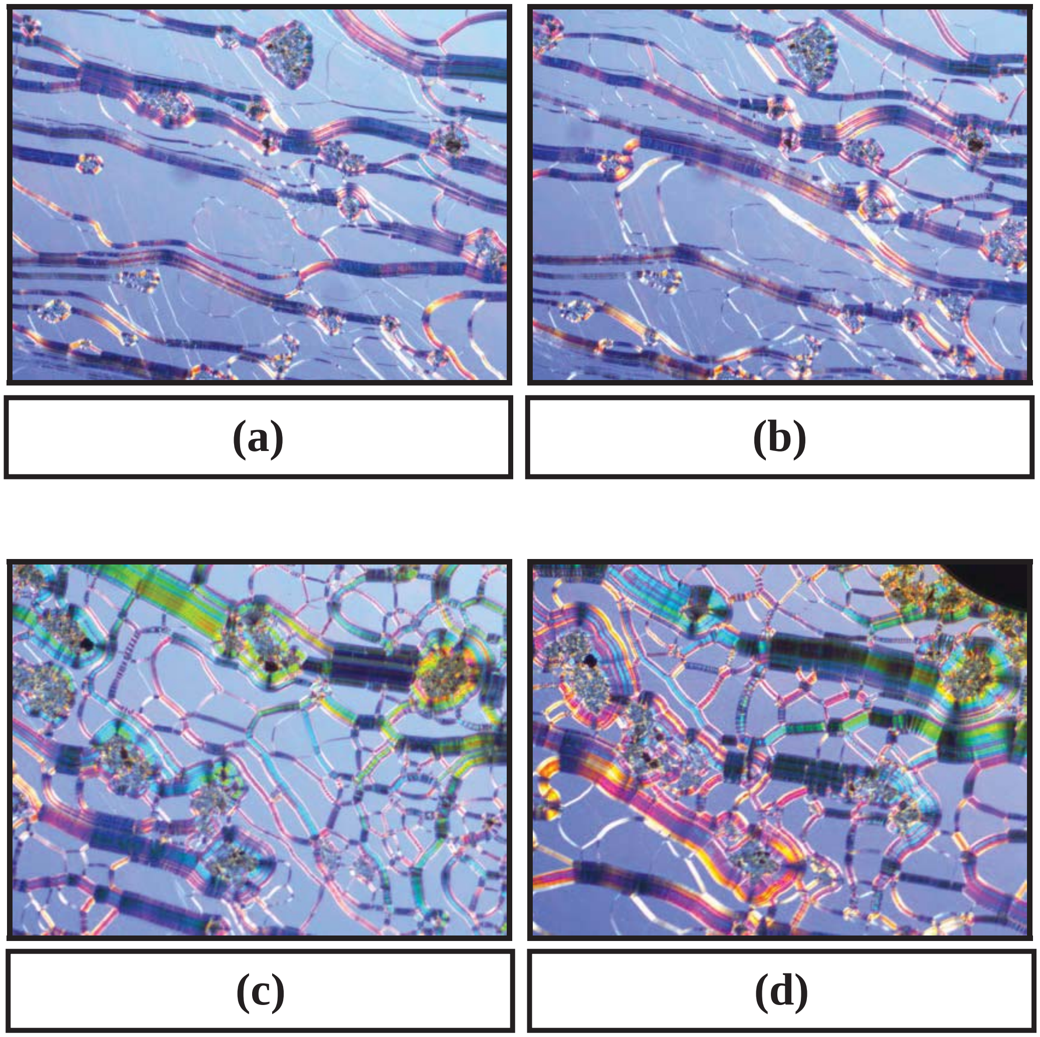


Figure 14. Polarised optical microphotographs of *n*-butyl derivative. (a) N*-oily streak texture observed at 210.0 °C on heating, (b) N*-oily streak texture observed at 228.5 °C on heating.



(a)

(b)

(c)

(d)

Figure 15. Polarised optical microphotographs of *n*-pentyl derivative. (a) N*-oily streak texture observed at 225.0 °C on heating, (b) N*-oily streak texture observed at 227.0 °C on heating, (c) N*-oily streak texture observed at 246.0 °C on heating and (d) N*-oily streak texture observed at 261.0 °C on heating.

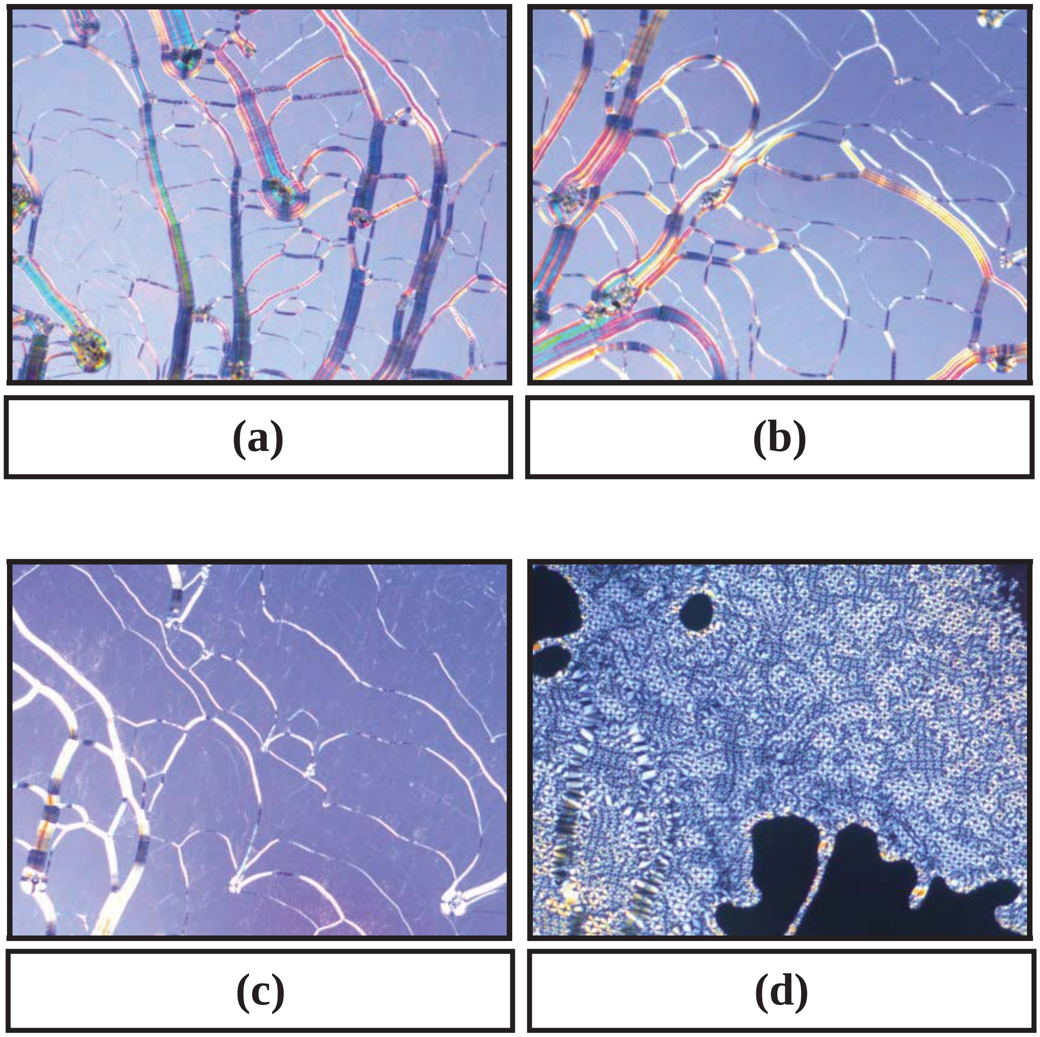


Figure 16. Polarised optical microphotographs of *n*-hexyl derivative. (a) N*-oily streak texture observed at 249.0 °C on heating, (b) N*-oily streak texture observed at 268.0 °C on heating, (c) N*-oily streak texture observed at 280.0 °C on heating and (d) N* to isotropic phase change observed at 306.0 °C on heating,

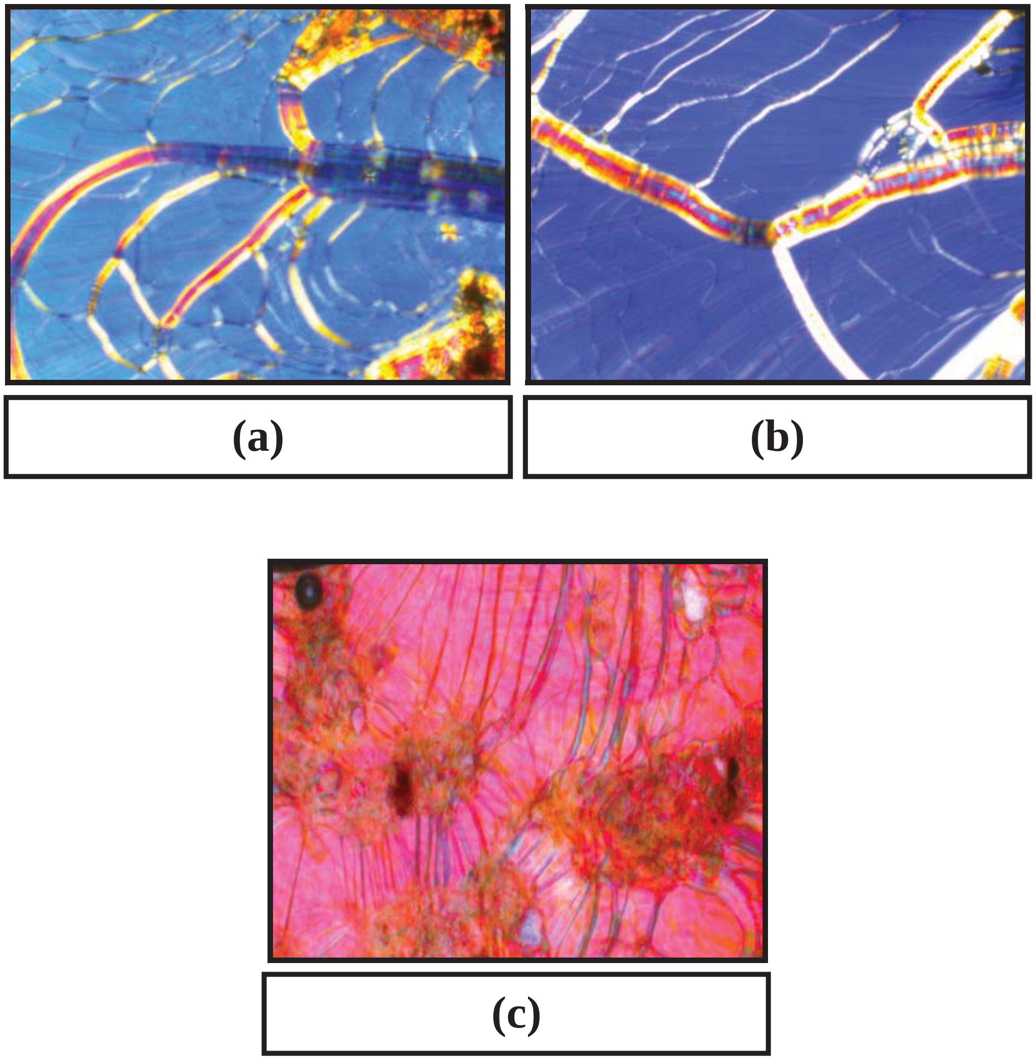
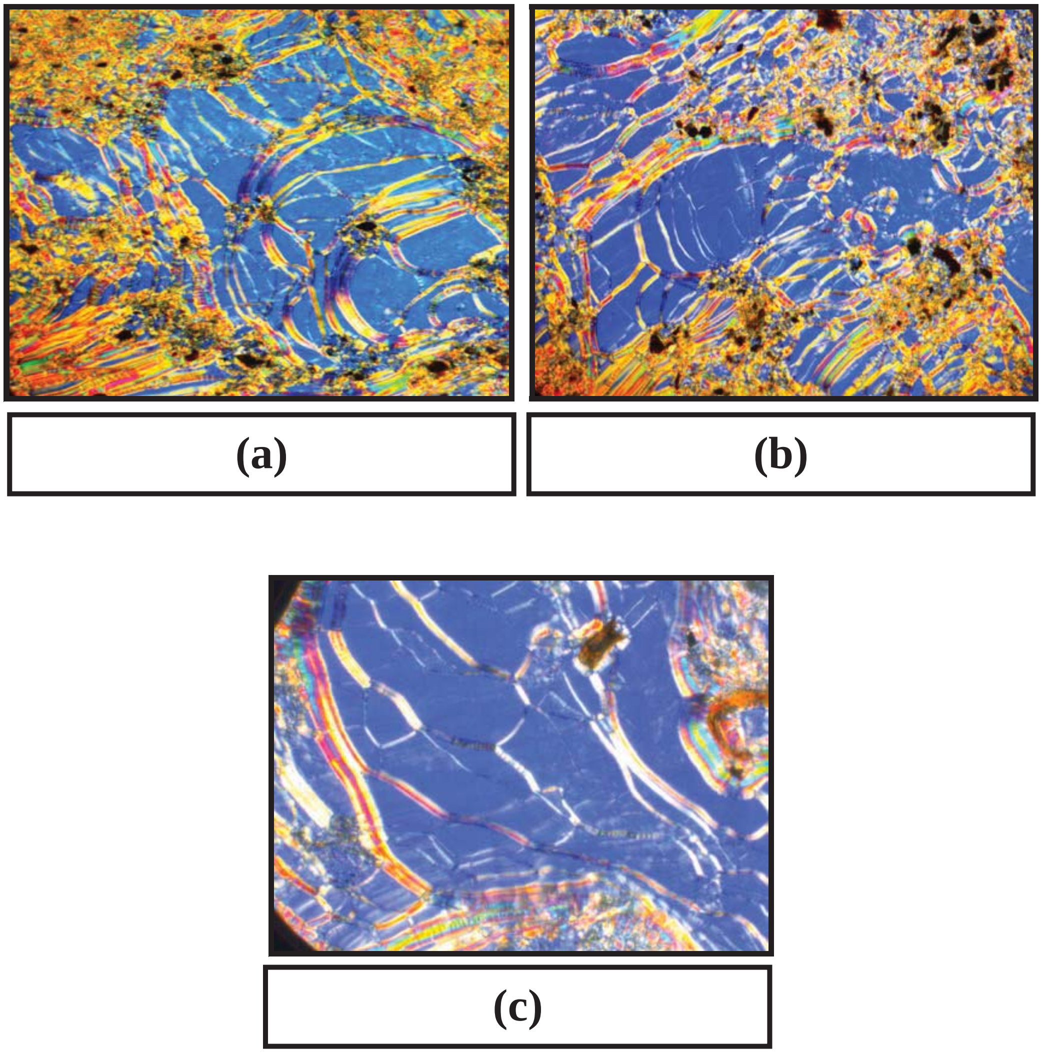


Figure 17. Polarised optical microphotographs of (a) *n*-heptyl derivative; N*-oily streak texture observed at 252.0 °C on heating, (b) *n*-heptyl derivative; N*-oily streak texture observed at 257.0 °C on heating, (c) *n*-octyl derivative; N*-oily streak texture observed at 247.1 °C on heating.



(a) (b)

(c)

Figure 18. Polarised optical microphotographs of (a) *n*-dodecyl derivative; N*-oily streak texture observed at 256.0 °C on heating, (b) *n*-dodecyl derivative; N*-oily streak texture observed at 260.0 °C on heating, (c) *n*-octadecyl derivative; N*-oily streak texture observed at 232.0 °C on heating.

3.4. References

[1] F. Reinitzer, *Wiener Monatsh. Chem.*, **9**, 421–441, 1888.

[2] T. Thiemann and V. Vill, *J. Phys. Chem. Ref. Data.*, **26**(2), 291-333, 1997.

[3] V. A. Mallia and N. Tamaoki, *Chem. Soc. Rev.*, **33**(2), 76-84, 2004.

[4] S. Bhattacharya and Y. Krishnan-Ghosh, *Mol. Cryst. Liq. Cryst.*, **381**(1), 33-41, 2002.

[5] N. Tamaoki, *Adv. Mater.*, **13**(15), 1135-1147, 2001.

[6] P. L. Carroll, *Cholesteric Liquid Crystals: Their Technology and Applications*, Ovum, London, 1973.

[7] G. W. Gray, *J. Chem. Soc.*, 3733-3739, 1956.

[8] G. W. Gray, *Molecular Structure and the Properties of Liquid Crystals*, Academic Press, New York, 1962.

[9] E. Daumer, *Diss. Halle-Wittenberg*, 1912.

[10] W. Elser, *Mol. Cryst.*, **2**(1-2), 1-13, 1966.

[11] J. S. Dave and R. A. Vora, *Indian J. Chem.*, **11**(1), 19-20, 1973.

[12] J. S. Dave and R. A. Vora, *Liquid Cryst. Ordered Fluids*, 477-487, 1970.

[13] J. S. Dave and G. Kurian, *Mol. Cryst. Liq. Cryst.*, **24**(3-4), 1, 1973.

[14] J. S. Dave and G. Kurian, *Indian J. Chem.*, **11**(8), 833, 1973.

[15] G. Kurian and J. S. Dave, *Mol. Cryst. Liq. Cryst.*, **42**(1), 193-201, 1977.

[16] J. S. Dave and R. Vora, *Mol. Cryst. Liq. Cryst.*, **14**(3-4), 319-327, 1971.

[17] S. W. Cha, J-I. Jin, M. Laguerre, M. F. Achard and F. Hardouin, *Liq. Cryst.*, **26**(9), 1325-1337, 1999.

[18] E. Ostuni and R. G. Weiss, *Liq. Cryst.*, **26**(4), 541-551, 1999.

[19] C. V. Yelamaggad, S. A. Nagamani, U. S. Hiremath and G. G. Nair, *Liq. Cryst.*, **28**(7), 1009-1015, 2001.

[20] C. V. Yelamaggad, M. Mathew, T. Fujita and N. Iyi, *Liq. Cryst.*, **30**(9), 1079-1087, 2003.

[21] C. V. Yelamaggad and M. Mathews, *Liq. Cryst.*, **30**(2), 125-133, 2003.

[22] A. S. Pandey, R. Dhar, A. S. Achalkumar and C. V. Yelamaggad, *Liq. Cryst.*, **38**(6), 775-784, 2011.

[23] N. Nagappa, J. Mahadeva, S. Mohyeddine, C. V. Yelamaggad, S. A. Nagami, U. S. Herimath, D. Revannasiddaiah and M. V. Krishnaswamy, *Mol. Cryst. Liq. Cryst.*, **508**(1), 242-248, 2009.

[24] V. K. Gupta, P. Bandhoria, M. Kalyan, M. Mathews and C. V. Yelamaggad, *Liq. Cryst.*, **32**(6), 741-747, 2005.

[25] R. K. Sharma, V. K. Gupta, M. Mathews and C. V. Yelamaggad, *Liq. Cryst.*, **35**(9), 1161-1167, 2008.

[26] R. K. Sharma, V. K. Gupta, M. Mathews and C. V. Yelamaggad, *Liq. Cryst.*, **36**(3), 225-230, 2009.

[27] V. K. Gupta, R. K. Sharma, M. Mathews and C. V. Yelamaggad, *Liq. Cryst.*, **36**(3), 339-343, 2009.

[28] C. V. Yelamaggad, S. A. Nagamani, D. S. Shankar Rao and S. Krishna Prasad, *J. Chem. Res.*, **2001**(11), 493-495, 2001.

[29] C. V. Yelamaggad, S. A. Nagamani, T. Fujita and N. Iyi, *Liq. Cryst.*, **29**(11), 1393-1399, 2002.

[30] C. V. Yelamaggad, A. S. Achalkumar, D. S. Shankar Rao and S. Krishna Prasad, *Org. Lett.*, **9**(14), 2641-2644, 2007.

[31] K. C. Majumdar, T. Ghosh, S. Chakravorty, N. Pal, D. S. Shankar Rao and S. Krishna Prasad, *Liq. Cryst.*, **37**(12), 1539-1547, 2010.

[32] K. C. Majumdar, T. Ghosh, D. S. Shankar Rao and S. Krishna Prasad, *Liq. Cryst.*, **38**(10), 1269-1277, 2011.

[33] K. C. Majumdar, S. Ponra and S. Chakravorty, *Mol. Cryst. Liq. Cryst.*, **528**(1), 113-119, 2010.

[34] K. C. Majumdar, P. K. Shyam, D. S. Shankar Rao and S. Krishna Prasad, *Liq. Cryst.*, **39**(11), 1358-1367, 2012.

[35] K. C. Majumdar, P. K. Shyam, D. S. Shankar Rao and S. Krishna Prasad, *Liq. Cryst.*, **39**(9), 1117-1123, 2012.

[36] A. T. M. Marcelis, A. Koudijs, E. A. Klop and E. J. R. Sudhölter, *Liq. Cryst.*, **28**(6), 881-887, 2001.

[37] A. T. M. Marcelis, A. Koudijs, Z. Karczmarzyk and E. J. R. Sudhölter. *Liq. Cryst.*, **30**(11), 1357-1364, 2003.

[38] V. A. Mallia and S. Das, *Liq. Cryst.*, **28**(2), 259-264, 2001.

[39] J. -W. Lee, J. -I. Jin, M. F. Achard and F. Hardouin, *Liq. Cryst.*, **30**(10), 1193-1199, 2003.

[40] T. Felekis, D. Tsiourvas, L. Tziveleka and C. M. Paleos, *Liq. Cryst.*, **32**(1), 39-43, 2005.

[41] W. -L. He, L. Wang, Z. Yang, H. Yang and M. -W. Xie, *Liq. Cryst.*, **38**(10), 1217-1225, 2011.

[42] M. Roohnikan, M. Ebrahimi, S. R. Ghaffarian and N. Tamaoki, *Liq. Cryst.*, **40**(3), 314-320, 2013.

[43] F. -B. Meng, C. -S. Cheng, B. -Y. Zhang and X. -Z. He, *Liq. Cryst.*, **32**(2), 191-195, 2005.

[44] D. Apreutesei, G. H. Mehl and D. Scutaru, *Liq. Cryst.*, **34**(7), 819-831, 2007.

[45] C. -C. Wu, *Liq. Cryst.*, **34**(3), 283-288, 2007.

[46] X. Zhan, X. Jing and C. Wu, *Liq. Cryst.*, 36(12), 1349-1354, 2009.

[47] J. Guo, J. Sun, K. Li, H. Cao and H. Yang, *Liq. Cryst.*, **35**(1), 87-97, 2008.

[48] L. Zhang, W. He, X. Yuan, W. Hu, H. Cao, H. Yang and S. Zhu, *Liq. Cryst.*, **37**(10), 1275-1280, 2010.

[49] L. Zhang, K. Li, W. Hu, H. Cao, Z. Cheng, W. He, J. Xiao and H. Yang, *Liq. Cryst.*, **38**(6), 673-677, 2011.

[50] C. Zhang, L. Jin, B. Yin, M. Jamil and Y. -J. Jeon, *Liq. Cryst.*, **35**(1), 39-44, 2008.

[51] T. Donaldson, P. A. Henderson, M. F. Achard and C. T. Imrie, *Liq. Cryst.*, **38**(10), 1331-1339, 2011.

[52] T. Donaldson, P. A. Henderson, M. F. Achard and C. T. Imrie, *J. Mater. Chem.*, **21**(29), 10935-10941, 2011.

[53] T. Donaldson, H. Staesche, Z. B. Lu, P. A. Henderson, M. F. Achard and C. T. Imrie, *Liq. Cryst.*, **37**(8), 1097-1110, 2010.

[54] H. -C. Lee, Z. Lu, P. A. Henderson, M. F. Achard, W. A. K. Mahmood. G. -Y. Yeap and C. T. Imrie, *Liq. Cryst.*, **39**(2), 259-268, 2012.

[55] J. -S. Hu, L. -Q. Yang, X. Zhang and Z. -W. Song, *Liq. Cryst.*, **37**(10), 1259-1268, 2010.

[56] J. -S. Hu, L. -Q. Yang, D. -S. Yao and Z. -W. Song, *Liq. Cryst.*, **37**(11), 1385-1392, 2010.

[57] Z. Cheng, K. Li, F. Wang, X. Wu, X. Chen, J. Xiao, H. Zhang, H. Cao and H. Yang, *Liq. Cryst.*, **38**(7), 803-812, 2011.

[58] Z.Chen, H. Cao, D. Zhao, W. Hu, W. He, X. Yuan, J. Xiao, H. Zhang and H. Yang, *Liq. Cryst.*, **38**(1), 9-15, 2011.

[59] Z. Cheng, K. Li, F. Wang, X. Wu, X. Chen, J. Xiao, H. Zhang, H. Cao and H. Yang, *Liq. Cryst.*, **39**(10), 1284-1290, 2012.

[60] D. D. Sarkar, R. Deb, N. Chakraborty, G. Mohiuddin, R. K. Nath and V. S. Rao Nandiraju, *Liq. Cryst.*, **40**(4), 468-481, 2013.

[61] R. C. Tandel and R. A. Vora, *Phase Transitions*, **81**(5), 421-429, 2008.

[62] J. S. Dave and G. Kurian, *Mol. Cryst. Liq. Cryst.*, **24**(3-4), 347-355, 1973.

[63] R. A. Vora and V. R. Teckchandani, *Mol. Cryst. Liq. Cryst.*, **209**(1), 279-283, 1991.

[64] G. -X. Sun, C. Kakei, E. Kume, T. Hatsui, S. Ujiie and A. Mori, *Liq. Cryst.*, **34**(8), 927-934, 2007.

[65] D. Kritchevsky, *J. Am. Chem. Soc.*, **65**(3), 480, 1943.

[66] G. Kurian and J. S. Dave, *Mol. Cryst. Liq. Cryst.*, **42**(1-3), 1203-1211, 1977.

[67] I. A. Pearl and D. L. Beyer, *J. Org. Chem.*, **16**(2), 216-220, 1951.

[68] R. Robinson and J. Shinoda, *J. Chem. Soc. Tran.*, **127**, 1973-1980, 1925.

[69] V.R. Teckchandani, *Studies on potential mesogenic materials*, Ph.D. Thesis, The M. S. University of Baroda, Vadodara, 1992.

[70] W. Maier and G. Baumgartner, *Z. Naturforsch*, **7**(a), 172, 1952.

[71] B. A. Veytsman, *Liq. Cryst.*, **18**(4), 595-600, 1995.

[72] Z. Sideratou, C. M. Paleos and A. Skoulios, *Mol. Cryst. Liq. Cryst.*, **265**(1), 19-26, 1995.

[73] M. Fukumasa, K. Takeuchi and T. Kato, *Liq. Cryst.*, **24**(2), 325-327, 1998.

[74] G. W. Gray and B. Jones, *J. Chem. Soc.*, 1467-1470, 1954.

[75] G. W. Gray and B. Jones, *J. Chem. Soc.*, 4179-4180, 1953.

[76] Y. Tian, X. Xu, Y. Ahao, X. Tang and T. Li, *Liq. Cryst.*, **22**(1), 87-96, 1997.

[77] J. -W. Lee, J. -I. Jin, M. F. Achard and F. Hardouin, *Liq. Cryst.*, **28**(5), 663-671, 2001.

[78] V. A. Mallia and S. Das, *Liq. Cryst.*, **28**(2), 259-264, 2001.

[79] T. Felekis, D. Tsiourvas, L. Tziveleka and C. M. Paleos, *Liq. Cryst.*, **32**(1), 39-43, 2005.

[80] C. M. Paleos and D. Tsiourvas, *Liq. Cryst.*, **28**(8), 1127-1161, 2001.

[81] P. A. Henderson, O. Niemeyer and C. T. Imrie, *Liq. Cryst.*, **28**(3), 463-472, 2001.

[82] C. T. Imrie, *Liq. Cryst.*, **6**(4), 391-396, 1989.

Chapter 4

LIQUID CRYSTALLINE 4-NITROBIPHENYL DERIVATIVES

LIQUID CRYSTALLINE 4-NITROBIPHENYL DERIVATIVES

4.1. Introduction

Biphenyl is a molecule interesting and fascinating itself, it has been the object, over many years, of many studies, both experimental [1-3] and theoretical [4, 5]. Such interest is mainly due to its relatively simple structure and to the strong conformational dependence of the molecule on the phase of the material.

Liquid crystalline materials have been studied for several decades in electrical, optical and life sciences fields not only for scientific interests but also for their practical applications. Formation of liquid crystalline phases relies on mesogenic groups having either calamitic or disc like shapes. These basic molecular structures can be further modified giving rise to controlled structural features of the mesophases. The calamitic liquid crystals can form two main classes of liquid crystal phases, the *nematic* and *smectic* phases. The mesomorphic properties of these materials can largely be influenced by various substituents. This can influence the melting points, the mesophase types, the dielectric properties, *etc.*

Linearity, rigidity and polarizability are also important factors for a molecule to display liquid crystalline properties [6]. Different aromatic moieties have been used as rigid core in synthesizing liquid crystals. Biphenyl can be seen as rigid core of many mesogenic compounds and liquid crystalline [7] or semi-crystalline aromatic polymers [8]. Biphenyl derivatives are able to undergo functionalization reactions, providing access to a variety of compounds. Mostly 4, 4'-substituted biphenyl derivatives exhibit one or more smectic phases and extraordinarily high clearing temperatures.

Isaacs *et al.* have studied the stability and phase behaviour of a series of alkylated dihydroxy biphenyl derivatives [9]. The results confirmed that the addition of oxygen to the polyether chain reduces the mesophase thermal stability and the possibility of smectic behaviour in a compound. It also seems that the chirality of the 2-methylbutyl group causes disruption in the crystal structure, thus reducing thermal stability and encouraging smectic phase behaviour.

Wilderbeek and co-workers have synthesized biphenyl-based liquid crystalline thiol-ene monomers [10]. The synthesis of these odourless monomers proved to be straightforward, and can easily be adapted to create further homologues. The type of mesophase can be tuned from the low ordered nematic and smectic A phase to highly ordered mesophases, e.g. crystal E phase, by the appropriate choice of bridging group and variation of the spacer lengths. Biphenyl-based thiol-ene monomers form a particularly interesting class of reactive materials that can be bulk polymerized to give main chain polymers with highly defined mechanical and optical or electro-optical properties resulting from the intrinsic high molecular order of the corresponding monomers.

Chen *et al.* [11] have studied the mesogenic properties of cycloalkylmethyl 4-(4’-octyloxybiphenyl-4-carbonyloxy) benzoate. All compounds exhibited SmA, SmC and SmX phases. Compounds with the three- or four-membered rings have the widest SmA phase, those with the five- or six-membered rings has the widest SmC phase. The structure of the cyclo alkyl ring in compounds does not affect the formation of the SmC phase, although both ring size and ring strain of these cyclo alkyl rings vary widely. Terminal groups can be effective for the formation of liquid crystals exhibiting SmC phases.

In order to evaluate structure property relationships in biphenyl mesogenic moiety-substituted acetylene derivatives in a more detailed fashion, Tang *et al.* [12] have described crystal structure and liquid crystalline properties of biphenyl-containing acetylene, [5-[(4’-heptyloxy-4-biphenylyl)carbonyloxy]-1-pentyne. Upon cooling from the isotropic phase, this compound packs in a monoclinic fashion exhibiting a SmA phase in the temperature range 72.4-53.6 °C. Further lowering of the temperature results in the formation of a SmC phase which exhibits a strong tendency towards crystallization.

The discovery of alkyl- and alkoxy-cyanobiphenyls was revolutionary in the field of liquid crystals [13]. These materials were the first known low melting stable nematics. They have become constituents of liquid crystal mixtures used in display technology and their various physical properties have been extensively studied [14, 15]. In order to attach these molecules to other molecules and to prepare dimers, oligomers and polymers, a number of terminally functionalized alkoxy cyanobiphenyls have been synthesized. Many interesting monomeric, oligomeric and polymeric materials have been derived from these functionalized cyanobiphenyls [16]. Sandeep Kumar [17] has first reported terminally thiol-functionalized alkoxy cyanobiphenyls. All the members of the series exhibited only the nematic phase. All the compounds form stable monolayers on a gold surface. In order to study the effect of sulphur atoms in the linking unit on mesomorphism and self-assembled monolayers, author have also first reported disulphide-bridged mesogenic alkoxy cyanobiphenyl dimers [18]. The formation of self-assembled monolayers by thiols, disulphides and thioethers on metals, particularly on gold, is well documented. Self-assembled monolayers provide a convenient, flexible and simple system for studies in nanoscience and nanotechnology. The dimers with shorter spacer exhibit only the nematic phase while dimers with a longer spacer display nematic as well as smectic phases.

Sauer *et al.* [19] have synthesized novel calamitic guanidinium salts with *p*-alkoxybiphenyl core unit utilizing the corresponding nitro compounds as synthetic intermediates. Compounds displayed broad SmA mesophases. Guanidinium salts with larger aromatic biphenyl cores exhibit broader and more stable mesophases than those with smaller phenyl cores. Furthermore, increasing the chain lengths of the aliphatic tails of the molecules leads to an increase of mesophase range and clearing points. Halides displaying much broader mesophases and lower melting points as compared with the corresponding tetrafluoroborates, hexafluorophosphates and thiocyanates, respectively, making guanidinium halides attractive for applications.

Dabrowski [20] have described the mesomorphic properties of 4-alkylcyclohexyl- and 4-alkylcyclohexylethyl and 4-alkylbicyclohexyl-3-fluoro- and 3,5-difluorobiphenyl-4-isothiocyanates. All compounds are low melting and show broad range nematic liquid crystals. Compounds are very useful for the formation of nematic mixtures of low viscosity and with a moderately high birefringence (0.3-0.35). The four ring compounds shows a strong dependence of the parallel electric permittivity constant on frequency, which makes them especially interesting for the formation of low viscosity dual frequency addressed mixtures.

Nandiraju and co-workers have synthesized stable achiral asymmetrical four ring banana-shaped molecules [21]. These molecules consist of a laterally fluoro-substituted 3,4’-disubstituted biphenyl unit with an ester linkage between the phenyl rings as the central unit in 4-(*N*-4’-*n*-alkyloxysalicylidene)aminophenyl [2-fluoro-5-(*N*-4’-*n*-alkyloxy-salicylidene) amino-benzoate]. These compounds are thermally and hydrolytically stable due to inter- or intramolecular hydrogen bonding and exhibit columnar phases. The materials possess interesting intrinsic light generating capacity in the region 450–580 nm with retention of banana polymorphism, which could be of value in practical applications.

Jiang and co-workers [22] have prepared but-3-enyl-based fluorinated biphenyl liquid crystals and studied the effect of the but-3-enyl terminal group and the lateral fluoro substituent on the mesomorphic properties. These compounds are composed of alkyl chain, trans-cyclohexane and biphenyl mesogenic core, ethylene linking group, lateral fluoro substitute, and but-3-enyl terminal groups. All these compounds exhibited a nematic mesophase of broad range with low melting points and high clearing points. The but-3-enyl terminal group and the lateral fluoro substituent were helpful to enhance the stability of the mesophase. These but-3-enyl-based biphenyl liquid crystals have potential for use in liquid crystal display mixtures. Author has also synthesized allyloxy-based biphenyl liquid crystals with multiple fluoro substituents [23]. The allyloxy terminal groups and the lateral fluoro substituents enhanced the stability of the mesophase and the negative dielectric anisotropy. These allyloxy-based biphenyl liquid crystals also have potential uses as LCD mixtures.

Piecek *et al.* have investigated liquid crystalline properties of a family of 4’-(ω-perfluoroalkanoyloxy)alkoxybiphenyl-4-yl(*S*)-4(1-methylheptyloxy)benzoates smectic liquid crystals [24]. The replacement of the alkyl terminal chain by the partially fluorinated one led to the increasing of the stability of the tilt SmC* phase. It was also observed that the presence of such a fluorinated unit promotes the high tilt of molecules in their smectic layers. The prepared compounds may be used as dopants of achiral smectic mixtures to change their electro-optical performance, as well as for the formulation low-tilt ferroelectric or antiferroelectric mixtures.

Kula and co-workers have synthesized 4-butyl-4’-[(4-butyl-2,6-difluorophenyl)ethynyl]biphenyl and its higher fluorinated analogues [25]. They have achieved many new liquid crystalline structures by modification of copper-catalyzed cross-coupling of aryl Grignard reagents with butyl bromides which are difficult to obtain by employing the conventional methods of synthesis. Basic properties of temperatures and enthalpies prove that these compounds are very promising as medium birefringent, low viscous components of novel liquid crystal applicable mixtures.

Recently, Zhang *et al.* [26] have reported series of 2-(4’-alkoxybiphenyl-4-yl)-1*H*-benzimidazole derivatives and discussed the effect of the length of alkoxy chain on mesomorphic properties. These compounds possessed 5-nitrobenzimidazole, benzimidazole or 5-methylbenzimidazole units at the end of the molecule. All compounds exhibited enantiotropic smectic mesophases with wide temperature domains for a carbon number in the alkoxy chain from 6 to 16. The substituent in the benzimidazole moiety was helpful in increasing the mesophase stability. Polar nitro substituent or flexible substituent in the benzimidazole moiety was helpful in enhancing the dipole-dipole interaction between the molecules, leading to the formation of more stable smectic mesophase. The formation of smectic phase was attributed to the lateral intermolecular hydrogen bonds resulting from benzimidazole groups of the compounds.

In 2006, Mori and co-workers [27] have investigated different types of 4,4’-bis(benzoyloxy)biphenyls and studied the effect of the lateral nitro group on appearance of mesophases as well as improvement of the mesomorphic property. The polar nitro group behaves differently depending on the types of molecules. In the case of 4,4’-bis-(4-alkoxybenzoyloxy)biphenyls and 4,4’-bis(3,4- and 2,4-dialkoxybenzoyloxy)biphenyls, their transition temperatures were reduced by the introduction of the nitro group because of the increase of the molecular breadth to reduce the molecular length-to-breadth ratio. The nitro group in 4,4’-bis(3,4,5-trialkoxybenzoyloxy)biphenyls enhanced the transition temperatures and mesomorphic properties since the trialkoxy derivatives without a nitro group were not mesomorphic and those with a nitro group had a hexagonal columnar phase. The introduction of the nitro group did not increase the molecular breadth of the trialkoxy derivatives because they already have the wide molecular breadth.

Geribaldi *et al.* [28] have synthesized series of smectic liquid crystalline 4,4’-biphenyl derivatives incorporating a perfluorinated segment and an allylic part. The synthesis has been performed from 2-Fluorobutylethyl iodide, 2-Fluorohexylethyl iodide or 2-Fluorooctylpropanoic acid. All the members of the series exhibit liquid crystalline phase of type smectic A and E. The molecular conception of these monomers from homologous compounds allowed to reach dimorphism and wide range smectic mesomorphism. This kind of structure is of a great interest for precursor of side chain liquid crystalline polymers.

Hentrich [29] have synthesized novel bolaamphiphilic triol and tetraol compounds by incorporating rigid structural units. He has pointed out that the liquid-crystalline phases of the bolaamphiphilic tetraols are significantly stabilized by the introduction of a rigid biphenylene unit. It can be also concluded that for bolaamphiphiles, a rigid unit consisting of at least two aromatic rings is necessary for the occurrence of mesophases.

Nishiyama *et al.* [30] have investigated homogeneous series of chiral trimeric compounds possessing three biphenyl mesogenic cores connected by flexible alkyl spacers. The micro-segregation between weakly distinct moieties, i.e., the aromatic rigid cores and the aliphatic flexible spacers, which was promoted by the trimeric molecular architecture, was proposed to produce the higher smectic order and thus to stabilized the anticlinic structure.

Biphenyl derivatives are also important in the formation of ferroelectric and anti-ferroelectric liquid crystals. Shashidhar and co-workers [31] have synthesized novel ferroelectric liquid crystals and copolymers containing biphenyl azobenzene and / or phenyl biphenyl carboxylate mesogenic groups. The copolymer show a SmC* phase over a large temperature range down to room temperature.

Chen *et al.* [32] have reported ferroelectric liquid crystals containing a phenyl biphenyl carboxylate mesogenic core, oligomethylene spacer and two different chiral moieties, (S)-2-methyl-butoxycarbonyl and (S)-1-methylheptoxycarbonyl. All the compounds display liquid crystalline phases. The spacer chain of methylene units favours a lowering of transition temperatures and an increasing temperature range of SmC* phase. The phase behaviours of the LC with (S)-1-methyl-heptoxycarbonyl are more complex than those with (S)-2-methylbutoxycarbonyl, due to the flexible tail in the former.

Shivkumar [33] have described the synthesis of the alkoxybiphenyl resorcylate and vanillate derivatives with a chiral moiety obtained from chloro analogues of L-leucine, L-valine and L-isoleucine. In all the synthesized compounds, the SmA phase is preceded by an enantiotropic SmC* phase over a wide temperature range, and in case of compounds with lateral methoxy group this ferroelectric phase is the predominant phase.

Pisipati [34] have designed novel wing shaped achiral antiferroelectric liquid crystalline compounds having wing units. The preliminary investigations on the ferroelectric properties of the present material show the presence of an antiferroelectric phase. The origin of antiferroelectric ordering in the molecule can be substantiated by the presence of conjugation, which is maintained throughout the molecule. The existence of this condition has a pronounced influence on the appearance of antiferroelectric ordering through the dipolar interactions (ester moieties) between the adjacent layers which intern enhances the inherent stabilization of the antiferroelectric phase. The resultant pairing of the transverse dipoles in the neighbouring layers is supposed to be the origin of antiferroelectric ordering.

Biphenyl moieties can also be incorporated into bent-core mesogens to exploit the effect on mesomorphism. But, from the view point of chemical structure, bent-core mesogens consisting of a biphenyl moiety have been less studied in the literature. Veena Prasad [35] have reported new bent-core mesogens containing biphenyl moieties. All compounds except the first homologue, exhibited B_7 to B_4 banana phases. It was observed that in bent-shaped compounds, when the phenyl rings on both ends of the molecule [36] is replaced with biphenyl rings, completely different mesomorphic properties were observed. In the case of compounds with phenyl ring, those with $n \geq 10$, exhibit only one type of mesophase B_2. However, in the compounds with biphenyl ring with $n = 10$ shows only one mesophase X_1 with textural features reminiscent of B_1, whereas those with $n \geq 12$ exhibit two types of banana phase B_4 and B_7. The compounds with $n =12$, 16 and 18 exhibit the phase sequence Cr-B_4-B_7-I which is very rare. The significance of this phase sequence lies in the fact that both phases B_4 and B_7 have helical structure.

Sadashiva [37] have also synthesized banana-shaped mesogens containing a biphenyl moiety and studied the effect of lateral substituents on seven-ring esters. Banana phases such as B_1, B_2 and B_6 were observed in the series of compounds. The lateral substituents have a strong influence in reducing the clearing temperatures. The larger ethyl substituent has a great effect in depressing the clearing temperature and suppressing the occurrence of a layered mesophase such as B_2, while enhancing the existence of the B_6 phase. It was also found that the ortho-fluoro substituted compounds gave rise to wide thermal ranges of the B_1 and B_2 mesophases, as compared with the meta-substituted analogues.

Clark *et al.* [38] have presented a series of mesogens composed of achiral bent molecules with thermally stable ester linkages and laterally substituted by a methoxy group symmetrically near the central benzene ring. In most of studied compounds, the antiferroelectric B_2 phase was found on cooling from the isotropic phase, followed by the B_7 phase at lower temperatures. The in-plane modulations observed in free-standing films in this phase are characteristic feature of the B_7 phase.

Novotná and co-workers [39] have synthesized and studied the mesomorphic properties of new non-symmetrical bent-shaped compounds containing a chiral moiety. These materials were built up from 3-hydroxybenzoic acid as a central unit with a chiral terminal group derived from lactic acid. The studied compounds exhibit one mesophase in a broad temperature range down to room temperature. Optical switching of the columnar phase has been observed for the studied compounds. All compounds prefer formation of the columnar phase with ferroelectric-like switching. A double bond in a terminal chain of the bent-shaped molecule is promising for the preparation of a new type of side-chain liquid crystalline polymer with polar properties.

Recently, Gude *et al.* [40] have designed new family of four-ring achiral bent-core compounds derived from 2-methyl 3-amino benzoic acid with the methyl group in the bent direction incorporated into the central core. These compounds possess an alkoxy chain attached at only one end of the bent core molecule, while the other arm consists of a biphenyl moiety possessing a highly polar cyano-group. All the compounds exhibited a wide-range enantiotropic nematic phases.

In this chapter, we have synthesized the mesogenic compounds containing 4-nitrobiphenyl moiety. To the best of our knowledge, liquid crystalline compounds having biphenyl moiety with nitro substituent are very rare. The present investigation was carried out with a view to study the effect of cinnamoyl linkage and nitrobiphenyl moiety on the mesomorphic properties of such molecules. The scientific interest in the synthesis and the better understanding of the structure-property correlations of biphenyl-based liquid crystals has prompted us to design and synthesize the series of 4’-Nitrobiphenyl trans-4-*n*-alkoxy-3-methoxy cinnamates. All the compounds exhibited stable enantiotropic mesophases during heating and cooling processes. The effect of length of alkoxy chain on mesomorphic properties was discussed. The structure-property relationships of biphenyl-based liquid crystals were investigated.

4.2. Experimental

4.2.1. Instrumentation

The synthetic route adopted for the series of mesogens is given in the Figure 1. All synthesized compounds were purified by column chromatography on silica gel (60-120 mesh). The purity of the samples was checked by thin-layer chromatography. The chemical structures of the compounds were determined by standard spectroscopic methods. IR spectra were determined for KBr pellets, using a Perkin Elmer-RX1 spectrophotometer. ^{1}H NMR spectra was recorded on a Bruker 400 MHz spectrometer using tetramethylsilane (TMS) as internal reference standard. Liquid crystalline properties were investigated using Leica DM 2500P polarizing optical microscope provided with a Linkam heating stage. The transition temperatures were confirmed by Differential Scanning Calorimeter on Mettler Toledo – DSC 822 system which was calibrated using indium as a standard.

4.2.2. Synthesis and Characterization

4.2.2.1. Trans-4-*n*-alkoxy-3-methoxycinnamic acids (1)

A mixture of 0.025 mol 4-hydroxy-3-methoxycinnamic acid [41, 42], 0.03 mol alkyl iodide or bromide, 0.062 mol potassium hydroxide and 50 ml ethanol was refluxed for 4-5 hr. After being cooled, the mixture was poured into a stirred mixture of concentrated hydrochloric acid and ice cold water. The product was then filtered off, washed with water, dried and recrystallized from ethanol until constant melting points were obtained. Purity of the compounds are checked by TLC and characterized by spectral data. The melting points are summarized in Table 1.

***n*-Butoxy derivative:** IR (KBr): 2594-2956 cm^{-1} -O-H stretch broad band superimposed upon C-H stretch, 2880, 2827 cm^{-1} –C-H stretch, 1683 cm^{-1} >C=O stretch, 1260 cm^{-1} C-O stretch, 979 cm^{-1} strong =C-H bending (Figure 2).

^{1}H NMR ($CDCl_3$, δ, ppm): 0.98-1.02 (t, 3H, CH_3), 1.49-1.55 (m, 2H, CH_2), 1.83-1.88 (m, 2H, CH_2), 3.92 (s, 3H, OCH_3), 4.06-4.10 (t, 2H, OCH_2), 6.31-6.35 (d, 1H, =CH-), 6.88-6.90 (d, 1H, Ar-CH), 7.09-7.10 (d, 1H, Ar-CH), 7.12-7.14 (dd, 1H, Ar-CH), 7.73-7.77 (d, 1H, -CH=) (Figure 3).

Mass spectra are given in Figure 4.

4.2.2.2. Trans-4-*n*-alkoxy-3-methoxycinnamoyl chlorides (2)

The acids were converted into their acid chlorides by treating them with thionyl chloride on water bath till evolution of hydrochloric acid ceased. The excess of thionyl chloride was distilled off. The crude product was used immediately in the next reaction without further purification.

4.2.2.3. 4-Benzoyloxy biphenyl (3) [43]

4-Hydroxy biphenyl (0.1 mol) was dissolved in 50 ml of dry pyridine and was added slowly with stirring to cold benzoyl chloride (0.1 mol) contained in a round bottom flask. The mixture was heated on a water-bath for 30 minutes and was allowed to cool upto room temperature. It was acidified with cold 1:1 hydrochloric acid and precipitates obtained were filtered, washed with water and dried. The ester was crystallized from ethanol to yield 87% product. Melting Point: 150 °C.

4.2.2.4. 4-Benzoyloxy-4'-nitrobiphenyl (4) [43]

4-Benzoyloxy biphenyl (0.145 mol) was taken in round bottom flask, 310 ml of glacial acetic acid was added in the flask and it was heated upto 80-90 °C. 100 ml fuming nitric acid was added slowly in such a way that the temperature remained between 80-90 °C. After complete addition, the reaction mixture was cooled to room temperature. The solid separated was filtered and washed with water and methanol. The product was crystallized from glacial acetic acid to yield 51% of product. Melting Point: 210 °C.

4.2.2.5. 4-Hydroxy-4'-nitrobiphenyl (5) [43]

4-Benzoyloxy-4'-nitrobiphenyl (0.18 mol) was taken in round bottom flask, 300 ml of ethanol was added to it and it was heated to reflux. An aqueous solution of potassium hydroxide (40 gms of KOH in 100 ml of water) was then added dropwise at reflux. After complete addition, the mixture was further refluxed for 30 minutes and cooled overnight. Next day, blue crystals of potassium salt were filtered, washed with tetrahydrofuran until washing was colourless. Pure 4-hydroxy-4'nitrobiphenyl was obtained by dissolving the salt in minimum amount of boiling water and adding

1:1 hydrochloric acid until acidic pH was obtained. The yellow solid was filtered, washed with water, dried and crystallized from ethanol. Melting Point: 203 °C.

4.2.2.6. 4’-Nitrobiphenyl trans-4-*n*-alkoxy-3-methoxy cinnamates (Series: I)

The respective 4-*n*-alkoxy-3-methoxycinnamoyl chloride (0.01 mol) was dissolved in about 5 ml of dry pyridine. The solution of compound **5** (0.01 mol) in 10 ml of dry pyridine was added slowly to a cold solution of the above acid chloride. The mixture was heated on a water bath for about half an hour and was allowed to stand overnight. It was acidified with cold 1:1 hydrochloric acid. Precipitates were filtered and washed with water followed by diluted sodium hydroxide solution and water. The residue was purified by column chromatography on silica gel with mixture of ethyl acetate and petroleum ether (10:90) as an eluent.

***n*-Butoxy derivative:** IR (KBr): 2958, 2872 cm^{-1} –C-H stretch, 1697 cm^{-1} >C=O stretch, 1602 cm^{-1} olefinic –C=C-stretch, 1295 cm^{-1} C-O stretch, 1504 cm^{-1} NO_2 asymmetric stretch, 1348 cm^{-1} NO_2 symmetric stretch, 1209 cm^{-1} C-N stretch, 1654, 1414, 1395 cm^{-1} ring breathing vibrations of C-H bending (Figure 5).

^1H NMR ($CDCl_3$, δ, ppm): 1.01-1.03 (t, 3H, CH_3), 1.52-1.58 (m, 2H, CH_2), 1.90-1.98 (m, 2H, CH_2), 4.02 (s, 3H, OCH_3), 4.13-4.17 (t, 2H, OCH_2), 6.33-6.37 (d, 1H, =CH-), 6.69-6.91 (d, 1H, Ar-CH), 7.25-7.27 (dd, 1H, Ar-CH), 7.34-7.36 (d, 1H, Ar-CH), 7.42-7.44 (d, 2H, Ar-CH), 7.57-7.61 (d, 1H, -CH=), 7.70-7.72 (d, 2H, Ar-CH), 7.76-7.78 (d, 2H, Ar-CH), 8.33-8.35 (d, 2H, Ar-CH) (Figure 6).

***n*-Heptyloxy derivative:** IR and ^1H NMR spectra are given in Figure 7 and 8, respectively.

4.2.3. Determination of transition temperatures with the help of a polarizing optical microscope

To determine the transition temperatures the Leica DM 2500P polarizing optical microscope equipped with a Linkam heating stage was used.

To determine the various transitions, a glass slide with a thin coating of material, covered with a glass cover slip, was observed under microscope. The slide was kept on the hot stage and the temperature was raised rapidly to find the approximate transition temperatures. The observations were repeated and the rate of heating was regulated to slowly near the transition, to determine the transition temperatures more precisely.

The heating device was standardized and its accuracy was checked by determining the transition temperatures of the known compounds, such as 4-*n*-alkoxy benzoic acids.

The members of the homologous series **I** exhibit enantiotropic mesomorphic states. The methyl to *n*-pentyl derivatives exhibit both Smectic and Nematic phases; the higher members, starting with the *n*-hexyl derivative, show only Smectic phase. The smectic phase shows smectic A type phase which was characterized by the formation of a typical focal conic texture. SmA phase also can be further confirmed by mixing with known SmA compound. The nematic phase showed a characteristic thread-like texture or schlieren texture under microscope.

4.2.4. Differential Scanning Calorimetry studies

The transition temperatures and enthalpies were investigated by Differential Scanning Calorimetry (DSC) using a Perkin Elmer Thermal Analyser with a heating and cooling rate of 5 °C min^{-1}. The instrument was calibrated using indium as a standard. The phase transition temperatures observed through polarizing optical microscope were found to be in reasonable agreement with the corresponding DSC thermograms. The thermograms and related discussions are given in the Results and Discussion section for the series **I** compounds.

4.3. Results and Discussion

Number of homologous series [44, 13] with biphenyl moiety is reported in literature. Most of these series have terminal cyano group in the moiety. Low melting mesogenic cyano biphenyl compounds gave impetus for applications [6]. Gray [44] mentioned that terminal nitro group normally imparts yellow colour hence they did not pursue it further. However, terminal nitro group has provided some interesting new mesogens. The effect of terminal nitro group on the commencement of smectic mesophase is quite interesting. It was thought quite interesting to synthesize and study the mesogenic properties of biphenyl derivatives having terminal nitro group.

Thirteen homologues were synthesized by condensing appropriate 4-*n*-alkoxy-3-methoxy cinnamoyl chlorides with 4-hydroxy-4'-nitrobiphenyl. All the homologues have enantiotropic mesophases. The methyl to *n*-pentyl derivatives exhibit both SmA and N phases; the higher members, starting with the *n*-hexyl derivative show only SmA phase. Series I was synthesized by the route shown in Figure 1. All the members of the series 4-*n*-alkoxy-3-methoxy cinnamic acids are non-mesogenic in nature. This behaviour is attributed to the presence of bulky lateral methoxy group. Lateral methoxy group hinders the packing of the molecules required for the mesomorphism. The transition temperatures of series **I** are summarized in Table 2. The mesophases exhibited by this series were identified according to their optical textures. These textures were observed by polarizing optical microscopy. The smectic phase shows smectic A type phase which was characterized by the formation of a typical focal conic texture. The nematic phase showed a characteristic thread-like texture or schlieren texture under microscope. Phase transition temperatures observed through thermal microscopy were found to be in reasonable agreement with the corresponding DSC thermograms. Optical textures are shown in Figures 15-18 (section 4.3.1).

Gray [45] and Major and Baumgartner [46] have suggested that the addition of each methylene unit simultaneously increase the overall polarizability of the molecules and the lateral intermolecular attraction. The lower homologues are SmA and N, the separation of aromatic nuclei is at minimum and the terminal cohesions are strongest. As we ascend the series, only SmA phase commences because as the alkyl chain length increases, the lateral cohesive forces are also increase and the molecules align themselves in the layer structure. Hence with increase in the alkyl chain length, the Smectogenic character should predominate at the expense of nematic mesophase.

Therefore in series **I,** at certain chain length of alkyl group, nematic mesophase would be observed and system would exhibit pure SmA phase. At this stage, SmA mesophase will directly pass into isotropic liquid stage presumably because the terminal intermolecular attractions are inadequate to maintain the parallel molecular orientation which is required for the normal nematogenic homologous series.

The plot of transition temperatures versus number of carbon atoms in the alkoxy chain is given in Figure 9. The SmA-Nematic and Nematic-Isotropic transition temperature curves exhibit zig-zag pattern in a lower derivatives (upto C_5) of series. The Nematic-Isotropic transition temperature curve raises steeply upto C_{10} derivative and then falls down upto the last member of the series.

There is a close relationship between liquid crystalline properties and molecular constitution of organic compounds, hence the thermal stability; a measure of liquid crystalline properties can be correlated with the molecular constitution of the compounds. The average thermal stabilities of different mesogenic homologous series are compared and recorded in Table 3.

Table 3. Average thermal stabilities (°C) of series I, A and B compounds.

Series	I	A	B
N / SmA - Iso (C_1-C_{18})	216.3	180.9	243.0
SmA - N	196.8 ($C_1 – C_5$)	148.1 ($C_7 – C_{14}$)	195.6 ($C_4 – C_8$)
Commencement of SmA mesophase	C_1	C_7	C_4

Comparison of molecular structure of present series **I,** 4’-Nitrobiphenyl trans-4-*n*-alkoxy-3-methoxy cinnamates, with reported Series:

(1) Biphenyl-4-Trans-p-*n*-Alkoxycinnamates; **Series: A** [47]

(2) 4(4”-*n*-Alkoxy benzoyloxy)-4’-nitrobiphenyls; **Series: B** [48]

The geometry of these series is given in Figure 10. The average isotropic thermal stabilities of series **I** is higher than those of series **A.** Series **I** and series **A** have the same molecular geometry except the terminal and lateral substituents. Series **I** have lateral methoxy and terminal nitro substituent. Introduction of lateral methoxy is expected to be deterrent to the thermal stability of the system but presence of polar nitro group increases significant intermolecular force of attraction which stabilizes the molecular orientation. It also increases the length and polarizability of the molecules. It shows increase in the thermal stability of the system [45]. Hence nematic and isotropic thermal stabilities of the series **I** is higher compare to series **A.** The difference between the isotropic thermal stabilities of series **I** and **A** is of the order of 35 °C. This shows potential effect of a terminal nitro group on the mesomorphic property of homologous series.

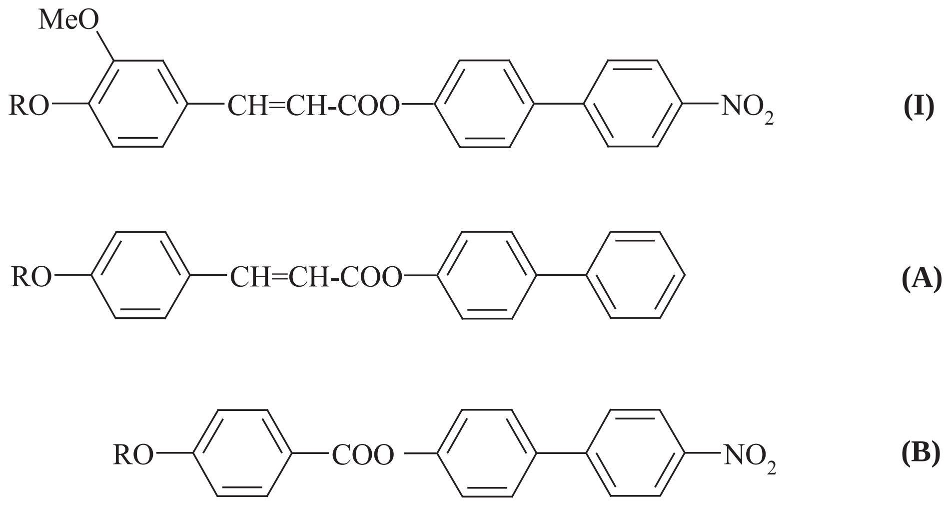


Figure 10. Comparative geometry of series I, A and B compounds.

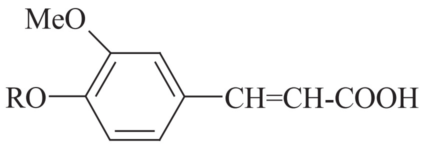
The Nematic thermal stabilities of series **I** and series **B** are almost same. They differ only in central linkage and lateral substituent at one end of the molecule. Methoxy group joined to phenyl ring at ortho position would have steric effect compared to the molecules of series **B.** However, the ortho methoxy group would not have fullest breadth increasing effect. Series **B** has a biphenyl nucleus and an ester linkage which could contribute appreciably to the polarizability of the molecule in the direction of molecular axis, thereby enhancing thermal cohesions. This would give higher nematic-isotropic transition temperatures than series **I.**

The mesogens were screened by DSC method and calorimetric data are recorded in Table 4. Figures 11 to 14 show DSC thermograms for *n*-butoxy to *n*-heptyloxy derivatives, respectively. *n*-Hexyloxy derivative was scanned at the heating rate of 3 °C min^{-1}, rest all derivatives were scanned at the heating rate of 5 °C min^{-1}. In the present study, SmA and nematic mesophases are inferred from the textures observed under Leica DM 2500P polarizing optical microscope provided with a Linkam heating stage.

Table 4. Differential Scanning Calorimetry (DSC) data.

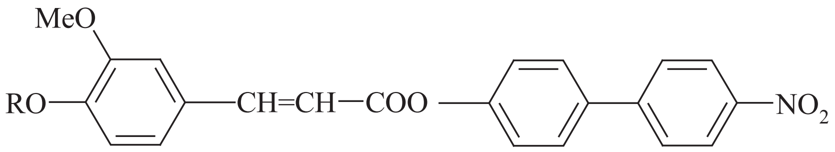
Sr. No.	R-*n*-alkyl group	Transition	Peak temperatures (microscopic reading) (°C)	ΔH kJ/mole
1	Butyl	Cr-SmA	185.2 (185.0)	10.45
		SmA-N	211.5 (211.0)	5.12
		N-Iso	222.7 (222.3)	1.83
2	Pentyl	Cr-SmA	164.5 (163.9)	10.68
		SmA-N	197.1 (196.5)	4.71
		N-Iso	210.0 (210.0)	1.84
3	Hexyl	Cr-SmA	174.8 (174.1)	19.27
		SmA-Iso	212.5 (213.2)	9.07
4	Heptyl	Cr-SmA	185.7 (185.0)	18.58
		SmA-Iso	227.7 (227.0)	7.22

Table 1. Melting points (°C) of trans-4’-*n*-alkoxy-3’-methoxycinnamic acid. (**5**)

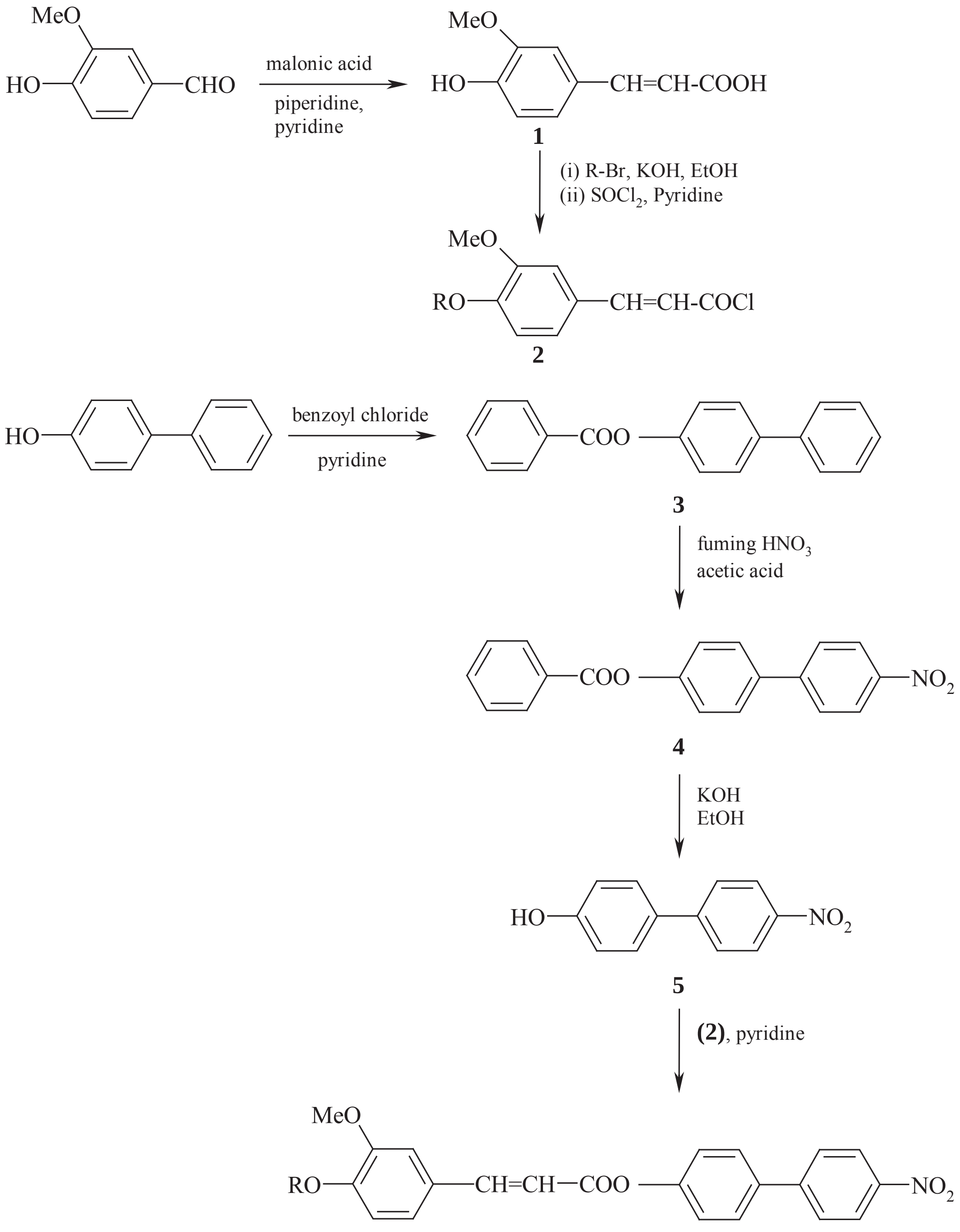


Sr. No.	R = *n*-alkyl group	Melting points (°C)
1	Methyl	181.0
2	Ethyl	178.0
3	Propyl	163.0
4	Butyl	149.0
5	Pentyl	132.0
6	Hexyl	125.0
7	Heptyl	120.0
8	Octyl	105.0
9	Decyl	103.0
10	Dodecyl	104.0
11	Tetradecyl	105.0
12	Hexadecyl	107.0
13	Octadecyl	107.0

Table 2. Transition temperatures of 4'-Nitrobiphenyl trans-4-*n*-alkoxy-3-methoxy cinnamates **(Series I).**



Sr. No.	R = *n*-alkyl group	Transition temperatures (°C)						
		Cr		SmA		N		I
1	Methyl	•	169.0	•	187.0	•	199.0	•
2	Ethyl	•	171.0	•	194.5	•	210.0	•
3	Propyl	•	174.0	•	195.0	•	205.0	•
4	Butyl	•	185.0	•	211.0	•	222.3	•
5	Pentyl	•	163.9	•	196.5	•	210.0	•
6	Hexyl	•	174.1	•	-	-	213.2	•
7	Heptyl	•	185.0	•	-	-	227.0	•
8	Octyl	•	182.2	•	-	-	229.5	•
9	Decyl	•	181.1	•	-	-	231.0	•
10	Dodecyl	•	181.0	•	-	-	229.3	•
11	Tetradecyl	•	175.9	•	-	-	221.8	•
12	Hexadecyl	•	177.4	•	-	-	216.0	•
13	Octadecyl	•	171.0	•	-	-	198.2	•



Series I

R = *n*-C$_n$H$_{2n+1}$, n = 1 to 8, 10, 12, 14, 16 and 18.

Figure 1. Synthetic route to series I.

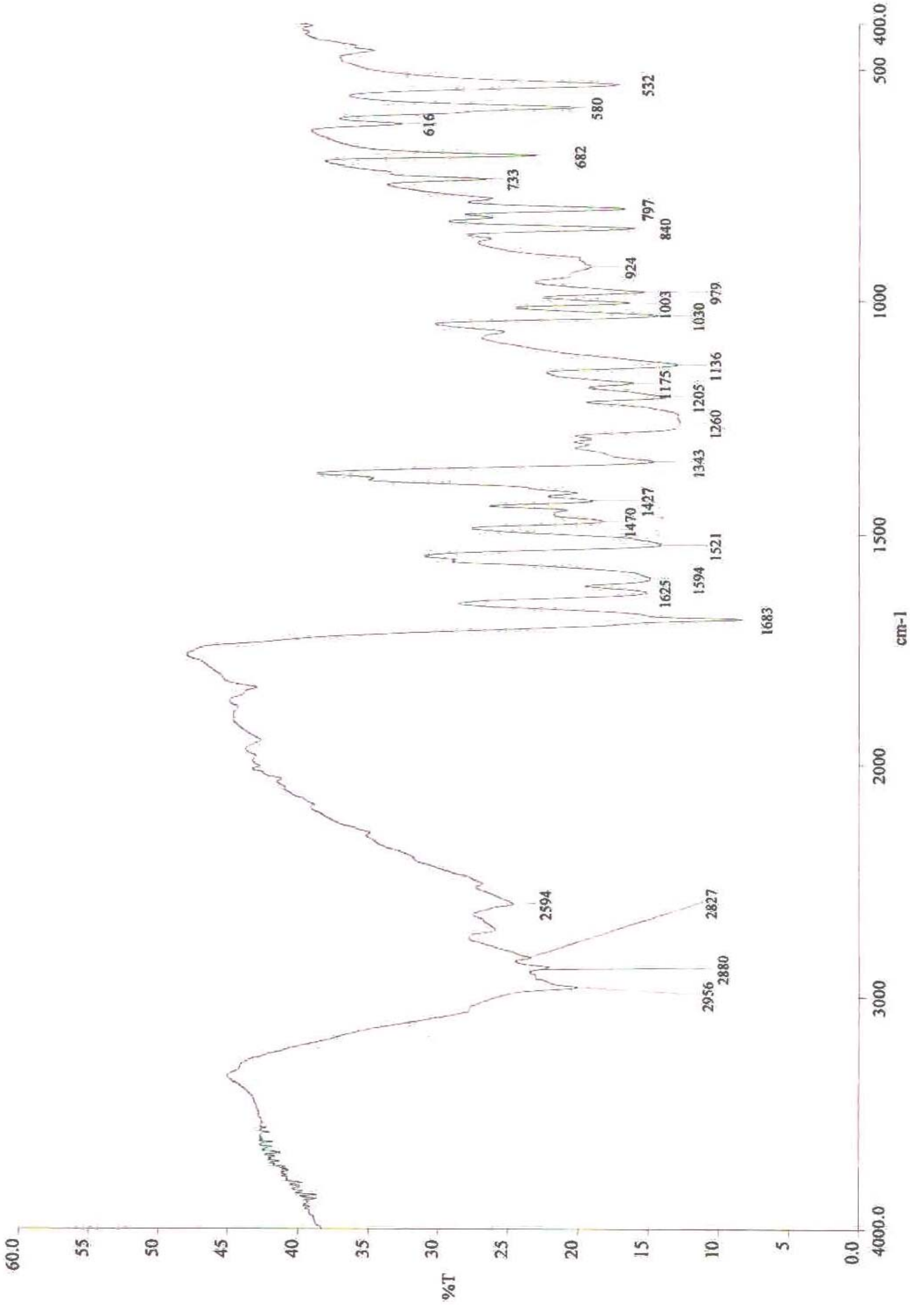
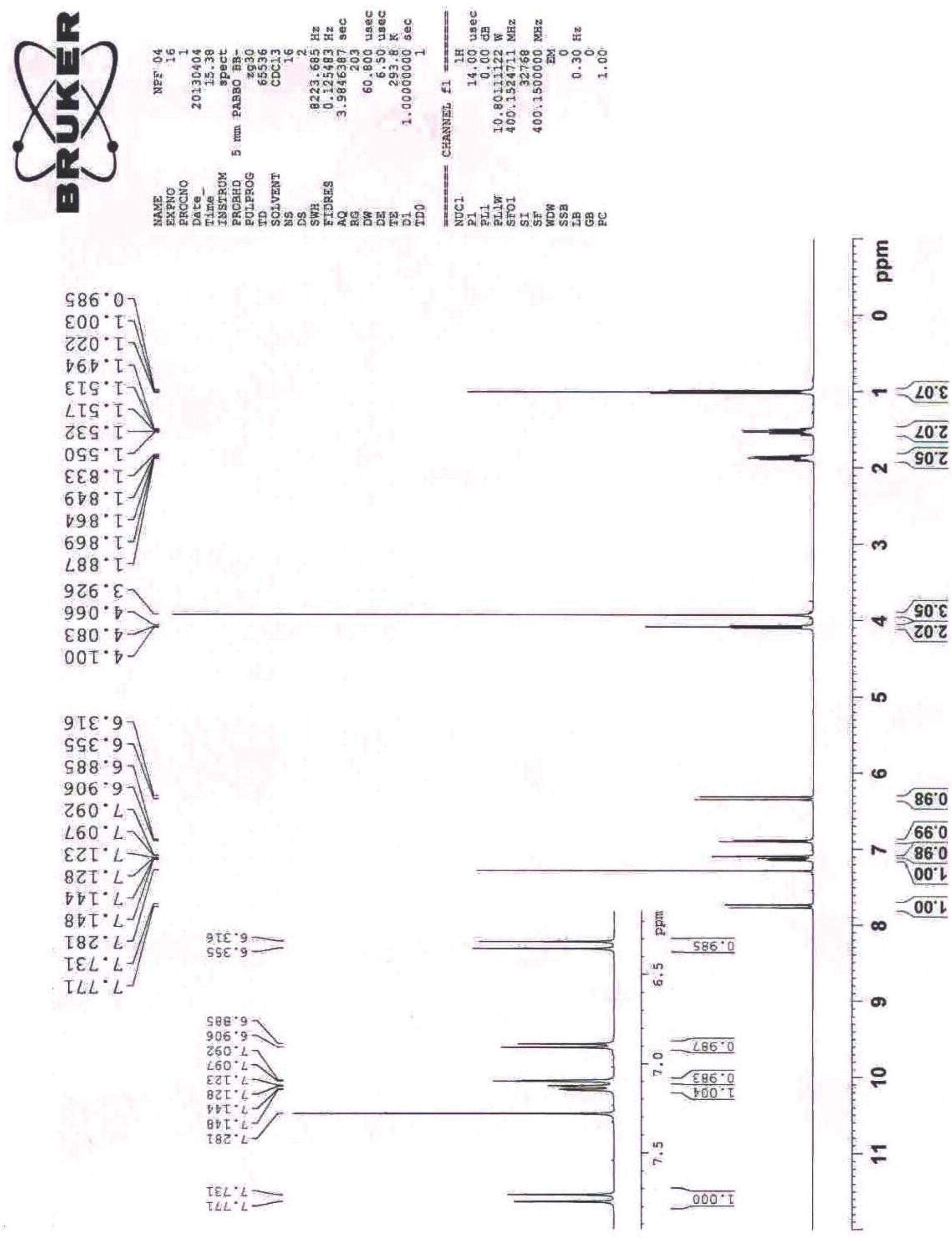


Figure 2. Representative IR spectra of 4-*n*-butoxy-3-methoxy cinnamic acid.



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PROCNO              1
Date_        20130404
Time            15.38
INSTRUM          spect
PROBHD   5 mm PABBO BB-
PULPROG          zg30
TD              65536
SOLVENT         CDCl3
NS                 16
DS                  2
SWH          8223.685 Hz
FIDRES       0.125483 Hz
AQ          3.9846387 sec
RG                203
DW             60.800 usec
DE               6.50 usec
TE              293.8 K
D1         1.00000000 sec
TD0                 1

======== CHANNEL f1 ========
NUC1               1H
P1              14.00 usec
PL1              0.00 dB
PL1W      10.80111122 W
SFO1      400.1524711 MHz
SI              32768
SF        400.1500000 MHz
WDW                EM
SSB                 0
LB               0.30 Hz
GB                  0
PC               1.00
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Figure 3. ^{1}H NMR spectra of 4-*n*-butoxy-3-methoxy cinnamic acid.

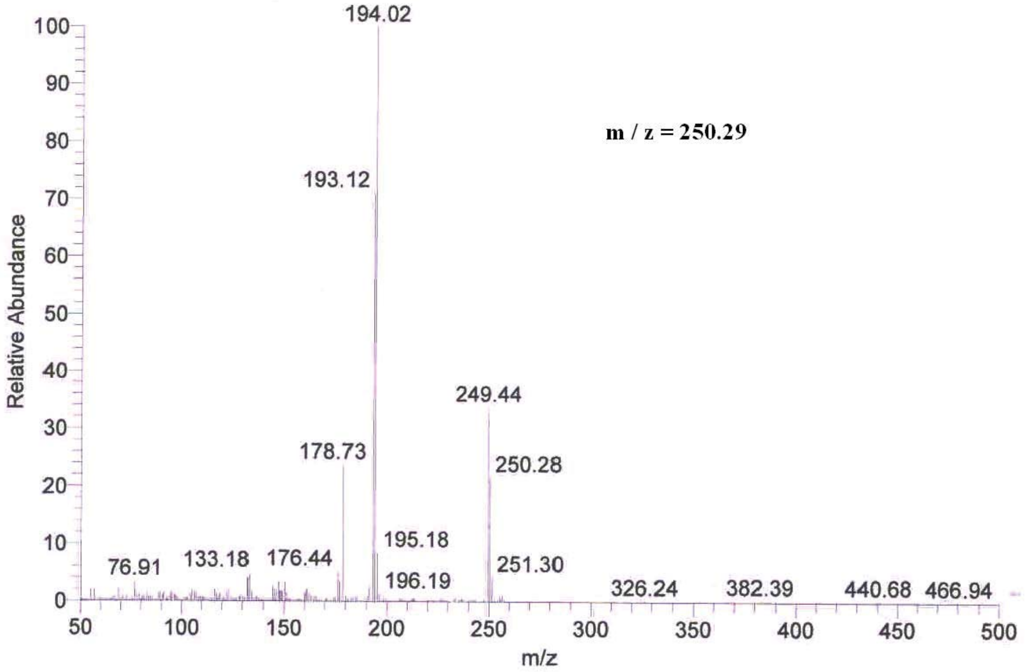


Figure 4. Mass spectra of 4-*n*-butoxy-3-methoxy cinnamic acid.

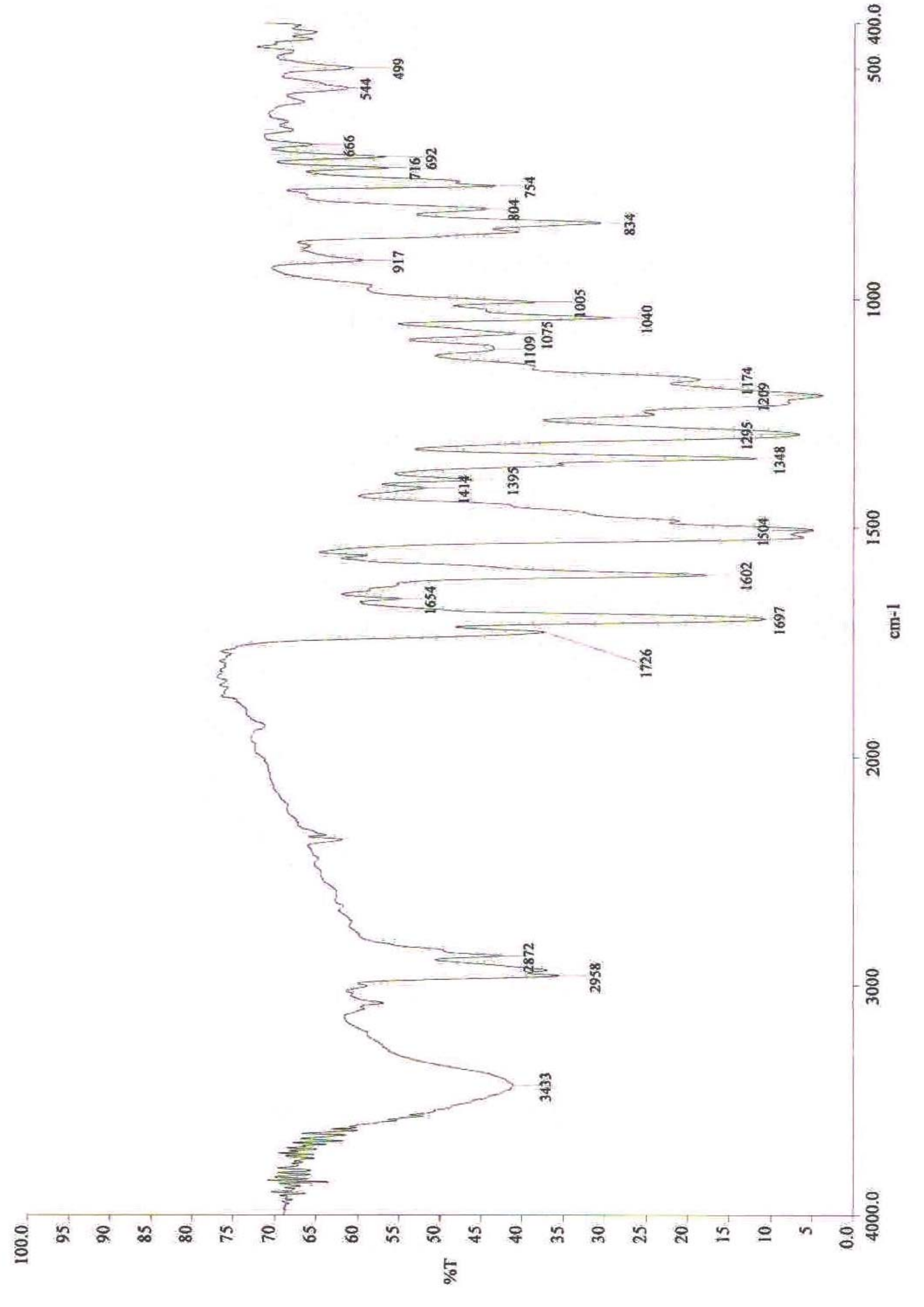


Figure 5. Representative IR spectra of 4'-Nitrobiphenyl trans-4-*n*-butoxy-3-methoxy cinnamate.

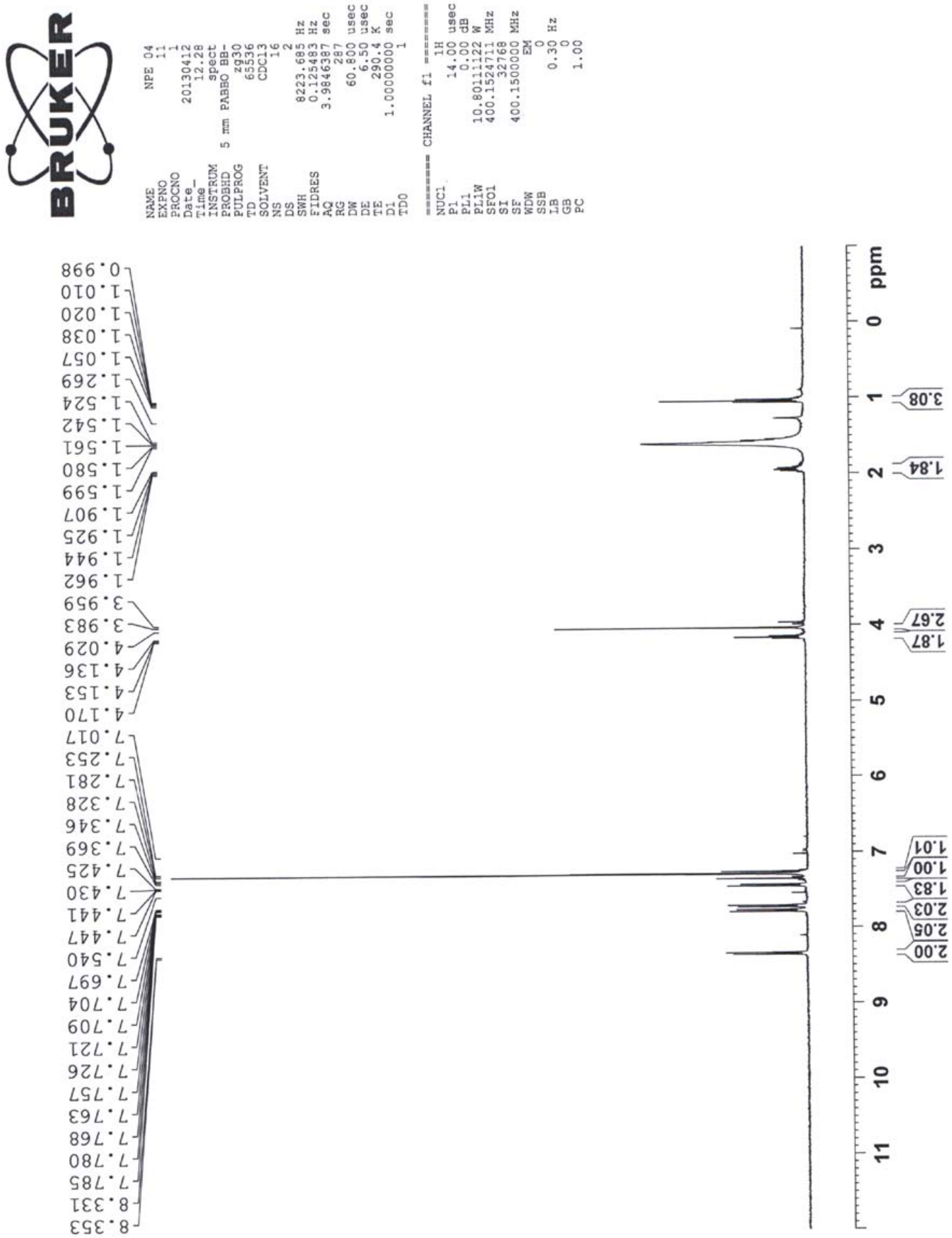


Figure 6. ^{1}H NMR spectra of 4’-Nitrobiphenyl trans-4-*n*-butoxy-3-methoxy cinnamate.

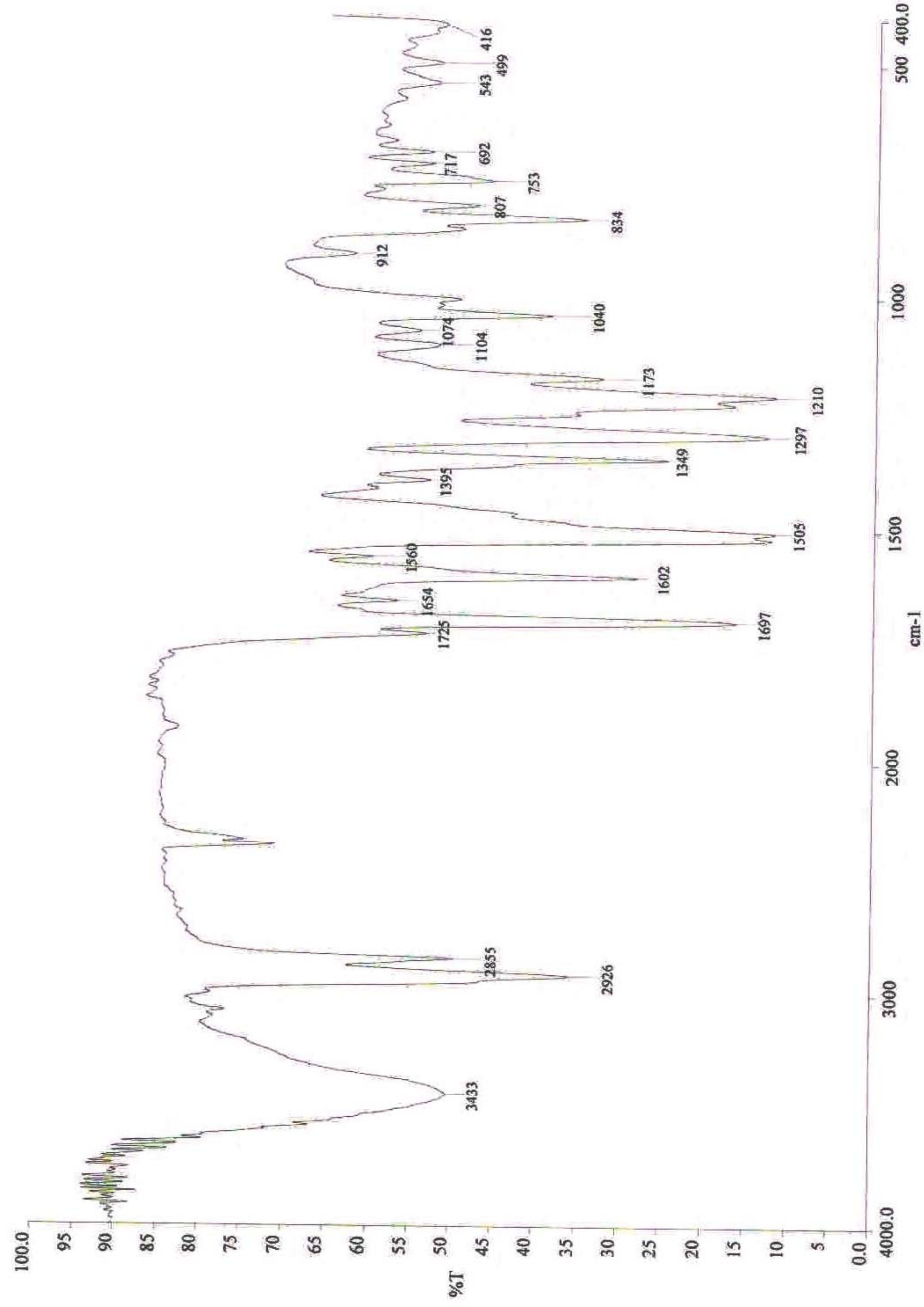


Figure 7. Representative IR spectra of 4'-Nitrobiphenyl trans-4-*n*-heptyloxy-3-methoxy cinnamate.

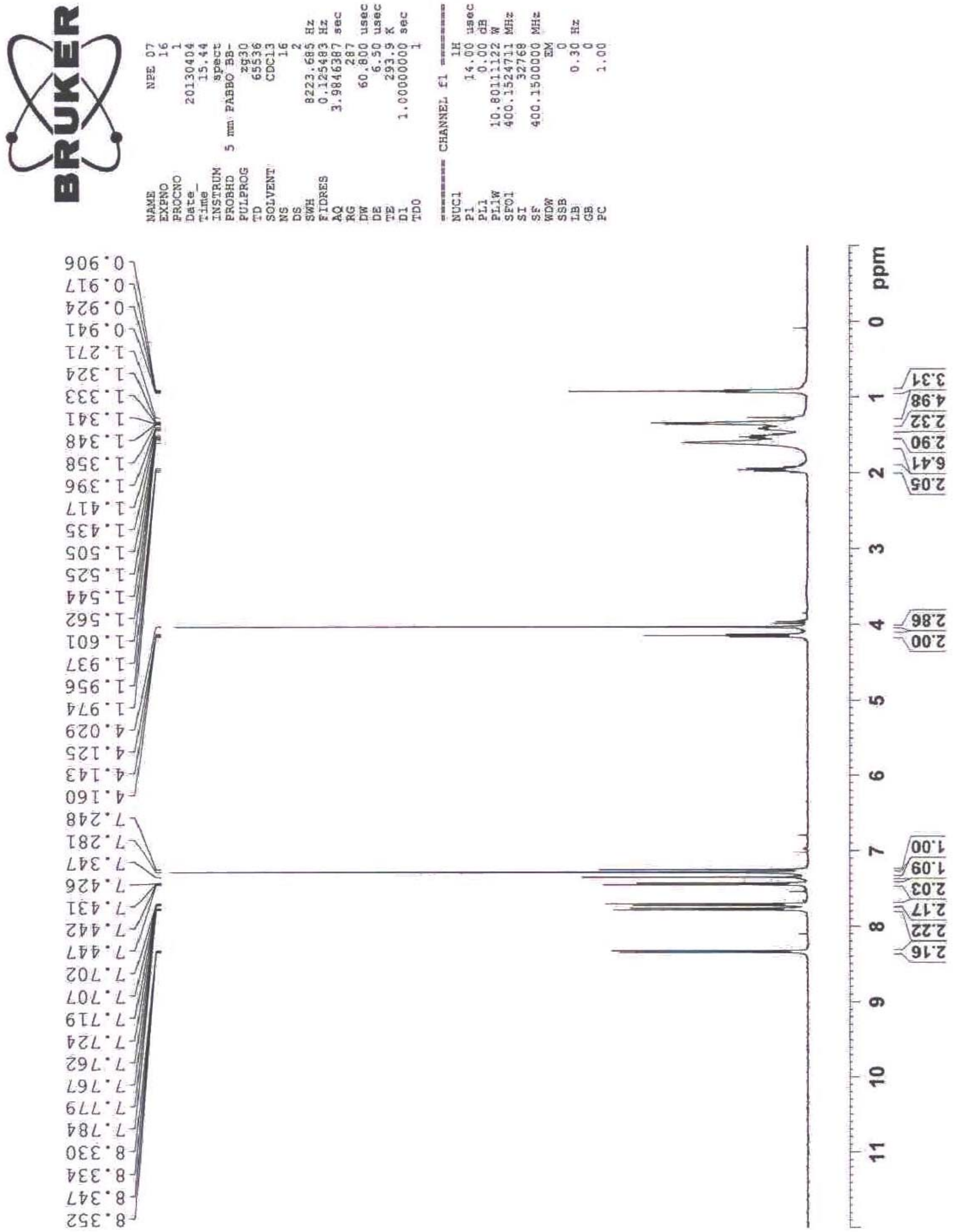


Figure 8. ^1H NMR spectra of 4’-Nitrobiphenyl trans-4-*n*-heptyloxy-3-methoxy cinnamate.

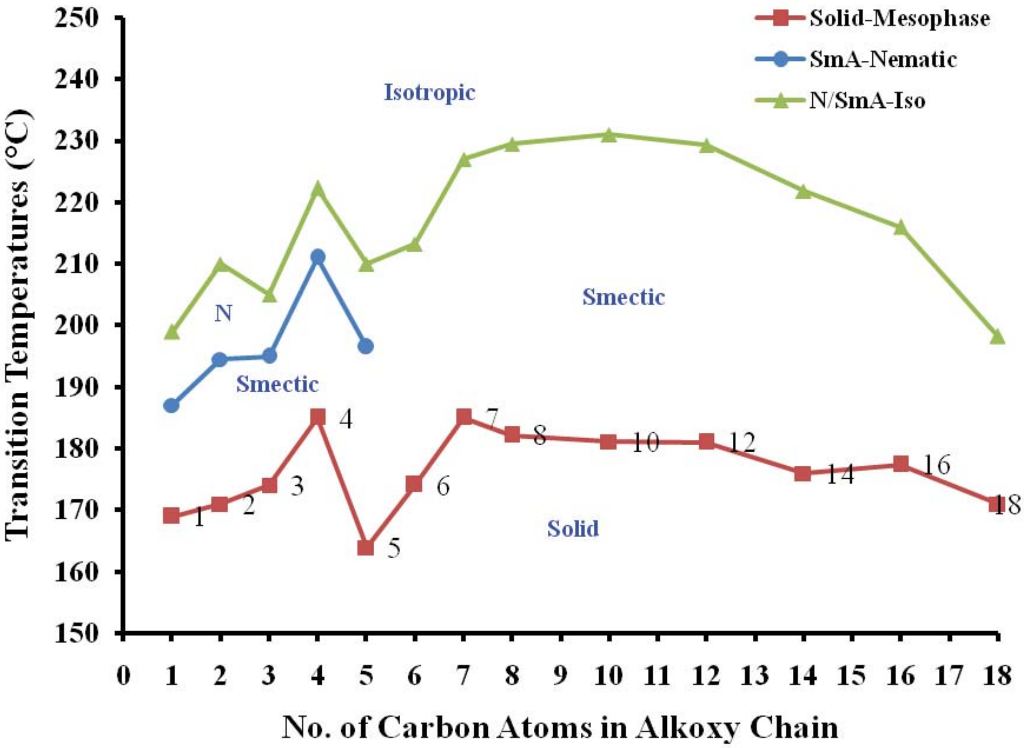


Figure 9. Plot of Transition temperatures (°C) versus number of carbon atoms in the alkoxy chain.

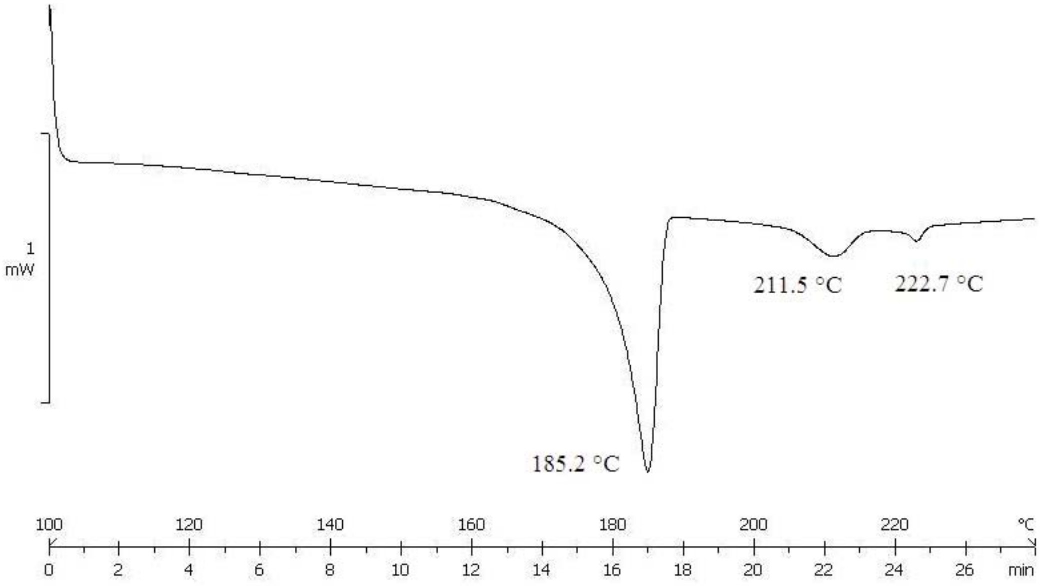


Figure 11. Representative DSC thermograms of *n*-butyloxy derivative at heating rate of 5 °C min^{-1}.

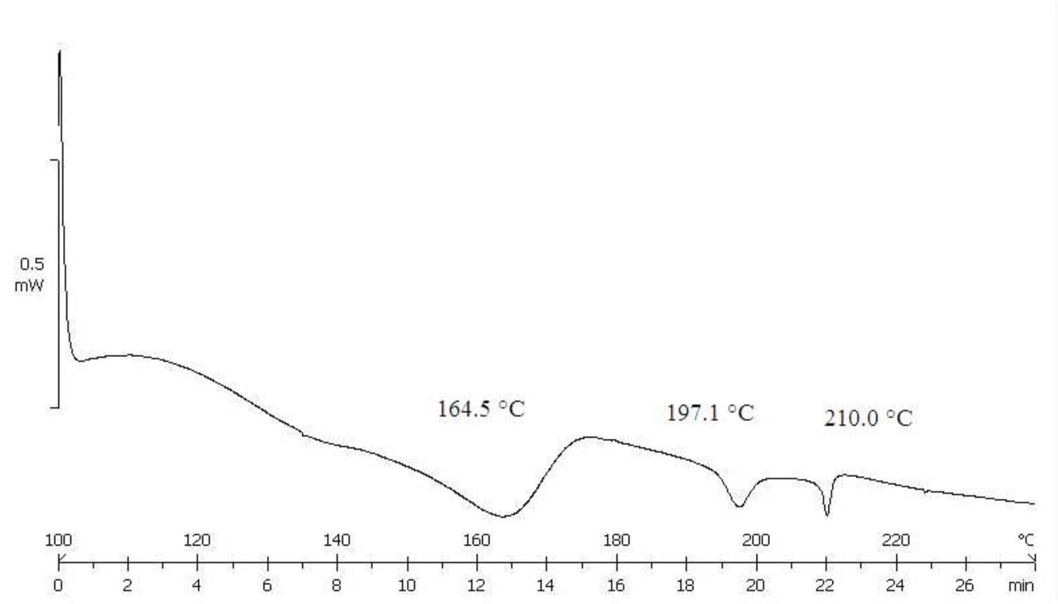


Figure 12. Representative DSC thermograms of *n*-pentyloxy derivative at heating rate of 5 °C min^{-1}.

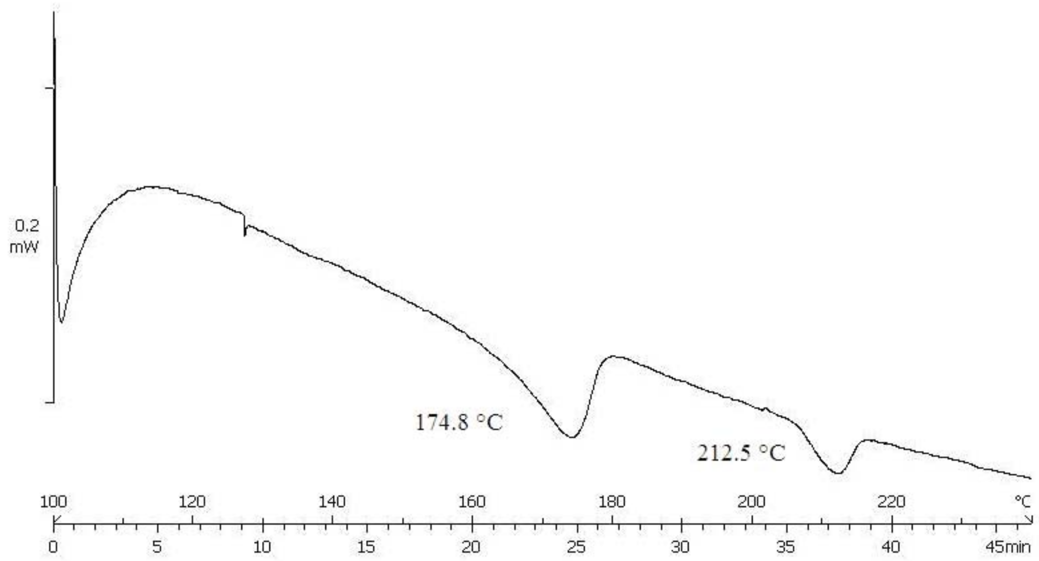


Figure 13. Representative DSC thermograms of *n*-hexyloxy derivative at heating rate of 3 °C min^{-1}.

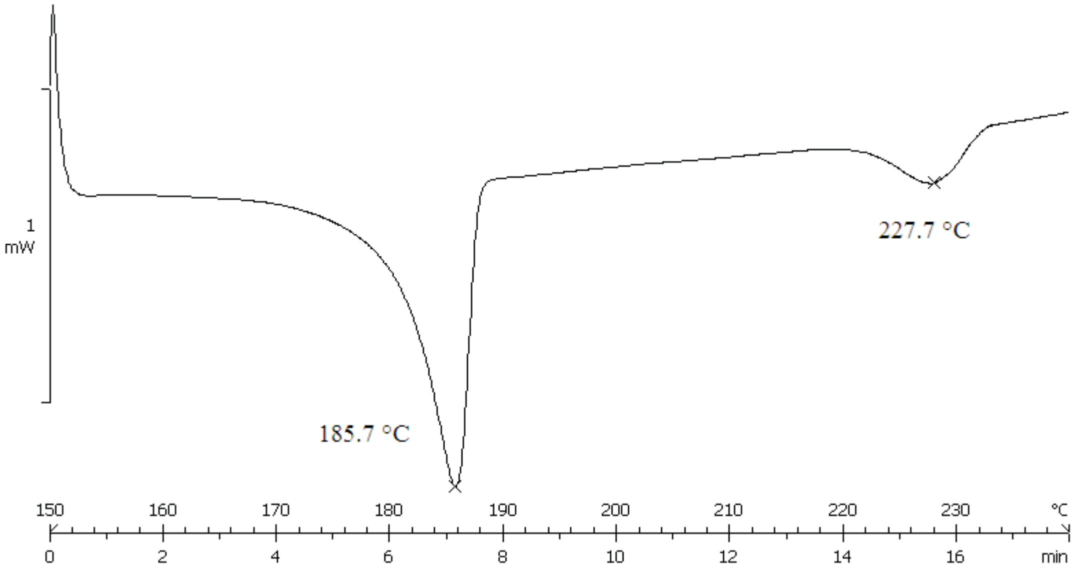
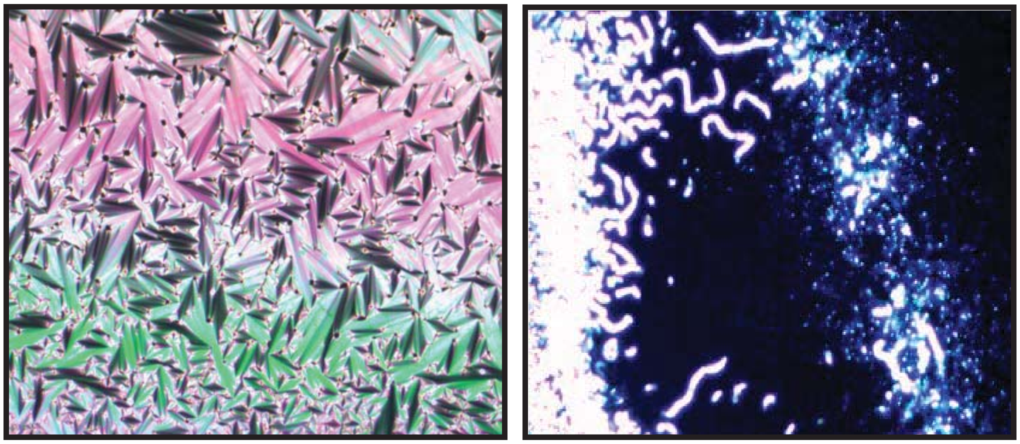


Figure 14. Representative DSC thermograms of *n*-heptyloxy derivative at heating rate of 5 °C min^{-1}.

4.3.1. Optical textures

The most widely used technique of liquid crystal phase identification is optical polarizing microscopy. This technique reveals that each different liquid crystal phase has a distinct optical texture. However, the identification of liquid crystal phases through optical polarizing microscopy is often difficult and requires a lot of experience. Optical polarizing microscopy enables the identification of the type of liquid crystal and other mesophases from the optical texture that is generated. The identification of mesophases through optical polarizing microscopy usually involves the magnified view of a thin sample of a mesogenic material sandwiched between a glass microscope slide and a glass cover-slip. The microscope slide of material is usually placed in a stage between polarisers which are crossed at 90° to each other.

All the compounds of the series **I** show mesomorphic properties and all are enantiotropic in nature. The lower members starting with methyl to *n*-pentyl derivatives exhibit both Smectic and Nematic phases; the higher member homologues starting with the *n*-hexyl derivative, show only Smectic phases and persists upto the last member of the series. The smectic and nematic phases were determined from optical texture observations under both heating and cooling cycles. The smectic phase is of smectic A type with characteristic focal conic or fan shape texture. The nematic phase showed a characteristic thread-like texture or schlieren texture under microscope. Optical textures of some of the compounds of the series **I** are shown in Figures 15-18.



(a) (b)

Figure 15. Polarised optical microphotographs of *n*-butyl derivative. (a) SmA-focal conic texture observed at 189.0 °C on heating, (b) Nematic-thread-like texture observed at 215.0 °C on heating.

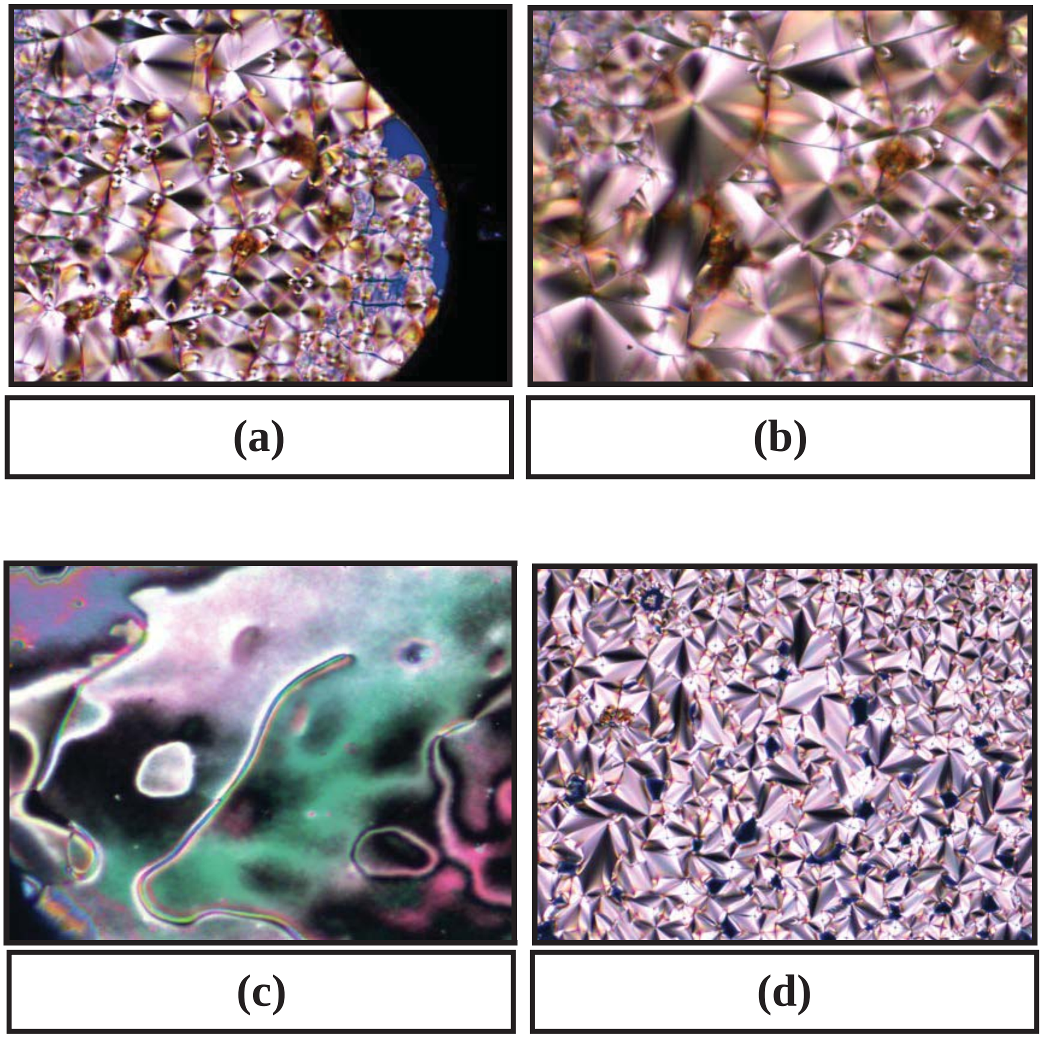


Figure 16. Polarised optical microphotographs of *n*-pentyl derivative. (a) SmA-focal conic texture observed at 190.0 °C on heating, (b) SmA-focal conic texture observed at 191.2 °C on heating, (c) Nematic-thread-like texture observed at 204.6 °C on heating and (d) SmA-focal conic texture observed at 189.3 °C on heating.

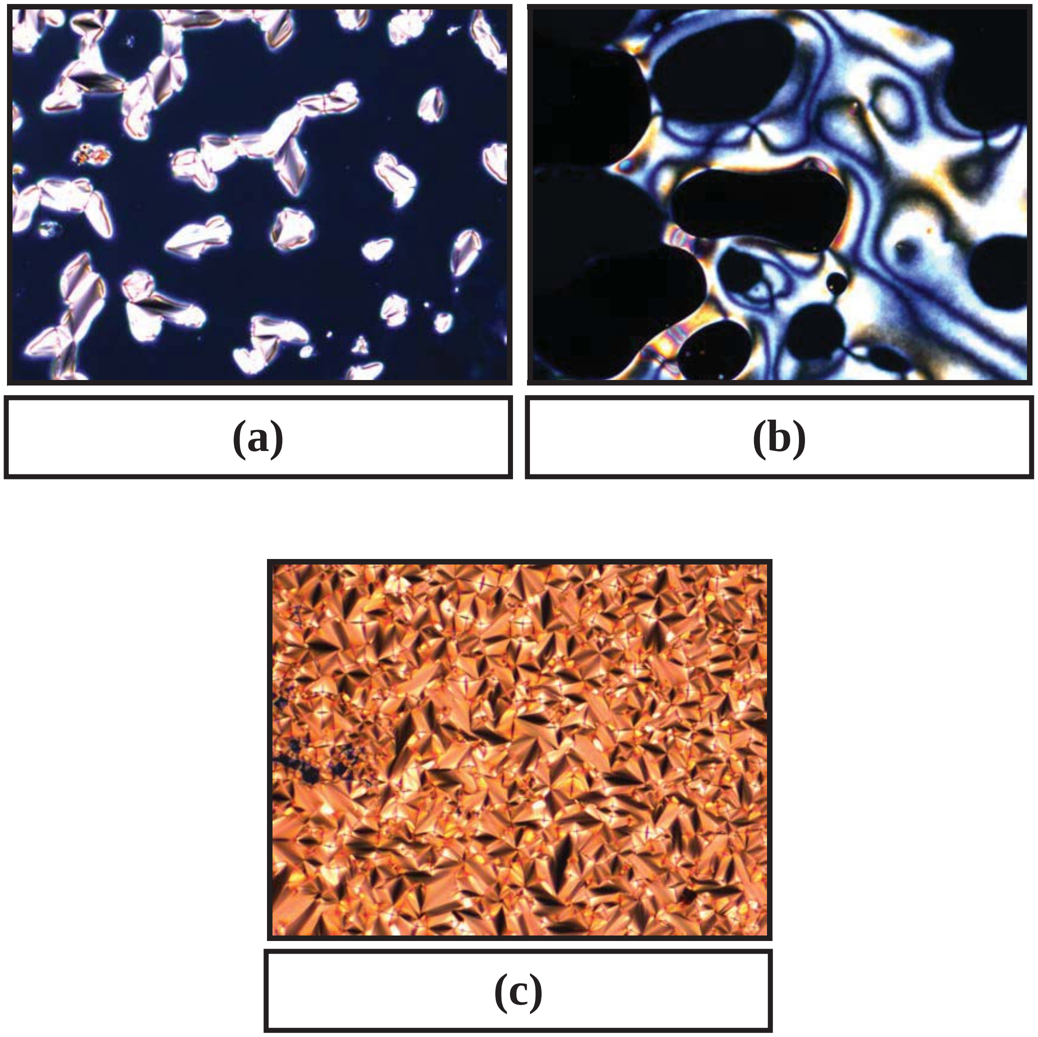


Figure 17. Polarised optical microphotographs of *n*-pentyl derivative. (a) SmA to Nematic phase change observed at 194.4 °C on heating, (b) Nematic to isotropic phase change observed at 210.6 °C on heating and (c) SmA-focal conic texture observed at 180.0 °C on cooling.

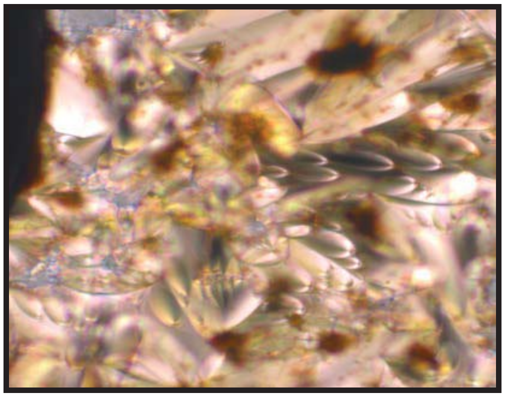


Figure 18. Polarised optical microphotograph of *n*-heptyl derivative; SmA-Polygonal texture observed at 203.0 °C on heating.

4.4. References

[1] A. Bree and M. Edelson, *Chem. Phys. Lett.*, **46**(3), 500-504, 1977.

[2] D. H. Barich, R. J. Pugmire, D. M. Grant and R. J. Iuliucci, *J. Phys. Chem. A*, **105**(28), 6780-6784, 2001.

[3] V.J. Eaton and D. Steele, *J. Chem. Soc. Faraday Trans. II.*, **69**(11), 1601-1608, 1973.

[4] I. Cacelli and G. Prampolini, *J. Phys. Chem. A*, **107**(41), 8665-8670, 2003.

[5] M. P. Johansson and J. Olsen, *J. Chem. Theory Comput.*, **4**(9), 1460-1471, 2008.

[6] P. J. Collings and M. Hird, *Introduction to Liquid Crystals Chemistry and Physics*, Taylor and Francis, London, 1997.

[7] R. H. Chen, *Liquid Crystal Displays: Fundamental Physics and Technology*, Wiley, New Jersey, 2011.

[8] P. Kovacic and M. B. Jones, *Chem. Rev.*, **87**(2), 357-379, 1987.

[9] A. J. Eagle, T. M. Herrington and N. S. Isaacs, *Liq. Cryst.*, **24**(5), 735-740, 1998.

[10] H. T. A. Wilderbeek, M. G. M. Van Der Meer, M. A. G. Jansen, L. Nelissen, H. R. Fischer, J. J. G. S. Van ES, C. W. M. Bastiaansen, J. Lub and D. J. Broer, *Liq. Cryst.*, **30**(1), 93-108, 2003.

[11] W. -L. Tsai, F. -M. Hsu and J. -N. Chen, *Liq. Cryst.*, **31**(2), 299-300, 2004.

[12] J. Geng, S. Wang, W. Ling, G. Li and E. Zhou, *Liq. Cryst.*, **31**(1), 71-79, 2004.

[13] G. W. Gray, K. J. Harrison, J. A. Nash, J. Constant, J.S. Hulme, J. Kirton and E. P. Raynes, *Liquid Cryst. Ordered Fluids*, **2**, 617-643, 1973.

[14] D. A. Dunmur, A. Fukuda, G. R. Luckhurst, *Physical Properties of Liquid Crystals: Nematics*, INSPEC, London, 2001.

[15] D. Demus, J. Goodby, G. W. Gray, H. -W. Spiess and V. Vill, *Hand Book of Liquid Crystals*, Wiley-VCH, Weinheim, 1998.

[16] C. T. Imrie, *Structure and Bonding*, D. M. P. Mingos (Ed.), p. 149, Springer-Verlag, Berlin, 2001.

[17] S. Kumar and S. K. Pal, *Liq. Cryst.*, **32**(5), 659-661, 2005.

[18] S. K. Pal, V. A. Raghunathan and S. Kumar, *Liq. Cryst.*, **34**(2), 135-141, 2007.

[19] S. Sauer, S. Saliba, S. Tussetschläger, A. Baro, W. Frey, F. Giesselmann, S. Laschat and W. Kantlehner, *Liq. Cryst.*, **36**(3), 275-299, 2009.

[20] R. Dabrowski, J. Dziaduszek, K. Garbat, M. Filipowicz, S. Urban, S. Gauza and G. Sasnouski, *Liq. Cryst.*, **37**(12), 1529-1537, 2010.

[21] R. K. Nath, D. D. Sarkar, D. S. Shankar Rao and V. S. Rao Nandiraju, *Liq. Cryst.*, **39**(7), 889-902, 2012.

[22] Y. Jiang, Z. An, P. Chen, X. Chen and M. Zheng, *Liq. Cryst.*, **39**(4), 457-465, 2012.

[23] Y. Jiang, L. Lu, P. Chen, X. Chen, J. Li and Z. An, *Liq. Cryst.*, **39**(8), 957-963, 2012.

[24] D. Ziobro, R. Dabrowski, M. Tykarska, W. Drzewiński, M. Filipowicz, W. Rejmer, K. Kuśmierek, P. Morawiak and W. Piecek, *Liq. Cryst.*, **39**(8), 1011-1032, 2012.

[25] P. Kula, A. Aptacy, J. Herman, W. Wójciak and S. Urban, *Liq. Cryst.*, **40**(4), 482-491, 2013.

[26] L. Zhang, X. Chen, F. Zhao, X. Fan, P. Chen and Z. An, *Liq. Cryst.*, **40**(3), 396-410, 2013.

[27] A. Mori, G. -X. Sun, K. Kubo, T. Hatsui, I. Akahoshi and S. Ujiie, *Mol. Cryst. Liq. Cryst.*, **458**, 27-34, 2006.

[28] E. T. de Givenchy, F. Guittard, L. Cailler, J. Munuera and S. Geribaldi, *Mol. Cryst. Liq. Cryst.*, **436**, 237-246, 2005.

[29] F. Hentrich, C. Tschierske, S. Diele and C. Sauer, *J. Mater. Chem.*, **4**(10), 1547-1558, 1994.

[30] I. Nishiyama, J. Yamamoto, J. W. Goodby and H. Yokoyama, *J. Mater. Chem.*, **13**(10), 2429-2435, 2003.

[31] Z. -S. Xu, R. P. Lemieux, A. Natansohn, P. Rochon and R. Shashidhar, *Liq. Cryst.*, **26**(3), 351-359, 1999.

[32] Y. Chen and W. -J. Wu, *Liq. Cryst.*, **25**(3), 309-318, 1998.

[33] Y. J. Jeon, J. C. Lee and B. Shivkumar, *Liq. Cryst.*, **26**(8), 1129-1133, 1999.

[34] P. A. Kumar and V. G. K. M. Pisipati, *Mol. Cryst. Liq. Cryst.*, **365**, 147-160, 2001.

[35] V. Prasad, *Liq. Cryst.*, **28**(7), 1115-1120, 2001.

[36] J. P. Bedel, J. C. Rouillon, J. P. Marcerou, M. Laguerre, M. F. Achard and T. Nguyen, *Liq. Cryst.*, **27**(1), 103-113, 2000.

[37] H. N. S. Murthy and B. K. Sadashiva, *Liq. Cryst.*, **29**(9), 1223-1234, 2002.

[38] V. Novotná, V. Hamplová, M. Kašpar, M. Glogarová, K. Knížek, S. Diele, G. Pelzl, C. Jones, D. Coleman and N. A. Clark, *Liq. Cryst.*, **32**(8), 967-975, 2005.

[39] V. Novotná, K. Mieczkowska, V. Hamplová, A. Domján, D. Pociecha, M. Kašpar and K. F-Csorba, *Liq. Cryst.*, **39**(10), 1252-1260, 2012.

[40] V. Gude, K. Upadhyaya, G. Mohiuddin and V. S. R. Nandiraju, *Liq. Cryst.*, **40**(1), 120-129, 2013.

[41] I. A. Pearl and D. L. Beyer, *J. Org. Chem.*, **16**, 216-220, 1951.

[42] R. Robinson and J. Shinoda, *J. Chem. Soc. Trans.*, **127**, 1973-1980, 1925.

[43] S. H. Ou, V. Percec, J. A. Mann, J. B. Lando, L. Zhou and K. D. Singer, *Macromolecules*, **26**(26), 7263-7273, 1993.

[44] G. W. Gray, *J. Physique Colloq.*, **36**, C1-337-C1-347, 1975.

[45] G. W. Gray, *Molecular Structure and the Properties of Liquid Crystals*, Academic Press, London, 1962.

[46] W. Major and G. Baumgartner, *Z. Naturforsch*, **7a**, 172-175, 1952.

[47] J. S. Dave and R. A. Vora, *Mol. Cryst. Liq. Cryst.*, **28**, 269-273, 1974.

[48] R. A. Vora and V. R. Teckchandani, Paper presented at the Thirteenth International Liquid Crystal Conference, Vancouver, Canada, July 22-27, 1990.

Chapter 5

LIQUID CRYSTALLINE BINARY MIXTURES

LIQUID CRYSTALLINE BINARY MIXTURES

5.1. Introduction

Binary mixtures of liquid crystals are of fundamental interest and of technological importance. Liquid Crystals with low crystal - mesophase transition temperatures and with wide phase length have been primary goal of organic chemists in recent years. Since the occurrence of single component, room temperature Liquid Crystal with wide mesophase is rare, it is necessary to mix two or more low melting materials which may give room temperature mesomorphic mixture with wide mesophase length. Just as the melting points of the solids are depressed by the addition of other substances, so also are the transition temperatures of liquid crystals lowered by the addition of other substances. Thus the nematogenic materials employed in electro-optic displays are multi-component mixtures whose nature and composition are selected to achieve particular display characteristics [1]. For example, the liquid crystalline range is enhanced by the addition of nematogens with high nematic-isotropic transition temperatures, such as the 4-*n*-alkyl-4”-cyano terphenyls, to materials with lower transitions such as the corresponding cyanobiphenyls. Solutions of pleochroic dyes in a nematogenic solvent are also of potential importance in display technology [2, 3]. Liquid crystalline mixtures are of fundamental interest because their properties provide a unique insight into the anisotropic interactions between unlike species.

In general, binary systems exhibiting mixed mesomorphism can be of three types:

1) Where both the components are mesomorphic,
2) Where only one component is mesomorphic and
3) Where both the components are non-mesomorphic

It has been observed in binary mixtures of polar compounds possessing a smectic A phase that the nematic phase is created or the range of the latter phase is extended at the cost of the smectic phase if the components differ significantly in their smectic layer spacing [4-6]. If the smectic layer spacings of the components of such mixtures differ significantly, a complete separation of the smectic phases by a nematic gap may even take place. The nematic gap is not observed at a definite smectic layer spacing ratio but at various values of that ratio depending on the smectic lattice energy and chemical structure of the compounds. Unexpectedly it was found that similar phase diagrams may be obtained for a mixture of two different compounds with the smectic phase A which have almost identical smectic layer spacings. Such behaviour was observed in some mixtures of compound belonging to cyanobiphenyl and halophenyl series [7].

Since the discovery of an induced smectic phase a variety of experiments have been performed in order to understand the nature of this phase [8-11]. In a number of cases such a phase is observed within some concentration range of the mixture when one of the components has a strongly polar cyano, nitro or isothiocyanate group, while the other has no group of this kind. On the other hand in some cases induced smectic phases appear when neither of the compounds has a strongly polar group, but both of them have an electron-donor character [12]. The kind of molecular interactions and the mechanism responsible for induced smectic phase formation have not been known accurately. Srikanta and Madhusudana [13] suggest that an induced smectic phase appears when charge transfer complex formation takes place between the two kinds of molecules, namely the highly polar component acting as an acceptor while the other component acts as a donor. These interactions appear to lead to the formation of a layered arrangement typical of smectic phases. Oh [14] has proposed a lamellar model to account for smectic phase formation. Waclawek *et al.* [15] and Sadowska *et al.* [16] suggest that 1:1 complexes, which occur during induced smectic phase formation, have a complexing energy which is smaller than that for complexes usually encountered with hydrogen bonds or charge transfer. Hence, they may be caused by Van der Waals forces. Griffin *et al.* [10] find that mixing two mesogens, one component of which has a tendency to form a bimolecular smectic phase and the other a monolayer smectic phase, leads to the induction of smectic mesomorphism. Raszewski [17] have investigated binary mixture systems by means of dielectric, refractometric and microscopic measurements to learn about the role of a strongly polar group, the effects of substituting a phenyl ring by a cyclohexyl one and the influence of the alkyl chain length in the process of induced smectic phase formation.

Studies of binary mixtures of mesogenic molecules offer a wide field of investigation since nematogenic or smectogenic pairs of compounds are, in general, totally miscible in the liquid-crystalline phases. This property was first used for the purpose of phase identification [18]. Moreover, the existence of a large domain of miscibility in the liquid-crystalline state gives us an opportunity to check the validity of additivity laws for many physical properties. In smectics, the fundamental feature is the occurrence of a one dimensional modulation of the density. The period is generally equal to the molecule length for pure compounds in a SmA state and varies linearly with the molar composition of the binary mixture. Levelut *et al.* [19] have studied the binary mixture of a liquid crystalline biforked molecule with derivatives of the *p*-terephtaldehyde-bis-alkyl-anilines. The phase diagrams and optical observations showed a continuous miscibility in the nematic and smectic C phase. Information on the molecular conformation of the biforked molecules was derived from X-ray diffraction studies of the binary mixtures.

Lohar have reported a binary system consisting of *p*-nitrophenyl-*p'*-*n*-amyloxy cinnamate and *p*-methoxyphenyl-*p'*-*n*-heptyloxy cinnamate which shows emergence of smectic mesophase in binary mixtures of pure nematogens [20]. The system transforms the original nematic texture into a mixed smectic A texture over a range of temperature and concentration. Both components individually are nematic liquid crystals. In their binary mixtures, a two dimensional more ordered mixed smectic A mesophase emerges between 5.0-92.5 mol% of *p*-methoxyphenyl-*p'*-*n*-heptyloxy cinnamate over a temperature range of about 50-105 ° at its maximum. Besides this phenomenon of emergence of the mixed smectic A mesophase out of a mixture of two purely nematic substances, the nematic mesophase also persists continuously in the phase diagram over a range of temperature and concentration.

Binary systems of two non-mesogens exhibiting polymesomorphism are rare. Vora *et al.* [21] have reported three binary systems of non-mesogens exhibiting smectic and / or nematic mesophases. One of the components is Schiff base and possesses strongly polar nitro end group. The transition temperature curves exhibit non-linear behaviour. In another binary system where one of the components exhibit monotropic nematic phase, induced smectic mesophase is observed and the monotropic nematic phase is converted to enantiotropic phase in certain concentration range. The binary systems of non-mesogens having identical structures (homologues) do not exhibit mesomorphism. Binary systems, where both the components are homologues and one of them is monotropic nematic, then, ideal behaviour is observed in their mixed mesomorphism. Vora have also evaluated the binary mesogenic systems comprised of ester mesogens and non-mesogens [22]. A non-mesogen as one of the components decreased the mesomorphic tendency of the system. The nematic phase remained enantiotropic for most of the compositions but the nematic-smectic curve went on falling up to about 50 % concentration and then the phase was eliminated from the system. In another binary system, the monotropic smectic phase is converted to enantiotropic phase. The smectogenic tendencies are enhanced with increasing carbon chain of alkoxy and ester substituent keeping with the trend observed in homologous series. Exhibition of induced mesophases in the binary system where one or both the components are non-mesogenic are also reported by Vora *et al.* [23]. In the three binary systems of both non-mesogenic components, induced nematic and smectic mesophases are observed in number of compositions. In the binary system where one of the components is monotropic nematic, an induced smectic phase is observed and the monotropic nematic phase is converted to an enantiotropic phase. The third binary systems where one component exhibits a monotropic smectic mesophase, an enantiotropic smectic mesophase is observed at comparatively lower temperatures. The terminal nitro substituent is responsible for the induced mesomorphic behaviour in the binary systems.

Alapati and co-workers [24] have also studied the liquid crystalline behaviour of binary mixtures of two non-mesogenic compounds. Binary mixtures of tetradecanol and orthophosphoric acid exhibited an interesting liquid crystalline phases in a large range of concentration and temperature. The mixtures in the concentration range between 10 to 60 % of tetradecanol in orthophosphoric acid exhibited SmA, SmD and SmE phases. The mixture with higher concentration of tetradecanol exhibited smectic phases.

Dave *et al.* [25] have reported binary systems consisting of structurally dissimilar mesogens and a non mesogens with a chiral terminal group and studied their effect on mixed mesomorphism, arising due to the differences in structural characteristics of these components. The molecular geometry of the two components in the binary mixture differ, N-I, Sm-N and Sm-Iso curves deviate from their linear nature. The rising tendency could be due to different moieties of terminal groups and central bridges. The deviation from linearity rule can be attributed to nitro group's high tendency of favouring the formation of oriented fluids. Most of the textures show super cooling below 35 °C.

Domingo [26] has studied mixtures of two different commercially available liquid crystals to formulate a technologically viable liquid crystal operating at room temperature. The study aimed to determine the mixture suitable for room temperature operations such as temperature sensors used in microchip production. Nematic E7 and cholesteric TM74A were mixed at different weight ratios with 10 % increments. The phase diagram showed the existence of three different phases for the temperature range of 10-80 °C cholesteric-nematic mesophase, SmA and isotropic. For mixtures that are largely nematic, the smectic phase has vanished and the cholesteric-nematic phase dominated from 30-60 °C.

Srivastava and Dhar [27] have reported the thermodynamic study of binary mixtures of cholesteryl myristate and dodecyloxybenzoic acid. Cholesteryl myristate have SmA and N* mesophases while dodecyloxybenzoic acid have SmC and N mesophases. The eutectic composition of the mixture has been found to be 30±5 mole % of dodecyloxybenzoic acid. Stability of SmA phase of cholesteryl myristate increases with the addition of dodecyloxybenzoic acid upto about 50 mole % of dodecyloxybenzoic acid but decreases thereafter and completely disappears at about 78 mol % of dodecyloxybenzoic acid.

Binary mixture of sodium lauryl sulphate and ethylene glycol is another example of the binary system where both components are non-mesogenic in nature [28]. This system exhibits a liquid crystalline phase over a large range of concentrations and temperatures. The concentration of 40 % of sodium lauryl sulphate exhibit I-SmA-SmE-Cr sequentially when the sample is cooled from the isotropic phase. Binary mixture of two non-mesogenic compounds viz., sodium oleate and ethylene glycol also exhibits very interesting liquid crystalline smectic phases at large range of concentration and temperatures [29]. The mixture with lower concentration of sodium oleate exhibits an I-SmA-SmD-SmB-SmE-Cr, sequentially when the specimen is cooled from its isotropic phase.

Luckhurst [30] have studied binary mixtures of intercalating, interdigitating and monolayer forming dimers to understand the origin of the different phase structures at the molecular level. The results indicated that the miscibility of the nematic and smectic A phases of these three forms of dimer are independent of the parity of the flexible spacer. The stability of the intercalated smectic A phase is, however, dependent on the compatibility of the spacer and terminal chain lengths, and also perhaps the compatibility of the mesogenic-mesogenic distance which is determined by the spacer length alone. In addition the intercalated and interdigitated smectic C phases have been show to be unstable to the addition of more than 20 mole % of even spacer dimer. For the mixtures with seemingly incompatible spacer and terminal chain lengths, the stability of the smectic phases is greatly reduced.

In the study of Li *et al.* [31], phase transitional properties of mixtures of azobenzene derivatives were reported in which one was a mesogen and the other a non-mesogen. The mixtures were found to exhibit a monotropic nematic phase which was converted to an enantiotropic phase in specific ranges of temperature and concentration. The unique low-temperature transitional property of this system has also been studied, with results showing that it was change of crystallite size caused enthalpic and morphological changes.

Nessim [32] has investigated phase behaviour of binary mixtures of 4-substituted phenyl 4'-*n*-alkoxybenzoates. Each series differs from the other by a substituent, which varies from the electron-donating -OCH_3 and -CH_3 groups to the electron-withdrawing -NO_2 and -CN groups, passing through the -Cl substituent which possesses opposing mesomeric and inductive effects, while the terminal alkoxy group changes between *n*-hexyloxy and *n*-hexadecyloxy. Such a variation in the molecular electronic properties could be a probe to investigate factors bearing on the phase transitions.

Jaishi and Mandal [33] have studied binary mixtures of 4-pentyloxy-4'-cyanobiphenyl and 4,4'-di(alkoxy)azoxybenzenes. Over a wide concentration range, the SmA phase was induced and the N phase of the parent compounds was absent. Instead of the tilted SmC phase of 4,4'-di(heptyloxy)azoxybenzenes an orthogonal SmA phase is observed when only 12 % of the host molecules are replaced by 4-pentyloxy-4'-cyanobiphenyl molecules. Moreover, in some mixtures the thermal stability of the induced SmA phase is found to be more than 1.6 times the stability of the mesophases in the pure compounds.

Liu and co-workers [34] have reported a study of the nematic-isotropic phase transition of three binary systems. The first system was simple and consisted of two nematic liquid crystals. The interaction between the two nematic molecules was found to be strong and the clearing temperature is slightly below the molar fraction-weighted arithmetic mean of the clearing temperatures of the components. The second system was a mixture of a nematic liquid crystal and a racemic liquid crystal, because chiral nematic liquid crystals are usually constructed from nematic hosts and chiral dopants. The interaction between the nematic and chiral molecules is weak and the clearing point temperature of the mixture was decreased. The third system was a mixture of positive and negative dielectric nematic liquid crystals, because mixing positive and negative dielectric liquid crystals is a method to adjust dielectric anisotropy. The interaction between the positive and negative dielectric nematic molecules was weaker and the clearing point temperature was significantly decreased. Author have used Maier-Saupe theory to study the nematic-isotropic transition and obtained good agreement with the experimental results.

Ma *et al.* [35] studied the binary system by mixing the unitary compound in various weight proportions and studied the temperature dependence of their physical properties. They have reported the temperature dependence of dielectric constants and splay elastic constants for fluorinated phenyl bicyclohexane binary liquid crystal mixtures. The results show that the proportions of the constituent elements of binary mixtures strongly influence their anisotropic dielectric constants. For mixtures in which meta-para- and ortho-para-fluorine-substituted molecules are in equal proportion, the effectiveness of the anisotropic dielectric is equal to that with a single para-fluorine- substituted compound. The proportions of a mixture seldom affect the threshold voltage and splay elastic constants in an anti-parallel measurement cell.

Fodor-Csorba [36] has prepared new bell-shaped compounds with symmetrical substitution in positions 3 and 5 of the central ring. Although this material was not mesogenic, it exhibited low melting and freezing points. Therefore this compound was suitable as a component for mixture study. Binary system was built with the rod-like 4-(*n*-octyloxy)phenyl 4-(*n*-hexyloxy)benzoate which exhibits enantiotropic nematic as well as monotropic SmC and SmX phases. It was found that the binary mixtures exhibit mesomorphic properties close to room temperature.

Recently, In a binary mixture system of ferroelectric and antiferroelectric liquid crystals whose major component shows an unusual reversed phase sequence of $\mathrm{SmC^*_A}(1/2)$ - SmC*, a new phase with ferrielectric order of five layers has been discovered by Vij and co-workers [37] by the electric field-induced birefringence (EFIB) measurements. The EFIB was measured using a photo-elastic modulator

(PEM) set up and by applying an in-plane electric field to a homeotropic aligned cell filled with the binary mixtures of compounds with ferroelectric and antiferroelectric compounds. The contours of constant birefringence in the electric field-temperature phase diagrams clearly indicate a distinct region corresponding to a new phase bordering the four-layer SmC*(1/2) on the low temperature side and SmC*$_\alpha$ on the high temperature side.

Nagappa [38] have reported binary mixtures of Cholesteryl 5-(4-((4-hexylphenylimino) methyl)-3-hydroxyphenoxy) pentanoate and *n*-Butyloxy-benzylidene-*p*-pentylaniline with interesting optical textures and phase behaviour. The samples with 1 % to 30 % of *n*-Butyloxybenzylidene-*p*-pentylaniline exhibit smectic and cholesteric phases. The intermediate concentrations ranging from 30 % to 70 % exhibit SmA, SmC*, SmG, SmF and SmB phases. The mixtures with higher concentrations from 71 % to 99 % show BP-N*-TGBA-TGBC-TGBC*-UTGBC*-SmA phases, sequentially.

Majumdar et al. [39] have performed miscibility study of two cholesterol based rod-shaped compounds. Both the compounds possess in common enantiotropic liquid crystalline phase sequence Cr-SmA-N*-Iso, which is generally exhibited by cholesterol-based compounds. Additionally, one of the rod-shaped compounds possesses a TGB phase over a short temperature range. In the binary mixture of this two rod-shaped compounds the TGB phase was stabilized over a long temperature range compared to that in the individual molecule. In the binary mixture up to 20 % (w/w) of one compound possessing the TGB phase exhibited enhancement of the temperature range of the TGB phase compared to that of individual compound. Further gradual increase of percentage of one compound in the binary mixture did not show any enhancement of the TGB phase compared to that of individual compound.

A binary mixture of cholesteryl ethyl carbonate and terephthal-bis-*p*-*n*-tetradecylaniline also exhibits a TGB phase as well as smectic polymorphic phases [40]. The mixture exhibits TGBA and TGBC phases at different concentrations and at different temperatures. Mixtures with higher concentrations of terephthal-bis-*p*-*n*-tetradecylaniline exhibit I-Ch-TGBA-TGBC-SmA-SmI-SmF phases sequentially when the specimen is cooled from its isotropic melt.

Binary mixtures of two non-mesogenic system tetradecyl trimethyl ammonium bromide (TTAB) and glacial acetic acid exhibits micellar nematic phase, SmA and

SmG mesophases [41]. The mixture exhibits very interesting schlieren texture of micellar nematic lyophase, SmA and SmG phases for all concentrations of TTAB sequentially when the specimen is cooled from its isotropic phase. The contribution of birefringence of the mixture is mainly due to TTAB. TTAB with non-mesogenic orthophosphoric acid also exhibits very interesting liquid crystalline smectic phase at large range of concentrations and temperature [42]. The mixture with lower and higher concentrations of TTAB exhibits SmA, SmD, SmB, and SmE phases, sequentially when the specimen is cooled from its isotropic phase.

Recently, Dave *et al.* [43] have studied many binary systems comprising three enantiotropic nematogens, namely 4-(4’-*n*-butyloxybenzoyloxy)phenylazo-4”-fluorobenzene, 4-(4’-*n*-butyloxybenzoyloxy)benzylidene-4”-fluoro aniline, and 4-(4’-*n*-heptyloxybenzoyloxy)phenylazo-4”-fluorobenzene; a monotropic nematogen, viz. 4-(4’-*n*-dodecyloxybenzoyloxy)naphthylazo-4”-fluorobenzene; and three non-mesogens, viz. 4-(4’-*n*-butyloxy benzoyloxy)benzaldehyde, 4-methoxybenzylidene-4’-chloroaniline, and 4-methoxybenzylidene-4’-toluidine. The central linkage, terminal group, and central ring system of the components have been varied systematically and the effect of these variations has been evaluated on the liquid crystalline properties of the binary mixtures.

In this chapter, we have synthesized two series of binary systems A and B containing 4-nitrobiphenyl moiety. The importance of understanding the behaviour of the mixtures is to produce better materials for applications. The present investigation was carried out with a view to synthesize such materials which can be useful for applications. Thus the effort in this investigation is in the direction of studying some of the variety and characterizing the difference in the mode or extent of formation of mixed liquid crystals.

5.2. Experimental

5.2.1. Instrumentation

The synthetic route adopted for the series of binary mixture systems A and B is given in the Figure 1. Liquid crystalline properties were investigated using Leica DM 2500P polarizing optical microscope provided with a Linkam heating stage.

5.2.2. Synthesis of Binary Systems

5.2.2.1. 4-(Benzoyloxy) biphenyl (1) [44]

4-Hydroxy biphenyl (0.1 mol) was dissolved in 50 ml of dry pyridine and was added slowly with stirring to cold benzoyl chloride (0.1 mol) contained in a round bottom flask. The mixture was heated on a water-bath for 30 minutes and was allowed to cool upto room temperature. It was acidified with cold 1:1 hydrochloric acid and precipitates obtained were filtered, washed with water and dried. The ester was crystallized from ethanol to yield 87% product. Melting Point: 150 °C.

5.2.2.2. 4-(Benzoyloxy)-4’-nitrobiphenyl (2) [44]

4-(Benzoyloxy) biphenyl (0.145 mol) was taken in round bottom flask, 310 ml of glacial acetic acid was added in the flask and it was heated upto 80-90 °C. 100 ml fuming nitric acid was added slowly in such a way that the temperature remained between 80-90 °C. After complete addition, the reaction mixture was cooled to room temperature. The solid separated was filtered and washed with water and methanol. The product was crystallized from glacial acetic acid to yield 51% of product. Melting Point: 210 °C.

5.2.2.3. Potassium salt of 4-hydroxy-4’-nitrobiphenyl (3) [44]

4-Benzoyloxy-4’-nitrobiphenyl (0.18 mol) was taken in round bottom flask, 300 ml of ethanol was added to it and it was heated to reflux. An aqueous solution of potassium hydroxide (40 gms of KOH in 100 ml of water) was then added dropwise at reflux. After complete addition, the mixture was further refluxed for 30 minutes and cooled overnight. Next day, blue crystals of potassium salt were filtered, washed with tetrahydrofuran until washing was colourless.

5.2.2.4. 4-*n*-Alkoxy-4’-nitrobiphenyl (4) (Components A1 and A2) [45-47]

The potassium salt of 4-hydroxy-4’-nitrobiphenyl (0.01 mol) was dissolved in 50 ml of dry DMF. To this solution alkyl halide (0.12 mol) was added. The whole mass was then refluxed for 3 to 4 hours on sand bath. The mixture was cooled upto room temperature then poured into cold water. It was then extracted with solvent ether. Ether layer was washed with water, diluted KOH solution and finally with water. Ether extract was dried over anhydrous calcium chloride and finally ether was evaporated. Solid obtained was further purified by recrystallization from ethanol several times till constant transition temperatures were obtained.

5.2.2.5. 4-hydroxy-4’-nitrobiphenyl (5) [44]

Pure 4-hydroxy-4’nitrobiphenyl was obtained by dissolving the potassium salt of 4-hydroxy-4’-nitrobiphenyl **(3)** in minimum amount of boiling water and adding 1:1 hydrochloric acid until acidic pH was obtained. The yellow solid was filtered, washed with water, dried and crystallized from ethanol. Melting Point: 203 °C.

5.2.2.6. 4-(*n*-Alkanoyloxy)-4’-nitrobiphenyl (6) (Components B1 and B2) [47]

Aliphatic acid (0.01 mol), 4-hydroxy-4’-nitrobiphenyl **5** (0.01 mol) and DMAP (0.001 mol) were dissolved in 100 ml dichloromethane at 0 °C. To this solution, DCC (0.011 mol) was added by maintaining the temperature at 0 °C. After 1 hr the solution was allowed to warm to room temperature and stirring was continued for 24 hrs. After 24 hrs, the precipitated dicyclohexylurea (DCU) was removed by filtration, dichloromethane was evaporated and the whole reaction mass was poured into cold water. The precipitated produced was filtered, washed with water and recrystallized from ethanol.

5.2.2.7. BINARY SYSTEM A (Series A)

The components A1 and A2 were weighted in known proportions and melted together in fusion tubes. They were thoroughly mixed in their melt to obtain a homogeneous mixture. After homogeneously mixing they were cooled to room temperature. This procedure was repeated 3 to 4 times. The solid obtained was finally ground and used for determining transition temperatures, by using Leica DM 2500P polarizing optical microscope provided with a Linkam heating stage. The transition temperatures of binary system **A** are summarized in Table 1.

5.2.2.8. BINARY SYSTEM B (Series B)

The components B1 and B2 were weighted in known proportions and melted together in fusion tubes. They were thoroughly mixed in their melt to obtain a homogeneous mixture. After homogeneously mixing they were cooled to room temperature. This procedure was repeated 3 to 4 times. The solid obtained was finally ground and used for determining transition temperatures, by using Leica DM 2500P polarizing optical microscope provided with a Linkam heating stage. The transition temperatures of binary system **B** are summarized in Table 2.

5.2.3. Determination of transition temperatures with the help of a polarizing optical microscope

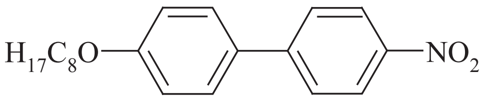
To determine the transition temperatures the Leica DM 2500P polarizing optical microscope equipped with a Linkam heating stage was used.

To determine the various transitions, a glass slide with a thin coating of material, covered with a glass cover slip, was observed under microscope. The slide was kept on the hot stage and the temperature was raised rapidly to find the approximate transition temperatures. The observations were repeated and the rate of heating was regulated to slowly near the transition, to determine the transition temperatures more precisely.

The members of the binary systems A and B both exhibit enantiotropic mesomorphic states. All the compounds show Smectic phases. The smectic phase shows smectic C type phase which was characterized by the formation of a typical broken focal conic texture or broken polygonal texture.

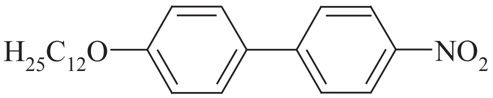
5.3. Results and Discussion

In the present investigation, we have synthesized two series of binary systems **A** and **B.** Series A was prepared by mixing components A1 and A2 which are both mesogenic in nature. Both components show smectic C phases. Structures of components A1 and A2 are shown in Figure 2. The transition temperatures of series A are recorded in Table 1. Components A1 and A2 were synthesized by the route shown in Figure 1. Optical textures of some of the compounds of the series **A** are shown in Figures 6-8.



Cr 50.0 SmC 63.4 Iso

Component A1



Cr 67.6 SmC 71.0 Iso

Component A2

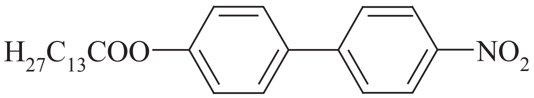
Figure 2. Components of binary system A.

In the above binary system A, component A1 differs from component A2 by a number of methylene units of the alkyl chain at the left terminal of the molecules and the difference is of four methylene units. In other words, as far as the molecular geometry of the components A1 and A2 is concerned, there is a difference of ‘four’ $-CH_2-$ units between them.

The plot of transition temperature versus mole % of component A1 is given in Figure 4. The Smectic-Isotropic curve exhibits falling tendency while Solid-Smectic curve decreases upto 50 mole % of component A1 and then rises till it reaches to the 100 mole % of component A1. This follows the principle of mixtures. Just as the melting points of the solids are depressed by the addition of other substances, so also are the transition temperatures of liquid crystals lowered by the addition of other component.

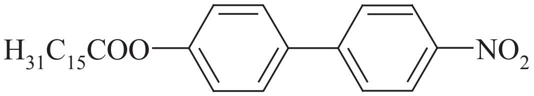
In pure component A2, the smectic phase appears from 67.6 °C and the phase stability is 3.4 °C and in pure component A1, the smectic phase appears from 50.0 °C and the phase stability is 13.4 °C. On addition of component A1 to component A2, smectic phase start appearing from 42.5 °C temperature which is near to room temperature and the smectic phase stability is increased upto 25.2 °C which is observed for compound 15 where both components A1 and A2 are in equal mole proportion.

Series B was prepared by mixing components B1 and B2 which are both mesogenic in nature. Both components show smectic C phases. Structures of components B1 and B2 are shown in Figure 3. The transition temperatures of series B are recorded in Table 2. Components B1 and B2 were synthesized by the route shown in Figure 1. Optical textures of some of the compounds of the series **B** are shown in Figures 9-11.



Cr 64.7 SmC 78.6 Iso

Component B1



Cr 73.5 SmC 81.9 Iso

Component B2

Figure 3. Components of binary system B.

In the above binary system B, component B1 differs from component B2 by a number of methylene units of the alkyl chain at the left terminal of the molecules and the difference is of two methylene units. In other words, as far as the molecular geometry of the components B1 and B2 is concerned, there is a difference of ‘two’ -CH_2- units between them.

The plot of transition temperature versus mole % of component B1 is given in Figure 5. The Smectic-Isotropic curve exhibits falling tendency while Solid-Smectic curve decreases upto 50 mole % of component B1 and then rises till it reaches to the 100 mole % of component B1. This also follows the same principle of mixtures. Just as the melting points of the solids are depressed by the addition of other substances, so also are the transition temperatures of liquid crystals lowered by the addition of other component.

In pure component B2, the smectic phase appears from 73.5 °C and the phase stability is 8.4 °C and in pure component B1, the smectic phase appears from 64.7 °C and the phase stability is 13.9 °C. On addition of component B1 to component B2, smectic phase start appearing from 49.3 °C temperature and the smectic phase stability is increased upto 30.5 °C which is observed for compound 25 where both components B1 and B2 are in equal mole proportion.

It should be emphasized that the mixed mesophases are quite wide and show up over a large area in the phase diagrams. The miscibility of the components in both the systems A and B seems to be of a high order giving rise to clear out mesophase texture. In the mixed conditions, the textures are clearly seen and they coexist at the boundaries. The changeover from one phase to another phase on raising or lowering of the temperature is also quite clear. The types of binary systems thus acquire importance; the mixed mesomorphism as exhibited by these binary systems only supports the mesomorphic characteristics in the pure state.

Table 1. Transition temperatures of Binary System **A. (Series A)**

Compound	Mole % of A1	Transition temperatures (°C)				
		Cr		SmC		I
A2	0	•	67.6	•	71.0	•
11	11.52	•	67.0	•	70.3	•
12	22.64	•	65.0	•	69.2	•
13	33.42	•	63.8	•	68.8	•
14	43.84	•	57.6	•	68.1	•
15	53.94	•	42.5	•	67.7	•
16	63.73	•	44.5	•	67.0	•
17	73.22	•	45.5	•	66.8	•
18	82.42	•	47.1	•	65.5	•
19	91.34	•	49.2	•	64.6	•
A1	100	•	50.0	•	63.4	•

Table 2. Transition temperatures of Binary System **B. (Series B)**

Compound	Mole % of B1	Transition temperatures (°C)				
		Cr		SmC		I
B2	0	•	73.5	•	81.9	•
21	10.58	•	72.9	•	81.5	•
22	21.04	•	70.4	•	81.1	•
23	31.36	•	69.2	•	80.4	•
24	41.54	•	63.1	•	80.2	•
25	51.59	•	49.3	•	79.8	•
26	61.52	•	51.5	•	79.2	•
27	71.33	•	52.6	•	79.1	•
28	81.00	•	56.4	•	78.9	•
29	90.55	•	60.5	•	78.7	•
B1	100	•	64.7	•	78.6	•

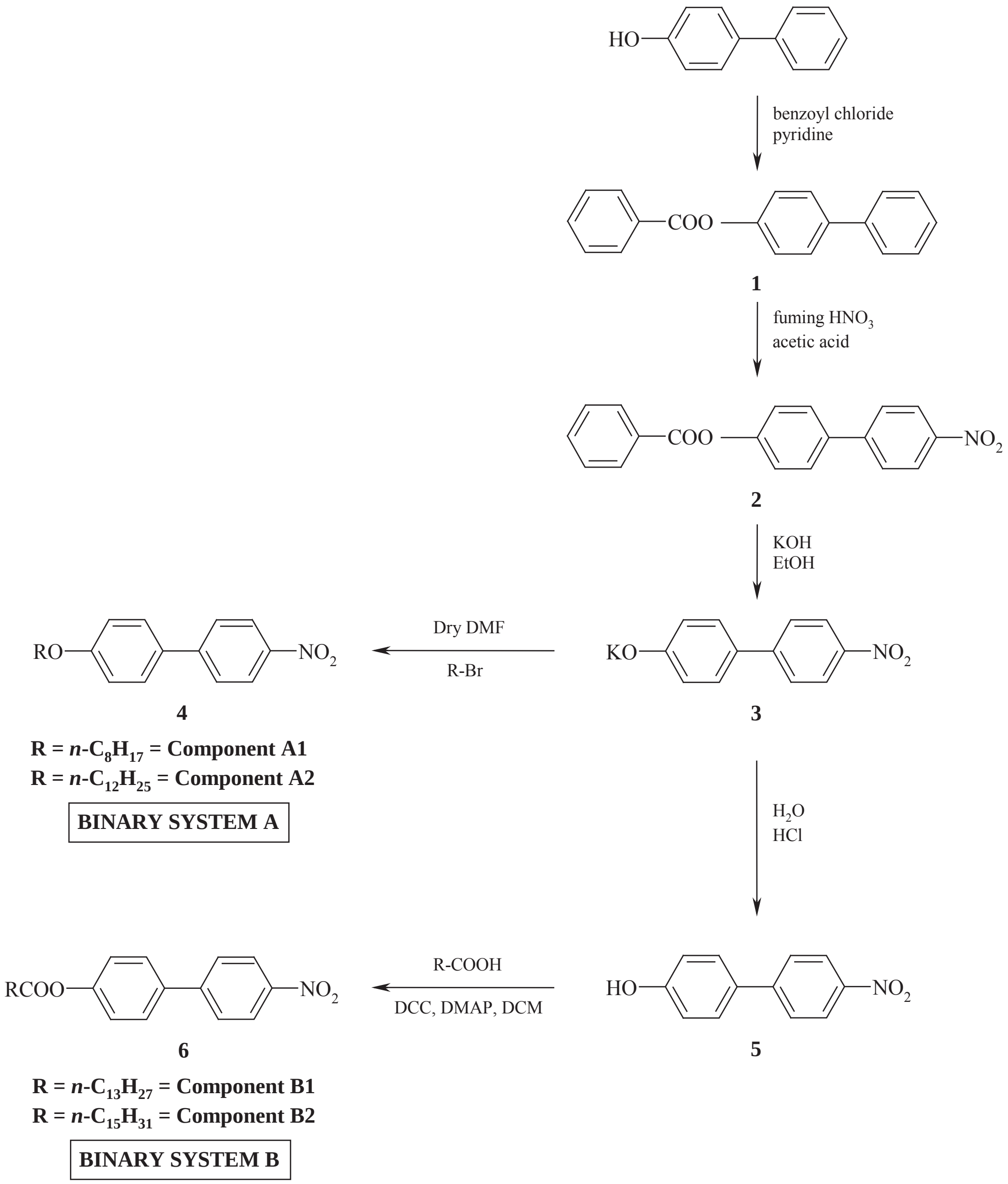


Figure 1. Synthetic route to Binary Systems A and B.

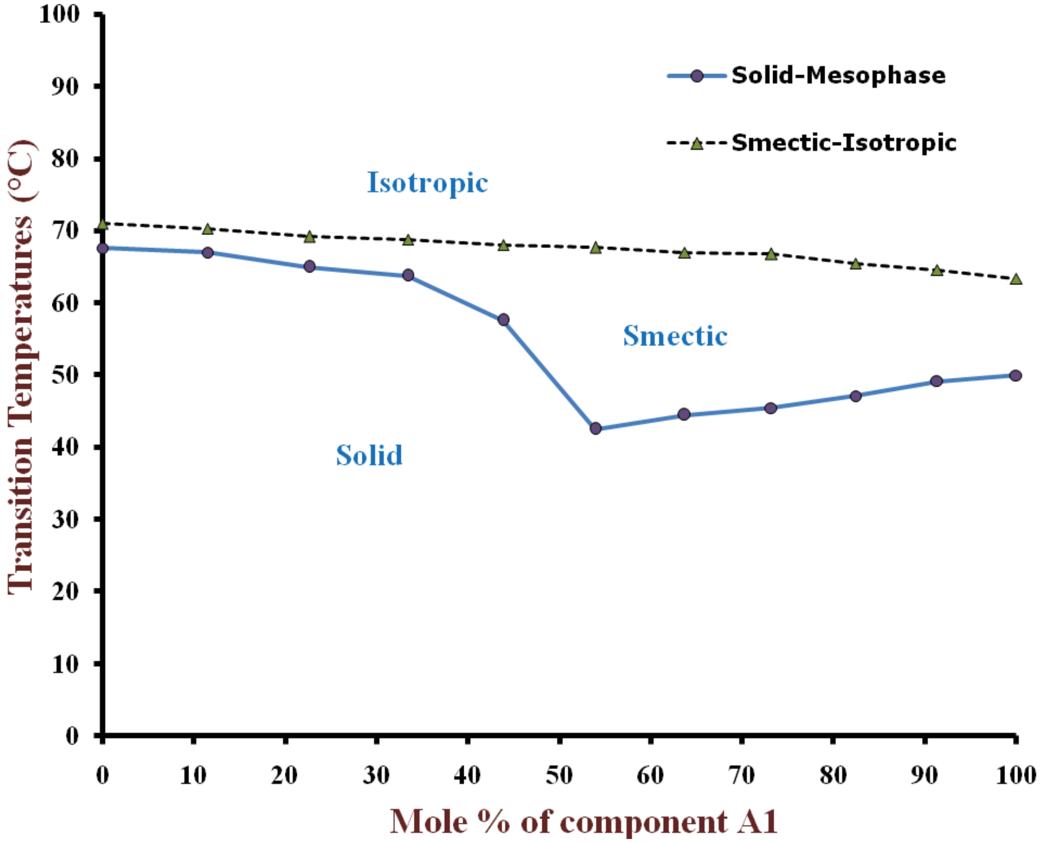


Figure 4. Plot of Transition temperatures (°C) versus mole % of component A1 in binary system A.

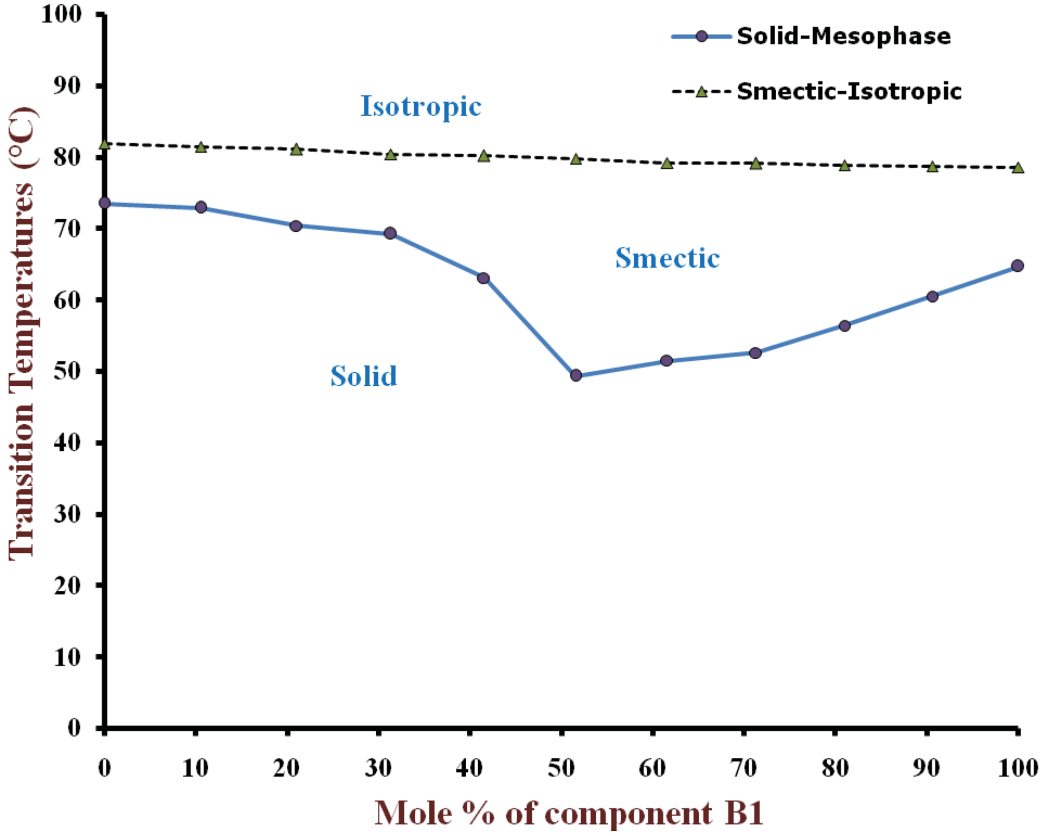


Figure 5. Plot of Transition temperatures (°C) versus mole % of component B1 in binary system B.

5.3.1. Optical textures

The most widely used technique of liquid crystal phase identification is optical polarizing microscopy. This technique reveals that each different liquid crystal phase has a distinct optical texture. However, the identification of liquid crystal phases through optical polarizing microscopy is often difficult and requires a lot of experience. Optical polarizing microscopy enables the identification of the type of liquid crystal and other mesophases from the optical texture that is generated. The identification of mesophases through optical polarizing microscopy usually involves the magnified view of a thin sample of a mesogenic material sandwiched between a glass microscope slide and a glass cover-slip. The microscope slide of material is usually placed in a stage between polarisers which are crossed at 90° to each other.

All the compounds of the series **A** and **B** show mesomorphic properties and all are enantiotropic in nature. All the compounds show Smectic phases. The smectic phases were determined from optical texture observations under both heating and cooling cycles. The smectic phase shows smectic C type phase which was characterized by the formation of a typical broken focal conic texture or broken polygonal texture. Optical textures of some of the compounds of the series **A** and **B** are shown in Figures 6-8 and 9-11 respectively.

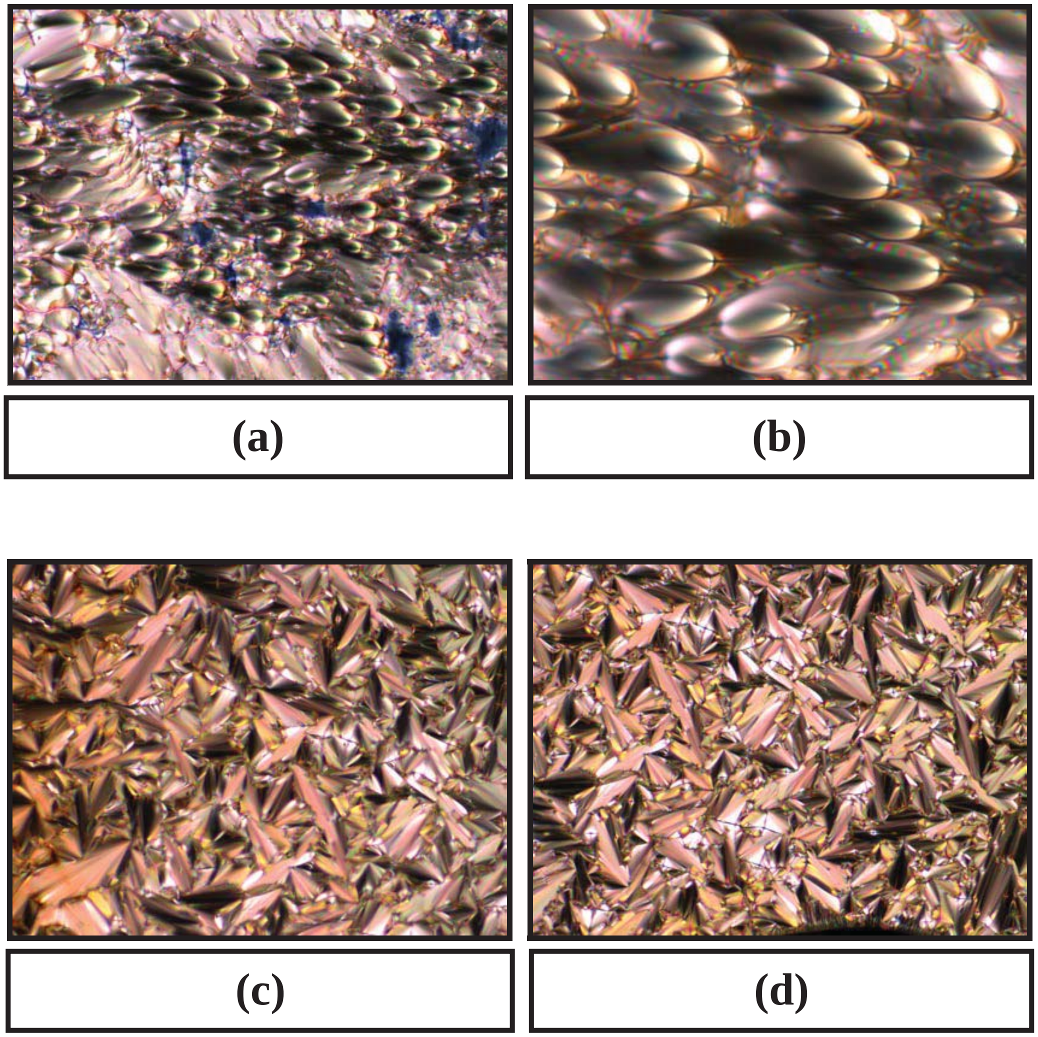


Figure 6. Polarised optical microphotographs (a) component A1, SmC-broken polygonal texture observed at 55.3 °C on cooling, (b) component A1, SmC-broken polygonal texture observed at 53.0 °C on cooling, (c) component A2, SmC-broken focal conic texture observed at 69.1 °C on cooling and (d) component A2, SmC-broken focal conic texture observed at 68.3 °C on cooling.

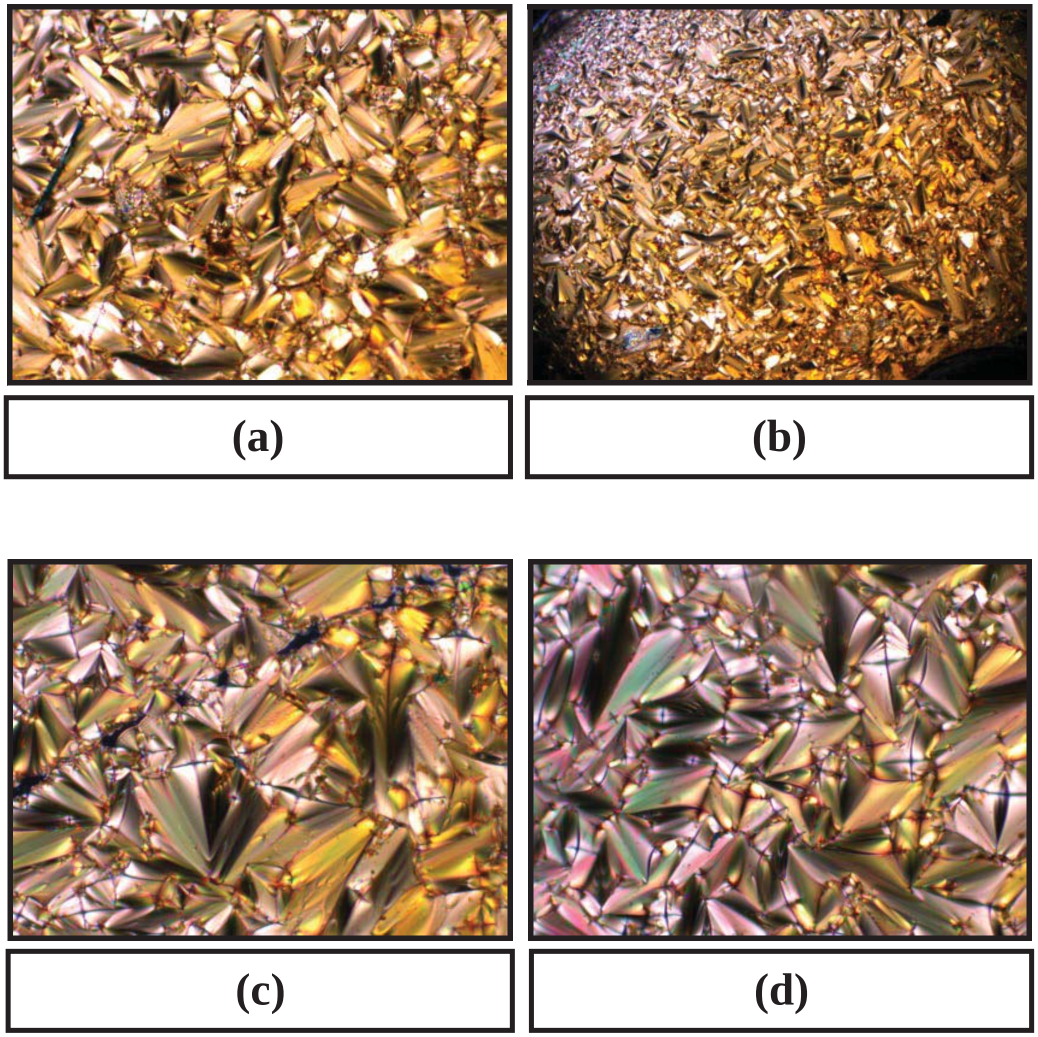


Figure 7. Polarised optical microphotographs (a) compound 11, SmC-broken focal conic texture observed at 69.6 °C on cooling, (b) compound 11, SmC-broken focal conic texture observed at 68.9 °C on cooling, (c) compound 15, SmC-broken focal conic texture observed at 53.5 °C on cooling and (d) compound 15, SmC-broken focal conic texture observed at 48.3 °C on cooling.

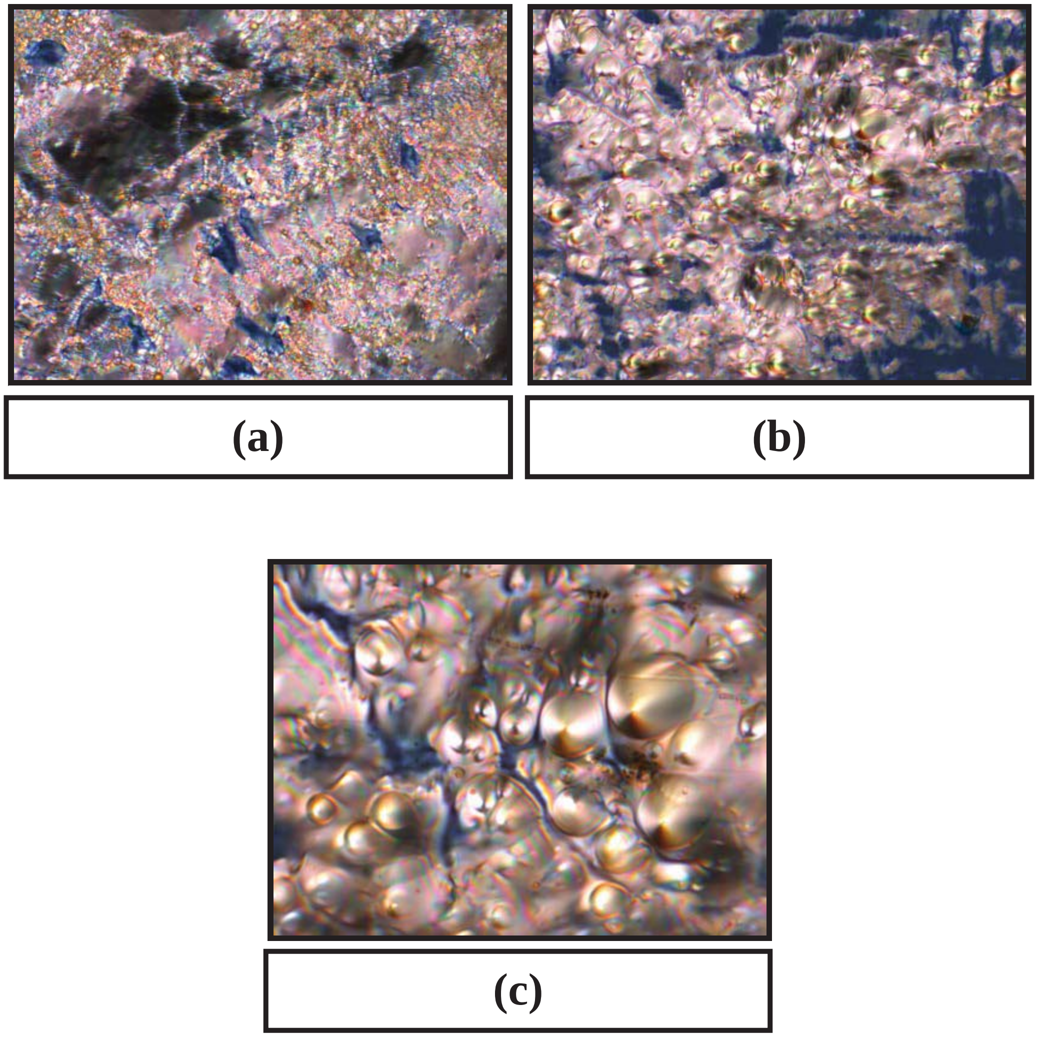
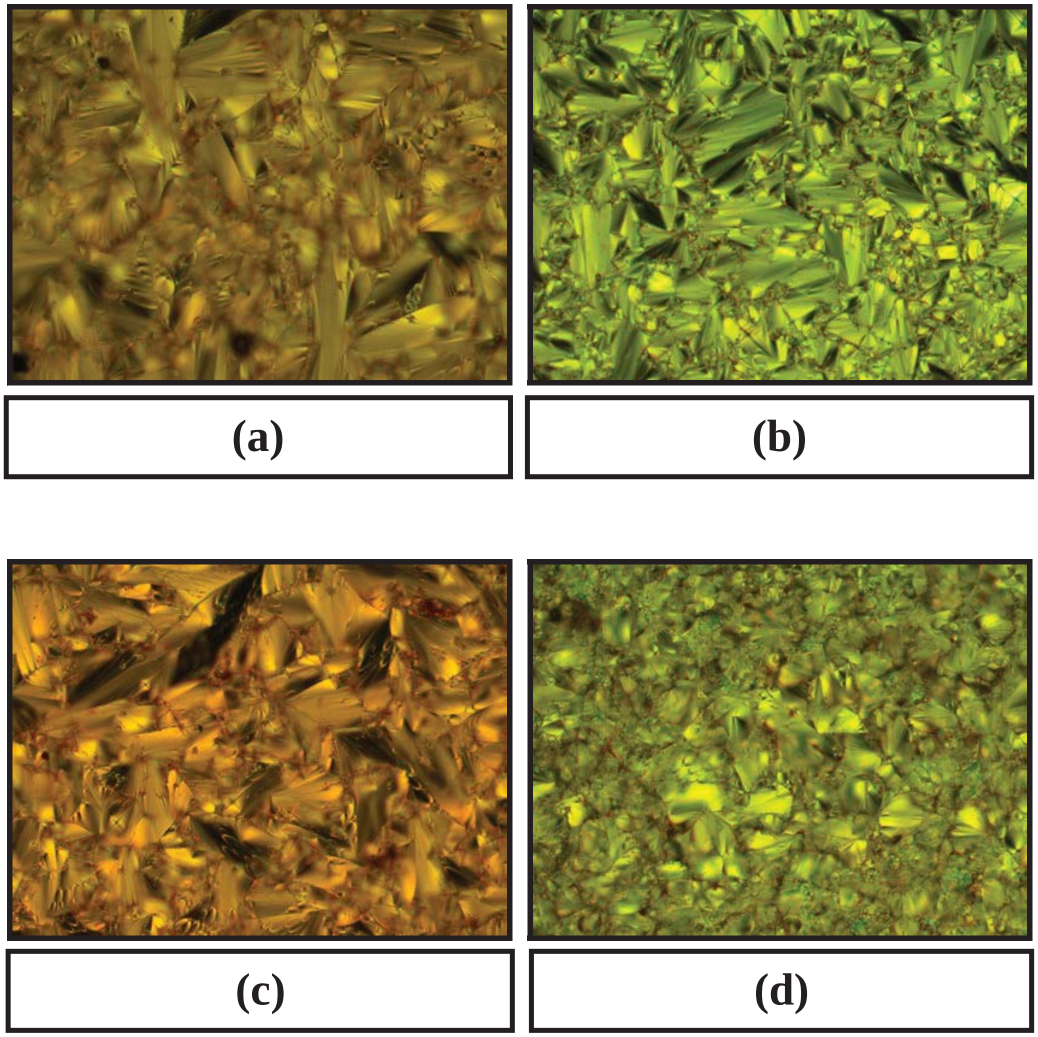


Figure 8. Polarised optical microphotographs of compound 19. (a) SmC-broken polygonal texture observed at 50.5 °C on heating, (b) SmC-broken polygonal texture observed at 51.5 °C on cooling and (c) SmC-broken polygonal texture observed at 62.4 °C on cooling.



(a) (b)

(c) (d)

Figure 9. Polarised optical microphotographs (a) component B1, SmC-broken focal conic texture observed at 67.2 °C on heating, (b) component B2, SmC-broken focal conic texture observed at 76.3 °C on cooling, (c) compound 21, SmC-broken focal conic texture observed at 75.4 °C on cooling and (d) compound 21, SmC-broken focal conic texture observed at 74.2 °C on cooling.

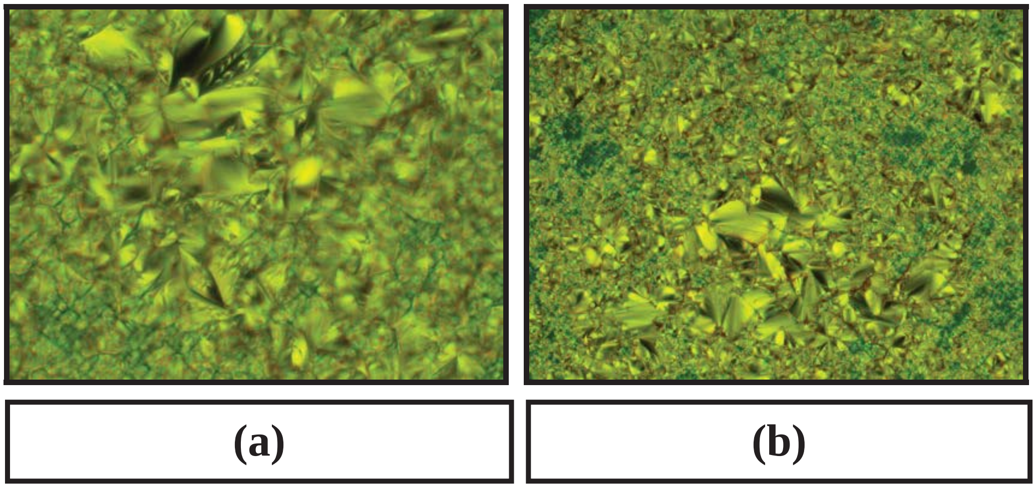
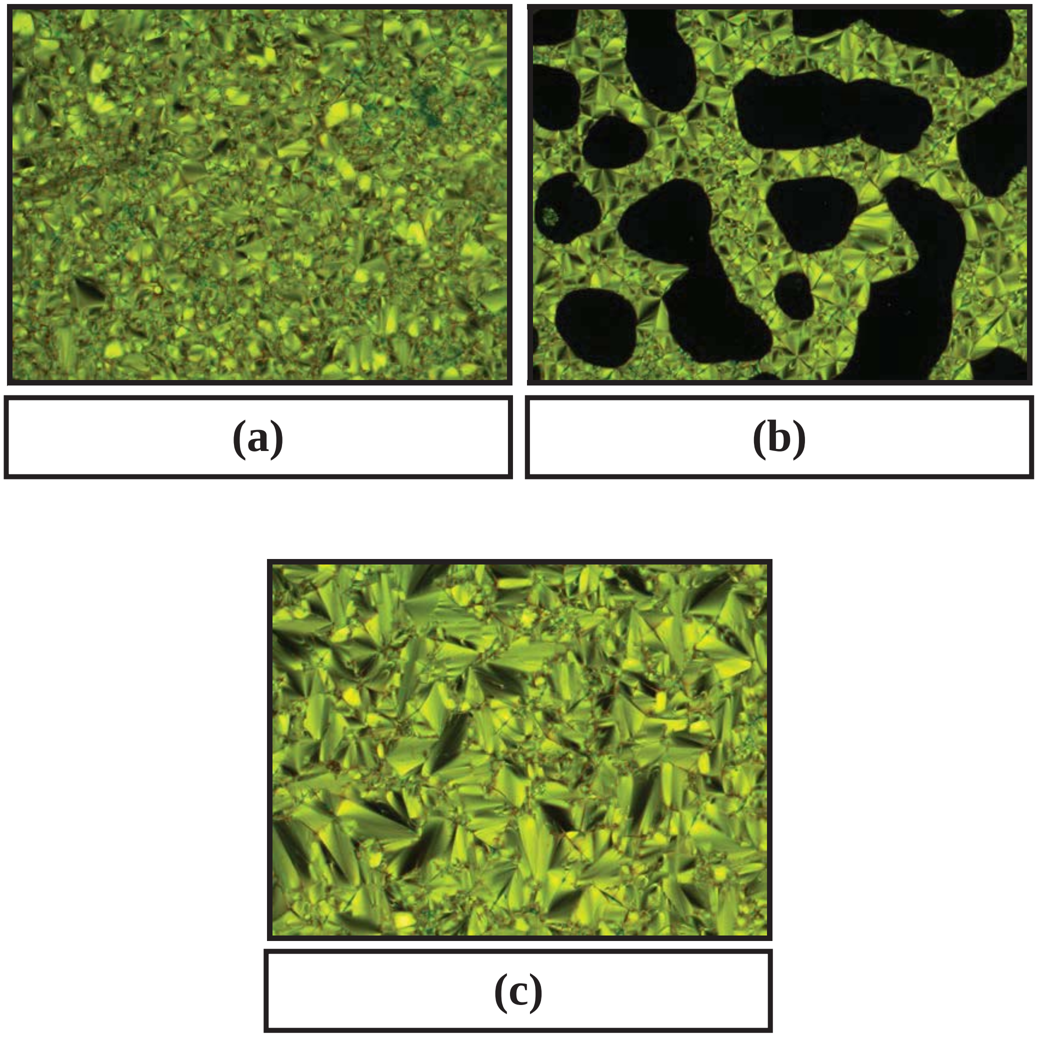

(a)
(b)

Figure 10. Polarised optical microphotographs of compound 25. (a) SmC-broken focal conic texture observed at 58.7 °C on cooling and (b) SmC-broken focal conic texture observed at 53.6 °C on heating.



(a)

(b)

(c)

Figure 11. Polarised optical microphotographs of compound 29. (a) SmC-broken focal conic texture observed at 66.7 °C on cooling, (b) SmC-Isotropic phase transition observed at 77.9 °C on heating and (c) SmC-broken focal conic texture observed at 73.3 °C on cooling.

5.4. References

[1] M. G. Clark, K. J. Harrison and E. P. Raynes, *Phys. Technol.*, **11**(6), 232-240, 1980.

[2] G. H. Heilmeier and L. A. Zanoni, *Appl. Phys. Lett.*, **13**(3), 91-92, 1968.

[3] D. L. White and G. N. Taylor, *J. Appl. Phys.*, **45**(11), 4718-4723, 1974.

[4] R. Dabrowski and K. Czuprynski, *Mol. Cryst. Liq. Cryst.*, **146**, 341-366, 1987.

[5] R. Dabrowski, B. Wazynska and B. Sosnowska, *Liq. Cryst.*, **1**(5), 415-428, 1986.

[6] B. Ziemnicka, A. De Vries, J. Doane and S. L. Arora, *Mol. Cryst. Liq. Cryst.*, **132**(3-4), 289-302, 1986.

[7] B. Wazynska, *Liq. Cryst.*, **3**(1), 85-93, 1988.

[8] J. W. Park, C. S. Bak and M. M. Labes, *J. Am. Chem. Soc.*, **97**(15), 4398-4400, 1975.

[9] J. L. Yu and M. M. Labes, *Mol. Cryst. Liq. Cryst.*, **54**(1-2), 1-8, 1979.

[10] A. C. Griffin, R. F. Fisher and S. J. Havens, *J. Am. Chem. Soc.*, **100**(20), 6329-6333, 1978.

[11] J. H. Macmillan, H. John and M. M. Labes, *Mol. Cryst. Liq. Cryst.*, **56**, 7-12, 1979.

[12] M. Domon and J. Billard, *J. Phys. Colloques*, **40**(3), 413-418, 1979.

[13] B. S. Srikanta and N. V. Madhusudana, *Mol. Cryst. Liq. Cryst.*, **99**(1-4), 203-221, 1983.

[14] C. S. Oh, *Mol. Cryst. Liq. Cryst.*, **42**(1-3), 1011-1024, 1977.

[15] W. Waclawek, R. Dabrowski and A. Domagala, *Mol. Cryst. Liq. Cryst.*, **84**(1-4), 255-265, 1982.

[16] K. W. Sadowska, A. Zywocinski, J. Stecki and R. Dabrowski, *J. Phys. France*, **43**(11), 1673-1678, 1982.

[17] Z. Raszewski, *Liq. Cryst.*, **3**(3), 307-322, 1988.

[18] H. Sackmann, *J. Phys. Colloques*, 40(C3), 5-8, 1979.

[19] A. M. Levelut, Y. Fang and C. Destrade, *Liq. Cryst.*, **4**(4), 441-448, 1989.

[20] J. M. Lohar and J. S. Dave Jr., *Mol. Cryst. Liq. Cryst.*, **103**, 181-192, 1983.

[21] R. Gupta and R. A. Vora, *Mol. Cryst. Liq. Cryst.*, **106**, 147-159, 1984.

[22] R. A. Vora and S. J. Rajput, *Mol. Cryst. Liq. Cryst.*, **209**, 265-277, 1991.

[23] R. A. Vora, R. Gupta and K. Patel, *Mol. Cryst. Liq. Cryst.*, **209**, 251-263, 1991.

[24] Nagappa, R. H. Nayak, J. Mahadeva, K. M. Lokanatha Rai and P. R. Alapati, *Mol. Cryst. Liq. Cryst.*, **301**, 7-12, 1997.

[25] J. S. Dave, M. R. Menon and P. R. Patel, *Mol. Cryst. Liq. Cryst.*, **365**, 581-591, 2001.

[26] S. Delica, M. Estonactoc, M. C. Micaller, L. Cada and Z. Domingo, *Mol. Cryst. Liq. Cryst.*, **366**, 101-106, 2001.

[27] S. L. Srivastava and R. Dhar, *Mol. Cryst. Liq. Cryst.*, **366**, 79-90, 2001.

[28] Nagappa, S. K. Naveen Kumar, J. Mahadeva and P. Nagaraj, *Mol. Cryst. Liq. Cryst.*, **409**, 1-8, 2004.

[29] J. Mahadeva, T. N. Govindaiah, K. Rajashekara Prasad and Nagappa, *Mol. Cryst. Liq. Cryst.*, **511**, 218-230, 2009.

[30] P. J. Le Masurier and G. R. Luckhurst, *Liq. Cryst.*, **25**(1), 63-72, 1998.

[31] M. Li, E. Zhou and J. Xu, *Liq. Cryst.*, **24**(3), 381-385, 1998.

[32] R. I. Nessim, *Liq. Cryst.*, **30**(2), 211-218, 2003.

[33] B. R. Jaishi and P. K. Mandal, *Liq. Cryst.*, **33**(7), 753-765, 2006.

[34] D.-K. Yang, Y. Yin and H. Liu, *Liq. Cryst.*, **34**(5), 605-609, 2007.

[35] H. Ma, X. Fu, H. Okada and H. Onnagawa, *Liq. Cryst.*, **36**(8), 835-838, 2009.

[36] D. Ž. Obadović, A. Vajda, A. Jákli, A. Menyhárd, M. Kohout, J. Svoboda, M. Stojanović, N. Éber, G. Galli and K. Fodor-Csorba, *Liq. Cryst.*, **37**(5), 527-536, 2010.

[37] A. D. L. Chandani, A. Fukuda, S. Kumar and J. K. Vij, *Liq. Cryst.*, **38**(5), 663-668, 2011.

[38] N. Nagappa, J. Mahadeva, S. Mohyeddine, C. V. Yelamaggad, S. A. Nagami, U. S. Herimath, D. Revannasiddaiah and M. V. Krishnaswamy, *Mol. Cryst. Liq. Cryst.*, **508**, 242-248, 2009.

[39] K. C. Majumdar, R. K. Sinha and S. Mondal, *Mol. Cryst. Liq. Cryst.*, **524**, 36-43, 2010.

[40] T. N. Govindaiah, Nagappa, P. M. Sathyanarayana, J. Mahadeva and H. R. Sreepad, *Mol. Cryst. Liq. Cryst.*, **548**, 120-125, 2011.

[41] T. N. Govindaiah, H. R. Sreepad, P. M. Sathyanarayana, J. Mahadeva and Nagappa, *Mol. Cryst. Liq. Cryst.*, **552**, 24-32, 2012.

[42] T. N. Govindaiah, H. R. Sreepad and Nagappa, *Mol. Cryst. Liq. Cryst.*, **557**, 11-17, 2012.

[43] J. S. Dave, P. D. Patel and H. S. Bhatt, *Mol. Cryst. Liq. Cryst.*, **575**, 8-21, 2013.

[44] S. H. Ou, V. Percec, J. A. Mann, J. B. Lando, L. Zhou and K. D. Singer, *Macromolecules*, **26**(26), 7263-7273, 1993.

[45] G. W. Gray, *J. Phys. Colloques*, **36**(C1), 337-347, 1975.

[46] G. W. Gray, K. J. Harrison, J. A. Nash, J. Constant, D. S. Hulme, J. Kirton and E. P. Raynes, *Liquid Crystals and Ordered Fluids*, **2**, 617-643, 1973.

[47] V. R. Teckchandani, *Studies of Potential Mesogenic Materials*, Ph. D. Thesis, The M. S. University of Baroda, Vadodara, 1992.

SUMMARY

Chapter 1

Liquid crystals are known for about hundred and twenty five years. The credit for the discovery of liquid crystalline phenomenon is given to an Austrian botanist Reinitzer. He observed that the compound cholesteryl benzoate appeared to have two melting points. At 145 °C the solid structure collapsed to form a turbid liquid (liquid crystal), which on further heating became transparent at 179 °C, giving a true isotropic liquid. The term Liquid Crystals suggests that a substance is in two quite different states of matter at the same time. A crystal can not possess the properties of a perfect liquid or vice versa. Conventionally, matter exists in one of the three well-defined states of aggregation, namely, solids, liquids and gases, each having properties characteristic of its own. The transition from one state to another normally occurs at a very precise temperature. When pure crystalline solid is heated beyond its melting temperature, it undergoes a single transition to isotropic liquid. There are, however, many organic compounds that do not immediately transform to liquid phase when heated beyond the melting temperature but exhibit more than a single transition from solid to liquid showing the existence of one or more intermediate phases, exhibiting the properties of both solids and liquids. Lehmann described this state as fluid crystals and established for the first time the terminology ‘liquid crystals’. Many other terms such as mesomorphic state, mesoform, mesophase, mesogen, anisotropic liquid, fluid crystals have been proposed and are used but the term ‘liquid crystals’ is still widely used.

Liquid crystals have been divided into two main categories, Thermotropic liquid crystals and Lyotropic liquid crystals in accordance with the manner in which these are obtained. Liquid crystals formed by heating solids are known as Thermotropic liquid crystals. The liquid crystalline systems formed when certain compounds are treated with a controlled amount of water or the polar solvent is known as Lyotropic liquid crystals.

With a large number of liquid crystalline substances available, Friedel carried out detailed optical studies of these compounds and classified them into three types as smectic, nematic and cholesteric. Smectic and nematic are the most common types of mesophases and the study of their optical properties made it possible to assign structures to them. These structures do not extend uniformly throughout the melt but the whole melt is composed of the random orientations of groups or swarms of molecules as proposed by Bose's swarm theory.

Many mesomorphic substances which have been studied are either of exclusively smectic structure or of exclusively nematic structure, but some can exist as both types of structures, smectic followed by nematic, and in these cases there are always definite transition temperatures defining the stability of different phases, which are completely reproducible. A few substances have been found to possess more than one phase and here also the temperature range of stability of the different phases are sharply defined. This is known as polymesomorphism.

Liquid crystalline materials are being exploited for their different applications. New developments have further encouraged chemists to explore structural variations in the liquid crystalline materials in search of new liquid crystals for different applications.

Chapter 2

This chapter deals with the syntheses and detailed characterization for the thirteen homologues of thiadiazole mesogens.

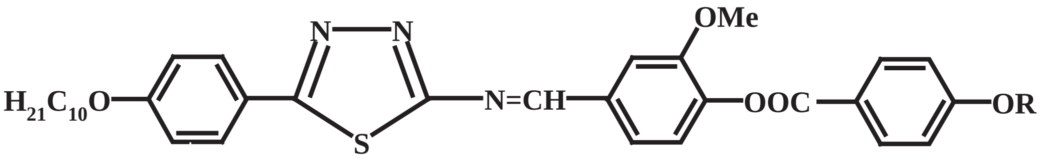
Heterocycles are of great important as core units in liquid crystals due to their ability to impart lateral and / or longitudinal dipoles combined with changes in the molecular shape. These materials hold great potential for use in spatial light modulation, all-optical signal processing, optical information storage, organic thin-film transistors, fast switching ferroelectric materials, fluorescent probes for the detection and analysis of biomolecules *etc*. Also, these materials have been patented in agricultural field as herbicides, fungicides and bactericides.

1,3,4-Thiadiazoles are relatively common in the liquid crystal literature although the variety of structural modifications that have been studied are actually very limited. The majority of systems have the 1,3,4-thiadiazole core substituted at the 2 and 5-positions by aryl units or a combination of aryl and alkyl / cyclo alkyl units. These materials are constructed through sulfurization and cyclization of appropriate diacylhydrazines. The 1,3,4-thiadiazole core imparts a large lateral dipole from S to the centre of the N-N bond.

In the present study it was proposed to synthesize low molecular weight materials with special structural features as well as to study the effect of rigidity on the liquid crystalline properties of the mesogenic systems. With this in view, we have synthesized homologous series **I** as shown in figure 1 and studied their mesogenic properties. The purity of the compounds was checked by thin layer chromatography (TLC) and mesogenic properties of these compounds were observed under polarizing optical microscope provided with a Linkam heating stage. The transition temperatures were confirmed by Differential Scanning Calorimeter. Lower members exhibit nematic phases and higher members exhibit both smectic and nematic phases. Nematic phase shows its thread like texture and smectic phase shows broken fan shape texture (figure 2). Smectic phase commences from *n*-heptyl derivative and persist upto last members of the series. The average thermal stability of compounds of series is higher than reported series due to the introduction of rigid phenyl core.

The plot of transition temperatures versus number of carbon atoms in alkoxy chain exhibits falling tendency for Nematic-Isotropic transition temperatures. Smectic C-Nematic transition temperature curve rises to the maximum and then falls off at *n*-octadecyloxy derivative. The Smectic C-Nematic transition temperature curve rises but does not merge with the falling Nematic-Isotropic transition temperature curve even in the *n*-octadecyloxy derivative.

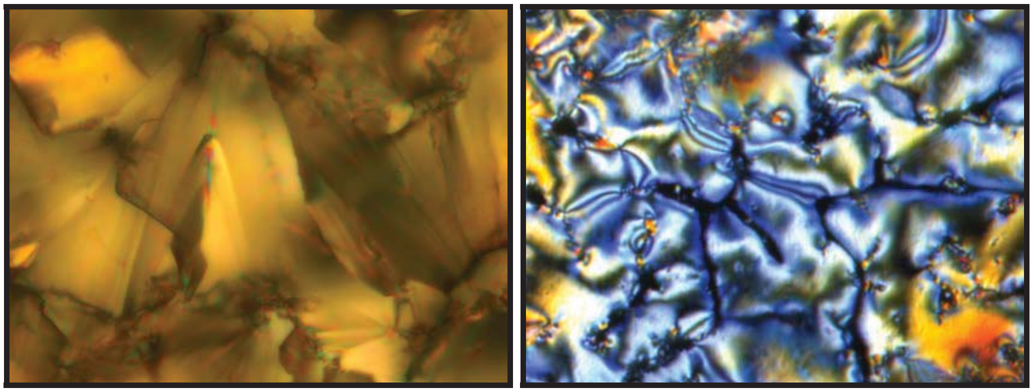
The calorimetric study has provided information of enthalpy changes involved in different phase transitions. It also helps in further confirmation of phases exhibited by the homologues.



Series I

Where, R = n-C_nH_{2n+1}, n = 1 to 8, 10, 12, 14, 16 and 18.

Figure 1. <u>Structure of the series I compounds</u>

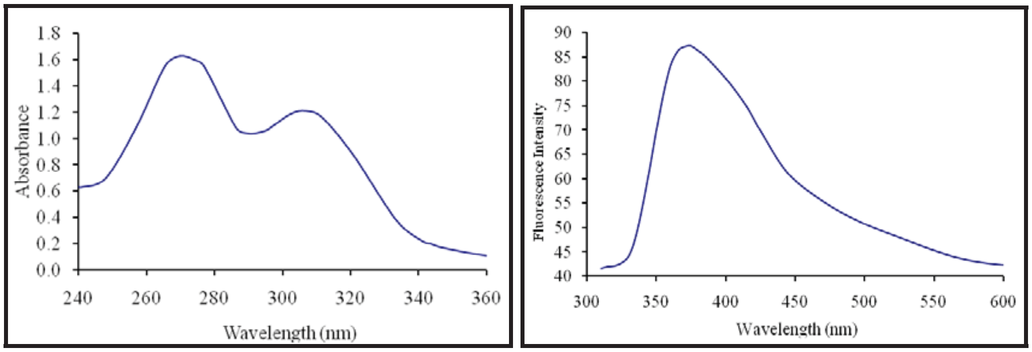


Smectic C texture at 138.6 °C

Nematic texture at 179.0 °C

Figure 2. Polarized optical microphotograph of homologue C_{14} on heating

1,3,4-Thiadiazoles have been investigated as a candidate for light-emitting materials due to their fluorescent properties. We were interested in studying some optical properties of our synthesized compounds. Hence, the ultraviolet-visible (UV-Vis) and fluorescence spectra were recorded. The UV-Vis absorption and fluorescence spectra of the homologue C_{14} in $CHCl_3$ solution are shown in figure 3. In UV-Vis absorption spectra, the λmax occurred at 307 nm. The fluorescent emission peak is observed at 375 nm. All homologues of the series exhibit fluorescence property.



UV-vis absorption spectra of homologue C_{14}

Fluorescence spectra of homologue C_{14}

Figure 3

Chapter 3

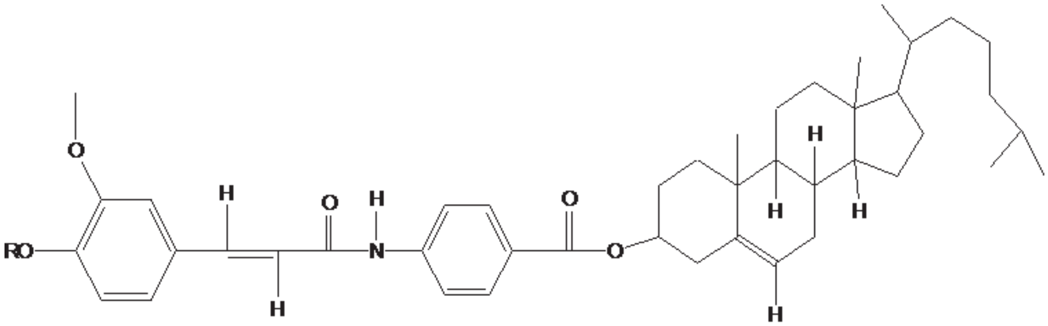
This chapter consists of the syntheses and characterization of the thirteen homologues having a terminal cholesteryl moiety.

Over the last decade, cholesterol-based liquid crystals have attracted attention from more and more researchers, because cholesterol is abundant in nature and a commercially available chiral compound. Moreover, cholesterol-based compounds have many unique optical properties, such as selective reflection, circular dichroism, electro-optical and magneto-optical effects; they could be applied to optical storage, optical switching, nonlinear optics and liquid crystal display devices.

Many liquid crystalline compounds consisting of a cholesteryl ester unit as a chiral segment joined to different mesogenic moieties such as benzoate ester, Schiff's base, azobenzene, biphenyl or tolane etc., through flexible spacers, have been synthesized and extensively studied. Their liquid crystalline properties are affected by spacer length and polarity, the length of the terminal group attached to the aromatic rings, as well as the type of linking group between the spacer and mesogenic units, such as ethers and esters. They have shown interesting mesomorphic phase behaviour including SmA phases, Twist Grain Boundary (TGB) phases, blue phases, and the chiral nematic (N*) mesophase. Highly viscous Cholesteric liquid crystalline materials show mechanical properties that make them very attractive for a new generation of mechanical sensors or materials able to visualize mechanical stress.

We have synthesized homologous series **II** possesses amide linkage and a terminus cholesteryl moiety as shown in figure 4 and studied their mesogenic properties. The cholesterol imparts chirality hence series is also chiral. Mesogenic properties of these compounds were checked by polarizing optical microscope provided with a Linkam heating stage. The transition temperatures were confirmed by Differential Scanning Calorimeter. All the compounds exhibit chiral nematic phase of broad range and high transition temperatures. Chiral nematic phase shows its oily streaks texture (figure 5). N* phase commences from methoxy derivative and persists upto last members of the series. Hence, it is purely nematogenic series. -CH=CH- spacer increases the flexibility and eliminates the Sm mesophase. The average thermal stability of compounds of series is lower than reported series due to the introduction of flexible spacer and lateral methoxy substituent.

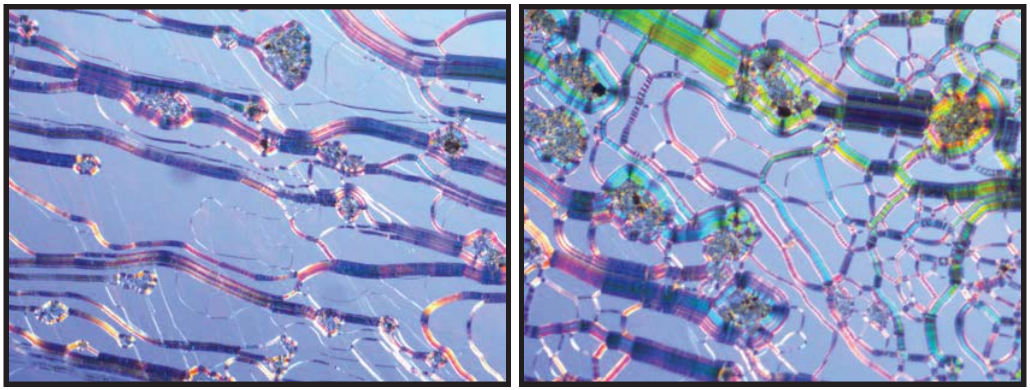
The plot of transition temperatures versus number of carbon atoms in alkoxy chain exhibits odd-even effect and falling tendency for N*-Isotropic transition temperatures.



Series II

Where, R = n-C_nH_{2n+1}, n = 1 to 8, 10, 12, 14, 16 and 18.

Figure 4. **Structure of the series II compounds**



Chiral N texture at 225.0 °C

Chiral N texture at 246.0 °C

Figure 5. **Polarized optical microphotograph of homologue C_5 on heating**

These cholesteric derivatives have been investigated for Specific Optical Rotation. The results for the homologues C_5 and C_6 are as follows:

Homologue	**[α]** **(degrees)**
C_5	+18.1
C_6	+17.7

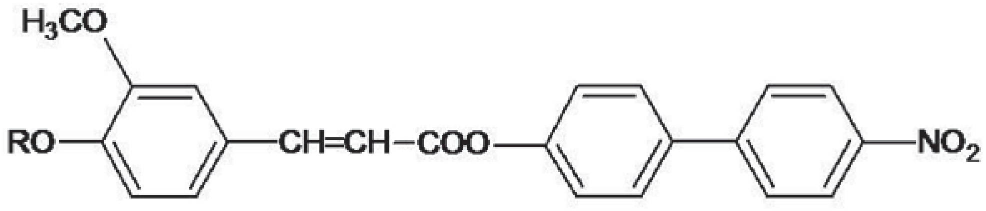
Chapter 4

This chapter includes the syntheses and detailed characterization of the thirteen compounds of biphenyl homologues.

Linearity, rigidity and polarizability are important factors for a molecule to display liquid crystalline properties. Different aromatic moieties have been used as rigid core in synthesizing liquid crystals. Biphenyl can be seen as rigid core of many mesogenic compounds and liquid crystalline or semi-crystalline aromatic polymers. Moreover, since biphenyl is a molecule interesting and fascinating itself, it has been the object, over many years, of many studies, both experimental and theoretical. Such interest is mainly due to its relatively simple structure and to the strong conformational dependence of the molecule on the phase of the material.

Biphenyl provides rich source of liquid crystals which are **thermally more stable** than those of benzene substituted analogues, which increase linearity and rigidity of the molecules. Biphenyl derivatives are also important in the formation of ferroelectric and anti-ferroelectric liquid crystals. Furthermore, biphenyl derivatives are able to undergo functionalization reactions, providing access to a variety of compounds. Mostly 4, 4’-substituted biphenyl derivatives exhibit one or more smectic phases and extraordinarily high clearing temperatures.

In present investigation, we have synthesized homologous series **III** as shown in figure 6 and carried out study of the effect of cinnamoyl linkage and nitrobiphenyl moiety on the mesomorphic properties. Mesogenic properties of these compounds were checked by polarizing optical microscope provided with a Linkam heating stage. The transition temperatures were confirmed by Differential Scanning Calorimeter.



Series III

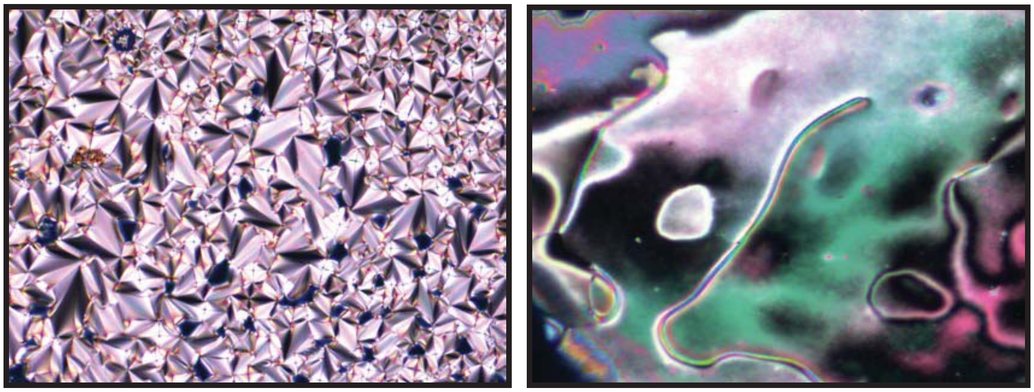
Where, R = n-C_nH_{2n+1}, n = 1 to 8, 10, 12, 14, 16 and 18.

Figure 6. **<u>Structure of the series III compounds</u>**

Lower members exhibit both smectic and nematic phases and higher members exhibit only smectic phase. Smectic phase shows focal conic texture and Nematic phase shows thread like texture as shown in figure 7. Smectogenic character should predominate at the expense of nematic mesophase. Smectic A phase commences from methoxy derivative and persist upto last member of the series. Nematic phase disappears from *n*-hexyloxy derivative. Introduction of methoxy group increases acoplanarity, which results in decrease in the transition temperatures and also the thermal stability of compounds.

In the plot of transition temperatures versus number of carbon atoms in the alkoxy chain, Smectic A-Nematic and Nematic-Isotropic transition temperature curves exhibit Zig-Zag patterns upto *n*-pentyloxy derivative of the series. The Nematic-Isotropic transition temperature curve raises steeply upto *n*-decyloxy derivative then falls off upto last member of the series.

The members of the series (I to III) are characterized by standard spectroscopic methods.



Smectic A texture at 189.3 °C

Nematic texture at 204.6 °C

Figure 7. Polarized optical microphotograph of homologue C_5 on heating

Chapter 5

This chapter deals with the syntheses and evaluation of liquid crystalline properties of model compounds and binary mixtures.

Number of model compounds having ester and amide linkages as well as ester and azoic linkages are synthesized to understand the mesogenic properties of the homologues. Most of the compounds exhibit mesomorphism. Structural aspects and mesogenic properties are correlated which throws good light on the subject.

Liquid Crystals with low crystal - mesophase transition temperatures and with wide phase length have been primary goal of organic chemists in recent years. Since the occurrence of single component, room temperature Liquid Crystal with wide mesophase is rare, it is necessary to mix two or more low melting materials which may give room temperature mesomorphic mixture with wide mesophase length. Just as the melting points of the solids are depressed by the addition of other substances, so also are the transition temperatures of liquid crystals lowered by the addition of other substances.

In general, binary systems exhibiting mixed mesomorphism can be of three types:

- Where both the components are mesomorphic,
- Where only one component is mesomorphic and
- Where both the components are non-mesomorphic

We have taken following system A and studied their binary mixtures.

System A:

Component a: 4-nitro-4’-*n*-octyloxy biphenyl

Component b: 4-nitro-4’-*n*-dodecyloxy biphenyl

We have also focused on binary mixture study of system B and studied their mesomorphic properties.

System B:

Component a: 4’-nitro-biphenyl-4-*n*-tetradecanoate

Component b: 4’-nitro-biphenyl-4-*n*-hexadecanoate

Binary mixtures are helpful in lowering the transition temperatures of liquid crystalline compounds by the addition of other substances. Binary mixtures are driving force for the liquid crystalline applications. Binary mixtures are also useful for phase identification.

References

[1] J. S. Dave, *J. Indian Chem. Soc.*, **72**(5), 293-306, 1995.

[2] A. Mohd and S. Kumar, *Eur. J. Med. Chem.*, **39**(6), 535-545, 2004.

[3] S. Sugita, S. Toda, T. Yamashita and T. Teraji, *Bull. Chem. Soc. Jpn.*, **66**(2), 568-572, 1993.

[4] M. Parra, J. Vergara, C. Zúñiga, E. Soto, T. Sierra and J. L. Serrano, *Liq. Cryst.*, **32**(4), 457-462, 2005.

[5] M. Parra, J. Vergara, P. Hidalgo, J. Barberá and T. Sierra, *Liq. Cryst.*, **33**(6), 739-745, 2006.

[6] A. S. Achalkumar, U. S. Hiremath, D. S. Shankar Rao and C. V. Yelamaggad, *Liq. Cryst.*, **38**(11-12), 1563-1589, 2011.

[7] H. -C. Lee, Z. Lu, P. A. Henderson, M. F. Achard, W. A. K. Mahmood, G.-Y. Yeap and C. T. Imrie, *Liq. Cryst.*, **39**(2), 259-268, 2012.

[8] S. Sauer, S. Saliba, S. Tussetschläger, A. Baro, W. Frey, F. Giesselmann, S. Laschat and W. Kantlehner, *Liq. Cryst.*, **36**(3), 275-299, 2009.

[9] Z. Cheng, H. Cao, D. Zhao, W. Hu, W. He, X. Yuan, J. Xiao, H. Zhang and H. Yang, *Liq. Cryst.*, **38**(1), 9-15, 2011.

[10] I. Nishiyama, J. Yamamoto, J. W. Goodby and H. Yokoyama, *J. Mater. Chem.*, **13**(10), 2429-2435, 2003.

[11] M. Brodzik and R. Dabrowski, *Liq. Cryst.*, **18**(1), 61-66, 1995.

[12] B. J. B. Folmar, R. P. Sijbesma, R. M. Versteegen, J. A. J. van der Rijt and E. W. Meijer, *Adv. Mater.*, **12**(12), 874-878, 2000.

[13] M. Li, C. Guo and Y. Wu, *Liq. Cryst.*, **29**(8), 1031-1037, 2002.

CONFERENCES / SEMINARS PRESENTATIONS

SYNTHESIS AND STUDY OF AZOIC LIQUID CRYSTALLINE COMPOUNDS HAVING DIFFERENT SUBSTITUENTS

Nilesh K. Patel and R. C. Tandel

Presented at
Regional Science Congress on “Science for Shaping the Future of India”
The M. S. University of Baroda, Vadodara
15th - 16th September 2012.

ABSTRACT

Thirteen compounds having ester and azo linkages have been synthesized and their mesogenic properties are studied. All the derivatives exhibit smectic (focal conic texture) as well as nematic mesophase (thread like textures). Compounds have terminal and lateral substituents (-Cl and -NO_2), due to this reason the molecules of series exhibit positive dielectric anisotropy. The presence of lateral substituents has resulted into lower solid-mesomorphic transition temperatures. Thermal stability of series I is higher than those of reported series. The effect of strong polar -CN and -NO_2 lateral / terminal groups would be comparable on the increased polarizability of the system. The plot of transition temperatures verses number of carbon atoms in the alkoxy chain exhibits usual odd-even effects of the nematic-isotropic transition temperatures. In this series the smectic-nematic transition temperature curve rises steeply to maximum and merges with the falling nematic-isotropic transition temperature curve at the hexadecyloxy member. The structure of the synthesized compounds were characterized by IR, NMR, Mass, DSC and TGA. The transition temperatures of the prepared compounds are confirmed by DSC and microscopic study. The purity of the compounds was checked by TLC. Series I: 4(4’-n alkoxy benzoyloxy)-2’’-chloro-4’’-nitroazo benzene.

SYNTHESIS AND STUDY OF MESOMORPHIC PROPERTIES OF SCHIFF'S BASES CONTAINING 1,3,4-THIADIAZOLE MOIETY

Nilesh K. Patel and R. C. Tandel

Presented at
17th National Conference on Liquid Crystals
Veer Narmad South Gujarat University, Surat
15th - 17th November 2010.

ABSTRACT

A New homologous series of Schiff's bases derived from substituted 2-amino 1,3,4-thiadiazole has been synthesized and their liquid crystalline properties investigated by Polarizing Optical Microscope and Differential Scanning Calorimetry. Thirteen homologues were synthesized by condensing substituted 4-*n*-alkoxy benzoyloxy benzaldehydes with substituted 2-amino 1,3,4-thiadiazole. The Methyl to *n*-hexyl derivatives exhibit only nematic phases. The *n*-heptyl to *n*-octadecyl derivatives exhibit smectic and nematic phases. The plot of transition temperatures versus number of carbon atoms in the alkoxy chain exhibits falling tendency for nematic-isotropic transition temperatures and raising tendency for smectic-nematic transition temperatures. The mesomorphic and thermal stability is compared with other homologous series. The result indicates that ester linkage enhances smectic thermal stability but decreases nematic thermal stability. The enhancement in smectic phase is much high. Compounds are characterized by elemental analysis, IR spectral data, Mass spectral data, DSC, NMR and microscopic study.

SYNTHESIS AND STUDY OF SOME MESOGENS HAVING CHALCONE LINKAGE

R. C. Tandel, Nilesh Patel and P. Rakshit

Presented at
16th National Conference on Liquid Crystals
University of Lucknow, Lucknow
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ABSTRACT

Chalcone is one of the important chemical compounds and is being studied extensively because of its significant use of application in various sectors. In the field of biology and biochemistry, chalcone has been claimed to be one of the compound that plays a vital role in antitumor, anti-inflammatory and anti-malarial activities. It has also been documented that the chalcone possesses a remarkable non-linear optical (NLO) property, which is an essential element for optical communications devices. Two chalcone system I and II were synthesized. In system I, intermediates ethyl 7-hydroxy coumarin-3-carboxylate, ethyl 7-alkoxy coumarin-3-carboxylate and 7-*n*-alkoxy coumarin-3-carboxylic acids were synthesized which are non-mesogenic in nature but when acid chloride of respective 7-*n*-alkoxy coumarin-3-carboxylic acid condenses with 4-hydroxy chalcone derivative having 3-amino as a terminal group exhibits smectic and nematic phases. The mesogenic-isotropic transition temperatures change in a regular manner hence series may show odd-even effect for smectic-nematic and nematic-isotropic transition temperatures. Compounds show high thermal stability of nematic phases. In the II system, compounds were synthesized by condensing two moles of respective 4-*n*-alkoxy benzoyl chloride with different chalcone derivatives containing 3-amino as a terminal group. Compounds show wide range of nematic thermal stability due to more polarizability. The study of the effect of chemical constitution on mesomorphic properties has revealed that the introduction of a terminal substitution increases the solid-mesomorphic and mesomorphic-isotropic transition temperatures but introduction of lateral substitutions decreases both that

temperatures. The structure of the synthesized compounds was characterized by elemental analysis and spectral data and the purity of the compounds were checked by TLC method.

THERMOTROPIC LIQUID CRYSTALLINE POLYESTERAMIDES WITH AZO LINKAGES AND FLEXIBLE SPACERS

A. B. Mistry, Nilesh K. Patel and R. C. Tandel

Presented at
15th National Conference on Liquid Crystals
Indian Institute of Science, Bangalore
13th - 15th October 2008.

ABSTRACT

Six main chain liquid crystalline polymers were synthesized and their different properties are studied. Polymeric azo mesogens were obtained by condensing substituted (methyl or chloro) 4-amino-4’-hydroxy azo benzenes with different diacid chlorides. The diacid moiety was changed and obtained from α, ω-bis(4’-carboxy phenoxy) alkanes (e.g. propane, butane and hexane) was conducive to mesomorphism and the polymers exhibited only nematic behavior. The lateral substituents affect the solid-mesogenic transition temperatures markedly. Polymers having lateral chloro and methyl substituents have lower solid-mesomorphic transition temperatures compared to unsubstituted polymers. Intrinsic viscosities of polymers were found in the range of 0.135-0.2dL/g in N-methyl-2-pyrrrolidone at 37 ± 1 °C. The polymers were characterized by elemental analysis, IR spectra, viscosity, TGA, conductivity, Fluorescent study etc.

SYNTHESIS AND STUDY OF CHOLESTERYL 4-(4’-*N*-METHOXY CINNAMOYL) AMIDE BENZOATES

Nilesh K. Patel and R. C. Tandel

Presented at
15th National Conference on Liquid Crystals
Indian Institute of Science, Bangalore
13th - 15th October 2008.

ABSTRACT

A new series of mesogenic compounds having a cholesteryl moiety has been synthesized by condensing *p*-amino benzoate of cholesterol and methoxy substituted 4-*n*-alkoxy cinnamoyl chlorides and their liquid crystalline properties has been studied. All the members of the series are enantiotropic and exhibit chiral nematic (N*) mesophase. The plot of transition temperatures versus number of carbon atoms in the alkoxy chain exhibits odd-even effect and falling tendency for N*-isotropic transition temperatures. The compounds exhibit oily streak textures that on slight disturbance change to the plane textures and show iridescent colours. High anisotropy, linearity and intermolecular hydrogen bonding confer rich mesomorphic properties on the system. Intermolecular hydrogen bonding arising from amide linkage can lead to supramolecular motifs.

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(Article in Press)

SYNTHESIS AND MESOMORPHIC BEHAVIOUR OF CALAMITIC LIQUID CRYSTALS WITH BIPHENYL MOIETY

R. C. TANDEL* AND NILESH K. PATEL
Chemistry Department, The M. S. University of Baroda, Vadodara - 390 002, India.

ABSTRACT

A new mesogenic homologous series having a biphenyl moiety has been synthesized condensing 4-hydroxy-4'-nitrobiphenyl and methoxy substituted 4-*n*-alkoxy cinnamoyl chlorides and their liquid crystalline properties have been studied. All the members of the series are enantiotropic. The methyl to *n*-pentyl derivatives exhibits both Smectic A (SmA) and Nematic (N) phases; the higher members, starting with the *n*-hexyl derivative show only SmA phases. The plot of transition temperatures versus number of carbon atoms in the alkoxy chain exhibits zig-zag pattern for Sm-N and N-Isotropic (Iso) transition temperature curves. The average thermal stability is compared with other related homologous series. Introduction of polar nitro group increases significant intermolecular force of attraction which stabilizes the molecular orientation. This results into the increase in the thermal stability of the system.

Keywords biphenyl moiety; cinnamates; calamitic liquid crystals; smectic; nematic

*Corresponding author. Email: tandelcy@yahoo.com

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Synthesis and mesomorphic properties of chiral nematic liquid crystals based on cholesterol

R.C. Tandel* and Nilesh K. Patel

Chemistry Department, Faculty of Science, The M.S. University of Baroda, Vadodara, India

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A new series of mesogenic compounds having a cholesteryl moiety has been synthesised by condensing *p*-amino benzoate of cholesterol and methoxy substituted 4-*n*-alkoxy cinnamoyl chlorides and their liquid crystalline properties has been studied. All the members of the series are enantiotropic and exhibit chiral nematic (N*) mesophase. The plot of transition temperatures versus number of carbon atoms in the alkoxy chain exhibits odd–even effect and falling tendency for N*–isotropic transition temperatures. The compounds exhibit oily streak textures that on slight disturbance change to the plane textures and show iridescent colours. High anisotropy, linearity and intermolecular hydrogen bonding confer rich mesomorphic properties on the system. Intermolecular hydrogen bonding arising from amide linkage can lead to supramolecular motifs.

Keywords: cholesteryl moiety; cinnamates; chiral nematic (N*) mesophases; intermolecular H-bonding; ester; amide

1. Introduction

Over the last decade, cholesterol-based liquid crystals have attracted attention from more and more researchers, because cholesterol is abundant in nature and a commercially available chiral compound. Moreover, cholesterol-based compounds have many unique optical properties, such as selective reflection, circular dichroism, electro-optical and magneto-optical effects; they could be applied to optical storage, optical switching, non-linear optics and liquid crystal display devices.[1–3]

Many liquid crystalline compounds consisting of a cholesteryl ester unit as a chiral segment joined to different mesogenic moieties such as benzoate ester, Schiff's base, azobenzene, biphenyl, tolane, etc., through flexible spacers, have been synthesised and extensively studied.[4–18] Their liquid crystalline properties are affected by spacer length and polarity, the length of the terminal group attached to the aromatic rings, as well as the type of linking group between the spacer and mesogenic units, such as ethers and esters. They have shown interesting mesomorphic phase behaviour including SmA phases, TGB phases, blue phases and the N* mesophases.

Highly viscous cholesteric liquid crystal materials show mechanical properties that make them very attractive for a new generation of mechanical sensors or materials able to visualise mechanical stress.[19,20] New cholesteric monomers and their corresponding smectic polysiloxanes based on cholesteryl groups were important for the structure–property relationships of new chiral monomers and polymers which are also useful to obtain piezoelectric liquid crystal networks by reaction of these monomers with a nematic cross-linking agent.[21,22] Zhang et al. have fabricated polymer-stabilised cholesteric liquid crystals by ultraviolet-induced polymerisation of photo polymerisable acrylate monomers mixed in a cholesteric liquid crystal.[23,24] Imrie and co-workers have designed cholesteryl-based trimers [25] and tetramers [26] and established that the formation of smectic phases is strongly dependent on the length and parity of the flexible spacers due to packing constraints, while the driving force for the phase formation is attributed to the specific electrostatic interactions. Majumdar et al. have synthesised number of cholesterol-based dimers and tetramers.[27–29] They have also reported an oxadiazole-base schiff's base dimers [30] and liquid crystalline trimers having cholesterol and ferrocene unit at the two terminal ends.[31] Pandey et al. have synthesised non-symmetrical liquid crystalline dimers [32] and Achalkumar et al. have also synthesised trimers and tetramers [33] derived from cholesterol. Lee et al. have synthesised cholesterol-based liquid crystal dimers which contain a sulphur–sulphur link in the flexible spacer.[34]

Recently, we have reported a series of mesogens having a cholesteryl moiety condensed with 4-(4′-*n*-alkoxy benzoyl) amido benzoyl chlorides.[35] In the present study, we have attempted to view the effect of non-mesogenic lateral methoxy cinnamic acids on cholesterol-based unit. We have synthesised a series of novel mesogenic compounds in which the cholesterol-based unit is connected to the 4-*n*-alkoxy-3-methoxy-cinnamic acids *via* an amide linkage and have investigated their liquid crystalline behaviour. Cholesteryl derivatives with amide linkages are rare. Kurian et al. have reported Schiff's bases containing

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*Corresponding author. Email: tandelcy@yahoo.com

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Synthesis and study of liquid crystalline properties of schiff's bases having 1,3,4-thiadiazole moiety

R.C. Tandel* and Nilesh K. Patel

Chemistry Department, Faculty of Science, The M.S. University of Baroda, Vadodara 390 002, India

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A new homologous series of Schiff's bases derived from substituted 2-amino 1,3,4-thiadiazole has been synthesised and their liquid crystalline properties investigated by Polarising Optical Microscope and Differential Scanning Calorimetry. Thirteen homologues were synthesised by condensing substituted 4-*n*-alkoxy benzoyloxy benzaldehydes with substituted 2-amino 1,3,4-thiadiazole. The methyl to *n*-hexyl derivatives exhibit only nematic phases. The *n*-heptyl to *n*-octadecyl derivatives exhibit smectic and nematic phases. The plot of transition temperatures versus number of carbon atoms in the alkoxy chain exhibits falling tendency for nematic–isotropic transition temperatures and rising tendency for smectic–nematic transition temperatures. The mesomorphic and thermal stability is compared with other homologous series. The result indicates that ester linkage enhances smectic thermal stability but decreases nematic thermal stability. The enhancement in smectic phase is much higher. Compounds are characterised by IR spectral data, NMR, DSC and microscopic study.

Keywords: 1,3,4-thiadiazoles; schiff's bases; mesogens; smectic C; nematic phases

1. Introduction

Heterocycles are of great importance as core units in liquid crystals due to their ability to impart lateral and/or longitudinal dipoles combined with changes in the molecular shape. These materials hold great potential for use in spatial light modulation,[1] all-optical signal processing, optical information storage,[2] organic thin-film transistors,[3,4] fast switching ferroelectric materials,[5] fluorescent probes for the detection and analysis of biomolecules, [6] etc. Also, some of these materials have been patented in agricultural field as herbicides, fungicides and bactericides.[7–9]

1,3,4-Thiadiazoles are relatively common in the literature although the variety of structural modifications that have been studied are actually very limited. The majority of systems have the 1,3,4-thiadiazole core substituted at the 2- and 5-positions by aryl units or a combination of aryl and alkyl/cyclo alkyl units.[10–15] These materials are constructed through sulphurisation and cyclisation of appropriate diacylhydrazines.[16–19] The 1,3,4-thiadiazole core imparts a large lateral dipole from S to the centre of the N–N bond (3.0 D) (Figure 1).[20]

In 1995, Tschierske et al. reported a novel synthesis of 2-alkylsulfanyl-5-aryl-1,3,4-thiadiazole for nonlinear optical (NLO) applications.[21] Tschierske et al. have also synthesised a number of 1,3,4-thiadiazole mesogens that are axially chiral by virtue of the incorporation of a chiral allene group.[10,18,22]

Parra et al. have reported different thiadiazole derivatives with amide,[23,24] imine [25–30] and azo [31,32] linking groups. They have also reported first amino-thiadiazole derivatives exhibiting columnar liquid crystalline behaviour.[33] This has opened an interesting possibility for designing new thiadiazole derivatives which might exhibit interesting columnar mesomorphic behaviour. Lai et al. have investigated complexes of azo compounds (with a terminal thiadiazole ring) with n-alkoxybenzoic acids.[34] Xu et al. have utilised a ring closure approach [35] whereby an appropriate thiosemicarbazone was chosen as the key precursor. Ester- linked ferroelectric 1,3,4-thiadiazole [36] and 1,3,4-thiadiazole-2-carboxylate esters have also been reported.[37] Some new 2,5-disubstituted 1,3,4-thiadiazole derivatives show antituberculosis activity.[38] They can also be used for the synthesis of novel fused heterocyclic system with a targeted 2,6-disubstituted imidazo[2,1-b] [1,3,4] thiadiazole involving various synthetic methodology.[39,40] Pati et al. have constructed macrocyclic compounds by incorporating a 2,5-thiadiazolo subunit into crown ether framework through carbon–oxygen linkages by the reaction of 2,5-dichloro-1,3,4-thiadiazole with polyethylene glycols. These compounds have been shown to possess unique chemical and biological properties.[41] Sato and co-workers have evaluated liquid

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*Corresponding author. Email: tandelcy@yahoo.com
Present address for R.C. Tandel: Applied Chemistry Department, Faculty of Technology and Engineering, The M. S. University of Baroda, Kalabhavan, Vadodara 390 001, India.

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Synthesis and Study of Main Chain Chalcone Polymers Exhibiting Nematic Phases

Tandel R.C., Gohil Jayvirsinh and Patel Nilesh K.
Chemistry Department, Faculty of Science, The M.S. University of Baroda, Vadodara, Gujarat, INDIA

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Abstract

The mesogenic main chain polymers of general structure-I were synthesized and their different properties are studied. All the polymers exhibit nematic phases. Classical nematic textures are observed in these polymers. None of the dihydroxy, amino-hydroxy or dicarboxy compounds shows liquid crystalline properties. The role of flexible methylene spacers, degree of polymerization and central linkage on exhibition of all the polymers is discussed. All the polymers are characterized by standard methods.

Keywords: : Liquid crystalline polymers, nematic phase, chalcone linkage, crystalline – crystalline etc.

Introduction

The rarity of mesogenic compounds having chalcone linkage and potential of polymers with this linkage for application prompted [1] to study the polymers with chalcone linkage. The first mesogenic homologous series with chalcone linkage have been reported [2] and studied polyesters and polyester-amides by varying flexible methylene spacers from $-(CH_2)_2-$ to $-(CH_2)$[illegible] in carboxy phenoxy diacid moiety[3,[illegible]]. They also varied the flexibility by using rigid and flexible dicarboxylic acids as comonomer. The chemistry and physics of high performance fiber spinning based on main chain liquid crystal polymer (MCLCP) solutions and melts was discussed, which is the largest industrial application of liquid crystal technology[5]. Recently Schiff base chalcone linkage thermotropic mesogens have synthesized and study the effect of substituent on liquid crystalline properties[[illegible],[illegible]]. The side chain liquid crystalline photoactive polymers with chalcone pendant chalcone moiety were synthesized and characterized[[illegible],9]. However polymers exhibited relatively higher transition temperatures.

The flexibility of the dicarboxylic acid moiety in the system increased by introducing 'oxyethylene spacers' in the place of methylene spacers[10,11]. Solid to mesomorphic and mesomorphic to isotropic transition temperatures were drastically reduced but florescent behavior was not affected. One striking feature of oxyethylene spacer polymers was that smectic mesophase was eliminated. This prompted us to investigate polymeric ester and ester-amide having chalcone linkage with increased flexibility by increasing number of methylene spacers to [illegible] and 10 i.e. $-(CH_2)$[illegible] and $-(CH_2)_{10}-$. With this in view polyester-amides and polyesters containing chalcone linkage were synthesized by the route given in figure 1.

It was proposed in the present study to concentrate on flexibility of carboxyl phenoxy diacid moiety by increasing flexibility with high number of methylene spacers to evaluate the effect of increased flexibility on mesogenic properties of polymers with this in view polymers were synthesized by route given in figure 1.

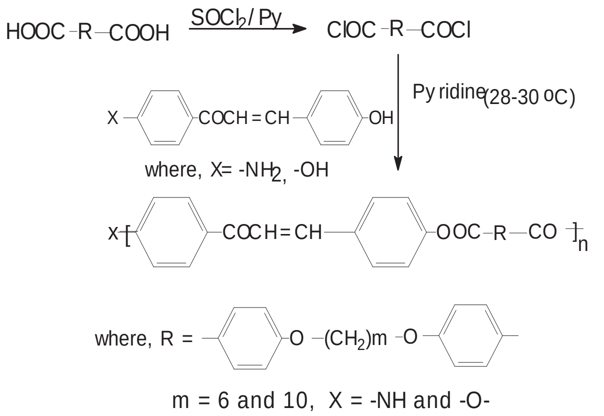
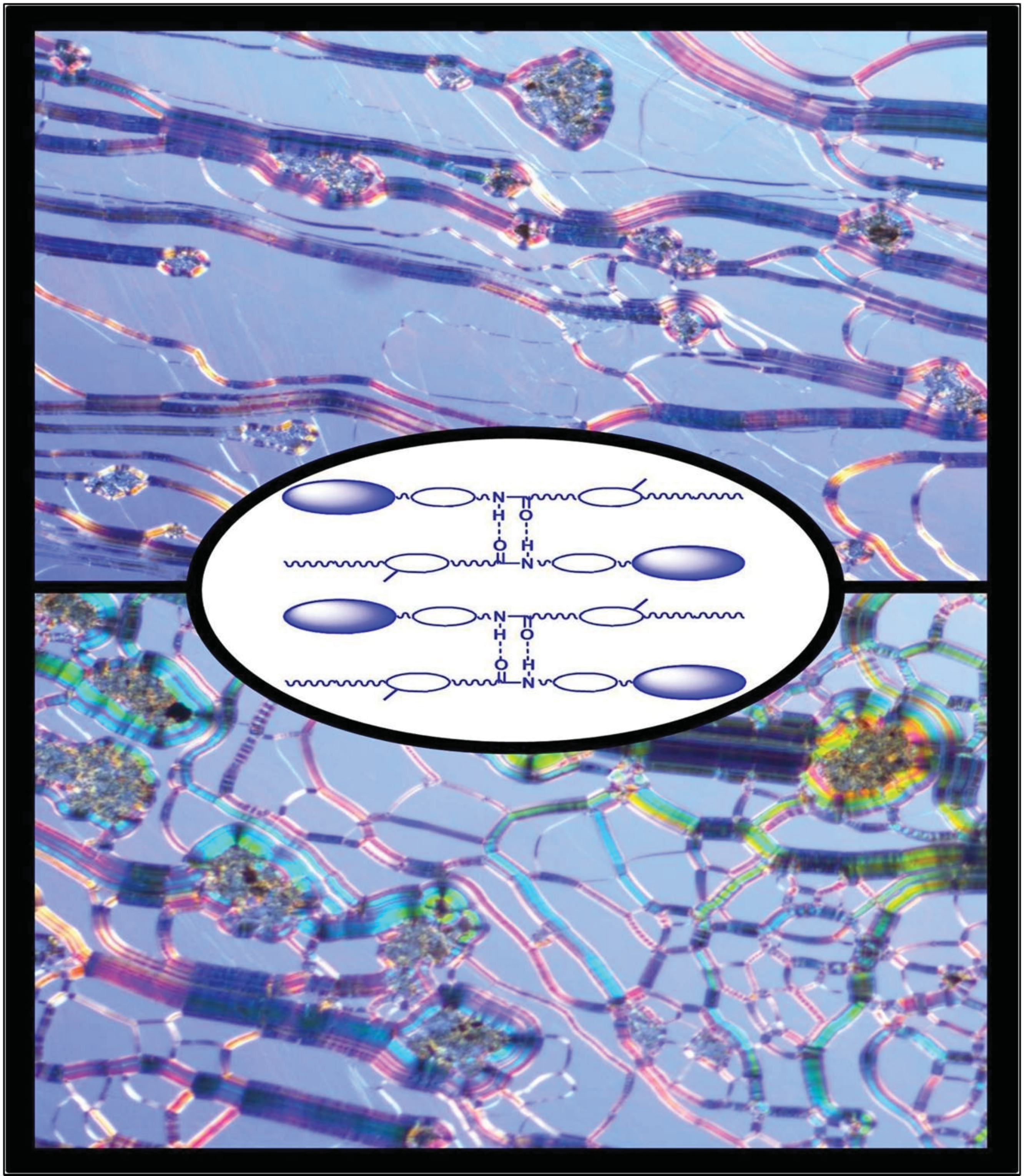


Figure-1
Synthetic route to Polychalcones

Measurements : The synthetic route adopted for the synthesis of polychalcones is shown in figure:1. Elemental analysis were performed with a Perkin Elmer 2[illegible]00, C,H,N analyzer. The IR of polymers was recorded on Perkin Elmer with KBr pellet. The optical textures of the polymers samples were studied with a Leitz Laborlux 12 Pol (Germany) polarizing microscope fitted with a Kofler heating stage. Ubbelohde viscometer was used for the measurement of viscosity of polymers in dimethyl formamide as a solvent.

SPECIAL
ACHIEVEMENT



The above research image has been invited as the COVER IMAGE on the April 2014 Issue of "Liquid Crystals" Journal (Taylor and Francis, UK) in which our research article will be published.

Synthesis and mesomorphic properties of chiral nematic liquid crystals based on cholesterol
R. C. Tandel* and Nilesh K. Patel
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