

**Azomethine Phenyl Benzoate Based Molecules: Synthesis,
Characterization and Mesomorphic Behaviour**



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by

ZAHIDA SADIQ

**Department of Chemistry
Quaid-i-Azam University Islamabad
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*In the name of ALLAH, the most
Compassionate, the most Merciful*

*“Allah will exalt those of
you who believe, and
those who are given
knowledge, in high
degrees; and Allah is
Aware of what you do.”*

(Surah Al Mujadilah 58:11)

The Prophet Hazrat Muhammad ﷺ said:

“If Allah wants to do good to a person, he makes him comprehend the religion and of course knowledge is attained by learning.”

(Bukhari 1/67)

*All efforts and
achievements are
dedicated to my loving
Parents*

Acknowledgement

*All praises be to the **Almighty Allah** who induced the man with intelligence, knowledge, sight to observe and mind to think. And showered His countless blessings throughout my life and give me patience and couragement to get through this difficult task. Peace and blessings of Allah be upon the **Holy Prophet Hazrat Muhammad** ﷺ who exhorted his followers to seek for knowledge from cradle to grave.*

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Abbreviation and Acronyms

Compd	Compound
CRT	Cathode ray tube
D	Doublet
DSC	Differential scanning calorimetry
EPR	Electron paramagnetic resonance
FETs	Field effect transistors
FLC	Ferroelectric liquid crystal
GH	Guest-host
IR	Infra-red
J	Coupling constant
LCDs	Liquid crystal displays
LCs	Liquid crystals
LLCs	Lyotropic liquid crystals
PLCs	Polymeric Liquid crystals
S	singlet
Sm A	Smectic A
Sm B	Smectic B
M	Multiplet
M.P	Melting point
NMR	Nuclear magnetic resonance
POM	Polarizing optical microscopy
Quin	Quintet
R_f	Retardation factor
Sm*	Chiral smectic
Sm C	Smectic C
STN	Super-twisted nematic
T	Triplet
TLCs	Thermotropic liquid crystals
TN	Twisted nematic
XRD	X-ray diffraction

Abstract

Liquid crystalline materials have been of great interest in recent past due to their wide applications in scientific and technological areas, such as non-linear optics, display devices, anisotropic networks, photo-conductor and semi-conductor materials. Azomethine based liquid crystals are used in many fields like catalysis, photochemistry, biochemistry and organometallic chemistry. Azomethinephenyl benzoate based mesogens have special importance in the field of electronics, electro-optical devices, electronic screens and are used as temperature sensors. Keeping in view the importance of azomethine phenylbenzoate liquid crystals in different fields and their growing demand in electro-optical devices, in the present project, azomethine phenyl benzoate was used as central core that is composed of three aromatic rings linked with each other through azomethine and ester linkages. Azomethine linkage increased the molecular length and polarizability of the molecule that enhance the liquid crystalline properties. Ester linkage generates a bend in the molecular structure that influence the anisotropic properties of liquid crystals and strengthens the mesomorphic properties.

In the present work, azomethine linkage was formed by the condensation of 4-aminophenol and 4-formylphenyl 4-methylbenzoate (**4**). Flexibility in the target mesogens was induced by alkylation of free hydroxyl group. Ten mesogens were synthesized with terminal methyl group at one end and varying chain length of 5-14 carbon-atoms at other end of the mesogen. The target mesogens (**8a-j**) were synthesized by coupling alkyl halide or alkyl tosylate and (*E*)-4-((4-hydroxyphenylimino)methyl)phenyl 4-methylbenzoate (**6**), itself synthesized by condensing 4-formyl phenyl 4-methylbenzoate (**4**) with 4-aminophenol (**5**). All the synthesized compounds were characterized using IR, ¹H NMR and ¹³C NMR spectroscopy.

Mesomorphic properties were studied using differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). All the synthesized compound showed liquid crystalline properties. Lower homologues of the synthesized series having alkyl chain length of five to ten carbon atoms exhibited nematic phase while higher homologues exhibited both nematic and smectic phases. Compound (**8j**) exhibited nematic phase in the temperature range from 181.6 to 175.1 °C during cooling scan, while smectic phase appeared in the range of 104.2-84.6 °C.

1.1 Liquid Crystals

Liquid crystal (LC) is a unique phase of matter having properties in between anisotropic crystalline solids and isotropic liquids. The term “Liquid Crystal” itself signifies the existence of a substance that flows like a liquid, exhibiting the properties of a liquid, like formation of droplets, coalescence, fluidity and incapability to withstand shear stress, and simultaneously exhibits the properties similar to crystals like optical, mechanical, electrical and magnetic properties. When a liquid crystal is heated, it melts and shows some thermodynamically stable states called mesophases, before being converted to an isotropic liquid. The term “mesophase” came from the Greek word “mesos” which means “intermediate”, signifying their nature intermediate between solids and liquids. Liquid crystals are anisotropic in nature because their physical properties are not identical in all directions.

Liquid crystals exhibit a significant difference in the molecular ordering and arrangement of atoms [1]. In crystalline state, molecules possess both orientational and positional order while in isotropic liquid state, there is no definite order and direction of atoms, and molecules diffuse randomly as shown in Figure 1.1.

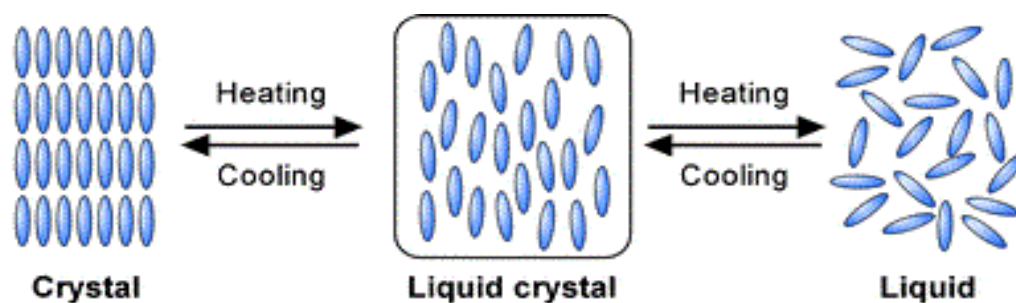


Figure 1.1: Phase transition from solid crystals to liquids (reproduced from <http://Pubs.rsc.org/en/content/articlehtml/2007/cs/b612546h>, retrieved on October 14, 2016).

1.2 Historical perspective

In 1888, an Austrian botanist, Friedrich Reinitzer [2] observed the liquid crystalline behaviour in certain esters of cholesterol. He observed two distinct melting points for cholesteryl benzoate, *i.e.*, at 145 °C white solid changed into a cloudy liquid and at 178.5 °C became a clear liquid. To understand this change in phase transition, he sent

a sample to Otto Lehmann, a leading crystallographer of that time. He observed that turbid liquid has a characteristic molecular order while clear liquid has a disordered state [3].

Lehmann [3] was the first scientist who recommended the name of liquid crystals and observed that it can show optical properties like solids and flow like liquids.

Around fifteen LCs had been recognized in the next decade although at that time scientists failed to develop a relationship between the liquid crystalline state and molecular structure. Further advancement and progress in the field of liquid crystals was made by chemists during the first half of 20th century. Daniel Vorlanders synthesized around 1100 compounds and found the relationship between molecular structure and liquid crystalline state [4]. He found that linearity in a molecule is a prerequisite for the existence of liquid crystalline state. He observed that all the synthesized compounds exhibited the phenomenon of polymorphism showing more than one phase.

George Friedel, in 1922 made an outstanding contribution in the field of liquid crystals and categorized them into different phases depending on the level of molecular order in the liquid crystalline state [5]. The mathematical explanation for LCs was given by Oseen [6] and Zocher [7]. Study on liquid crystals by Lehmann and Friedel, along with the work of Oseen and Zocher, formed the scientific bases of liquid crystal research.

In the middle of 1960s, a French Physicist, Pierre-Gilles de Gennes, worked on the analogies between liquid crystals and magnetic materials as well as superconductors. His research work was awarded with Nobel Prize in physics and his work greatly influenced the development of LCs science [8]. In 1960s, G. H. Heilmere provided the first signal for an application of liquid crystals in the field of electro-optical display devices, which tremendously increased the interest in the liquid crystal research [9].

In late 1960s, interest in liquid crystals was re-energized by pioneering work of UK's Royal Radar Establishment. Inspired by the work of Gray and his coworkers on cyanobiphenyl liquid crystals, Radio Corporation of America in 1968, introduced the first operational liquid crystal display [10].

A microscopic theory of liquid crystals was framed by Maier and Saupe [11], whereas later continuum theories for static and dynamic systems was developed by Frank [12], Leslie [13] and Erickson [14].

In 1970, Chandrasekhar [15] and his colleagues stated that there are some disc-like molecules that also exhibit mesophases. Such disc-like molecules are commonly called discotic molecules.

On the basis of shape, there is another class of liquid crystals commonly called banana shaped liquid or bent core LCs [16]. Bent core liquid crystals consist of an angular core that is attached to a linear rigid core by linking groups [17]. Non-chiral banana-shaped LCs show ferroelectric phenomena that created an interest in the research activity [18]. Research on liquid crystals exploded during 1970s and 1980s. As a result, in late 1980s scientists were successful in manufacturing full color liquid crystal displays which lead the display industry into new millennium [19].

1.3 Liquid Crystal Molecular Design

Geometry of molecule is important in determining the molecular packing and nature of liquid crystalline phase. However, it is not always possible to predict the nature of liquid crystalline phase on the basis of molecular structure. The essential feature for a molecule to act as a liquid crystal is that it should consist of rigid core, linking group, terminal group, lateral group and a flexible alkyl chain. Here is an example of a representative liquid crystalline molecule [20].

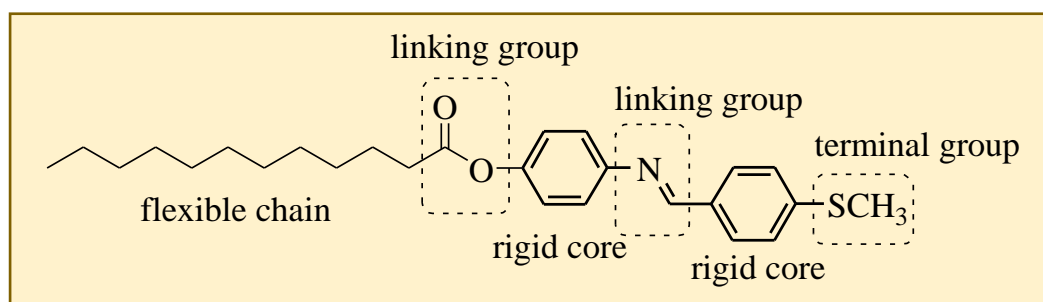
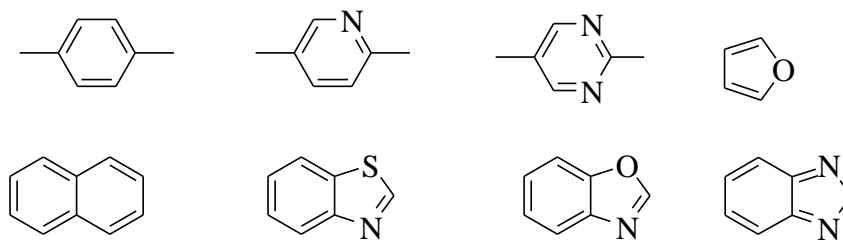


Figure 1.2: An example of a liquid crystal molecule.

1.3.1 Rigid Core

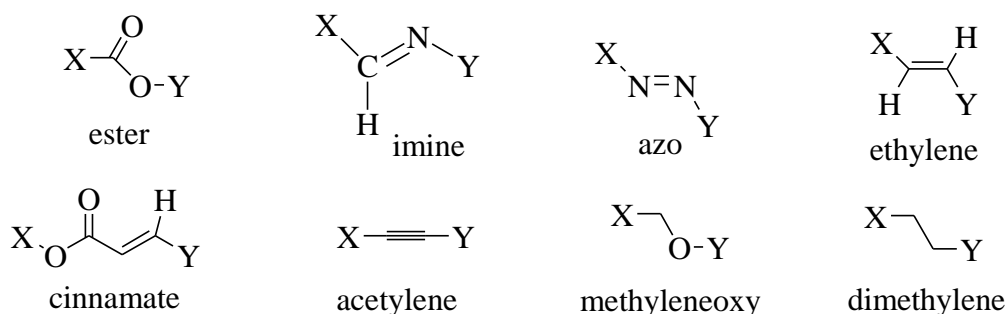
The most important part of liquid crystals is the rigid core. Rigid core is the essential requirement of a molecule to exhibit mesophase state and show anisotropic behaviour. The rigid core mostly consists of aromatic rings which may be carbocyclic or heterocyclic connected with one another by linking groups [21]. The melting point of a molecule depends on the number of aromatic rings. With the increase in number of

aromatic rings, conjugation in the molecule increases that result in the intermolecular interactions and increases the melting point [21]. Most commonly used rigid cores are:



1.3.2 Linking Group

Linking groups are the small chemical groups that connect one part of the core to another. They are also used to link the rigid core with the flexible part and increase the molecular length which provide flexibility and polarizability anisotropy to the molecular core in order to enhance the liquid crystalline phase stability [22]. Most commonly used linking groups are:



1.3.3 Terminal Group

Terminal group of a molecule plays an important role in mesomorphic properties. The role of terminal group in generating the liquid crystalline phase is not fully understood yet. However, the presence of alkyl or alkoxy chain increases the molecular length and adds flexibility to the rigid core that tends to decrease the melting point and stabilize the molecular orientation which is necessary for a molecule to exhibit liquid crystalline phases. Different alkyl chains and terminal substituents (F, Cl, Br, CN, OH, CH₃, SCH₃, etc.) influence anisotropic properties of liquid crystals [23].

1.3.4 Lateral Group

The lateral group is any group that sticks out of the linear axis of the molecule, usually on the side of an aromatic core. It usually disrupts the molecular packing which is sometimes useful for a molecule to exhibit the liquid crystalline properties and exhibit

the physical properties required for electrical displays. The most commonly used lateral substituents are F, Cl, Br, CN, OH, CH₃, *etc.* [24].

1.3.5 Flexible Chain

It plays a vital role in mesomorphic behaviour as it establishes Van der Waals interactions and provide flexibility to mesogens. Flexibility of end chain suppresses crystallization and leads to stability of the mesophase [25].

1.4 Classification of liquid crystals

The classification of liquid crystals has always been a difficult job because over the last two decades a huge number of LCs has been synthesized. Liquid crystals are classified into two groups on the basis of their physical parameters, as shown in the flow chart (Figure 1.3).

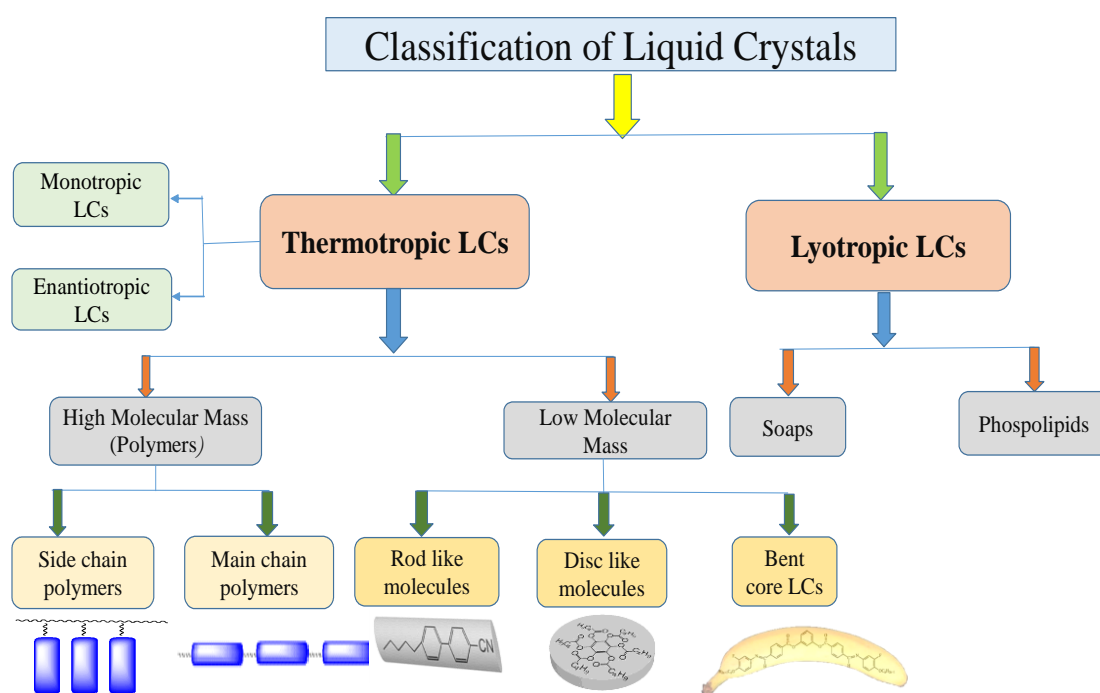


Figure 1.3: Flow chart showing classification of liquid crystals.

1.4.1 Thermotropic liquid crystals (TLCs)

The mesophase of TLCs depends on the variation in temperature. TLCs show liquid crystalline phases on heating having some mechanical and symmetric properties in-between isotropic liquid and crystalline solid. The essential requirement of a TLC is that it should be composed of central core usually derived from aromatic rings and a

flexible part formed of an alkyl chain. Thermotropic mesophases occur because of anisotropic dispersion forces between the molecules and because of packing interactions [26]. Thermotropic LCs may be enantiotropic or monotropic.

(a) Enantiotropic liquid crystals

Enantiotropic liquid crystals show liquid crystalline states by heating the sample to an isotropic liquid or cooling the isotropic liquid to crystalline solid [26].

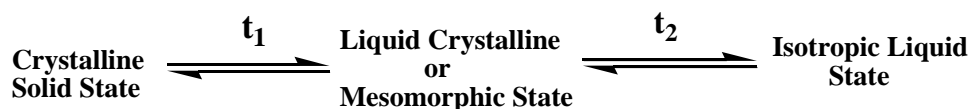


Figure 1.4: Phase change to enantiotropic liquid crystal.

(a) Monotropic liquid crystals

This type of thermotropic liquid crystals show liquid crystalline state in one direction only, *i.e.*, either on heating the sample to isotropic liquid or cooling it to crystalline solid. It has been observed in many compounds that monotropic LCs show liquid crystalline state on heating but do not show liquid crystalline properties on cooling and *vice versa*. [26].

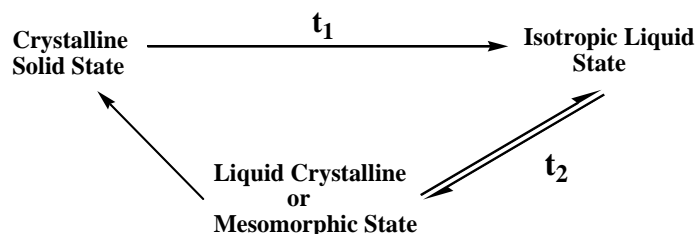


Figure 1.5: Phase change to monotropic liquid crystal.

Thermotropic LCs are classified into two categories depending on their molecular masses: low molecular mass and high molecular mass thermotropic liquid crystals.

1.4.1.1 Low molecular mass thermotropic liquid crystals

Low molecular mass thermotropic liquid crystals, depending on their structural features, are classified into three main groups: calamitic liquid crystals, discotic liquid crystals and bent core liquid crystals.

1.4.1.1.1 Calamitic liquid crystals

Calamitic LCs are also called rod-like LCs because they are elongated in shape having greater molecular length as compared to molecular breadth (Figure 1.6), which is responsible for anisotropy of the molecule [27]. Calamitic LCs consists of two or three aromatic rings and flexible alkyl chains. These are bonded together by linking groups like N=N, CH=N, COO, CH=CH, *etc.*, which increase the molecular length, maintains the rigidity of the molecule through conjugation and enhances the polarizability of the molecule.

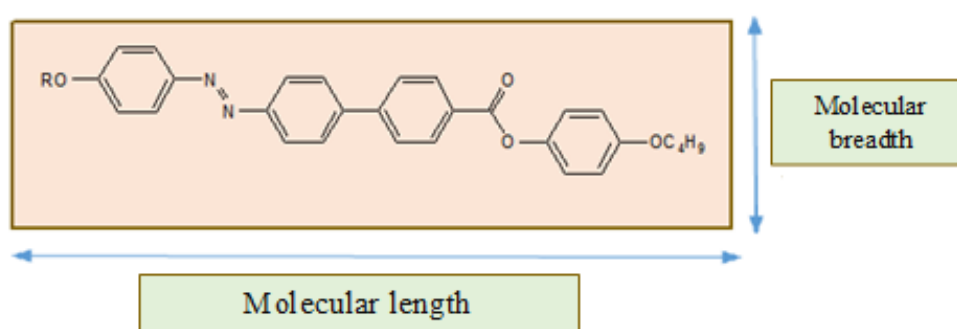


Figure 1.6: An example of calamitic LC demonstrating the general shape [28].

1.4.1.1.2 Discotic liquid crystals

Those compounds that have disc-like core in their structure and show liquid crystalline properties are called discotic LCs. First discotic liquid crystals consisting of hexa-substituted benzene derivatives were discovered by S. Chandrasekhar in 1977 [15]. Discotic LCs consist of central rigid core usually comprised of aromatic rings, which is surrounded by flexible peripheral groups having four to eight carbon chains [29]. Such type of LCs have molecular diameter much larger than disc thickness, which is responsible for the anisotropic behaviour of the molecule [30].

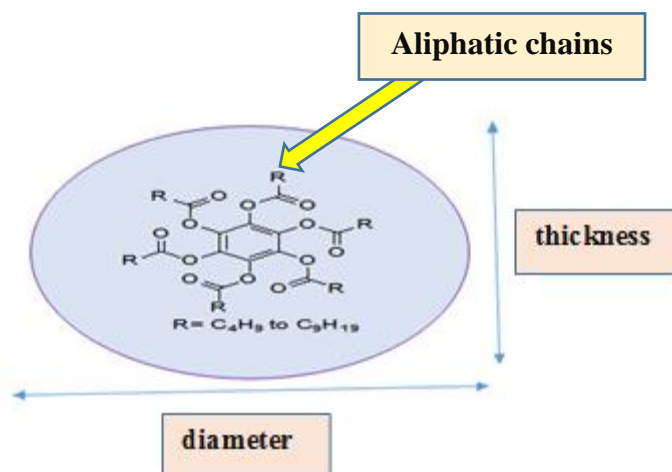


Figure 1.7: First discotic LCs: hexasubstituted benzene derivatives [15].

Discotic LCs exhibit different types of mesophases depending on the varying degree of organization in the molecule. Among them, is the discotic nematic phase which is the least ordered and more symmetric mesophase [31] while in columnar phase, there is a self-organization of molecules and they arrange themselves into hexagonal or rectangular arrays [30].

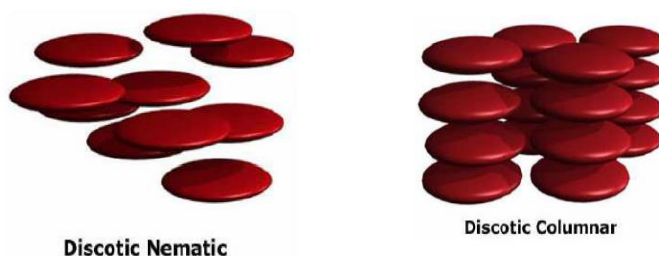


Figure 1.8: A representation of the molecular order in phases of discotic liquid crystals (reproduced from http://barrettgroup.mcgill.ca/tutorials/liquid_crystals/LC04.htm, retrieved on October 25, 2016).

1.4.1.1.3 Bent core liquid crystals

Bent core LCs, also called banana shaped LCs, provide a path for the synthesis of unique types of molecules that are used in the field of supramolecular chemistry [32]. Bent core liquid crystals were first proposed by Vorlanders in 1929 [33]. Bent core LCs find applications in non-linear optics, photoconductivity, flexoelectricity and design of biaxial nematic phase, *etc.* [34]. Bent core LCs generate a number of mesophase ranges from B_1 - B_7 on the basis of order in their discovery. The bend in

these LCs is responsible for the reduction in the rotational disorder of the molecule. Bent shaped LCs consist of three units: angular central core, two linear rigid units and terminal chains. Banana shaped LCs are similar to calamitic LCs because they have molecular length significantly greater than molecular breadth [35].

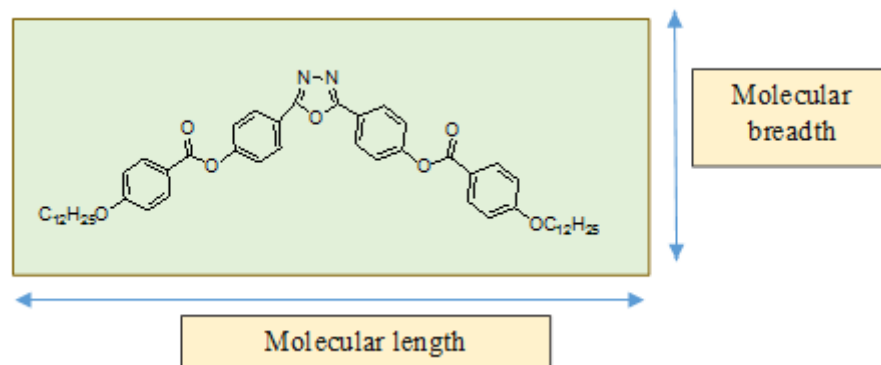


Figure 1.9: An example of a bent core LC depicting general shape [34].

1.4.1.2 High molecular mass thermotropic liquid crystals

High molecular mass thermotropic liquid crystals are also known as polymeric liquid crystals (PLCs). Polymeric liquid crystals exhibit mesophase states because of the unique properties of polymers and anisotropic properties of liquid crystals. The phenomena of polymorphism are seen in those compounds that have more than one smectic phase and show significant range of stability of different phases. Depending on the site of attachment of mesogen unit to the polymeric backbone, polymeric liquid crystals are classified as side-chain and main-chain PLCs. PLCs exhibit higher viscosity as compared to their monomers and have been used for optical storage applications [36].

1.4.2 Lyotropic liquid crystals (LLCs)

The formation of mesophase in lyotropic liquid crystals is influenced by the solvent. When compound is dissolved in a solvent, it does not form a clear liquid rather it forms a cloudy liquid or mesophase, which means it can possess the properties of liquid crystals. Lyotropic mesogens are composed of hydrophilic head and a flexible hydrophobic tail that helps in the formation of micellar structure in the presence of a solvent as hydrophilic part lies on the surface of the solution while hydrophobic part lies inside the solution. When the concentrated solution is cooled then the size of micelles increase and eventually coalesce which results in the formation of different

mesophases. Lyotropic liquid crystals can be converted into isotropic liquid by dissolving it in excess amount of solvent or by heating it at high temperature [37]. Examples of lyotropic liquid crystals are soaps and detergents that form micelle in solution as shown in Figure 1.10.

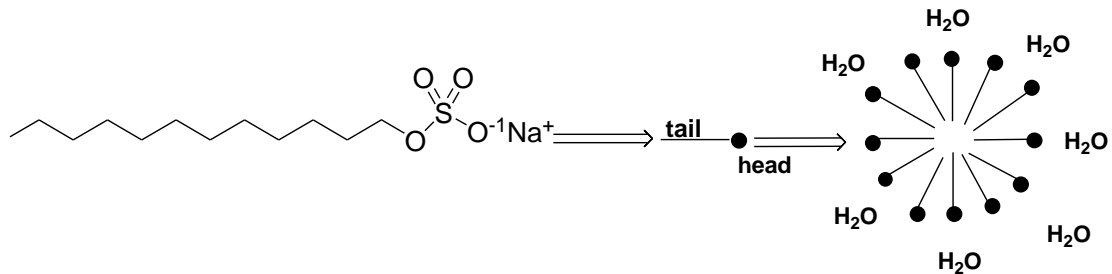


Figure 1.10: Sodium dodecylsulfate (soap) forming micelles [37].

1.5 Types of phases

Friedel classified different types of mesophase states depending on the basis of level of order that molecules possess [5]. These types include: nematic phase, cholesteric phase and smectic phase.

1.5.1 Nematic phase

The word “nematic” originated from “Nema”-a Greek word, which means “thread-like”. This phase is named nematic because the texture obtained from polarizing microscope is thread-like in appearance [38]. It is the simplest of all the liquid crystalline phases and more closely related to isotropic liquids having no positional order but possess orientational order. Molecules in the nematic phase are unidirectional having long range orientational order and are directed parallel to each other along the molecular axis which is represented by the vector ‘ n ’ [39].

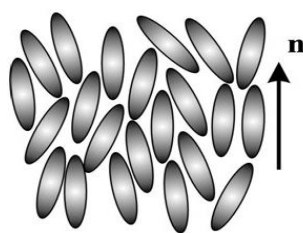


Figure 1.11: Representation of nematic phase (reproduced from <http://www.g.eng.cam.ac.uk/CMMPE/lcintro2.html>, retrieved on October 15, 2016).

Nematic phase has fluidity like liquids and has low viscosity. They can align themselves on applying external magnetic and electric fields. The physical properties of a nematic liquid crystal change with the change in direction of unit vector due to their anisotropy in the distribution of electrical charge [40]. Textures formed under polarizing microscope by 3-hydroxy-4-((*p*-tolyl diazenyl)methyl)phenyl-4-(methylthio)benzoate exhibit nematic phase and show nematic marble texture during heating scan while schlieren nematic texture during cooling scan [41].



Figure 1.12: (a) Representation of a marble texture for nematic phase in 3-hydroxy-4-((*p*-tolyl diazenyl)methyl)phenyl-4-(methylthio)benzoate at 150 °C during heating (b) Schlieren texture for nematic phase in same compound at 234 °C during cooling [41].

1.5.2 Cholesteric phase

Cholesteric phase is also called chiral nematic phase and was first observed by Reintizer in the cholesterol benzoate LCs because of the presence of chiral moiety (cholesterol) in the mesogens [2]. In this phase, asymmetry of the constituent molecules causes slight and gradual rotational of the director 'n' from one layer to the other due to helical

structure. A chiral nematic phase may be produced by adding a chiral dopant into nematic material as shown in Figure 1.13. The characteristic feature of the cholesteric phase is the pitch which can be defined as a distance covered by a director to complete its full turn in a helix. The pitch can be changed either by changing the temperature or by adding some chiral dopant into achiral molecules [42].

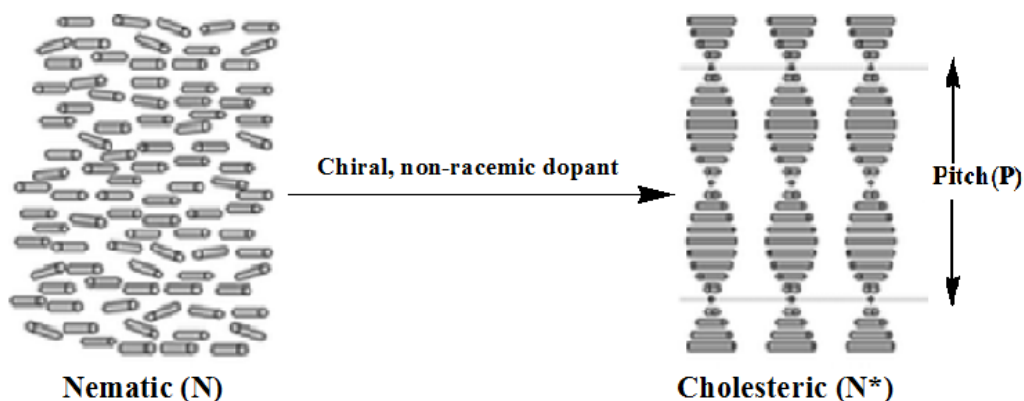


Figure 1.13: Diagrammatic representation of cholesteric phase induced by chiral dopant (reproduced from [http://Pubs.rsc.org/en/content/ ArticleHtml/ 2006/OB/ b6087 49c](http://Pubs.rsc.org/en/content/ArticleHtml/2006/OB/b608749c), downloaded on October 20, 2016).

Chiral nematic liquid crystals exhibit interesting properties like low-threshold laser emission and Bragg's reflection if the pitch is equal to the wavelength of visible light. These LCs are optically active and reflect circularly polarized light [43]. Texture observed under polarizing microscope (Figure 1.14) for compound (*S*)-(benzylidene-4'-methylaniline)-2''-methylbutyl-4'''-(4''''-phenoxy)benzoateoxy) hexanoate shows fan-like structure at 140 °C and appear as oily streaks at 120 °C [44].

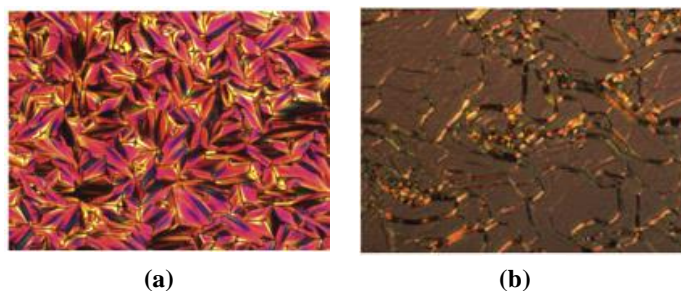


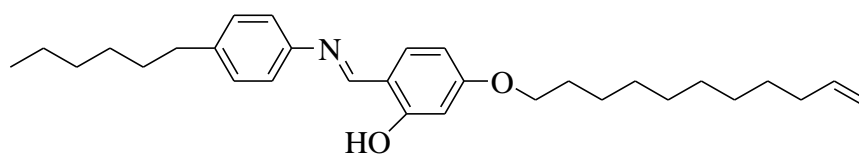
Figure 1.14: Mesophases in *(S)*-(benzylidene-4'-methylaniline)-2''-methylbutyl-4'''-(4''''-phenoxy)benzoateoxy)hexanoate: **(a)** Cholesteric phase having fan-like structure at 140 °C, **(b)** oily streak texture of chiral nematic phase at 120 °C [44].

1.5.3 Smectic Phase

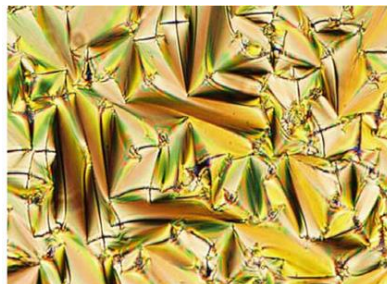
The word smectic originated from the Greek word "smegma", means soap-like. This phase is named because the substance which shows smectic phase is slippery in nature. Smectic phase is more ordered than nematic phase and it is more closely related to solids, characterized by both orientational and positional order. Molecules in the smectic phase possess two dimensional order and align themselves in the form of layers, providing flexibility to the molecules due to their interlayer spacing [45]. Depending on the molecular arrangements within the layer and the extent of interlayer spacing, the smectic phase is classified into various types which are designated as Sm A, Sm B, Sm C, Sm E, Sm H and Sm G. These smectic phases can be classified into two categories depending on the orientation of molecules; whether they are tilted or not. Sm A, Sm B and Sm E phase are not tilted, their unit vector is perpendicular to the layer plane, while Sm C, Sm H and Sm G are tilted phases.

1.5.3.1 Smectic A phase

In Smectic A phase, the molecules are aligned parallel to their long axes represented by director 'n' and perpendicular to the plane formed by layers. They possess short range crystalline order. Optical texture seen under polarizing microscope for 5-(10-undecenyloxy)-2-[[[4-hexylphenyl]imino]methyl]phenol exhibit focal conic or fan-like texture at 352 K (Figure 1.15) which is the characteristic of smectic A phase [46].



(a)



(b)

Figure 1.15: (a) Structure of 5-(10-undecenyloxy)-2-[[[4-hexylphenyl]imino]methyl]phenol, (b) texture of Sm A mesophase at 352 K [46].

1.5.3.2 Smectic C phase

In Smectic C phase, the molecules are tilted and make an angle with the layer plane which is represented by director 'n'. The tilt angle increases with the decrease in temperature. Optical texture observed under polarizing microscope for 5-(10-undecenyloxy)-2-[[[4-hexylphenyl]imino]methyl]phenol at 321 K exhibits broken focal-conic texture (Figure 1.16), which is characteristic of smectic C phase [46].



Figure 1.16: Representation of Sm C mesophase in 5-(10-undecenyloxy)-2-[[[4-hexylphenyl]imino]methyl]phenol at 321 K [46].

1.5.3.3 Smectic C* phase

In this phase, the direction of molecules changes from one layer to the next and directed at some angle other than 90 degrees to the normal plane [39]. POM study for (S)-

(benzylidene-4'-ethyl-aniline) - 2"- methylbutyl-4'''-(4'''-phenoxy)benzoateoxy)hexanoate revealed chiral smectic phase (Figure 1.17).

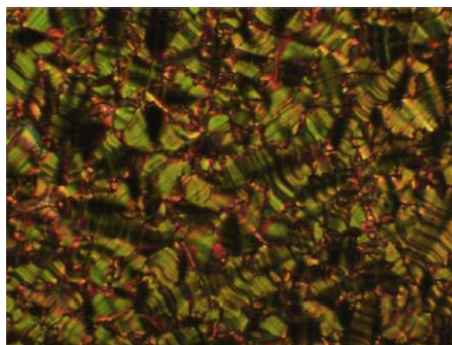


Figure 1.17: Representation of chiral smectic C phase in (*S*)-(benzylidene-4'-ethyl-aniline)-2"-methylbutyl-4'''-(4'''-phenoxy)benzoateoxy) hexanoate [44].

In Sm E phase, there is rhombic arrangement of molecules and director 'n' is perpendicular to the layer plane. In Sm G phase, the director 'n' is inclined to the layer plane and molecules are arranged in layers. In Sm H phase, the centre of mass lies in one plane but the director 'n' is inclined to layers and molecules are arranged in the form of hexagons.

1.6 Identification of liquid crystal phases

Liquid crystals consist of a number of phases that are characterized and identified by techniques like differential scanning calorimetry (DSC), polarizing optical microscopy (POM) and X-ray diffraction analysis (XRD). It is necessary to determine the thermal stability of the sample by thermogravimetric analysis before performing DSC to know the safe temperature limit upto which the sample can be heated without decomposition.

1.6.1 Differential scanning calorimetry (DSC)

DSC is a preliminary technique used for the identification of mesophases present in the liquid crystalline molecules. The phase transitions in a molecule can be detected by the difference in enthalpy change associated with each phase transition [47]. DSC in conjunction with polarizing optical microscope is used to determine the type of mesophase in a molecule. The enthalpy change at a transition cannot determine the type of phase but the magnitude of enthalpy change is directly proportional to the ordering

of the phases involved [48]. If enthalpy change is around 30 to 50 KJ/mol, it means considerable structural change is occurring and transition from solid to liquid crystal or to isotropic liquid is taking place. However, liquid crystal to liquid crystal and liquid crystal to isotropic liquid transition corresponds to smaller enthalpy change that is around 4 to 6 KJ/mol.

DSC consists of two furnaces, one is used to heat the sample which is under observation and the other is used to heat the inert reference, usually gold. These furnaces are independently heated but connected by two control loops, to maintain the temperature constant in both furnaces during heating and cooling cycles. The temperatures are monitored by platinum resistance thermometers present inside the holders [49]. When a substance is heated, it changes from solid to liquid state, this phase change requires heat from surroundings. On the other hand, the crystallization of liquids is an exothermic process. DSC measures the difference in the amount of heat which is required to maintain the temperature of sample and reference at the same level. It is necessary that both sample and reference should be at same temperature during the whole experiment. DSC thermogram of 2-(4'-heptyloxybiphenyl-4-yl)-benzoxazole in Figure 1.18 exhibited the liquid crystalline phases on heating and cooling scans.

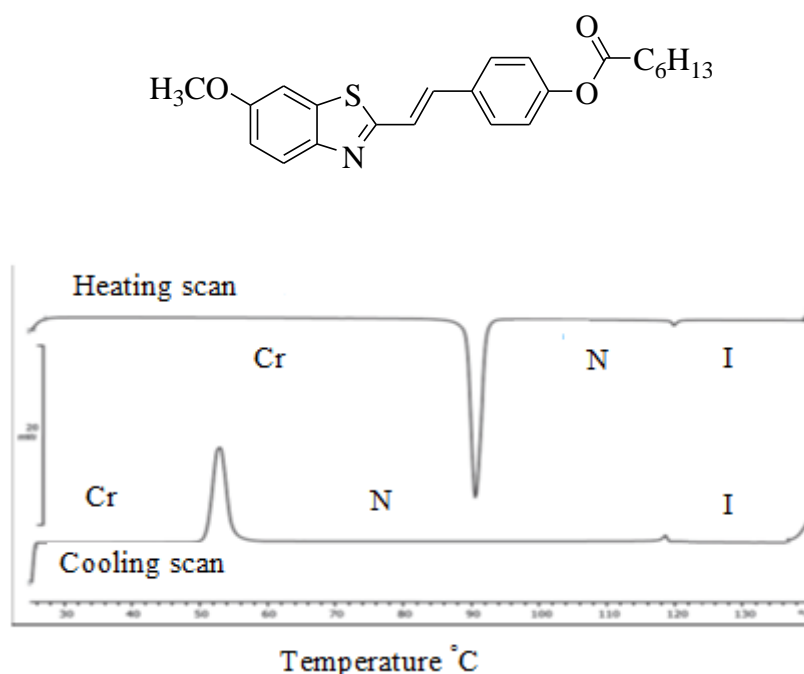


Figure 1.18: DSC thermogram of methoxy-2-(4-hexyloxybenzylideneamino)-benzothiazole [50].

1.6.2 Polarizing optical microscopy (POM)

Polarizing optical microscopy is used to identify the type of liquid crystalline phases in a molecule and shows a distinct optical texture for each liquid crystal phase. Textures are the pictures obtained under microscope through the polarizers and it defines the alignment of molecules in the liquid crystal phase. Moreover, it is used to distinguish between anisotropic and isotropic materials and gives information about their composition [51]. Darkness is observed through the analyzer when isotropic solvent is used because polarized light is not affected by the sample molecules. However, for an anisotropic material polarized light is not gratified and optical textures is obtained that gives information about alignment of molecules in liquid crystalline material [52]. POM is also helpful for the identification of physical properties of a mesogen like spontaneous polarization, ferroelectric properties, tilt angle and switching time of certain liquid crystal phases [53]. When polarized light passes from a liquid crystal, it experiences birefringence due to characteristic textures such as smectic, nematic, *etc* [54]. The (*E*)-*N*-(4-(dodecyloxy)benzylidene)-4-(3-bromopropoxy)benzene amine shows different textures upon cooling [55] as shown in Figure 1.19.

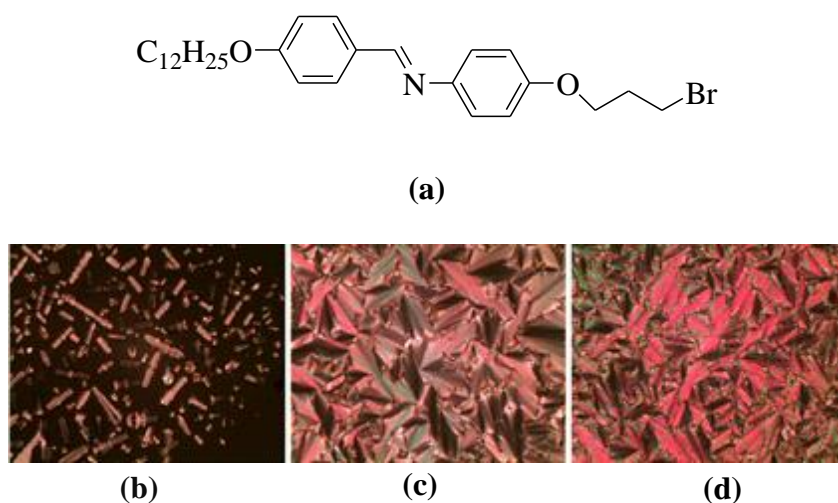


Figure 1.19: (a) Structure of (*E*)-*N*-(4-(dodecyloxy)benzylidene)-4-(3-bromopropoxy) benzene amine, (b) formation of batonets from isotropic liquid on cooling, (c) the focal conic fan-shaped texture of Sm A phase, (d) the appearance of broken fan-shaped texture characteristics of the Sm C phase [55].

1.6.3 X-ray diffraction analysis (XRD)

X-ray diffraction (XRD) is a fundamental technique used for the confirmation of type of mesophase. XRD analysis is used to determine the phase structure and classify the liquid crystalline phase on the basis of positional order in liquid crystals. It provides information related to the inter-planar distance and also measures the relative orientation of different sets of planes. Each mesophase has its own specific peak, angle and pattern shape [56]. XRD analysis follows the Bragg's law and generally it has been observed that nematic and cholesteric phases give broad low intensity peak between 16° to 20° in XRD curves while in case of smectic mesophase a sharp high intensity peak can be seen around 3° to 4° . XRD analysis gives useful results if aligned sample is used [57]. An XRD pattern of the 4-chlorobenzylidene-4'-dodecanoyloxyaniline showed sharp reflection peak at 2θ of 2.55° at 90°C , corresponding to the smectic layer spacing. The interlayer spacing was 30.1 \AA upon cooling from isotropic liquid to Sm A phase whereas the molecular length was 27.1 \AA . The Sm A layer suggests that molecules are arranged in monolayer [58].

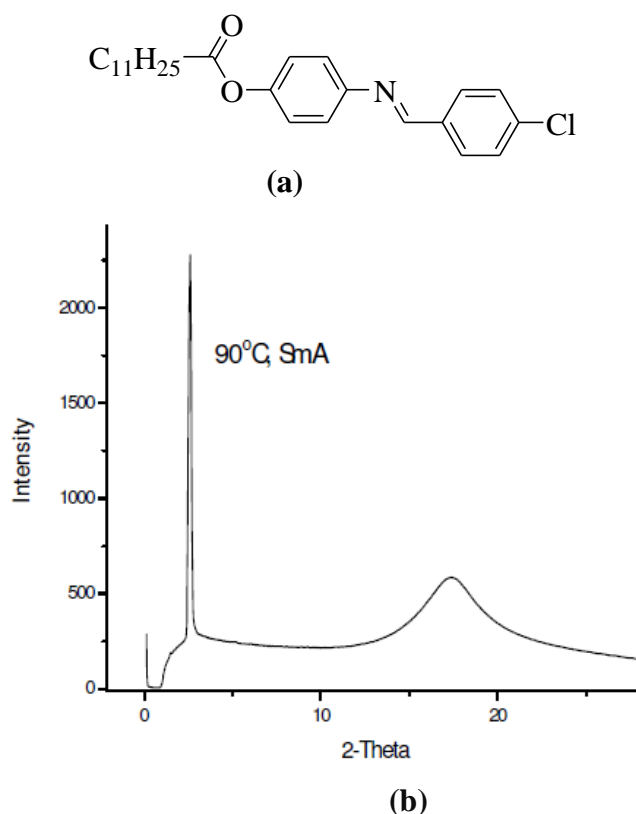


Figure 1.20: (a) Structure of 4-chlorobenzylidene-4'-dodecanoyloxyaniline, (b) XRD diffractogram for the same compound at 90°C during cooling cycle [58].

1.7 Applications of Liquid Crystals

Liquid crystals have found numerous application in various fields of science and technology.

1.7.1 Liquid crystals displays (LCDs)

Liquid crystal displays are the most common application of liquid crystals that has shown extensive development in the field of science and technology [59]. LCDs consist of digital readout devices that are used in televisions, watches, calculators, mobile phones and several other electrical appliances [60]. Cathode ray tube (CRT) has been replaced by LCDs because of its flat and compact size. Moreover, it uses low power consumption as compared to CRT such as in twisted nematic displays. The contrast and colour in twisted nematic displays do not change with the intensification of light [61]. Majority of the electro-optic effects in the LCDs used today include twisted nematic (TN), super-twisted nematic (STN), guest-host (GH) mode and ferroelectric liquid crystal (FLC) displays [62].

In host-guest display LCs can be used in military air-crafts. Liquid crystals are also used to control the solar energy and fabricate it with the phase change host guest mixture. Glass cover made from liquid crystals is used to control transmittance of incident light on solar cell. This helps the solar cell to maintain constant output of voltage under load shedding situation [63]. In guest host display, the nematic host orients the dye molecule when it is added into it and the colour of dye depends on the orientation of dye molecule. It can be used in the optical storage devices due to increase in thermal back relaxation time because of the addition of the dye (4-chloro-1,3-phenylene *bis*-[4-(4-allyloxyphenylazo)benzoate]) to the liquid crystals [64].

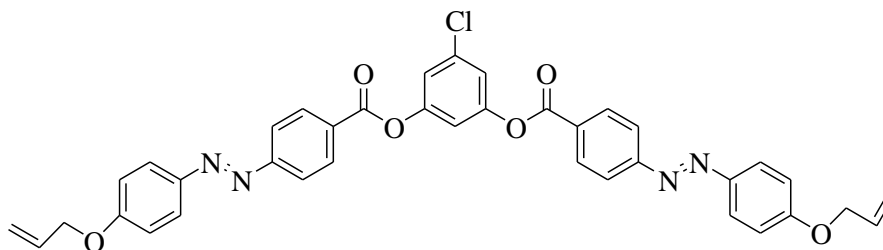


Figure 1.21: Liquid crystal used in guest-host display [64].

1.7.2 Chromatography

Liquid crystals are used as stationary phase in gas and liquid chromatography due to their molecular structure possessing the properties of both anisotropic solid and

isotropic liquid. Separation of similar compounds is possible due to their anisotropic orientational ordering created by using LCs [65]. It can also be used to differentiate the isomers of disubstituted benzene or naphthalene derivatives [66].

1.7.3 Spectroscopy

Spectroscopic techniques are used for the identification and characterization of unknown compounds. Recent studies reveal that liquid crystals can be used as anisotropic solvent in NMR, EPR and optical spectroscopic techniques. Mostly nematic mesophase is used in NMR spectroscopy to restrict the motion of the solute molecules. This technique gives valuable information about chemical shifts and molecular geometry [67].

1.7.4 Chemical reactions

In many bimolecular and photochemical reactions, thermotropic liquid crystals are employed as solvents [68]. The anisotropic property of LCs is employed to elucidate the reaction mechanism, control the specificity and effectiveness in microsynthesis [69]. LCs having proper morphology may be used to control solute reactivity [70].

1.7.5 Temperature sensors

Liquid crystals having cholesteric phase (chiral nematic phase) are mainly used as temperature sensors. They reflect a light of wavelength equal to the magnitude of the pitch. As pitch depends on temperature, reflected colour of light is also temperature dependent. With the help of liquid crystals, such as cholesteric LCs, it is possible to predict the temperature just by looking at the colour. Devices of different temperature range can be made by mixing different cholesteric liquid crystals and can be employed in various disciplines like medicine, packing industry and electronics [71]. Cholesteric LCs have been used in disposable thermometers as fever strips. Thermal LC sensors when attached to skin show a thermal map which is useful in diagnosis of the problems like tumor cells that have a different temperature than the neighbouring tissue [72] They are also used to find out a wrong connection on a circuit board by analyzing characteristic higher temperature [73].

1.7.6 Gynecology

In gynecology, liquid crystals are employed to locate the placenta when cesarian section is needed in order to avoid the need for x-ray diagnosis [74].

1.7.7 Drug delivery

Liquid crystalline materials are used to deliver drugs to the desired targets. Permeability of drug through skin is enhanced by liquid crystals due to interaction with intercellular lipids of the skin [75,76].

1.7.8 Cosmetics

Liquid crystals have also found applications in cosmetic industry by providing milky and silky appearance to the skin care products. Lamellar gel, an innovative skin care product, was developed, that forms lamellar phase similar to LCs. It interacts with the intercellular layer of lipids in skin, providing hydration to stratum corneum [77].

1.7.9 Optical imaging

Liquid crystals have also found applications in optical imaging and recording. This technology is the most promising area of liquid crystals. In optical imaging, the conductivity of material is enhanced by applying light on photoconductor in which LC cell is placed. Corresponding to intensity of light, an electric field is produced in liquid crystal. Image is recorded by transmitting the electric pattern to the electrode [78].

1.7.10 Creative arts

LCs are temperature sensitive and change colour at various temperature and give lustrous look to the material. Therefore, it can be used in creative arts [79].

1.7.11 High strength fibres

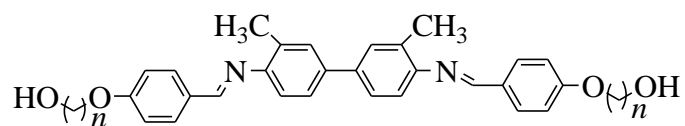
Polymeric liquid crystals are very useful in high strength fiber industry. Kevlar fibers, used in making of strong lightweight materials, *e.g.*, helmets and bulletproof vests, are one of the polymer liquid crystal material [80].

1.8 Azomethine based liquid crystals

Azomethines (Schiff bases) are the compounds having -CH=N- group, formed by the condensation reaction between a carbonyl compound and an amine. Being isoelectronic with *p*-phenylene vinylene, it exhibits interesting electronic, luminescent and non-linear optical properties [81,82]. It is used as a linking group in liquid crystals because it provides higher thermal stability, excellent mechanical strength, good semiconducting and optoelectronic properties to liquid crystals [83]. Azomethine compounds are sensitive to acids, therefore, they can exhibit photochromic properties [84]. Azomethine based LCs have their utility in display devices, light valves, biosensors, pressure and temperature sensors, *etc.* They are used as active layer in optoelectronic devices like LCDs, FETs, Solar cells and Lasers [85].

Azomethine unit is incorporated into the molecular structure because it increases the molecular length and polarizability of the molecule and thus enhances the liquid crystalline properties of the molecule [86]. Schiff base liquid crystals have gained importance after the discovery of 4-methoxybenzylidene-4'-butylaniline (MBBA) which exhibits nematic phase at room temperature.

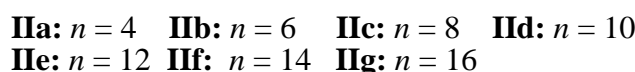
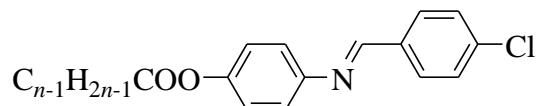
In a recent work of Issam *et. al.* [87] a homologous series of azomethine mesogens (**Ia-d**) derived from *N,N'*-bis(4-hydroxyl)benzylidene-*o*-tolidine containing even numbered carbon-atom chains was synthesized and characterized by FT-IR, CHN, ¹H-NMR and ¹³C-NMR spectroscopy. It was observed that mesogen **Ia** do not exhibit any liquid crystalline properties while mesogen **Ib** and **Ic** exhibit enantiotropic nematic phase. Smectic mesophase is shown by mesogen **Id**. The results from DSC analysis showed that there is a decrease in phase transition temperature with the increase in chain length of carbon-atoms. The presence of terminal hydroxyl group increases the geometrical anisotropy and polarizability of the molecule.



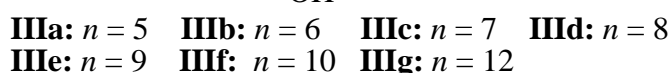
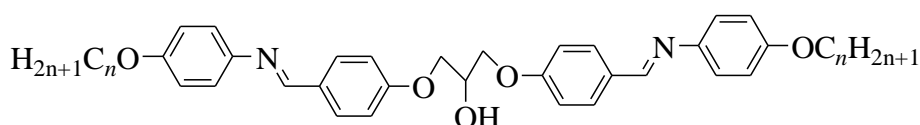
Ia: $n = 4$ **Ib:** $n = 6$ **Ic:** $n = 8$ **Id:** $n = 10$

Calamitic Schiff base ester (**IIa-g**) have been synthesized by Ha *et. al.* [88]. This calamitic mesogen consists of two aromatic rings having a flexible alkanoyloxy chain

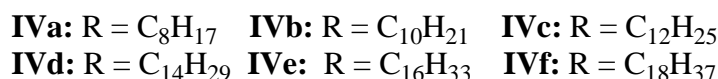
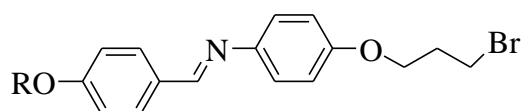
and a terminal chloro group. It has been found that mesogen **IIa** does not exhibit mesomorphic properties but mesogen **IIb** exhibit monotropic smectic phase while compounds **IIc-g** were smectogens. Moreover, melting point decreases with the increase in carbon atom due to the dilution of core system.



A new series of symmetrical dimer (**IIIa-g**) have been synthesized consisting of two azomethine linking units connected by 2-hydroxy-1,3-dioxypyrolylene moiety [89]. All these LC dimers showed smectic phase except compound **IIIa**. Compound **IIIf** and **IIIg** exhibited smectic A as well as smectic C phase while rest of the dimers exhibited only smectic A phase. **IIIa** do not show any liquid crystalline property possibly due to the short chain and imbalance in the ratio of flexible and rigid part. Presence of polar hydroxyl group increases the molecular polarizability and clearing temperature.

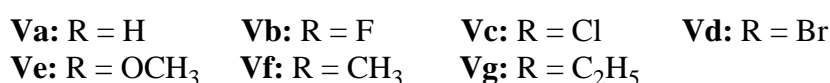
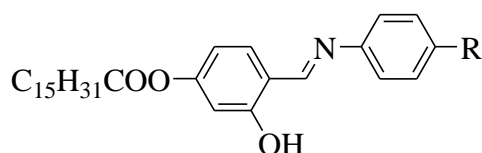


It has been reported [55] that a new homologous series of Schiff base liquid crystals named 4-(4-bromopropoxy)-4'-(4-alkyloxybenzylidene)anilines (**IVa-f**) has been synthesized and their mesomorphic behaviour studied. It was found that compounds **IVa-e** showed enantiotropic mesophase except compound **IVf**, which shows only monotropic mesophase. Due to the presence of bromine atom, the polarizability of the molecule increases and it promotes the formation of smectic phase.

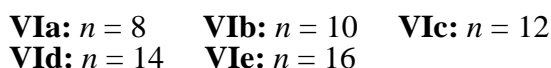
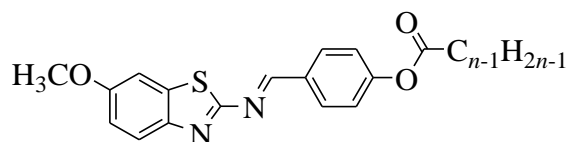


A new series of compounds (**Va-g**) has been synthesized by condensation reaction between *p*-substituted aniline and *o-n*-hydroxy-*p-n*-hexadecanoyloxybenzaldehyde,

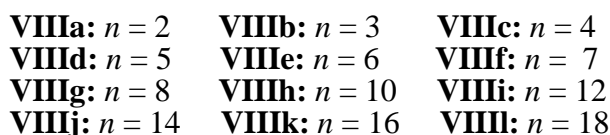
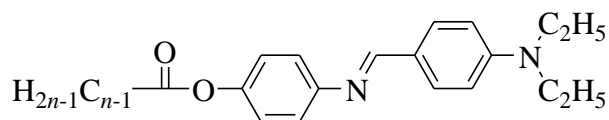
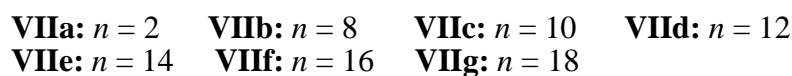
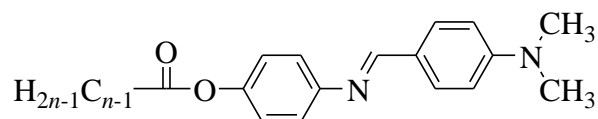
itself synthesized by esterification reaction between 2,4-dihydroxybenzaldehyde with palmitic acid [90]. All the compounds exhibit mesomorphic properties. Mesogens **Va-e** exhibited smectic A mesophase while **Vf** and **Vg** were monotropic and exhibited smectic C phase. The presence of lateral hydroxyl group causes the mesophase stability for short alkyl terminal groups. Therefore, mesogen **Vf** is more polarizable than mesogen **Vg**.



It has been reported [50] that Schiff base LCs having benzothiazole ring possess good hole-transporting properties and used in organic light emitting devices. Benzothiazole based LCs were synthesized by condensation of 4-hydroxybenzaldehyde and 2-amino-6-methoxybenzothiazole and then followed by steglich esterification with suitable fatty acids in the presence of DCC and DMAP. It was found that mesogen **Via**, **Vic**, **Vid** and **Vie** exhibited enantiotropic nematic phase, while **Vib** exhibited enantiotropic smectic C phase.

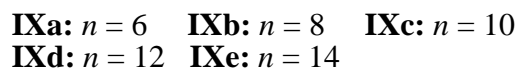
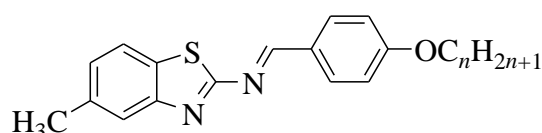


The presence of dialkyl amino terminal group affects the mesomorphic properties of the molecules [91]. Ha *et. al.* synthesized mesogens **VIIa-g** by coupling (*E*)-4-(4-(dimethylamino)benzylideneamino)phenol with aliphatic fatty acids. It has been found that mesogen **VIIa-g** having dimethyl amino group exhibited mesomorphic properties while mesogens **VIIIa-l** having diethyl amino terminal group do not exhibit any liquid crystal phase.



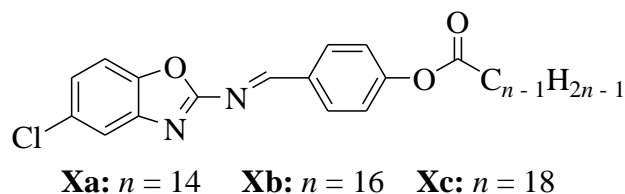
All those compounds having terminal dimethyl amino group (**VIIa-g**) were monotropic mesogens, while all the members of diethyl amino terminal group (**VIIIa-l**) were non-mesogenic because the longer alkyl group in dialkyl amino group, perturbs the packing of molecules.

Ha *et. al.* studied the effect of terminal methyl on mesomorphic properties of benzothiazole Schiff based liquid crystals [92]. It has been observed that mesogen **IXa** exhibit enantiotropic nematic phase, mesogen **IXb** shows only smectic A monotropic phase, while compounds **IXc-e** exhibit enantiotropic smectic A phase. Due to the presence of ordered smectic phase in the structure, it becomes a topic of interest in the electrical studies for device application.

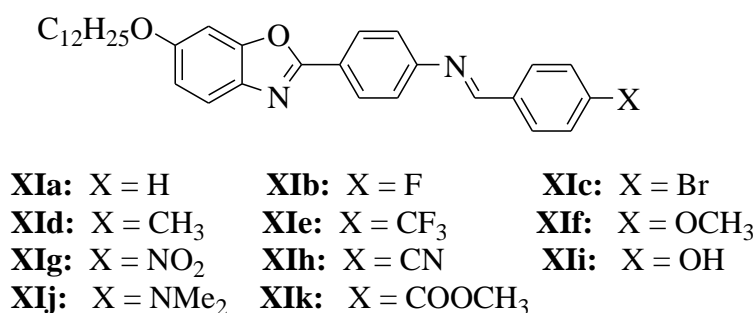


Benzoxazole based LCs having azomethine linking unit have found applications in organic light emitting diodes, non-linear optics and polymeric materials [93]. Benzoxazole based Schiff base liquid crystals were synthesized by coupling of 2-amino-5-chlorobenzoxazole with 4-hydroxybenzaldehyde in DCM at reflux temperature for 24 hours which was then subjected to steghlic esterification using appropriate fatty acids in the presence of DCC and DMAP. It has been observed that

compounds **Xa–c** exhibited enantiotropic smectic A phase due to the presence of polar chloro and ester linking group.



Relationship between polar substituents and mesomorphic behaviour was studied by Wang *et. al.* [94]. It was found that polar substituents induced better mesophases. Compound **XIa** was the only one in the series that formed a crystalline phase whereas **XIb–k** exhibited nematic or smectic A phase except for **XIi**. All the electron donating substituents (as in compounds **XId**, **XIf** and **XIj**) exhibited nematic phase whereas electron withdrawing substituents (as in compounds **XIb**, **XIc**, **XIe**, **XIg**, **XIh** and **XIk**) exhibited smectic A phase.

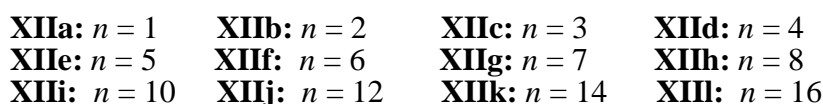
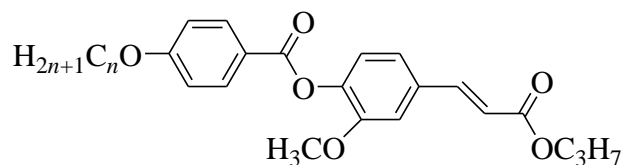


1.9 Benzoate based liquid crystals

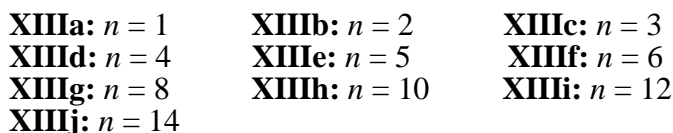
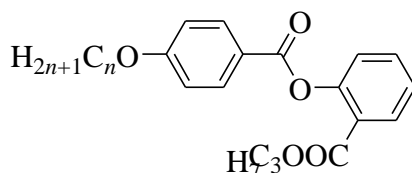
Benzoate based derivatives possess liquid crystalline properties and find their applications in pharmaceutical, biological and analytical fields. Moreover, it is also used in the manufacture of electronic devices, electronic screens, conventional and non-conventional LCD indicators, *etc.* [95]. Ester moiety is used as a linking group and increases the molecular length of a molecule by connecting either the two aromatic rings or an aromatic ring with the flexible part. Ester is a polar group, it dislocates longitudinal polarizability by generating bend in the molecular structure and strongly influences the properties like birefringence and dielectric anisotropy. Furthermore, it increases the anisotropy and polarizability of the molecule and strengthens the mesomorphic properties [22].

Benzoate based derivatives **XIIa–I** have been synthesized in order to study the effect of lateral OCH₃ substituent on mesomorphic behaviour [96]. It was observed that

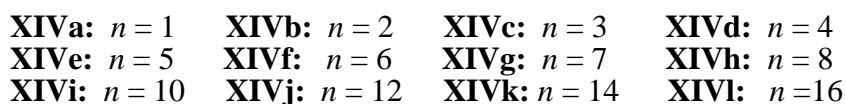
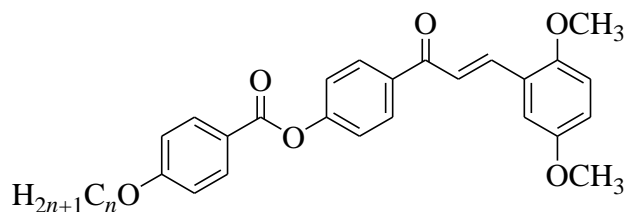
compounds **XIIa-d** are non-mesogenic while compounds **XIIe-j** are smectogens as well as nematogens. Compounds **XIIk** and **XIII** are only smectogens. The textures of smectic and nematic phases obtained by POM are A or C type and threaded or schlieren, respectively.



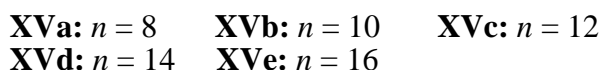
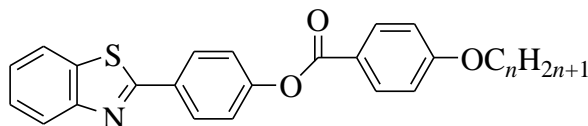
Ten new compounds of *n*-propyl-*o*-[*p*'-*n*-alkoxybenzoyloxy]benzoates (**XIIIa-j**) were synthesised to study the effect of benzoate derivatives on the mesomorphic behaviour of *n*-propyl group [97]. Compounds **XIIIa** and **XIIIb** were non-mesogenic while rest of the members of the series (**XIIIc-j**) were mesogenic. Compound **XIIIc-g** showed enantiotropic nematic phase. Compound **XIIIh** showed both enantiotropic nematic and smectic phase while **XIIIi** and **XIIIj** exhibited enantiotropic smectic phase.



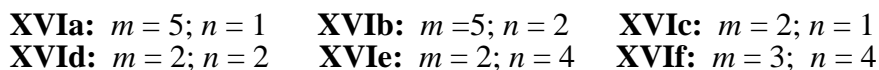
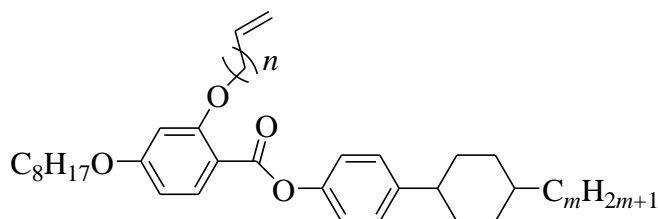
A homologous series of thermotropic liquid crystals (**XIVa-l**) consisting of benzoate linkages were synthesized [98]. The target molecules have found application in electronic devices like LCDs. It was observed that compounds **XIVa-h** are nematogens while compounds **XIVi-k** are smectogens as well as nematogens. Compound **XIVl** showed only smectic phase. All synthesized compounds show liquid crystalline property. Nematic phase showed thread or schlieren texture while the texture obtained for nematic phase was focal conical fan-shaped. The average thermal stability for nematic phase was 117 °C and that for smectic phase was 93 °C.



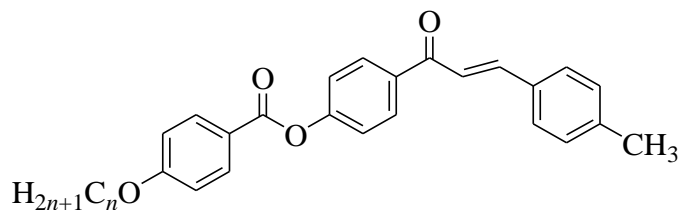
It has been reported [99] that all the synthesized compounds **XVa-e** show enantiotropic nematic phase with high thermal stability (>168 °C). Monotropic smectic phase was observed for **XVb** whereas compounds **XVc-e** showed enantiotropic smectic phase. Because of the occurrence of smectic phase in the compounds, they become an interesting molecule for electronic devices.



In a reported method [100], a series of nematic liquid crystals (**XVIa-f**) having reactive substituent on the lateral side of the molecule was synthesized. Compounds **XVIa** and **XVIb** exhibited enantiotropic nematic phase while compounds **XVIc-f** showed monotropic nematic phase during cooling cycle. Molecules having double bond have low viscosity, low melting point and good thermal stability.



Thermotropic liquid crystals (**XVIIIa-l**) having chalconyl benzoate central core have been synthesized [101]. All the synthesized compounds exhibited smectic mesophase. Textures obtained from smectic phase were fan-shaped or battonet type of smectic A or smectic C phase.

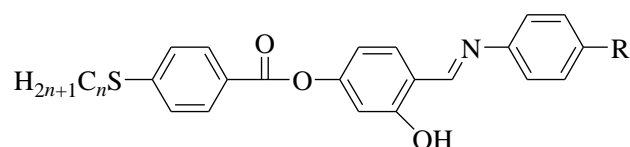


XVIIa: $n = 1$	XVIIb: $n = 2$	XVIIc: $n = 3$	XVIId: $n = 4$
XVIIe: $n = 5$	XVIIf: $n = 6$	XVIIg: $n = 7$	XVIIh: $n = 8$
XVIIi: $n = 10$	XVIIj: $n = 12$	XVIIk: $n = 14$	XVIIl: $n = 16$

1.10 Azomethine phenyl benzoate based liquid crystals

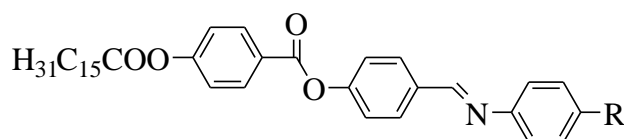
Azomethine benzoate based liquid crystals possess two linking groups, *i.e.*, ester and azomethine. LCs based on these linking groups possess interesting properties in the field of optics and photonics [102]. Such type of LCs also found their applications in the manufacture of electronic devices, electronic screens, electro-optical devices and can also act as temperature sensors. In such type of LCs, azomethine linkage provides a stepped core structure and maintains the molecular linearity, thus enhancing the liquid crystalline properties. Ester linkage increases the anisotropy and polarizability of the molecules and strengthens the mesomorphic properties. Both ester and azomethine linking units are useful components for generating the mesomorphism in compounds with two or three aromatic rings [103].

In a recent work, Al-Hamdani *et. al.* synthesized two series containing azomethine phenyl benzoate as a central core having terminal CH_3 and COCH_3 on one end of the series **XVIIIa-j** and **XVIIIk-p**, respectively, and thioalkyl group on other side in both series [104]. All the compounds (**XVIIIa-j**) showed nematic phase because of the large size of sulfur atom that makes it difficult for the molecules to be assembled to form more organized liquid crystalline phases (Sm phase). All the compounds **XVIIIk-p** showed liquid crystalline behaviour. Nematic phase was observed for compound **XVIIIk**. For compounds **XVIIIk-n** Smectic A as well as nematic phase was observed. For longer alkyl chain compounds, **XVIIIo** and **XVIIIp**, only Sm A phase was observed.



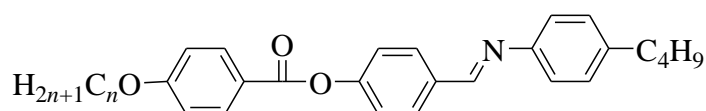
- | | | |
|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|
| XVIIIa: R = CH ₃ ; n = 1 | XVIIIb: R = CH ₃ ; n = 2 | XVIIIc: R = CH ₃ ; n = 3 |
| XVIIId: R = CH ₃ ; n = 4 | XVIIE: R = CH ₃ ; n = 5 | XVIIIf: R = CH ₃ ; n = 6 |
| XVIIIg: R = CH ₃ ; n = 7 | XVIIIh: R = CH ₃ ; n = 8 | XVIIIi: R = CH ₃ ; n = 9 |
| XVIIIj: R = CH ₃ ; n = 10 | XVIIIk: R = CH ₃ CO ; n = 2 | XVIIIl: R = CH ₃ CO ; n = 3 |
| XVIIIm: R = CH ₃ CO ; n = 4 | XVIIIn: R = CH ₃ CO ; n = 5 | XVIIIo: R = CH ₃ CO ; n = 6 |
| XVIIIp: R = CH ₃ CO ; n = 8 | | |

Azomethine benzoate based liquid crystals (**XIXa- d**) having flexible hexadecanoyl moiety on one side of the molecule and various substituents at the other end of molecule have been synthesized by Ha *et. al.* [105]. All these compounds exhibited mesomorphic properties except compound **XIXc**. Compounds **XIXb** and **XIXd** showed nematic phases while compound **XIXa** was smectic in nature.



- | | |
|---------------------|----------------------------------|
| XIXa: R = CN | XIXb: R = OH |
| XIXc: R = SH | XIXd: R = NO ₂ |

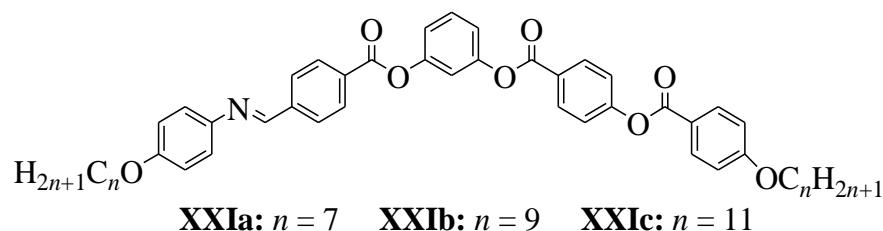
The alkoxy substituent contributes to the molecular polarizability due to strong dipole moment and thus affects intermolecular interactions, hence resulting in nematic polymorphism [106]. Schiff base ester derivatives (**XXc-h**) were prepared by coupling 4-butylaniline with 4-[4'-*n*-alkoxybenzoyloxy]benzaldehyde. Short chain alkoxy groups such as methoxy (**XXa**) and ethoxy (**XXb**) are non-mesogenic while from **XXc-f** exhibit enantiotropic nematogenic phase. Compound **XXg** and **XXh** exhibited smectogenic phase due to increase in the flexibility of molecule.



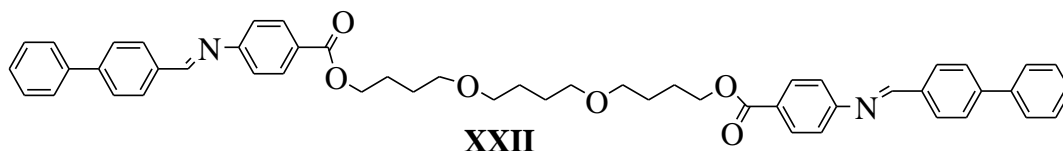
- | | | |
|-------------------|-------------------|-------------------|
| XXa: n = 1 | XXb: n = 2 | XXc: n = 3 |
| XXd: n = 4 | XXe: n = 5 | XXf: n = 6 |
| XXg: n = 7 | XXh: n = 8 | |

Some of the bent shape liquid crystals having asymmetric core with equal chain length on both sides of the rigid core were synthesized *via* coupling of 4-alkoxyaniline with 3-(4-(4-(alkyloxy)benzoyloxy)benzoyloxy)phenyl 4-formylbenzoate. Compound

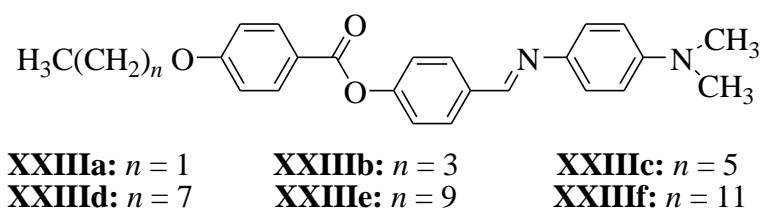
XXIa exhibited B₁ mesophase while **XXIb** and **XXIc** showed antiferroelectric B₂ mesophase. Compound **XXIc** also showed good electro-optical properties [107].



An imine linkage was formed by Iwan *et. al.* via condensation of biphenyl-4-carboxaldehyde with poly(1,4-butanediol)bis(4-aminobenzoate)[108]. The compound **XXII** showed smectic A and B phases during heating and cooling cycles. Compound **XXII** is used in active layer optoelectronic devices.

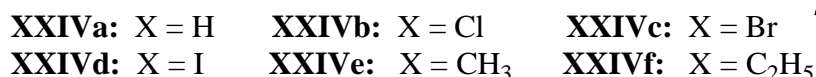
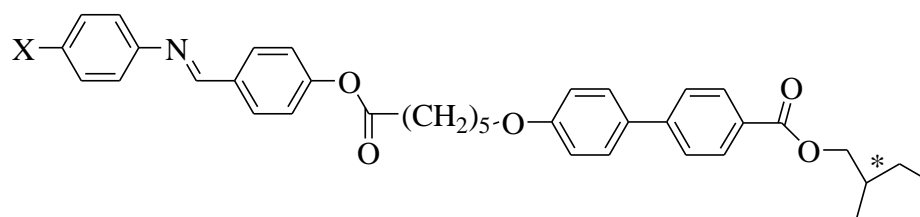


Narasimhaswamy *et. al.* synthesized 4-octyloxybenzoic acid 4-[(4-dimethylamino phenylimino)methyl]phenyl ester via coupling of 4-dimethylaminoaniline with 4-octyloxybenzoic acid 4-formylphenyl ester, itself synthesized by treating 4-octyloxybenzoyl chloride with 4-hydroxybenzaldehyde. All the synthesized compounds (**XXIIIa-f**) showed enantiotropic nematic phase and excellent phase stability [109]. In compound **XXIIIc**, smectic A phase was observed. Due to dimethylamino terminal group, the charge-transfer characteristics of LCs are reduced.

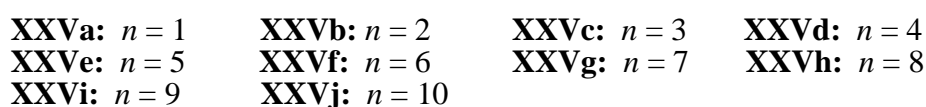
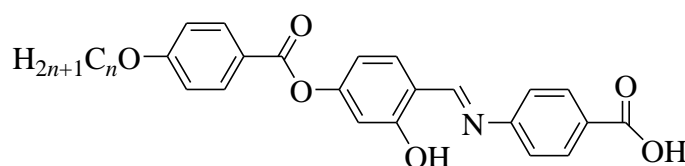


Using a reported method [110], six chiral non-symmetric dimers (**XXIVa-f**) consisting of azomethine and benzoate linkages were synthesized. All the synthesized compounds exhibited enantiotropic chiral nematic phase. It has been observed that **XXIVf** exhibited enantiotropic monolayer chiral smectic C phase, this formation take place due to the molecular inhomogeneity which arises from longer alkyl part. All halogen derivatives

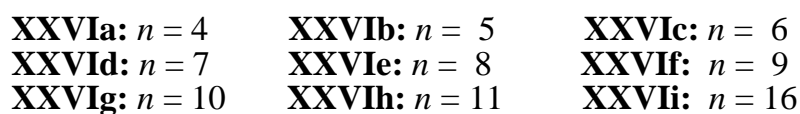
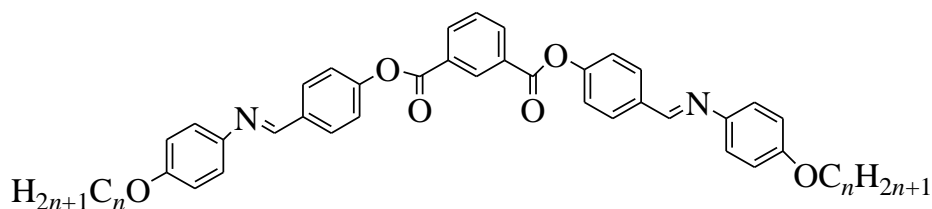
(XXIVb –d) showed weak tendency towards smectic phase due to repulsive dipolar interaction between the halogens and the presence of ester linkage in the intercalated smectic arrangement.



Schiff base esters (XXVa –j) consisting of terminal carboxylic acid group and a flexible alkoxy chain have been synthesized by Ridha *et. al.* [111]. It has been found that compounds XXVa–c exhibit enantiotropic nematic phase while compounds XXVd–g exhibit both smectic and nematic phase. Compounds XXVh–j showed only smectic phase.



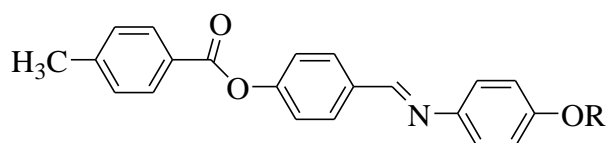
Banana shape liquid crystals (XXVIa-i) consisting of isophthalic acid as central core to which two azomethine phenyl benzoate units are attached have been reported [112]. All the synthesized compounds exhibit enantiotropic liquid crystalline B₁ phase except compound XXVif which shows nematic phase along with B₁ phase.



Liquid crystals have gained popularity due to their interesting properties of birefringence and optical properties. Liquid crystals having calamitic mesogens found applications in the field of electronic devices, electronic screens, non-linear optical devices and can also be used as temperature sensors. After the comprehensive study of literature, it has been found that azomethine phenyl benzoates are of great importance as a central core in LCs due to their interesting properties in the field of optics and photonics. They can be used in the manufacture of electronic devices, as temperature sensors and show good thermal and optoelectronic properties.

Liquid crystals have been a topic of interest in recent past due to their increasing demand in the scientific and technological areas such as display devices, organic light emitting diodes, photoconductors and semi-conductor materials. Liquid crystalline molecules using azomethine phenylbenzoate as a central core are used in the field of optics, photonics and used in electronic devices, and show thermochromic and photochromic properties due to the presence of azomethine linkage.

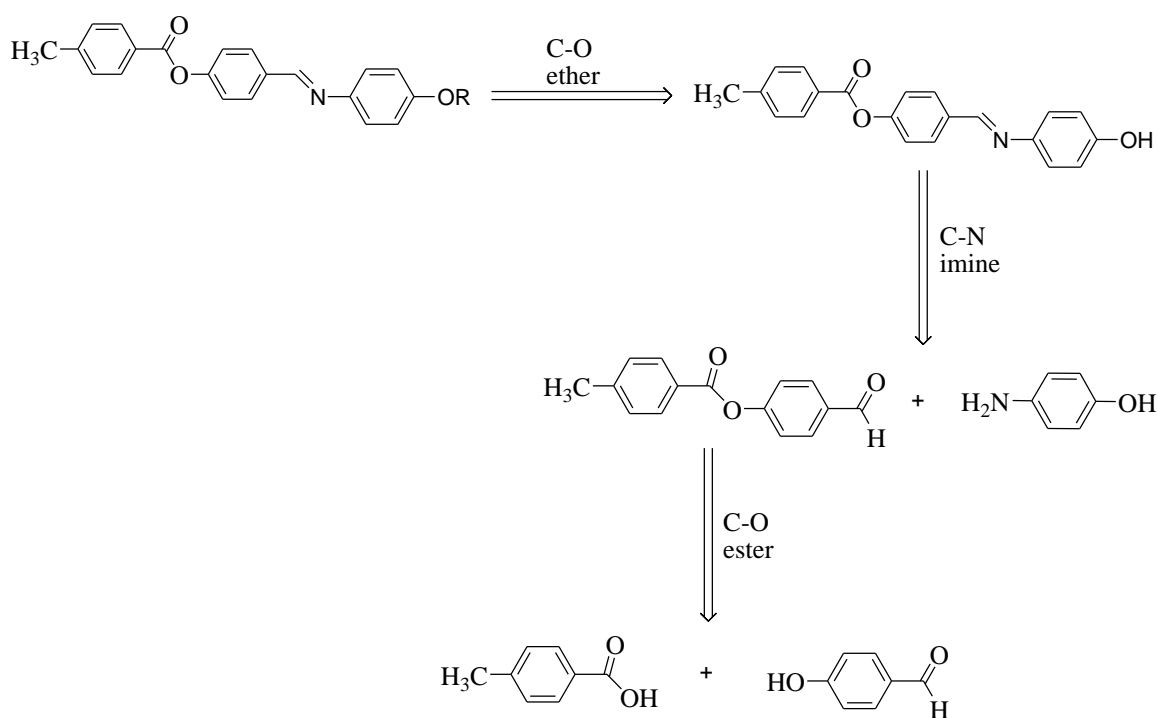
Keeping in mind the growing applications of azomethinephenyl benzoate liquid crystals in different fields, it was planned to synthesize different derivatives of azomethinephenyl benzoates. Different derivatives may be synthesized by introduction of flexible alkoxy end group to explore its effects on the phase transition temperature and mesomorphic nature. The target molecule may comprise of three aromatic rings as a rigid core which are linked to each other *via* azomethine and ester linkages. Ester being a polar group is expected to increase the polarizability of the molecule and influence the properties like birefringence and dielectric anisotropy, while azomethine linkage is supposed to maintain the molecular linearity and provide mechanical strength and enhance the liquid crystalline properties. Both ester and azomethine linkages make the system highly conjugated, provide rigidity to the molecule and enhance the liquid crystalline properties. (*E*)-4-((4-alkyloxyphenylimino)methyl)phenyl 4-methyl benzoate was suggested as a target molecule for the synthesis and evaluation of liquid crystalline properties.



Where R = Alkyl groups

2.1 Retrosynthetic analysis

Keeping in view the above target mesogen consisting of azomethinephenyl benzoate derivatives with ether, azomethine and ester linkages, retrosynthetic analysis of (*E*)-4-((4-alkyloxyphenylimino)methyl)phenyl 4-methylbenzoate leads to simple and commercially available starting materials as depicted in Scheme 2.1.

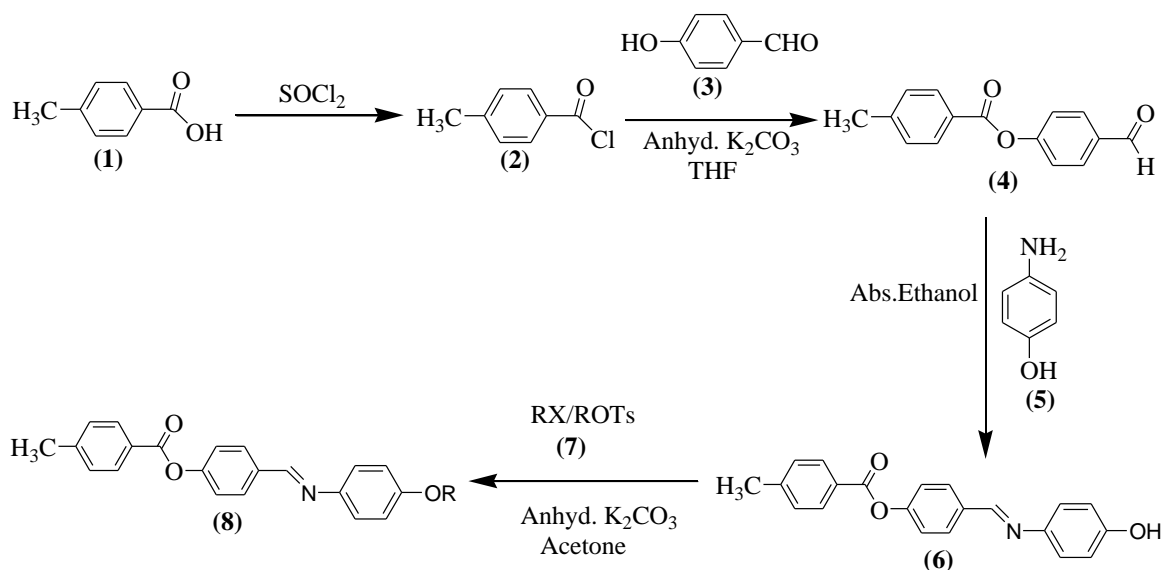


Scheme 2.1: Retrosynthetic analysis for (*E*)-4-((4-alkyloxyphenylimino)methyl) 4-methylbenzoates.

2.2 Synthesis of target compound

According to retrosynthetic analysis, following reaction sequence may be followed while synthesizing (*E*)-4-((4-alkyloxyphenylimino)methyl)phenyl 4-methylbenzoate. 4-Formylphenyl 4-methylbenzoate (**4**) may be synthesized by the esterification reaction between 4-hydroxybenzaldehyde (**3**) and 4-methylbenzoylchloride (**2**). Compound **2** itself may be synthesized by the reaction of 4-methylbenzoic acid (**1**) with thionyl chloride. 4-Formylphenyl 4-methylbenzoate (**4**) may be condensed with 4-aminophenol (**5**) and to give (*E*)-4-((4-hydroxyphenylimino)methyl)phenyl 4-methylbenzoate (**6**). Flexibility in the molecule may be generated by the alkylation of the free hydroxyl group in compound **6** using alkyl halide or alkyl tosylate (**7**) to afford the target molecule, (*E*)-

4-((4-alkoxyphenylimino)methyl) phenyl 4-methylbenzoates (**8**). The synthetic route is given in Scheme 2.2



Scheme 2.2: Synthesis of (*E*)-4-((4-alkoxyphenylimino)methyl) phenyl 4-methylbenzoate (**8**).

2.3 Structure characterization

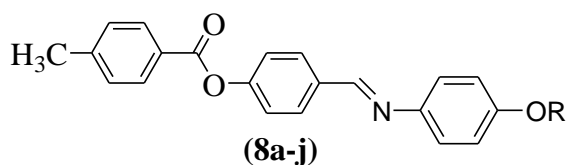
All the synthesized compounds will be characterized using Infrared (IR) spectroscopy, ^1H NMR and ^{13}C NMR spectroscopy. The molecular formula will be verified using mass spectrometry.

2.4 Study of mesomorphic properties

Mesomorphic properties of all the synthesized compounds will be studied using differential scanning calorimetry (DSC), polarizing optical microscopy (POM) and X-ray diffraction (XRD) analysis.

Azomethinephenyl benzoate liquid crystals have been in focus during past years due to their interesting properties in the fields of optics and photonics. Azomethine linkage is incorporated into the molecular structure to maintain the molecular linearity and enhance the mesomorphic properties. An ester linkage is used to increase the molecular polarizability and anisotropy of molecule. The retrosynthetic analysis of the target mesogen, as designated in scheme 2.1, leads to the possible pathway for the synthesis from easily available starting materials, *i.e.*, 4-methylbenzoyl chloride and 4-hydroxy benzaldehyde. Alkyl chain was varied in the synthesized derivatives to determine the structure-property relationship between flexible chain length and mesomorphic behaviour.

The (*E*)-4-((4-alkyloxyphenylimino)methyl)phenyl 4-methylbenzoates (**8a-j**) were synthesized in a multistep sequence according to Scheme 2.2. In the first step, 4-methylbenzoic acid (**1**) was converted to 4-methylbenzoyl chloride in the presence of thionyl chloride. The 4-formylphenyl 4-methylbenzoate (**4**) was synthesized by the esterification reaction between 4-hydroxybenzaldehyde (**3**) and 4-methylbenzoyl chloride (**2**) in the presence of anhydrous potassium carbonate using THF as a solvent. The 4-formylphenyl 4-methylbenzoate (**4**) was condensed with 4-aminophenol (**5**) using absolute ethanol as a solvent under reflux conditions to afford (*E*)-4-((4-hydroxyphenylimino)methyl)phenyl 4-methylbenzoate (**6**). The target molecule (*E*)-4-((4-alkyloxyphenylimino)methyl)phenyl 4-methylbenzoates (**8a-j**) were synthesized by *O*-alkylation of the free hydroxyl group with alkyl bromides or alkyl tosylates (**7**) using anhydrous potassium carbonate as a base and acetone as a solvent.



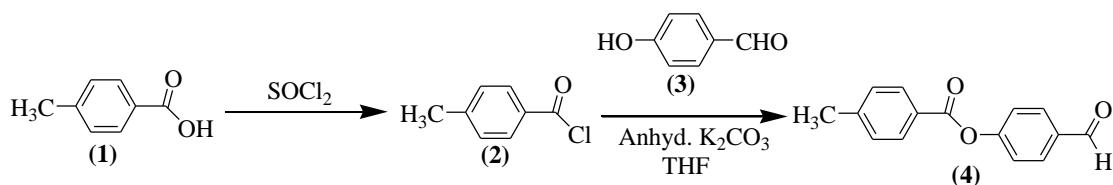
8a: R = C₅H₁₁
8d: R = C₈H₁₇
8g: R = C₁₁H₂₃
8j: R = C₁₄H₂₉

8b: R = C₆H₁₃
8e: R = C₉H₁₉
8h: R = C₁₂H₂₅

8c: R = C₇H₁₅
8f: R = C₁₀H₂₁
8i: R = C₁₃H₂₇

3.1 Synthesis of 4-formylphenyl 4-methylbenzoate (4)

Synthesis of 4-formylphenyl 4-methylbenzoate (**4**) was accomplished through conversion of 4-methylbenzoic acid (**1**) to 4-methylbenzoyl chloride (**2**) using a reported method [113], followed by condensation with 4-hydroxybenzaldehyde (**3**) [114, 115] (Scheme 3.1).



Scheme 3.1: Synthesis of 4-formylphenyl 4-methylbenzoate (**4**).

The synthesized compound 4-formylphenyl 4-methylbenzoate (**4**) was purified by column chromatography (*n*-hexane: ethylacetate; 95:5). White crystalline solid was obtained in 78 % purified yield and melted in the range of 97-98 °C.

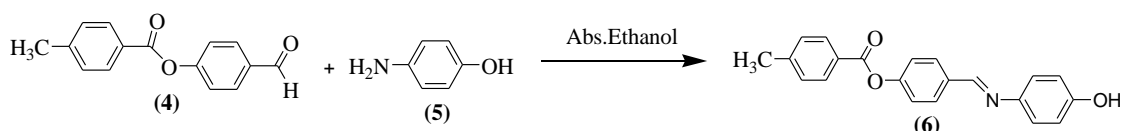
The formation of ester linkage between 4-methylbenzoyl chloride and 4-hydroxybenzaldehyde was indicated in IR spectrum. In IR spectrum, a band with strong intensity for C=O stretching vibrations of ester appeared at 1732 cm^{-1} and C=O of aldehyde group show stretching vibration at 1697 cm^{-1} . Absorption bands for C-H stretching of aldehyde were observed at 2742 cm^{-1} .

^1H NMR spectral data confirmed the formation of 4-formylphenyl 4-methylbenzoate (**4**). The most deshielded signal at 10.03 ppm was assigned to aldehyde proton whereas a singlet at 2.48 ppm was attributed to the terminal methyl attached to aromatic ring. Aromatic protons, integrating to eight protons, appeared in the range of 7.31– 8.12 also confirmed the condensation reaction.

In ^{13}C NMR spectrum of compound (**4**), the signal for carbonyl carbon of ester appeared at 164.58 ppm whereas aldehyde carbonyl carbon resonated at 191.04 ppm further confirming the formation of the product. Signal for methyl carbon appeared at 21.84 ppm while in the range of 122.61-155.81 ppm aromatic carbon resonate.

3.2 Synthesis of (*E*)-4-((4-hydroxyphenylimino)methyl)phenyl 4-methylbenzoate (**6**)

The compound (*E*)-4-((4-hydroxyphenylimino)methyl)phenyl 4-methylbenzoate (**6**) was synthesized *via* condensation reaction between 4-formylphenyl 4-methylbenzoate (**4**) and 4-aminophenol (**5**) as depicted in Scheme 3.2 using a reported method [88].



Scheme 3.2: Synthesis of (*E*)-4-((4-hydroxyphenylimino)methyl)phenyl 4-methylbenzoate.

Purification of Schiff bases was carried out by washing with warm ethylacetate followed by recrystallization from ethanol. The synthesized compound (**6**) was obtained as shiny light brown solid in a purified yield of 82 %. It showed a wide melting temperature range from 205-218 °C.

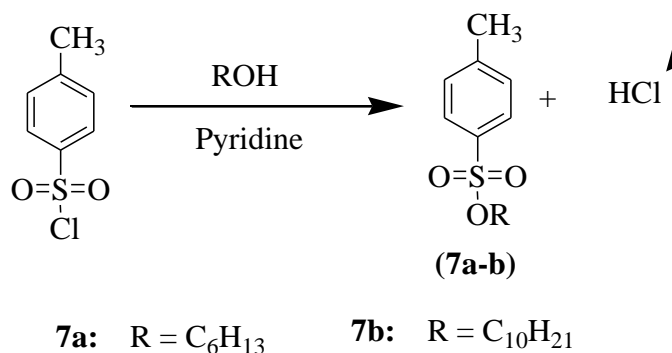
The formation of imine linkage (CH=N) between 4-formylphenyl 4-methylbenzoate (**4**) and 4-aminophenol (**5**) was indicated in IR spectroscopy by the appearance of stretching vibrations of CH=N at 1603 cm⁻¹. Appearance of broad peak at 3628 cm⁻¹ also indicated the successful conversion of compound (**4**) to compound (**6**). A band with strong intensity at 1742 cm⁻¹ was assigned to C=O of ester.

The coupling reaction was confirmed in ¹H NMR spectrum by the appearance of a singlet for imine proton at 8.65 ppm. The phenolic OH proton resonated at 9.54 ppm further confirming the formation of product. Aromatic protons integrating to twelve protons, appeared in the range of 6.80–8.06 ppm. The terminal methyl attached to aromatic ring appeared at 2.50 ppm.

In ¹³C NMR spectrum, appearance of new signal in the range of 156.86 confirmed the formation of CH=N bond. Moreover, the disappearance of signal at 191.04 ppm for carbonyl carbon of aldehyde further confirmed the condensation reaction. The ester carbonyl carbon shifted slightly downfield from 164.58 in the reactant (**4**) to 164.84 ppm in the product. Terminal methyl carbon attached to aromatic ring resonate at 21.75 ppm whereas aromatic carbon appeared in the range of 116.81-156.86 ppm.

3.3 Synthesis of alkyl tosylates (7a-b)

Alkyl tosylates (**7a-b**) were synthesized using a reported method [116] as shown in Scheme 3.3. Primary alcohols were made to react with 4-methylbenzenesulfonyl chloride, using pyridine as a solvent, as well as a base, to afford alkyl tosylates (**7a-b**).



Scheme 3.3: Synthesis of alkyl tosylates (**7a-b**).

Both alkyl tosylates were transparent golden yellow liquids at room temperature. The synthesized tosylates were obtained in good yields and with enough purity to be used in the next step. Physical data of alkyl tosylates is tabulated in Table 3.1.

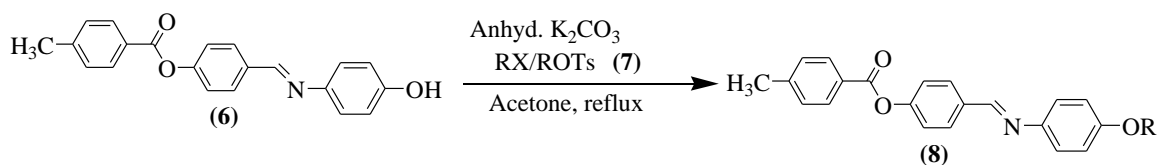
Table 3.1: Physical data of alkyl tosylates (**6a-b**)

Compound	R	Yield (%)	*R _f
6a	C ₆ H ₁₃	92	0.92
6b	C ₁₀ H ₂₁	90	0.88

**n*-hexane:ethyl acetate (7:3) on silica gel 60F₂₅₄

3.4 Synthesis of (*E*)-4-((4-alkyloxyphenylimino)methyl)phenyl 4-methylbenzoates (**8a-j**)

The compound **6** was *O*-alkylated using either an alkyl tosylate or alkyl bromide employing anhydrous potassium carbonate as a base to afford the target molecules [92]. The synthesis is shown in Scheme 3.4.



8a: R = C₅H₁₁

8d: R = C₈H₁₇

8g: R = C₁₁H₂₃

8j: R = C₁₄H₂₉

8b: R = C₆H₁₃

8e: R = C₉H₁₉

8h: R = C₁₂H₂₅

8c: R = C₇H₁₅

8f: R = C₁₀H₂₁

8i: R = C₁₃H₂₇

Scheme 3.4: Synthesis of (*E*)-4-((4-alkoxyphenylimino)methyl)phenyl 4-methylbenzoates (**8a-j**).

The synthesized compounds (**8a-j**) were purified by repeated recrystallization from *n*-hexane resulting in white crystalline solids. The physical data of compounds **8a-j** is tabulated in Table 3.2.

Table 3.2: Physical data of (*E*)-4-((4-alkoxyphenylimino)methyl)phenyl 4-methylbenzoates (**8a-j**)

Compound	Yield (%)	R _f [*]	Melting point (°C)
8a	33	0.69	135 - 280
8b	32	0.70	127 - 263
8c	31	0.71	124 - 248
8d	33	0.71	121 - 231
8e	43	0.73	116 - 227
8f	35	0.76	112 - 218
8g	30	0.77	108 - 212
8h	33	0.79	111 - 204
8i	40	0.80	114 - 198
8j	31	0.81	112 - 190

The appearance of aliphatic C-O stretching bands in the region of 1253-1249 cm⁻¹ and 1020-1016 cm⁻¹ in the IR spectra of (*E*)-4-((4-alkoxyphenylimino)methyl)phenyl 4-methylbenzoates (**8a-j**), indicated the formation of ether linkage. Sharp absorption peaks in the region of 1742-1739 cm⁻¹ were assigned to carbonyl group of ester. Moreover, the absence of broad signal for phenolic hydrogen at 3628 cm⁻¹, observed in

the IR spectrum of compound **6**, also indicated successful *O*-alkylation. IR spectroscopic data of compound **8a-j** is summarized in Table 3.3.

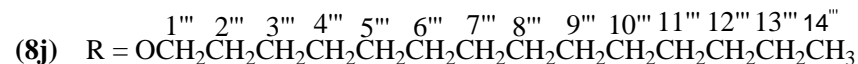
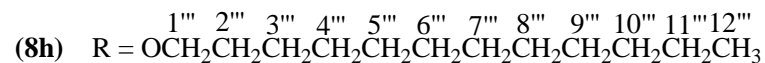
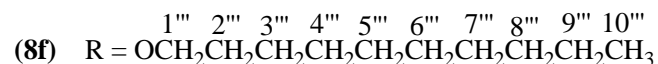
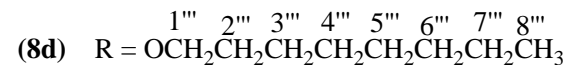
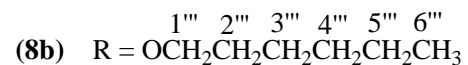
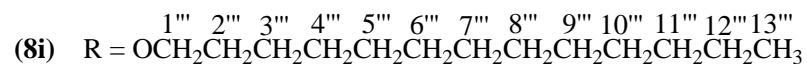
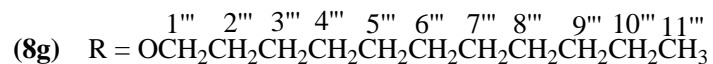
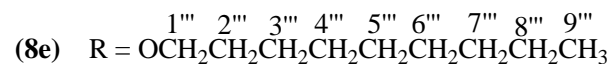
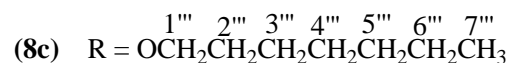
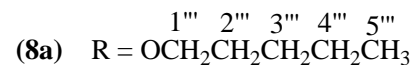
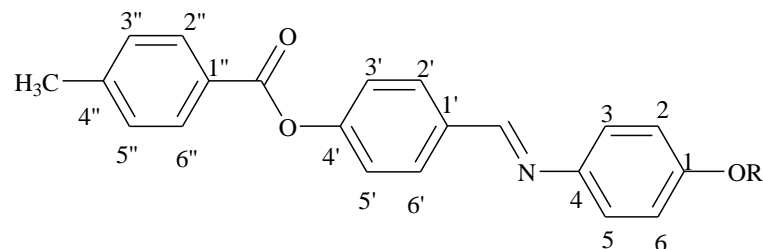
Table 3.3: IR spectroscopic data of (*E*)-4-((4-alkyloxyphenylimino)methyl)phenyl 4-methylbenzoates (**8a-j**)

Compound	Absorptions(cm ⁻¹)				
	Sp ³ C-H str.	CH=N Str.	C=O Ester str.	C-O-C Str.	C=C arom str.
8a	2957, 2862	1604	1742	1250, 1019	1573, 1474
8b	2934, 2860	1606	1742	1249, 1076	1573, 1473
8c	2920, 2852	1607	1739	1251, 1060	1572, 1473
8d	2920, 2857	1605	1741	1251, 1066	1574, 1473
8e	2951, 2848	1606	1742	1272, 1037	1574, 1472
8f	2917, 2849	1606	1742	1274, 1078	1574, 1473
8g	2915, 2847	1605	1742	1249, 1077	1574, 1472
8h	2916, 2848	1606	1742	1252, 1078	1574, 1473
8i	2915, 2847	1605	1742	1214, 1077	1574, 1472
8j	2915, 2848	1606	1742	1253, 1078	1574, 1472

Alkylation was confirmed in ¹H NMR spectra by the appearance of a triplet in the range of 3.98-4.07 ppm. This signal was attributed to methylene protons next to oxygen-atom. Additional signal for the rest of alkyl chain protons appeared in the aliphatic region of 0.94-1.89 ppm. Moreover, the disappearance of phenolic proton in the region of 9.54 ppm further confirmed the formation of ether linkage. The ¹H NMR spectral data of compound **8a-j** is given in Table 3.4.

Table 3.4

¹H NMR data of (*E*)-4-((4-alkoxyphenylimino)methyl)phenyl 4-methylbenzoates (**8a-j**)



(Continued)

Table 3.4: Continuation

Protons	Chemical shifts (ppm), intensity, multiplicity and coupling constants (<i>J</i>)									
	8a	8b	8c	8d	8e	8f	8g	8h	8i	8j
CH = N	8.46 (1H, s)	8.42 (1H, s)	8.42 (1H, s)	8.42 (1H, s)	8.42 (1H, s)	8.42 (1H, s)	8.42 (1H, s)	8.46 (1H, s)	8.42 (1H, s)	8.44 (1H, s)
H-2'', 6''	8.12 (2H, d, <i>J</i> = 8.1 Hz)	8.12 (2H, d, <i>J</i> = 8.1 Hz)	8.12 (2H, d, <i>J</i> = 8.1 Hz)	8.12 (2H, d, <i>J</i> = 8.1 Hz)	8.12 (2H, d, <i>J</i> = 8.1 Hz)	8.12 (2H, d, <i>J</i> = 8.1 Hz)	8.11 (2H, d, <i>J</i> = 8.1 Hz)	8.11 (2H, d, <i>J</i> = 8.1 Hz)	8.12 (2H, d, <i>J</i> = 8.1 Hz)	8.10 (2H, d, <i>J</i> = 8.4 Hz)
H-3', 5'	7.92 (2H, d, <i>J</i> = 8.7 Hz)	7.86 (2H, d, <i>J</i> = 8.7 Hz)	7.91 (2H, d, <i>J</i> = 8.7 Hz)	7.90 (2H, d, <i>J</i> = 8.7 Hz)	7.86 (2H, d, <i>J</i> = 8.7 Hz)	7.92 (2H, d, <i>J</i> = 8.7 Hz)	7.84 (2H, d, <i>J</i> = 8.7 Hz)	7.84 (2H, d, <i>J</i> = 8.7 Hz)	7.87 (2H, d, <i>J</i> = 8.4 Hz)	7.84 (2H, d, <i>J</i> = 8.7 Hz)
H-3, 5	7.22-7.38	7.22-7.35	7.23-7.38	7.23-7.35	7.22-7.35	7.22-7.35	7.22-7.35	7.22-7.35	7.22-7.35	7.24-7.35
H-2', 6'	(6H, <i>m</i>)	(6H, <i>m</i>)	(6H, <i>m</i>)	(6H, <i>m</i>)	(6H, <i>m</i>)	(6H, <i>m</i>)	(6H, <i>m</i>)	(6H, <i>m</i>)	(6H, <i>m</i>)	(6H, <i>m</i>)
H-3'', 5''										
H-2, 6	6.96 (2H, d, <i>J</i> = 8.7 Hz)	6.99 (2H, d, <i>J</i> = 8.7 Hz)	6.99 (2H, d, <i>J</i> = 8.7 Hz)	6.99 (2H, d, <i>J</i> = 8.7 Hz)	6.99 (2H, d, <i>J</i> = 8.7 Hz)	7.00 (2H, d, <i>J</i> = 8.7 Hz)	7.00 (2H, d, <i>J</i> = 8.7 Hz)	7.00 (2H, d, <i>J</i> = 8.7 Hz)	7.00 (2H, d, <i>J</i> = 8.7 Hz)	7.00 (2H, d, <i>J</i> = 8.7 Hz)
CH₃	2.48 (3H, s)	2.47 (3H, s)	2.46 (3H, s)	2.48 (3H, s)	2.48 (3H, s)	2.48 (3H, s)	2.47 (3H, s)	2.47 (3H, s)	2.48 (3H, s)	2.47 (3H, s)
H-1'''	4.04 (2H, t, <i>J</i> = 6.6 Hz)	4.04 (2H, t, <i>J</i> = 6.6 Hz)	4.05 (2H, t, <i>J</i> = 6.6 Hz)	4.05 (2H, t, <i>J</i> = 6.6 Hz)	4.04 (2H, t, <i>J</i> = 6.6 Hz)	4.05 (2H, t, <i>J</i> = 6.6 Hz)	4.04 (2H, t, <i>J</i> = 6.6 Hz)	4.04 (2H, t, <i>J</i> = 6.6 Hz)	4.04 (2H, t, <i>J</i> = 6.6 Hz)	4.05 (2H, t, <i>J</i> = 6.6 Hz)

(Continued)

Table 3.4: Continuation

H-2'''	1.84 (2H, quin, $J = 6.9$ Hz)	1.83 (2H, quin, $J = 6.9$ Hz)	1.83 (2H, quin, $J = 6.9$ Hz)	1.83 (2H, quin, $J = 6.9$ Hz)	1.82 (2H, quin, $J = 6.9$ Hz)	1.83 (2H, quin, $J = 6.9$ Hz)	1.83 (2H, quin, $J = 6.9$ Hz)	1.83 (2H, quin, $J = 6.9$ Hz)	1.83 (2H, quin, $J = 6.9$ Hz)	1.83 (2H, quin, $J = 6.9$ Hz)
H-3'''	1.38-1.51	1.34-1.52 6H, m	1.34-1.511 8H, m	1.31-1.49 10H, m	1.30-1.49 12H, m	1.30-1.49 14H, m	1.29-1.51 16H, m	1.29-1.51 18H, m	1.29-1.51 20H, m	1.28-1.49 22H, m
H-4'''	4H, m									
H-5'''	0.96 (3H, t, $J = 6.9$ Hz)									
H-6'''	-----									
H-7'''	-----	0.93 (3H, t, $J = 7.2$ Hz)	0.90 (3H, t, $J = 6.9$ Hz)	0.91 (3H, t, $J = 7.2$ Hz)	0.91 (3H, t, $J = 7.2$ Hz)					
H-8'''	-----	-----	-----	-----	-----					
H-9'''	-----	-----	-----	-----	-----					

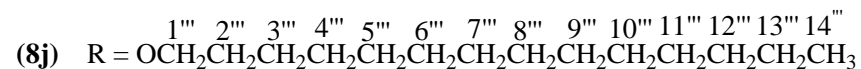
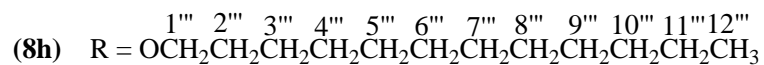
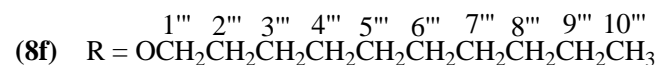
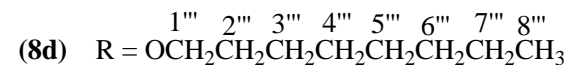
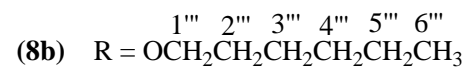
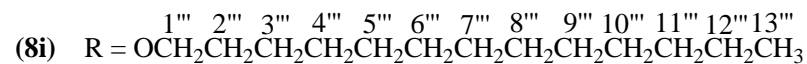
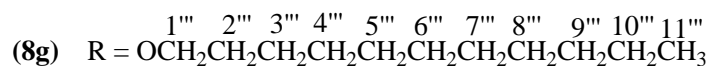
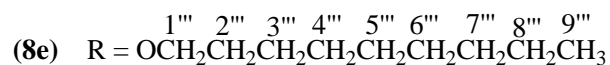
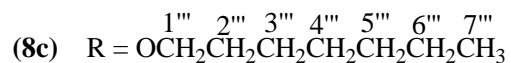
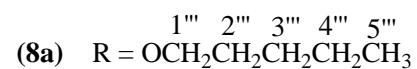
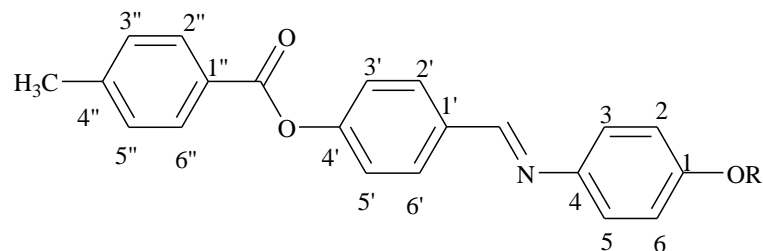
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Table 3.4: Continuation

H-10'''	----	----	----	----	----	0.90 (3H, t, <i>J</i> = 6.9 Hz)				
H-11'''	----	----	----	----	----	----	0.90 (3H, t, <i>J</i> = 6.9 Hz)			
H-12'''	----	----	----	----	----	----	----	0.90 (3H, t, <i>J</i> = 6.9 Hz)		
H-13'''	----	----	----	----	----	----	----	----	0.90 (3H, t, <i>J</i> = 6.9 Hz)	
H-14'''	----	----	----	----	----	----	----	----	----	0.90 (3H, t, <i>J</i> = 6.9 Hz)

In ^{13}C NMR spectra of compounds **8a-j**, appearance of OCH_2 carbon signal in the range of 68.21-68.44 ppm confirmed the formation of C-O-C bond. Aliphatic carbon atoms appeared in their respective region. The ester carbonyl carbon shifted slightly downfield from 166.70 in the reactant to 166.90-167.05 ppm in the product. The detailed ^{13}C NMR data of compounds **8a-j** is presented in Table 3.5.

Table 3.5: ^{13}C NMR data of (*E*)-4-((4-alkyloxyphenylimino)methyl)phenyl 4-methylbenzoates (**8a-j**)



(Continued)

Table 3.5: Continuation

Carbons	Chemical shifts (ppm)									
	8a	8b	8c	8d	8e	8f	8g	8h	8i	8j
C=O	165.41	165.41	165.36	165.41	165.41	165.36	165.36	165.37	165.38	165.39
CH = N	161.96	161.96	160.07	161.96	161.96	160.14	160.14	160.05	160.04	160.04
C-1	159.96	159.97	159.96	159.98	159.96	-----	-----	-----	-----	-----
C-4'	150.03	150.02	150.02	150.03	150.03	-----	-----	-----	-----	-----
C-4	148.80	148.79	148.78	148.78	148.79	-----	-----	-----	-----	-----
C-4''	144.43	144.44	144.49	144.51	144.44	144.53	144.52	144.48	144.49	144.45
C-1'	130.55	130.56	130.55	130.56	130.55	130.73	130.71	130.73	130.73	130.65
C-2'', 6''	130.23	130.23	130.25	130.25	130.24	130.25	130.25	130.25	130.25	130.24
C-2', 6'	129.31	129.31	129.33	129.33	129.31	129.34	129.33	129.33	129.34	129.32
C-3'', 5''	128.92	128.92	128.92	128.90	128.92	128.92	128.92	128.92	128.92	128.92
C-3, 5	126.81	126.80	126.73	126.79	126.80	126.68	126.70	126.75	126.71	126.78
C-3', 5'	122.31	122.32	122.33	122.32	122.32	122.34	122.48	122.41	122.44	122.36
C-1''	121.79	121.79	121.98	121.89	121.79	121.90	121.87	121.84	121.88	121.82

Table 3.5: Continuation

C-2, 6	114.71	114.71	114.75	114.99	114.71	114.75	114.75	114.75	114.75	114.75
CH₃	21.79	21.79	21.80	21.80	21.79					
C-1'''	68.21	68.22	68.44	68.22	68.23	68.44	68.44	68.44	68.28	68.26
C-2'''	28.22	25.70	25.98	26.03	26.02	25.98	26.01	26.02	26.03	26.01
C-3'''	29.01	29.15	29.16,	29.37,	29.54,	29.39,	29.63,	29.67,	29.72,	29.74,
C-4'''	22.47	31.58	29.07	29.26,	29.41,	29.34,	29.57,	29.62,	29.70,	29.68,
C-5'''	14.04	22.61	31.79	29.19	29.28,	29.24,	29.41,	29.60,	29.64,	29.62,
C-6'''	-----	14.06	22.63	31.83	29.19	29.13,	29.36,	29.41,	29.61,	29.59,
C-7'''	-----	-----	14.12	22.69	31.89	29.06	29.15,	29.38,	29.41,	29.48,
C-8'''	-----	-----	-----	14.14	22.69	31.91	29.07	29.17,	29.37,	29.39,
C-9'''	-----	-----	-----	-----	14.14	22.70	31.93	29.07,	29.26,	29.28,
C-10'''	-----	-----	-----	-----	-----	14.15	22.72	31.94	29.17	29.17,
C-11'''	-----	-----	-----	-----	-----	-----	14.14	22.72	31.96	29.07
C-12'''	-----	-----	-----	-----	-----	-----	-----	14.16	22.74	31.95
C-13'''	-----	-----	-----	-----	-----	-----	-----	-----	14.14	22.72
C-14'''	-----	-----	-----	-----	-----	-----	-----	-----	-----	14.14

3.5 Mesomorphic properties of synthesized compounds

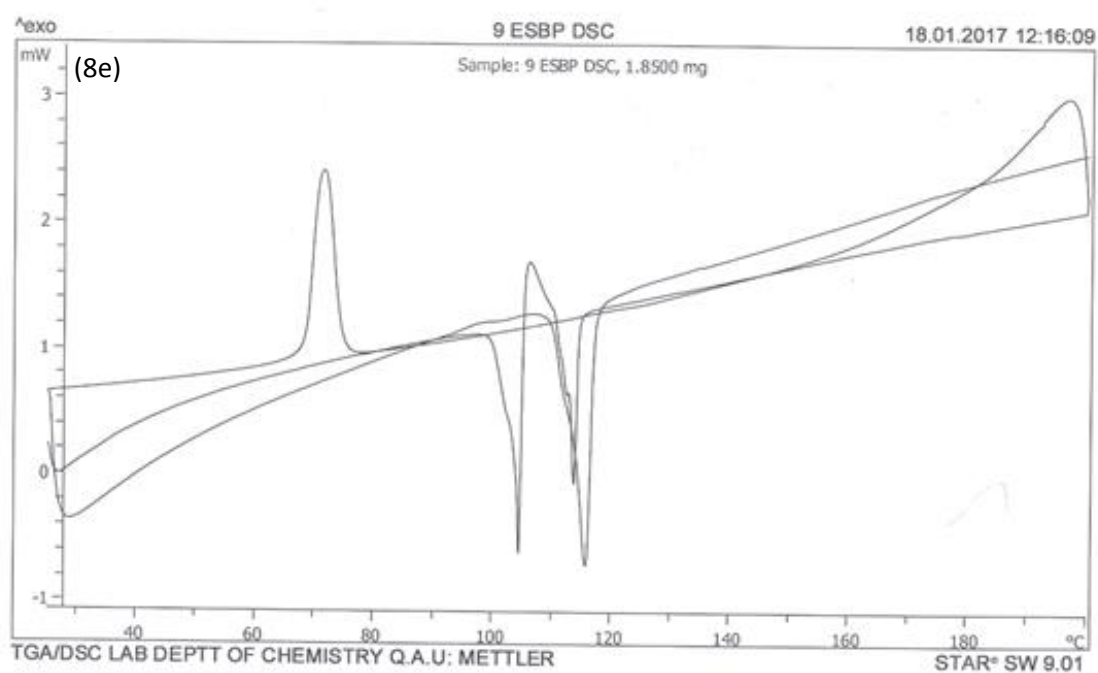
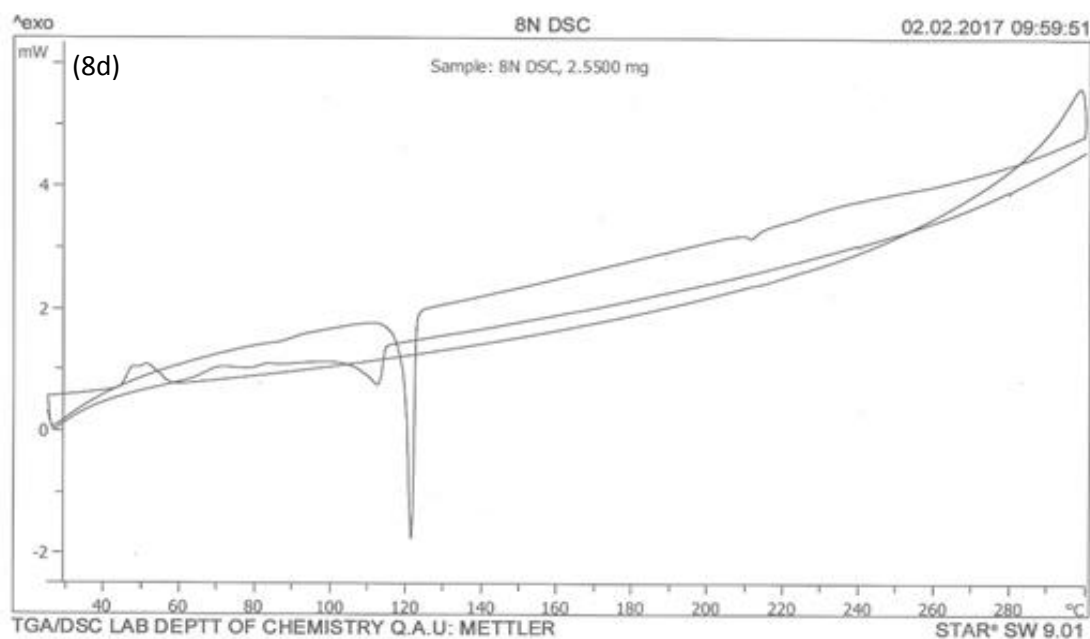
Mesomorphic properties of the synthesized (*E*)-4-((4-alkyloxyphenylimino)methyl)phenyl 4-methylbenzoates (**8a-j**) were studied using differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). DSC was used for the determination of number of liquid crystalline phases, their phase transition temperatures and enthalpy changes. The transitions observed in DSC were further confirmed under POM, where specific optical textures were observed for each transition.

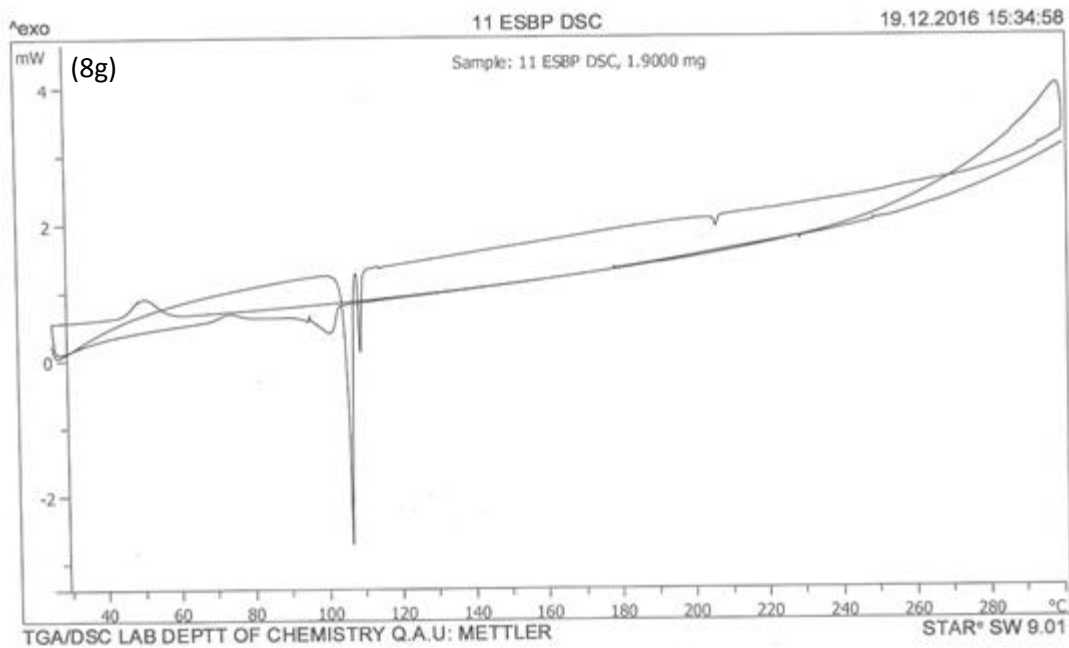
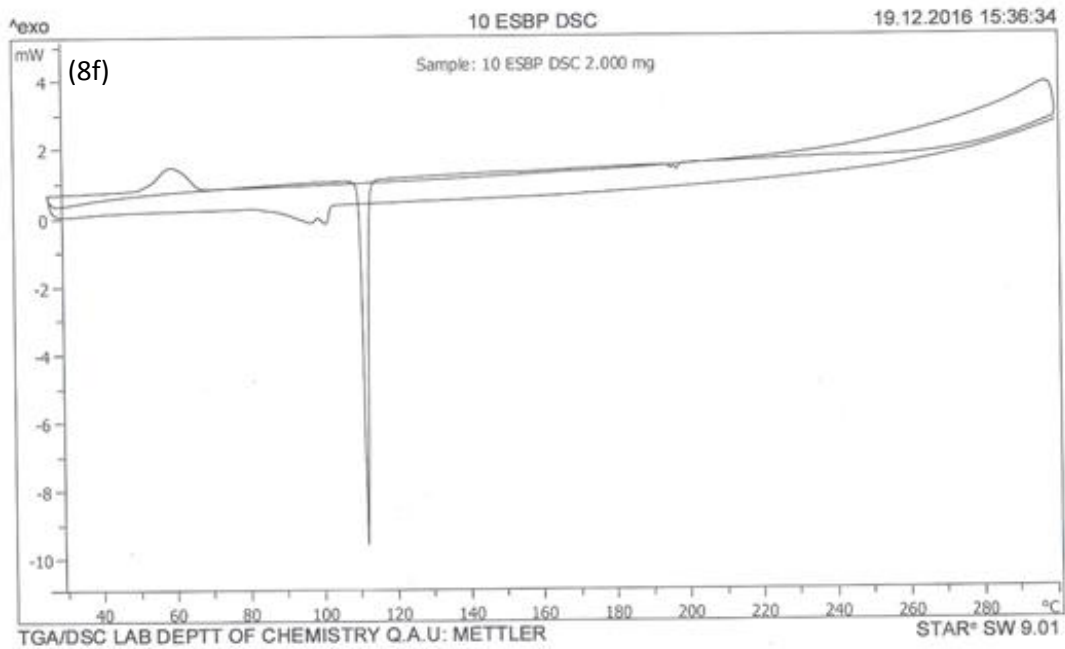
3.5.1 Mesomorphic properties of (*E*)-4-((4-alkyloxyphenylimino)methyl)phenyl 4-methylbenzoates (**8a-j**)

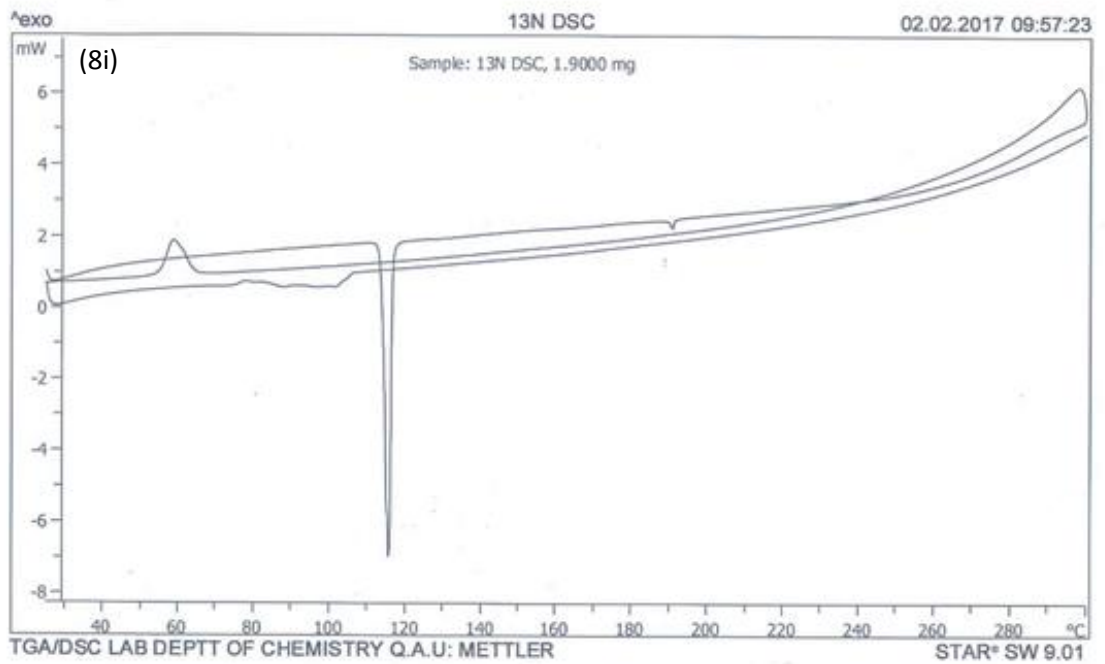
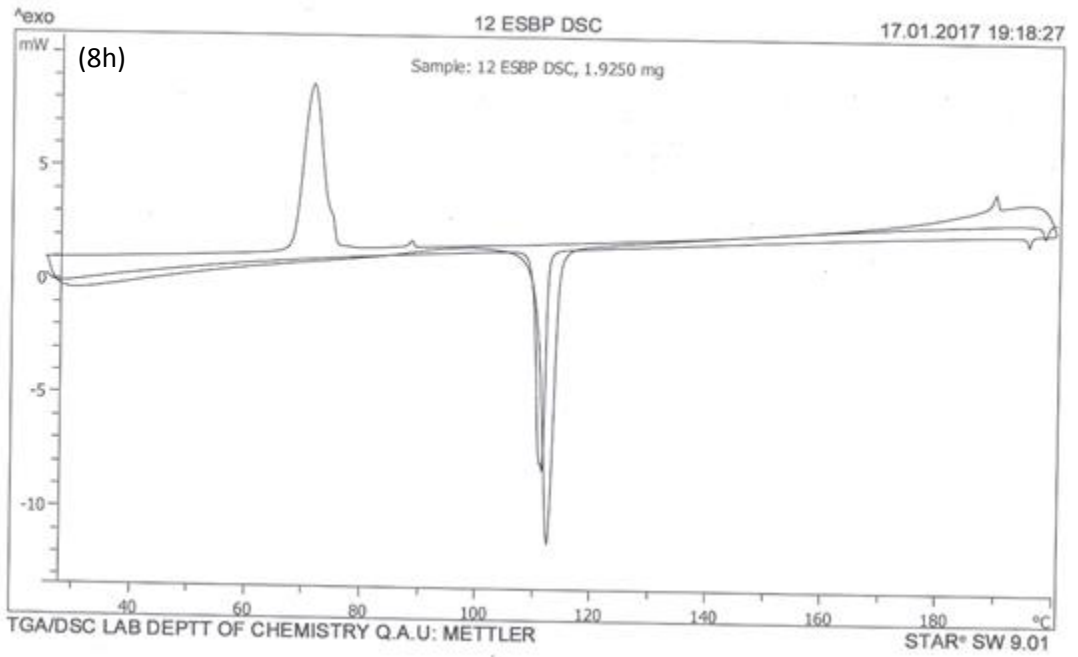
DSC thermograms of synthesized compounds were obtained at a heating rate of 5 °C per minute. Multiple transitions were observed both on heating and cooling scans. The transitions correspond to crystalline, liquid crystalline and isotropic phases.

In DSC thermogram of compound **8d**, two transitions were obtained, one in the range of 119.5-130.2 °C (-4.96 cal/mol) that shows the transition from crystalline solid to liquid crystalline state and the second in the range 220.6-225.8 °C (-0.03 cal/mol) showing the transition from liquid crystalline state to isotropic liquid. In DSC thermogram of compound **8e**, a peak at 102.4 °C corresponds to enthalpy change of -3.94 cal/mol indicating the melting temperature which changed to isotropic phase at 227.0 °C (-3.44 cal/mol). The DSC trace for compound **8f**, exhibited monotropic liquid crystalline phases between 110.1–195.2 °C during heating scan with the enthalpy change of -10.66 to -0.25 cal/mol. The DSC thermogram of compound **8g**, showed enantiotropic mesomorphic behaviour and melted at 104.9 °C whereas isotropic liquid phase was observed at 204.8 °C. Differential scanning calorimetric analysis of compound **8h** exhibited a number of transitions both on heating as well as on cooling cycles. During cooling cycle, compound **8h** changed from isotropic liquid to first mesophase state at 190.3 °C having enthalpy changed of 0.30 cal/mol which then transformed to the second mesophase state at 89.1 °C (0.10 cal/mol), further cooling changed it into solid crystalline state at 74.4 °C. The compound **8i**, showed transition from 113.6-208.7 °C during heating scan. The compound **8j** showed three peaks, the first one at 178.8 °C (0.11 cal/mol) from isotropic liquid to first mesophase state, which changed into second mesophase at 101.7 °C (0.075 cal/mol), followed by phase change

at 86.5 °C, which upon further cooling changed into solid crystalline state at 84.0 °C. The DSC thermograms of compounds **8d-j** are presented in Figure 3.2.







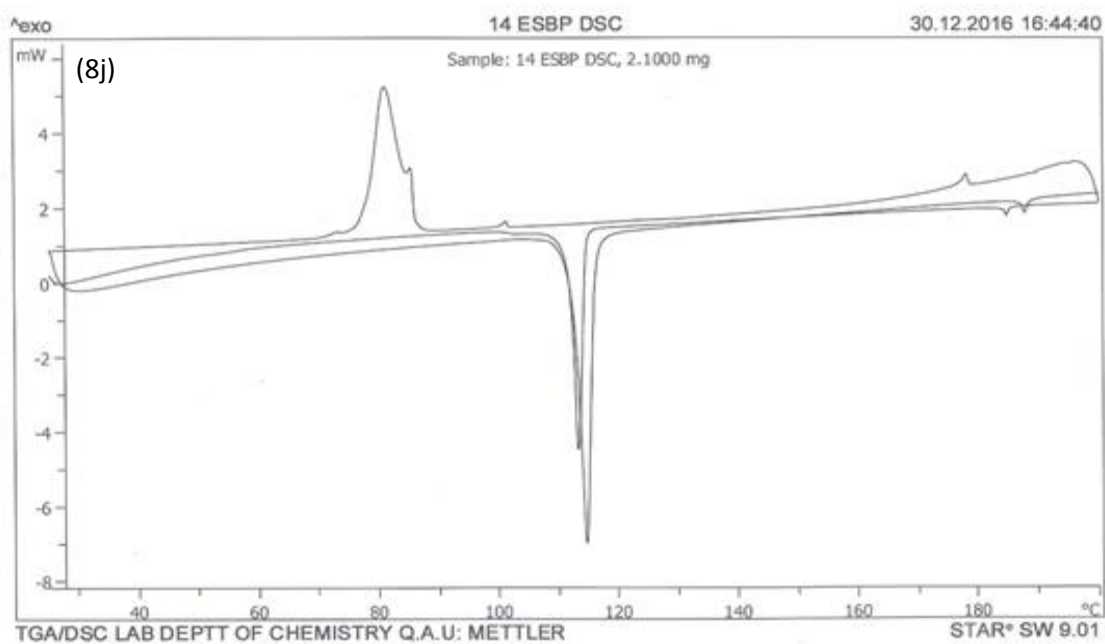


Figure 3.1: DSC thermograms of (*E*)-4-((4-alkyloxyphenylimino)methyl)phenyl 4-methylbenzoates (**8d-j**).

The transition temperatures, number of phases and enthalpy values for compounds **8d-j** are tabulated in Table 3.6.

Table 3.6: Transition temperature and enthalpy values of of (*E*)-4-((4-alkyloxyphenylimino)methyl)phenyl 4-methylbenzoates (**8d-j**)

Compounds	Transition Temperature (°C)		Enthalpy ΔH (Cal/mol)
	Cooling / heating		
8d	I 209.78 N 72.32 Cr		I 0.07 N 1.33 Cr
	Cr 119.5 N 220.49 I		Cr 4.96 N -0.03 I
8e	I 193.38 N 74.53 Cr		I -5.67 N 2.19 Cr
	Cr 102.40 Sm 195.41 I		Cr -3.94 Sm -3.44 Cr
8f	I 66.34 Cr		I 0.016 Cr
	Cr 110.10 N 195.22 I		Cr -10.66 N -0.25 I
8g	I 57.38 Cr		I 1.56 Cr
	Cr 104.93 Sm 108.08 N 204.84 I		Cr -4.04 Sm -0.64 N -4.93 I
8h	I 190.38 N 89.12 Sm 74.5 Cr		I 0.30 N 0.10 Sm 9.98 Cr
	Cr 109.53 N 194.81 I		Cr -12.38 N -0.29 I
8i	I 64.23 Cr		I 4.00 Cr
	Cr 113.80 N 189.71 I		Cr -11.35 N -0.20 I
8j	I 178.74 N 101.75 Sm X 86.58		I 0.11 N 0.05 Sm X 0.13
	Sm C 84.05 Cr		Sm C 2.85 Cr
	Cr 111.71 N 184.14 I		Cr -7.04 N -0.12 I

The liquid crystalline properties of the synthesized compounds **8a-j** were further confirmed through POM analysis. Photomicrographs of the samples were taken by heating the sample at a rate of 1 °C/min to isotropic liquid and then cooling at the same rate to crystalline solid. The textures were captured during cooling scans. All the synthesized compounds showed nematic phase and smectic phases. In some of the compounds (**8f-j**), some peaks in DSC thermograms could not be observed during cooling scan, however, POM studies indicated phase transition temperatures. In some of the compounds (**8f-j**), some peaks in DSC thermograms could not be observed during cooling scan, however, POM studies indicated phase transition temperatures.

The snapshots for compounds **8a** were captured during cooling scan. POM micrographs displayed nematic phase (Figure 3.2). The nematic phase was recognized by the appearance of droplets at 274.2 °C, which was then changed into schlieren nematic texture having two brushes at 273.4 °C and 272 °C. Thread-like texture was obtained at 270.5 °C.

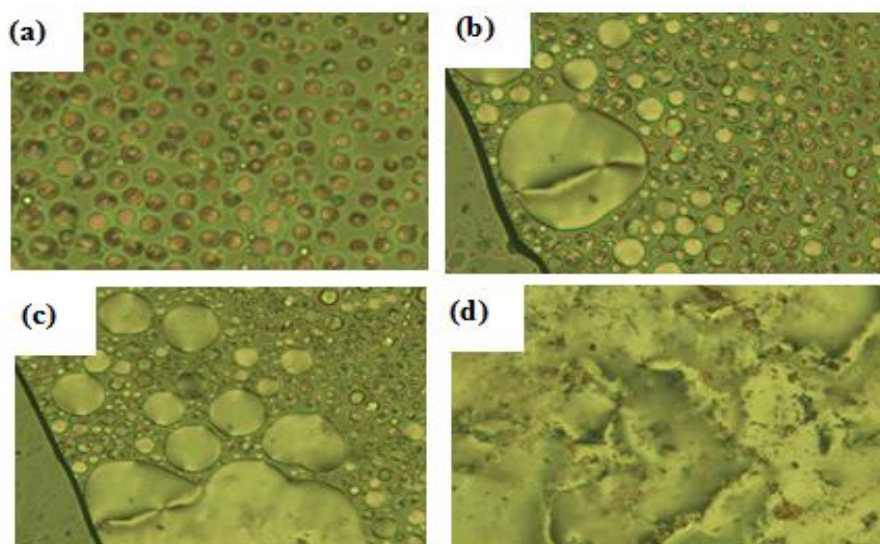


Figure 3.2: POM micrographs of compound **8a** at different temperatures during cooling scan at: **a)** 274.2 °C **b)** 273.4 °C **c)** 272.0 °C **d)** 270.5 °C.

During cooling scan, POM micrographs for compound **8b** were collected. It was observed that compound **8b** exhibited nematic phase that was confirmed by the appearance of droplets at 254.3 °C and schlieren textures at 252.5 °C and 251.8 °C (Figure 3.3).

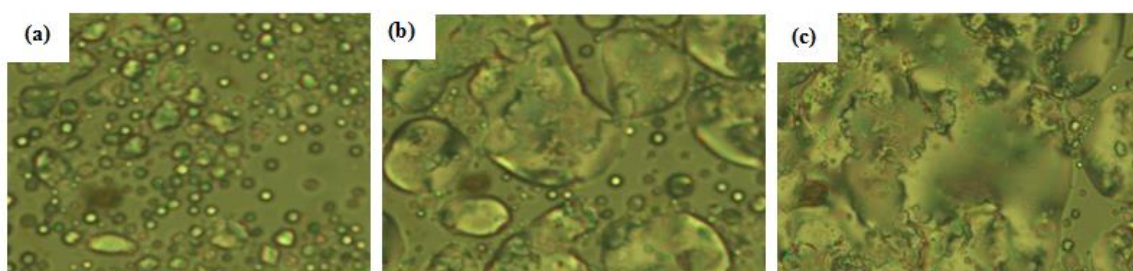


Figure 3.3: POM snapshots of compound **8b** during cooling scan at: **a)** 254.3 °C **b)** 252.5 °C **c)** 251.8 °C.

The pictures for compound **8c** were taken during heating scan. Optical micrographs demonstrated nematic phase. Appearance of thread like textures at 225.3 °C forming loops as well as the appearance of nematic droplets having fan-like structure at 245.6 °C and 247.3 °C depicted the presence nematic phase (Figure 3.4).

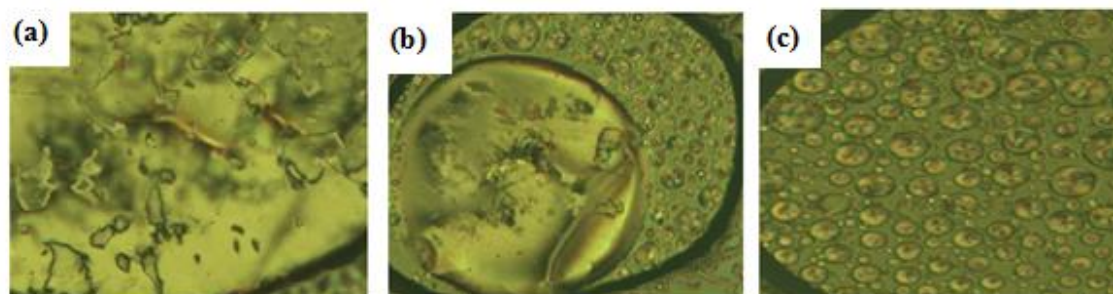


Figure 3.4: POM snapshots of compound **8c** during heating scan at: **a)** 225.3 °C
b) 245.6 °C **c)** 247.3 °C.

Optical micrographs for compound **8d** were captured on cooling the compound **8d** from isotropic liquid phase. Nematic phase was observed at different temperatures (Figure 3.5). The nematic phase was confirmed by the appearance of nematic droplets at 221.5 °C, schlieren nematic texture at 220.1 °C and planar textures with thread like loops at 211.8 and 207.3 °C.

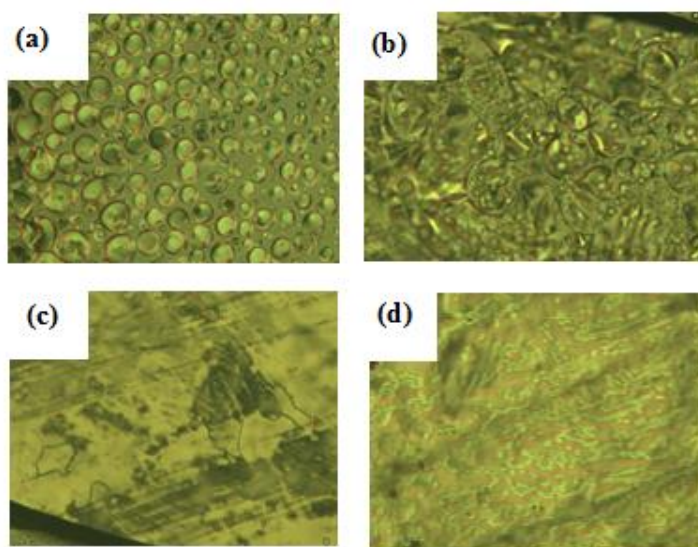


Figure 3.5: POM snapshots of compound **8d** during cooling scan at: **a)** 221.5 °C
b) 220.1 °C **c)** 211.8 °C **d)** 207.3 °C.

The POM textures were obtained on heating the crystalline compound **8e** to isotropic liquid. The appearance of schlieren texture at 124.5 °C, 142.2 °C and 165.6 °C demonstrated the Smectic C phase. An additional nematic phase was observed by the appearance of Schlieren nematic texture as well as nematic droplet texture at 181.9 °C, 235.3 °C and 247.5 °C as depicted in Figure 3.6.

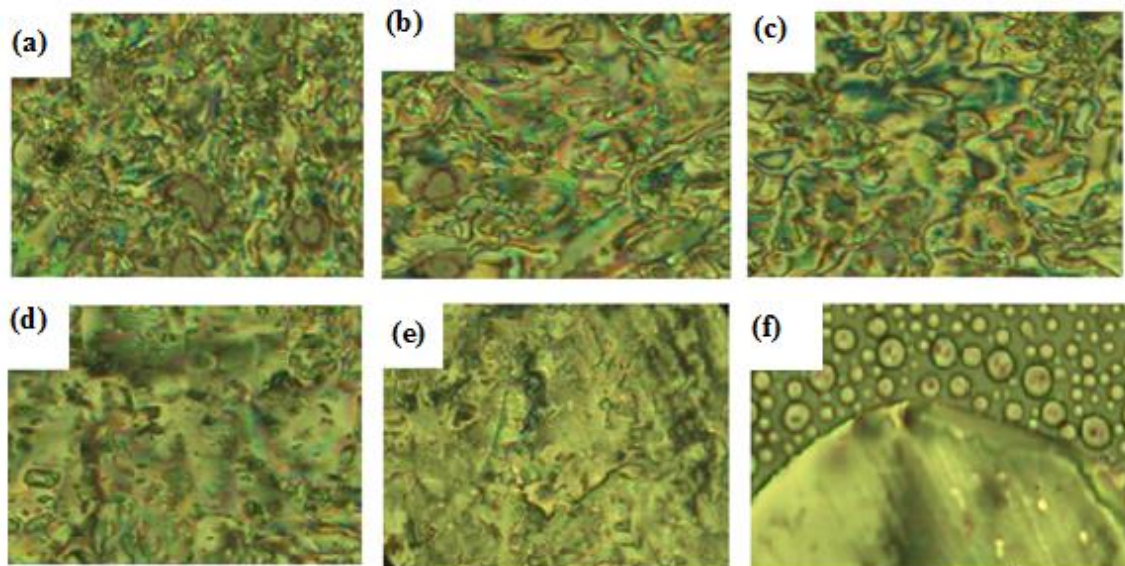


Figure 3.6: POM snapshots of compound **8e** during heating scan at: **a)** 124.5 °C **b)** 142.2 °C **c)** 165.6 °C **d)** 181.9 °C **e)** 220.8 °C **f)** 226.3 °C.

Optical micrographs for compound **8f** were collected during cooling scan as shown in Figure 3.7. Nematic droplets having fan-like texture appeared at 213.7 °C, schlieren nematic texture having two and four brushes appeared at 205.8 °C, while thread-like texture was observed at 167.2 °C.

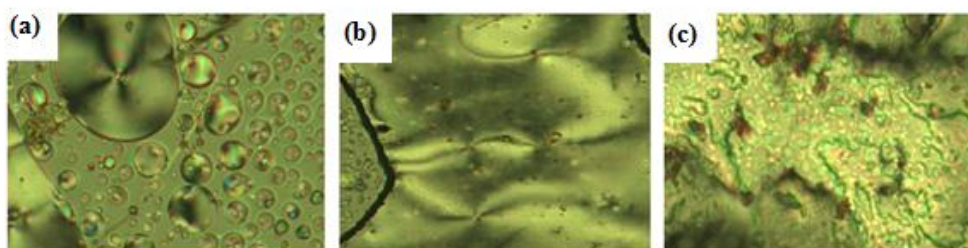


Figure 3.7: POM textures of compound **8f** during cooling scan at: **a)** 213.7 °C **b)** 205.8 °C **c)** 167.2 °C.

The photomicrographs for compound **8g** were captured during cooling scan (Figure 3.8). The compound **8g** exhibited nematic phase which was recognized by the appearance of droplets at 203.8 °C, which then changed into schlieren nematic texture having four brushes at 202.1 °C. Smectic phase was confirmed by the appearance of schlieren texture, characteristic of smectic C phase at 89.0 °C.

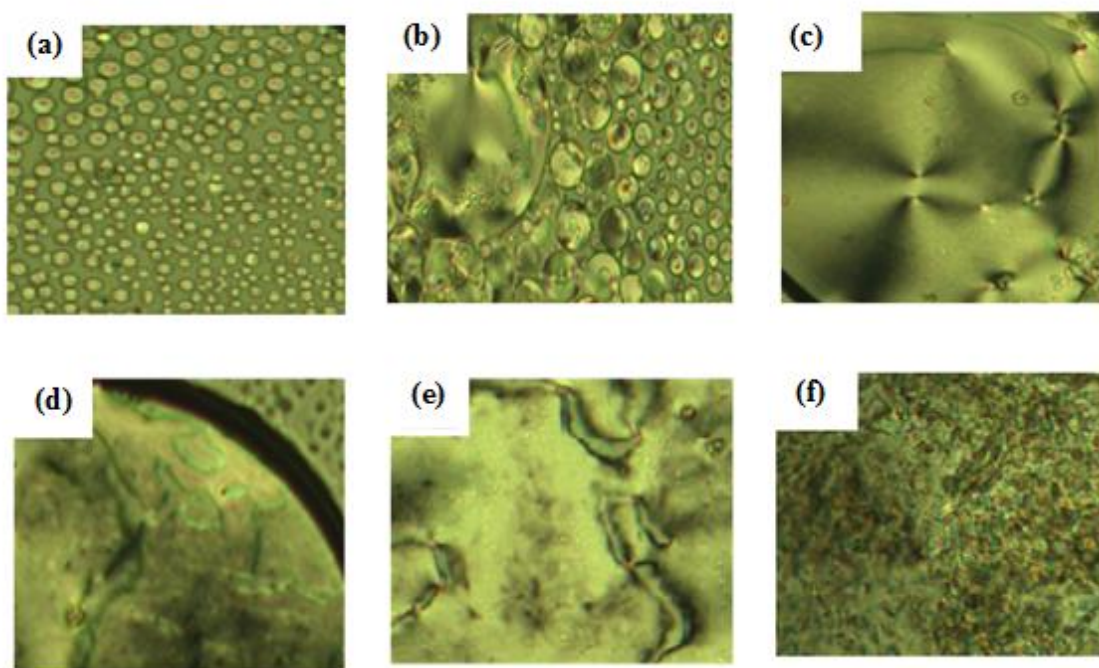


Figure 3.8: POM snapshots of compound **8g** during cooling scan at: **a)** 203.8 °C **b)** 202.1 °C **c)** 200.6 °C **d)** 195.0 °C **e)** 192.0 °C **f)** 89.0 °C.

The pictures for **8h** were taken at 200.0 °C, 189.0 °C, 85.0 °C and 81.0 °C on cooling the compound **8h** from isotropic phase to crystalline solid. POM micrographs displayed nematic and smectic phases (Figure 3.9). The nematic phase was confirmed by the appearance of nematic droplet texture as well as the appearance of planar texture with long dark lines, also called threads, characteristics of nematic phase. The smectic phase was confirmed by the appearance of focal conic structure at 81.0 °C.

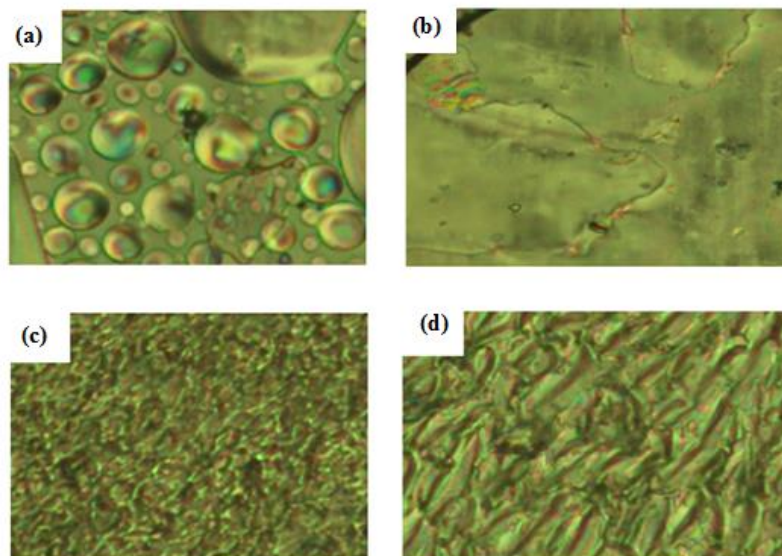


Figure 3.9: Optical textures of compound **8h** at different temperatures: **a)** 200.0 °C **b)** 189.0 °C **c)** 85.0 °C **d)** 81.0 °C, on cooling.

The photomicrographs of **8i** were collected on cooling the sample from isotropic liquid. The appearance of schlieren texture at 207.0 °C, 206.0 °C and 204.0 °C is the characteristic of nematic phase and additional smectic C phase was also observed at 100.0 °C by the appearance of schlieren texture (Figure 3.10).

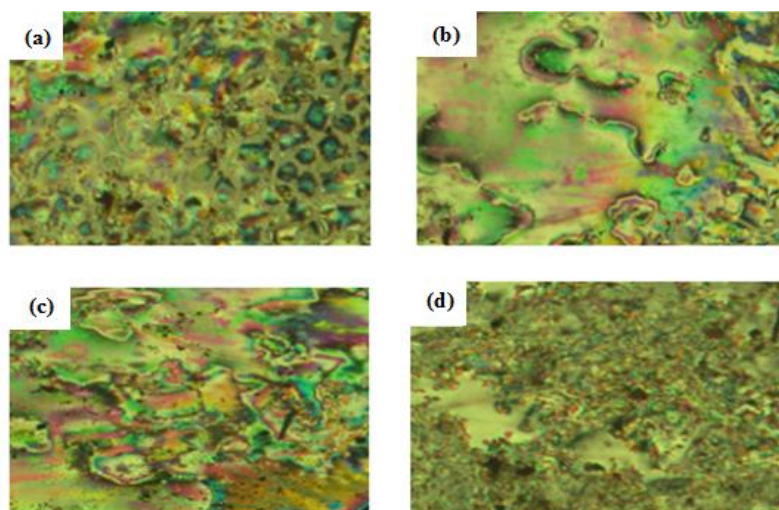


Figure 3.10: Photomicrographs of compound **8i** at: **a)** 207.0 °C **b)** 206.0 °C **c)** 204.0 °C **d)** 100.0 °C during cooling scan.

The POM textures of compound **8j** were obtained on cooling from isotropic liquid. Nematic droplet and Schlieren nematic textures appeared at 180.0 °C and 178.0 °C during cooling scan confirming the nematic phase. Smectic X and Smectic C phases appeared at 112.0 °C, 85.0 °C and 84.0 °C (Figure 3.10).

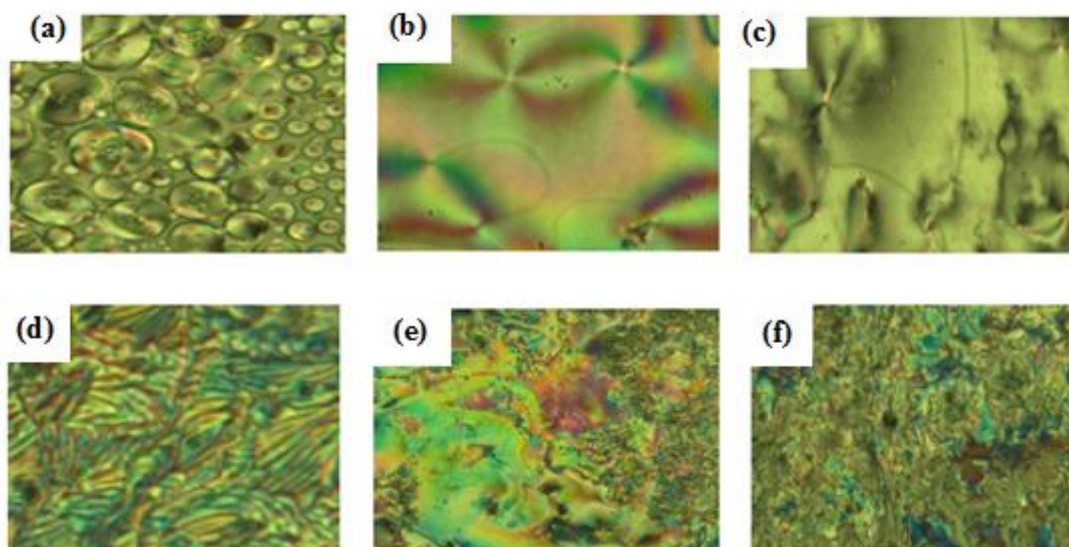


Figure 3.11: Photomicrographs of compound **8j** at: **a)** 180.0 °C **b)** 178.0 °C **c)** 170.0 °C **d)** 112.0 °C **e)** 85.0 °C **f)** 84.0 °C during cooling scan.

3.6 Conclusions

Azomethine phenyl benzoate derivatives (**8a-j**) having different alkyl chain lengths were successfully synthesized in a multistep sequence. All the synthesized compounds (intermediates and target compounds) were characterized by IR and NMR spectroscopic techniques. Liquid crystalline properties of synthesized compounds were studied using DSC and POM. All the synthesized compounds **8d-j** exhibited mesomorphic behaviour. Compounds **8a-f** having lower alkyl chain (5-10 carbon atoms) showed only nematic phase. Compounds **8g-j** having higher alkyl chain (11-14 carbon atom) showed nematic and smectic phases with good mesophase ranges.

3.7 Future Plans

All the synthesized compounds will be characterized by more spectral techniques. TGA, DSC and XRD analysis of the synthesized compounds will be performed.

4.1 Materials

Thionyl chloride, sodium hydroxide, 1-bromopentane, 1-hexanol, 1-bromooctane, 1-bromononane, pre-coated TLC aluminium sheets coated with silica gel 60F₂₅₄ were purchased from Merck (Germany). 4-Methyl benzoic acid, anhydrous potassium carbonate, anhydrous magnesium sulphate and concentrated sulphuric acid, were the products of Fluka. Tetrahydrofuran (THF), chloroform, carbon tetrachloride, methanol, pyridine, concentrated hydrochloric acid, 1-octanol and 1-decanol were supplied by Riedel-deHaën (U.S.A). *p*-Toluene sulphonyl chloride, 1-bromoheptane, 1-bromoundecane, 1-bromododecane, 1-bromotridecane, 1-bromotetradecane and 4-hydroxy benzaldehyde were obtained from Sigma Aldrich (Germany). Acetone, ethyl acetate, *n*-hexane and ethanol were purchased from commercial sources and distilled prior to use.

4.2 Instrumentation

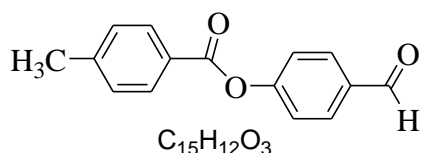
The Gallenkamp melting point apparatus MPD350.BM3.5 (UK) was used to determine the melting points of the synthesized compounds in open capillaries. FT-IR spectra were recorded on Bruker FTIR Tensor-II spectrophotometer (Germany). Bruker Avance 300 MHz NMR spectrophotometer (Switzerland) was used to record ¹H and ¹³C NMR spectra and signals were calibrated with respect to the residual signal of the solvent. Mettler Toledo DSC 823e (Switzerland) was used to determine the liquid crystalline phases of the compounds. Optical textures were studied on LEICA, DM 2500P polarizing optical microscope (Germany) equipped with Linkam hot-stage LK-600PM.

4.3 Preparation of 4-formylphenyl 4-methylbenzoate (4)

The 4-methylbenzoic acid (5g, 0.036 mol) was refluxed for 5-6 hours in 6-8 mL thionyl chloride. Excess thionyl chloride was distilled off by vacuum distillation. 4-Methyl benzoyl chloride solution (in 10 mL THF) was added dropwise at 0°C to a stirring solution of 4-hydroxybenzaldehyde in 30 mL THF containing anhydrous potassium carbonate. After the complete addition of 4-methylbenzoyl chloride, the reaction mixture was stirred for 3 hours at room temperature. The reaction was monitored through TLC. After the completion of reaction as indicated by TLC, the reaction

mixture was filtered, solvent removed on rotary evaporator and the white solid product obtained purified through column chromatography (*n*-hexane: ethylacetate; 95:5).

Yield: 78 %; white solid; m.p. = 97-98 °C; $R_f = 0.81$ (*n*-hexane:ethylacetate; 7:3); IR



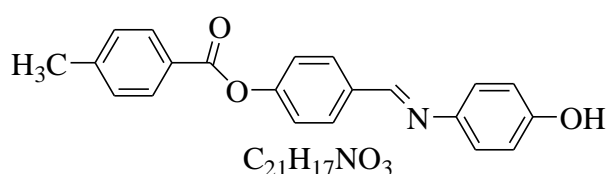
Mol. Wt.: 240.25

(neat, $\bar{\nu}$, cm^{-1}): 27421, 1732, 1697, 1596, 1419, 1312, 1265, 1178, 1156, 1099, 1011, 875, 791, 685, 669, 649, 626, 513, 472, 419; ^1H NMR (CDCl_3): δ (ppm) 10.03 (1H, s), 8.11(2H, d, $J = 8.1$ Hz), 7.92 (2H, d, $J = 8.7$ Hz), 7.42 (2H, d, $J = 8.7$ Hz), 7.34 (2H, d, $J = 8.1$ Hz), 2.48 (3H, s); ^{13}C NMR (CDCl_3): δ (ppm) 191.04, 164.58, 155.81, 145.02, 133.98, 131.28, 130.35, 129.47, 126.12, 122.61, 21.84.

4.4 Preparation of (*E*)-4-((4-hydroxyphenylimino)methyl)phenyl 4-methylbenzoate (6)

To a solution of 4-formylphenyl 4-methylbenzoate in 30 mL absolute ethanol, 4-aminophenol was added. The reaction mixture was refluxed for about 6 hrs. After the completion of reaction as indicated by TLC, the reaction mixture was cooled down to room temperature and filtered. A crude shiny light brown product was purified by washing with ethylacetate and followed by recrystallization from ethanol.

Yield: 82 %; shiny light brown solid; m.p. = 205-218 °C; $R_f = 0.64$ (*n*-hexane:ethylacetate; 7:3); IR (neat, $\bar{\nu}$,



Mol. Wt.: 331.36

cm^{-1}): 3628, 2666, 1724, 1603, 1508, 1420, 1269, 1165, 1064, 1016, 832, 724, 647, 519, 471, 423; ^1H NMR (CDCl_3): δ (ppm) 9.54 (1H, s), 8.65 (1H, s), 8.06-7.97 (4H, *m*), 7.44-7.39 (4H, *m*), 7.22 (2H, d, $J = 8.7$ Hz), 6.81(2H, d, $J = 8.7$ Hz), 2.50 (3H, s); ^{13}C NMR (CDCl_3): δ (ppm) 164.84, 156.86, 156.63, 152.97, 145.17, 142.82, 130.46, 130.05, 129.95, 126.43, 123.39, 122.88, 116.18, 21.75.

4.5 General method for the synthesis of alkyl tosylates (7a-b)

To an ice cooled solution of primary alcohol (0.01 mol) in 30 mL pyridine, 2g (0.01 mol) of *p*-toluenesulphonyl chloride was added in small portions. The reaction mixture was stirred for 4 hours at 0°C. The product was extracted in ethylacetate (3 × 50 mL) and washed with 6N HCl (2 × 50 mL) to remove pyridine. The organic layer was

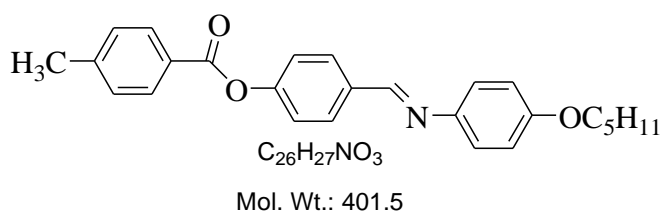
separated and dried over anhydrous MgSO₄. The desiccant was removed by filtration and solvent was evaporated under vacuum. A yellow oily liquid was obtained with enough purity to be used in the next step.

4.6 General Method for the synthesis of (E)-4-((4-alkyloxy phenyl imino)methyl)phenyl 4- methylbenzoate (8a-j)

The compound (E)-4-((4-hydroxyphenylimino)methyl)phenyl 4-methylbenzoate (0.5g, 0.001mol) was refluxed in acetone with a slight excess of anhydrous potassium carbonate (0.31g, 0.002mol). Alkyl halide or alkyl tosylate (0.001mol) was slowly added to the reaction mixture. After the addition of alkyl halide or alkyl tosylate, the reflux was continued while the reaction was monitored using TLC. After the completion of reaction (TLC), the reaction mixture was cooled to room temperature and filtered. The filtrate contains the desired product and solvent was removed under vacuum. The crude solid product was purified by repeated recrystallization from *n*-hexane. Pure white solid product was obtained which was dried in a desiccator.

(E)-4-((4-pentyloxyphenylimino)methyl)phenyl 4-methylbenzoate (8a)

Yield: 33 %; white solid; m.p. = 135-280 °C; R_f = 0.69 (*n*-hexane:ethylacetate; 7:3); IR

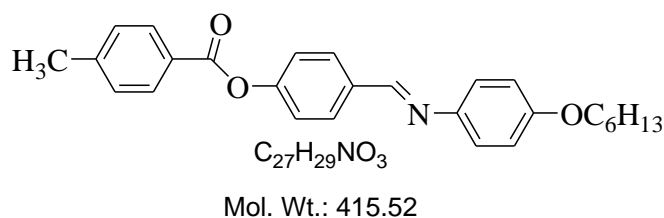


(neat, $\bar{\nu}$, cm⁻¹): 2957, 2862, 1742, 1604, 1573, 1507, 1474, 1395, 1250, 1075, 1019, 877, 836, 741, 685, 602, 547, 473, 422; ¹H NMR

(CDCl₃): δ (ppm) 8.46 (1H, s), 8.12 (2H, d, *J* = 8.1 Hz), 7.92 (2H, d, *J* = 8.7 Hz), 7.38–7.22 (6H, *m*), 6.96 (2H, d, *J* = 8.7 Hz), 4.04 (2H, t, *J* = 6.6 Hz), 2.48 (3H, s), 1.84 (2H, quin, *J* = 6.9 Hz), 1.51–1.38 (4H, *m*), 0.96 (3H, t, *J* = 6.9 Hz); ¹³C NMR (CDCl₃): δ (ppm) 165.41, 161.96, 159.96, 150.03, 148.80, 144.43, 130.55, 130.23, 129.31, 128.92, 126.81, 122.31, 121.79, 114.71, 68.21, 29.01, 28.22, 22.47, 21.79, 14.04.

(E)-4-((4-hexyloxyphenylimino)methyl)phenyl 4-methylbenzoate (8b)

Yield: 32 %; white solid; m.p. = 127-263 °C; R_f = 0.70 (*n*-hexane:ethylacetate; 7:3); IR

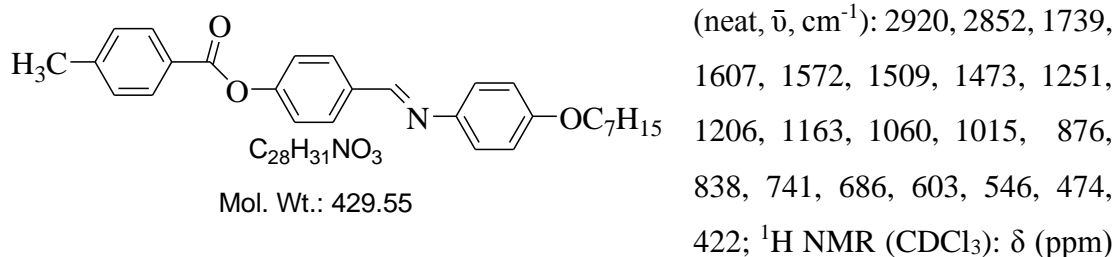


(neat, $\bar{\nu}$, cm⁻¹): 2934, 2860, 1742, 1606, 1573, 1508, 1473, 1395, 1249, 1169, 1076, 1028,

878, 839, 820, 741, 686, 603, 547, 473, 426; ^1H NMR (CDCl_3): δ (ppm) 8.42 (1H, s), 8.12 (2H, d, $J = 8.1$ Hz), 7.86 (2H, d, $J = 8.7$ Hz), 7.35–7.22 (6H, *m*), 6.99 (2H, d, $J = 8.7$ Hz), 4.04 (2H, t, $J = 6.6$ Hz), 2.47 (3H, s), 1.83 (2H, quin, $J = 6.9$ Hz), 1.52–1.34 (6H, *m*), 0.93 (3H, t, $J = 7.2$ Hz); ^{13}C NMR (CDCl_3): δ (ppm) 165.41, 161.96, 159.97, 150.02, 148.79, 144.44, 130.56, 130.23, 129.31, 128.92, 126.80, 122.32, 121.79, 114.71, 68.22, 31.58, 29.15, 25.70, 22.61, 21.79, 14.06.

(E)-4-((4-heptyloxyphenylimino)methyl)phenyl 4-methylbenzoate (8c)

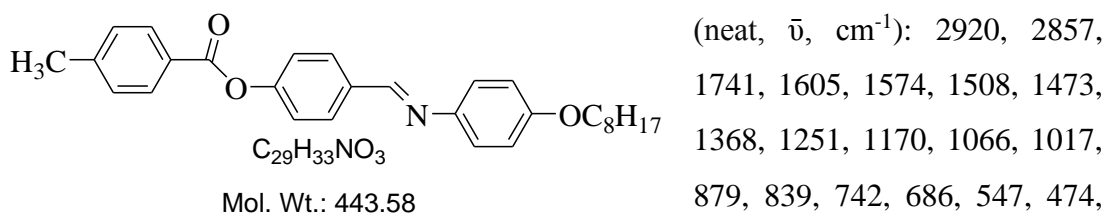
Yield: 31 %; white solid; m.p. = 124-248 °C; $R_f = 0.71$ (*n*-hexane:ethylacetate; 7:3); IR



8.42 (1H, s), 8.12 (2H, d, $J = 8.1$ Hz), 7.91 (2H, d, $J = 8.7$ Hz), 7.38–7.23 (6H, *m*), 6.99 (2H, d, $J = 8.7$ Hz), 4.05 (2H, t, $J = 6.6$ Hz), 2.46 (3H, s), 1.83 (2H, quin, $J = 6.9$ Hz), 1.51–1.34 (8H, *m*), 0.90 (3H, t, $J = 6.9$ Hz); ^{13}C NMR (CDCl_3): δ (ppm) 165.36, 160.07, 159.96, 150.02, 148.78, 144.49, 130.55, 130.25, 129.33, 128.92, 126.73, 122.33, 121.98, 114.75, 68.44, 31.79, 29.16, 29.07, 25.98, 22.63, 21.80, 14.12.

(E)-4-((4-octyloxyphenylimino)methyl)phenyl 4-methylbenzoate (8d)

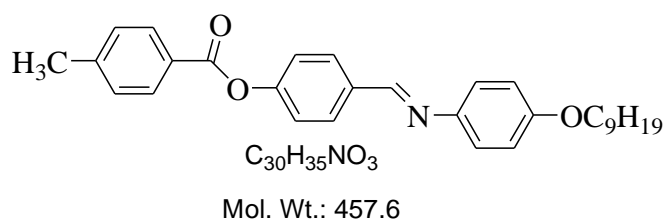
Yield: 33 %; white solid; m.p. = 121-231 °C; $R_f = 0.71$ (*n*-hexane:ethylacetate; 7:3); IR



427; ^1H NMR (CDCl_3): δ (ppm) 8.42 (1H, s), 8.12 (2H, d, $J = 8.1$ Hz), 7.90 (2H, d, $J = 8.7$ Hz), 7.35–7.23 (6H, *m*), 6.99 (2H, d, $J = 8.7$ Hz), 4.05 (2H, t, $J = 6.6$ Hz), 2.48 (3H, s), 1.83 (2H, quin, $J = 6.9$ Hz), 1.49–1.31 (10H, *m*), 0.91 (3H, t, $J = 7.2$ Hz); ^{13}C NMR (CDCl_3): δ (ppm) 165.41, 161.96, 159.96, 150.03, 148.79, 144.44, 130.55, 130.24, 129.31, 128.90, 126.80, 122.32, 121.89, 114.99, 68.22, 31.83, 29.37, 29.26, 29.19, 26.03, 22.69, 21.80, 14.14.

(E)-4-((4-nonyloxyphenylimino)methyl)phenyl 4-methylbenzoate (8e)

Yield: 43 %; white solid; m.p. = 116-227 °C; R_f = 0.73 (*n*-hexane:ethylacetate; 7:3); IR

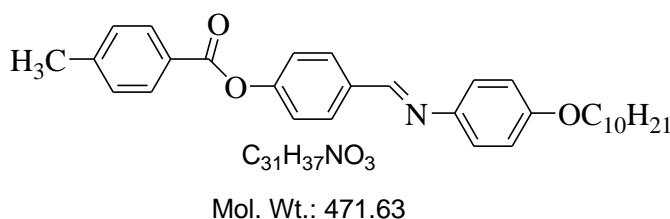


(neat, $\bar{\nu}$, cm^{-1}): 2951, 2848, 1742, 1606, 1574, 1508, 1472, 1272, 1185, 1109, 1037, 980, 879, 788, 635, 500, 474, 424; 1H NMR (CDCl₃): δ (ppm) 8.42 (1H, s),

8.12 (2H, d, J = 8.1 Hz), 7.86 (2H, d, J = 8.7 Hz), 7.35–7.22 (6H, *m*), 6.99 (2H, d, J = 8.7 Hz), 4.04 (2H, t, J = 6.6 Hz), 2.48 (3H, s), 1.82 (2H, quin, J = 6.9 Hz), 1.49–1.30 (12H, *m*), 0.91 (3H, t, J = 7.2 Hz); ^{13}C NMR (CDCl₃): δ (ppm) 165.41, 161.96, 159.96, 150.03, 148.79, 144.51, 130.55, 130.24, 129.31, 128.92, 126.80, 122.32, 121.79, 114.71, 68.23, 31.89, 29.54, 29.41, 29.28, 29.19, 26.02, 22.69, 21.79, 14.14.

(E)-4-((4-decyloxyphenylimino)methyl)phenyl 4-methylbenzoate (8f)

Yield: 35 %; white solid; m.p. = 112-218 °C; R_f = 0.76 (*n*-hexane:ethylacetate; 7:3); IR

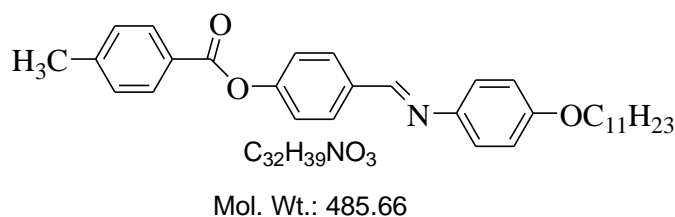


(neat, $\bar{\nu}$, cm^{-1}): 2917, 2849, 1742, 1606, 1574, 1473, 1274, 1184, 1170, 1100, 1078, 960, 839, 686, 603, 548, 473, 422; 1H NMR (CDCl₃): δ (ppm) 8.42

(1H, s), 8.12 (2H, d, J = 8.1 Hz), 7.92 (2H, d, J = 8.7 Hz), 7.35–7.22 (6H, *m*), 7.00 (2H, d, J = 8.7 Hz), 4.05 (2H, t, J = 6.6 Hz), 2.48 (3H, s), 1.83 (2H, quin, J = 6.9 Hz), 1.49–1.30 (14H, *m*), 0.90 (3H, t, J = 6.9 Hz); ^{13}C NMR (CDCl₃): δ (ppm) 165.36, 160.14, 144.53, 130.73, 130.25, 129.34, 128.92, 126.68, 122.34, 121.90, 114.75, 68.44, 31.91, 29.39, 29.34, 29.24, 29.13, 29.06, 25.98, 22.70, 21.80, 14.15.

(E)-4-((4-undecyloxyphenylimino)methyl)phenyl 4-methylbenzoate (8g)

Yield: 30%; white solid; m.p. = 108-212 °C; R_f = 0.77 (*n*-hexane:ethylacetate; 7:3); IR

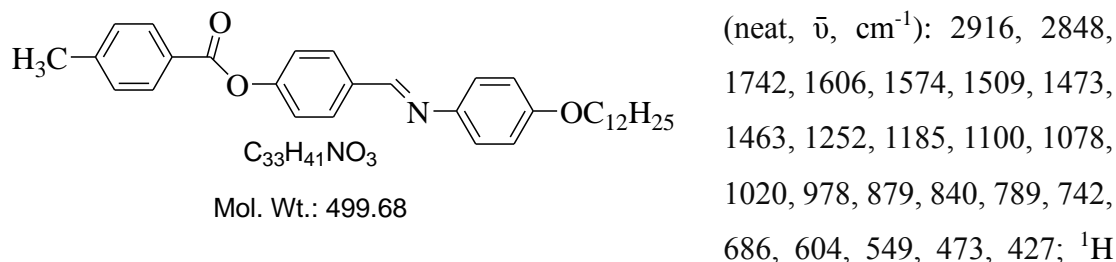


(neat, $\bar{\nu}$, cm^{-1}): 2915, 2847, 1742, 1605, 1574, 1508, 1472, 1249, 1169, 1077, 1016, 879, 840, 816, 741, 686, 634, 603,

549, 474, 430; ^1H NMR (CDCl_3): δ (ppm) 8.42 (1H, s), 8.11 (2H, d, $J = 8.1$ Hz), 7.84 (2H, d, $J = 8.7$ Hz), 7.35–7.22 (6H, m), 7.00 (2H, d, $J = 8.7$ Hz), 4.04 (2H, t, $J = 6.6$ Hz), 2.47 (3H, s), 1.83 (2H, quin, $J = 6.9$ Hz), 1.51–1.29 (16H, m), 0.90 (3H, t, $J = 6.9$ Hz); ^{13}C NMR (CDCl_3): δ (ppm) 165.36, 160.14, 144.48, 130.73, 130.25, 129.33, 128.92, 126.70, 122.48, 121.87, 114.75, 68.44, 31.93, 29.63, 29.57, 29.41, 29.36, 29.15, 29.07, 26.01, 22.72, 21.81, 14.14.

(E)-4-((4-dodecyloxyphenylimino)methyl)phenyl 4-methylbenzoate (8h)

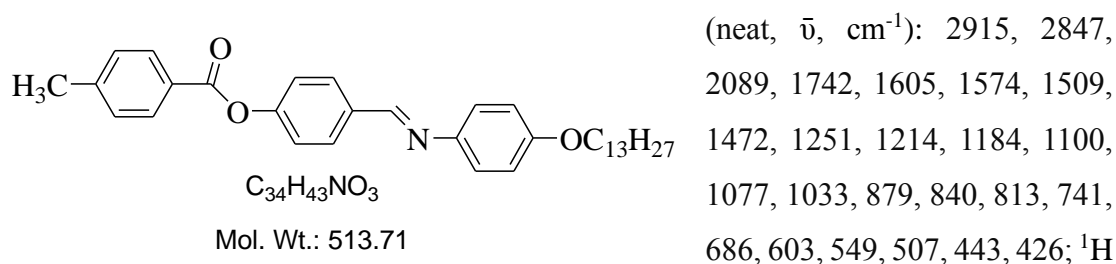
Yield: 33 %; white solid; m.p. = 111-204 °C; $R_f = 0.79$ (*n*-hexane:ethylacetate; 7:3); IR



NMR (CDCl_3): δ (ppm) 8.46 (1H, s), 8.12 (2H, d, $J = 8.1$ Hz), 7.84 (2H, d, $J = 8.7$ Hz), 7.35–7.22 (6H, m), 7.00 (2H, d, $J = 8.7$ Hz), 4.04 (2H, t, $J = 6.6$ Hz), 2.47 (3H, s), 1.83 (2H, quin, $J = 6.9$ Hz), 1.51–1.29 (18H, m), 0.90 (3H, t, $J = 6.9$ Hz); ^{13}C NMR (CDCl_3): δ (ppm) 165.37, 160.05, 144.48, 130.73, 130.25, 129.33, 128.92, 126.75, 122.41, 121.84, 114.75, 68.44, 31.94, 29.67, 29.62, 29.60, 29.41, 29.38, 29.17, 26.02, 22.72, 21.80, 14.16.

(E)-4-((4-tridecyloxyphenylimino)methyl)phenyl 4-methylbenzoate (8i)

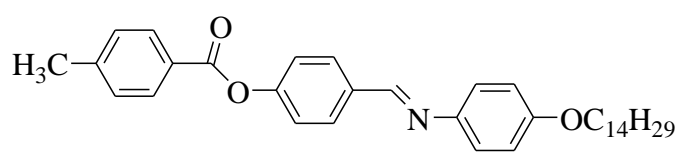
Yield: 40 %; white solid; m.p. = 114-198 °C; $R_f = 0.80$ (*n*-hexane:ethylacetate; 7:3); IR



NMR (CDCl_3): δ (ppm) 8.42 (1H, s), 8.12 (2H, d, $J = 8.1$ Hz), 7.87 (2H, d, $J = 8.4$ Hz), 7.35–7.22 (6H, m), 7.00 (2H, d, $J = 8.7$ Hz), 4.04 (2H, t, $J = 6.6$ Hz), 2.48 (3H, s), 1.83 (2H, quin, $J = 6.9$ Hz), 1.51–1.29 (20H, m), 0.90 (3H, t, $J = 6.9$ Hz); ^{13}C NMR (CDCl_3): δ (ppm) 165.38, 160.04, 144.49, 144.49, 130.73, 130.25, 129.34, 128.92, 126.71, 122.44, 121.88, 114.75, 68.28, 31.96, 29.72, 29.70, 29.64, 29.61, 29.41, 29.37, 29.26, 29.17, 26.03, 22.74, 21.38, 14.14.

(E)-4-((4-tetradecyloxyphenylimino)methyl)phenyl 4-methylbenzoate (8j)

Yield: 31 %; white solid; m.p. = 112-190 °C R_f = 0.81 (*n*-hexane:ethylacetate; 7:3); IR



$C_{35}H_{45}NO_3$

Mol. Wt.: 527.74

(neat, $\bar{\nu}$, cm^{-1}): 2915, 2848,
1742, 1606, 1574, 1509, 1472,
1253, 1215, 1170, 1100, 1078,
1020, 879, 840, 741, 686, 603,
549, 473, 424; 1H NMR

($CDCl_3$): δ (ppm) 8.44 (1H, s), 8.10 (2H, d, $J = 8.4$ Hz), 7.84 (2H, d, $J = 8.7$ Hz), 7.35–7.24 (6H, m), 7.00 (2H, d, $J = 8.7$ Hz), 4.05 (2H, t, $J = 6.6$ Hz), 2.47 (3H, s), 1.83 (2H, quin, $J = 6.9$ Hz), 1.49–1.28 (22H, m), 0.90 (3H, t, $J = 6.9$ Hz); ^{13}C NMR ($CDCl_3$): δ (ppm) 165.39, 160.04, 144.45, 130.65, 130.24, 129.32, 128.92, 126.78, 122.36, 121.82, 114.75, 68.26, 31.95, 29.74, 29.68, 29.62, 29.59, 29.48, 29.39, 29.28, 29.17, 29.07, 26.01, 26.01, 21.80, 14.14.

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