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Synthesis, Characterization and Study the Liquid Crystalline Properties of New Discotic Compounds

A Thesis

Submitted to the College of Science/ Al-Nahrain University as a partial fulfillment of the requirements for the Degree of Master in Science in Chemistry.

By

Ali Hassan Dawood Al Hadeethi

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Supervised By
Dr. Nasreen R. Jber

(Assist. Prof.)

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Supervisor Certification

I, certify that this thesis entitled "Synthesis, Characterization and Study the Liquid Crystalline Properties of New Discotic Compounds" was prepared by "**Ali Hassan Dawood**" under my Supervision at the College of Science/ Al-Nahrain University as a partial fulfillment of the requirements for the Degree of Master of Science in chemistry.

Signature:
Name: **Dr.Nasreen R. Jber**
Scientific Degree: Assistance Professor
Date:

In view of the available recommendation, I forward this **thesis** for debate by the examining committee.

Signature:
Name: **Dr.Nasreen R. Jber**
Scientific Degree: Assistance Professor
Title: Head of the Department of Chemistry / Al-Nahrain University
Date:

Committee's Certification

We, the Examining Committee, certify that we read this **thesis** and examined the student "Ali Hassan Dawood" in its contents and that, in our opinion; it is accepted for the Degree of Master of Science, in Chemistry.

Signature:
Name: **Prof. Dr. Entesar O. Al-Tamimi**
Scientific Degree: Proffesor
Date:
(Chairman)

Signature:
Name: **Dr. Ahmed A. Ahmed**
Scientific Degree: Assistance Professor
Date:
(Member)

Signature:
Name: **Dr. Nisreen H. Karam**
Scientific Degree: Assistance Professor
Date:
(Member)

Signature:
Name: **Dr.Nasreen R. Jber**
Scientific Degree: Assist. Prof.
Date:
(Member/**Supervised**)

I, hereby certify upon the decision of the examining committee.

Signature:
Name: **Dr. Hadi M. A. Abood**
Scientific Degree: Assistance Professor
Title: Dean of the college of Science
Date:

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وَيَسْأَلُونَكَ عَنِ الرُّوحِ ۖ قُلِ الرُّوحُ مِنْ
أَمْرِ رَبِّي وَمَا أُوتِيتُم مِّنَ الْعِلْمِ إِلَّا قَلِيلًا

سورة الإسراء الآية ٨٥

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Ali Hassan Dawood Al Hadeethi

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Chapter Three Results & Discussion

List of abbreviations

LCs	Liquid crystals
DLCs	Discotic liquid crystals
S	Order parameter
T_c	Clearing temperature
CMC	critical micelle concentration
5CB	4-Cyano-4'-pentylbiphenyl
LCD	Liquid crystal displays
N_D	Discotic nematic liquid crystal phase
Col_h	Discotic hexagonal columnar liquid crystal phase
Col_r	Discotic rectangular columnar liquid crystal phase
S_m	Smectic phase
N	Nematic phase
POM	Polarizing Optical Microscope
DSC	Differential scanning calorimeter
TMS	Tetramethylsilane
S_Ni	Internal nucleophilic substitution mechanism
IL	Isotropic liquid
Cr	Crystal
PSB-X-n	1,3,5-Tris{4-[(4-substitutedphenylimino) methyl]phenoxy}-n-alkyloxy benzene, (X = Cl, Br ; n = 3,4,5,6)
PAZ-X-n	1,3,5-Tris{4-[(4-substitutedphenyl) diazenyl]phenoxy}-n-alkyloxy benzene,(X = Cl, Br ; n = 3,4,5,6)

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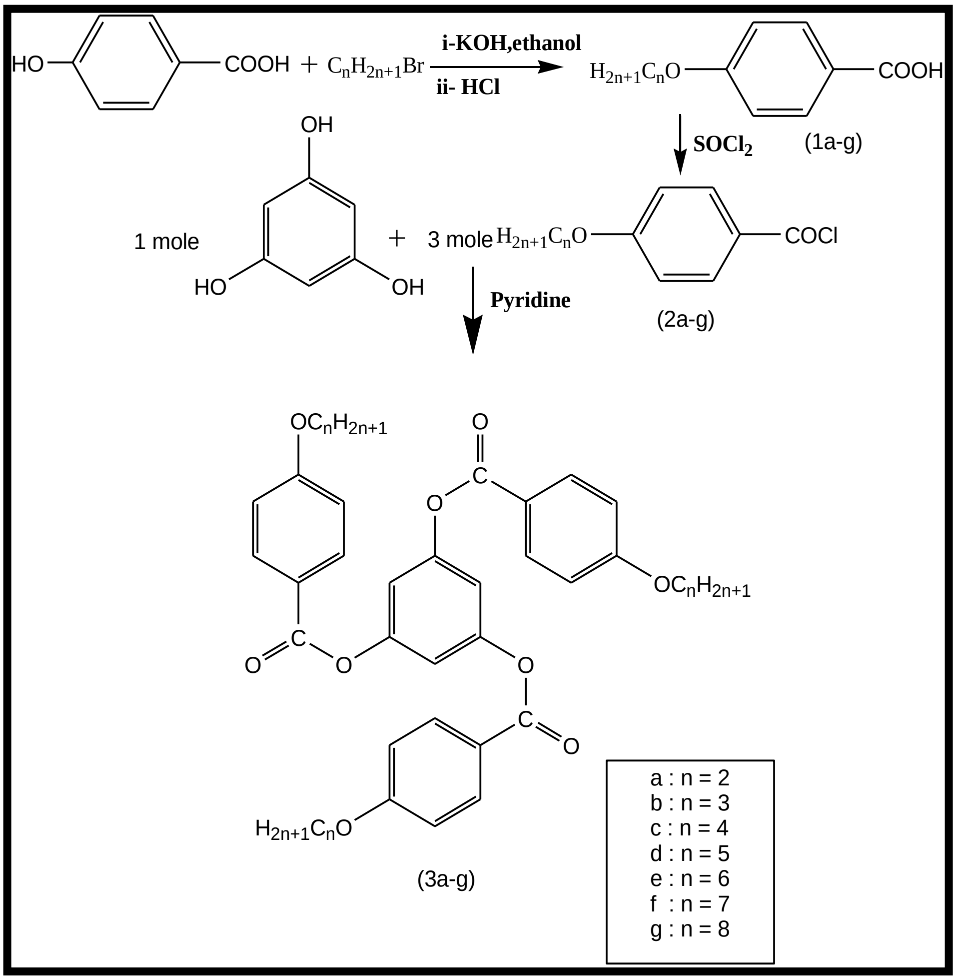
Summary

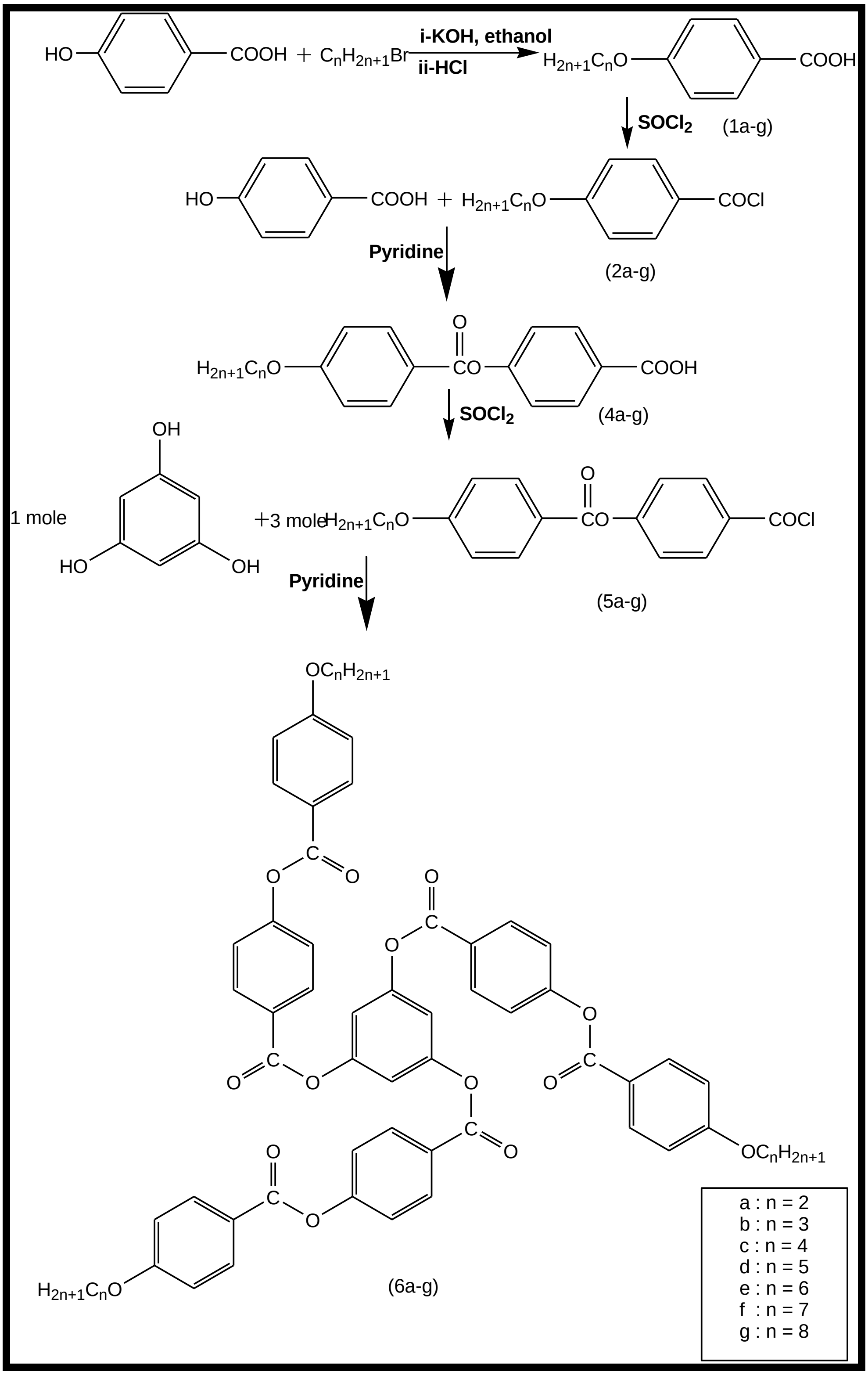
This study deals with the synthesis and study characterization of two sets (3a-g) and (6a-g) as tri-substitution derived from 1,3,5-trihydroxybenzene (Phluroglucinol).

The first series (3a-g), scheme 1 was synthesized from the reaction of 1,3,5-trihydroxybenzene with *p*-alkoxybenzoyl chloride.



Scheme 1.

The second series (6a-g) were synthesized by the reaction of 1,3,5-trihydroxybenzene (Phluroglucinol) with *p*-alkoxybenzoyloxybenzoyl chloride, scheme 2.



Scheme 2

The synthesized compounds were characterized using FTIR spectroscopy, ^{1}HNMR spectroscopy for some of them and elemental analysis.

The liquid crystalline behavior of the two series have been examined by means of hot – stage polarizing microscopy and differential scanning calorimetry (DSC) for the determination of phase transition temperatures and the type of mesophases. For the first series the first compound (3a) do not reveal any liquid crystalline behavior, but simply changes from the solid crystalline state to the isotropic liquid at 130°C. Compounds (3b-g) display enantiotropic mesomorphism. The texture observed by POM on heating the solid crystal are consistent with the presence of columnar mesomorphism, with fan-shaped typical to columnar phases for compounds (3c, 3e, and 3g) and fan shaped focal conic typical to a columnar hexagonal for compound (3b, 3d, and 3f).

For the second series all the synthesized compound show Star-shaped mesogens with the alkoxy terminal groups show nematic phases in their liquid crystalline state when viewed under a polarized optical microscope.

Chapter One

Introduction

Chapter One

Introduction

1.1 Liquid Crystal:

Matters, in general, have three distinct states: solid, liquid, and gas (1). The differences between these three states can be attributed to the temperature of the substance. Temperature is a measure of the randomness of the molecules and therefore the higher the temperature the less order they exist. Increasing temperature will cause the transition from a solid to a liquid and then to a gas (2). However, there are states of matter which do not meet the necessary requirements of any of these three categories. Many materials exhibit more than a single transition when passing from solid to liquid, which proves the presence of one or more intermediate phases (1). The new phases have mechanical, optical and structural properties between those of crystalline solid and the corresponding isotropic liquid. These phases are referred to as liquid crystalline phases (3, 4).

The liquid crystal phase is a well-known state of matter, which lies between the crystalline solid and isotropic liquid phases. The study of liquid crystals began in 1888 when Reinitzer (5) observed the fact that cholesteryl benzoate had two distinct melting points. Reinitzer increased the temperature of the solid state and then observed the change of the solid into a hazy liquid. When the temperature increased further the material changed its phase into a transparent liquid. This experiment showed that cholesteryl benzoate has another phase between solid and liquid that has the properties between these two phases.

The liquid crystal state (mesomorphic state) is characterized by having a long-range orientational order and possible partial positional order (3). The distinguishing characteristic of the liquid crystalline state is the tendency of the molecules (mesogens) to point along a common axis, called the director (n). This is in contrast to molecules in the solid phase, which are highly ordered and have little translational freedom. The molecules in liquid state have no intrinsic order. The characteristic orientational order of the liquid crystal state is between the traditional solid and liquid phases and this is the origin of the term mesogenic state, which used synonymously with liquid crystal state. Figure (1.1) shows the alignment of the molecules in each of the above phases.

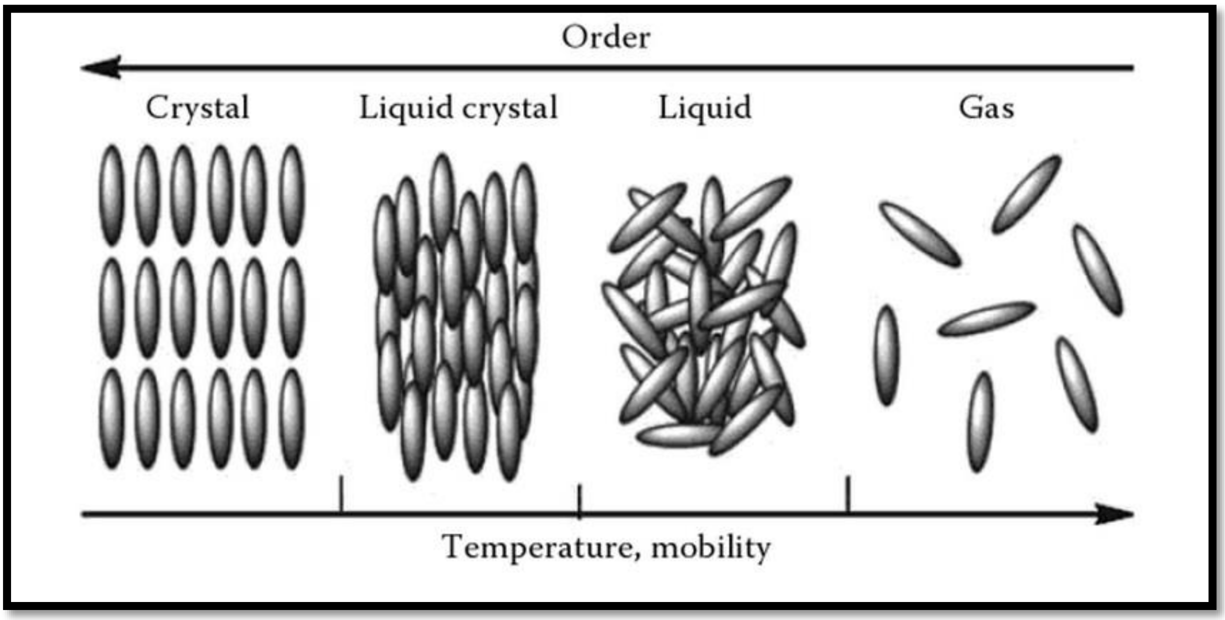


***Figure 1.1** Alignment of the molecules for solid, liquid crystal, liquid and gas phases.*

To quantify just how much order is present in a material, an order parameter (S) is defined. Traditionally, the order parameter is given as follows:

$$S = \left\langle \frac{3\cos^2\theta - 1}{2} \right\rangle$$

Where θ is the angle between the director and the long axis of each molecule. The brackets denote an average over all of the molecules in the sample. In an isotropic liquid, the average of the cosine terms is zero, and therefore the order parameter is equal to zero. For a perfect crystal, the order parameter evaluates to one. Typical values for the order parameter of a liquid crystal range between 0.3 and 0.9, with the exact value a function of temperature, as a result of kinetic molecular motion as shown in figure (1.2) (1).

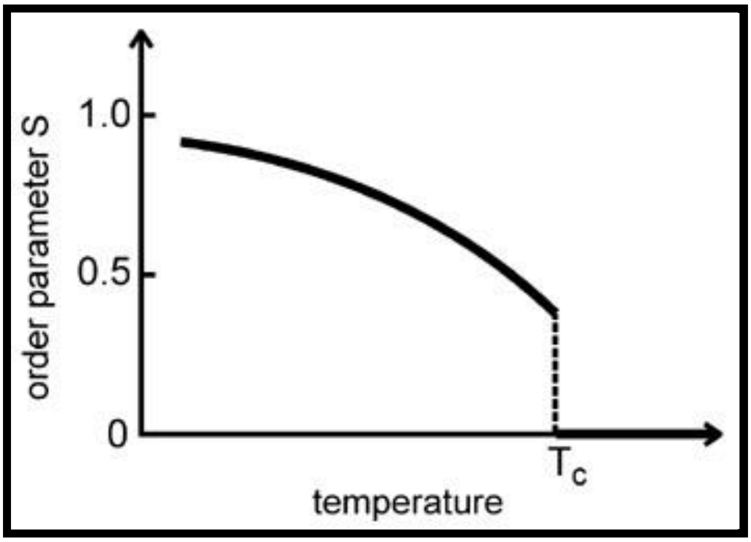


Figure 1.2 *Order parameter S vs. temperature: Tc is clearing temperature (1).*

The tendency of the liquid crystal molecules to point along the director leads to a condition known as anisotropy. The term means that the properties of a material depend on the direction in which they are measured. The anisotropic nature of liquid crystals is responsible for the unique optical properties (6). Liquid crystal materials, generally, have several common characteristics. Among these are rod-like molecular structures, rigidness of the long axis, and strong dipoles and/or easily polarizable. Liquid crystalline properties are exhibited by several different types of systems. In addition to certain classes of organic molecules, micellar solutions of surfactants, main and side chain polymer, and a large number of biological systems are known to be liquid crystalline (7).

1.2 Classification of Liquid crystals:

There are various ways of classifying LCs based on the molar mass of the constituent molecules, that is, low molar mass (monomeric and oligomeric) and high molar mass (polymeric) LCs; based on how the liquid crystalline phase has been obtained, that is, by adding solvent (lyotropic) or by varying the temperature (*thermotropic*); based on the nature of the constituent molecules (organic, inorganic, and organometallic); based on the geometrical shape of the molecules (rod-like, disk-like, banana-like); and based on the organization of the molecules in the liquid crystalline phase (nematic, smectic, columnar, helical, B phases, etc.). The classification of LCs is shown in figure (1.3). However, the most widely recognized and used classification of LCs is into two major categories: (a) thermotropic LCs (mesophase formation is temperature dependent) and (b) lyotropic LCs (mesophase formation is solvent and concentration dependent). If a compound displays both thermotropic and lyotropic liquid crystalline phases, then it is called *amphotropic* LC (8).

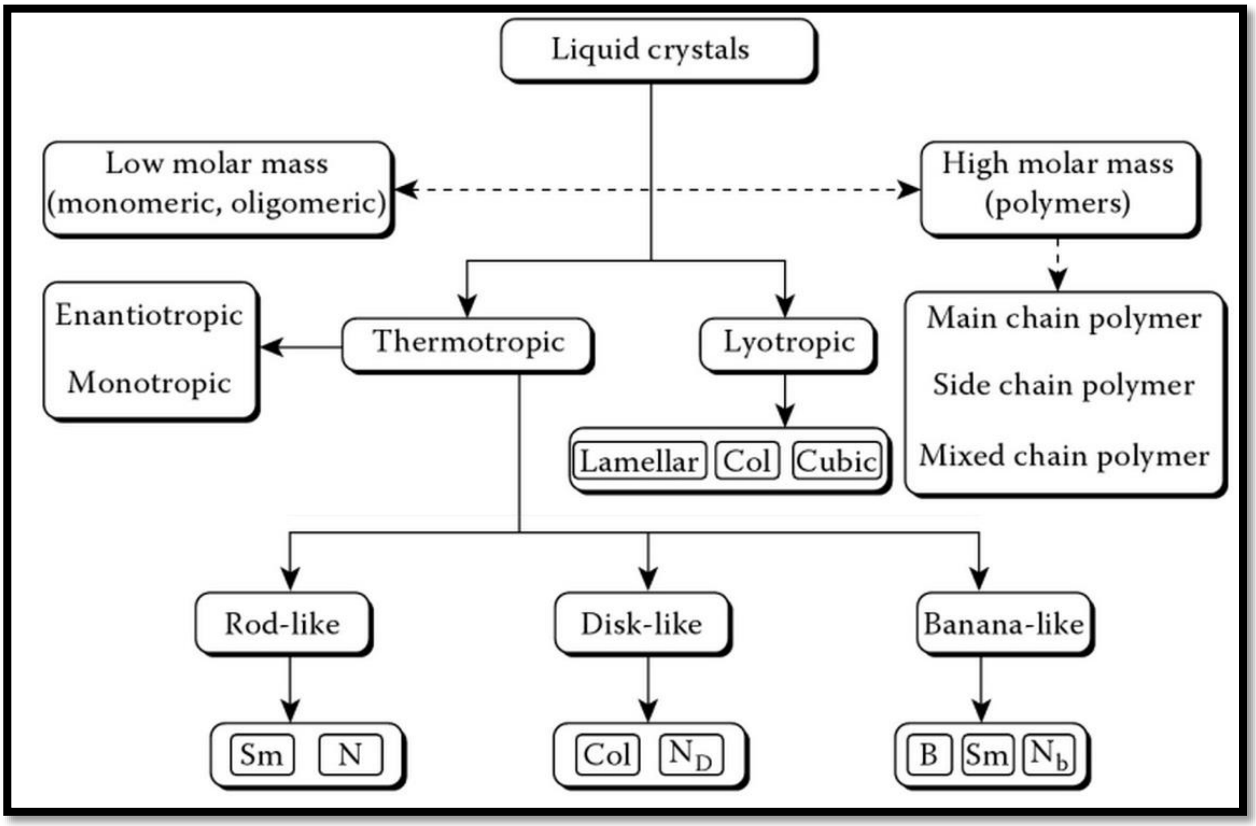


Figure1.3 *Classification of LCs.* (8)

1.3 Lyotropic Liquid Crystals:

Lyotropic LCs also known as anisotropic solutions, are formed by dissolving amphiphilic compounds in suitable solvents under appropriate conditions of concentration and temperature. The amphiphilic compounds are characterized by two distinct parts of contrasting character: a hydrophilic polar head and a hydrophobic nonpolar tail. Apart from temperature, both the concentration of the solute and the solvent (most often water) also play a very significant role in lyotropic LC systems. Typical examples of lyotropic LCs are soaps in water and various phospholipids. Lyotropic LC phases can have positional order in one (lamellar) two (columnar hexagonal), or three (cubic) dimensions. When a small amount of amphiphilic material is dissolved in a polar solvent such as water, it goes into the solution. As the concentration of the material is increased, the hydrophobic tails assemble together and present the hydrophilic polar heads to the solvent, thereby arranging themselves into spheres called *micelles* figure (1.4). So the polar head groups are on the surface of the *micelle* and the nonpolar hydrocarbon chains are toward the center. The micelles are stable as long as the amount of amphiphilic material is above a certain concentration called *critical micelle concentration* (CMC). (8)

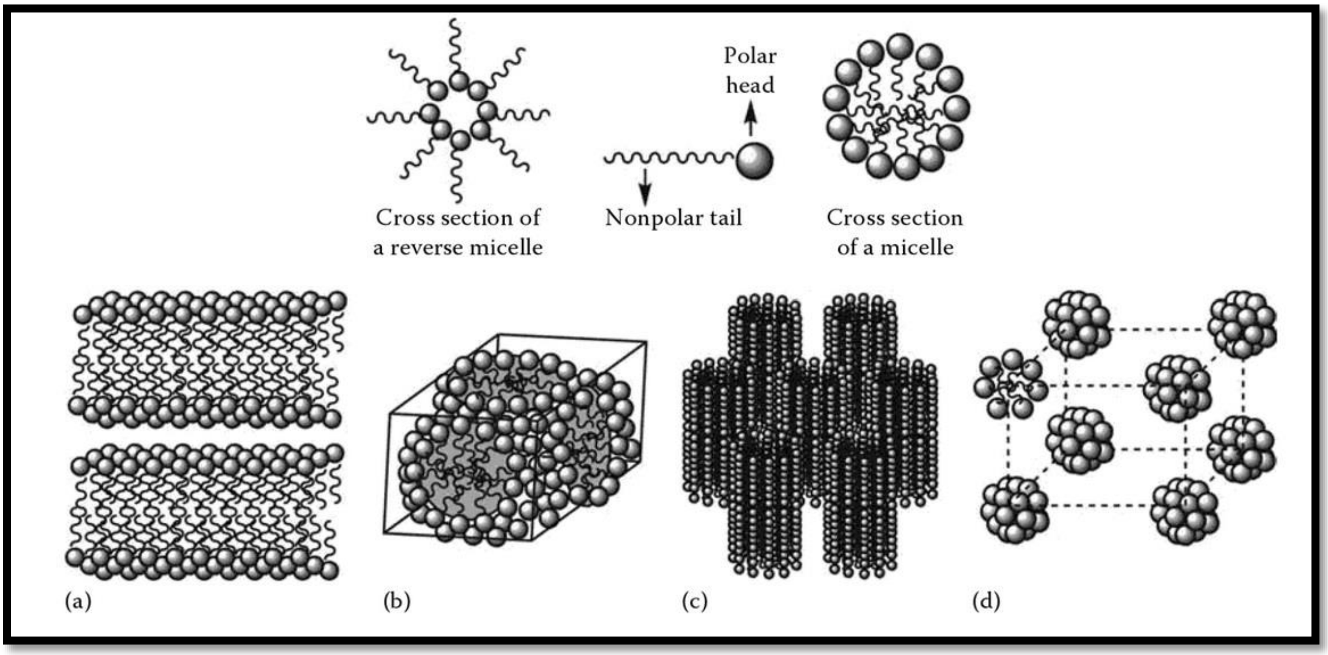


Figure1.4 *Cross sections of micelles and reverse micelles formed by surfactant molecules and lyotropic liquid crystalline phases: (a) lamellar, (b) bicontineous cubic, (c)hexagonal columnar, and (d) miceller cubic.* (8)

1.4 Thermotropic Liquid Crystals:

When the liquid crystalline phases are obtained by varying the temperature of the compounds, they are called thermotropic LCs. If the temperature increases, thermal motion will destroy the order of the LC phase, pushing the material into a conventional isotropic liquid phase. At too low temperature, most LC materials will form a conventional crystal.(4)(9)Thermotropic divided into three main classes according to the shape and structure of the molecules , the three classes are rod like (calamitic), disk like (discotic) and banana like LCs.(8) Figure (1.5) show the classes of thermotropic LCs.

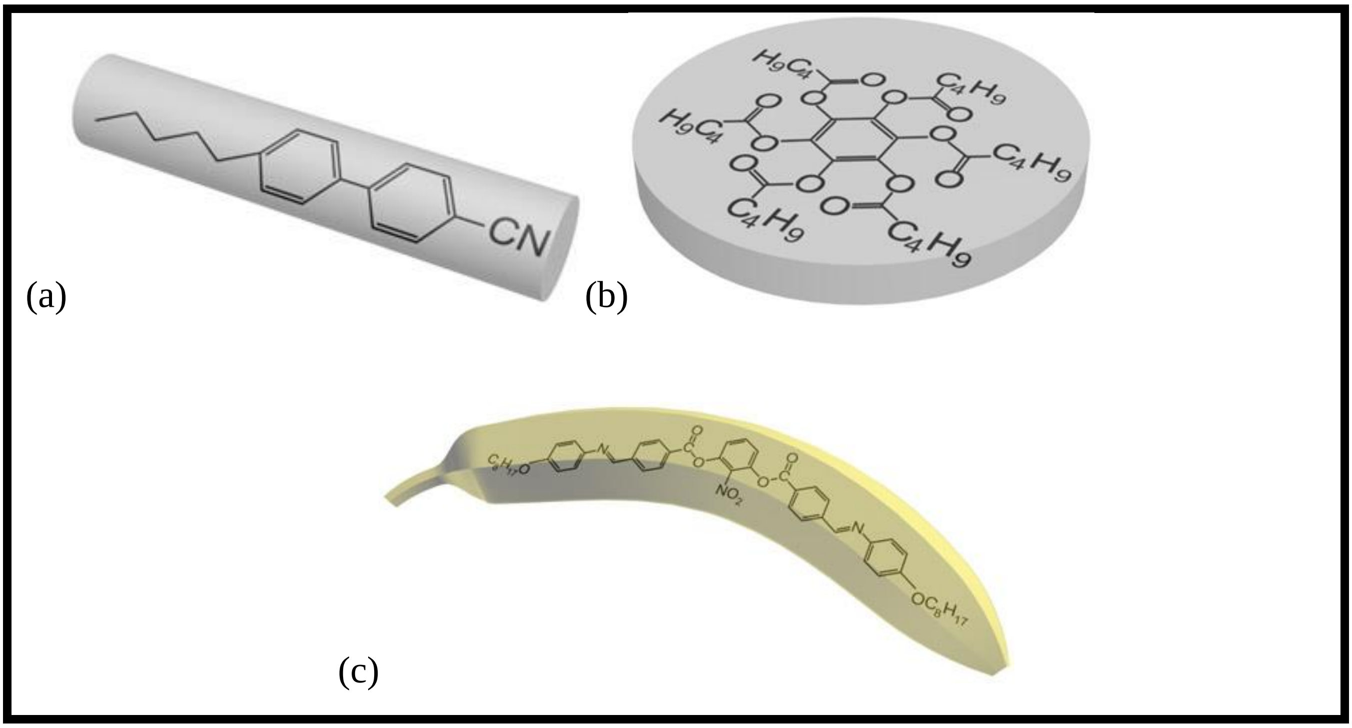


Figure 1.5 *Molecular structure of the three classes of thermotropic LCs (a) rod like [5CB], (b) disc like (benzene-hexa-n-alkanoate derivatives), and (c) banana-shaped liquid crystals.*(10)

1.4.1 Calamitic Liquid Crystals (rod like):

The most common type of molecules that form thermotropic mesophase are rod-like molecules. These molecules possess an elongated shape, that is, the molecular length (l) is significantly greater than the molecular breadth (b), as depicted in figure (1.6).

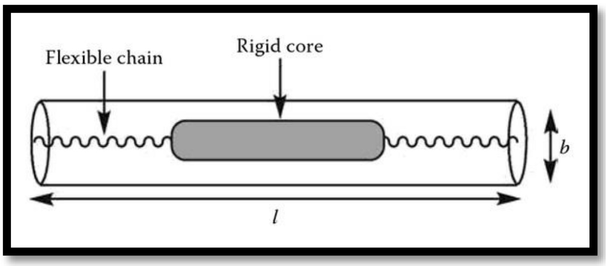


Figure 1.6 *Representation of a calamitic LC molecule where l>>b.* (8)

The geometric shape anisotropy in combination with interaction anisotropy and microsegregation of incompatible parts in calamitic LCs leads to a number of mesophase morphologies. Most of the calamitic liquid crystalline compounds consist of two or more ring structures, bonded together directly or via linking groups. They usually have terminal hydrocarbon chains and sometimes lateral substituents as well. The typical chemical structure of these molecules can be represented by the general template, as shown in figure (1.7), where A and B are core units (benzene, naphthalene, biphenyl, etc.), R and R' are flexible moieties such as normal and/or branched alkyl groups, M and N are generally small lateral substituents ($-Cl$,$-Br$, $-NO_2$,$-CH_3$,$-OCH_3$,$-CN$, etc.). Y is a linking group to the core units and X and Z are linking groups of terminal chains and core units like (S, N, O, NH, CO, etc.). The nature of the central core, linking groups, and lateral substituents impart significant effect on the mesophase morphology and physical properties of calamitic LCs. Calamitic LCs generally exhibit two types of mesophases: (a) nematic and (b) smectic.

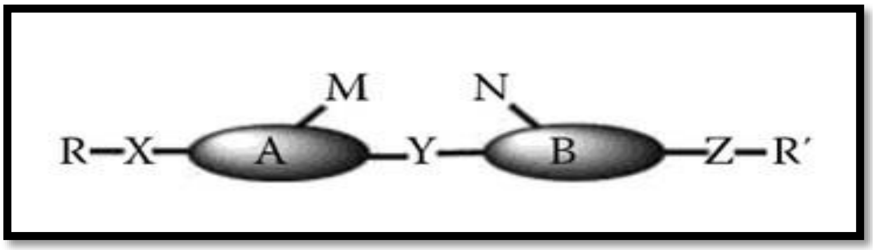


Figure 1.7 *General template for calamitic LC molecules.*(8)

1.4.1.1 Nematic phases:

One of the most common LC phases is the nematic. The word *nematic* comes from the Greek word *nema* which means "thread". In a nematic phase, the *calamitic* or rod-shaped organic molecules have no positional order, but they self-align to have long-range orientational order with their long axes roughly parallel.(11) Thus, the molecules are free to flow and their center of mass positions are randomly distributed as in a liquid, but still maintain their long-range directional order. Most nematics are uniaxial: they have one axis that is longer and preferred, with the other two being equivalent (can be approximated as cylinders or rods). However, some liquid crystals are biaxial nematics, meaning that in addition to orienting their long axis, they also orient along a secondary axis.(12) Nematics have fluidity similar to that of ordinary (isotropic) liquids but they can be easily aligned by an external magnetic or electric field. Aligned nematics have the optical properties of uniaxial crystals and this makes them extremely useful in liquid crystal displays (LCD).(13)

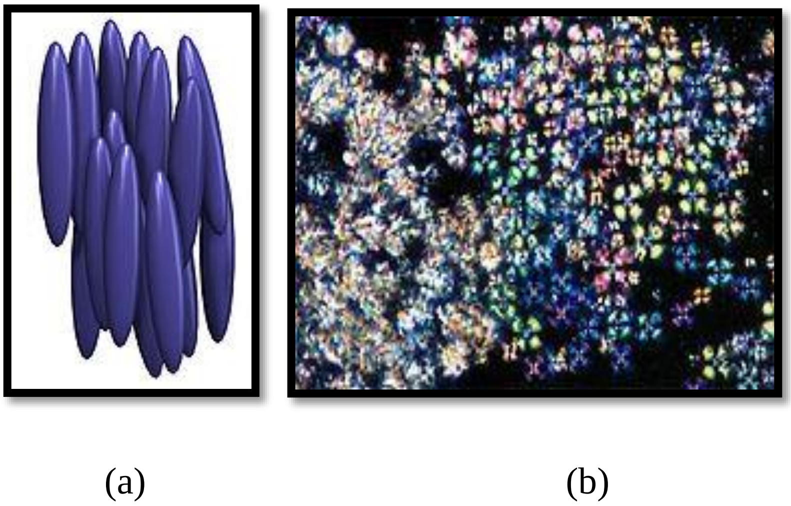

(a) (b)

Figure 1.8 *(a) Alignment in a nematic phase (b) Phase transition between a nematic (left) and smectic A (right) phases observed between crossed polarizers. The black color corresponds to isotropic medium.* (12)

1.4.1.2 Smectic phases:

The smectic phases at low temperatures form characteristic layers that can slip over one another in a manner similar to that of soap. The word "smectic" originates from the Latin word "smecticus", means cleaning, or having soap like properties. The smectics are thus positionally ordered along one direction. In the Smectic A phase, the molecules are oriented along the layer normal, while in the Smectic C phase they are tilted away from the layer normal. These phases are liquid-like within the layers. There are many different smectic phases, all characterized by different types and degrees of positional and orientational order. (4)(14)

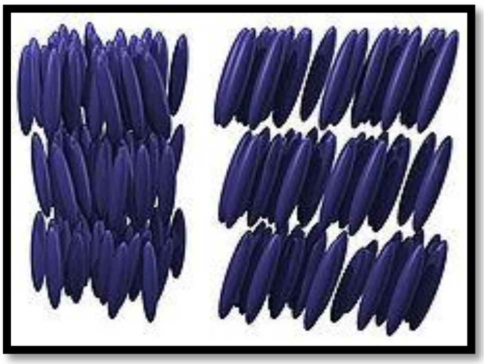


***Figure 1.9** Schematic of alignment in the smectic phases. The smectic A phase (left) has molecules organized into layers. In the smectic C phase (right), the molecules are tilted inside the layers.*(12)

1.4.2 Discotic Liquid Crystals (disk like):

In September 1977,(15) Chandrasekhar and colleagues at Raman Research Institute, India reported the first observation of thermotropic mesomorphism in pure, single component systems of relatively simple plate like, or more appropriately disk-like molecules. They designed and synthesized a number of benzene hexa-n-alkanoates and investigated possible mesomorphism in this novel molecular architecture. By thermodynamic, optical, and x-ray studies, they could establish that these materials form a new class of LCs in which molecules are stacked one on top of the other in columns, and the columns in turn constituted a 2D hexagonal arrangement. Self-organization of disk-like molecules forms an entirely new class of LC, quite different from the classical LCs formed by rod-like molecules that had been known since they were observed by Friedrich Reinitzer in 1888.(5) The disk-like molecules spontaneously self-assemble into 1D stacks, which in turn self-organize on various 2D lattices; the third dimension has no translational order figure (1.10).(8)

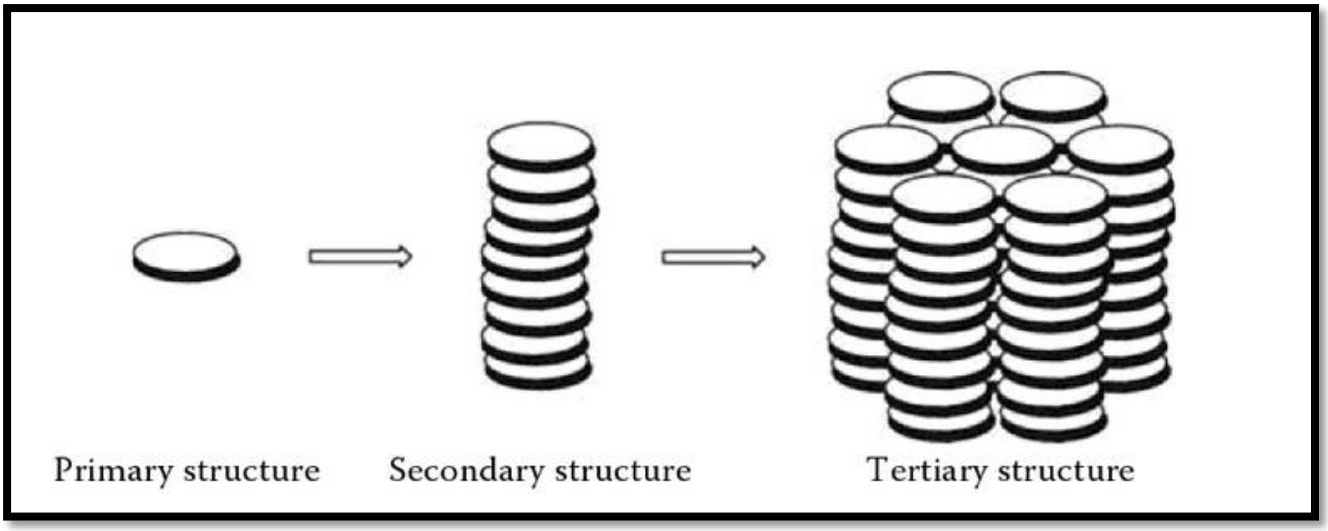


Figure 1.10 *Self-assembly and self-organization of discotic liquid crystalline molecules into columnar phases.*(8)

1.4.2.1 Types of Discotic Liquid Crystal Mesophase:

There are two types of discotic liquid crystal mesophase. First, the *Nematic* phase or the least ordered mesophase (usually occur at highest temperature). Disk-like molecules in such a phase have orientational order but no positional order. Only few examples of discogens have this mesophase.

The other mesophase is *Columnar* phase in which the molecules are stacked into columns, the columns then being organized in a two-dimensional lattice. Molecules in such a phase have a positional order in two dimensions and are disordered in the third. Columnar phases are very rich and are normally classified at three levels; according to the symmetry of the two-dimensional array, the orientation of the core with respect to the column axis, and finally the degree of order within the column. The columnar phase divided into hexagonal and rectangular columnar phases as shown in figure (1.11). (16)

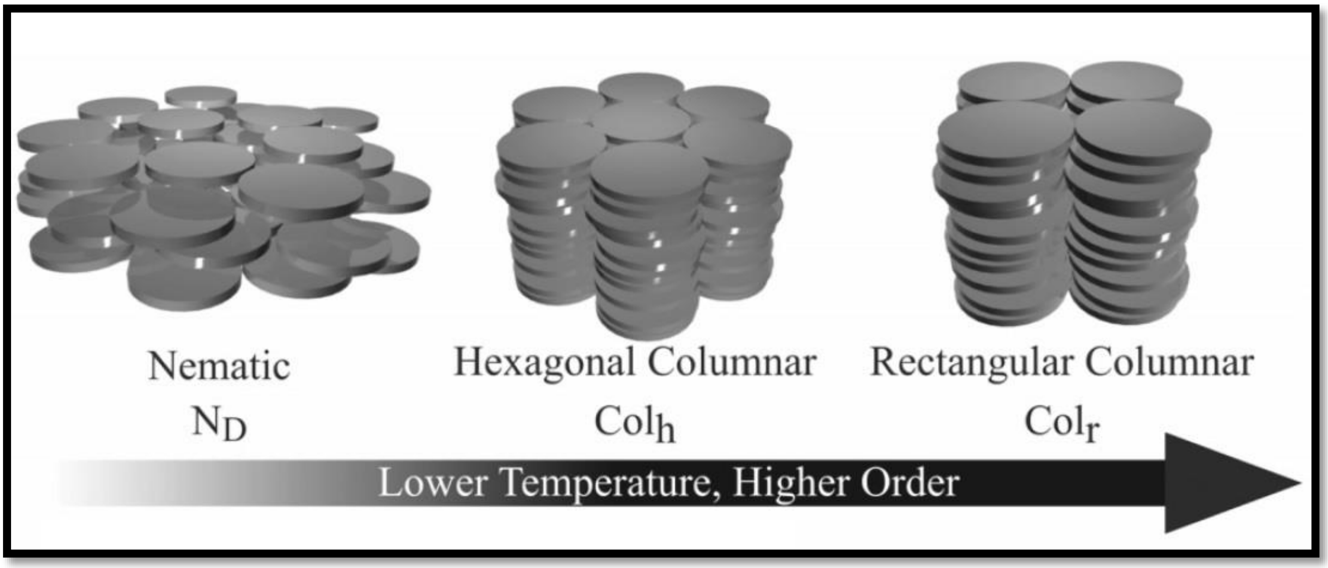


Figure 1.11 *The phases formed by disc-like molecules are characterized by the degree of positional order and symmetry.*(16)

1.4.2.2 Structure of the Discotic Mesogens:

Molecules forming DLCs are typically made of a central discotic core substituted by 3-12 saturated chains of three or more carbon atoms phthalocyanines and triphenylenes are the typical examples of discotic molecules figure (1.12).

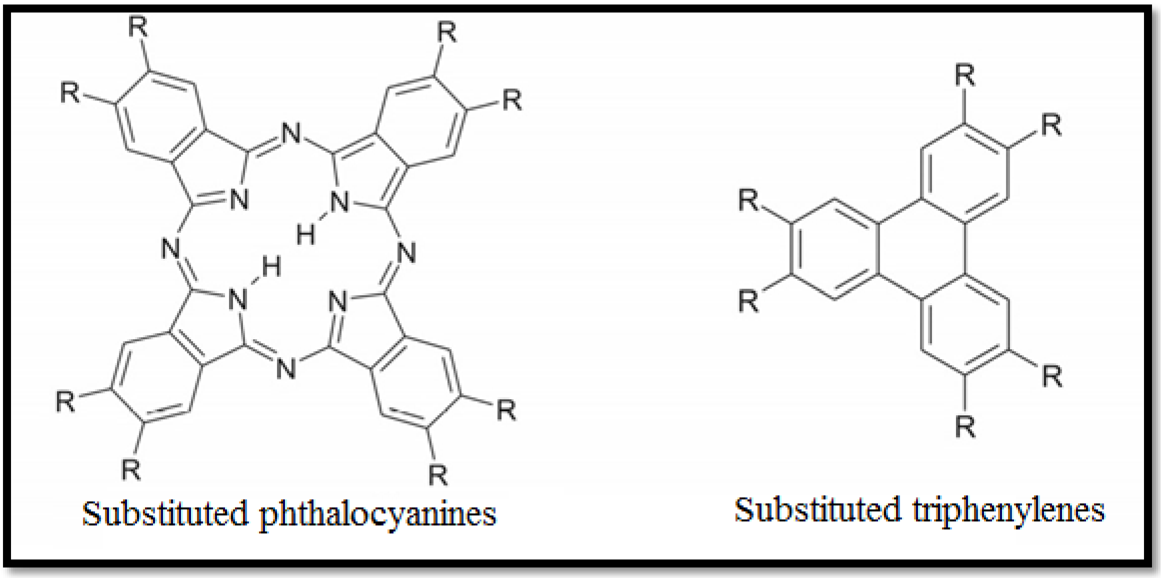


Figure 1.12 *Typical examples of discotic molecules.*

These materials often have two-, three-, four-, or six-fold rotational symmetry. However, there are many exceptions, and materials with low symmetry, a nonplanar, nonaromatic core having shorter number of chains are also documented. The liquid crystallinity results from the microsegregation of the two constituents: the crystalline character is promoted by the interaction between the conjugated cores while the liquid character originates from the melting of the saturated alkyl chains in the mesophase. Such discotic molecules organize spontaneously in the form of 1D columns, which can be oriented easily and possess self-healing properties, that is, the capacity of repairing structural defects in contrast to crystalline materials. The search for such mesophases is mostly ruled by subtle changes in the number, size, and nature of the lateral chains in addition to the central core. A general template for discotic mesogens is shown in figure (1.13). By tailoring the shape, size, and nature of the central core as well as the type of the attached side chains, compounds with different abilities to self-organize into different mesophase morphologies can be obtained.(8)

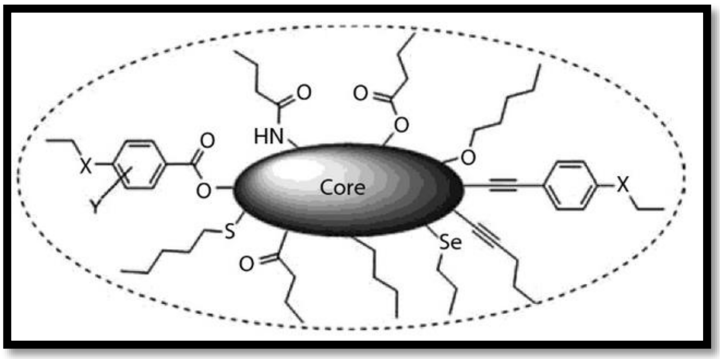


Figure 1.13 *General template for DLC molecular architecture . X is a linking group like (NH,COO,S,O, etc.),Y is a lateral group like (Cl, Br, CH_3, OCH_3, CN, NO_2, etc.).(8)*

1.4.3 Bent-Core Liquid Crystals (Banana like):

Vorlander (17), a pioneer in the field of LC synthesis, has synthesized several bent-core LCs and reported the mesogenic properties in 1929, mentioning that the thermal stability of the mesophase is low compared to straight core analogues. Matsunaga (18) and coworkers also synthesized bent-core mesogens in the early 1990s but did not realize the physical importance of the molecules before the discovery of polar switching in these compounds in 1996. Bent-shaped molecules provide access to mesophase with polar order and supramolecular chirality despite the mesogens being achiral. Typically, their molecular structure can be regarded as being composed of three units: an angular central core, two linear rigid cores, and terminal chains figure (1.14). (8)

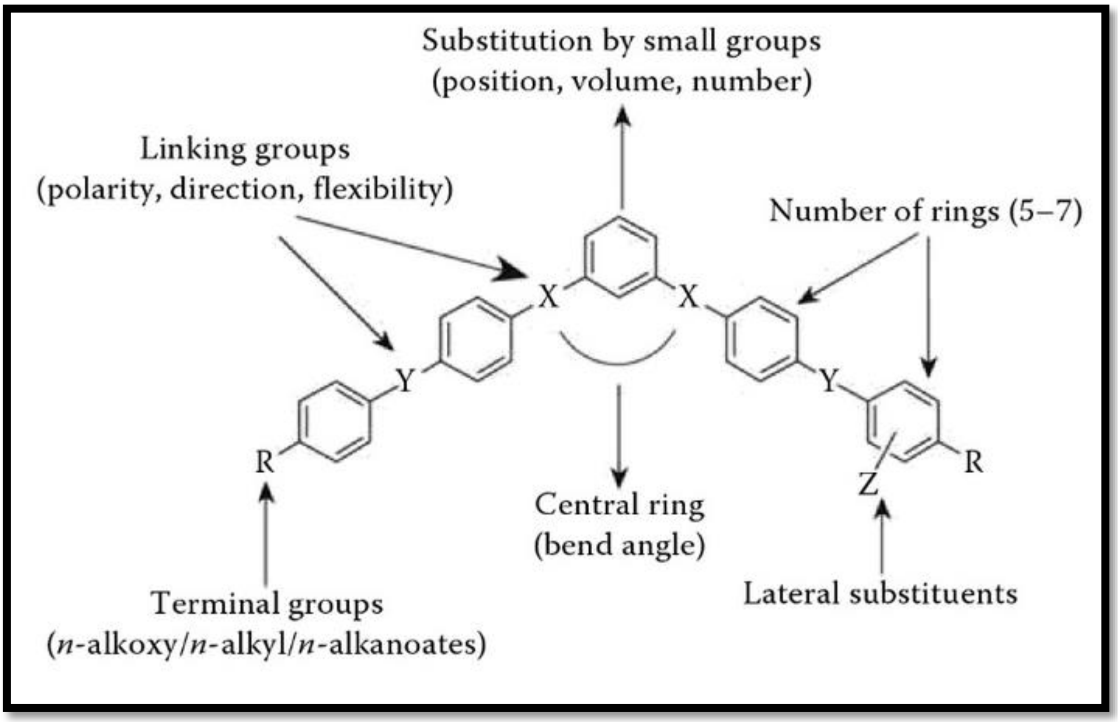


Figure 1.14 *General template for banana LC molecules, X, Y are linking groups like (NH, S, O, COO, etc.), Z lateral substituents like (NO_2, OCH_3, CH_3, OH, Cl, Br, CN,etc.).*

1.5 Application of Liquid Crystals:

Liquid crystals have a large number of applications due to their electro-optical, magneto-optical, electro-chromic and thermo-chromic properties, which are important in industrial and medical applications. These applications include display-device technology, medical applications, gas-liquid chromatography, and cosmetics applications.

The major use of liquid crystal displays is currently in watches and small portable calculators …. etc. Liquid crystal displays visibility in high ambient light, easily changed pattering and size, variation in color, operation in transmissive or reflective mode and more. (19)

Liquid crystals have gained a great interest as stationary phase in gas liquid chromatography (G.L.C.). They are used in the separation of close boiling compounds on the bases of their molecular shape. One of the most interesting separations that have been achieved on liquid crystals is in separation of optical isomers. Certain liquid crystal stationary phases are suitable for programmed-temperatures gas chromatography and for work at temperature of about 300°C. (20)

The medical applications of liquid crystals such as cholesteric nematic type, include disposable oral thermometry, neurology, oncology, pediatrics surgery, and podiatry. To be more specific these medical applications include detection of breast cancer, location of the placenta, blood flow patterns in extremities of the human anatomy and observation of skin temperature change following blockage of the sympathetic nervous system. Liquid crystals used in many skin care products. The first and probably most successful product is Eyzon, which incorporates very attractive coils of iridescent liquid crystal in a clear gel. It is probable that vitamin A palmitateis mixed with the liquid crystal. (21)

Since 1977 when Chandrasekhar et al. first discovered discotic liquid crystals (DLCs)(4), DLCs have become an important member of liquid crystals. DLCs can easily self-assembly to be highly ordered columnar mesophases, which allow the electrons or holes to migrate along the columnar structures. These properties, as a result, have made DLCs an excellent candidate for photo-electronic semiconductor materials (22).

The synthesis route of a discotic liquid crystal was investigated, because these molecules have potentially important industrial applications due to unique properties. Discotic liquid crystals are well ordered types of liquid crystal that make their liquid crystal state easy to control. In addition, they can be easily polymerized and they have conducting properties. All these properties make discotic liquid crystals of particular interests especially if they are intended for electronic devices. (23)

1.6 Literature Survey:

In 1984, S. Takenaka, et. al (24) synthesized a triester derivative of benzene which exhibit a discotic nematic phase.

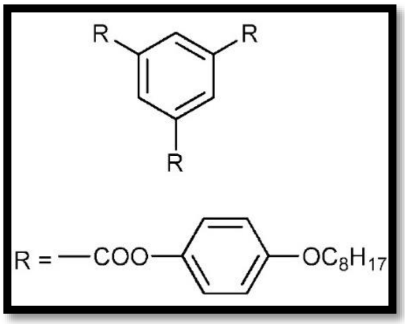


Figure 1.15 *Triester derivative of benzene.*

In 2001, B. G. Kim and coworkers synthesized compounds containing oxadiazole side arms figure (1.16) exhibit discotic nematic phase behavior. (25)

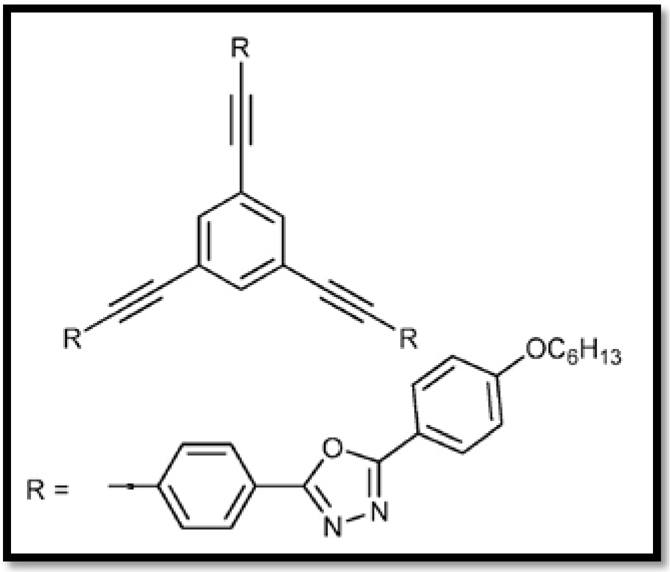


Figure 1.16 *Oxadiazole side arms discotic compounds.*

In 2001, J. H. Lee and coworkers synthesized a various hydrogen bonded supramolecular discotic compounds, which exhibit the N_D phase (26) figure (1.17).

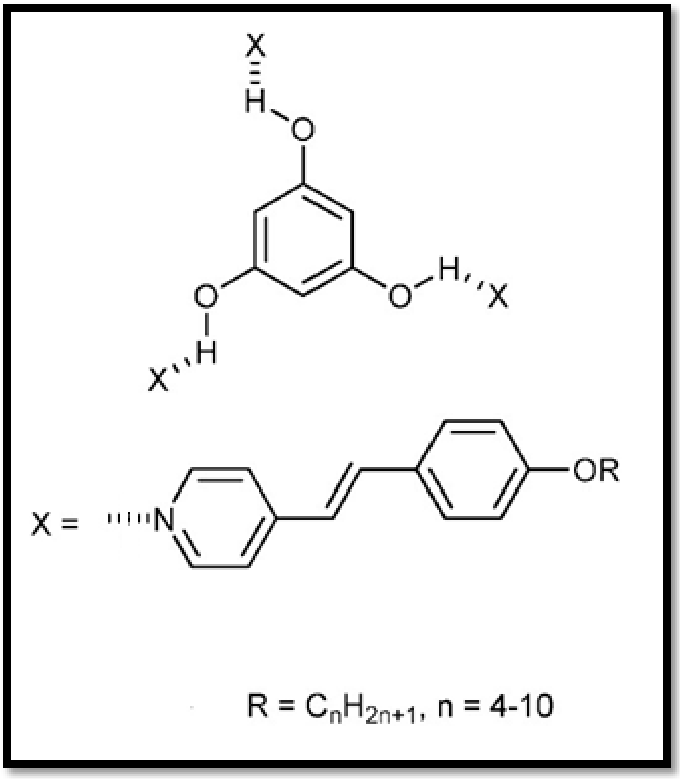


Figure 1.17 *Various hydrogenbonded supramolecular discotic compounds.*

In 2004, H. Meier and coworkers synthesized a stilbinoid side arms discotic compounds figure (1.18) which exhibit discotic nematic phase behavior. (27)

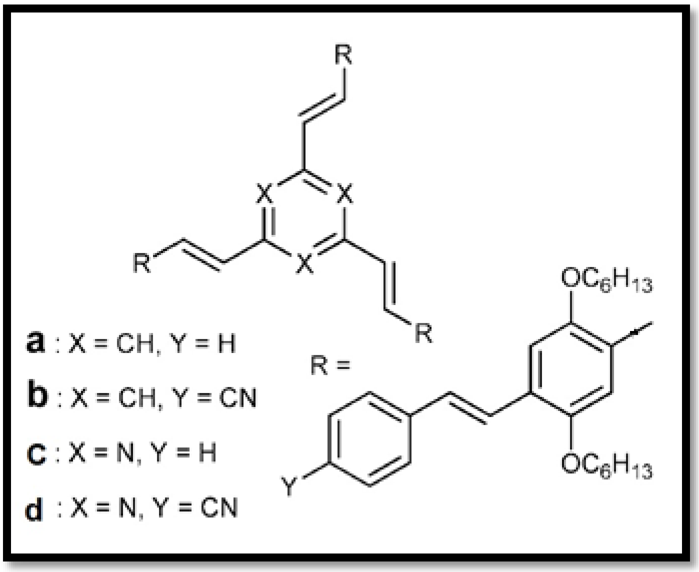


Figure 1.18 *Stilbinoid side arms discotic compounds.*

In 2005, A. Grafe, et. al (28) synthesized a discotic liquid crystalline trimers (a-d) figure (1.19) containing benzene as the central core show only the columnar nematic phase in the pure compounds.

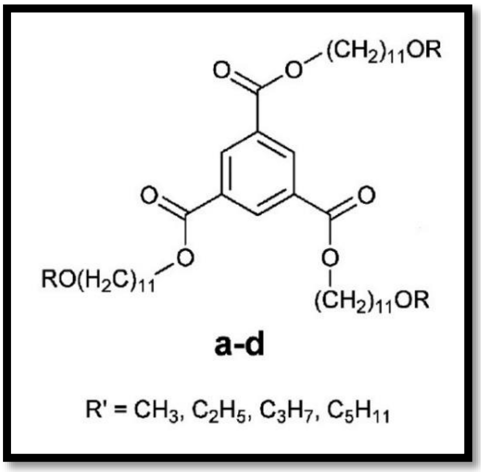


Figure 1.19 *Discotic liquid crystalline trimers containing benzene as the central core.*

In 2006, M. J. Jeong and coworkers synthesized a hydrazone -based side-arms discotic compounds figure (1.20) which exhibit discotic nematic phase behavior. (29)

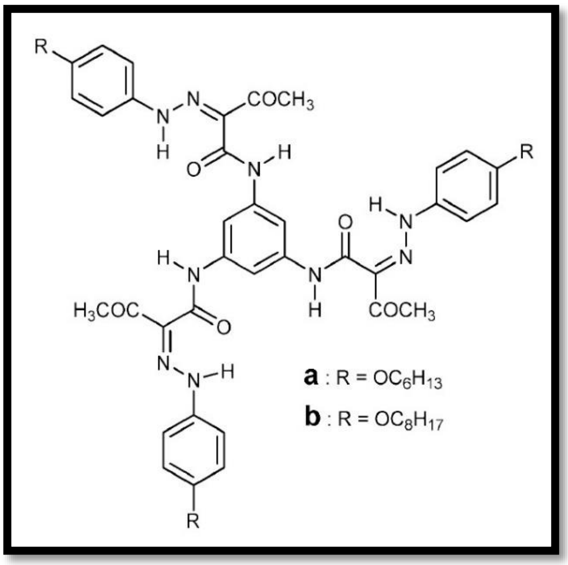


Figure 1.20 *Hydrazone based side arms discotic compounds.*

In 2011, S. Kumar and S. K. Gupta (30) synthesized a novel discotic core by fusing imidazole unit with well-known triphenylene discotic core as in figure (1.21). Two (new imidazole fused unsymmetrically substituted triphenylene) derivatives were prepared and characterized. These triphenylenoimidazole derivatives were found to exhibit hexagonal columnar mesomorphism over a wide temperature range.

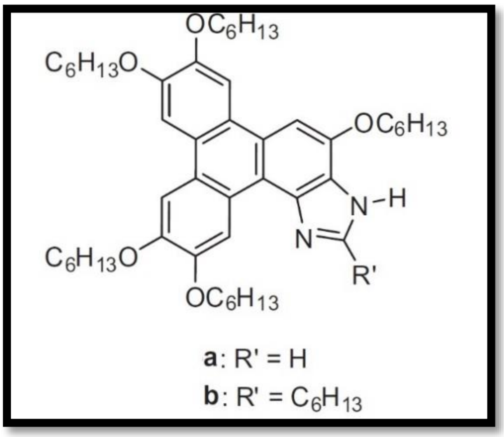


Figure 1.21 *New imidazole fused unsymmetrically substituted triphenylene derivatives.*

In 2014, G. Y. Yeap and coworkers synthesized a symmetrical trimeric star-shaped mesogens based on 1,3,5-trisubstituted benzene incorporating Schiff base and azobenzene fragments as the peripheral units figure (1.22). **PSB-Cl-5** show during the cooling cycle from the isotropic, (a) Schlieren texture two- and four-fold brushes of N phase appeared followed by the (b) SmC phase. **PSB-Br-5** exhibiting the focal conic fan-shaped texture of SmA phase. **PAZ-Cl-4** show (a) Schlieren texture of N phase upon cooling and followed by the (b) fan-shaped texture characteristic of S_{mA} phase. **PAZ-Br-5** upon cooling showing the appearance of transition bars across the fan-shaped during the S_{mA} to S_{mB} phase transition.(31)

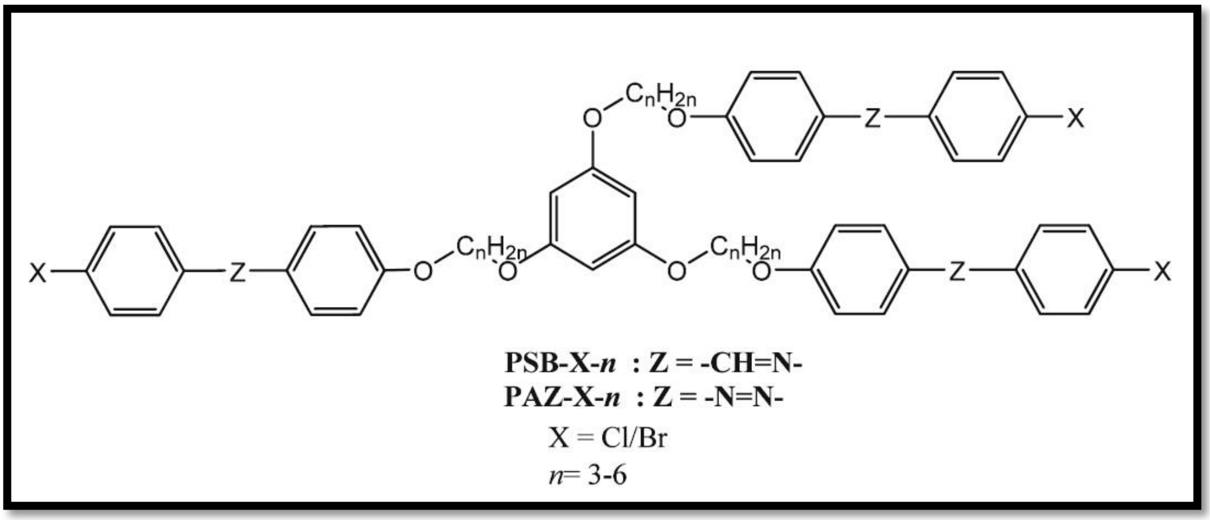


Figure 1.22 *Three-armed star-shaped mesogens* ***PSB-X-n*** *and* ***PAZ-X-n****.*

1.7 Aim of the work:

The purpose of this study is synthesis and characterization of two new series of discotic liquid crystals compounds derived from 1,3,5-trihydroxy benzene (phluroglucinol core) and substituted by three alkoxybenzoyl groups and alkoxybenzoyloxy benzoyl groups, and elucidate the liquid crystalline properties of the synthesized compounds.

Chapter Two

Experimental

Chapter two

Experimental

2.1 Chemicals:

The chemicals used and their suppliers are listed in table (2.1)

Table (2.1) *chemical and their suppliers.*

No.	Materials	Supplier company
1	Phluroglucinol (1,3,5-trihydroxy benzene)	TCI Chemicals
2	Potassium hydroxide	BDH
3	Absolute ethanol	Scharlau
4	n-Ethyl bromide	BDH
5	n-Propyl bromide	Alfa Aesar
6	n-Butyl bromide	Ferak
7	n-Heptyl bromide	Fluka
8	n-Octyl bromide	Fluka
9	n-Pentanol	BDH
10	n-Hexanol	BDH
11	Hydrochloric acid	BDH
12	Magnesium sulfate	Aldrich
13	Sodium bicarbonate	BDH
14	Hydrobromic acid	BDH
15	Thionyl chloride	Merck Schuchardt OHG
16	Pyridine	Merck
17	p-Hydroxy benzoic acid	Acros Organics
18	Sulphuric acid	Fluka
19	Distilled water	Local

2.2 Apparatus used:

1- Fourier Transform Infrared Spectrophotometer (FT-IR)

FT-IR spectra in the range (4000-400) cm^{-1} were recorded using potassium bromide disc on FT-IR instrument Model 8300 Shimadzu Spectrophotometer, Japan. The analysis were carried out in Al-Nahrain University.

2- ^{1}H Nuclear magnetic resonance spectrometer (^{1}H-NMR):

1H Nuclear Magnetic Resonance (^{1}H-NMR) spectra were recorded on Brüker ACF 300 spectrometer at 300 MHz, using deuterated chloroform ($CDCl_3$) as solvent with TMS as an internal standard, in the University of Exeter, England.

3- Melting point:

Uncorrected melting points were recorded on hot stage Gallen kamp melting point apparatus (U.K.).

4- Differential scanning calorimeter (DSC):

Transition temperatures and enthalpies were scanned by LINSEIS DSC PT-1000 differential scanning calorimeter with a heating rate of 10.0◦C/min in air and it was calibrated with indium (156.6◦C, 28.45 J/g) at Al Nahrain University.

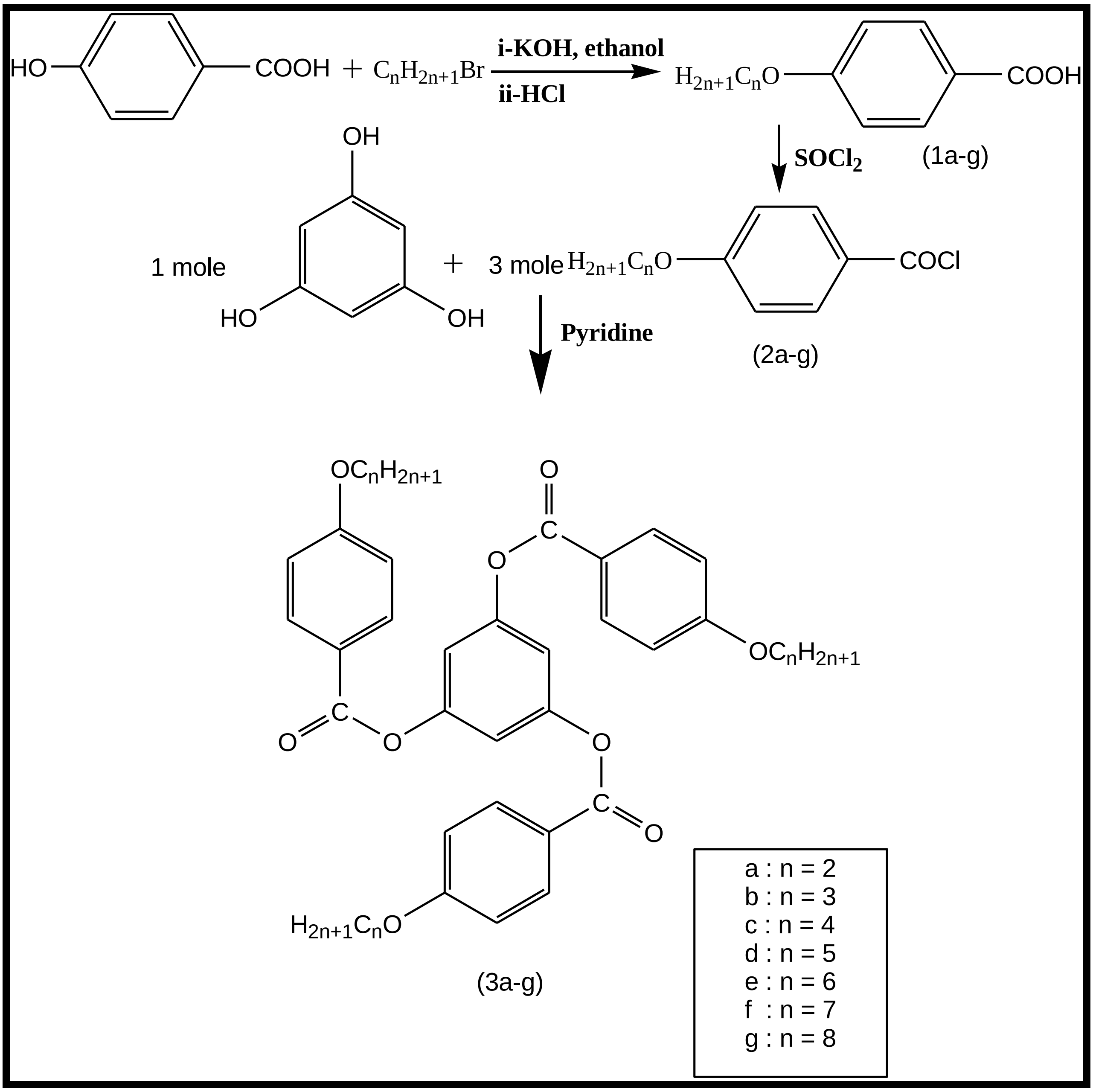
5- Hot stage Polarizing Microscope:

Liquid crystalline properties were investigated by using a (Meiji MT9000) Polarizing Optical Microscope attached to an INSTEC Hot stage. The texture of the compounds were observed using polarized light with crossed polarizers, the sample being prepared as a thin film sandwiched between a glass slide and a cover. A camera (Lumenera) was installed on the polarizing microscope. The analysis were carried out in Al-Nahrain University.

6- Elemental analysis (CHNS-O): Elemental analysis (CHNS-O) was carried out using EURO EA elemental analyzer instrument. The analysis were carried out in Al-Nahrain University.

2.3 Preparation procedures of 1,3,5-tri[4-n-alkoxybenzoyloxy] benzene (3a-g):

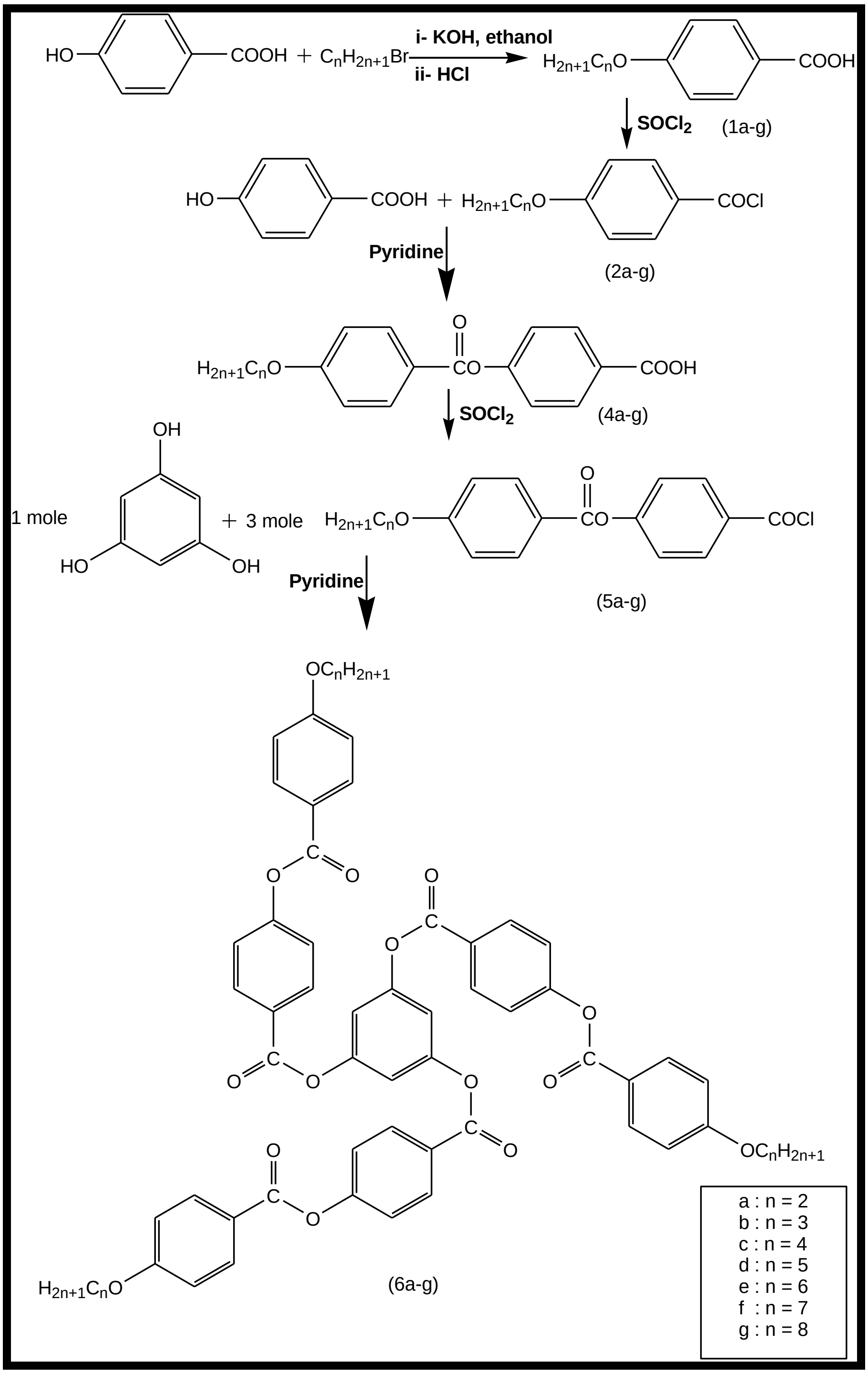
The intermediates and discotic compounds (3a-g) were prepared according to scheme (2.1):



Scheme 2.1 *The synthetic pathway for the discotic compounds (3a-g).*

2.3 Preparation procedures of 1,3,5-tri-[4-{4'-n-alkoxybenzoyloxy}benzoyloxy] benzene (6a-g):

The intermediates and discotic compounds (6a-g) were prepared according to the scheme 2.2:



***Scheme 2.2** The synthetic pathway for the discotic compounds (6a-g).*

2.3.1 Preparation of n-pentylbromide and n-hexylbromide:

To 71 mL of 48% hydrobromic acid contained in a 500 mL round-bottomed flask, 16 mL of concentrated sulfuric acid was added in portion with shaking and cooling (some hydrogen bromide may be evolved). A 0.5 mole of l°-alcohol (*n-pentylalcohol and n-hexylalcohol)* was added, followed by 2.75 mL of H_2SO_4 in Several portions. The reaction mixture was heated under reflux until the appearance of two phases. During this period the formation of n-alkyl bromide was almost completed and two layers were formed. After cooling, and discarding the aqueous phase, the organic layer was washed first with an equal volume of 10% HCI, and then the organic layer was separated and washed with an equal volume of 10% sodium bicarbonate solution. Then the organic layer was separated and the anhydrous magnesium sulphate was added to remove the water completely from organic layer. The solution was filtered to give n-alkylbromide (n-pentylbromide and n-hexylbromide) (32).

2.3.2 Preparation of 4-n-Alkoxy benzoic acid (1a-g):

Dissolving 5 g (0.036) mole of 4-Hydroxybenzoic acid in 20 mL ethanol. 5.1 g, 0.091 mole KOH was added with stirring, the mixture was placed in 250 mL round bottom flask and cooled to room temperature, then 0.036 mole of appropriate alkyl bromide was added drop wise. The solution was refluxed overnight. 1.12 g, 0,02 mole KOH dissolved in a little amount of water (~ 5mL) was added to the reaction mixture and heated for (1-3) hour. The solvent was evaporated and equal volume of water was added. The solution was heated till became clear. Acidification with conc. HCl yielded white precipitate. Recrystallization from ethanol gave the desired product. (33)

Table (2.2) *Physical properties of compounds (1a-g).*

Comp. name	Comp.No.	Yield %	m.p (°C)	Color
4-ethoxybenzoic acid	1a	90%	158-163	white
4-n-propyloxybenzoic acid	1b	92%	136-138	white
4-n-butyloxybenzoic acid	1c	88%	180-183	white
4-n-pentyloxybenzoic acid	1d	83%	112-117	white
4-n-hexyloxybenzoic acid	1e	91%	96-101	white
4-n-heptyloxybenzoic acid	1f	95%	185-190	white
4-n-octyloxybenzoic acid	1g	94%	160-164	white

2.3.3 Preparation of 4-n-Alkoxy benzoyl chlorides (2a-g):

4-n-alkoxy benzoyl chlorides were prepared by reflux the corresponding 4-n-alkoxy benzoic acid (0.03 mole) with thionyl chloride (15 ml) in water bath till evolution of hydrogen chloride gas cased. Excess of thionyl chloride was distilled off under reduce pressure using water pump. The acid chloride left behind were directly used for further reaction without purification. (34)

2.3.4 Synthesis of 1,3,5-tri[4-n-alkoxybenzoyloxy] benzene (3a-g):

A mixture of 1,3,5-trihydroxybenzene (0,008 mole**,** 1 g) and 4-n-alkoxybenzoylchloride (0.024 mole) with 10 mL pyridine were stirred for three hours in an ice bath. The mixture was poured onto cold water, acidification with HCl and filtered. The product was washed with cold water (35).

Table (2.3) *Physical properties of compounds (3a-g).*

Comp. name	**Comp.No.**	**Yield %**	**m.p (°C)**	**Color**
1,3,5-tri[4'-ethoxybenzoyloxy]benzene	3a	81%	125-130	white
1,3,5-tri[4'-n-propyloxybenzoyloxy]benzene	3b	58%	112-116	white
1,3,5-tri[4'-n-butyloxybenzoyloxy]benzene	3c	67%	115-120	white
1,3,5-tri[4'-n-pentyloxybenzoyloxy]benzene	3d	73%	120-125	white
1,3,5-tri[4'-n-hexyloxybenzoyloxy]benzene	3e	62%	70-75	white
1,3,5-tri[4'-n-heptyloxybenzoyloxy]benzene	3f	50%	93-98	yellow
1,3,5-tri[4'-n-octyloxybenzoyloxy]benzene	3g	41%	89-94	white

2.3.5 Preparation of 4-[4'-n-alkoxybenzoyloxy] benzoic acid (4a-g):

A mixture of 4-Hydroxybenzoic acid (0,008 mole**,** 1.14 g) and (0.008 mole) of 4-n-alkoxybenzoylchloride (2a-g) with 10 mL pyridine were stirred for three hours in an ice bath. The mixture was poured onto cold water, acidification with HCl and filtered. The product was washed with cold water (35).

Table (2.4) *Physical properties of compounds (4a-g).*

Comp. name	**Comp.No.**	**Yield %**	**m.p (°C)**	**Color**
4-[4'-n-ethoxybenzyloxy]benzoic acid	4a	70%	120-123	white
4-[4'-n-propyloxybenzyloxy]benzoic acid	4b	65%	133-136	white
4-[4'-n-butyloxybenzyloxy]benzoic acid	4c	85%	140-144	white
4-[4'-n-pentyloxybenzyloxy]benzoic acid	4d	81%	135-138	white
4-[4'-n-hexyloxybenzyloxy]benzoic acid	4e	59%	139-143	white
4-[4'-n-heptyloxybenzyloxy]benzoic acid	4f	66%	170-174	white
4-[4'-n-octyloxybenzyloxy]benzoic acid	4g	45%	166-170	white

2.3.6 Preparation of 4-[4'-n-alkoxybenzoyloxy] benzoyl chloride (5a-g):

4-[4'-n-alkoxybenzoyloxy] benzoyl chlorides were prepared by reflux the corresponding 4-[4'-n-alkoxybenzoyloxy] benzoic acid (0.03 mole) with thionyl chloride (15 ml) in water bath till evolution of hydrogen chloride gas cased. Excess of thionyl chloride was distilled off under reduce pressure using water pump. The acid chloride left behind were directly used for further reaction without purification. (34)

2.3.7 Synthesis of 1,3,5-tri-[4-{4'-n-alkoxybenzoyloxy} benzoyloxy] benzene (6a-g):

A mixture of 1,3,5-trihydroxybenzene (0,008 mole**,** 1.14 g) and 4-[4'-n-alkoxybenzoyloxy] benzoyl chloride (0.024 mole) with 10 mL pyridine were stirred for three hours in an ice bath. The mixture was poured onto cold water, acidification with HCl and filtered. The product was washed with cold water. (35)

Table (2.5) *Physical properties of compounds (6a-g).*

Comp. name	**Comp.No.**	**Yield%**	**m.p(°C)**	**Color**
1,3,5-tri[4-{4'-ethoxybenzoyloxy}benzoyloxy]benzene	6a	78%	160-165	white
1,3,5-tri[4-{4'-n-popyloxybenzoyloxy}benzoyloxy]benzene	6b	63%	105-110	white
1,3,5-tri[4-{4'-n-butyloxybenzoyloxy}benzoyloxy]benzene	6c	66%	110-115	white
1,3,5-tri[4-{4'-n-pentyloxybenzoyloxy}benzoyloxy]benzene	6d	58%	120-130	white
1,3,5-tri[4-{4'-n-hexyloxybenzoyloxy}benzoyloxy]benzene	6e	71%	118-123	yellow
1,3,5-tri[4-{4'-n-heptyloxybenzoyloxy}benzoyloxy]benzene	6f	51%	105-112	yellow
1,3,5-tri[4-{4'-n-octyloxybenzoyloxy}benzoyloxy]benzene	6g	43%	130-136	yellow

Chapter Three

Results & Discussion

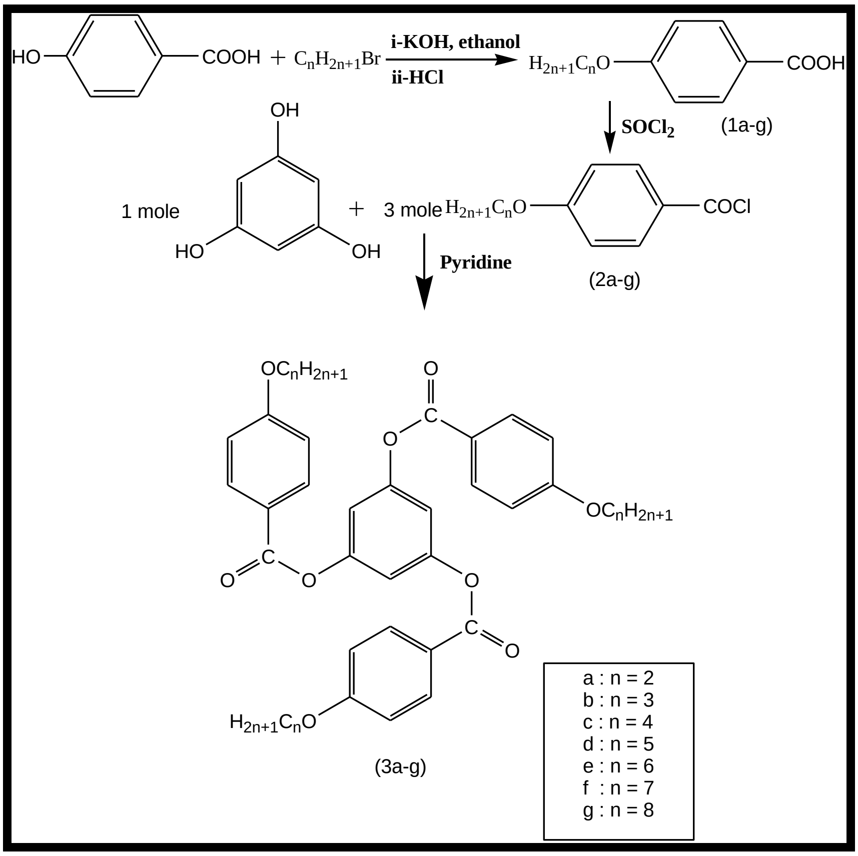
Chapter Three

Results & Discussion

Discotic liquid crystals (DLCs) with nematic phase have been commercially utilized in the liquid crystal display industry as optical compensating films for widening the view angles (36). More interestingly, DLCs can self-organize into columnar mesophases with a high degree of order, and show fast unidirectional charge migration properties, and have been studied as soft organic semiconductors (37). In this thesis, we report two series of star-shaped DLC trimers derived from 1,3,5-trihydroxybenzene.

3.1 Synthesis and Characterization of 1,3,5-tri-[4-n-alkoxybenzoyloxy] benzene (3a-g):

The titled compounds were synthesized as shown in scheme (3.1):

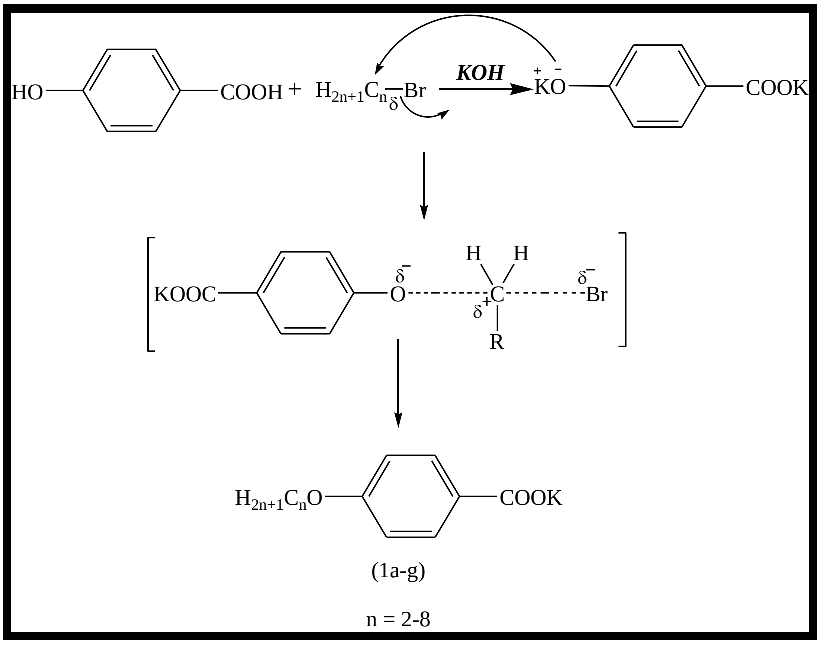


Scheme 3.1 *The synthetic pathway for the discotic compounds (3a-g).*

3.1.1 Preparation of 4-alkoxybenzoic acid (1a-g):

4-alkoxybenzoic acids were prepared in the easiest fashion by the alkylation of 4-hydroxybenzoic acid with appropriate alkyl halides in boiling alcohol (34) according to bimolecular nucleophilic substitution mechanism (S_N2) (38), in this mechanism, there is backside attack. The nucleophile approaches the substrate from a position 180° away from the leaving group. The reaction is a one-step process with no intermediate.

The C-Y bond is formed as the C-X bond is broken to generate transition state as follow:



Eq. 3.1 *Mechanism for preparation of 4-n-alkoxybenzoic acids (1a-g).(38)*

Structures of the acids were confirmed by its melting points, the melting points agree well with that reported in the literature (39). Also by its FTIR spectra, Table (3.1) which displayed the disappearance of the phenolic (O – H) stretching absorption bands and the appearance of (C – H) aliphatic stretching bands, FT-IR spectrum of 4-butyloxybenzoic acid (1c) is shown figure (3.1).

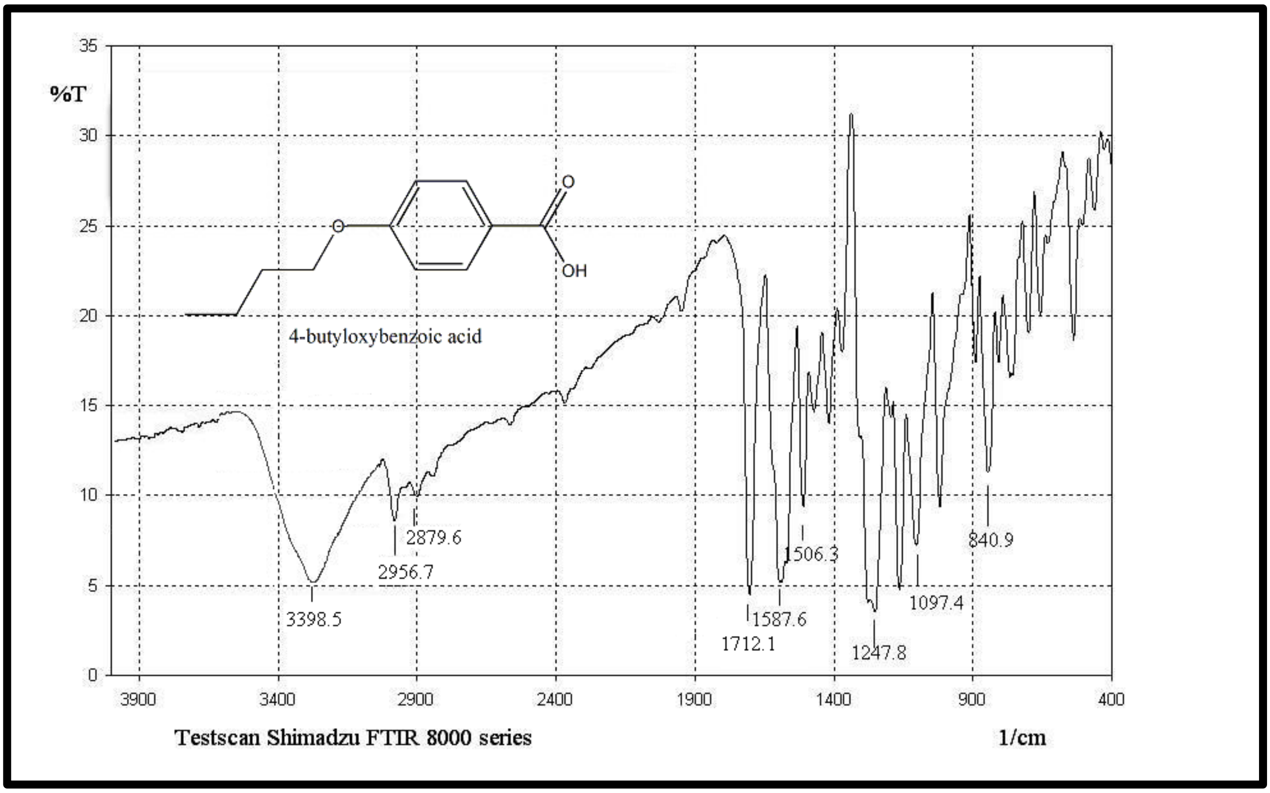


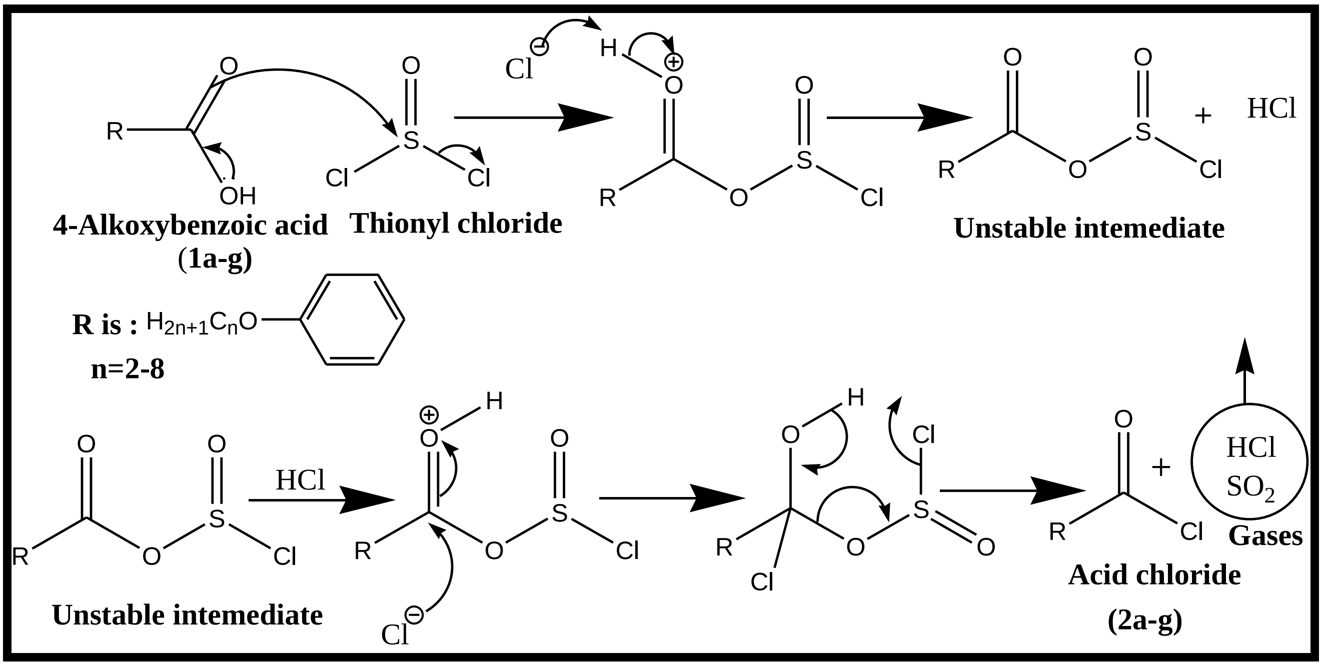
Figure 3.1 *FTIR spectrum of 4-butyloxybenzoic acid 1c.*

Table 3.1 *Characteristic FTIR absorption bands (cm^{-1}) of synthesized compounds (1a-g).*

Comp.No.	**υ O-H (COOH)**	**υ C-H aromatic**	**υ C-H aliphatic**	**υ C=O carboxyl**	**υ C=C aromatic**	**υ C - O**
1a	2790	3045	2985 & 2827	1678	1606	1261
1b	2750	3050	2961 & 2875	1680	1599	1245
1c	2782	3070	2956 & 2879	1712	1587	1247
1d	2744	3035	2950 & 2864	1678	1602	1259
1e	2760	3066	2942 & 2864	1682	1607	1247
1f	2773	3072	2927 & 2858	1685	1614	1253
1g	2759	3064	2926 & 2865	1684	1615	1254

3.1.2 Preparation of 4-alkoxy benzoyl chlorides (2a-g):

Reaction of *4*-alkoxybenzoic acid with thionyl chloride afforded the titled compounds, the mechanism of reaction involve S_Ni mechanism (40) as follow:



Eq. 3.2 *S_Ni mechanism for preparation of 4-alkoxybenzoyl chlorides (2a-g)(40).*

The prepared acid chlorides were characterized by using FTIR, figure (3.2), showed infrared spectrum of 4-pentyloxybenzoyl chloride (2d), which indicate the disappearance of hydroxyl carboxylic group and appearance of absorption band at 646 cm^{-1} could be attributed to *v* (C – Cl) band.

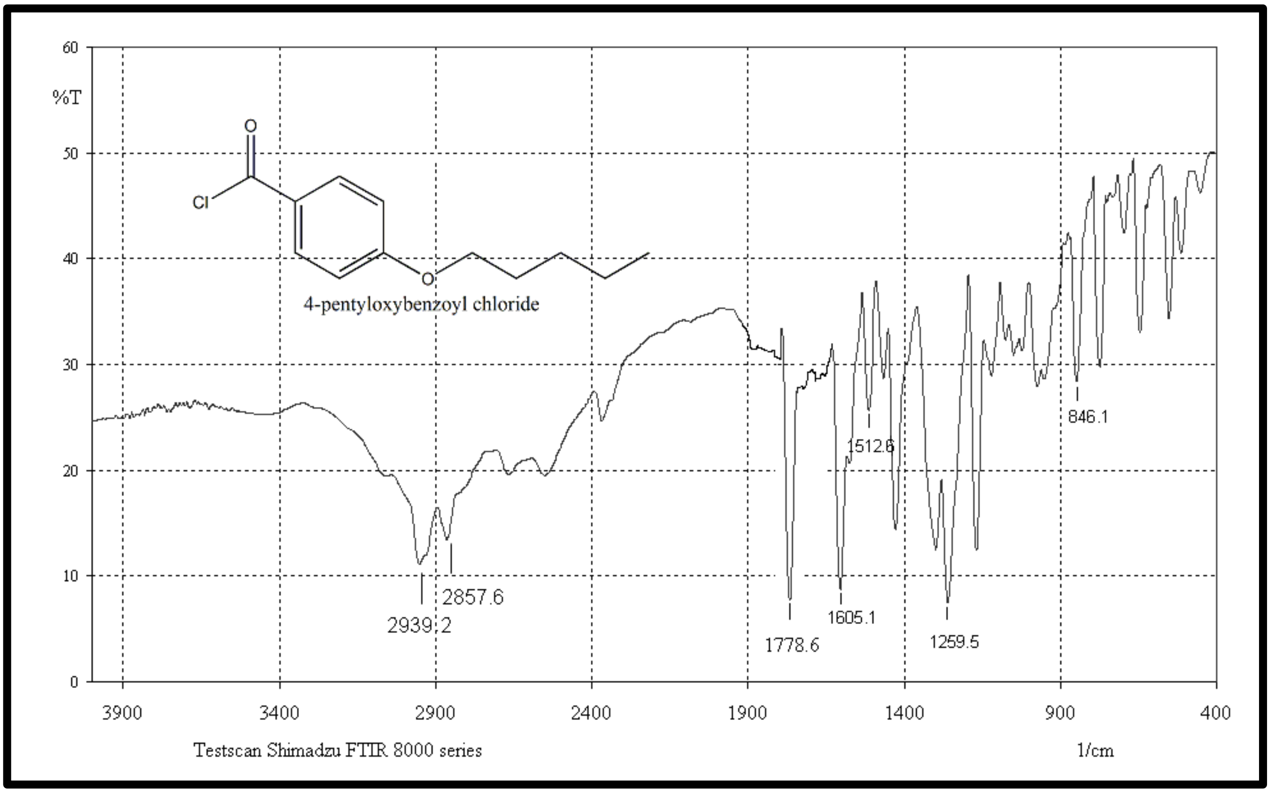
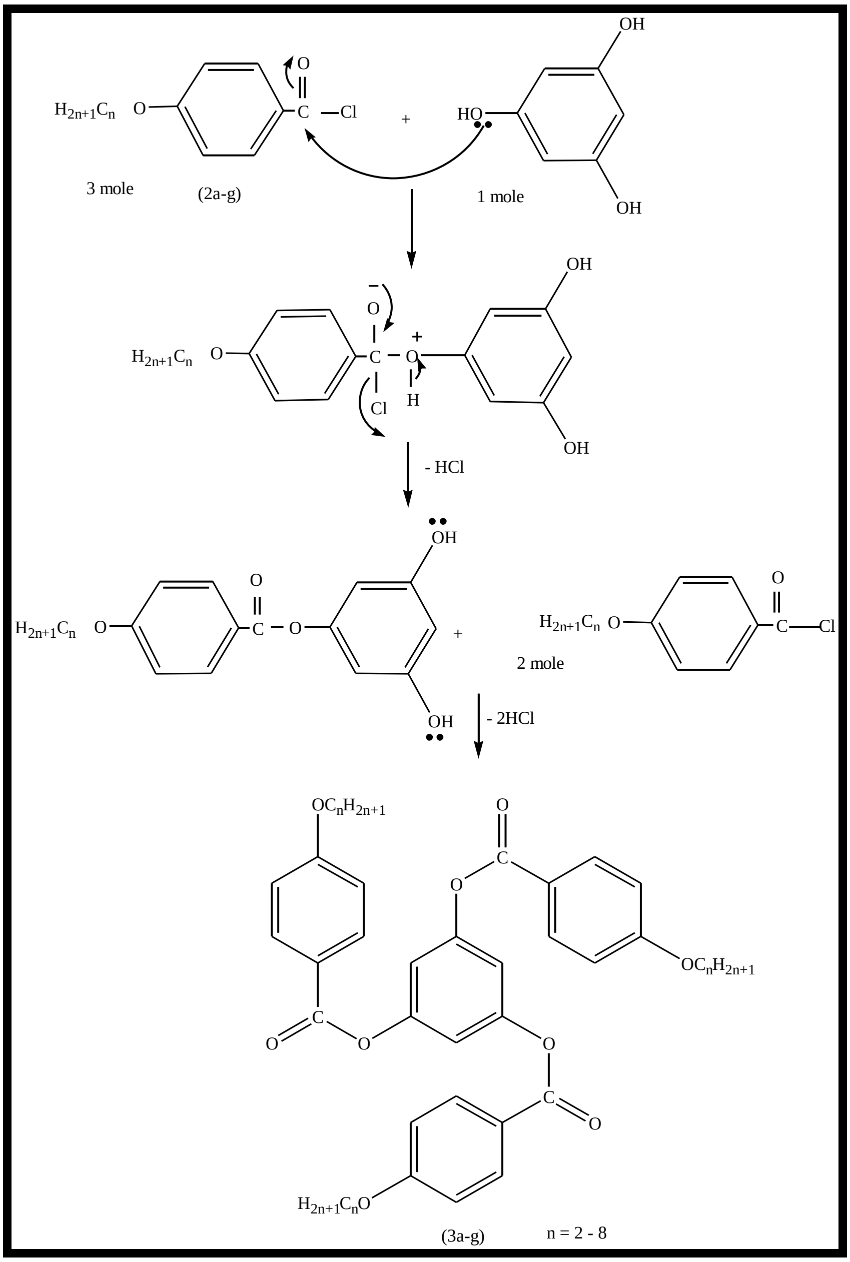


Figure 3.2 *FTIR spectrum of 4-pentyloxybenzoyl chloride 2d.*

The target compounds were used at once in the second step.

3.1.3 Synthesis of 1,3,5-tri[4-n-alkoxybenzoyloxy]benzene(3a-g):

1,3,5-tri[4-n-alkoxybenzoyloxy]benzene (3a-g) have been synthesized by the reaction of compounds (2a-g) with 1,3,5-trihydroxybenzene (Phluroglucinol) in presence of pyridine as solvent and proton acceptor, the mechanism involved (tetrahedral mechanism) (41) by two step firstly is the addition of the nucleophile (OH) to the carbon of the carbonyl group and secondly is the elimination of the leaving group (Cl), as in equation 3.3:



Eq. 3.3 *Mechanism for synthesis of 1,3,5-tri[4-n-alkoxybenzoyloxy]benzene (3a-g)* (41).

Structures of all products were identified by using FTIR and some of them by ^{1}HNMR. The resultant data of the spectra were in accordance with expected values. The purities of compounds were confirmed by using an elemental analysis. The elemental analysis of series (3a-g) compounds synthesized above is listed in Table (3.2). The observed values are in well agreement with theoretical values indicating structure of respective compounds.

Table 3.2 *Elemental analysis (CHNS-O) for compounds (3a-g).*

Comp. No.	**Formula**	**%C**		**% H**	
		Calc.	**Found**	**Calc.**	**Found**
3a	$C_{33}H_{30}O_9$	69.47	68.99	5.26	5.21
3b	$C_{36}H_{36}O_9$	70.58	69.78	5.88	5.74
3c	$C_{39}H_{42}O_9$	71.55	71.53	6.42	6.40
3d	$C_{42}H_{48}O_9$	72.41	72.13	6.89	6.83
3e	$C_{45}H_{54}O_9$	73.17	72.98	7.31	7.30
3f	$C_{48}H_{60}O_9$	73.84	74.09	7.69	7.66
3g	$C_{51}H_{66}O_9$	74.45	74.56	8.02	8.03

The spectroscopic observation of compound 3a for example is given: FT-IR (KBr, cm^{-1}) figure (3.3) : 1736 cm^{-1} (C = O of ester stretching), 3080 cm^{-1} (C–H aromatic), 2966–2887 cm^{-1} (ν C–H, aliphatic stretching), 1591 cm^{-1} (ν C=C aromatic), 1261 cm^{-1} (νC−O). Table (3.3) includes FTIR spectral data of compounds (3a-g).

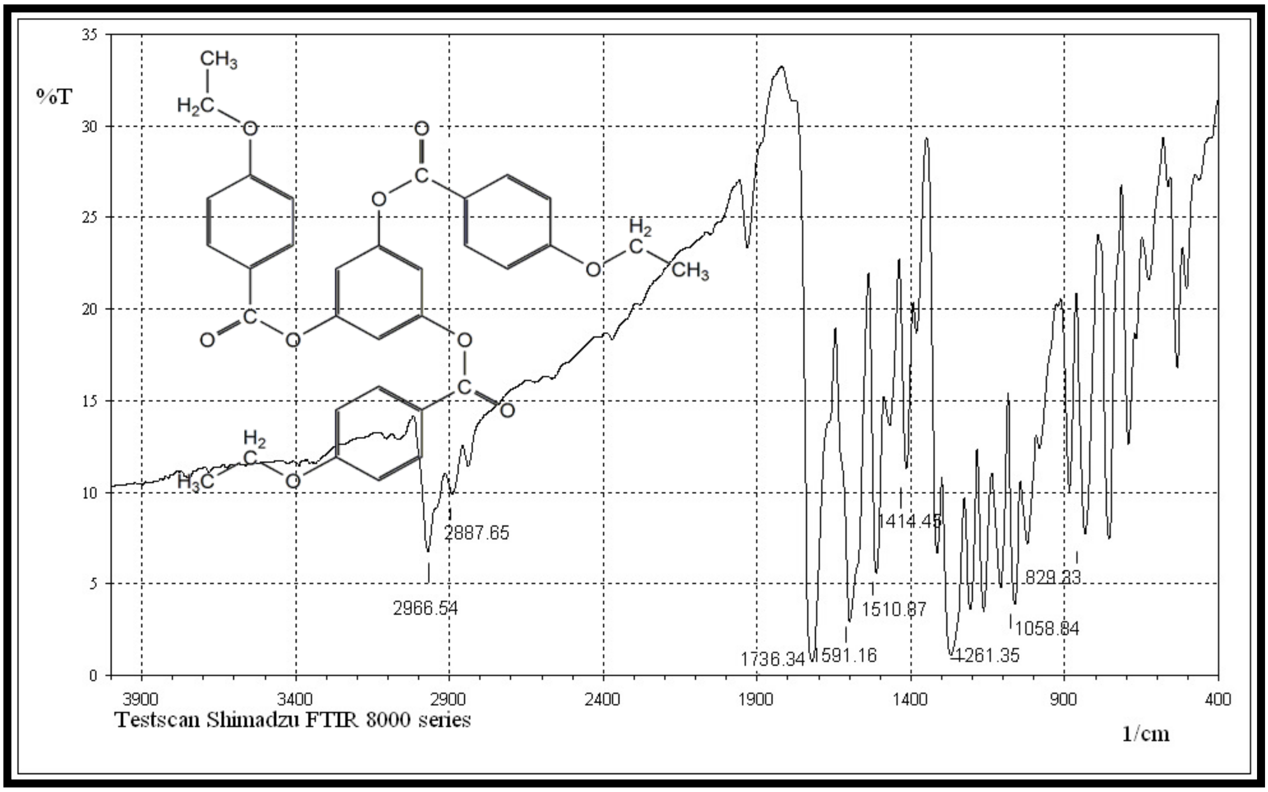


Figure 3.3 *FTIR spectrum of 1,3,5-tri[4-ethoxybenzoyloxy]benzene 3a.*

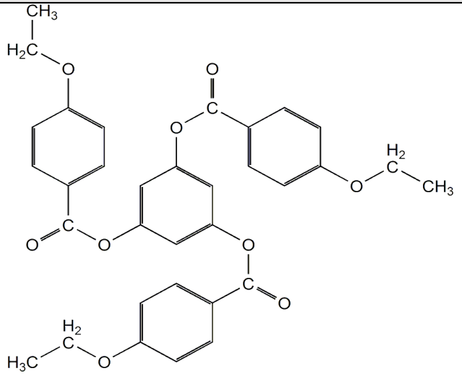
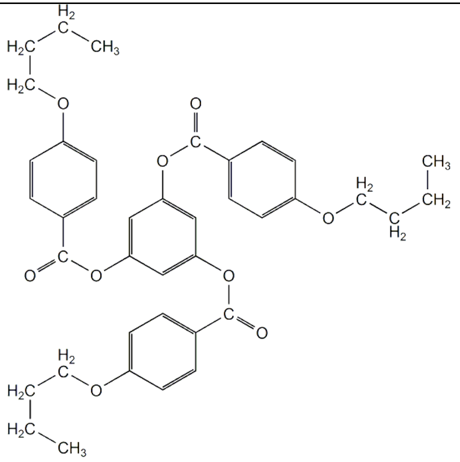
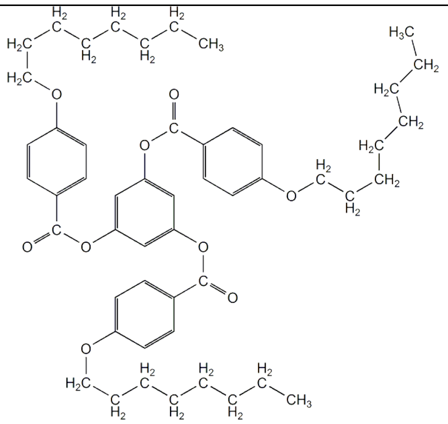
Table 3.3 *Characteristic FTIR absorption bands (cm^{-1}) of synthesized compounds (3a-g).*

Comp.No	**υ C-H arom.**	**υ C-H aliph.**	**υ C=O Ester**	**υ C=C arom.**	**υ C - O**
3a	3080	2966&2887	1736	1591	1261
3b	3060	2950 & 2868	1730	1598	1250
3c	3062	2945 & 2860	1730	1600	1251
3d	3051	2931 & 2848	1736	1598	1253
3e	3075	2963 & 2865	1747	1602	1254
3f	3056	2931 & 2844	1738	1598	1245
3g	3045	2924 & 2839	1733	1597	1249

^{1}H-NMR spectrum of compound 3a, is shown in figure (3.4). The following characteristic chemical shifts (CDCl$_3$, ppm) were appeared: two pairs of double doublet at δ 7.72-7.51 ppm (d-d, 12H, aromatic H), that could be attributed to the twelve protons of the aromatic phenyl ring. ^{1}HNMR spectrum also showed a singlet at δ 6.98 – 6.96 ppm that could be assigned to the three protons of benzene nucleus. A six proton quartet at δ 2.95-2.88 ppm might be assigned to the –OCH$_2$ group. Also the spectrum show triplet signal at δ 0.91- 0.87 which assigned for the nine protons of (-CH$_3$) group, Singlet signal at 7.25 ppm for CHCl3 (solvent) because CDCL3 is not 100% deuterated so signals for the residual protons are observed. Singlet signal at 1.54 ppm for H2O due to moisture. Therefore, the ^{1}HNMR spectrum of this compound together with the FTIR spectrum were good evidence for the suggested structure for compound 3a. Table (3.4) explain the ^{1}H-NMR spectra for compounds (3a, 3c and 3g).

Figure 3.4 *^{1}HNMR spectrum of 1,3,5-tri[4-ethoxybenzoyloxy]benzene 3a.*

Table 3.4 *^{1}H-NMR data of compounds (3a, 3c and 3g) in ppm.*

Comp. No.	Structures	NMR data of (δ-H) in ppm	Fig. No.
3a		(7.72-7.51) doublet of doublet of 12H of aromatic phenyl rings, (6.98 – 6.96) singlet of 3H of benzene nucleus, (2.95-2.88) quartet of 6H of $–OCH_2$, (0.91-0.87) triplet of 9H of CH_3 groups, (7.25-7.22) singlet for $CHCl_3$ solvent, (1.43-1.54) singlet for H_2O due to moisture.	3.4
3c		(7.73-7.53) doublet of doublet of 12H of aromatic phenyl rings, (6.99) singlet of 3H of benzene nucleus, (4.03-4.10) triplet of 6H of $–OCH_2$, (1.72-1.71) pentet of 6H of CH_2, (1.30-1.34) pentet of 6H of CH_2, (0.98-0.95) triplet of 9H of CH_3 groups, (7.25-7.22) singlet for $CHCl_3$ solvent, (1.43-1.54) singlet for H_2O due to moisture.	3.7
3g		(7.74-7.60) doublet of doublet of 12H of aromatic phenyl rings, (6.99-6.97) singlet of 3H of benzene nucleus, (3.72-3.71) triplet of 6H of $–OCH_2$, (1.72-1.71) pentet of 6H of CH_2, (1.32-1.30) pentet of 6H of CH_2, (1.29-1.28) pentet of 6H of CH_2, (1.27-1.26) pentet of 6H of CH_2, (1.25-1.24) pentet of 6H of CH_2, (1.23-1.22) pentet of 6H of CH_2, (0.97-0.95) triplet of 9H of CH_3 groups, (7.25-7.22) singlet for $CHCl_3$ solvent, (1.43-1.54) singlet for H_2O due to moisture.	3.11

The FTIR and ^{1}HNMR spectra for the compounds (3a-g) are shown in the following figures:

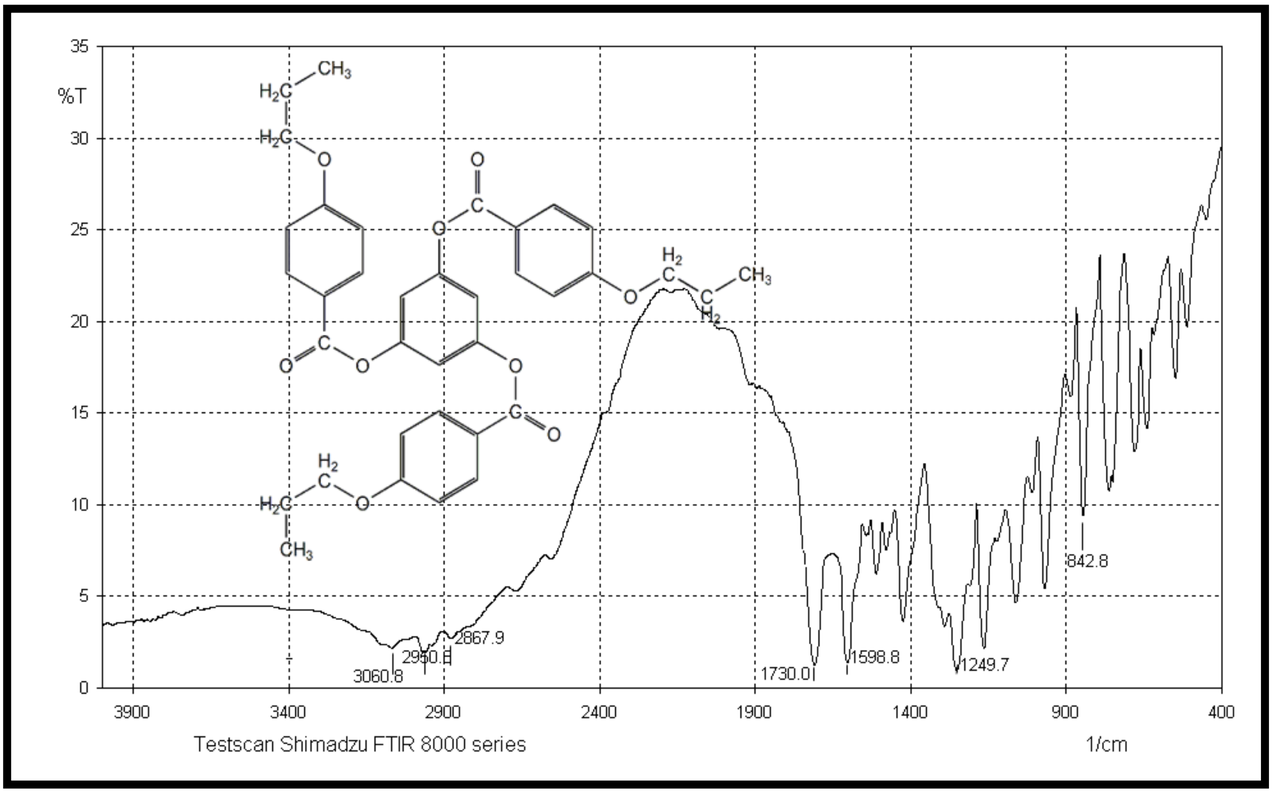


Figure 3.5 *FTIR spectrum of 1,3,5-tri[4-propyloxybenzoyloxy]benzene 3b.*

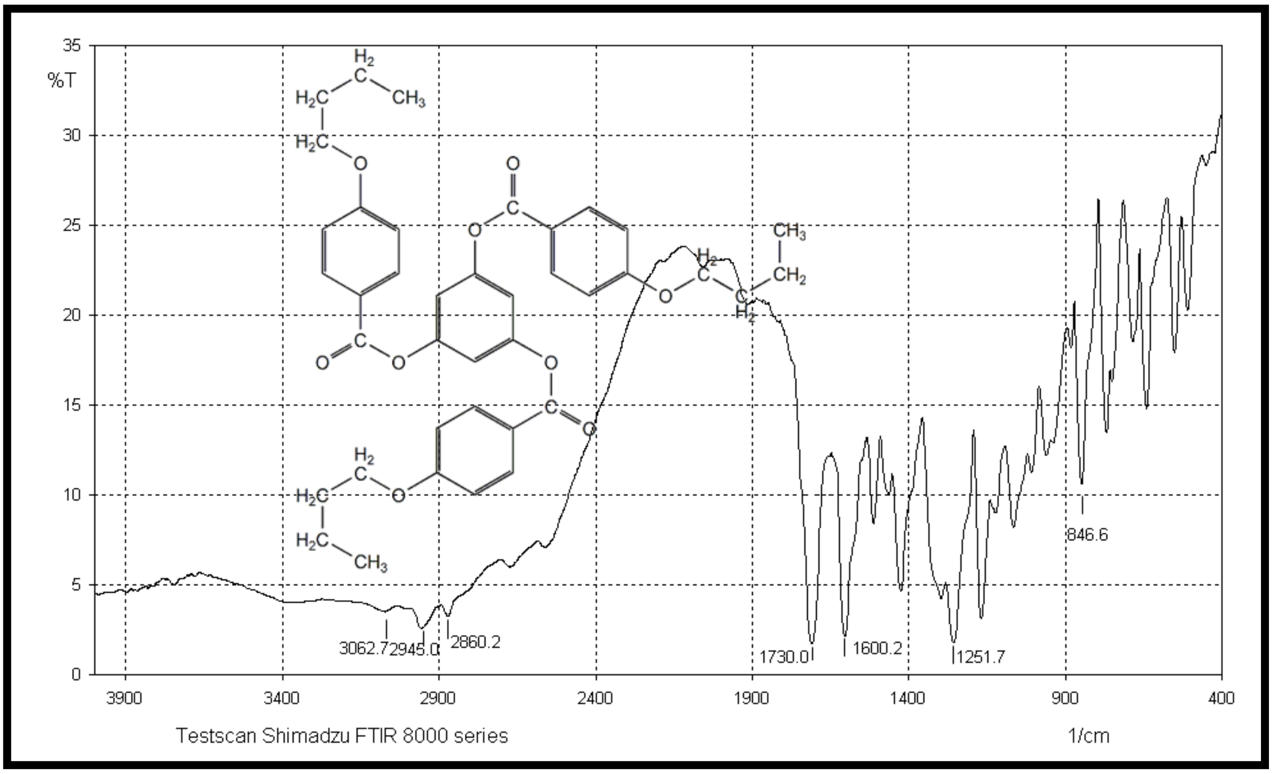


Figure 3.6 *FTIR spectrum of 1,3,5-tri[4-butyloxybenzoyloxy]benzene 3c.*

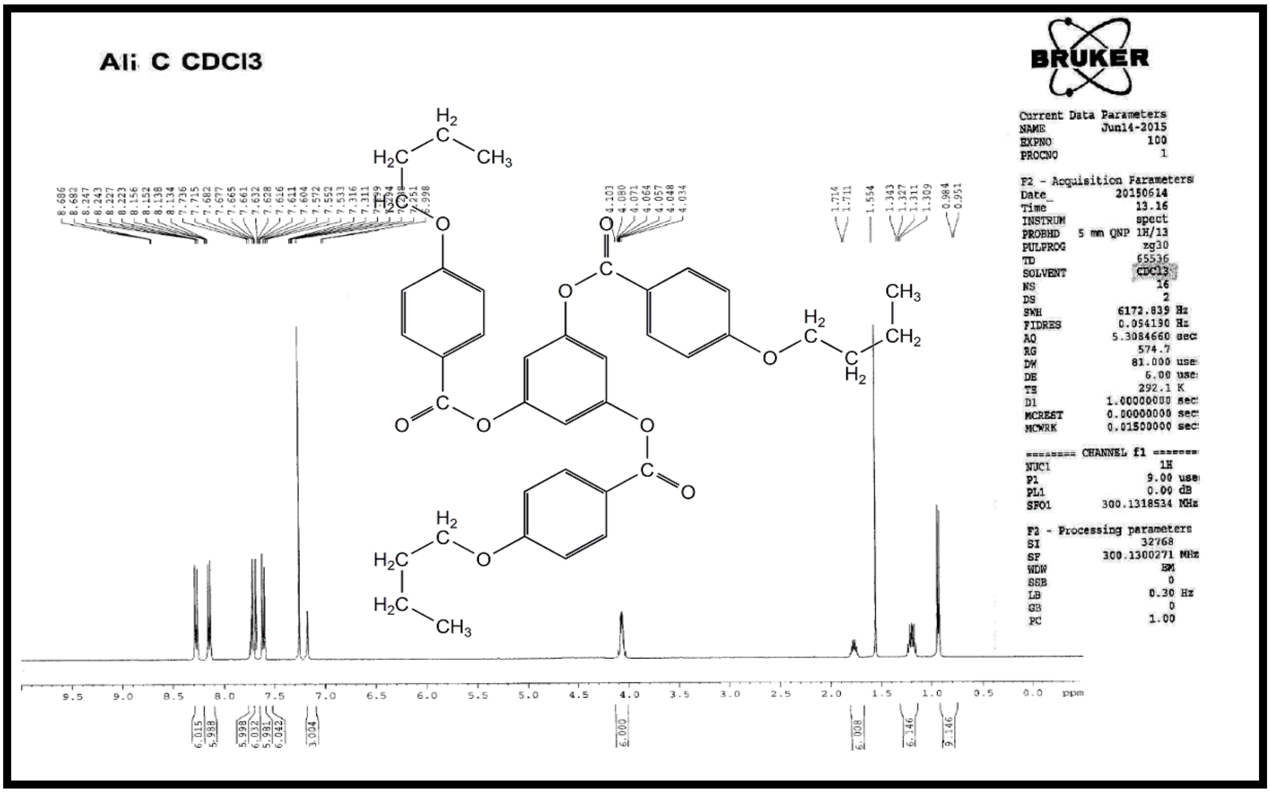


__Figure 3.7__ ^{1}HNMR spectrum of 1,3,5-tri[4-butyloxybenzoyloxy]benzene 3c.

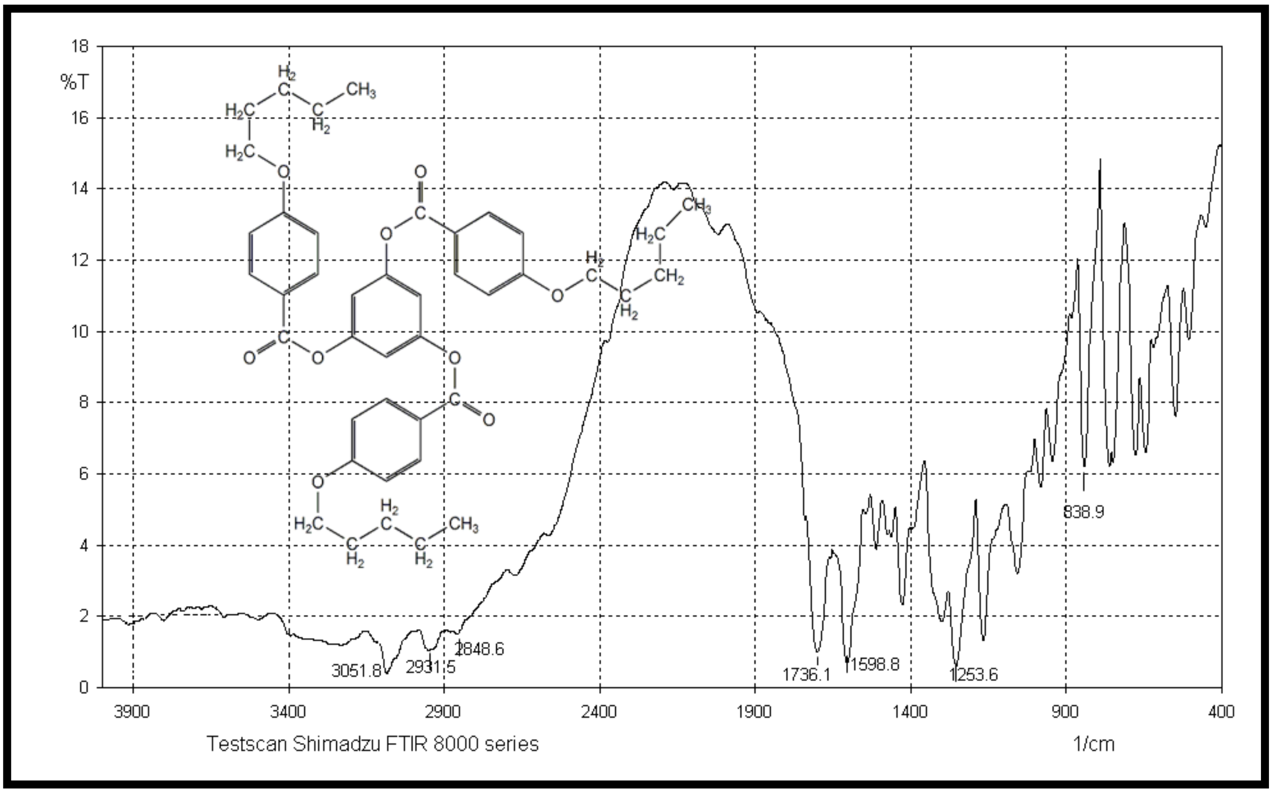


__Figure 3.8__ FTIR spectrum of 1,3,5-tri[4-pentyloxybenzoyloxy]benzene 3d.

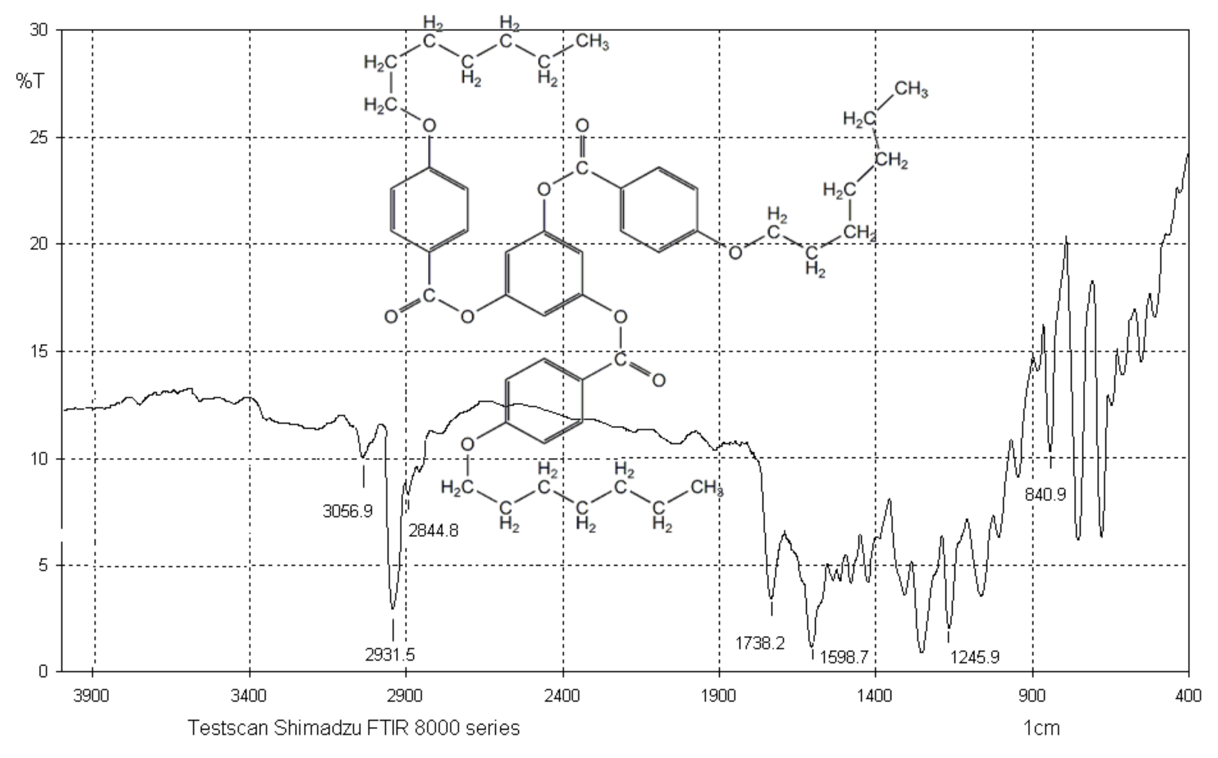


Figure 3.9 *FTIR spectrum of 1,3,5-tri[4-heptyloxybenzoyloxy]benzene 3f.*

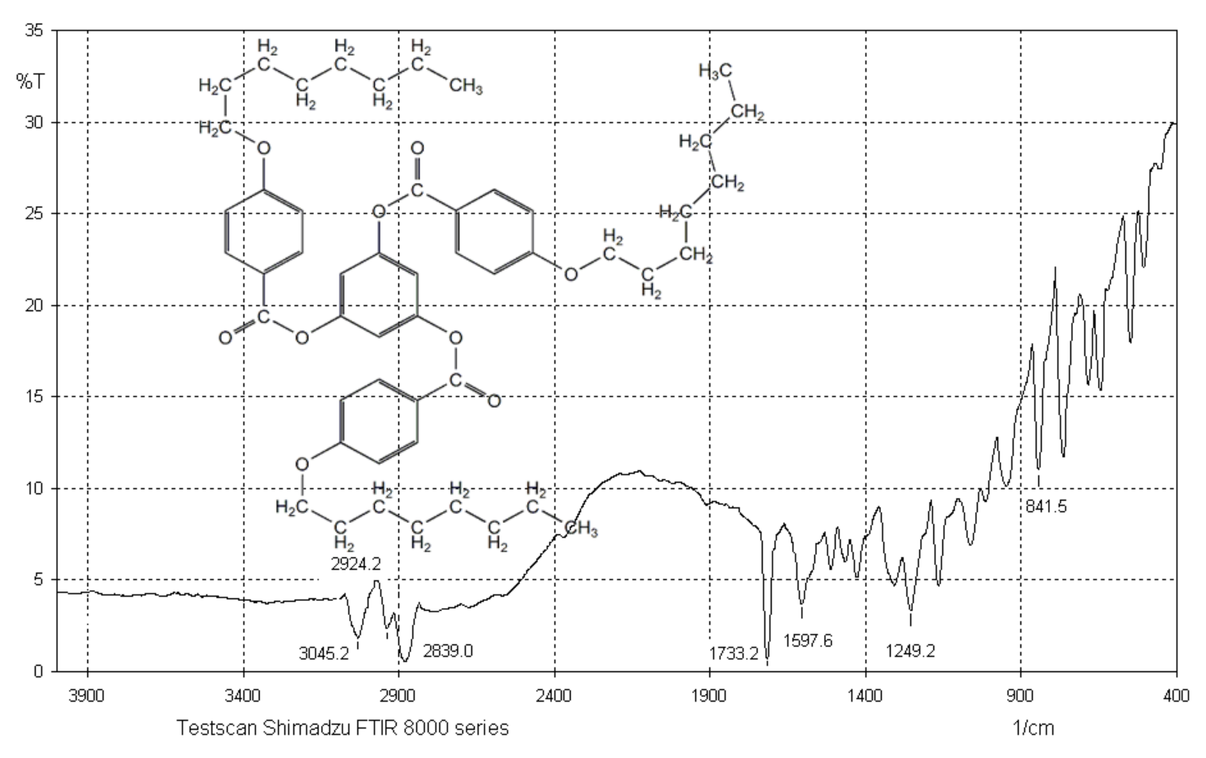


Figure 3.10 *FTIR spectrum of 1,3,5-tri[4-octyloxybenzoyloxy]benzene 3g.*

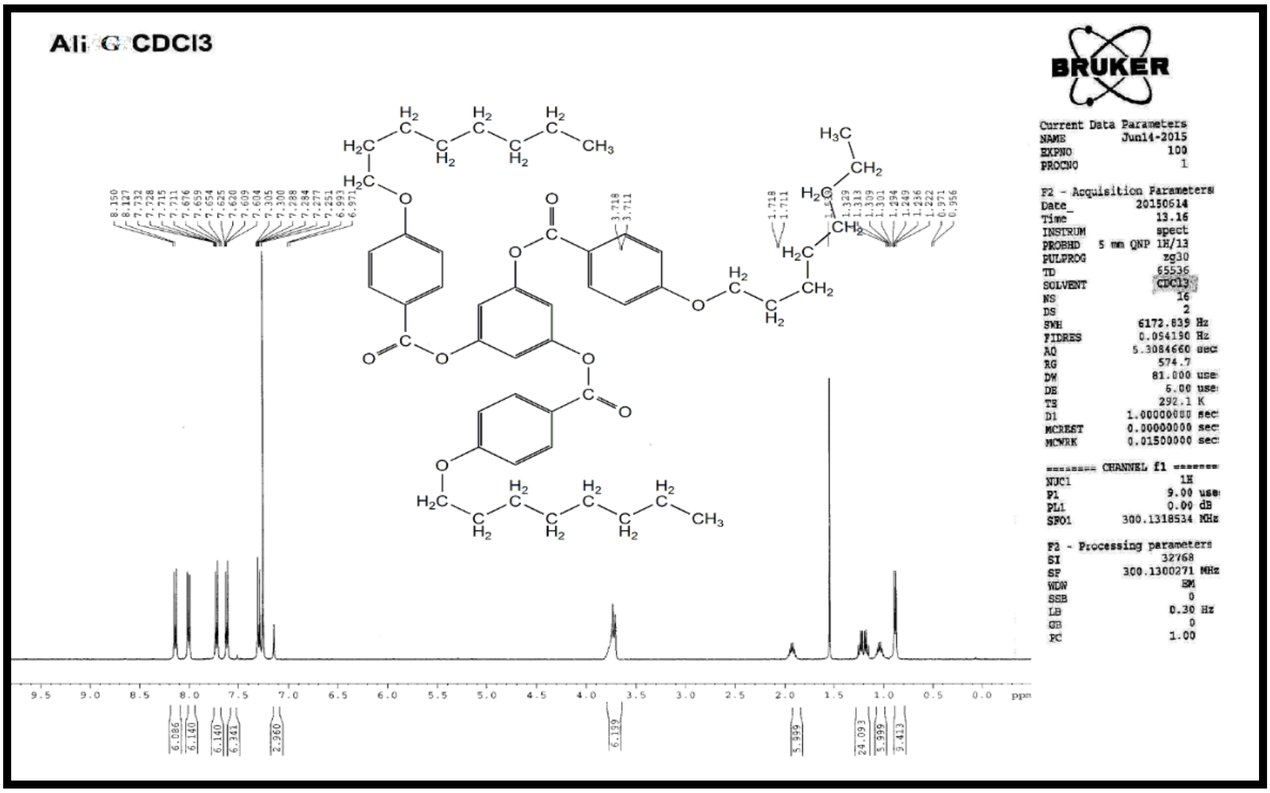
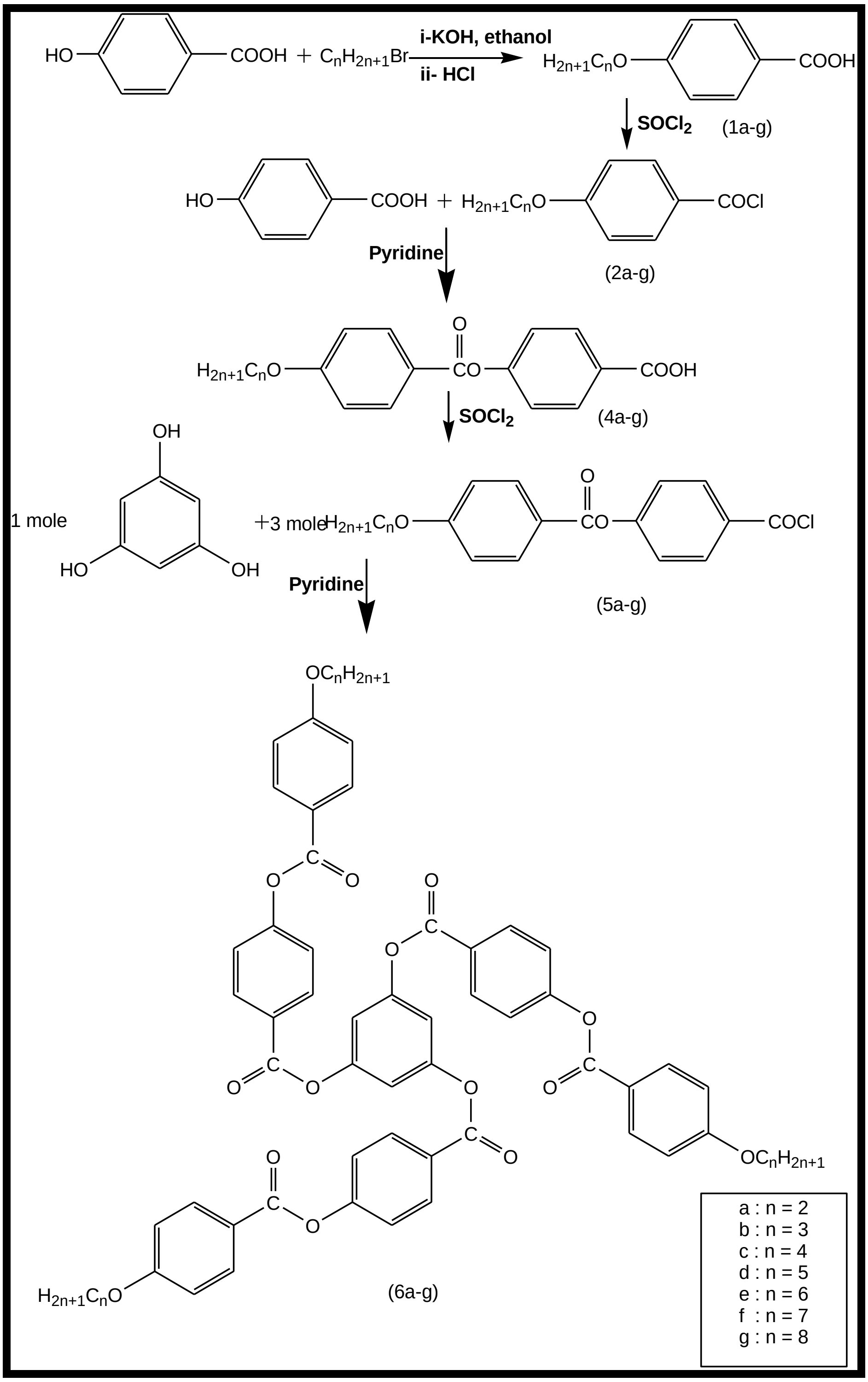


Figure 3.11 *^{1}HNMR spectrum of 1,3,5-tri[4-octyloxybenzoyloxy]benzene 3g*.

3.2 Synthesis of 1,3,5-tri-[4-{4'-n-alkoxybenzoyloxy}benzoyloxy]benzene (6a-g):

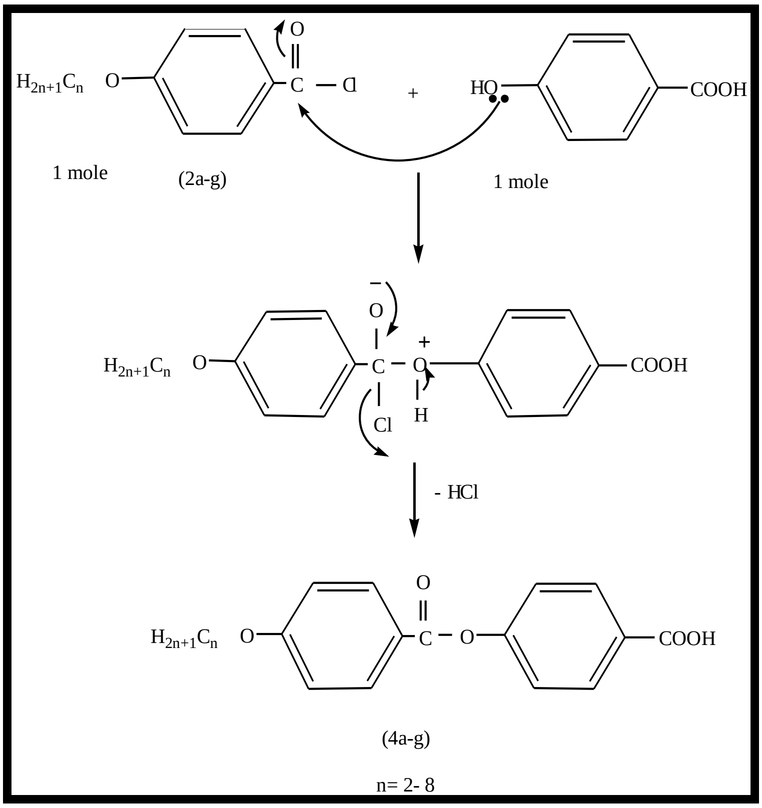
The titled compounds were synthesized as shown in scheme (3.2):



Scheme 3.2 *The synthetic pathway for the discotic compounds (6a-g).*

3.2.1 Preparation of 4-[4'-n-alkoxybenzoyloxy] benzoic acid (4a-g):

Reaction of 4-n-alkoxy benzoyl chlorides (2a-g) with 4-hydroxybenzoic acid gave 4[4'-n-alkoxybenzoyloxy] benzoic acid (4a-g) according to nucleophilic substitution (tetrahedral mechanism)$^{(41)}$ as in equation 3.4:



Eq. 3.4 *Mechanism for preparation of 4-[4'-n-alkoxybenzoyloxy] benzoic acid (4a-g)$^{(41)}$.*

The structures of these acids were confirmed by its FTIR spectra, which displayed the disappearance of the phenolic (O – H) stretching absorption bands and the appearance of (C – H) aliphatic stretching bands. The spectroscopic observation of (4b) for example is given: FT-IR (KBr, cm^{-1}) figure (3.12): 2740 cm^{-1} (ν O–H) stretching for carboxylic group), 1733.9 cm^{-1} (ν C = O of ester stretching), 3064.6 cm^{-1} (ν C–H aromatic), 2937–2877 cm^{-1} (ν C–H, aliphatic stretching), 1600 cm^{-1} (ν C=C aromatic), 1257 cm^{-1} (ν C−O). Table (3.5) includes FTIR spectral data of compounds (4a-g).

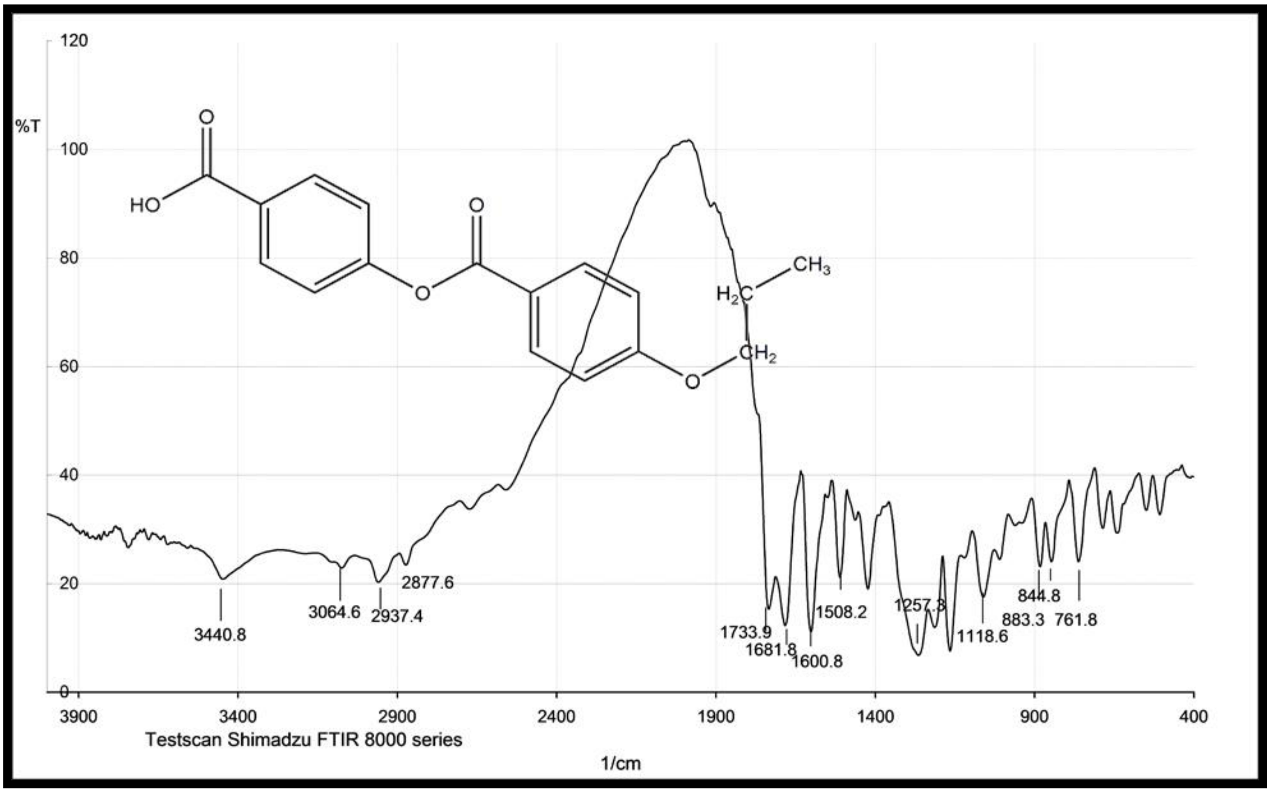


Figure 3.12 *FTIR spectrum of 4-[4’-n-propyloxybenzoyloxy] benzoic acid 4b.*

Table 3.5 *Characteristic FTIR absorption bands (cm^{-1}) of synthesized compounds (4a-g).*

Comp. No	**υ O-H (COOH)**	**υ C-H aromatic**	**υ C-H aliphatic**	**υ C=O (COOH)**	**υ C=O (ester)**	**υ C=C aromatic**
4a	2800	3058	2970 & 2867	1670	1731	1600
4b	2740	3064	2937 & 2877	1681	1733	1600
4c	2711	3074	2958 & 2873	1683	1733	1600
4d	2690	3049	2931 & 2840	1679	1733	1597
4e	2640	3058	2935 & 2850	1676	1734	1602
4f	2610	3062	2921 & 2844	1674	1731	1598
4g	2595	3058	2928 & 2842	1672	1734	1600

3.2.2 Preparation of 4-[4'-n-alkoxybenzoyloxy] benzoyl chloride (5a-g):

Reaction of 4-alkoxybenzoyloxy benzoic acid with thionyl chloride afforded the preparation of the titled compounds, the mechanism of reaction involve S_Ni mechanism(40) as shown in section 3.1.2 using 4-[4'-n-alkoxybenzoyloxy]benzoic acid instead of 4-n-alkoxybenzoic acid, the prepared compounds were used immediately in the second reaction.

3.2.3 Synthesis of 1,3,5-tri-[4-{4'-n-alkoxybenzoyloxy}benzoyloxy]benzene (6a-g):

1,3,5-Tri-[4-{4'-n-alkoxybenzoyloxy}benzoyloxy]benzene (6a-g) were prepared by reaction of 4-[4'-n-alkoxybenzoyloxy]benzoyl chloride with 1,3,5-trihydroxybenzene in pyridine.

The structures of all products were identified using FTIR and ^{1}HNMR for some of them. The FTIR spectra of 1,3,5-tri-[4-{4'-n-alkoxybenzoyloxy} benzoyloxy] benzene (6a-g) give the evidence for the formation of the titled compounds through, the disappearance of the hydroxyl group bands and the appearance of the ester carbonyl bands. The purities of compounds were confirmed by using an elemental analysis. Elemental analyses of series (6a-g) compounds are listed in (Table 3.6). The observed values are in well agreement with theoretical values proving structure of respective compounds.

***Table 3.6** Elemental analysis (CHNS-O) for compounds 6a-g.*

Comp. No.	**Formula**	**%C**		**% H**	
		Calc.	**Found**	**Calc.**	**Found**
6a	$C_{54}H_{42}O_{15}$	69.67	70.01	4.55	4.58
6b	$C_{57}H_{48}O_{15}$	70.36	70.21	4.97	4.89
6c	$C_{60}H_{54}O_{15}$	70.99	70.97	5.36	5.28
6d	$C_{63}H_{60}O_{15}$	71.58	71.56	5.72	5.80
6e	$C_{66}H_{66}O_{15}$	72.12	72.36	6.05	6.09
6f	$C_{69}H_{72}O_{15}$	72.63	72.87	6.36	6.33
6g	$C_{72}H_{78}O_{15}$	73.09	72.98	6.64	6.62

The spectroscopic observation of compound 6c for example is given: FT-IR (KBr, cm^{-1}) figure (3.13): 1741 cm^{-1} (ν C = O of ester stretching), 3040 cm^{-1} (ν C–H aromatic), 2948–2841 cm^{-1} (ν C–H, aliphatic stretching), 1608 cm^{-1} (ν C=C), 1251 cm^{-1} (ν C−O). Table (3.7) includes FT-IR spectral data of compounds (6a-g).

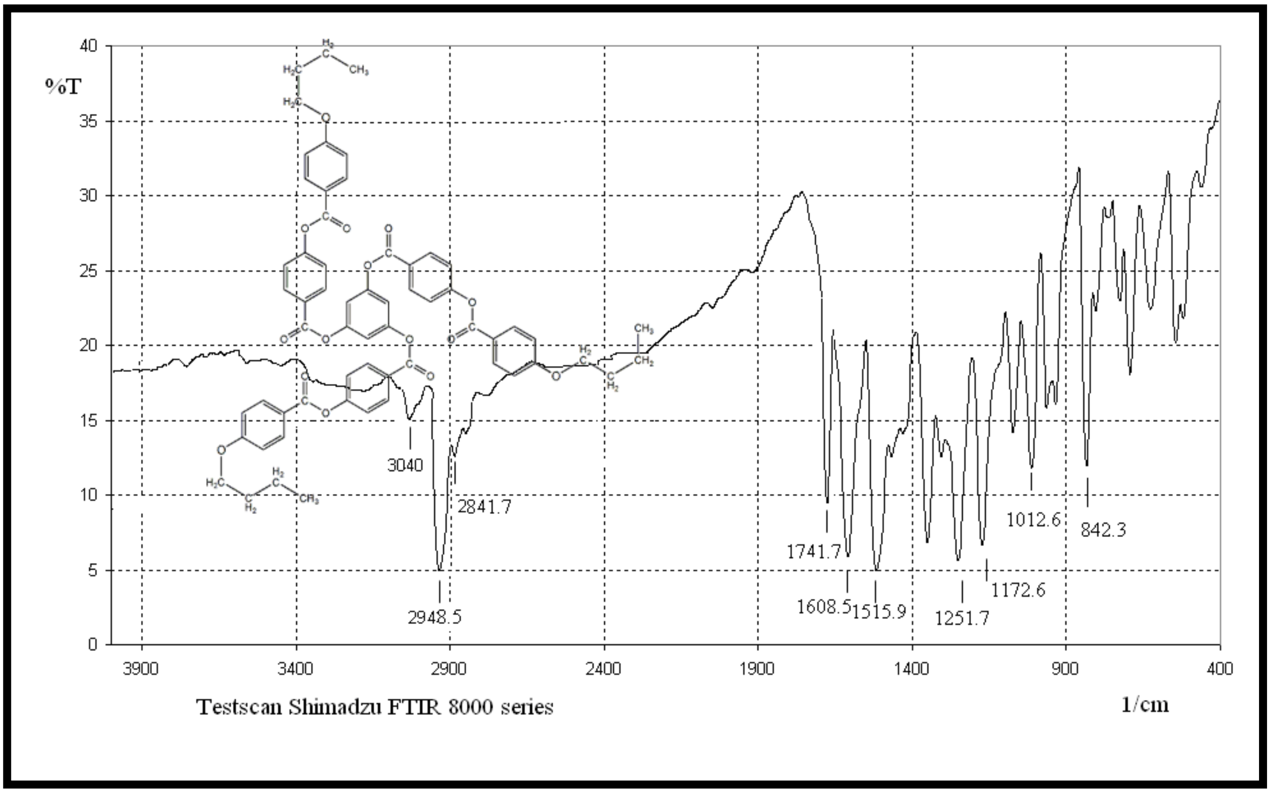


Figure 3.13 *FTIR spectrum of 1,3,5-tri-[4-{4'-n-butyloxybenzoyloxy}benzoyloxy]benzene 6c.*

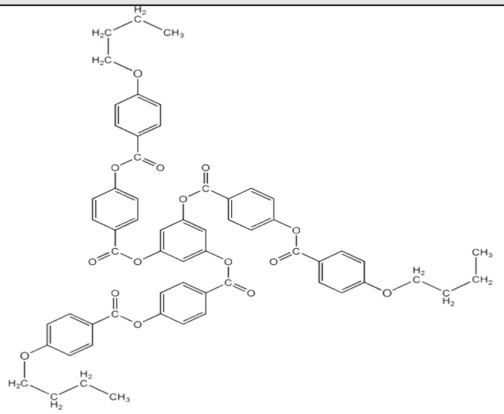
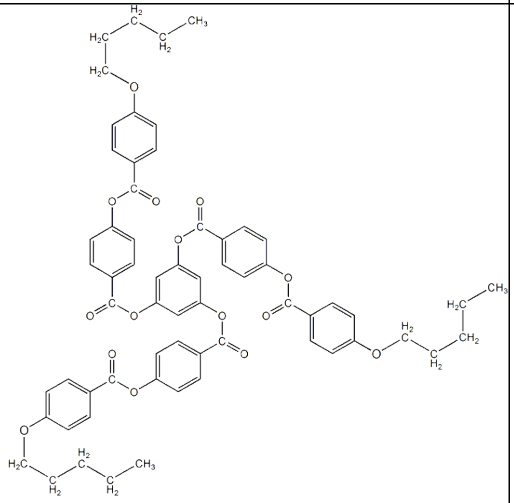
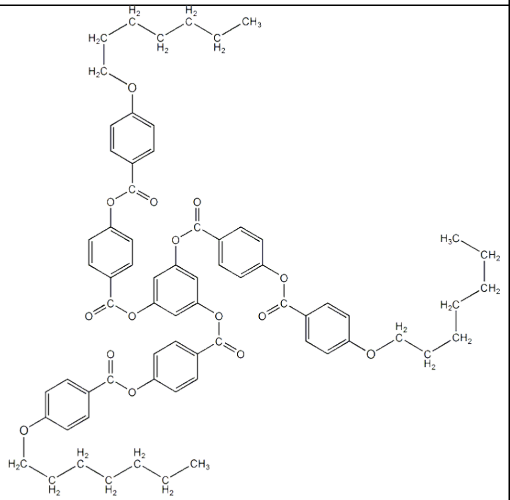
Table 3.7 *Characteristic FTIR absorption bands (cm^{-1}) of synthesized compounds (6a-g).*

Comp.No	**υ C-H aromatic.**	**υ C-H aliphatic.**	**υ C=O Ester**	**υ C=C aromatic**	**υ C – O**	**γ (*Para*- sub.)**
6a	3064	2974 & 2887	1733	1597	1257	842
6b	3062	2962 & 2867	1734	1595	1247	840
6c	3040	2948 & 2841	1741	1608	1251	842
6d	3058	2956 & 2871	1735	1602	1261	846
6e	3064	2927 & 2862	1737	1604	1257	844
6f	3062	2941 & 2842	1732	1597	1249	842
6g	3055	2927 & 2850	1735	1596	1251	841

^{1}H-NMR spectrum of compound 6c in figure 3.14 shows the following features ($CDCl_3$, ppm): two pairs of double doublet at δ 8.15-7.53 ppm leaning on each other which could be attributed to the twenty four protons of the three 4-substituted benzene rings. ^{1}H-NMR spectrum also showed a singlet at δ 7.2 – 6.9 ppm that could be assigned to the three protons of centered benzene ring. A six protons triplet at δ 4.04-3.9 ppm which could be assigned to OCH_2 protons due to the splitting caused by the adjacent CH_2 protons. A twelve protons multiplet at δ 2.48-2.41 due to CH_2CH_2 is also observed in this spectrum, while the CH_3 group appeared as a nine protons triplet at δ 1.15-1.14 ppm. Table (3.8) explain the ^{1}H-NMR spectra for compounds (6c, 6d and 6f).

Figure 3.14 *^{1}HNMR spectrum of compound 1,3,5-tri-[4-{4'-n-butyloxybenzoyloxy}benzoyloxy]benzene 6c.*

Table 3.8 *^{1}H-NMR data of compounds (6c, 6d and 6f) in ppm.*

Comp. No.	Structures	NMR data of (δ-H) in ppm	Fig. No.
6c		(8.15-7.53) doublet of doublet of 24H of aromatic phenyl rings, (7.20 – 6.9) singlet of 3H of benzene nucleus, (4.04-3.9) triplet of 6H of –OCH_2 , (2.48-2.41) pentet of 6H of CH_2, (2.48-2.41) pentet of 6H of CH_2, (1.15-1.14) triplet of 9H of CH_3 groups, (7.25-7.22) singlet for $CHCl_3$ solvent, (1.43-1.54) singlet for H_2O due to moisture.	3.14
6d		(8.12-7.54) doublet of doublet of 24H of aromatic phenyl rings, (6.99 – 6.97) singlet of 3H of benzene nucleus, (3.72-3.71) triplet of 6H of –OCH_2 , (2.47-2.42) pentet of 6H of CH_2, (1.32-1.30) pentet of 6H of CH_2, (1.29-1.22) pentet of 6H of CH_2, (0.97-0.95) triplet of 9H of CH_3 groups, (7.25-7.22) singlet for $CHCl_3$ solvent, (1.43-1.54) singlet for H_2O due to moisture.	3.18
6f		(8.14-7.59) doublet of doublet of 24H of aromatic phenyl rings, (6.79 – 6.69) singlet of 3H of benzene nucleus, (3.96) triplet of 6H of –OCH_2 , (1.80-1.67) pentet of 6H of CH_2, (1.36) pentet of 6H of CH_2, (1.15-1.12) pentet of 6H of CH_2, (1.10-1.05) pentet of 6H of CH_2, (1.00-0.95) pentet of 6H of CH_2, (0.90) triplet of 9H of CH_3 groups, (7.25-7.22) singlet for $CHCl_3$ solvent, (1.43-1.54) singlet for H_2O due to moisture.	3.21

The other FTIR and ^{1}H-NMR spectra for the compounds (6a-g) are shown in following figures:

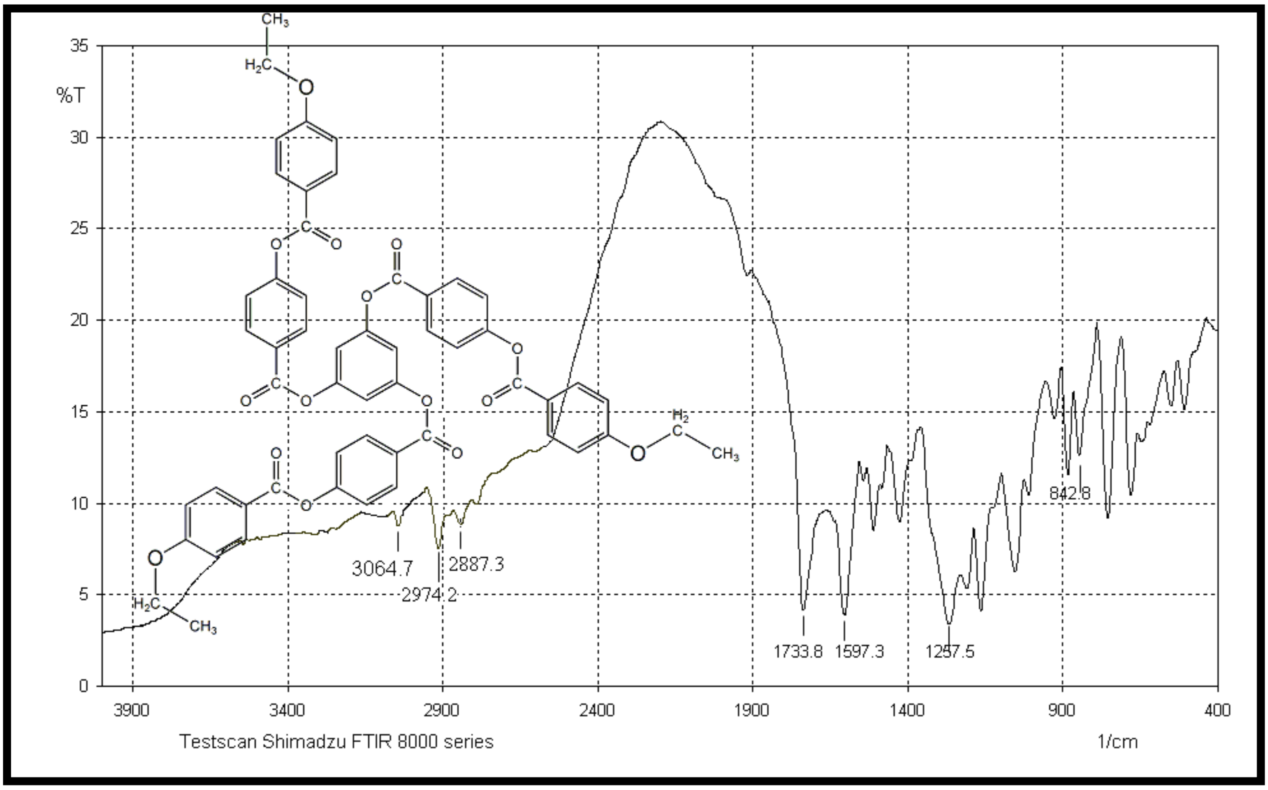


Figure 3.15 *FTIR spectrum of 1,3,5-tri-[4-{4'-ethyloxybenzoyloxy}benzoyloxy]benzene 6a.*

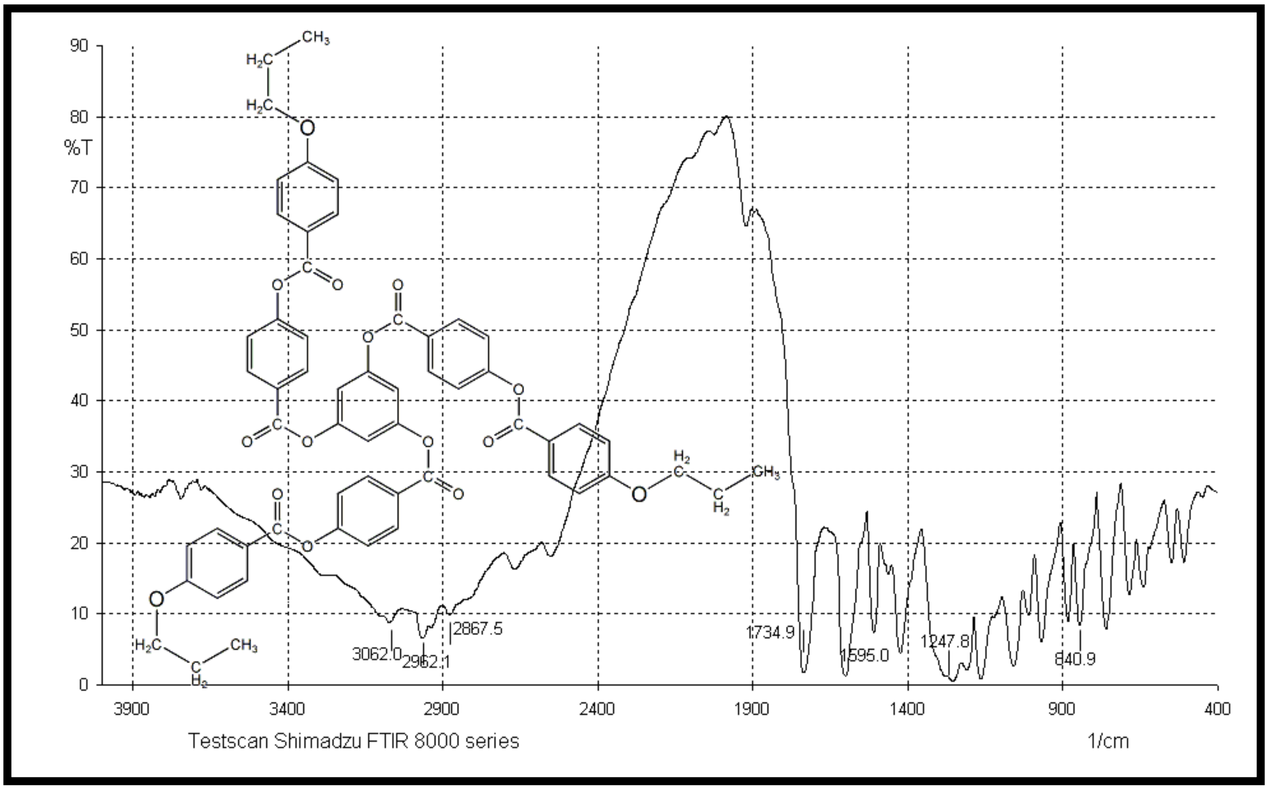


Figure 3.16 FTIR spectrum of 1,3,5-*tri-[4-{4'-n-propyloxybenzoyloxy}benzoyloxy]benzene 6b.*

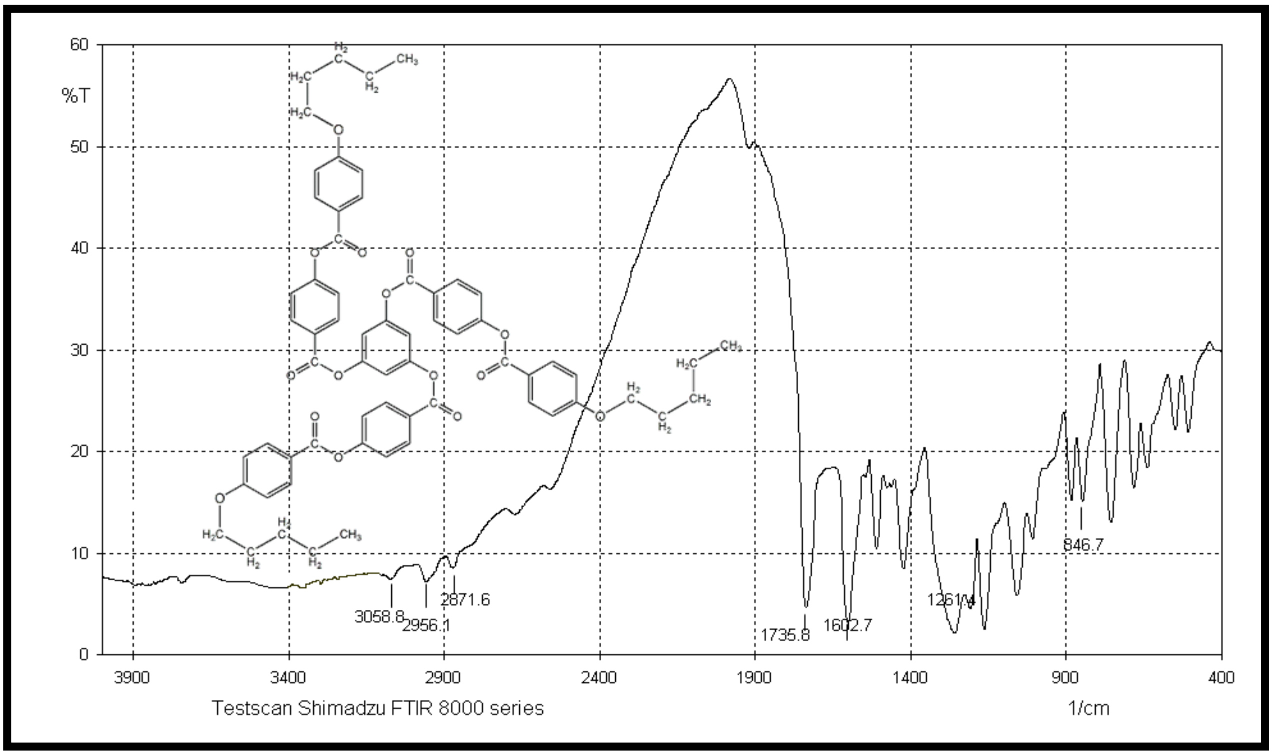


Figure 3.17 FTIR spectrum of 1,3,5-*tri-[4-{4'-n-pentyloxybenzoyloxy}benzoyloxy]benzene 6d.*

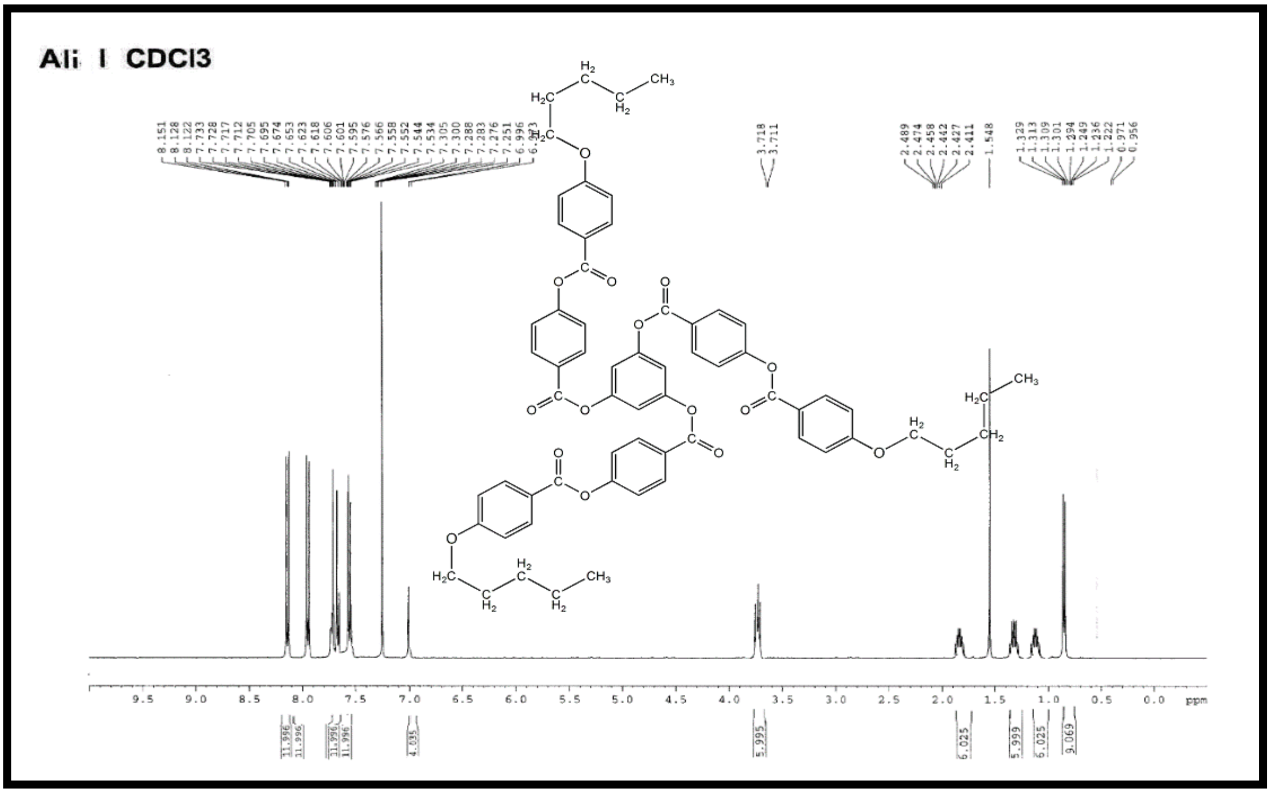


Figure 3.18 *^{1}HNMR spectrum of compound 1,3,5-tri-[4-{4'-n-pentyloxybenzoyloxy}benzoyloxy]benzene 6d.*

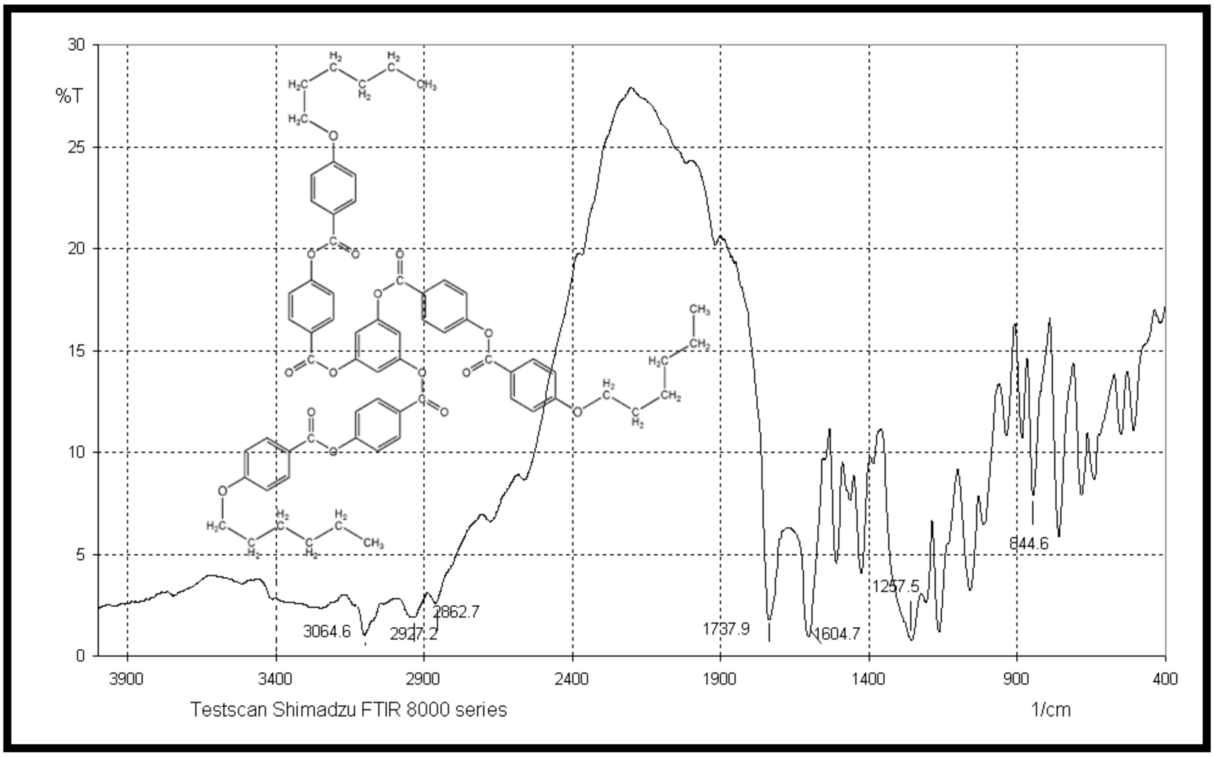


Figure 3.19 *FTIR spectrum of 1,3,5-tri-[4-{4'-n-hexyloxybenzoyloxy} benzoyloxy]benzene 6e.*

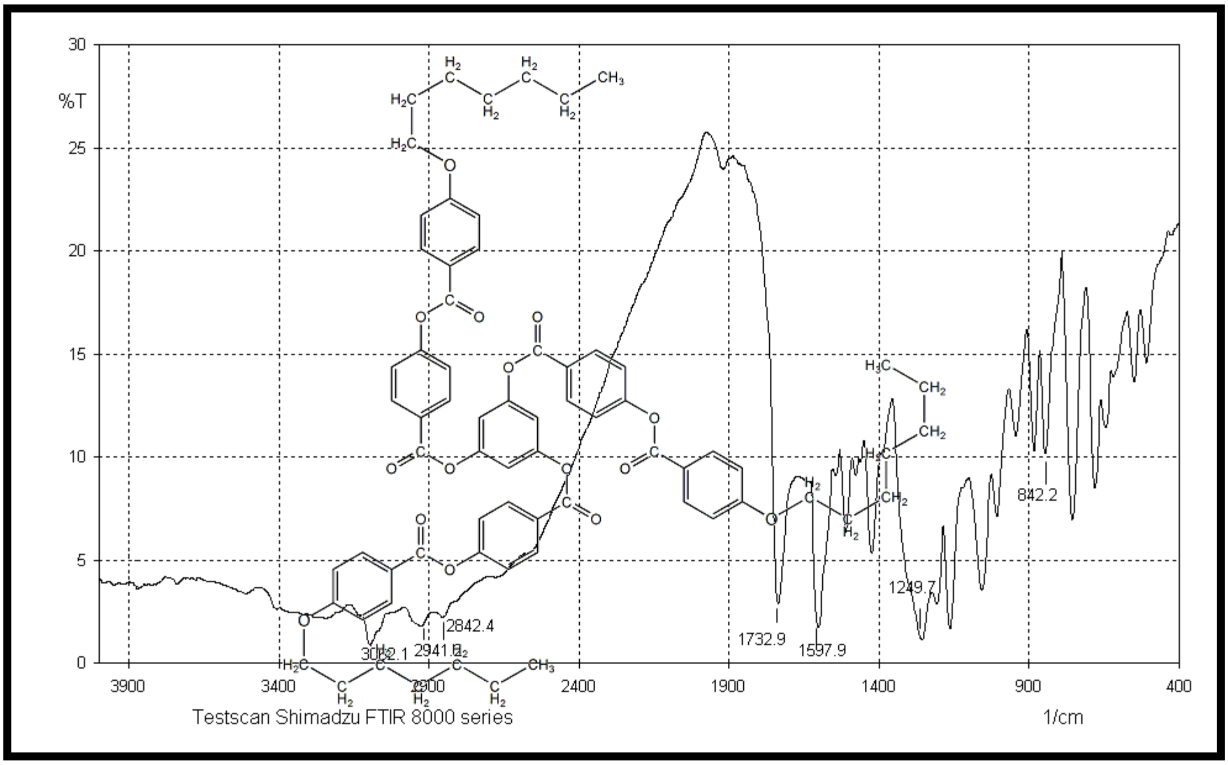


Figure 3.20 *FTIR spectrum of 1,3,5-tri-[4-{4'-n-heptyloxybenzoyloxy}benzoyloxy]benzene 6f.*

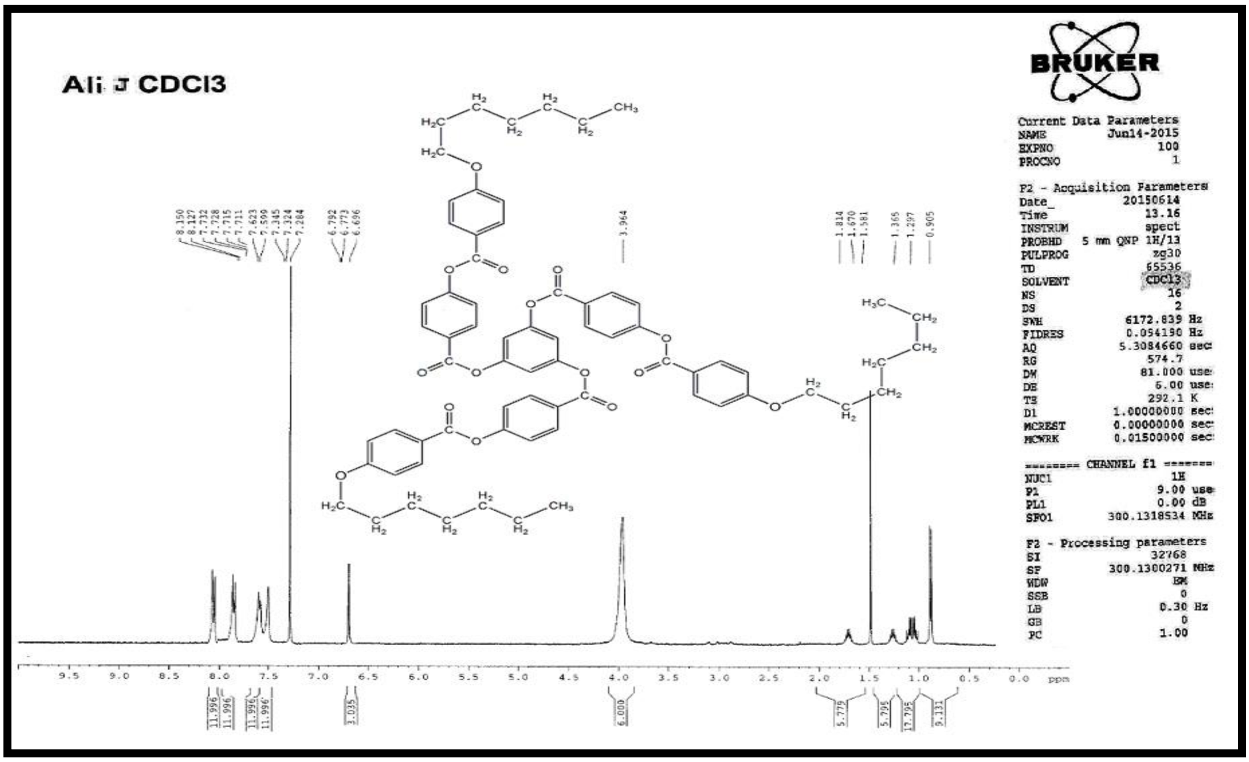


Figure 3.21 *^{1}HNMR spectrum of compound 1,3,5-tri-[4-{4'-n heptyloxybenzoyloxy}benzoyloxy]benzene 6f.*

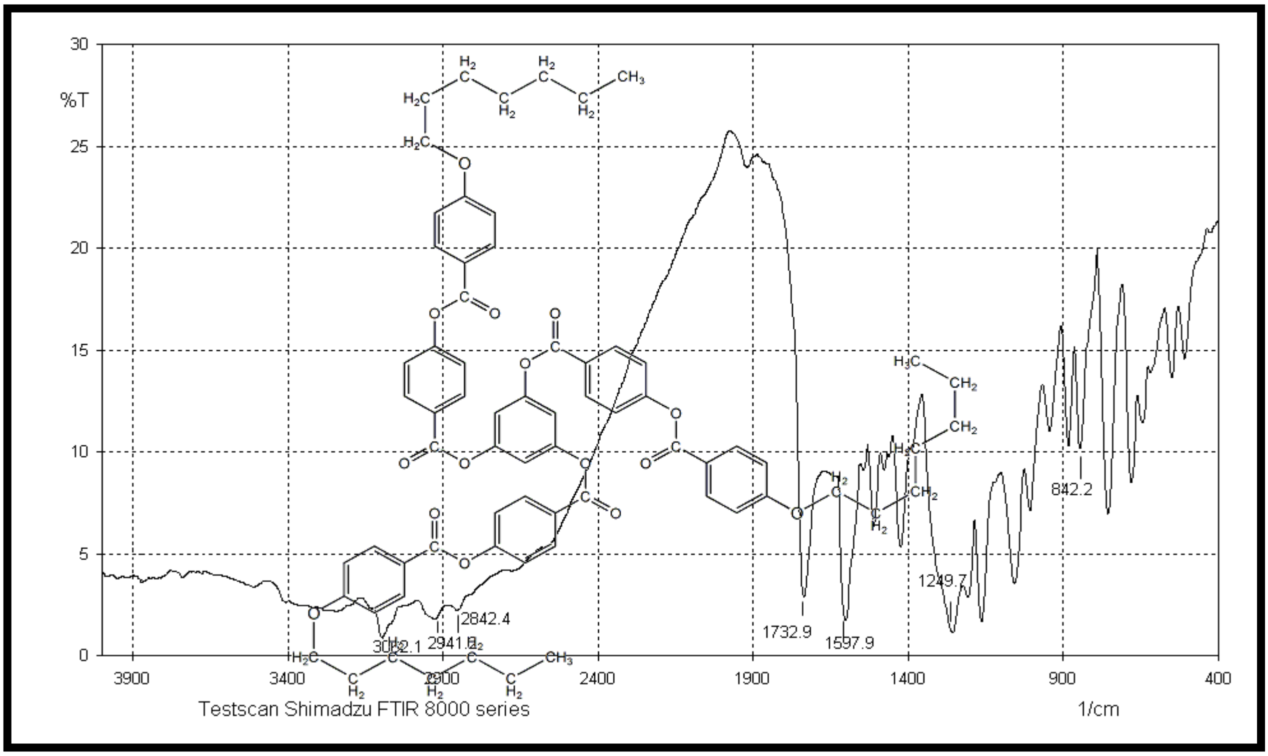


Figure 3.22 *FTIR spectrum of 1,3,5-tri-[4-{4'-n-octyloxybenzoyloxy} benzoyloxy]benzene 6g.*

3.3 Liquid Crystalline Properties of the Synthesized Compounds:

Liquid crystalline behavior has been observed mainly in two types of molecules: linear or rod-like molecules that form calamitic phases and disc-like molecules that form discotic phases. The structure of liquid crystalline phases is characterized by the arrangement of the molecules, the conformation of the molecules, and the intermolecular interactions. (42)

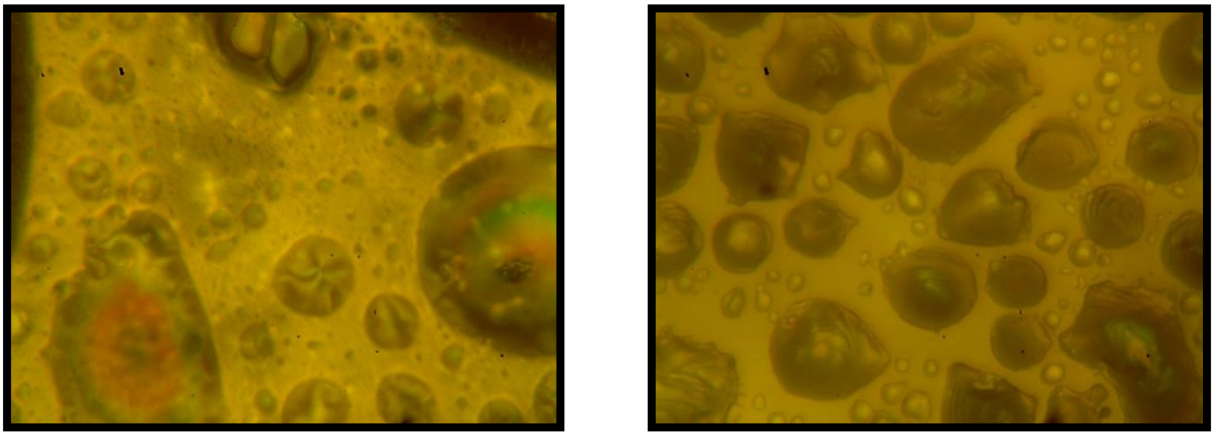
3.3.1 Mesomorphic Properties of the 1,3,5-tri-[4-n-alkoxybenzoyloxy]benzene(3a-g):

Liquid crystalline materials are found to have an important role in new and emerging electro-optical technologies. Thermotropic liquid crystals consist of either linear or disc-like organic molecules. The general architecture for linear thermotropic liquid crystals consists of linearly linked ring systems and flexible chains, the permanent dipoles and polarizable moieties also being requirements. The rings may be linked to each other either directly or through some linking group (e.g. ester, olefinic, acetylenic, azo, azoxy, dimethylene or oxymethylene) that maintains the linearity of the core (43) . The flexible alkyl chains may be linked either directly with the ring or through the intervening hetero atoms such as oxygen, sulfur and nitrogen. These polar groups may also impart dielectric anisotropy to the molecules (44). The thermal stability of the mesophase is determined by the nature of the molecule, steric and electronic factors. It has also been reported in the literature (45-46) that the linking units capable of maintaining the rigidity and linearity of the molecule also promote mesophase stability. Results of the DSC studies, which used heating and cooling rates of 10 °C/min, are show in table (3.9) and figures (3.24), (3.25), (3.26), (3.27), (3.28) and (3.29). The phase transitions of compounds (3a-g) series were studied using polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). The phase transition temperatures observed by POM agree well with the corresponding DSC thermograms. For the mesomorphism of the synthesized compounds all the compounds display different phase-transition temperatures related to the length of the chain.

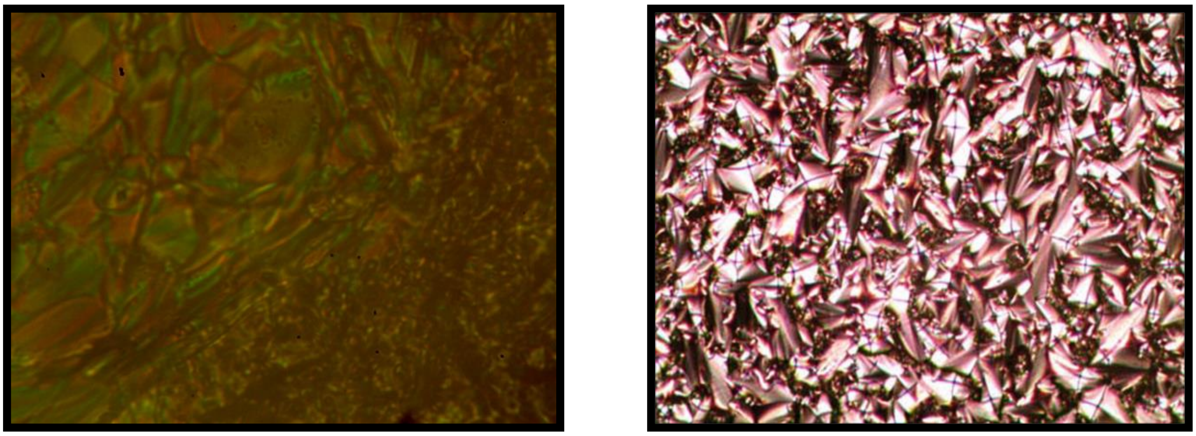
Table 3.9 *Mesophase-transition temperature ranges obtained from DSC thermograms for series (3b-g).*

Comp. No.	Mesophase temperature ranges	No. of figure
3b	(71 – 132) °C	3.24
3c	(73 – 130) °C	3.25
3d	(85 – 140) °C	3.26
3e	(74 – 143) °C	3.27
3f	(66 – 120) °C	3.28
3g	(64 – 134) °C	3.29

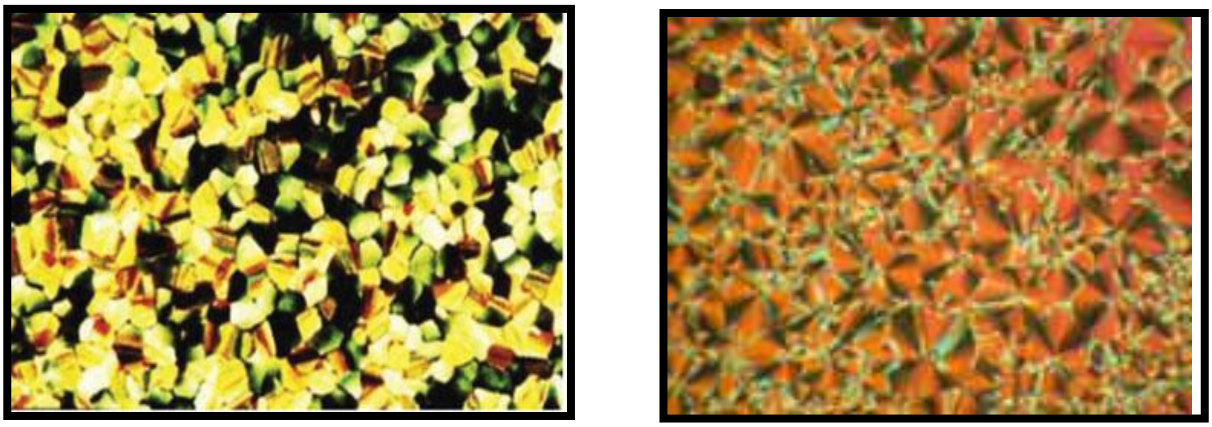
The first compound (3a) do not reveal any liquid crystalline behavior, but simply changes from the solid crystalline state to the isotropic liquid at 130°C. Compounds (3b-g) display enantiotropic mesomorphism. The texture observed by POM on heating the solid crystal are consistent with the presence of columnar mesomorphism, with fan-shaped typical to columnar phases for compounds (3c, 3e, and 3g) and fan shaped focal conic typical to a columnar hexagonal for compound (3b, 3d, and 3f) as shown in figure (3.23).



a (Fan shaped columnar) *b (Focal conic columnar)*



c (Fan shaped columnar) *d (Focal conic columnar)*



e (Fan shaped columnar) *f (Fan shaped focal conic columnar)*

Figure 3.23 *Cross-polarizing Optical textures of the columnar mesophase obtained on heating and cooling (Magnification 200×) for compounds of series (3b-g), (a) (3b) at 118°C, (b) (3c) at 123°C, (c) (3d) at 128°C, (d) (3e) at 79°C, (e) (3f) at 80°C, (f) (3g) at 95°C.*

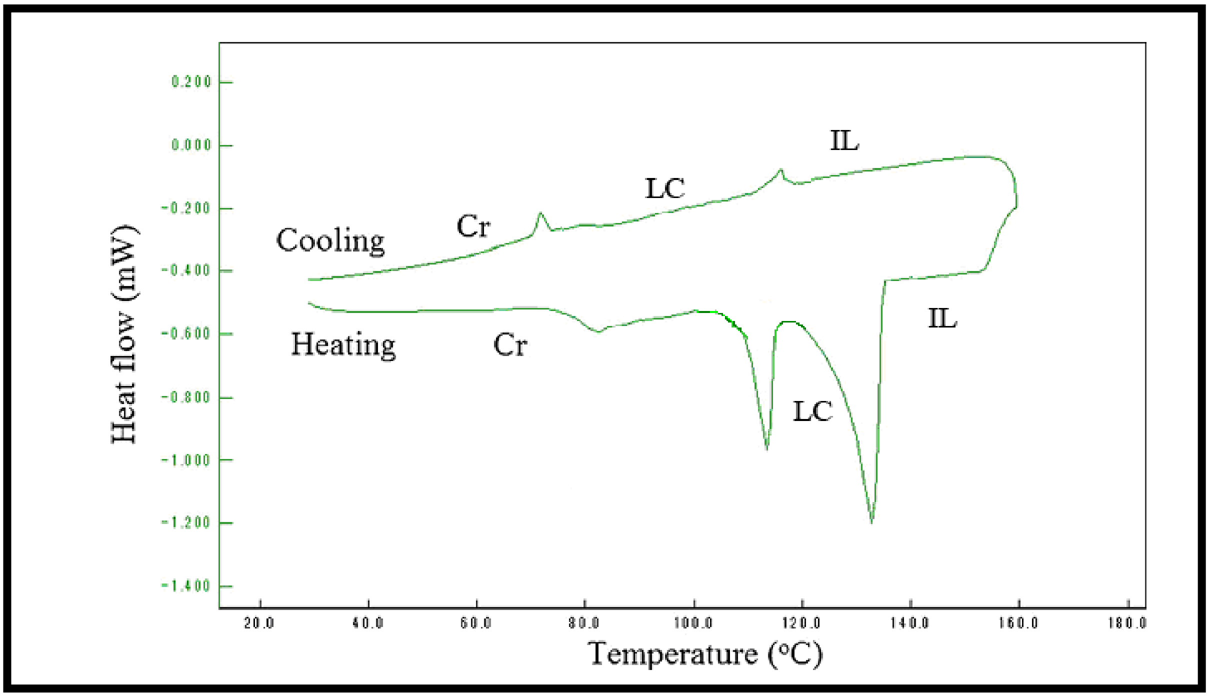


Figure 3.24 *DSC thermograms at 10 °C/min for compound 3b.*

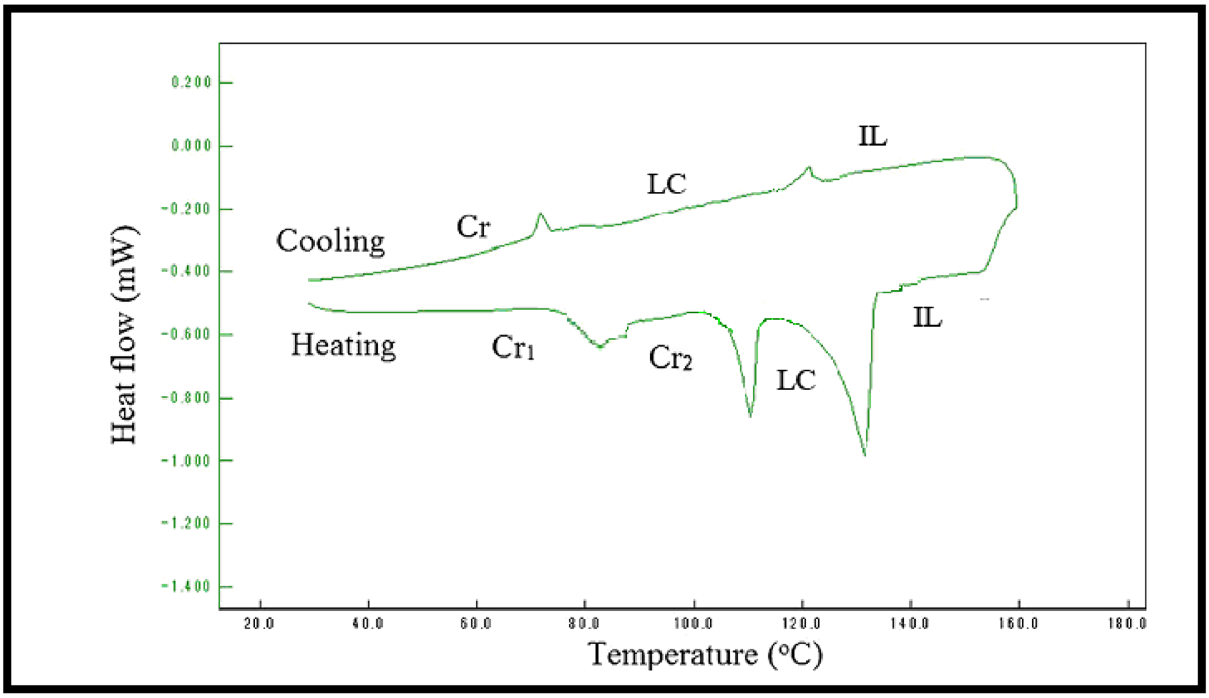


Figure 3.25 *DSC thermograms at 10 °C/min for compound 3c.*

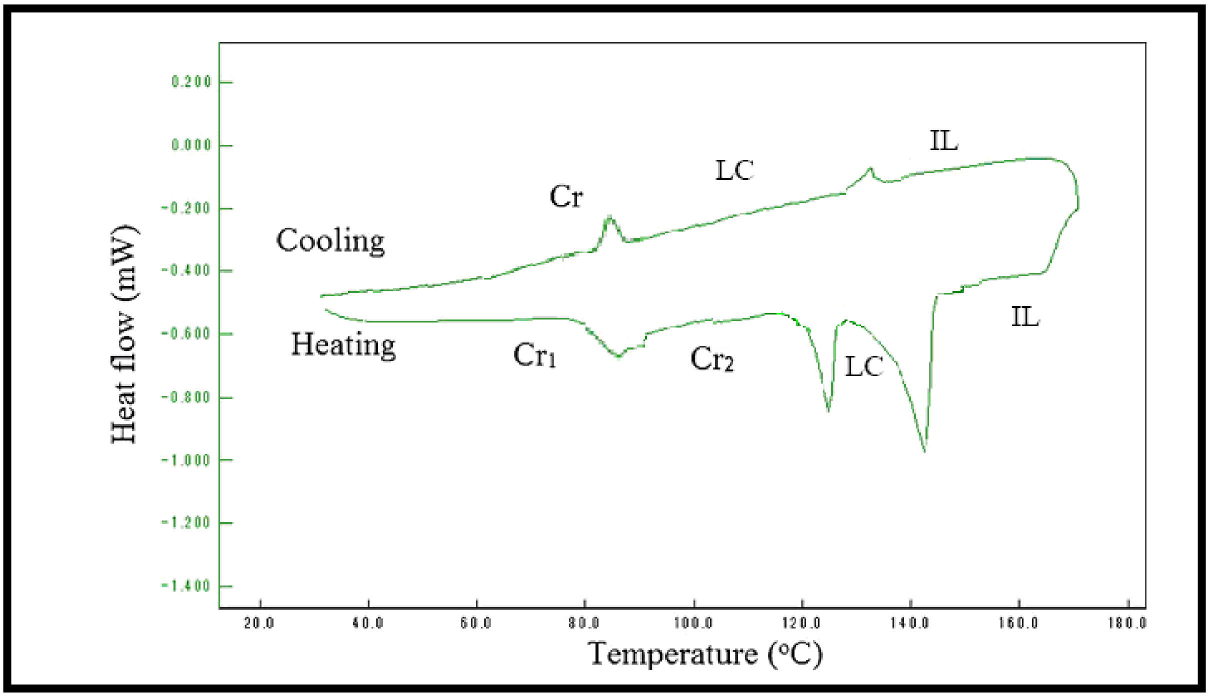


Figure 3.26 *DSC thermograms at 10 °C/min for compound 3d.*

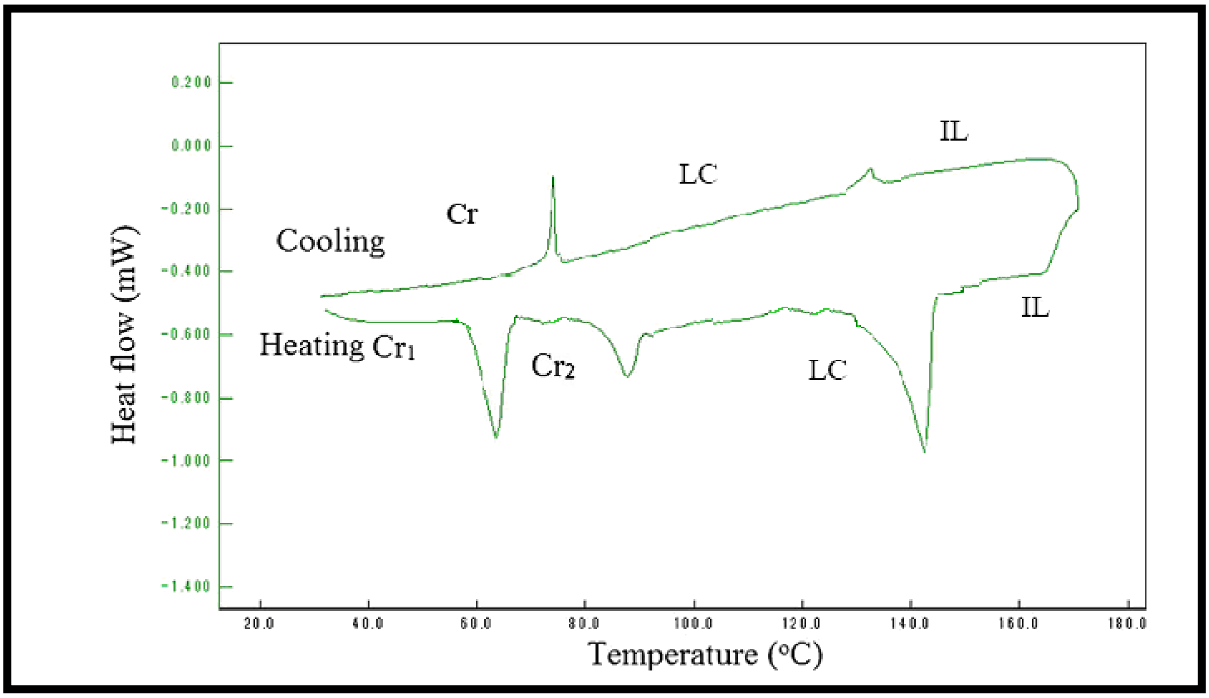


Figure 3.27 *DSC thermograms at 10 °C/min for compound 3e.*

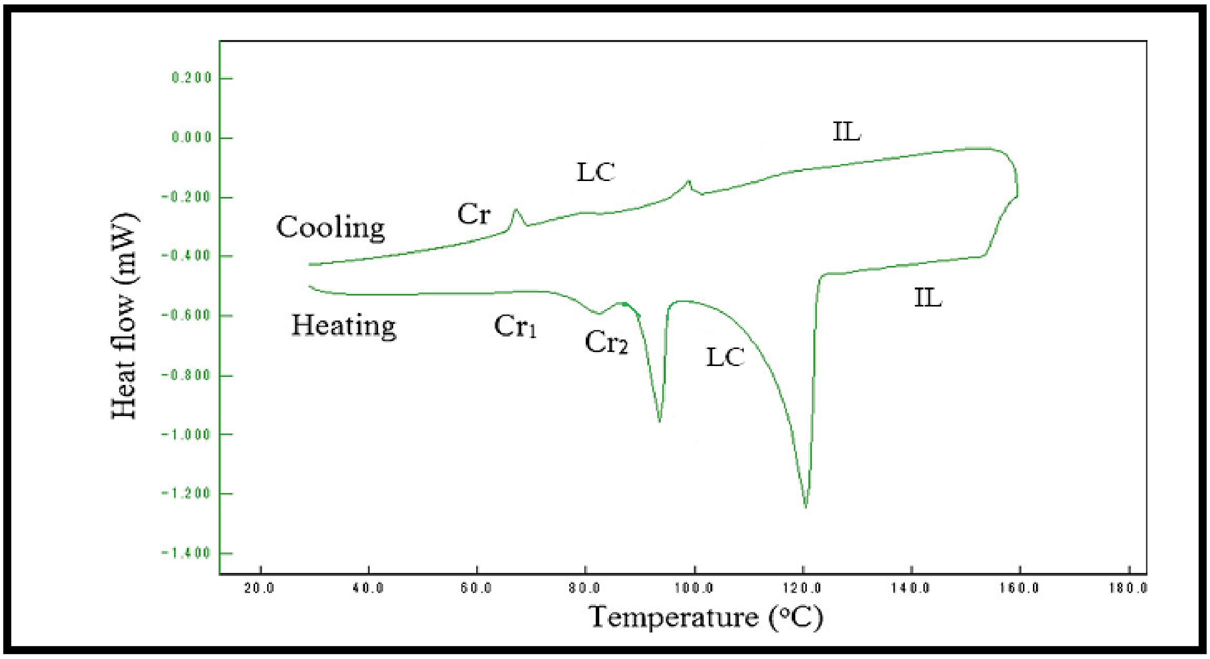


Figure 3.28 *DSC thermograms at 10 °C/min for compound 3f.*

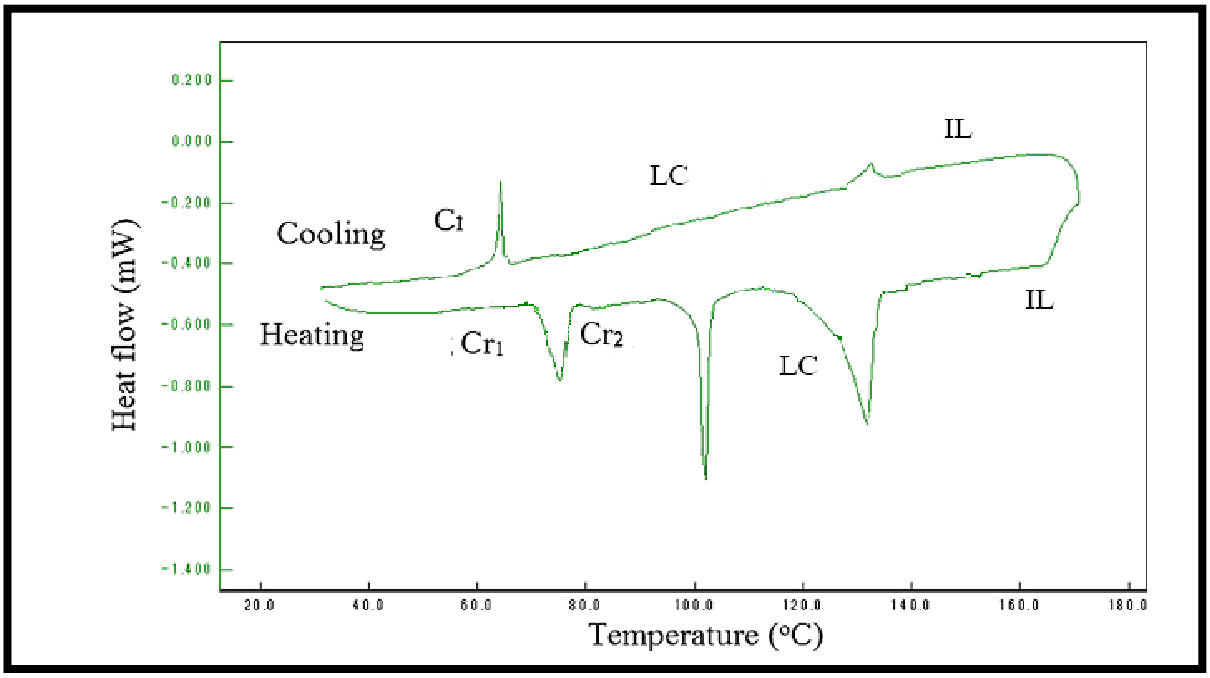


Figure 3.29 *DSC thermograms at 10 °C/min for compound 3g.*

All the star-shaped mesogens exhibit liquid crystalline behavior except for the homologues possessing the shortest alkyl spacer (n = 2). These compounds undergo direct isotropization on heating and crystallization on cooling, thus indicating the non-mesogenic properties. In addition, the non-mesogenic properties can also be inferred from the DSC thermograms of these homologues which display only one endotherm and exotherm upon heating-cooling cycle. The absence of mesophase is presumably due to the short flexible spacer as the short chain may tend to hinder the peripheral units from the appropriate anisotropic arrangement in forming liquid crystalline properties (47). Furthermore, shorter alkyl spacer also does not increase the polarity and polarizability of the molecules (48). Therefore, phase generation is usually less apparent especially in molecule having short alkyl chain. The formation of a columnar mesophase was found to be dependent on the number of methylene units in alkoxy terminal chains attached to the rigid. The mesophase's stability was found to be poor for the first synthesized compound.

3.3.2 Mesomorphic Properties of 1,3,5-tri-[4-{4'-n-alkoxybenzoyloxy} benzoyloxy] benzene (6a-g):

Thermal phase behavior of 1,3,5-tri-[4-{4'-n-alkoxybenzoyloxy}benzoyloxy]benzene (6a-g) was studied using differential scanning calorimetry (DSC), polarizing optical microscopy (POM). Results of the DSC studies, which used heating and cooling rates of 10 °C/min, are shown in table (3.10) and figures (3.30), (3.31), (3.32), (3.33), (3.34), (3.35) and (3.36).

Table 3.10 *Mesophase-transition temperature ranges obtained from DSC thermograms for series (6a-g).*

Comp. No.	Mesophase temperature ranges	No. of figure
6a	(94 – 170) °C	3.30
6b	(74 – 132) °C	3.31
6c	(111 – 149) °C	3.32
6d	(100 – 140) °C	3.33
6e	(123 – 152) °C	3.34
6f	(126 – 154) °C	3.35
6g	(122 – 157) °C	3.36

Star-shaped mesogens with the alkoxy terminal groups show nematic phase in their liquid crystalline state when viewed under a polarized optical microscope as show in figure (3.37).

The effects of the terminal chain length on the transition temperatures and phases behavior observed in this series are in accordance with those observed for nematic discotic mesogens (49).

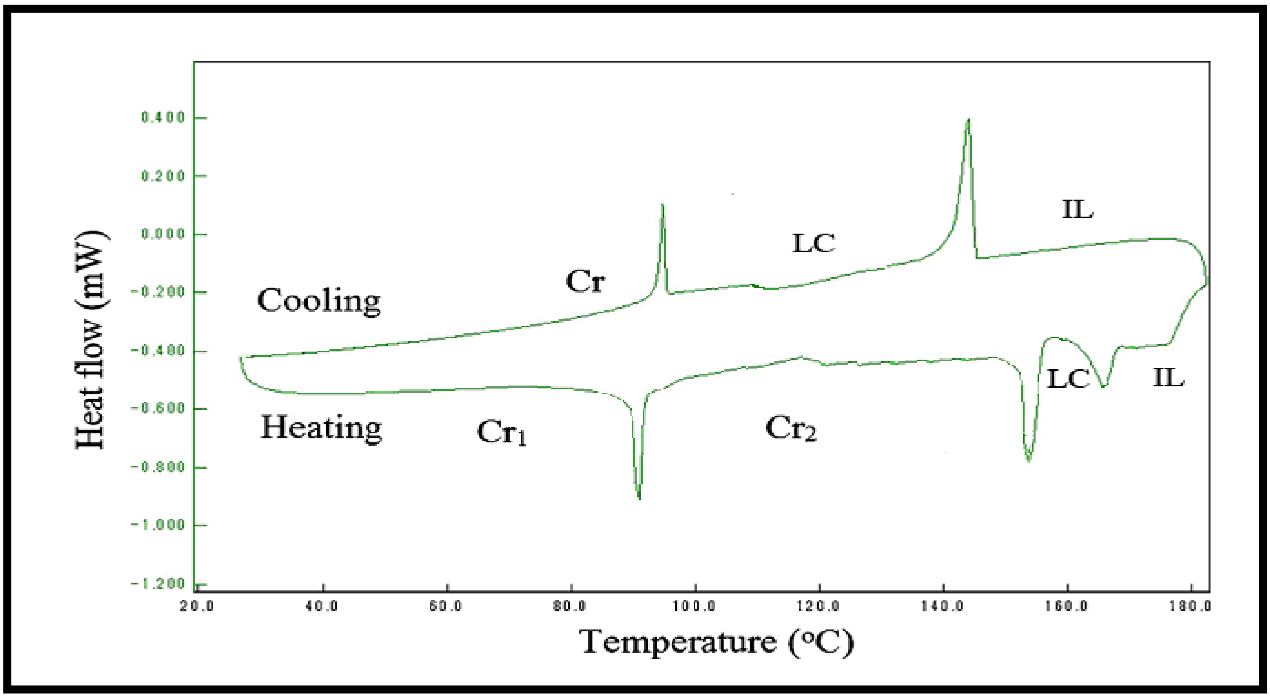


Figure 3.30 *DSC thermograms at 10 °C/min for compound 6a.*

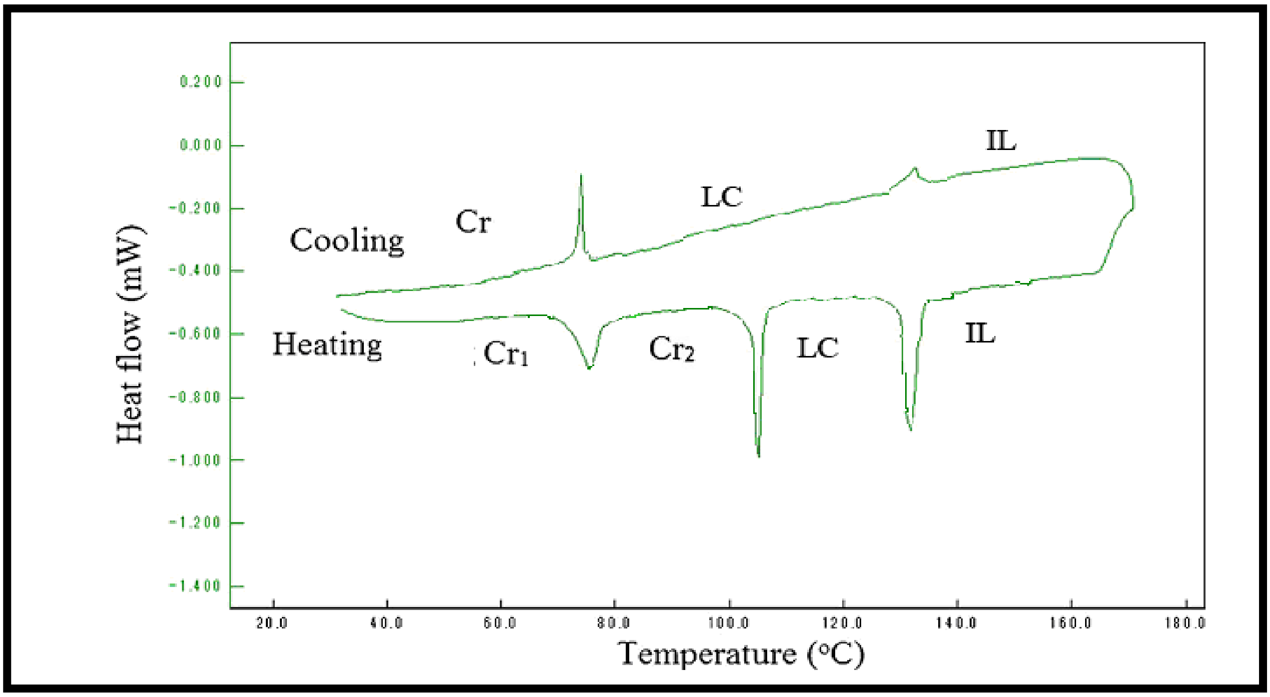


Figure 3.31 *DSC thermograms at 10 °C/min for compound 6b.*

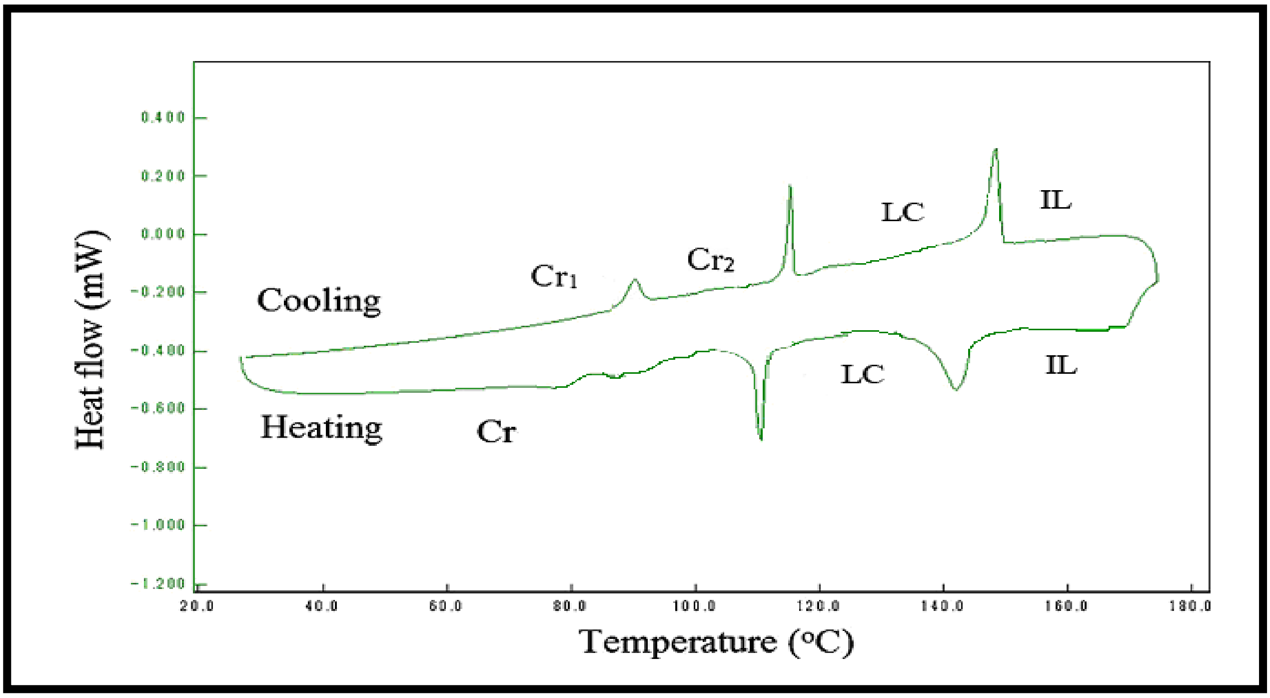


Figure 3.32 *DSC thermograms at 10 °C/min for compound 6c.*

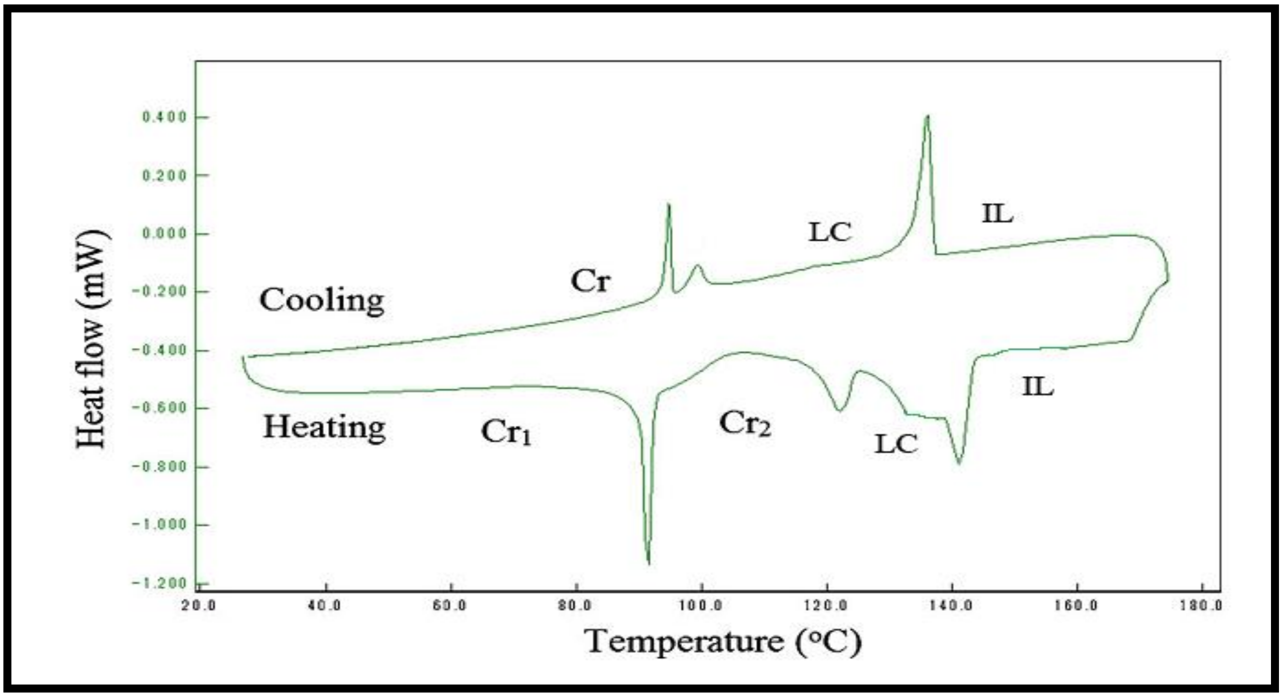


Figure 3.33 *DSC thermograms at 10 °C/min for compound 6d.*

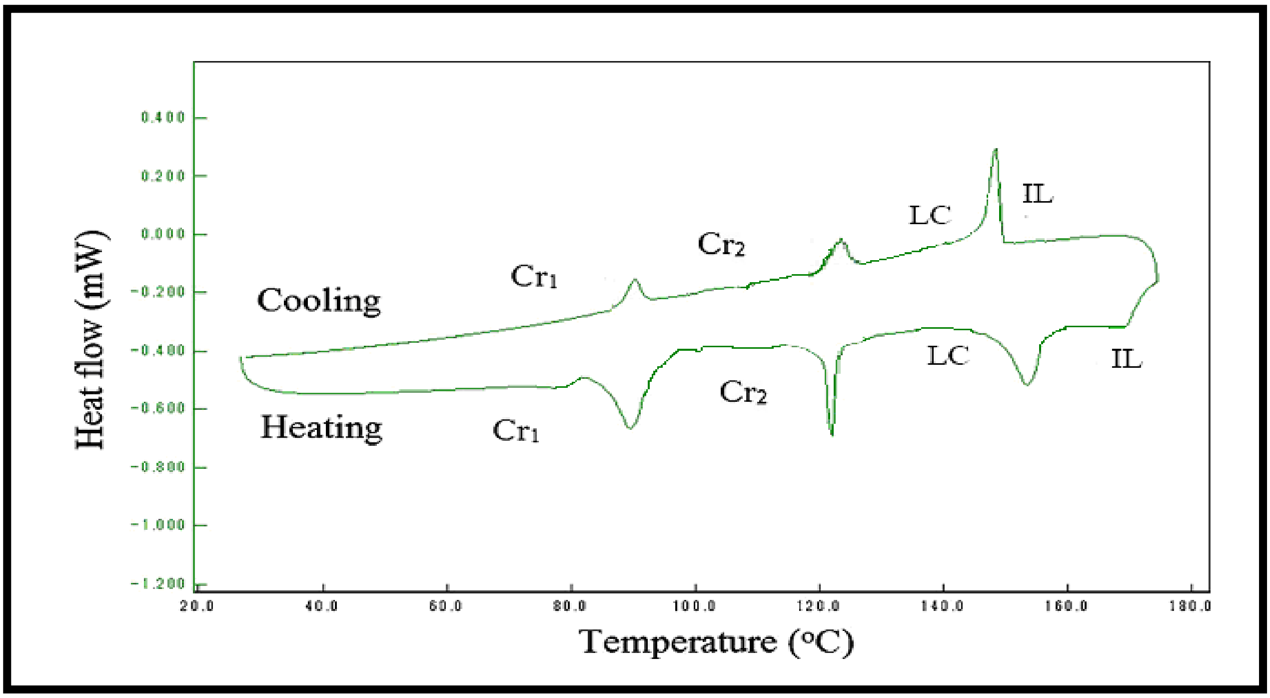


Figure 3.34 *DSC thermograms at 10 °C /min for compound 6e.*

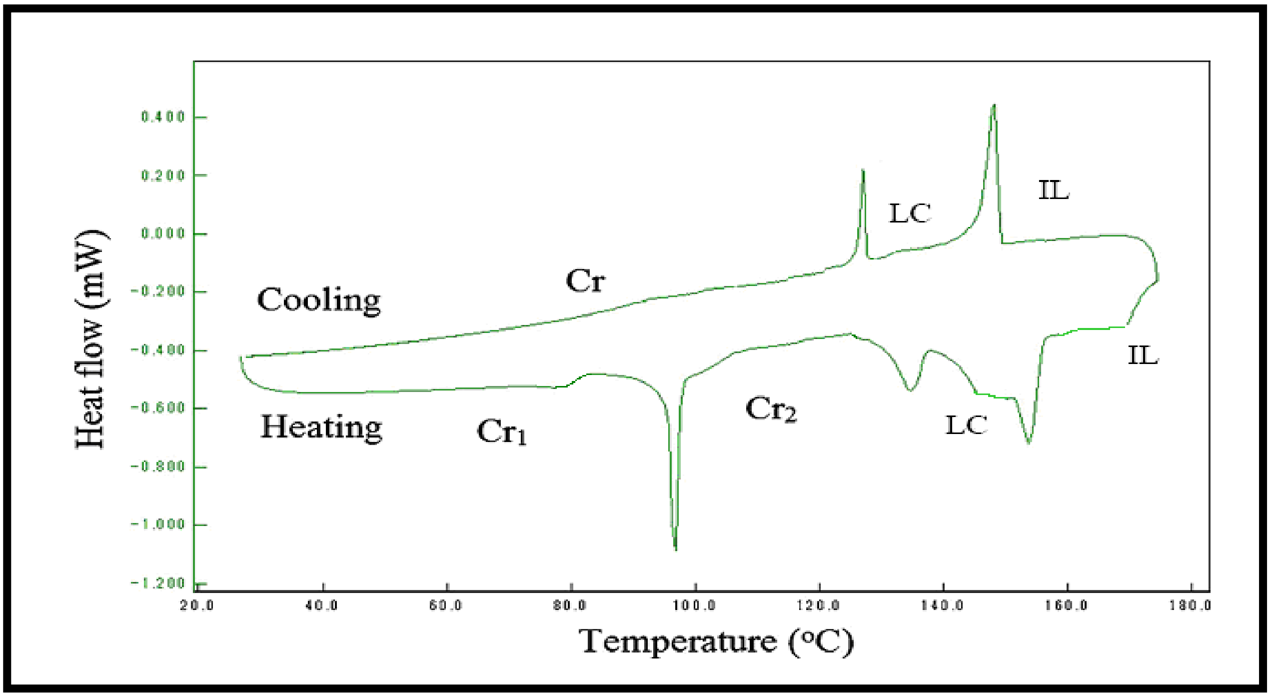


Figure 3.35 *DSC thermograms at 10 °C/min for compound 6f.*

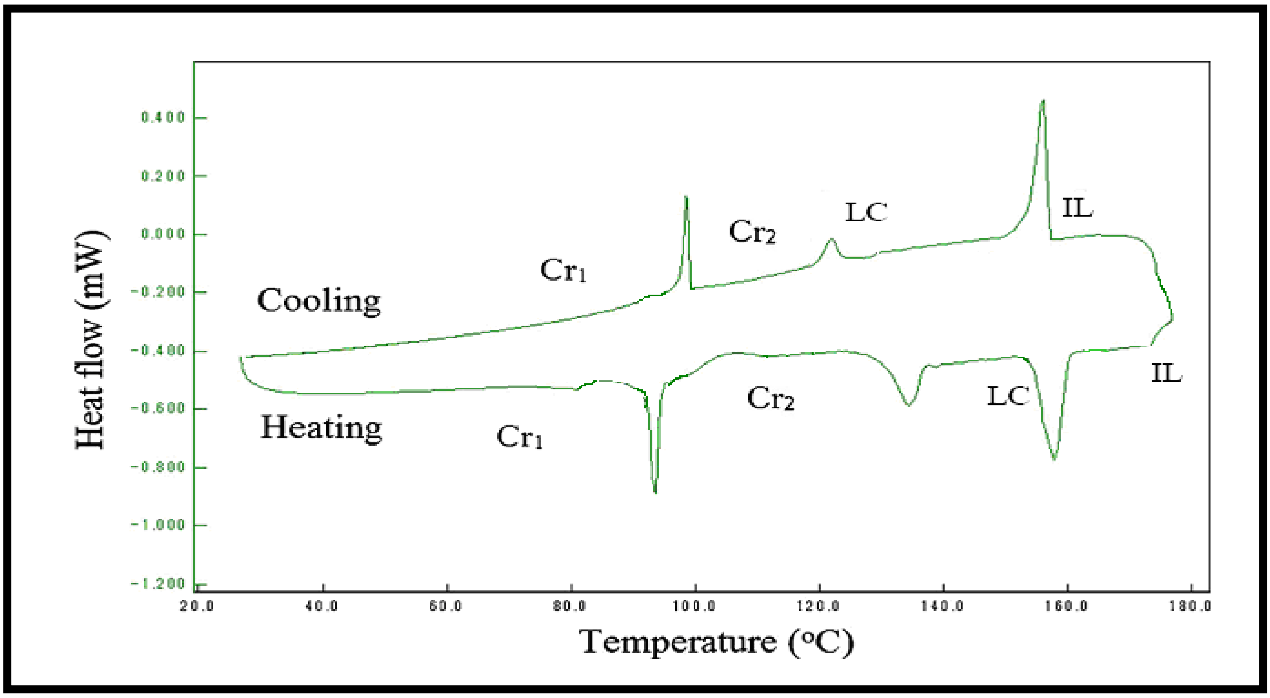
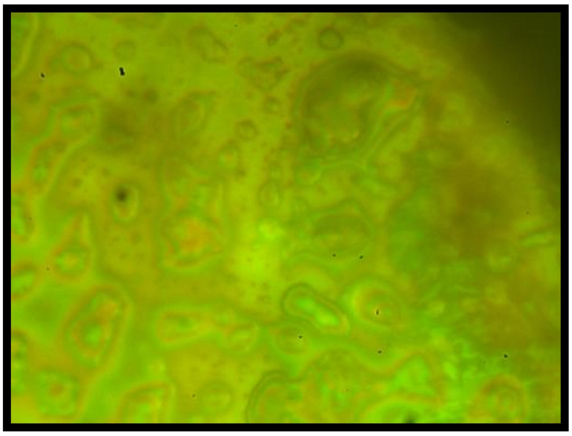
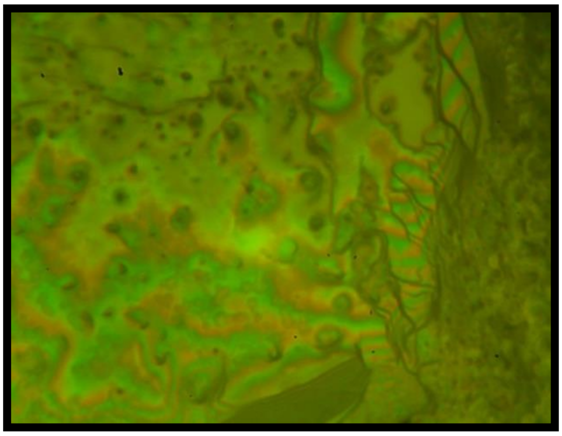


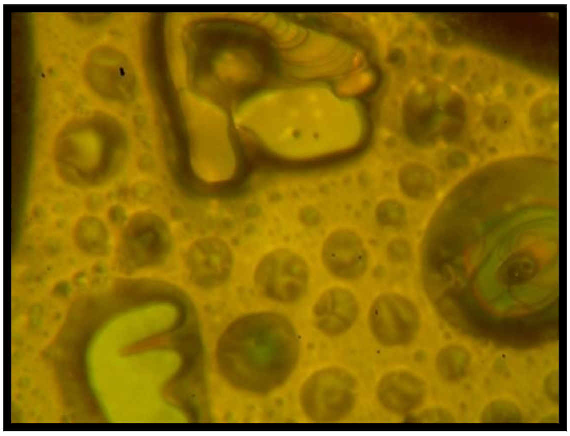
Figure 3.36 *DSC thermograms at 10 °C/min for compound 6g.*



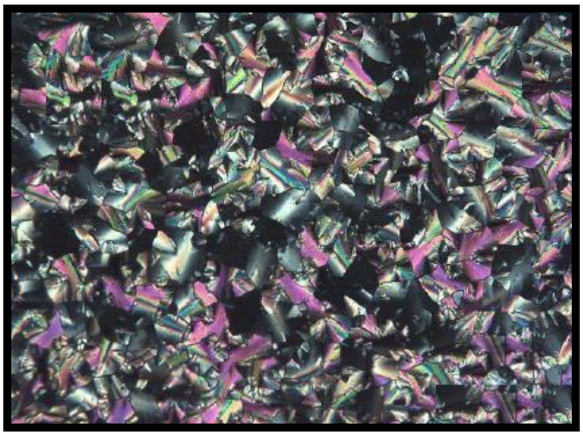
a (Threaded nematic)



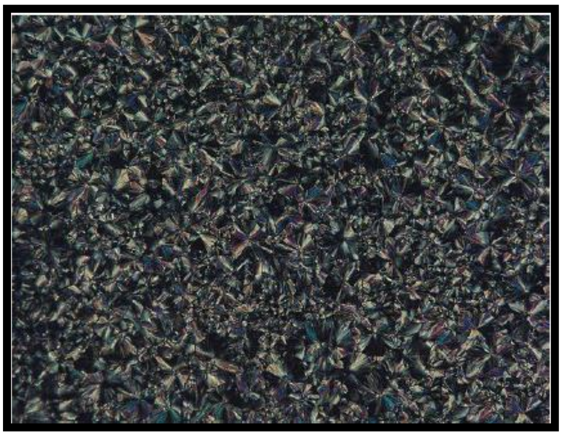
b (Threaded nematic)



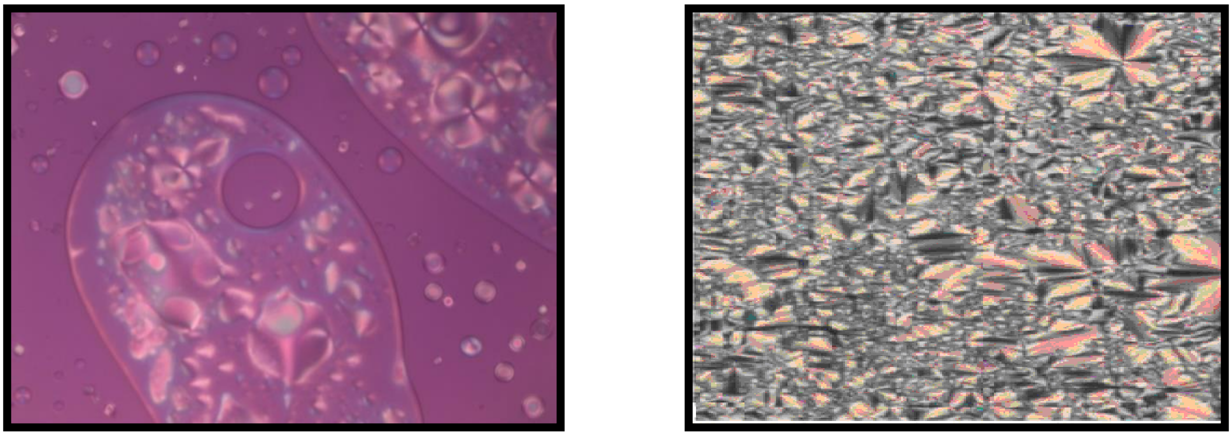
c (Fan shaped nematic)



d (Fan shaped focal conic nematic)



e (Fan shaped nematic)



f (Droplet nematic) *g (Fan shaped nematic)*

Figure 3.37 *Cross-polarizing Optical textures of the nematic mesophase obtained on heating and cooling (Magnification 200×) for compounds of series (6a-g), (a) (6a) at 167°C, (b) (6b) at 112°C, (c) (6c) at 118°C, (d) (6d) at 135°C, (e) (6e) at 122°C , (f) (6f) at 115°C, (g) (6g) at 135°C .*

There is close relationship between mesomorphism and molecular constitution of organic compounds. Hence thermal stability, a measure of mesomorphism, can be correlated with the molecular constitution of the compounds. The different mesomorphic properties arises due to the presence of different right terminal groups which differ in their sizes and polarities.

The presence of an untwisted alkoxy-substituted diphenyl section aids mesomorphic properties by enhancing the longitudinal polarizability of the core and hence, enables a discotic phase to be revealed in all the synthesized compounds.

Conclusions

A new series of discotic liquid crystalline based on 1,3,5-trihydroxybenzene derivatives with two pendant alkoxybenzoyl group and alkoxybenzoyloxy benzoyl group were designed and synthesized by varying alkoxy terminal chain length (*n*=2–8). The formation of a columnar mesophase was found to be dependent on the number of methylene unit in alkoxy terminal chains. The compounds with $n \geq 3$, exhibited an enantiotropic columnar phase; however, compound with $n = 2$ formed a crystalline phase for series (3a-g) but compound 6a show a nematic phase due to increasing the aromatic ring to seven ring.

Suggestion for further work

We wish in the future to prepare a phloroglucinol based core discotic liquid crystals and changing the side arms by Schiff base.

Also we want to insert a lateral group on the synthesized compounds and watch the effect of these groups on the liquid crystalline behavior and make a comparison between it and the same compounds without inserting a lateral group.

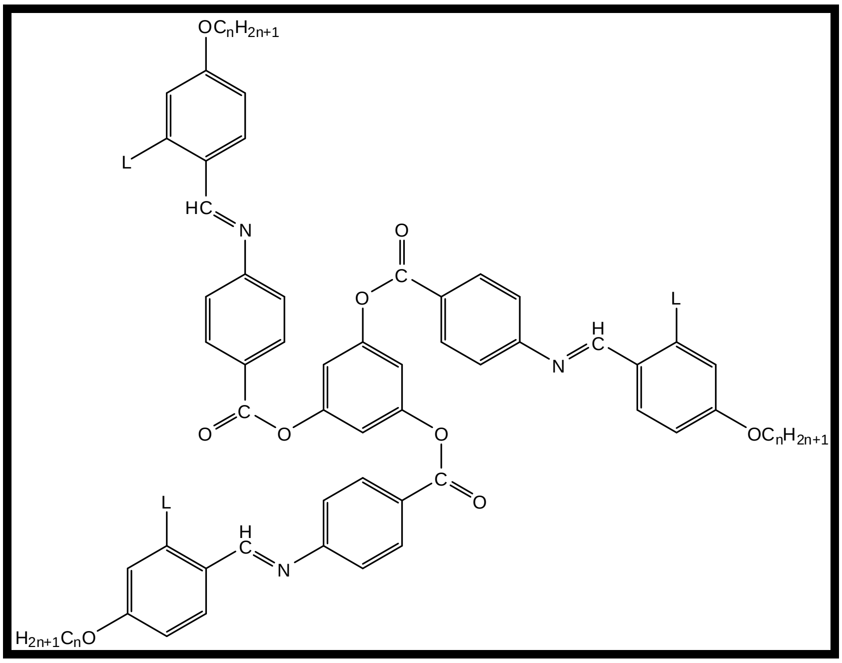


***Figure 3.38** Discotic compounds contain phluroglucinol core and Shiff base linking groups.*

L: lateral group like halogens, nitro, acyl, methyl, methoxy groups.

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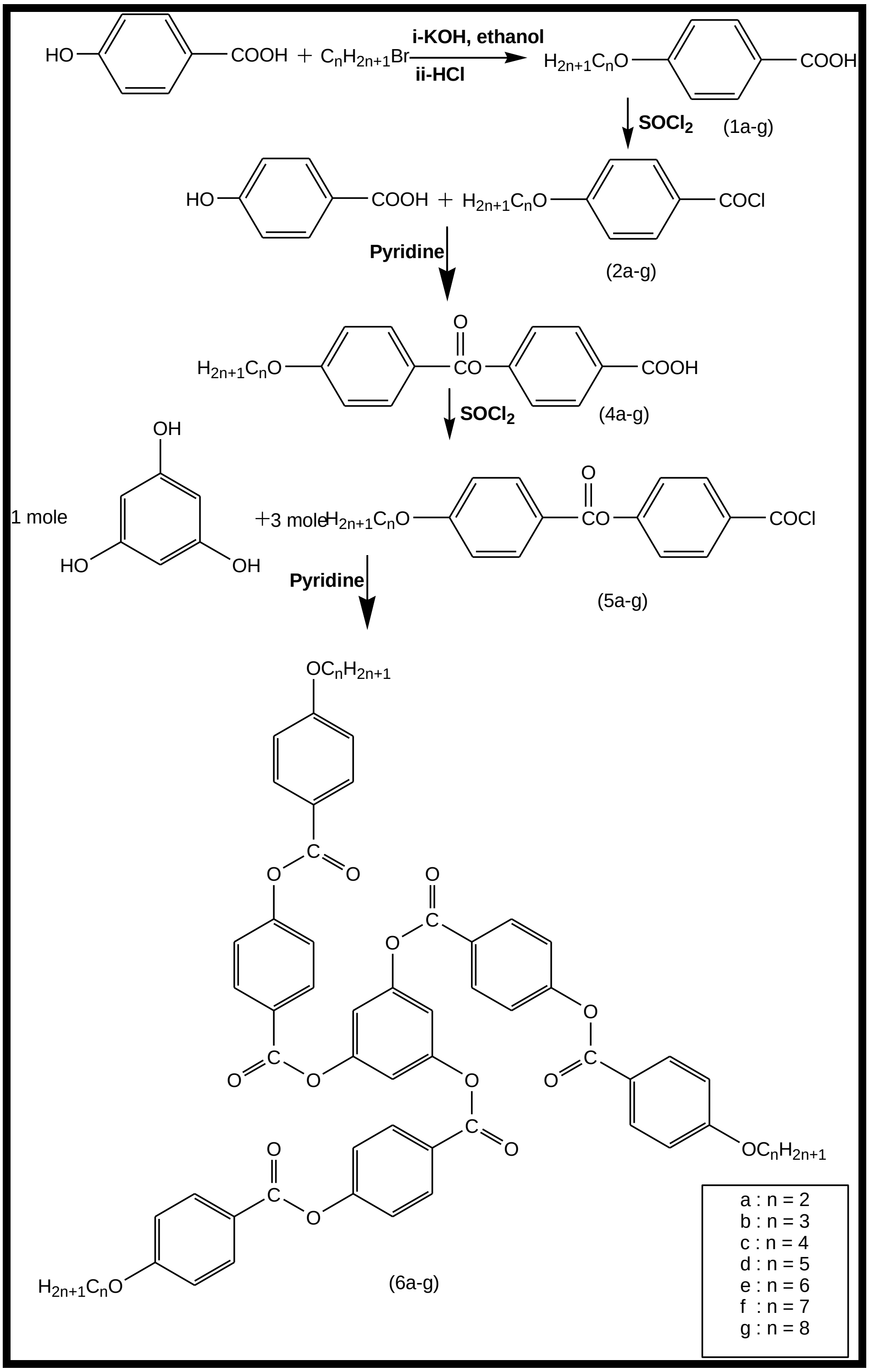
الملخص

المركب الأول (3a) في السلسلة الأولى لا يمتلك طور بلوري سائل, لكن بسهولة يتحول من الطور الصلب الى الطور السائل عند درجة حرارة 130°C.

المركبات (3b-g) أظهرت أطوار بلورية سائلة إنانتيوتروبك (Enantiotropic) . النسيج الذي ظهر في المجهر الضوئي المستقطب polarizing optical microscope (POM) أثبت وجود اطوار بلورية سائلة عمودية , مع اطوار ذات شكل المروحة النموذجي الى الشكل العمودي للمركبات (3c, 3e, and 3g) و أطوار ذات شكل المروحة المخروطي البؤري للمركبات (3b, 3d, and 3f).

أما بالنسبة للسلسلة الثانية فإن كل مركباتها أظهرت أطوار بلورية سائلة نيماتيكية Nematic ذات الشكل النجمي عند فحصها بالمجهر الضوئي المستقطب polarizing optical microscope (POM) .



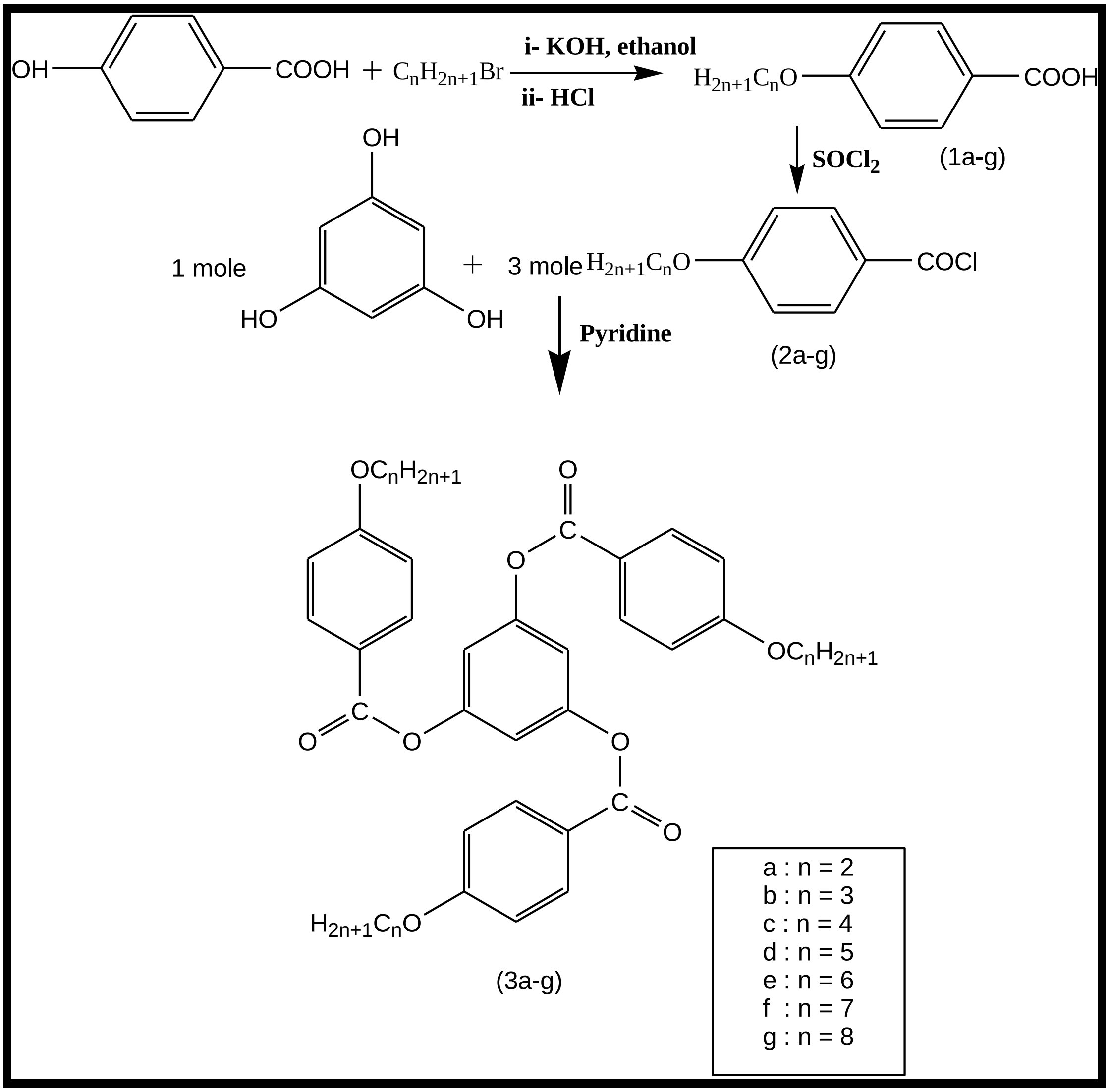
المركبات المحضرة تم تشخيصها باستخدام طيف الاشعة تحت الحمراء FTIR وطيف الرنين المغناطيسي النووي ^{1}HNMR لبعض منها والتحليل الذري للعناصر CHNS-O.

الاطوار البلورية السائلة للسلسلتين تم فحصها بإستخدام المجهر الضوئي المستقطب المزود بمنصة ساخنة ومسعر المسح التفاضلي DSC من أجل معرفة درجات الحرارة للاطوار الانتقالية ونوع الاطوار البلورية السائلة.

الملخص

هذه الدراسة تختص في تحضير ودراسة خواص السلسلتين (3a-g) و (6a-g) التي هي عبارة عن تعويض ثلاثي مشتق من ٥,٣,١- ثلاثي هيدروكسي البنزين (فلوروكلوسينول).

السلسلة الأولى (3a-g) موضحة في المخطط ١ تم تحضيرها من تفاعل فلوروكلوسينول مع بارا الكوكسي كلورايد البنزويل.



المخطط ١

السلسلة الثانية (6a-g) موضحة في المخطط ٢ تم تحضيرها من تفاعل الفلوروكلوسينول مع بارا الكوكسي بنزويل اوكسي كلورايد البنزويل.

جمهورية العراق
وزارة التعليم العالي والبحث العلمي
كلية العلوم / جامعة النهرين
قسم الكيمياء

تحضير وتشخيص ودراسة الخواص البلورية السائلة لمركبات قرصية جديدة

رسالة

مقدمة الى مجلس كلية العلوم/ جامعة النهرين
كجزء من متطلبات نيل درجة الماجستير في علوم الكيمياء

من قبل

علي حسّان داود الحديثي

بكالوريوس ٢٠١٢(جامعة النهرين)

إشراف

أ.م.د. نسرين رحيم جبر

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