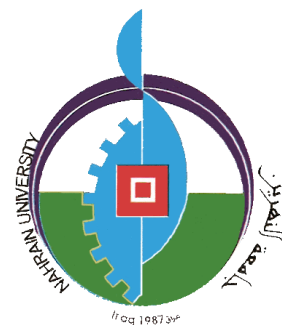


*Republic of Iraqi
Ministry of Higher Education
And Scientific Research
Al-Nahrain University
College of Science
Department of Chemistry*



***Separation of isomeric hydrocarbons by
Gas Chromatography using Liquid
Crystalline Materials as Stationary Phases***

*A thesis
Submitted to the College of Science
Al-Nahrain University
In partial fulfillment of Requirements
For the Degree of Master in Science of Chemistry*

***BY
Mohammed Muayad Shukur
B.SC. (Baghdad University 2010)***

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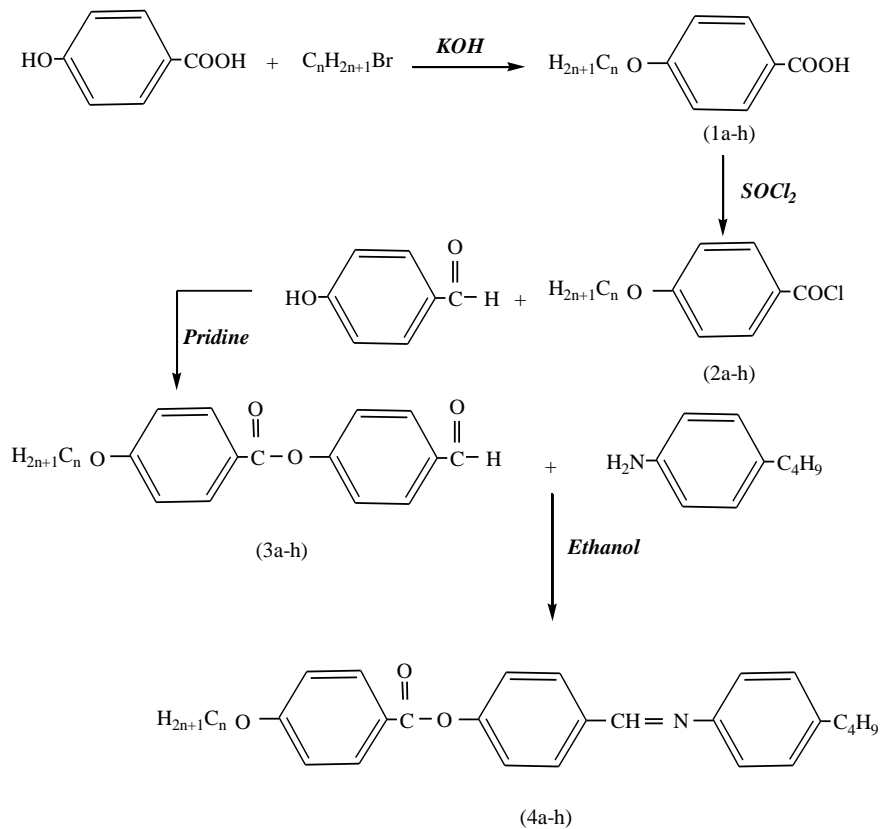
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Abstract

This thesis consists of the synthesis of new liquid crystalline compounds N-{(n-alkoxy-4'-benzoyloxy)-4'-benzylidene}-4-butyl aniline which were synthesized according to the following Scheme:



a : n = 1
b : n = 2
c : n = 3
d : n = 4
e : n = 5
f : n = 6
g : n = 7
h : n = 8

The synthesized compounds were characterized using FTIR, ^1H NMR ^{13}C NMR, EI-Mass spectroscopy and CHN analysis. The liquid crystalline properties of the prepared compounds which were verified using differential scanning calorimeter (DSC) and hot-stage polarizing optical microscope (POM) were discussed. The relation between the liquid crystalline behavior with chemical constitution was discussed on the basis of the effect of terminal group (Alkoxy group). Compound (4d) was used as stationary phases in gas chromatography for separation of positional isomer hydrocarbons (*o*-, *m*-, *p*-cresol) and poly aromatic hydrocarbons (naphthalene, flourene, phenanthrene and anthracene).

Stationary phase for gas chromatography were prepared by loading the 4d compound on solid support (chromosorb W/AW 60-80 mesh) at 20%. These stationary phases were packed on glass gas chromatographic columns. A gas- liquid chromatographic study of the interaction and elution characteristics of positional isomer hydrocarbons and poly aromatic hydrocarbons using liquid crystalline phases and at different column temperatures of 100°C-180°C for 2.

The best chromatographic conditions for the separation of hydrocarbons were characterized by measuring column efficiency N_{eff} , resolution R_s , and selectivity factors α in order to assess the performance and separation ability of these columns. It was found that best chromatographic performance can be achieved with operating temperature at which the thermal stability of the nematic mesophase starts to form.

Chapter One

Introduction

Chapter One

Introduction

1.1 Liquid Crystals

Liquid crystalline molecules are ‘*soft materials*’, representing a special states of matter (also called the fourth state of matter) which is recognized by it’s long range order (as in crystals) and mobility (as in liquid)⁽¹⁾.

Liquid crystals are substances that exhibit a phase of matter that has properties between those of a conventional isotropic liquid, and those of a solid crystal, as shown in Figure 1.1⁽²⁾.

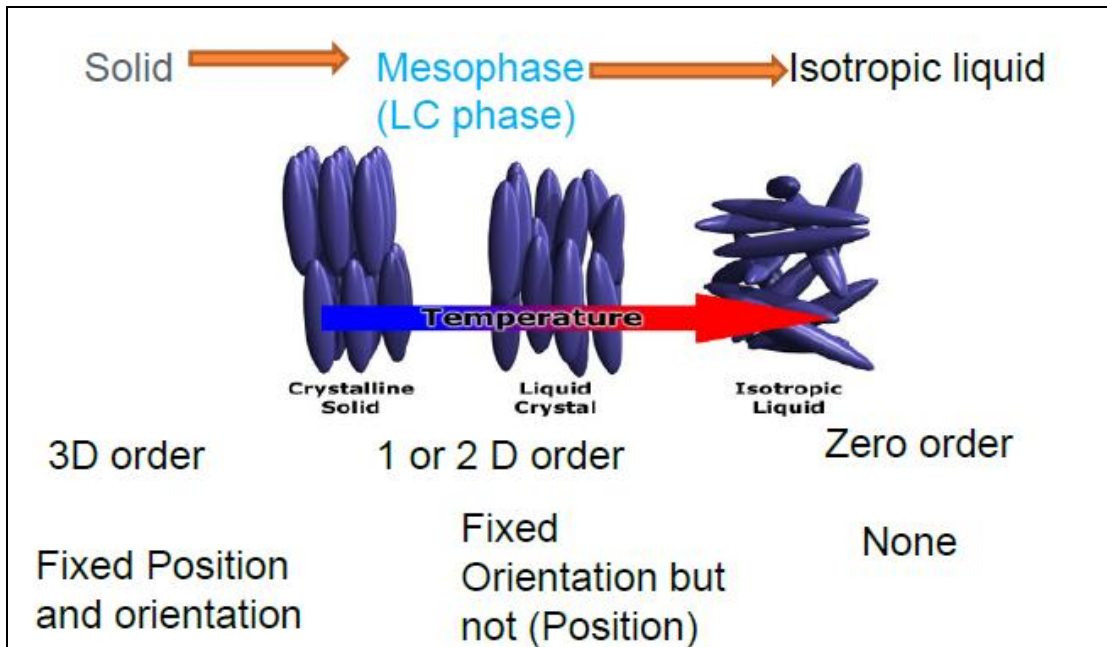


Figure (1.1): Alignment of the molecules for solid, liquid crystal and liquid phases.

In a solid state, molecules are arranged very close together and cannot move around which shown in the Figure 1.2 (a). It is in a regular structure, which arranged in a well ordered pattern. Crystalline solids have molecules that are arranged in fixed geometric patterns or lattices with repeating unit cells extending in all three spatial dimensions. As shown in Figure 1.2 (c), the molecules in a liquid are close together but do not have

fixed positions and can move around freely. In contrast, the molecules in a liquid crystal have an arrangement of that in between a solid and a liquid as shown in the Figure 1.2(b). They can be considered to be crystals which have lost some or all of their positional order, while maintaining full orientational order or as a liquid whose component particles, atoms or molecules, tend to arrange themselves with a degree of order far exceeding that found in ordinary liquids and approaching that of solid crystals⁽³⁾.

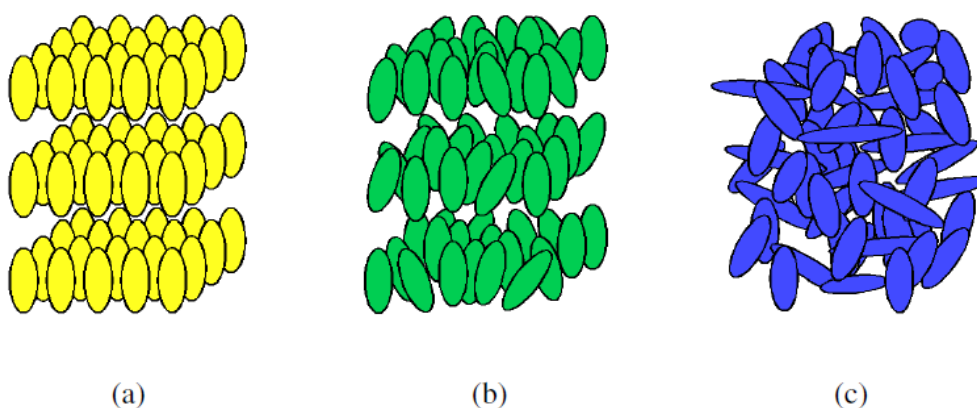


Figure (1.2): (a) Arrangement of molecules in a crystalline solid
(b) Arrangement of molecules in a liquid crystal
(c) Arrangement of molecules in a liquid

1.1.1 History and Development of Liquid Crystals

In 1888, the Austrian chemist Friedrich Reinitzer, working in the Institute of Plant Physiology at the University of Prague, discovered a strange phenomenon. Reinitzer was conducting experiments on a cholesterol based substance trying to figure out the correct formula and molecular weight of cholesterol. When he tried to precisely determine the melting point, which is an important indicator of the purity of a substance, he was struck by the fact that this substance seemed to have two melting points. At 145.5 °C the solid crystal melted into a cloudy liquid which existed until 178.5 °C where the cloudiness suddenly disappeared, giving

way to a clear transparent liquid. At first Reinitzer thought that this might be a sign of impurities in the material, but further purification did not bring any changes to this behaviour⁽⁴⁾.

Puzzled by his discovery, Reinitzer turned for help to the German physicist Otto Lehmann, who was an expert in crystal optics. Lehmann became convinced that the cloudy liquid had a unique kind of order. In contrast, the transparent liquid at higher temperature had the characteristic disordered state of all common liquids.

Eventually he realized that the cloudy liquid was a new state of matter and coined the name "liquid crystal," illustrating that it was something between a liquid and a solid, sharing important properties of both. In a normal liquid the properties are isotropic, i.e. the same in all directions. In a liquid crystal they are not; they strongly depend on direction even if the substance itself is fluid⁽⁴⁾.

In 1922 in Paris, France, Georges Freidel suggested the classification scheme which is used today with different phases of liquid crystals called nematic, smectic and cholesteric⁽⁵⁾.

1.2 Categories of Liquid Crystals

Compounds consist such unusual phases are also known as mesogens and their various phases in which they can exist are termed as mesophases⁽⁴⁾. Liquid crystals are grouped into a few general groups which are well known and widely studied such as thermotropics, lyotropics, and metallotropic phases⁽⁴⁾. There are a lot of different types of molecules form liquid crystals phases at various temperature and pressure. At atmospheric pressure, if temperature is the major physical variable in determines a liquid crystal's phase, that particular types of liquid crystals are termed as thermotropic liquid crystals.

Meanwhile, there are other types of liquid crystalline materials which formed from anisotropic objects immersed in a solvent. The phases of these materials are mainly determined by the composition of the mixture. These types of liquid crystals are termed as lyotropic liquid crystals⁽⁶⁾. Lyotropic liquid crystals commonly exhibit in disk shaped or rod shaped. Figure 1.3 below shown typical rod shaped or disk shaped liquid crystal:

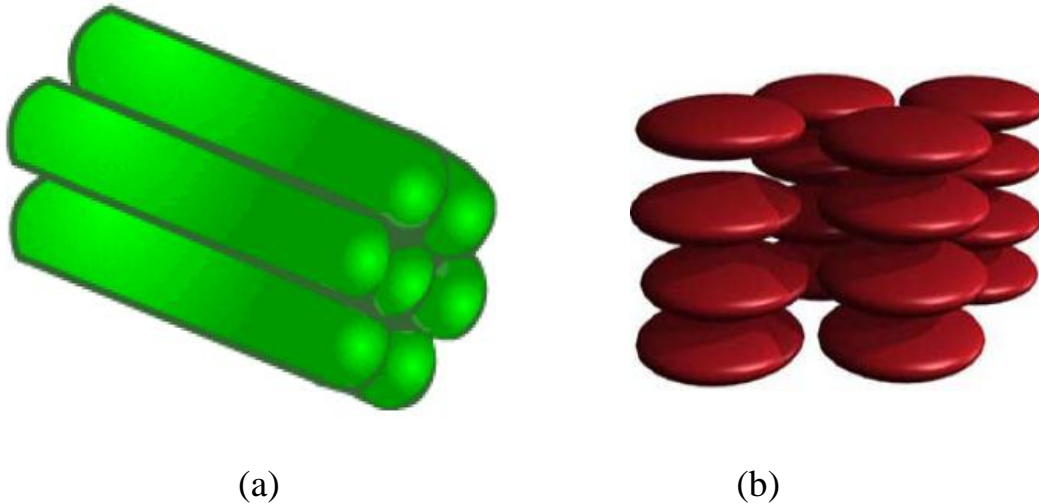


Figure (1.3): (a) A schematic representation of a rod shaped liquid crystal
(b) A schematic representation of a disc shaped liquid crystal

Liquid crystals can be classified into two main categories: thermotropic liquid crystals, and lyotropic liquid crystals. These two types of liquid crystals are distinguished by the mechanisms that drive their self-organization, but they are also similar in many ways.

Thermotropic transitions occur in most liquid crystals, and they are defined by the fact that the transitions to the liquid crystalline state are induced thermally. That is, one can arrive at the liquid crystalline state by raising the temperature of a solid and/or lowering the temperature of a liquid. Thermotropic liquid crystals can be classified into two types: enantiotropic liquid crystals, which can be changed into the liquid crystal state from either lowering the temperature of a liquid or raising of the temperature of a solid, and monotropic liquid crystals, which can only be changed into the liquid crystal state from either an increase in the

temperature of a solid or a decrease in the temperature of a liquid, but not both. In general, thermotropic mesophases occur because of anisotropic dispersion forces between the molecules and because of packing interactions.

In contrast to thermotropic mesophases, lyotropic liquid crystal transitions occur with the influence of solvents, not by a change in temperature. Lyotropic mesophases occur as a result of solvent-induced aggregation of the constituent mesogens into micellar structures. Lyotropic mesogens are typically amphiphilic, meaning that they are composed of both lyophilic (solvent attracting) and lyophobic (solvent-repelling) parts. This causes them to form into micellar structures in the presence of a solvent, since the lyophobic ends will stay together as the lyophilic ends extend outward toward the solution. As the concentration of the solution is increased and the solution is cooled, the micelles increase in size and eventually coalesce. This separates the newly formed liquid crystalline state from the solvent.

A very large number of chemical compounds are known to exhibit one or several liquid crystalline phases. Despite significant differences in chemical composition, these molecules have some common features in chemical and physical properties. There are two types of thermotropic liquid crystals: discotics and rod-shaped molecules. Discotics are flat disc-like molecules consisting of a core of adjacent aromatic rings. This allows for two dimensional columnar ordering. Rod-shaped molecules have an elongated, anisotropic geometry which allows for preferential alignment along one spatial direction.

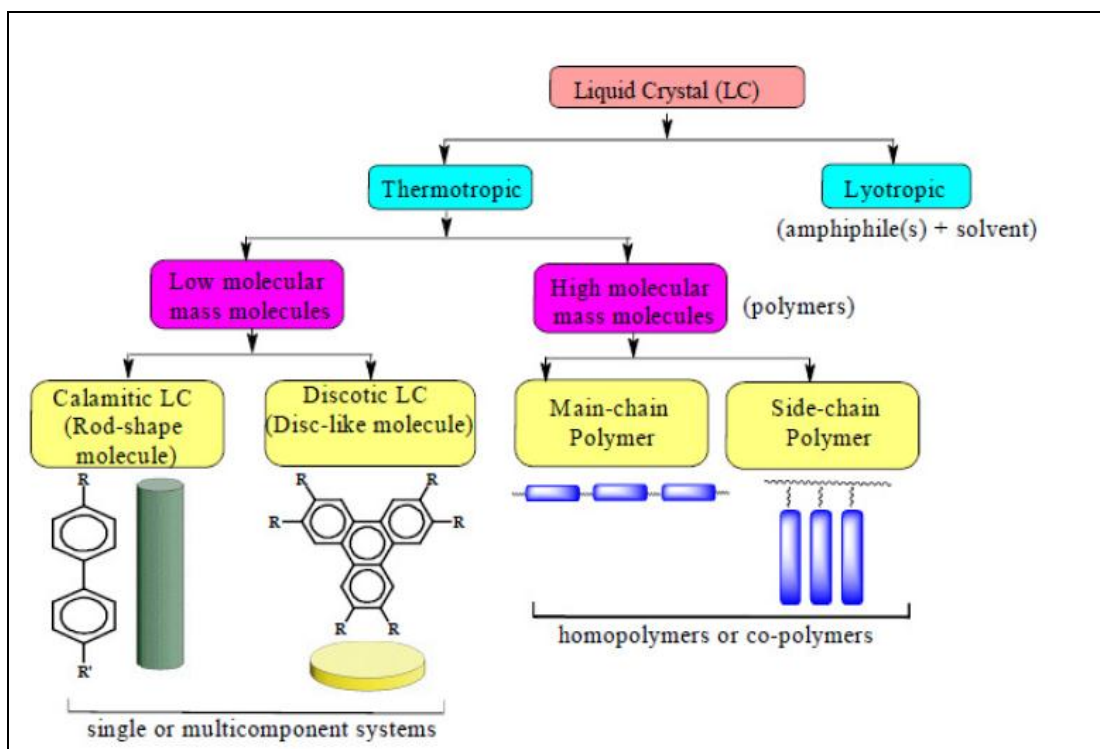


Figure (1.4): Classification of Liquid Crystal⁽⁷⁾

1.2.1 Calamitic Liquid Crystals

A compound must possess a certain requirement in order to exhibit liquid crystals properties. Figure 1.5 provides the basic structure of the most commonly occurring liquid crystals. A typical example of aromatic compounds contained benzene rings which may also referred as benzene derivatives.

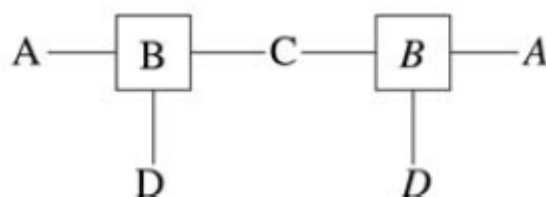


Figure (1.5): Typical rod-like structures of nematic LC molecules⁽³⁾.

A typical structure of the nematic rod-like molecule is shown in Figure (1.5). It consists of the two (less three or four) ring systems (B, B),

sometimes with lateral substituents (D, D), and a linking group C between them. The groups A and A are the terminal groups (tails of the molecules). Examples of side-chain and terminal groups are alkyl (C_nH_{2n+1}), alkoxy ($C_nH_{2n+1}O$), and others such as acyloxy, alkylcarbonate, alkoxy-carbonyl, nitro, and cyano groups. The example of the linkage groups are simple bonds or groups such as ethylene ($-CH=CH-$), ester ($-COO-$), Schiff base ($-CH=N-$), azo ($-N=N-$), acetylene ($C\equiv C$), and diacetylene ($C\equiv C-C\equiv C$). The names of liquid crystals are often termed after the linkage group like Schiff-base liquid crystal. There are few types of non-aromatic available. These include saturated cyclohexane, unsaturated phenyl, biphenyl, terphenyl in various combinations. The majority of liquid crystals are benzene derivatives which have mentioned previously⁽⁴⁾.

That is, in order for a molecule to display the characteristics of a liquid crystal, it must be rigid and rod-shaped. This is accomplished by the interconnection of two rigid cyclic units. The interconnecting group should cause the resulting compound to have a linear planar conformation. Linking units containing multiple bonds such as $-(CH=N)-$, $-N=N-$, $(CH=CH)_n-$, $-CH=N-N=CH-$, etc. are used since they restrict the freedom of rotation. These groups can conjugate with phenylene rings, enhancing the anisotropic polarizability. This increases the molecular length and maintains the rigidity.

1.2.2 Liquid Crystals Phases

1.2.2.1 Nematic Phase:

The nematic phase is the least ordered liquid crystal phase, with molecules only possessing orientational order, but no positional order. Thus it is usually the least viscous mesophases. The preferred direction, *i.e.* the direction, where the long axis of the molecule is most likely to point, is called the director, usually \mathbf{n} . Figure 1.6 shows this phase⁽⁸⁾.

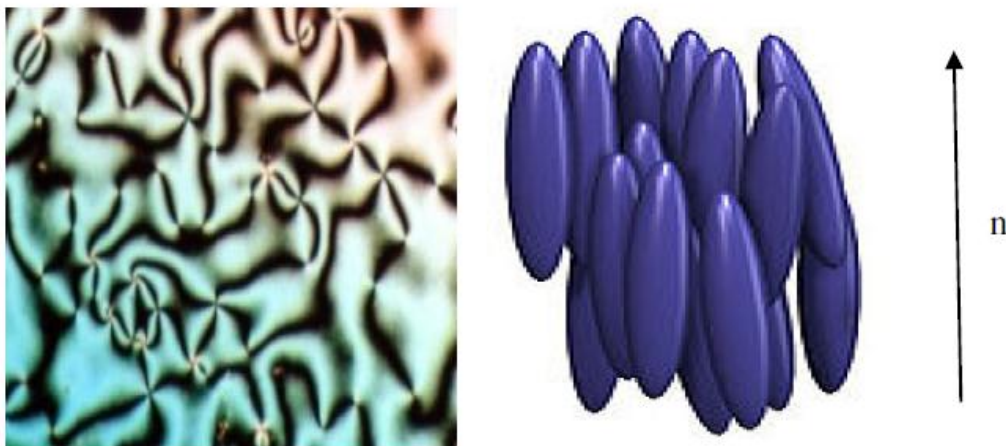


Figure (1.6): Texture and molecular arrangement of typical nematic liquid crystal

1.2.2.2 Smectic Phase:

Smectic phases show orientational order, and also some positional order. The molecules are preferably pointing in one direction, just like in the nematic phase. Additionally, the molecules form layers. There are several different types of smectic mesophases. The most important ones are smectic A (SmA), smectic C (SmC) and smectic C* (SmC*). In SmA the director \mathbf{n} is perpendicular to the planes of the layers, whereas in SmC and SmC* the molecules are directed with an angle other than 90° to the plane and direction of molecules varies continuously from layer to layer respectively. The molecules in smectic A are in random position while molecules that form smectic C phase are either a racemic mixture or non-chiral which are randomly positioned within each layer⁽⁹⁾.

Under the observation of polarized optical microscope (POM), SmA appears to be observed as fonic-fan texture whereas SmC and SmC* are observed broken-fan shape and colour when viewed under POM respectively⁽⁹⁾. All smectic phases are layered structures with well-defined layer structured. Motions are restricted within these planes. The texture and molecular arrangement of smectic liquid crystals are shown in Figure 1.7 (a) –(c).

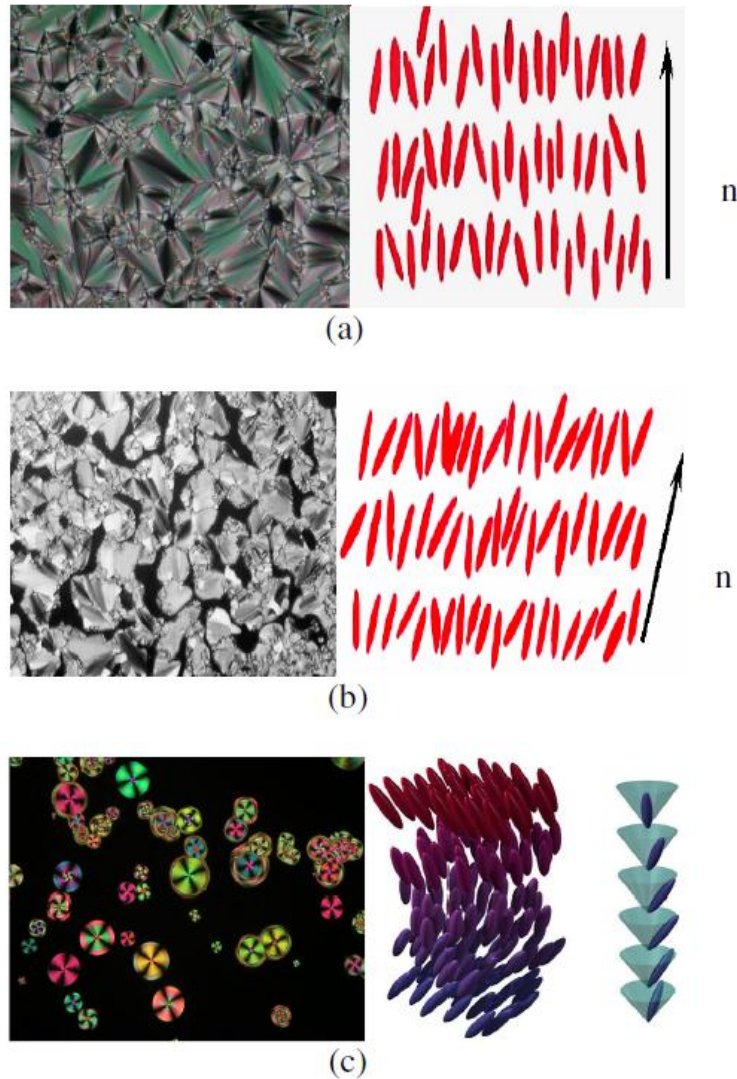


Figure (1.7): (a) Texture and molecular arrangement of typical smectic A liquid crystal. (b) Texture and molecular arrangement of typical smectic C liquid crystal. (c) Texture and molecular arrangement of typical smectic C* liquid crystal

1.2.2.3 Cholesteric Phase

The cholesteric or known as chiral nematic is a liquid crystal phase is typically composed of nematic mesogenic molecules containing a chiral centre which produces intermolecular forces that favour alignment between molecules at a slight angle to one another. This leads to the formation of a structure which can be visualized as a stack of very thin 2-D nematic- like layers with the director in each layer twisted with respect to those above and below⁽¹⁰⁾.

The molecules shown are merely representations of the many chiral nematic mesogens lying in the slabs of infinitesimal thickness with a distribution of orientation around the director. Figure 1.8 shows the texture and molecular arrangement of cholesteric liquid crystals⁽¹⁰⁾.

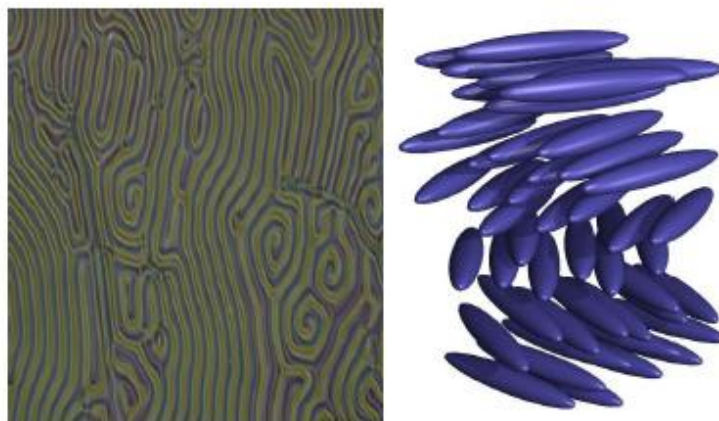


Figure (1.8): *Texture and molecular arrangement of typical cholesteric liquid crystal*

1.3 Applications of Liquid Crystals

The most common application of liquid crystal technology is liquid crystal displays. This field has grown into a multi-billion dollar industry, and many significant scientific and engineering discoveries have been made.

A liquid crystal display (LCD) is a thin, flat electronic visual display that uses the light modulating properties of liquid crystals (LCs). LCs does not emit light directly. They are used in a wide range of applications, including computer monitors, television, instrument panels, aircraft cockpit displays, signage, etc.

They are common in consumer devices such as clocks, watches, calculators, and telephones. LCDs have displaced cathode ray tube (CRT) displays in most applications. They are available in a wider range of screen sizes than CRT and plasma displays, and since they do not use phosphors, they cannot suffer image burn-in. Besides that, liquid crystals also applied in making thermometer. This is due to chiral nematic (cholesteric) liquid

crystals reflecting light with a wavelength equal to the pitch. Because the pitch is dependent upon temperature, the colour reflected also is dependent upon temperature. Liquid crystals make it possible to accurately gauge temperature just by looking at the colour of the thermometer. By mixing different compounds, a device for practically any temperature range can be built⁽¹¹⁾. In addition of that, more important and practical applications have been developed in such diverse areas as medicine and electronics⁽¹²⁾. Special liquid crystal devices can be attached to the skin to show a "map" of temperatures. This is useful because often physical problems, such as tumours, have a different temperature than the surrounding tissue. Liquid crystal temperature sensors can also be used to find bad connections on a circuit board by detecting the characteristic higher temperature⁽¹³⁾.

1.4 The separation mechanism on liquid-crystalline stationary phases:

The chromatographic separation of compounds of mixtures using most of the conventional stationary phases is associated with the polarity of these phases and with the polarity and polarizability of the chromatographed substances as well as the subsequent intermolecular interactions. The mechanism of the chromatographic separation on LCSPs is mostly connected with the differentiation of the structure of molecules of chromatographed substances. The differentiation of the structure of molecules of chromatographed substances results from the ordering of the liquid crystal structure and depends on the type of mesophase and thermodynamic effects of dissolution of solutes in LCSP⁽¹⁴⁾. The use of low-molecular-mass (low-*Mr*) liquid crystals as an analytical tool was first reported in the 1960s by Kelker and Dewar and Schröder chromatography (GC)⁽¹⁵⁾. Liquid crystals exhibit ordered arrangement of molecules in the temperature range of the existence of the mesophase and, hence, found

wide application as stationary liquid phases in gas chromatography for the separation of closely boiling structural isomers. One of the advantages of liquid-crystal phases is their universality, which is due to a drastic change in sorption capacity on changing the phase state of the mesogen⁽¹⁶⁾. Liquid crystals have potential as mesogenic stationary phases which can have extra retention for stationary phases which can have extra retention for some solute molecules by receiving them into an oriented molecular structure. This is their nematic condition, which exists when the solid state melts to give the liquid crystal, up until a higher transition temperature at which it becomes a normal isotropic liquid with the usual randomly oriented molecules. Above this transition temperature, it can still function as a normal liquid phase, but presumably without any extra solute selectivity. The nematic temperature range of some liquid crystal states is quite narrow from just 112 –116°C with cholesteryl acetate, for example⁽¹⁷⁾.

1.5 Factors Effecting the Separation of Mixture Components on LCSP's

1.5.1 Kind of Mesophase of the Liquid Crystal

A nematic liquid crystal would be expected to show a selective affinity for linear molecules, since these should be able to fit better into its “lattice”. On this basis, one might expect columns of nematic to retain selectivity *p*-disubstituted benzene, relative to the ortho and meta isomers.

In general it is assumed that nematic liquid crystals have better separation properties than those of smectics, and that smectics with a low degree of ordering of the mesophase (S_A , S_B) have better separation properties than those of a high degree of ordering⁽¹⁸⁾.

A possible explanation for this feature seems to be that smectic stationary phases may not, like normal liquids, operate under equilibrium conditions. The viscosity of a smectic liquid crystal is extremely anisotropic, being very great for shear across the planes of two-dimensional liquid⁽¹⁹⁾. This is a consequence of the layered structure, the mechanical properties of a smectic phase being similar to those of graphite. It therefore, seems possible that diffusion through a smectic stationary phase may be slow enough to affect the residence time. In this case two factors could operate in the transition from smectic to nematic; the decrease in order would lead to an increase in retention time, while the viscosity effect should lead to a decrease.

1.5.2 Molecular Structure of the Liquid Crystal and of the Chromatographed Substances

A fact of intermolecular reactions or interactions between the liquid crystal and the chromatographed substances is important for the understanding of the phenomena taking place in the chromatographic column. The structure of the molecules and their polarity and polarizability affect, as well as, the solubility of the chromatographed substances in the liquid crystal plays an important influence on the separation.

The process of dissolution dominates in the column during chromatography on a liquid crystal. However, as liquid crystals are usually phases of medium polarity⁽²⁰⁾, the mechanism of the retention of the substances chromatographed on them is accompanied by adsorption. Nevertheless, the contribution of adsorption to the total retention is usually much smaller than that of dissolution.

The properties of the liquid crystal stationary phases depend both on the structure of the main chain of the molecule and on the terminal substituents which strongly affect the polarity of the molecules⁽²¹⁾. However, an equally important or even greater effect on the chromatographic properties of liquid crystals is exerted by the lateral substituents. These substituents not only affect the intermolecular reactions between the liquid crystal and the chromatographed substance but also the liquid crystal – liquid crystal interactions. The lateral substituents also affect the selectivity of the liquid crystal owing to the changes they produce in the distance between its molecules⁽²²⁾. This relates not only to monomers but also polymers⁽²³⁾.

The direct quantitative correlation between the retention of the chromatographed substances and their molecular structure has been studied in several studies⁽²⁴⁾. It is generally assumed that the ratio of the length to the smallest transverse dimension of the molecule, (L/D) (shape factor), is a decisive quantity for the retention of chromatographed substance on liquid crystal stationary phases.

1.5.3 Effect of the Support

Although great attention has been paid to the practical applications of liquid crystal stationary phases, relatively little concern has been devoted to fundamental studies of interactions of the liquid crystals with the surface of the support⁽²⁵⁾.

The effect of the surface of the substrate on which the liquid crystals are deposited in the chromatographic column is rarely accounted for in analytical practice. This is also the case with other stationary phases. However, this effect may be important on separations, although sometimes this effect may be positive⁽²⁶⁾.

The surface of the support or the column wall may not only contribute substantially to the retention of the chromatographed substances but may also influence the orientation of the liquid crystal molecules in various ways. The distribution of the liquid crystal on the support and hence the properties of the whole system are affected not only by the chemical characters (silanized or non-silanized) and porous structure of the support, but also by the amount of the liquid crystal deposited on its surface⁽²⁷⁾. The effect of the support surface also manifests itself by the changes in the phase transition temperatures of the deposited liquid crystal. This effect is related to the conditions under which the column filling is heat treated. During heating, a redistribution of the liquid crystal on the support takes place and as a result the properties of the system are changed⁽²⁸⁾. In some instances conditioning at high temperatures leads to a more advantage order of the liquid crystals in the column. Therefore, if this treatment is not long enough or is conducted at an insufficiently high temperature, sometimes the selectivity of the column may change in the course of its use⁽²⁹⁾. The occurrence of this phenomenon is related to the kind of liquid crystal used and the properties of the surface on which it has been deposited.

The selectivity of the system depend strongly on the kind of support used and on the amount of the liquid crystal deposited on it⁽³⁰⁾. The selectivity also depends on the thickness of the liquid crystal layer on the column wall and the character of the wall surface⁽³¹⁾. The reproducibility and reliability of the retention data are better when the surface of the column wall is inactive and the thickness of the liquid crystal layer is relatively thick (140 nm)⁽³²⁾.

The liquid crystal molecules may be introduced on the support in two states as a film on the surface or in bulk form in the columns. The

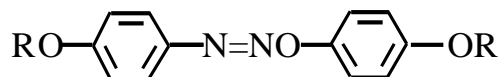
proportion of the two states influences the properties of the system and depends on the kind of the support and the kind and amount of the deposited liquid crystal.

The interaction of the support surface with the liquid crystal stationary phase may give specific effects. One is lowering the melting point of the liquid crystal by 7°C owing to its contact with silanized surface⁽³³⁾. The lowering of the melting point is due to the formation, under the influence of the support, of a layer phase with a crystalline structure different from that of the bulk liquid crystal beyond the support. This effect is not related to the kind of substance chromatographed but depends on the kind and amount of the liquid crystal deposited on the support and is a feature of the liquid crystal–silanized support system. It appears when the amount of the liquid crystal on the support exceeds 3% and manifests itself by a new phase transition not observed thermo–optically. Hence this effect differs from the normal interactions of the liquid crystal with the support at small converges which manifest themselves by a shift of the phase transition connected with the liquid crystal melting point and not by a new phase transition.

The nature of the surface of the support considerably affects the relative retention of the chromatographed substance. On silanized chromosorb P, the relative retention are greater compared with the same, small converges of the supports with the liquid crystal stationary phase on the silanized support. The observed difference decreases with increasing converge of the support.

1.6 Literature Survey

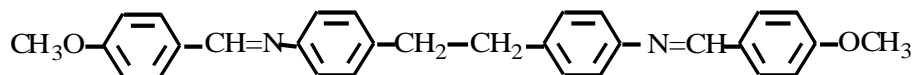
The use of liquid crystals as stationary phase in gas liquid chromatography (GLC) for hydrocarbon analysis began in 1963. Kelker⁽³⁴⁾ used the mesophase 4-4-azoxyphenetol [1] as a liquid stationary phase GLC for the separation of some aromatic compounds and xylene isomers.



[1]

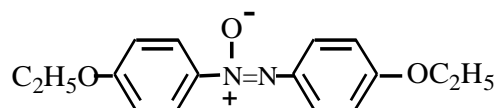
$R = \text{CH}_3, \text{C}_2\text{H}_5, n\text{-C}_6\text{H}_{13}, n\text{-C}_7\text{H}_{15}$.

Pailer and Hlozek⁽³⁵⁾ separated azo heterocyclic compounds α -pinene, eucalyptol, fenchone, 4-terpfenchone, 4-terpineol and α -terpineol using the mesophase bismethoxy-benilidinebitoluidine [2].

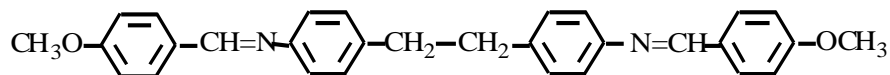


[2]

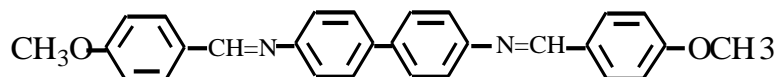
Eight cyclic monoterpene volatile oil constituents of short retention time were studied using three liquid crystals as gas chromatographic stationary phases in packed columns⁽³⁶⁾. Two phases azoxy diphentole [3], bismethoxy-benilidinebitoluidine [4] exhibited a different solute elution sequence after melting and supercooling. The third bis-(methoxy-benilidineanilchloroaniline) [5], did not, but still showed fairly good resolution.



[3]

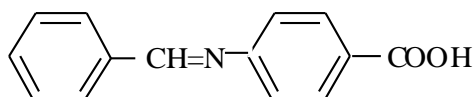


[4]

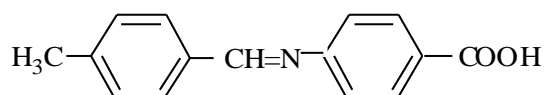


[5]

The chromatographic behavior of liquid crystalline compounds [6,7] as stationary phases for the separation of dimethylphenol isomers was also studied⁽³⁷⁾. It was found that isomer separation was obtained with 20% loading for both liquid crystal materials [6] and [7].

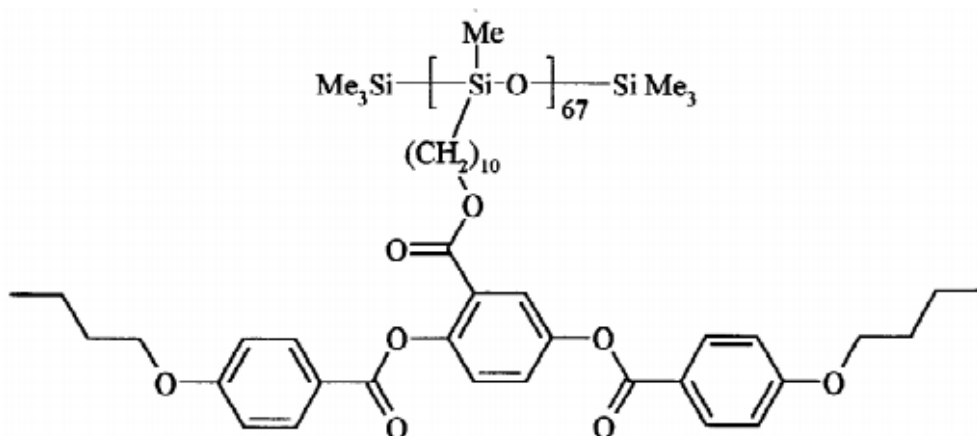


[6]



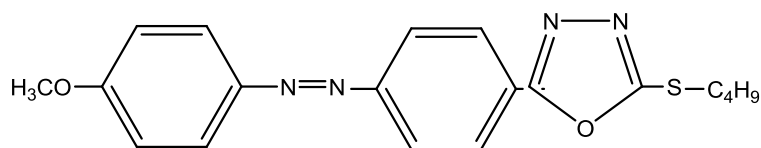
[7]

The molecular diffusion coefficients, D , of naphthalene, fluorene, pyrene and *o*-terphenyl have been determined at different temperatures the nematic phase [8] of the LCP as well as in the isotropic melt by F. Gritti *et al.*⁽³⁸⁾

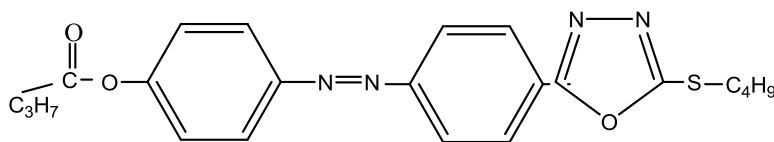


[8]

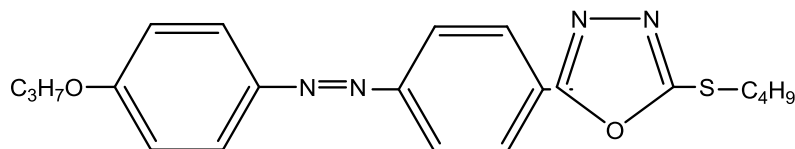
The investigation of the analytical properties of three liquid crystals 5-(4-methoxyphenyl)-azophenyl)-2-butylthio-1,3,4-oxadiazole [9], 5-(4-(carboxymethylphenyl)-azophenyl)-2-butylthio-1,3,4-oxadiazole [10] and 5-(4-(propoxyphenyl)-azophenyl)-2-butylthio-1,3,4-oxadiazole [11] was carried out by gas chromatography using glass capillary columns. For this purpose, 79 solutes belonging to various families were injected. Among these compounds which have different polarities and volatilities, we studied the retention of 16 alkylbenzenes, 7 polar substituted benzenes, 24 polar and non-polar phenols, 12 substituted naphthalenes and 20 constituents of natural products⁽³⁹⁾.



[9]

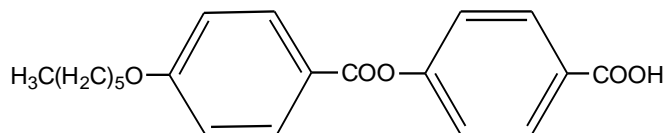


[10]



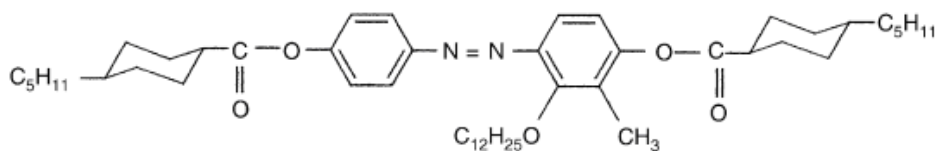
[11]

Zainab M. Abdul Allah *et al.*; studied the chromatographic behavior of Aldehyde and Ketone compounds on two different stationary phases. The first one was liquid crystalline type 1,4-n-Hexyloxy benzoate-4-benzoic acid [12] while the second one was conventional type of stationary phase PEG. Various aldehyde and ketone compounds with different functional groups were analyzed on the two columns in order to emphasize the differences on their retention behaviors⁽⁴⁰⁾.

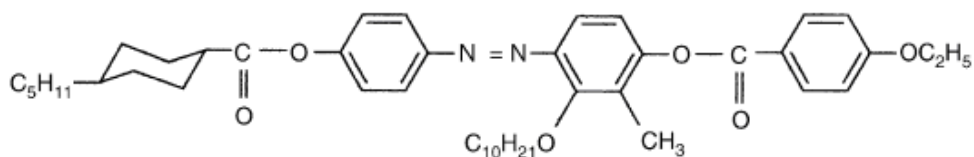


[12]

D. Beläidi *et al.*; studied the analytical performances of two liquid crystals and their mixture as stationary phases in capillary gas chromatography, [13] and [14], for isomeric separation of aromatics, polyaromatics, phenols⁽⁴¹⁾.

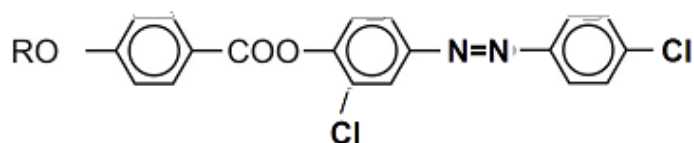


[13]



[14]

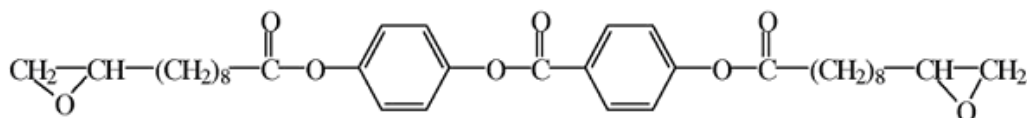
Chauhan. B. C. and Doshi. A. V., synthesized new homologous azoester series entitled p-(p'-n-alkoxybenzoyloxy)-m-Chlorophenylazo-p''-Chlorobenzenes [15] is predominantly nematogenic and partly smectogenic. They noticed that lateral substitution reduces average thermal stability and transition temperatures⁽⁴²⁾.



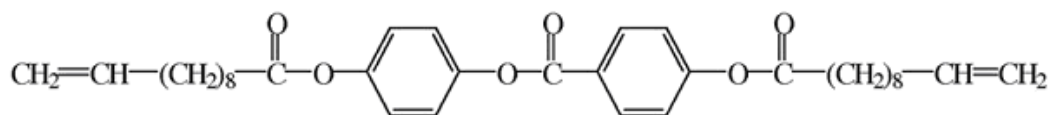
[15]

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

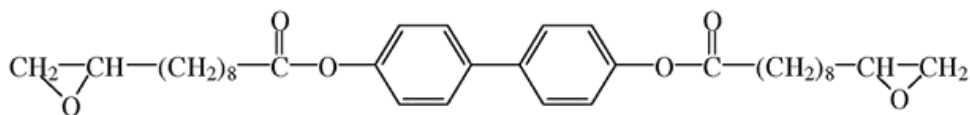
B. Mossety, H. Galina and M. Wlodarska, study the physical properties of the four synthesized compounds with two different functional groups[16], [17], [18] and [19]. It was observed that replacing the functional group in the tails visibly changes the temperatures and sequences of phase transitions⁽⁴³⁾.



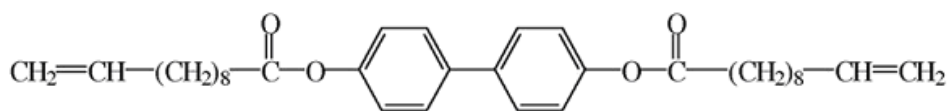
[16]



[17]

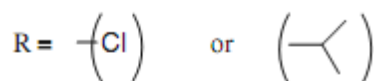
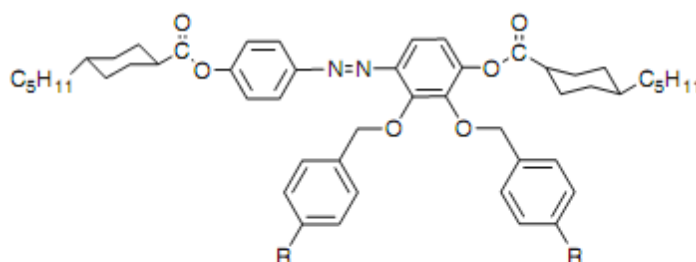


[18]



[19]

Fatiha Athman *et al* ;in their comparative gas chromatographic applications obtain a good efficiency in retention time for the two liquid crystalline phases[20] ,which are able to separate different kinds of solutes such as aromatics, polyaromatics hydrocarbons, phenols, cis and trans isomers and volatile aromatic compounds. The thermal properties were established by differential scanning calorimetry. The optical characterization of the liquid crystal was made by using polarizing optical microscopy⁽⁴⁴⁾.



[20]

1.7 Aim of the work

- Synthesis and characterization of liquid crystalline Schiff bases compounds with related structural properties.
- Elucidated the structure of the synthesized compounds using different spectroscopic technique like FTIR, ^1H NMR, ^{13}C NMR, EI-Mass Spectrometry and CHN analysis.
- Study the properties of liquid crystals compounds using DSC and POM (polarizing optical microscopy).
- Study the properties of gas-chromatographic columns packed with the synthesized liquid crystal compounds.
- Study the interaction and elution characteristics of positional isomers and poly aromatic hydrocarbons by determination the thermodynamic and physical properties.

Chapter Two

Experimental Part

Chapter Two Experimental

2.1 Chemicals

The following chemicals were used directly from their mentioned suppliers, without further purification:

Table (2.1): Chemicals and their manufactures.

Material	Supplied from	Purity %
<i>p</i> -hydroxybenzoic acid	BDH	99
Anisic acid	Fluka	98
<i>p</i> -hydroxybenzaldehyde	BDH	99
Calcium chloride	Hannover	98
Chloroform	Hopkin and Williams	98
Dimethylformamide (DMF)	BDH	98
Ethanol	BDH	99.9
Methanol	BDH	99
Hydrochloric acid	Merck	97
Potassium hydroxide	BDH	98
Pyridine	Merck	98
Thionyl chloride	Merck	97
<i>P</i> -butyl aniline	Sigma	99
Hydro bromic acid	Merck	99
Heptanol	Fluka	98
Octanol	Fluka	98
Chromosorb W/Aw DMCA 60-80 mesh	Merck	99
Sodium bicarbonate	BDH	99
Sulphuric acid	Fluka	98
anhydrous magnesium sulphate	Fluka	97

Continued Table (2.1): Chemicals and their manufactures.

Material	Supplied from	Purity %
Ethyl bromide	BDH	98
Propyl bromide	BDH	98
Butyl bromide	BDH	98
Pentyl bromide	BDH	98
Hexyl bromide	BDH	98

2.2 Instruments and Equipments

● *Fourier Transform Infrared Spectrometer (FTIR)*

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

● *Proton Nuclear Magnetic Resonance Spectrometer (^1H & ^{13}C NMR)*

^1H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were recorded in DMSO using a Bruker 300 MHz NMR Spectrometer with Trimethylsilane (TMS) as the internal standard. The analyses were carried out in University of Ahal AL-Bait, Jordon.

● *Mass Spectrometer (GCMS)*

Electron ionization mass spectrum (EI-MS) was recorded using a Shimadzu GCMS-QP2010 Ultra/SE mass spectrometer operating at 70 eV ionizing energy. The analyses were carried out in Al-Mustansirya University.

● *Elemental Analysis (CHN)*

Microanalyses were carried out on Euro EA Elemental analyzer A- 3000. The analyses were carried out in Al-Mustansirya University.

● *Melting Points*

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

● *Differential Scanning Calorimeter (DSC)*

All DSC measurements were made with a *Perkin-Elmer DSC-6* in unsealed aluminum pans in a dry nitrogen atmosphere with an empty aluminum pans as reference. Indium (156.6 °C) of purity 99.999 standards was used for temperature calibration. These analyses were carried out in University of Ahal AL-Bait, Jordon.

● *Hot-stage Polarizing Microscope*

Liquid crystalline properties were investigated by POM using a (Meiji MT9000) Polarizing Optical Microscope attached to a INSTRON 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 analyses were carried out in Al-Nahrain University.

● *Gas Chromatograph (GC)*

The gas chromatograph used in this work was *Pye-Unicam*, England, which has been equipped with flame ionization detector. The analyses were carried out in ministry of technology and Sciences.

● *Rotary Evaporator*

The rotary evaporator used in evaporating processes of organic solvents, was Buchi 461.

- ***Vacuum Pump***

Vacuum pump type Edwards, 50 Hz, (England), was used for packing the columns.

- ***Shaker***

Shaker type national, 110V, (Japan) was used in packing the columns.

- ***Flow meter***

The flow rate of the carrier gas has been measured using soap bubble flow-meter.

- ***Hydrodynamics Syringe***

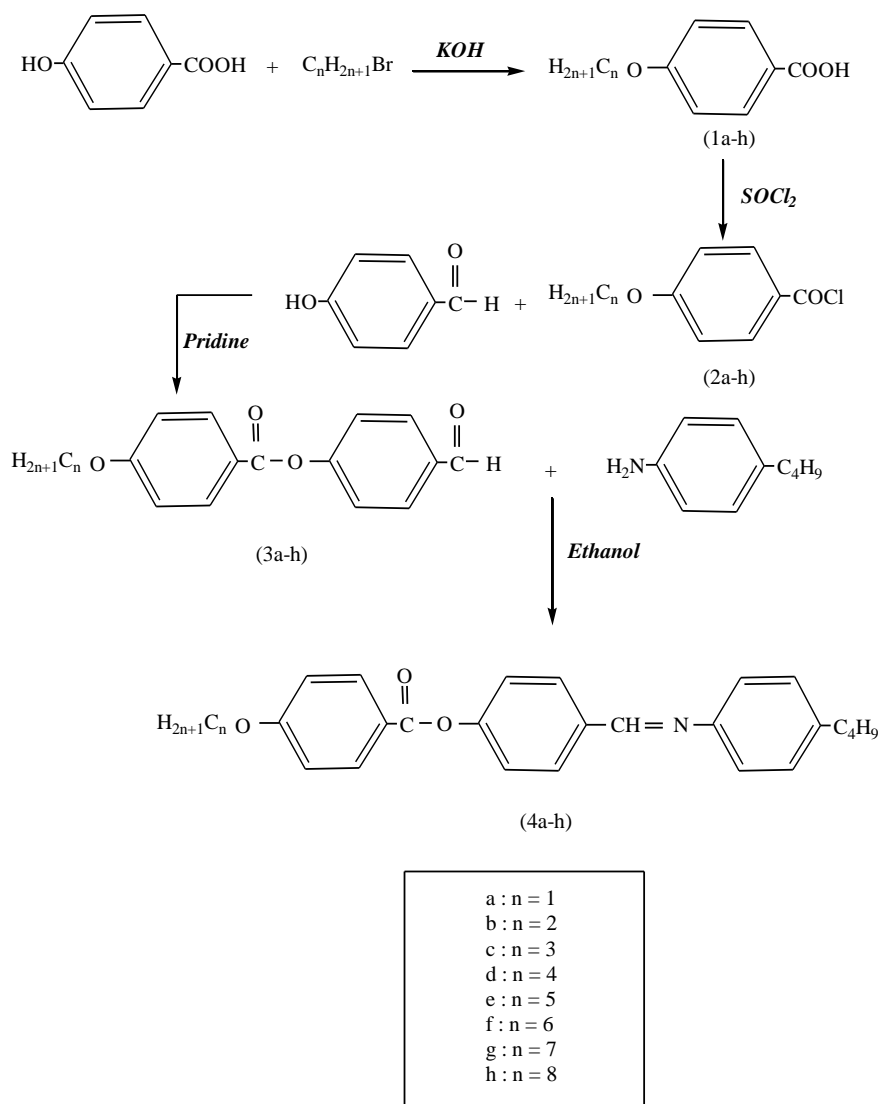
Samples were injected using a calibrated 1 ml hydrodynamics syringe type Hamilton 7002 NCH.

- ***Column***

The dimensions of the glass column are 1.75 m in length, 3.0 mm internal diameter (i.d).

2.3 Preparation Procedures of N- $\{(n\text{-alkyloxy-4''-bezoyloxy})\text{-4''-benzylidene}\}\text{-4-butyl aniline (4a-h):$

The intermediate and title compounds were prepared according to the following scheme:



Scheme (2.1): The synthetic pathway for the titled compounds.

2.3.1 Preparation of *n*-alkyl bromide⁽⁴⁵⁾

To 71 mL of 48% hydrobromic acid contained in a 500 mL round-bottomed flask, 16 mL of concentrated sulfuric acid was added in portions with shaking and cooling (some hydrogen bromide may be evolved). A 0.5 mol of 1°-alcohol was added, followed by 2.75 mL of H₂SO₄ in several portions. The reaction mixture was heated under reflux until the appearance of two phases or for 5 hours. 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% HCl and water, and

then the organic layer was separated and washed with an equal volume of 10% sodium bicarbonate solution and water. Then the organic layer was separated and the anhydrous magnesium sulphate was added to remove the water completely from the organic layer. The solution was filtered to give n-alkyl bromide.

2.3.2 Preparation of *p-n-alkyloxy benzoic acids*⁽⁴⁶⁾

p-Hydroxy benzoic acid (1.38 g, 0.1 mole) corresponding alkyl halides (0.12 mole) and KOH (0.25 mole) were dissolved in 10 ml methanol and reaction mixture was refluxed for 3 to 4 hr. 10% aqueous KOH solution (20 ml) was added and refluxing continued for further two hours to hydrolysis any ester formed. The solution was cooled and acidified with HCl to precipitate. The corresponding alkyloxy acids of the higher members the total refluxing period was extended to 7 to 8 hours. The alkoxy acids were crystallized from ethanol or acetic acid.

2.3.3 Preparation of *p-n- alkyloxy benzoyl chlorides*⁽⁴⁶⁾

p-n-alkyloxy benzyl chlorides were prepared by refluxed the corresponding *p-n* alkoxy benzoic acids (0.01 mole) with freshly distilled thionyl chloride (5 ml) in water bath till evolution of hydrogen was gas ceased. The excess thionyl chloride was distilled off under reduce pressure using water pump. The acid chlorides left behind were directly used for further reaction without purification.

2.3.4 Synthesis of 4-[4'-*n-alkyloxybezoyloxy*]benzaldehyde⁽⁴⁷⁾:

(0.01 mole, 1.22 g) of 4-hydroxybenzaldehyde and (0.01 mole) of 4-*n*-alkyloxybezoylchloride, along with 10 ml of dry pyridine were stirred for three hours in an ice bath. The mixture was poured onto cold water acidified with HCl and filtered. The product was washed with cold water.

2.3.5 Synthesis of *N*-{(*n*-alkyloxy-4'-bezoyloxy)-4'-benzylidene}-4-butyl aniline⁽⁴⁸⁾:

A mixture 4-[4'-*n*-alkyloxybezoyloxy]benzaldehyde (0.01 mole) and 4-*n*-butylaniline(0.01 mole, 1.6 mL), were dissolved in 30 ml of absolute ethanol are refluxed for three hours. The mixture was cooled to room temperature and filtered. The yellow product was recrystallized from ethanol until its transition temperature remained constant

2.4 preparation Stationary phases⁽³⁷⁾

The stationary phases were prepared by coating each of the liquid crystal compounds on chromosorb W/AW 60 – 80 mesh size, solid support. Different weights of the liquid crystal compounds (2g) and (8g) of the solid support were used, to prepare liquid crystal stationary phase with coating percentage 20%. The liquid crystal compounds were first dissolved in 50 mL chloroform; the solid support was then added slowly to the solution with stirring to form slurry. The stirring was continued for 72 hours to ensure complete homogeneity and uniform coating of the liquid crystal on the solid support particles. The solvent was then evaporated using rotary evaporator. The resulting stationary phase was then dried at 100°C for 2 hours.

2.5 Packing and Conditioning Process⁽⁴⁹⁾

The Pyrex glassy column was packed by 20% (loading percent) of the liquid crystal stationary phases. The methodology of packing process is described below.

A piece of glass wool was inserted at one end of the column, where it was connected to a vacuum pump. A plastic funnel was fixed on the top of the other end. After drying of the prepared stationary phases, it

was added onto the column through the funnel to ensure a complete and homogeneous packing as shown in Figure (2.1). Vibration was used in addition to the vacuum pump. This would reduce the porosity between particles of stationary phases and eliminate all dead spaces in the column. After completion of the packing process, a glass wool was then inserted at the other end of the column.

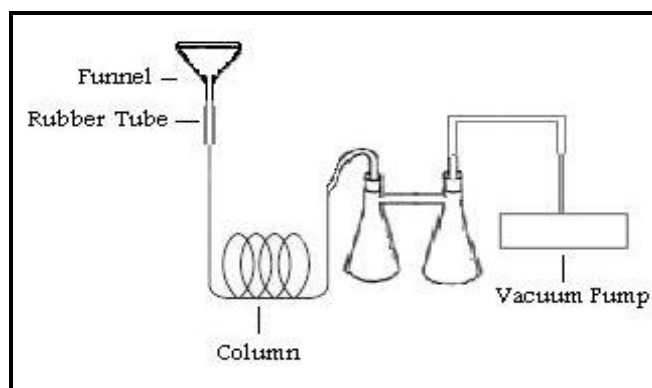


Figure (2.1): Packing assembly layout.

The prepared columns were conditioned as follows: the column was maintained at (10–15°C) above the maximum temperature at which the column was used, with a stream of nitrogen gas passing through the column. The column was kept for 48 hours at these conditions. This column conditioning was vital to remove the remaining solvent, humidity and any other volatiles.

The above conditioning procedure was repeated every day for about 1 hour prior analysis to ensure good reproducibility as indicated from the base line stability. In addition, the column was weighted before and after packing to ensure complete and consistent packing without losing the stationary phase.

Each stationary phase was examined separately by increasing column temperature 10 or 20°C between each run to cover the whole

transition temperature ranges of the specific liquid crystal. A 1 μL of each sample was introduced to the system by direct injection, with a flow rate 20 mL/min.

A soap-bubble flow meter was used to measure the flow rate of the carrier gas; by connecting it to the outlet from the detector.

Chapter Three

Result & Discussion

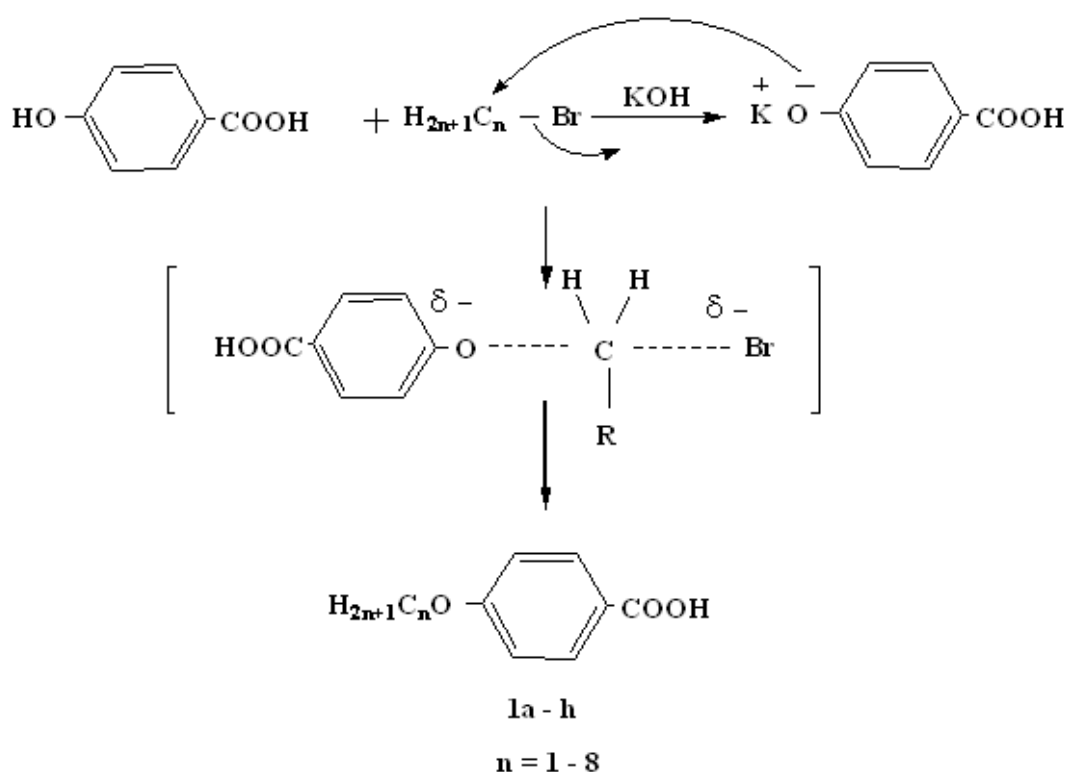
Chapter Three

Results and Discussion

3.1 Synthesis and Characterization of *N*-{(*n*-alkyloxy-4'-bezoyloxy)-4'-benzylidene}-4-butyl aniline (**4a-h**):

These compounds were prepared as previously shown in scheme (2.1).

3.1.1 4-*n*-alkyloxybenzoic acid (1a-h**):** These compounds were prepared by the reaction of 4-hydroxy benzoic acid with *n*-alkyl halide in boiling alcohol⁽⁴⁶⁾ according to bimolecular nucleophilic substitution mechanism (S_N2) as follow:



The observed and reported⁽⁷⁾ melting point of these compounds were tabulated in Table 3.1. They were also identified by FTIR spectroscopy.

Figure (3.1) shows the FTIR spectrum of **1e** using KBr disc which showed the disappearance of the phenolic hydroxyl group and the appearance of bands at 2991.7 and 2895.2 for C–H aliphatic stretching. The spectrum give bands at 3326.9, 1705.4 (the characteristic band for carboxylic acid O – H stretching and C = O stretching), the out of plane bending of *para* disubstituted benzene ring occurs at 844.6.

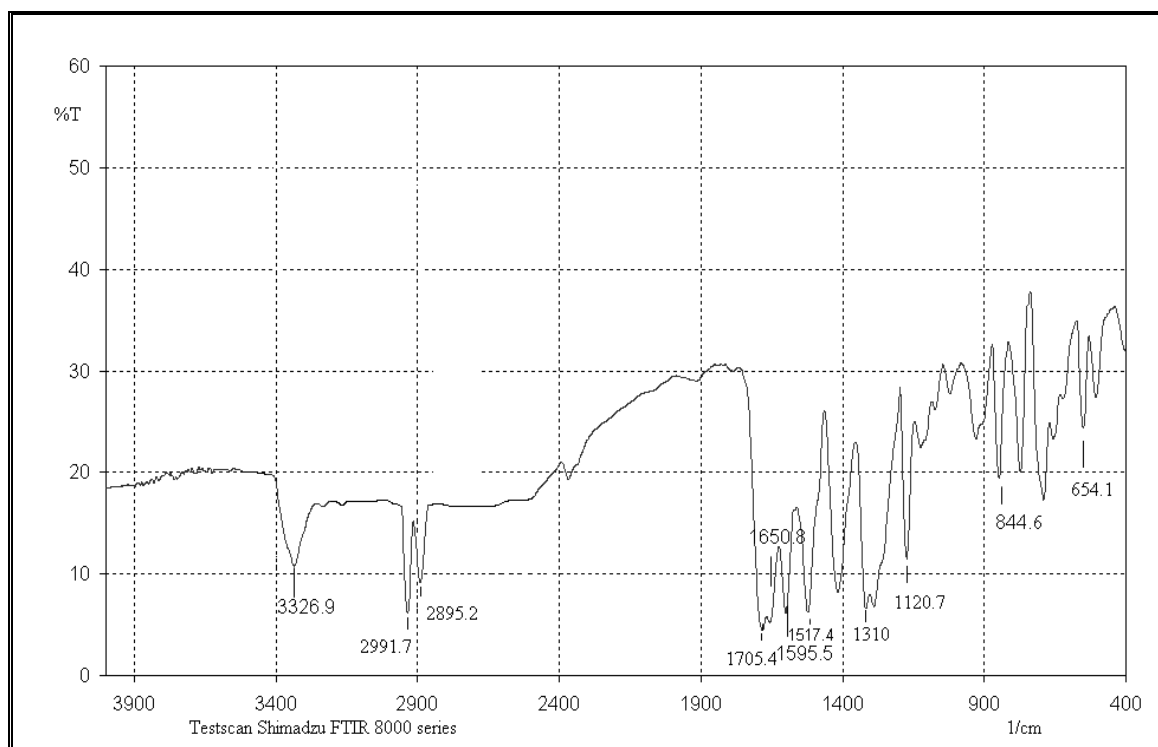
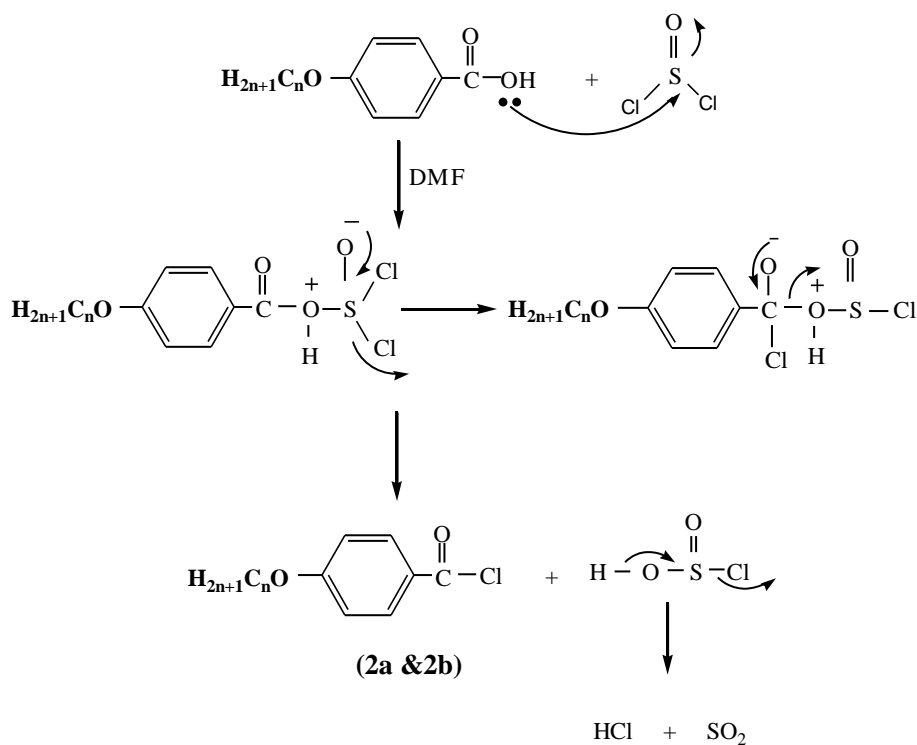


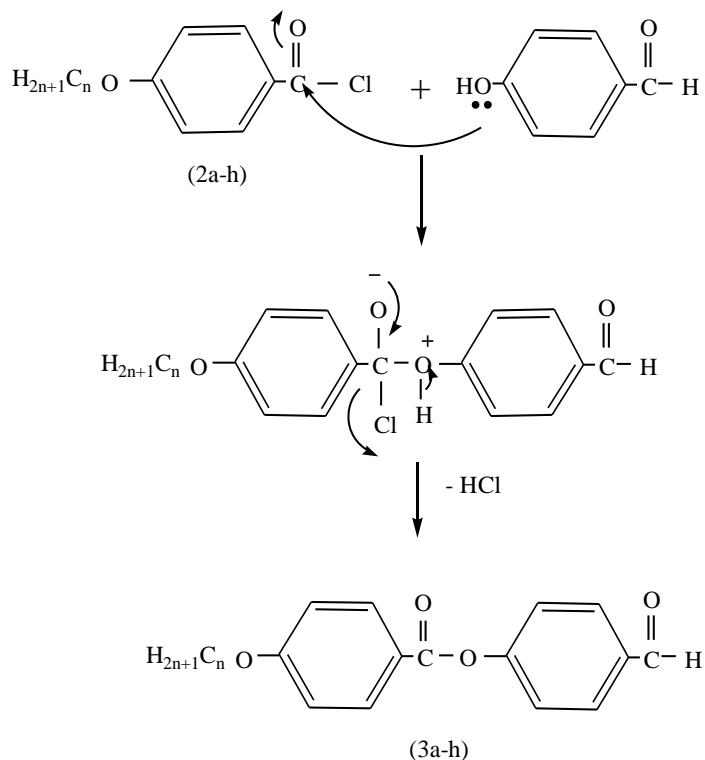
Figure (3.1): FTIR spectrum of 4-pentyloxybenzoic acid (1e)

3.1.2 4-Alkyloxybenzoyl chloride (2a-h): These compounds were prepared by the internal nucleophilic substitution (S_Ni) reaction between the prepared 4-alkyloxybenzoic with thionyl chloride as show below:



3.1.3 4-[4'-n-alkoxybenzoyloxy]benzaldehyde (3a-h):

The reaction of the synthesized 4-alkoxybenzoylchloride with 4-hydroxybenzaldehyde will give 4-[4'-n-alkoxybenzoyloxy]benzaldehyde (3a-h) the reaction were carried out through nucleophilic substitution (tetrahedral mechanism) by the two step: firstly, the addition of nucleophile (O – H) to the carbon of the carbonyl group, secondly the elimination of the leaving group (Cl).



The products were verified by FTIR, ^1H NMR, ^{13}C NMR spectroscopy and CHN analysis. The FTIR spectrum of compound 3d is shown in Figure (3.2). The appearance of bands at 2800.2 cm^{-1} , 2728.5 cm^{-1} and 1728.1 cm^{-1} that are due to proton and carbonyl group stretching of aldehyde. A new stretching bands appeared at 1747.3 cm^{-1} and 1253.6 cm^{-1} which could be attributed to $\text{C}=\text{O}$ stretching of ester and $\text{C}-\text{O}-\text{C}$ stretching. Out of plane bending of para-substituted benzene ring was appeared at 848.6 cm^{-1} . Table (3.1) summarizes the FTIR spectral data of compounds 3a-h.

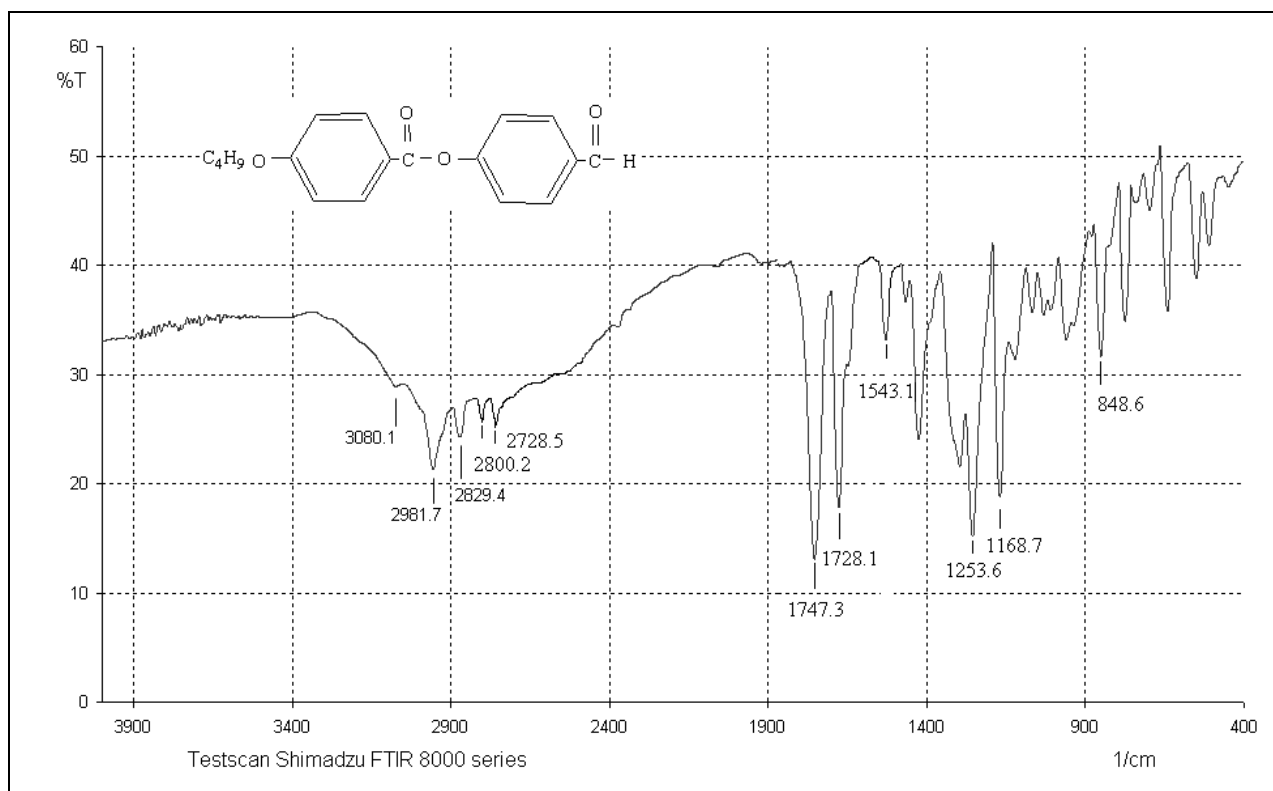


Figure (3.2): FTIR spectrum of 4-[4'-n-butyloxybenzoyloxy]benzaldehyde (3d).

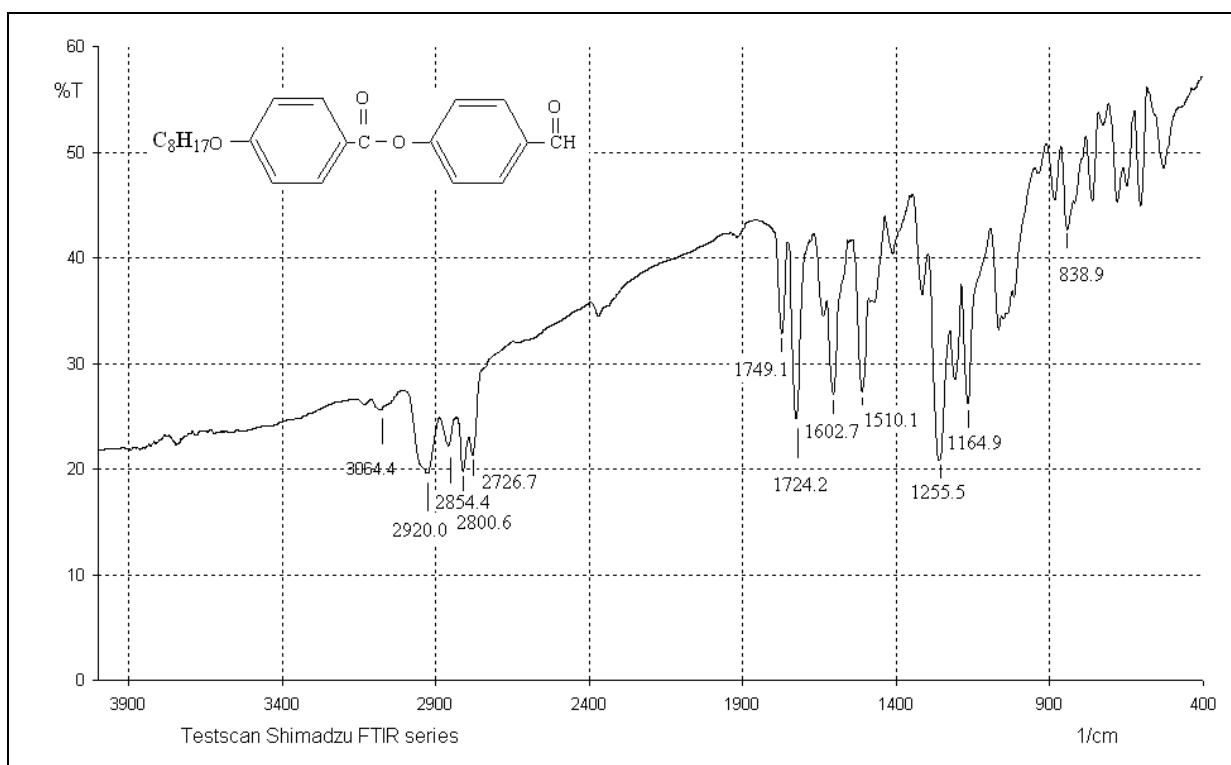


Figure (3.3): FTIR spectrum of 4-[4'-n-octyloxybenzoyloxy]benzaldehyde (3h).

Table (3.1): FTIR spectral data for 4-[4'-n-alkoxybenzoyloxy]benzaldehyde (3 a-h).

Comp. No.	RO- group	ν C-H Aro. cm^{-1}	ν C-H Aliph. cm^{-1}	ν O=C-H cm^{-1}	ν C=O cm^{-1} Ald.	ν C=O cm^{-1} Ester	ν C=C cm^{-1}	γ -out of plane bending
3a	-OCH ₃	3078.9	2904.5,2856.3	2803.1 & 2722.4	1722.1	1741.8	1590.9	841.2
3b	-OC ₂ H ₅	3025.3	2953.8,2839.0	2800.3 & 2725.6	1728.5	1747.2	1583.1	838.3
3c	-OC ₃ H ₇	3096.4	2935.5,2875.7	2804.0 & 2723.1	1728.3	1736.5	1547.9	944.9
3d	-OC ₄ H ₉	3080.1	2981.7,2829.4	2810.2 & 2724.5	1738.1	1747.3	1534.1	848.6
3e	-OC ₅ H ₁₁	3076.5	2974.0,2864.1	2801.1 & 2725.4	1730.6	1745.4	1551.8	830.2
3f	-OC ₆ H ₁₃	3075.3	2931.7,2843.7	2800.6 & 2729.0	1728.9	1744.0	1572.9	832.8
3g	-OC ₇ H ₁₅	3081.2	2927.8,2847.4	2803.5 & 2721.9	1727.2	1742.9	1600.5	845.0
3h	-OC ₈ H ₁₇	3064.4	2920.2 , 2854.4	2800.6 & 2726.7	1724.2	1749.1	1602.7	838.9

The ^1H NMR spectrum of **3c** is shown in Figure (3.4). The following characteristic chemical shifts (DMSO, ppm) were appeared: a doublet of doublets leaning on each other at δ 7.9 – 8.1 that could be attributed to the four protons of the alkyloxy phenyl ring (Hb, Hc), while the other two doublet at δ 6.9- 7.4 suggesting the attribution of the four protons of the benzene nucleus attached to the aldehyde group (Hd, He).

The spectrum also showed a singlet at δ 9.2 that could be assigned to the aldehydic proton (Ha)⁽⁵⁰⁾. A three proton triplet at δ 4.1 ppm could be assigned to the $-\text{OCH}_2$ group (Hf). The ^1H NMR spectrum also showed three protons triplet at δ 0.94 could be assigned to CH_3 protons (Hh) which was due to the splitting caused by the adjacent CH_2 protons. A two protons (Hg) quintet at δ 1.3- 1.7 due to CH_2 were also observed in this spectrum. The ^1H NMR spectrum is in agreement with the proposed structure.

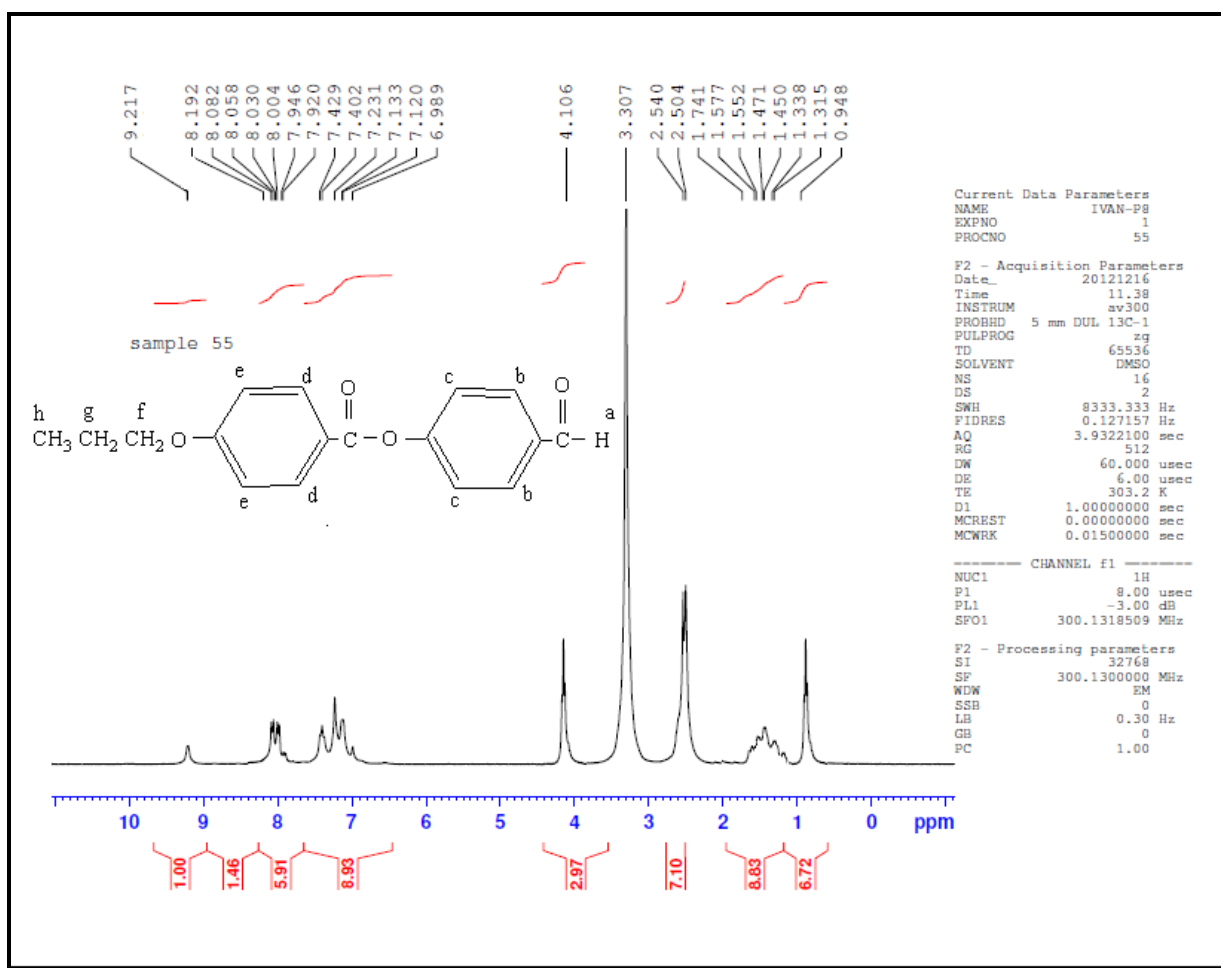


Figure (3.4): ^1H NMR spectrum of 4-[4'-n-propyloxybenzoyloxy]benzaldehyde (**3c**).

The structures of the synthesized compounds are elucidated by using ^{13}C NMR analysis technique as well. The representative compound for elucidate is 3c Figure (3.5).

The signal appears at the most low field region at = 191.9 ppm is due to the carbonyl of aldehyde group, C=O at C1. This followed by the signal appeared at δ = 163.6 ppm is assigned to carbonyl of ester group, C=O at C6. This is because oxygen is the electronegative atoms in the compound which causing the electron pulling away from the carbon and shifted both C1 and C6 to the most down field in spectrum. The signals appeared to be at the most high field in the spectrum is the more shielded carbon. At the region from δ = 13.5-31.1, C13, C12 ppm, the carbons that contributed to these signals at the region is mainly the carbon atoms that attached to the alkyloxy chain. Signal appears at δ =67.7 ppm was attributed to carbon attached to oxygen atom, C11. The signals appeared at the low field region in between δ = 114.7-163.4 ppm in fact attributed by the aromatic carbons as follow: δ = 114.7 ppm (C9), δ = 120.2 ppm (C4), δ = 122.3 ppm (C7), δ = 131-133 ppm (C2, C3 and C8), δ = 155.3 ppm (C5), δ = 163.4 ppm (C10)⁽⁵¹⁾.

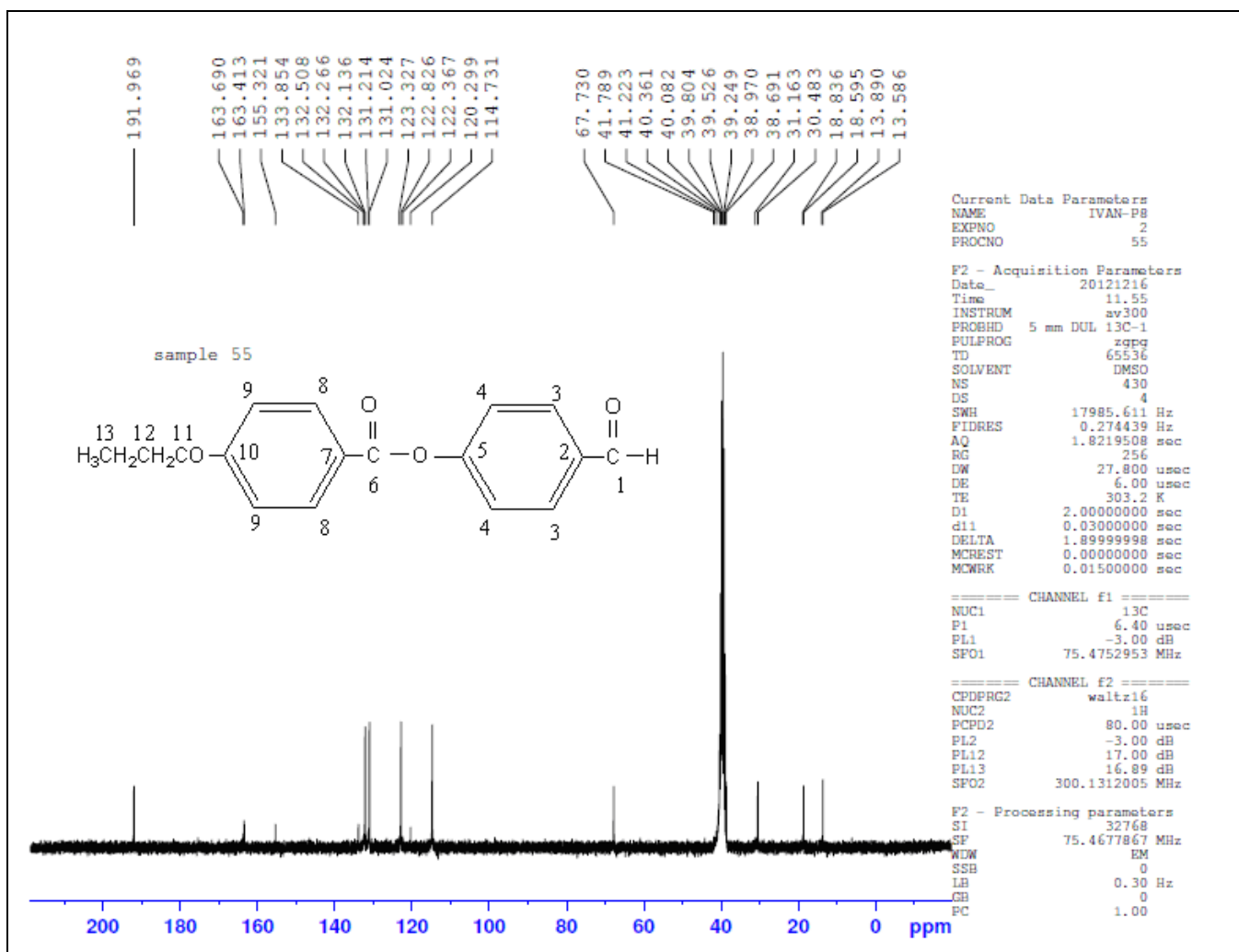
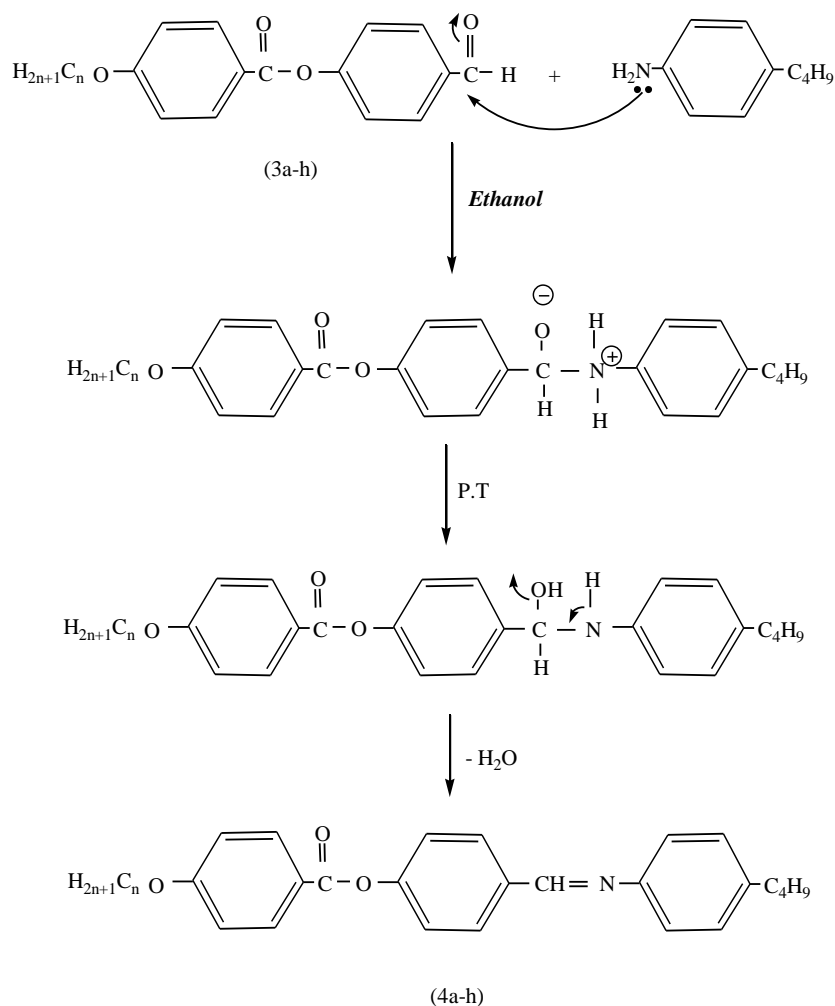


Figure (3.5): ^{13}C NMR spectrum of 4-[4'-n-propyloxybenzoyloxy]benzaldehyde (3c).

3.1.4 N-{(n-alkyloxy-4''-benzoyloxy)-4'-benzylidene}-4-butyl aniline (4a-h):

The N-{(n-alkyloxy-4''-benzoyloxy)-4'-benzylidene}-4-butyl aniline 4a-h were prepared by the condensation of 4-[4'-n-alkyloxybenzoyloxy]benzaldehyde (3 a-h) with 4-n-butylaniline in the presence of ethanol as solvent.



The products were verified by FTIR, ¹HNMR, ¹³CNMR, mass spectroscopy and CHN analysis. The FTIR spectrum of compound 4e is shown in Figure (3.6). The disappearance of bands at 2810 cm⁻¹, 2724 cm⁻¹ and 1738 cm⁻¹ that are due to proton and carbonyl group stretching of aldehyde and appeared band at 1620 cm⁻¹ that due to C = N of imine group. Table (3.2) summarizes the FTIR spectral data of compounds 4a-h. Table (3.3) summarized the elemental analysis data for some synthesized compounds.

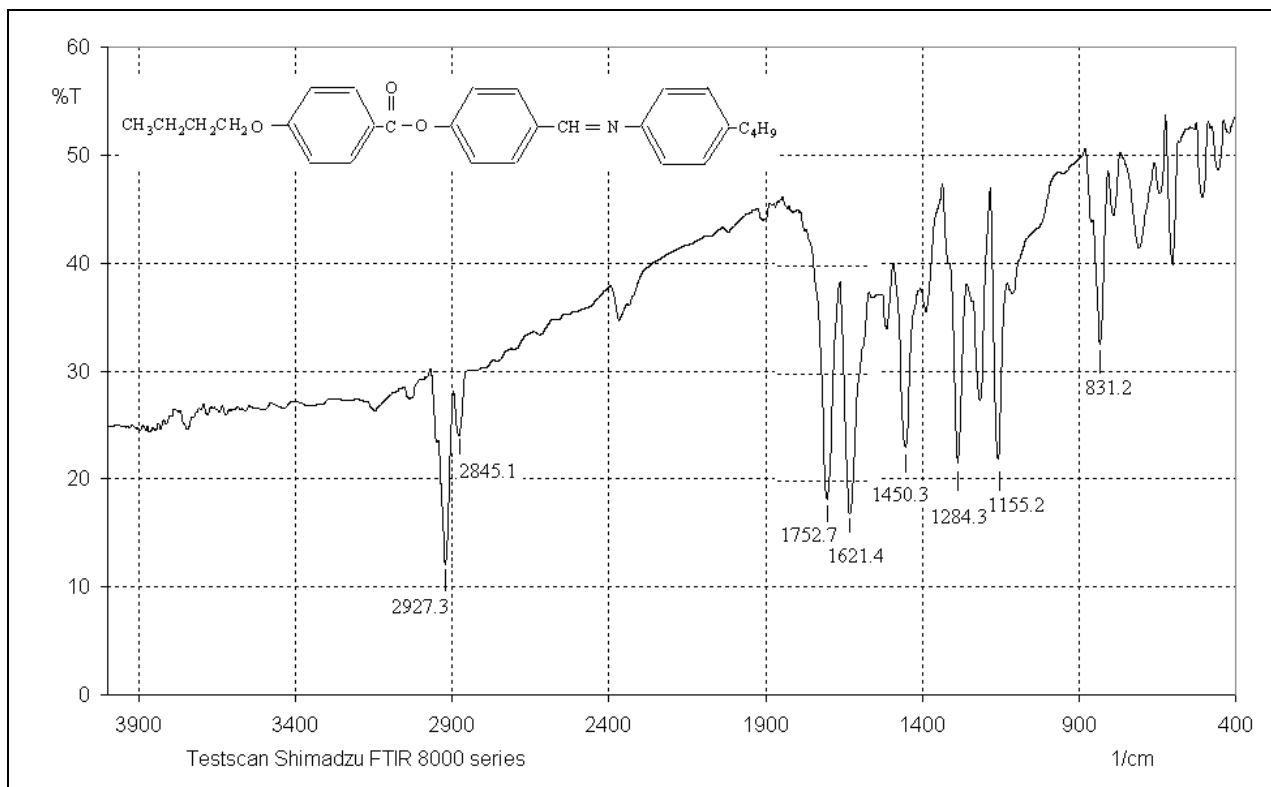


Figure (3.6): FTIR spectrum of *N*-(*n*-butyloxy-4'-benzoyloxy)-4'-benzylidene-4-butyl aniline (4d).

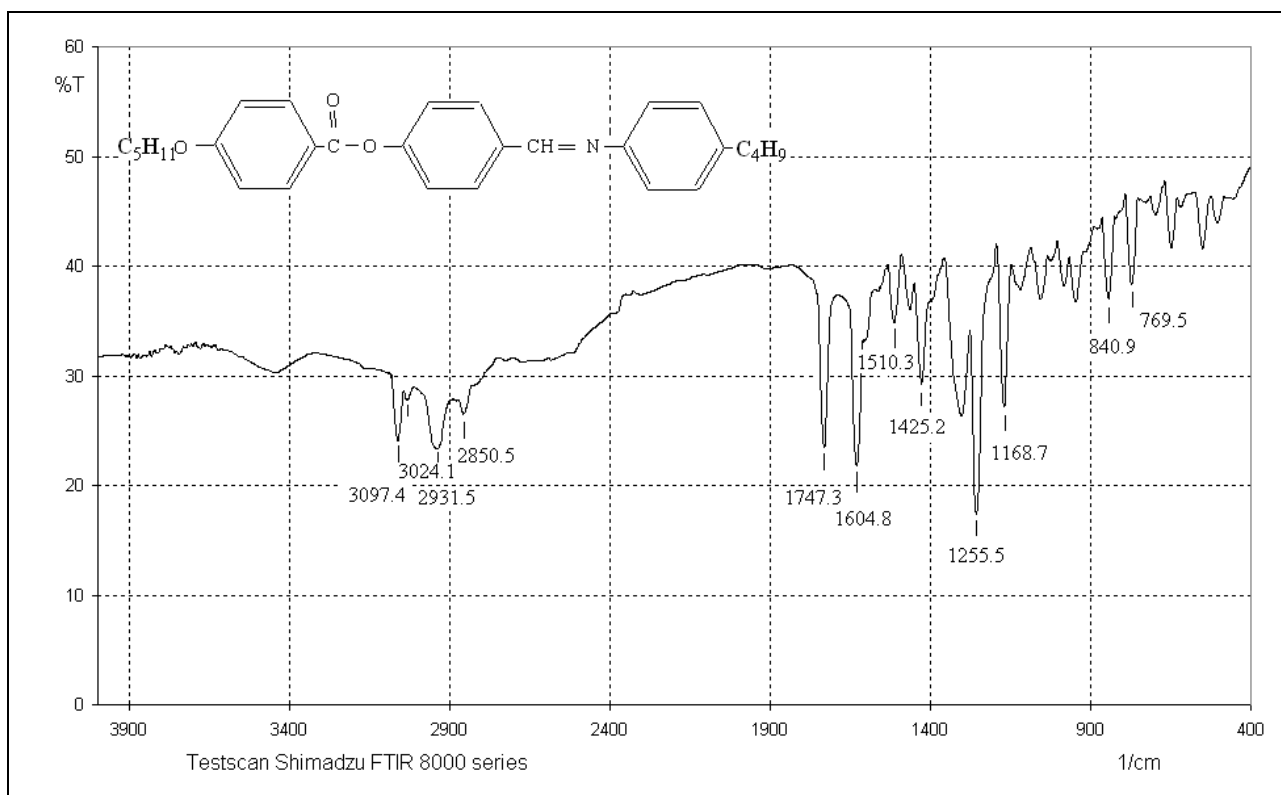


Figure (3.7): FTIR spectrum of *N*-(*n*-pentyloxy-4'-benzoyloxy)-4'-benzylidene-4-butyl aniline (4e).

Table (3.2): FTIR spectral data for *N*-{(*n*-alkoxy-4'-bezoyloxy)-4'-benzylidene}-4-butyl aniline (4a-h).

Comp. No.	RO-group	ν C-H Aro. cm^{-1}	ν C-H Aliph. cm^{-1}	ν H - C = N cm^{-1}	ν C = N cm^{-1}	ν C=O cm^{-1} Ester	ν C=C cm^{-1}	γ -out of plane bending
4a	-OCH ₃	3025.3	2953.8,2839.0	3100.3	1618.2	1742.9	1572.9	841.1
4b	-OC ₂ H ₅	3076.5	2974.0,2864.1	3097.5	1620.0	1735.2	1551.8	843.0
4c	-OC ₃ H ₇	3035.0	2943.7,2863.1	3090.4	1623.1	1747.0	1534.6	835.5
4d	-OC ₄ H ₉	3080.1	2927.3,2845.1	3110.0	1621.4	1752.7	1530.3	831.2
4e	-OC ₅ H ₁₁	3024.1	2935.7,2848.7	3097.4	1604.8	1747.3	1581.5	840.9
4f	-OC ₆ H ₁₃	3081.3	2968.1,2852.4	3102.6	1628.8	1738.1	1562.3	835.9
4g	-OC ₇ H ₁₅	3046.9	2942.5,2876.2	3099.5	1622.4	1743.2	1549.6	840.9
4h	-OC ₈ H ₁₇	3062.1	2984.3,2861.4	3097.6	1626.2	1744.0	1575.2	838.7

Table (3.3): Percentage yields and analytical data for synthesized compound.

Compound	Yield (%)	Formula	% Found (% Calc.)		
			C	H	N
3a	84.5	C ₁₅ H ₁₂ O ₄	70.42(70.31)	4.51(4.68)	-
3d	88.3	C ₁₈ H ₁₈ O ₄	72.53(72.48)	5.99(6.04)	-
3h	80.2	C ₂₂ H ₂₆ O ₄	74.43(74.57)	7.28(7.34)	-
4a	67.9	C ₂₅ H ₂₅ O ₃ N	77.58(77.51)	6.34(6.45)	3.58(3.61)
4b	78.6	C ₂₆ H ₂₇ O ₃ N	77.89(77.80)	6.69(6.73)	3.45(3.49)
4c	77.0	C ₂₇ H ₂₉ O ₃ N	78.11(78.07)	6.88(6.98)	3.32(3.37)
4d	75.3	C ₂₈ H ₃₁ O ₃ N	78.41(78.32)	7.17(7.22)	3.29(3.26)
4e	76.9	C ₂₉ H ₃₃ O ₃ N	78.64(78.55)	7.39(7.44)	3.10(3.16)

The ¹HNMR spectrum of compound 4d, is shown in Figure (3.8). The following characteristic chemical shifts (DMSO, ppm) were appeared: The most upfield triplet signals appeared at $\delta = 0.94$ ppm was caused by the two methyl protons at the end of the long alkyl and alkyloxy chain which the three protons are chemically and magnetically equivalent. These six hydrogens in the methyl groups (H1 & H8) are the most highly shielded type of proton and therefore shown the NMR signal at the lowest chemical shift. Meanwhile, the multiplet signals at $\delta = 1.31 - 1.47$ ppm were owned to the methylene protons, (H2 & H7) present. As quintet signals appeared at $\delta = 1.57 - 1.74$ ppm is typically due to four proton, (H3 & H6). This because based on the (n+1) rules, which 2 adjacent protons from the H2 and H4, H5 and H7 respectively affecting the splitting and induced the quintet splitting. For the most intense singlet triplet signal at approximately $\delta = 3.94$ ppm is due to the two protons,

H5. Whereas at the region $\delta = 2.50$ ppm, signal were detected. This is mainly caused by the H4 because the two adjacent protons from the H3 has obeyed the (n+1) rules and give rise to triplet splitting.

As for the most deshielded singlet signal appeared at $\delta = 8.66$ ppm region was due to proton of imine linking group, H9⁽⁵¹⁾. The signal appeared as singlet is mainly because there are no adjacent protons. Existence of sp² hybridisation in double bond and electron withdrawing effect of nitrogen atom shifted the H9 to the most downfield. There were signals appeared at $\delta = 6.98$ -8.19 ppm region are mainly due to the presence of three aromatics rings.

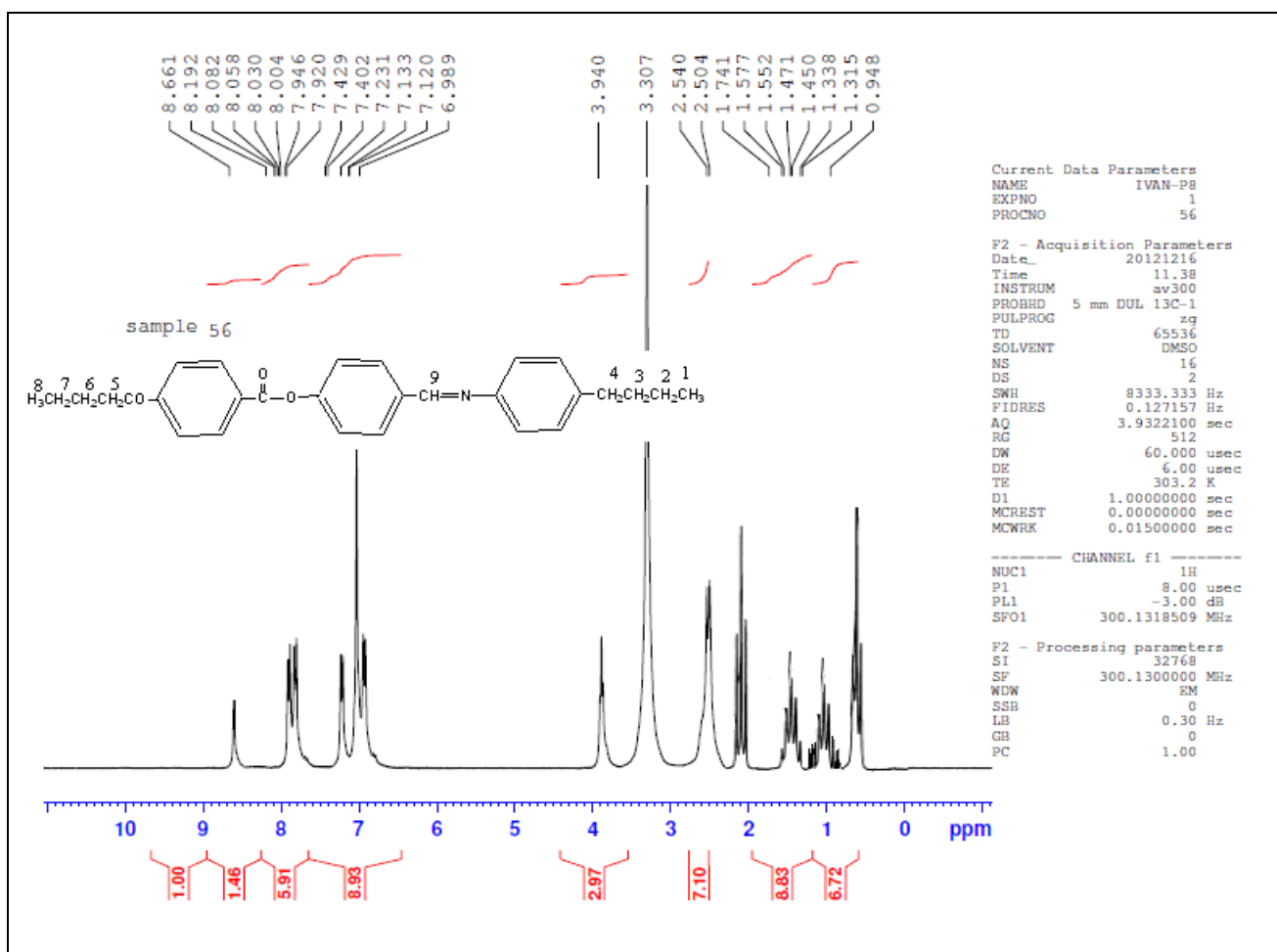


Figure (3.8): ¹H NMR spectrum for compound N-*(n*-butyloxy-4'-bezoyloxy)-4'-benzylidene}-4-butyl aniline (4d).

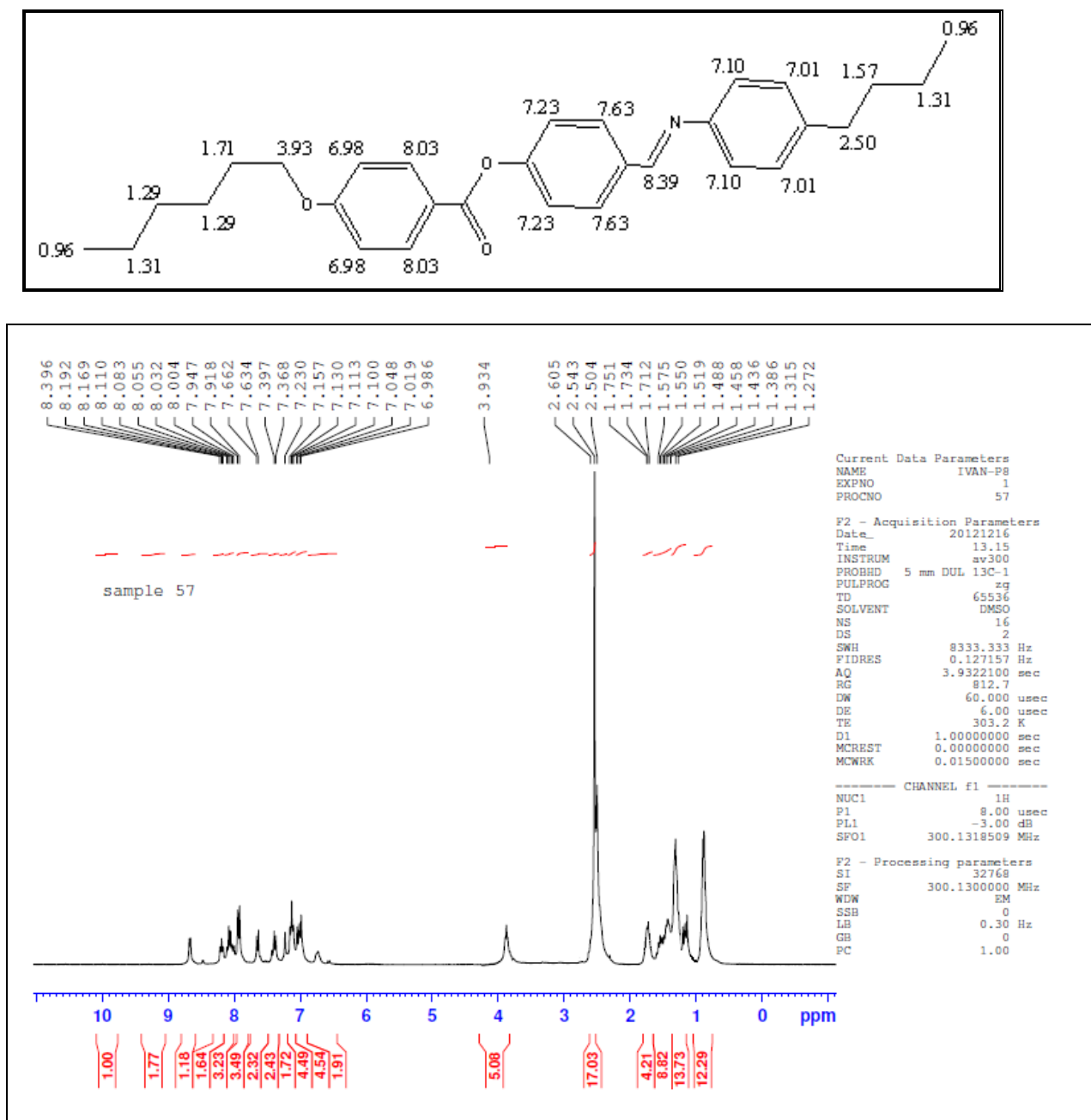


Figure (3.9): ¹H NMR spectrum for compound N-{(n-hexyloxy-4'-bezoyloxy)-4'-benzylidene}-4-butyl aniline (4f).

The ¹³C NMR spectrum of compound 4d, is shown in Figure (3.10). The following characteristic chemical shifts (DMSO, ppm) were appeared:

The signal appears at the most low field region at $\delta = 191.9$ ppm is due to the carbonyl group of ester, C=O at C10. This followed by the signal appeared at $\delta = 163.6$ ppm is assigned to imine carbon, C=N at C9. This is because both oxygen and nitrogen are the electronegative atoms in the compound which

causing the electron pulling away from the carbon and shifted both C10 and C9 to the most down field in spectrum. The signals appeared at the low field region in between $\delta = 113.9\text{--}163.1$ ppm in fact attributed by the aromatic carbons. The aromatic carbon attached to a double bond and thus deshielded due to sp^2 hybridization and diamagnetic anisotropy. Amongst all the aromatic carbons, C11, C14, C15, and C18 are having the lowest intensity. This is mainly due to these four carbons are ipso carbon which is without hydrogen as the substituent directly attached⁽⁵²⁾. Thus, these four carbons have relatively weak signals due to a long relaxation time and a weak nuclear overhauser enhancement (NOE) effect⁽⁵³⁾.

The chemical shift at $\delta = 63.6$ ppm is assigned to C5. This carbon is relatively low field compared to long alkyl chain because it is directly bonded to an oxygen atom which can act as an electron withdrawing atom and causes the chemical shift lower compared to the alkyl chain.

The signals appeared to be at the most high field in the spectrum is the more shielded carbon. At the region from $\delta = 13.7\text{--}40.8$ ppm, the carbons that contributed to these signals at the region is mainly the carbon atoms that attached to the alkyl chain.

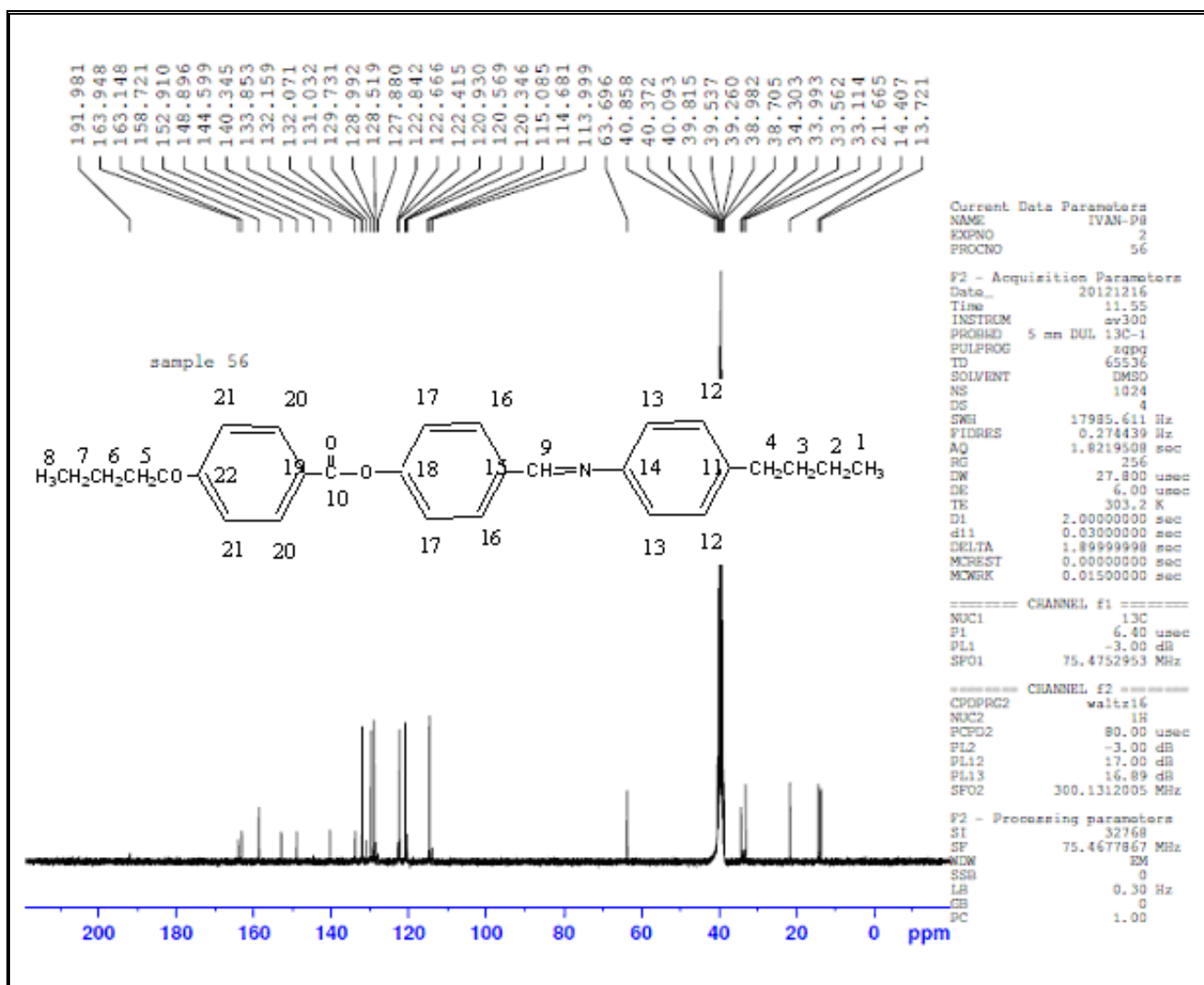


Figure (3.10): ^{13}C NMR spectrum for compound *N*-{(*n*-butyloxy-4'-bezoyloxy)-4'-benzylidene}-4-butyl aniline (**4d**).

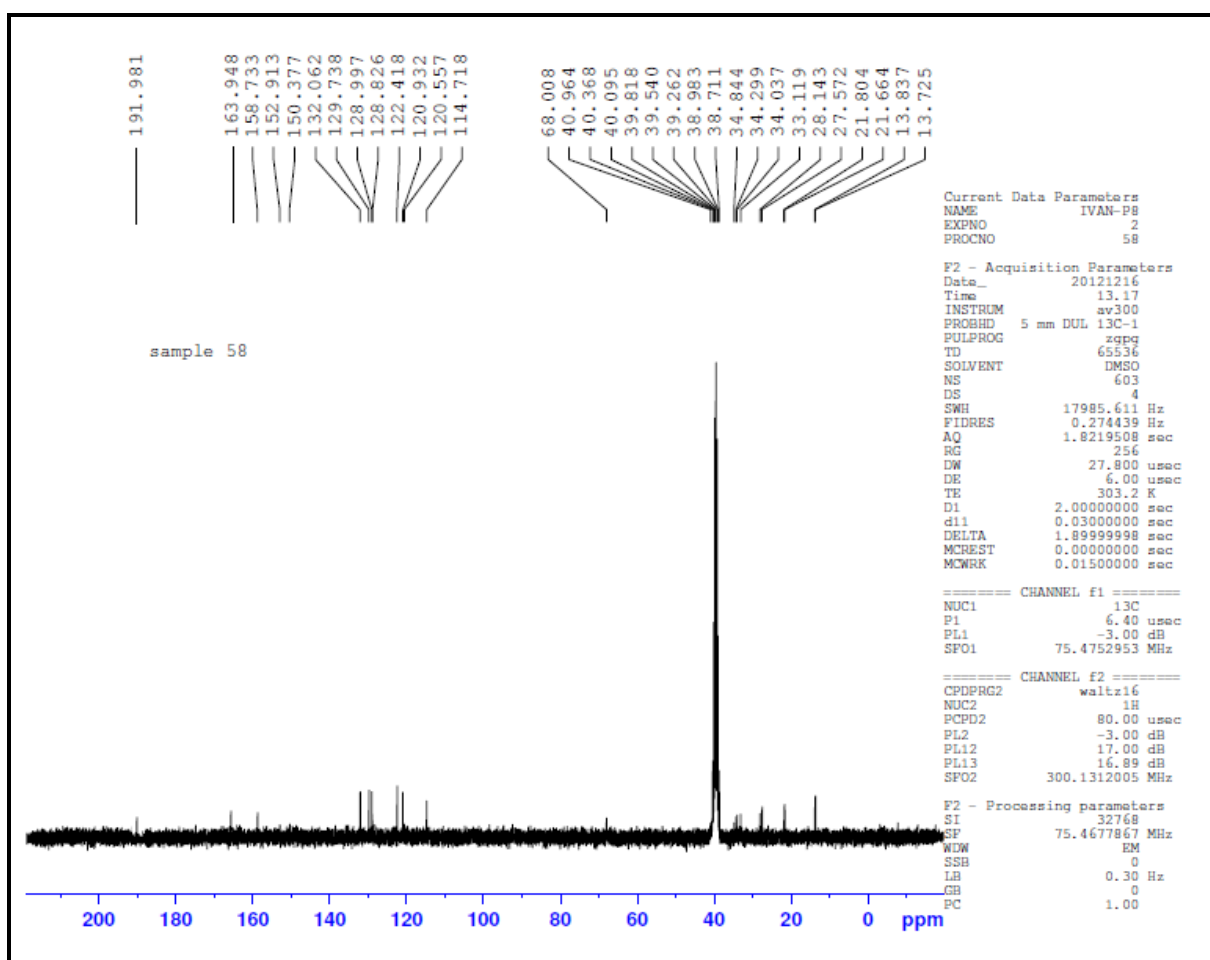
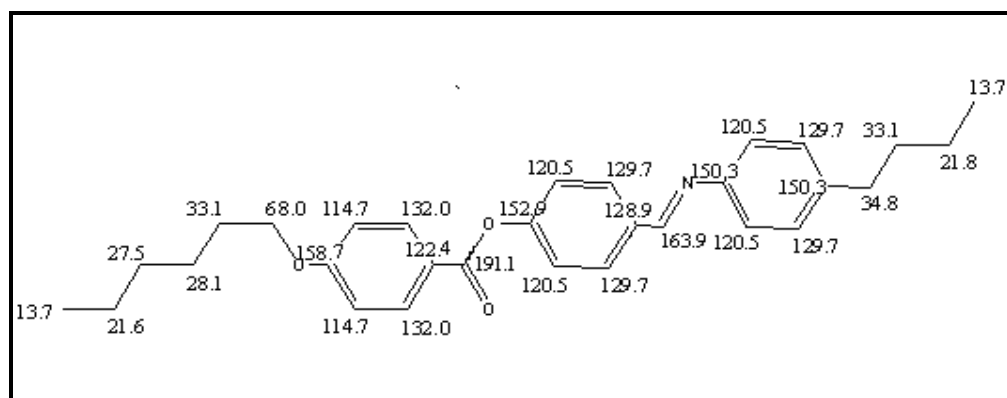


Figure (3.11): ^{13}C NMR spectrum for compound *N*-{(*n*-hexyloxy-4'-benzoyloxy)-4'-benzylidene}-4-butyl aniline (4f).

The structure and the purity of the synthesized compound 4d are elucidated by using EI-Mass Spectrometry analysis technique. The structure of the respective compound, *N*-{(*n*-butyloxy-4'-benzoyloxy)-4'-benzylidene}-4-butyl aniline (4d) Figure (3.12) with the m/z values and the proposed

fragments of the compound are shown in scheme (3.2). Molecular ion peak, M^+ for 4d is distinguishable. It appears at $m/z=429$ with a molecular formula of $(C_{28}H_{31}NO_3)$.

First of all, the α -cleavage on the molecular ion produces the acylium and the phenoxy⁽⁵¹⁾ ion respectively (I) and (II). As the result of cleavage, the peak found at $m/z=177$ in the spectrum of 4d, represents the stable acylium in which the relative abundance is 70. As consecutive fragmentation, acylium ion undergoes β -cleavage by eliminating the alkyl chain, $[C_4H_9]^+$. It is giving rise to the highest relative abundance base peak at $m/z=121.0$. The m/z value for that particular peak is 43.1 which indicated the presence of $C_3H_7^+$.

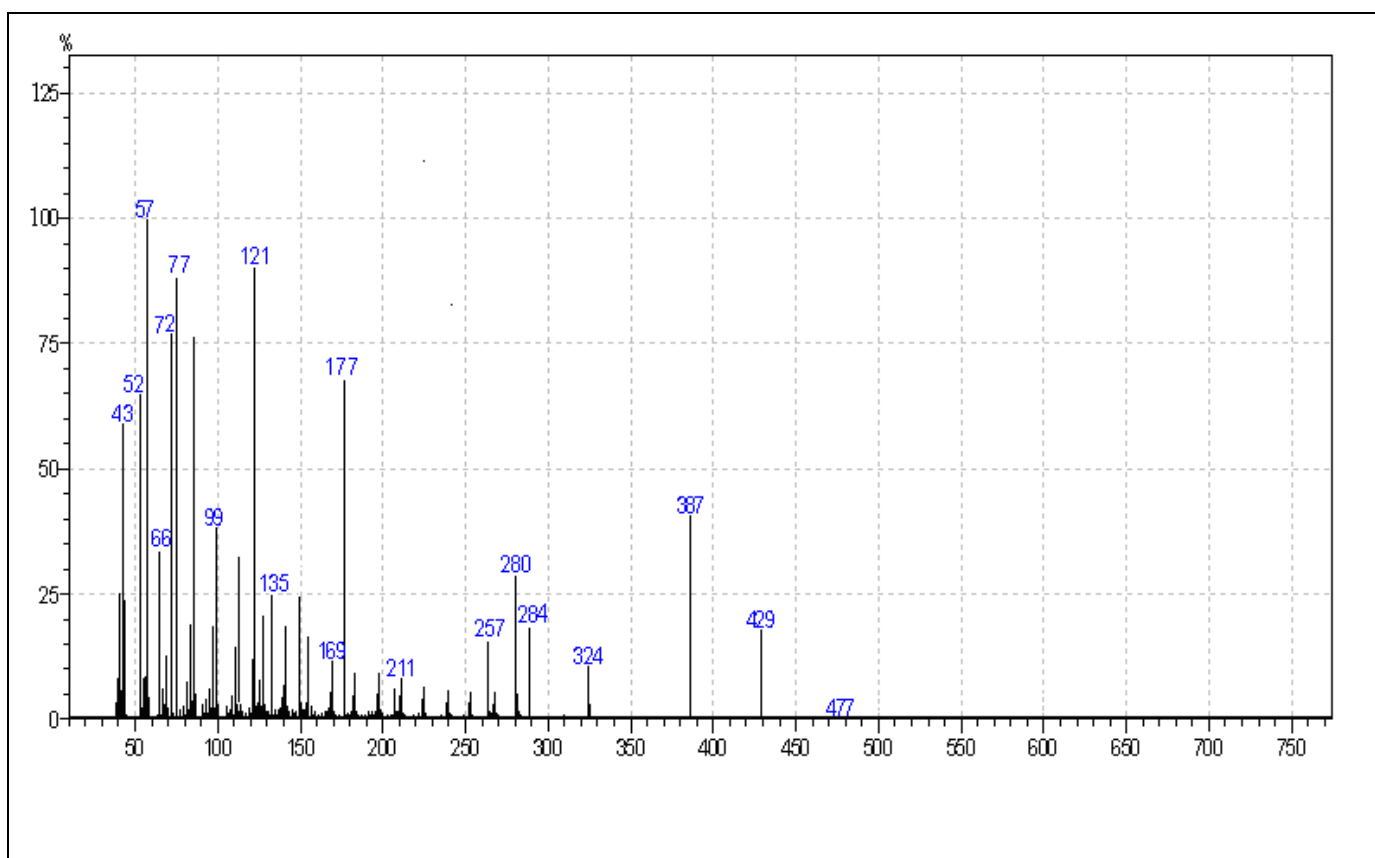
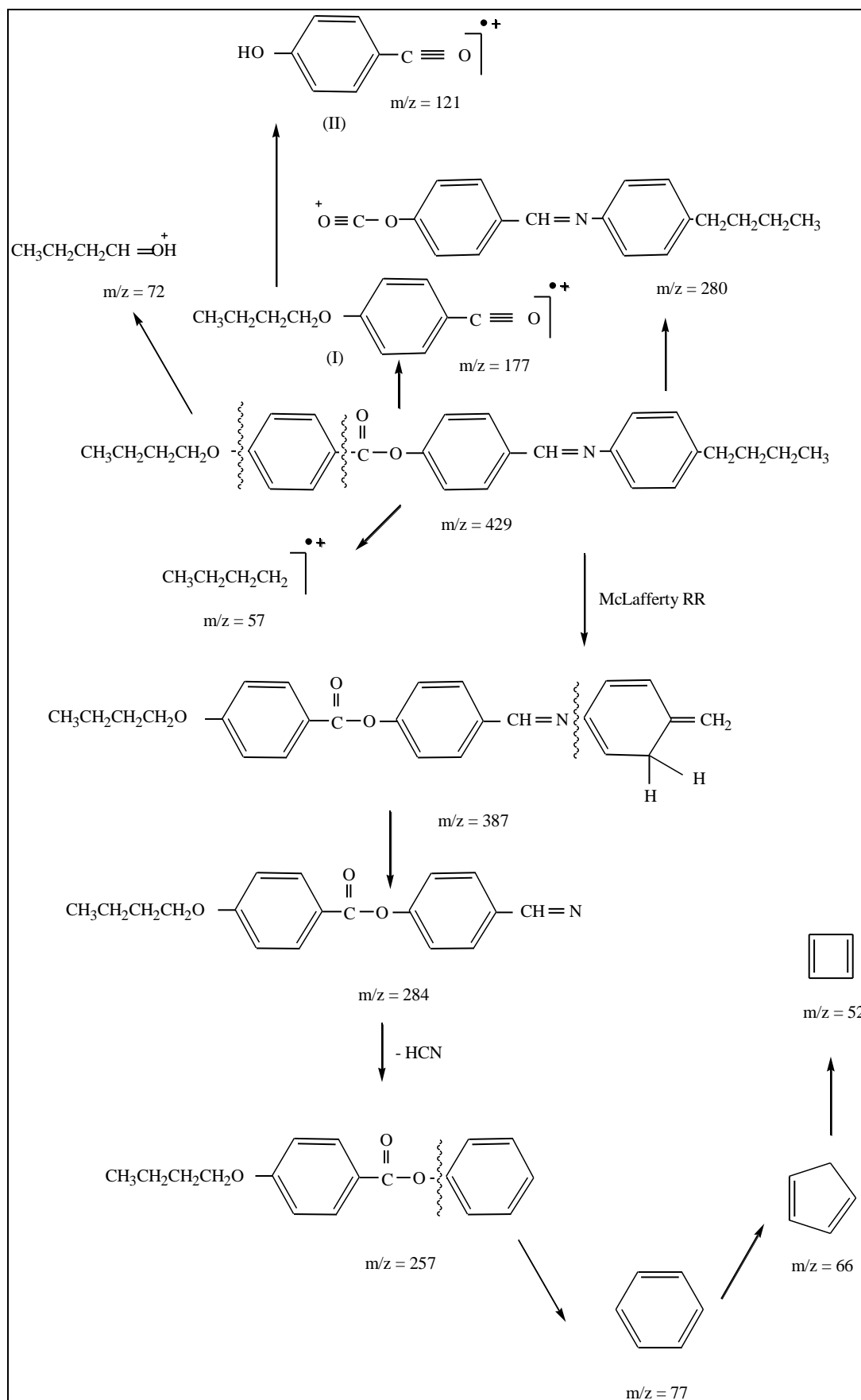


Figure (3.12): EI-MS Spectrum of compound *N*-{(*n*-butyloxy-4'-bezoyloxy)-4'-benzylidene}-4-butyl aniline (4d).



Scheme (3.1): The fragmentation modes for compound *N*-{(*n*-butyloxy-4'-bezoyloxy)-4'-benzylidene}-4-butyl aniline (**4d**).

3.2 Mesomorphic Properties Analysis *N*-{(*n*-alkyloxy-4'-bezoyloxy)-4'-benzylidene}-4-butyl aniline (4a-h).

3.2.1 Differential Scanning Calorimetry (DSC) Thermogram Analysis of 4e and 4h:

DSC analyses have been carried out for compounds 4d and 4h. The thermogram of the representative compounds, are shown in Figure (3.13) and Figure (3.14):

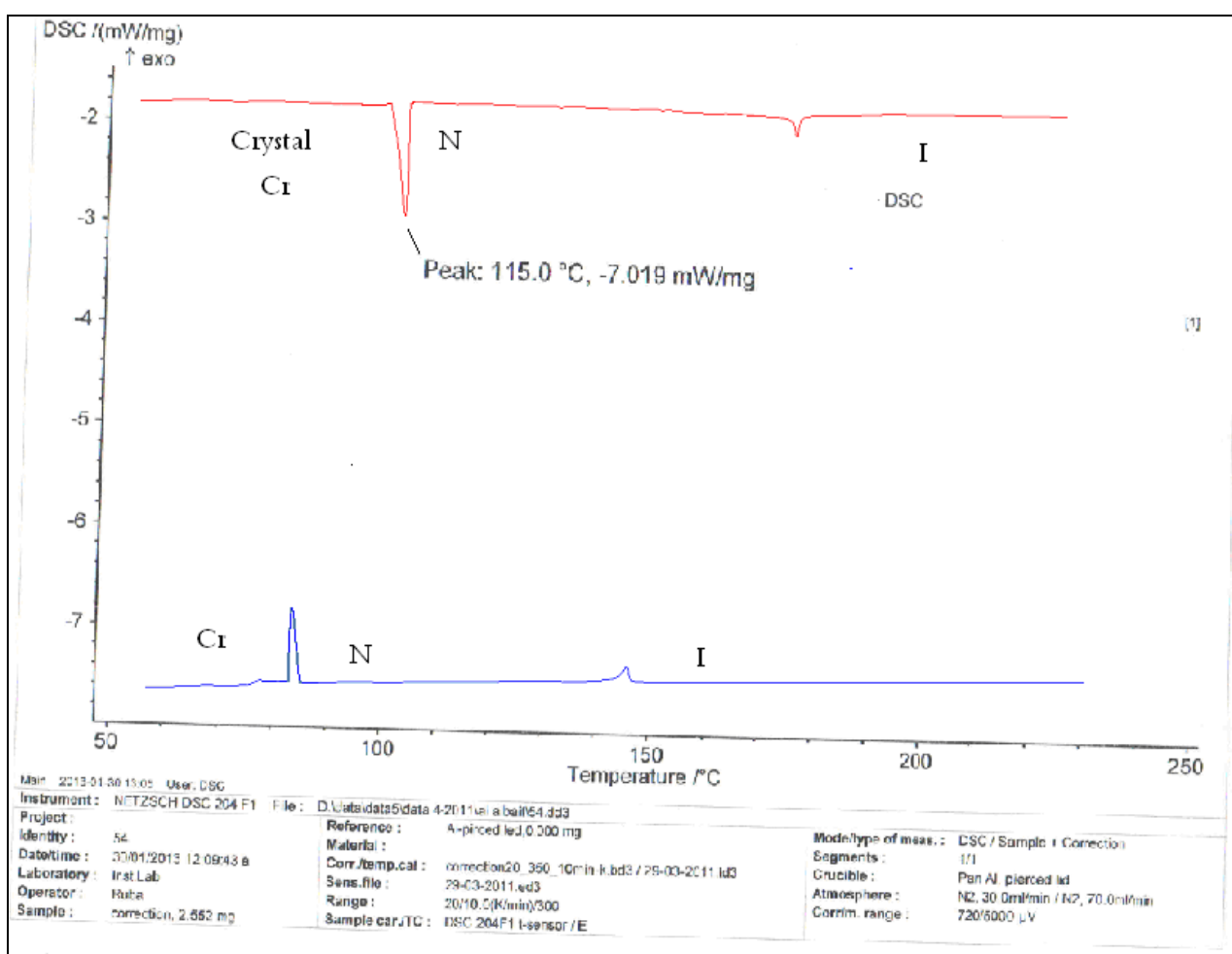


Figure (3.13): DSC thermogram of *N*-{(*n*-butylloxy-4'-bezoyloxy)-4'-benzylidene}-4-butyl aniline (4d)

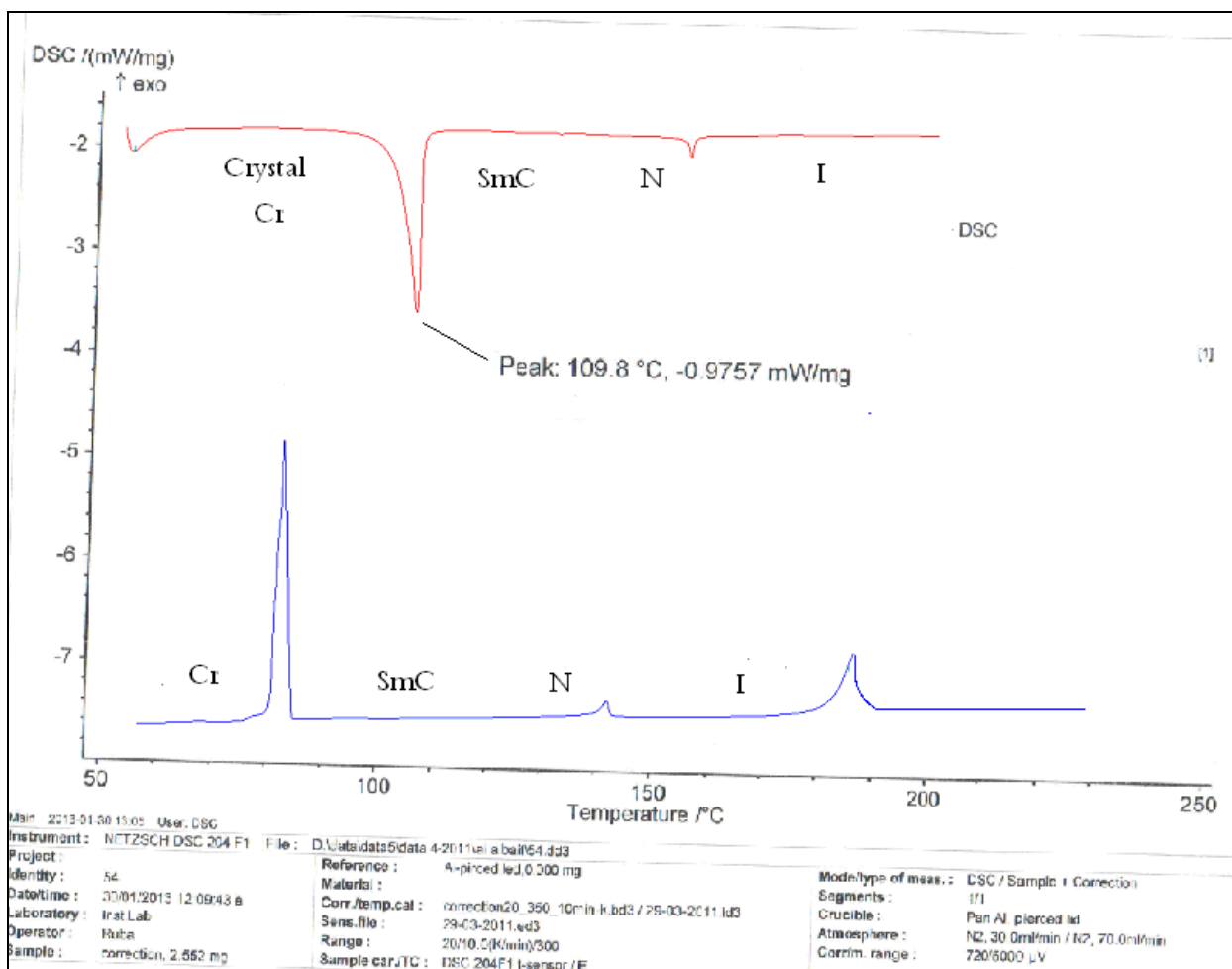


Figure (3.14): DSC thermogram of N-((n-octyloxy-4'-bezoyloxy)-4'-benzylidene)-4-butyl aniline (4h)

Upon heating of compound 4d, two peaks can be observed in the heating cycle at 115.0°C where crystal is melted to a nematic (N) phase liquid crystal. Further heating, to 182.43°C, isotropic (I) liquid formed. All of the peaks indicated the endothermic energy absorbed the crystal molecules to break the intermolecular forces between molecules apart. It can be observed that the enthalpy change of Cr – N phase transition is smaller than the N – I phase transition.

This can be explained because due to liquid crystal are more similar to liquid, lesser latent heat is needed to convert liquid crystal to liquid compared to solid to liquid crystal.

There are two peaks which are observed in the cooling cycle. As the cooling cycle proceed, conversion of I – N occur at 148.43°C, follows by phase transition of N – Cr at 86.7°C. These two peaks represent the exothermic energy was take place during the cooling cycle. This energy was released to reform the intermolecular bond.

The DSC thermogram of compound 4h show the following: Upon heating, three peaks can be observed in the heating cycle at 109.8°C where crystal is melted to a smectic C (SmC) phase liquid crystal. Further heating, to 159.2°C, nematic (N) liquid crystal was formed. When the heating is continued to 200.5°C, isotropic (I) liquid formed. There are three peaks which are observed in the cooling cycle. As the cooling cycle proceed, conversion of I – N occur at 185.43°C, follows by phase transition of N – SmC at 143.15°C. As the cooling process continues SmC – Cr take part at 84.8°C. All these three peaks represent the exothermic energy was take place during the cooling cycle. This energy was released to reform the intermolecular bond.

As the DSC analysis done for the 4h, the molecular orientation of the molecules is as below:

Crystal \longrightarrow Smectic C \longrightarrow Nematic \longrightarrow Isotropic



Increasing order

3.2.2 Polarising Optical Microscopy Studies of N-((n-alkoxy-4'-bezoyloxy)-4'-benzylidene)-4-butyl aniline (4a-h).

The synthesized compounds exhibited interesting thermotropic properties and its melting behavior was carefully monitored by POM during both heating and cooling scans. The results from the POM observation were verified by the DSC measurements. The transition temperatures and phase sequences are summarizing in Table (3.4). Phase identification was based on the optical textures, and the magnitude of isotropization on enthalpies is

consistent with the assignment of each mesophase type, using the classification systems reported by Sackmann and Demus (1966) and Gray and Goodby (1984)⁽⁵⁴⁾. Under POM, nematic texture was observed Figure (3.13). Out of the eight compounds, the first two members (4a and 4b) did not possess mesomorphic properties. These molecules with short alkyloxy chains are too rigid, therefore have high melting points, thus impeding their liquid crystal properties⁽⁵⁵⁾. Once the length of the terminal chain is increased, the molecule becomes more flexible, hence promoting a single mesophase in a particular compound. Therefore, the 4c – 4f members exhibited nematic mesophase. All compounds, from 4c and 4h are enantiotropic liquid crystals because the stable mesophases were observed during both heating and cooling processes. From the graph, the lower member of the homologous series, C3, possessed the highest melting temperature ($T_m = 176.1^\circ\text{C}$). The melting point decreased as the length of the chain increased to the C8 member ($T_m = 110^\circ\text{C}$). This resulted from the increase in the flexibility of the molecule owing to the longer alkyl chain. It is also common that the melting temperature increases from the medium chain member onwards following a decrease from the short to the medium chain members⁽⁵⁶⁾. This ascending trend could have been attributed to the increase in the Van der Waals attractive forces between the molecules⁽⁵⁷⁾. As the series ascends from the 4a to the 4b member, the Cr – I transition temperatures attenuates consistently. The even members possessed high clearing temperatures compared to their odd member counterparts. Such attenuation of the melting temperatures has been observed in various homologous systems of liquid crystals⁽⁵⁷⁾. While the 4c to 4f members exhibited an increase in their transition temperatures during the N – I transition, 4g and 4h exhibited smectic mesophase, the terminal intermolecular attractions play a role in determining the N – I transition temperatures, that is, the destruction of the nematic molecular order is determined by the fact that the terminal attractions become

weaker, allowing partial interpenetration of the layers to occur more easily as the alkoxy chains grow longer, in turn depressing the Sm – I transition temperatures⁽⁵⁸⁾.

Table (3.4): Melting points and type of transition for compounds 4a-h.

Comp. No.	Melting point°C	Transition
4a	176 – 179	C → I
4b	168 – 170	C → I
4c	154 – 166	C → N
4d	143 – 152	C → N
4e	120 – 140	C → N
4f	121 – 130	C → N
4g	117 - 125	C → Sm
4h	110 – 119	C → Sm

C = Crystal; Sm = Smectic ; N = Nematic; I = Isotropic liquid.

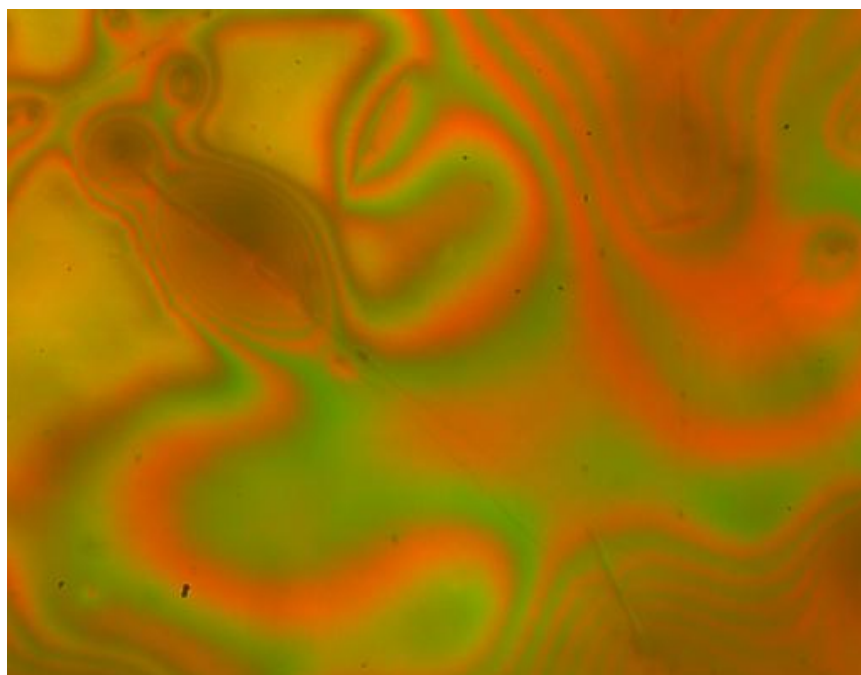


Figure (3.15): Nematic texture of *N*-{(*n*-butyloxy-4'-bezoyloxy)-4'-benzylidene}-4-butyl aniline (4d)

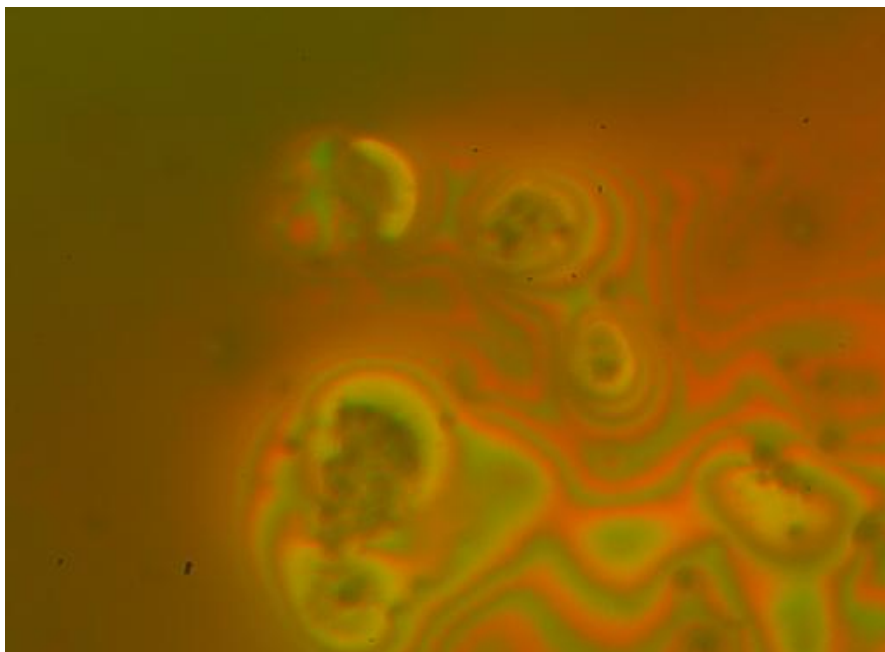


Figure (3.16): Nematic texture of N-((n-hexyloxy-4'-bezoyloxy)-4'-benzylidene)-4-butyl aniline (4f).

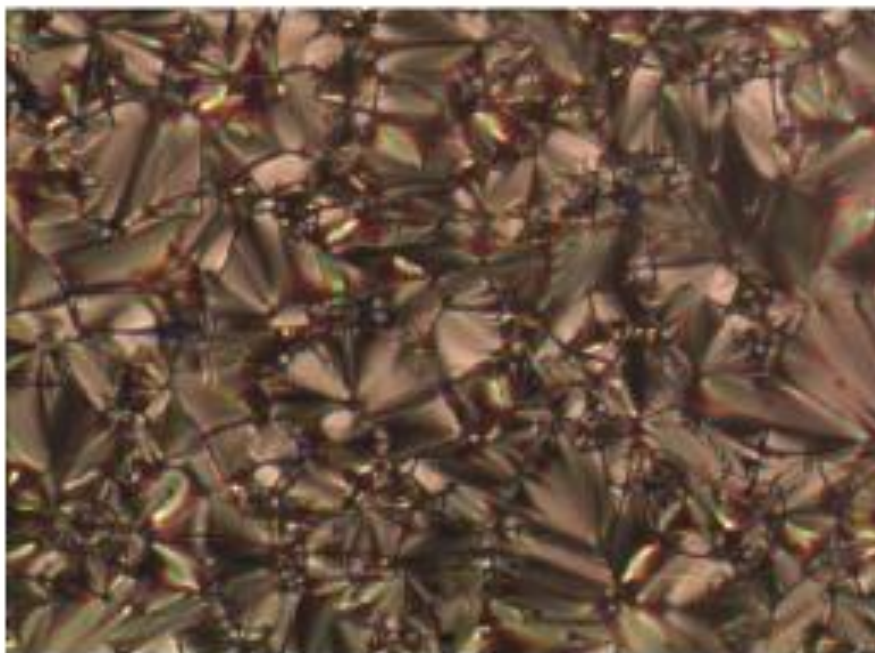


Figure (3.17): Smectic texture of N-((n-octyloxy-4'-bezoyloxy)-4'-benzylidene)-4-butyl aniline (4h).



Figure (3.18): Nematic texture of *N*-{(n-propylxy-4'-bezoyloxy)-4'-benzylidene}-4-butyl aniline (4c).

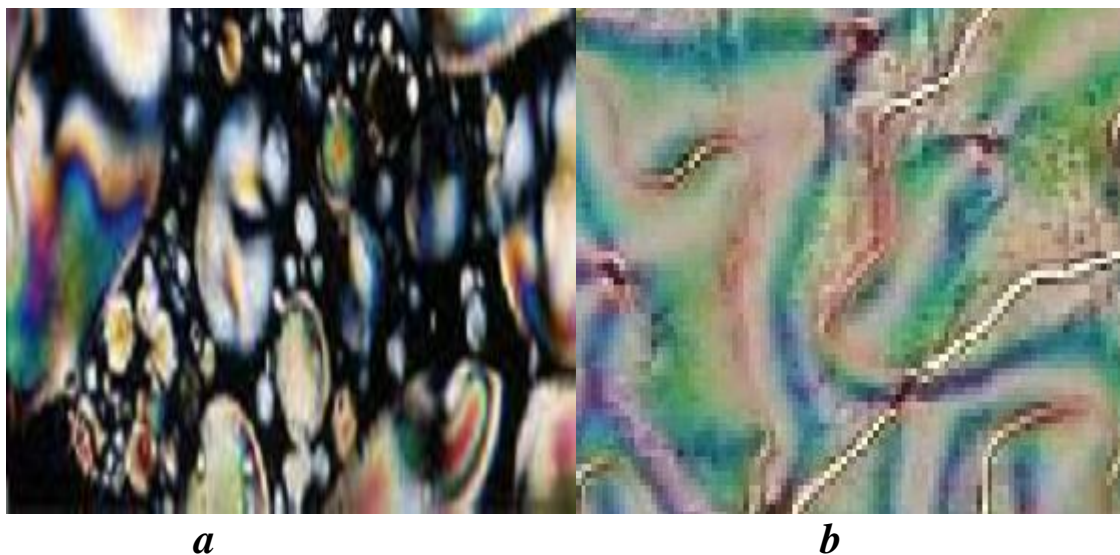


Figure (3.19): a Nematic texture of *N*-{(n-pentylpxy-4'-bezoyloxy)-4'-benzylidene}-4-butyl aniline (4e), b Smectic texture of *N*-{(n-heptyloxy-4'-bezoyloxy)-4'-benzylidene}-4-butyl aniline (4g).

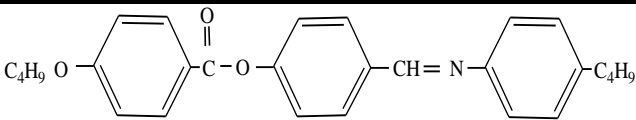
3.3 Column Chromatography

3.3.1 The packing ratio

Gas-liquid chromatography were obtained with an chromatograph Pye-Unicam using nitrogen as carrier gas and a flame ionization detector.

The column packing contained 20 wt.% of liquid crystal stationary phase deposited on the solid support, Chromosorb W(60-80 mesh). The column were conditioned at 15°C above the nematic-isotropic (N-I) transition temperature of the crystal phase stationary liquid for 24 hr. before use. Table (3.5) list the liquid crystal stationary phase used in this work.

Table (3.5): The liquid crystal stationary phase

Stationary phase	Molecular weight	Chemical name and structural formula	Max. analysis Temp.°C
4d	429	 <chem>CCCCOC1=CC=C(C(=O)OC2=CC=C(C=N3C=CC=C3C4)C=C14)C=C2</chem>	200
PEG	6000	HO-CH ₂ CH ₂ O) _n -H Polyethylene glycol	255

We choose 20% coating percentage as reported in previous studies to give best chromatographic performance, therefore no attention was made to use other coating percentage⁽⁵⁹⁾. The retention time is affected by several factors such as column length, nature and type of stationary phase, how well the column is packed the speed of carrier gas, the pressure as well as the nature of the analyzed compounds. In order to be more accurate, we calculate t'_R (Adjusted) retention time, by measuring t_m , the time of unretained species (ethanol) in this case and calculating t'_R using this equation:

$$t'_R = t_R - t_m \quad \dots 3.1$$

Table (3.6) shows the times for unretained species for the three columns.

Table (3.6): The time of unretained species t_m (min.) of Ethanol

No.	Packing material	100°C	110°C	120°C	130°C	140°C	150°C	160°C	170°C	180°C
1	4d	3.350	3.310	3.280	3.240	3.200	3.170	3.130	3.100	3.050
2	PEG 20%	2.449	2.403	2.352	2.301	2.251	2.203	2.155	2.102	2.063

3.3.2 Column performance evaluation

For each value the retention time was measured and the corrected retention time t'_R was calculated using equation 3.1. The effective plate number N_{eff} was calculated for each value of t'_R using:

$$N_{\text{eff}} = 16 (t'_R/w)^2 \quad \dots 3.2$$

3.3.3 *N*-{(n-butyloxy-4'-bezoyloxy)-4'-benzylidene}-4-butyl aniline (4d) as a stationary phase:

The analysis of positional isomer o-, m- and p-cresol (mixture A) and poly-aromatic hydrocarbons (PAH) naphthalene, fluorene, phenanthrene and anthracene (mixture B) were performed on 20% of the above liquid crystal column. The retention time of each compound in the mixtures was measured at the mesophase transition range 100 – 180°C.

The analysis of mixture A is shown in Figure (3.20), while the analysis of mixture B is shown in Figure (3.21). The data of the retention times are listed in Tables (3.7) and (3.8). In order to make comparison with the separation on the traditional column, the separation of mixture B was done on column 20% PEG and at the same conditions, no separation was obtained, this work is assessed the importance of liquid crystal as stationary phase. Figure (3.20) show the separation of mixture B on column 20% PEG.

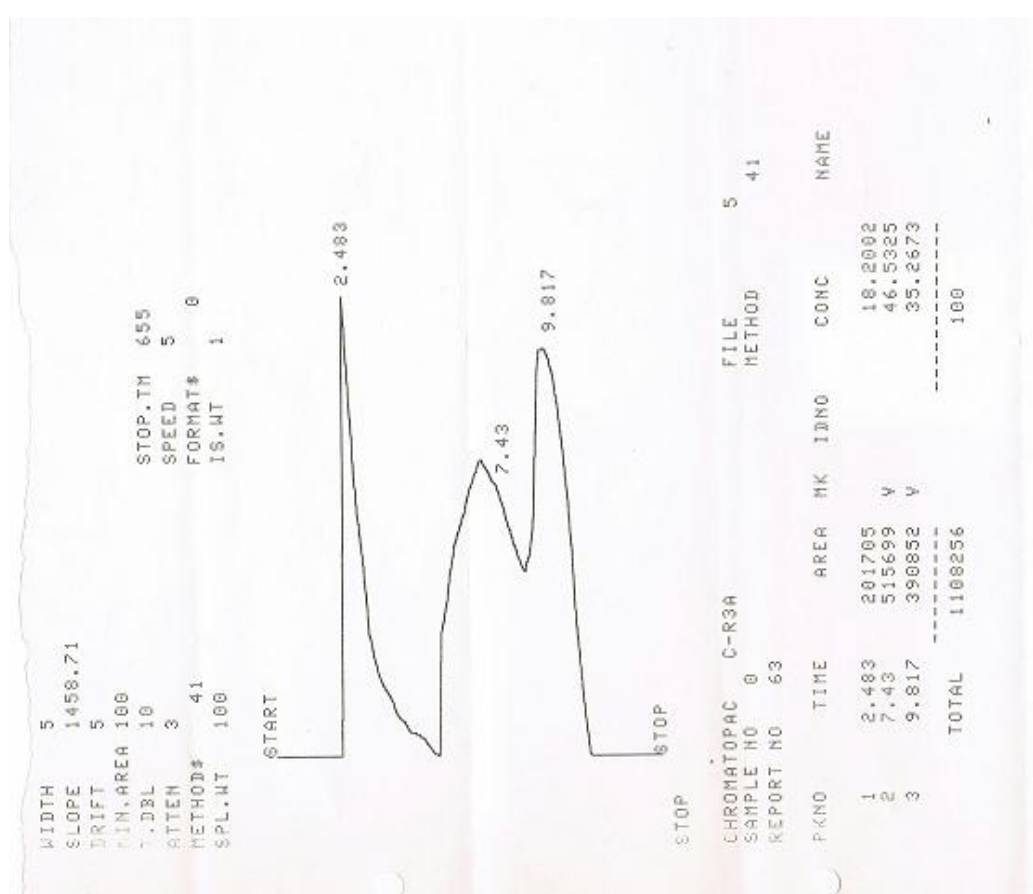


Figure (3.20): Chromatogram of positional isomers (cresols) of *N*-{(*n*-butyloxy-4'-bezoyloxy)-4'-benzylidene}-4-butyl aniline (4d) Condition oven temperature 110°C; F_c 25 ml/min and detector temperature 200°C, peak: *o*-cresol 1, *p*-cresol 2, *m*-cresol 3.

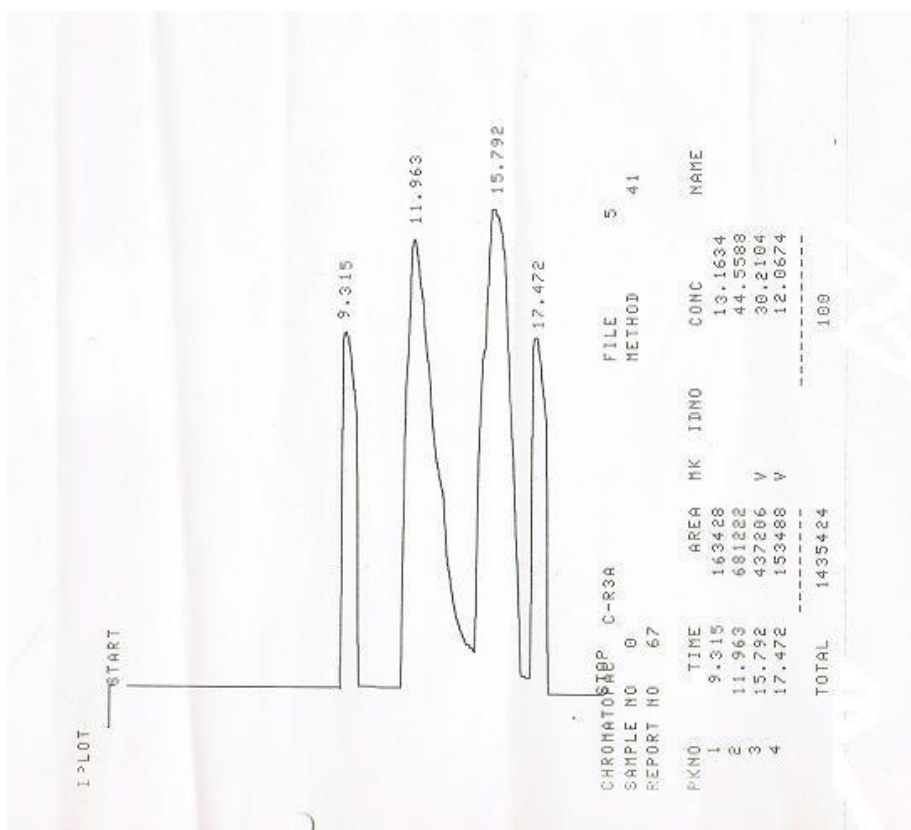


Figure (3.21): Chromatogram of of PAHs (mixture B) of *N*-{(n-butyloxy-4'-bezoyloxy)-4'-benzylidene}-4-butyl aniline (4d) Condition oven temperature 120°C; F_c 25 ml/min and detector temperature 200°C, peak: naphthalene 1, fluorine 2, phenanthrene3, anthracene 4.

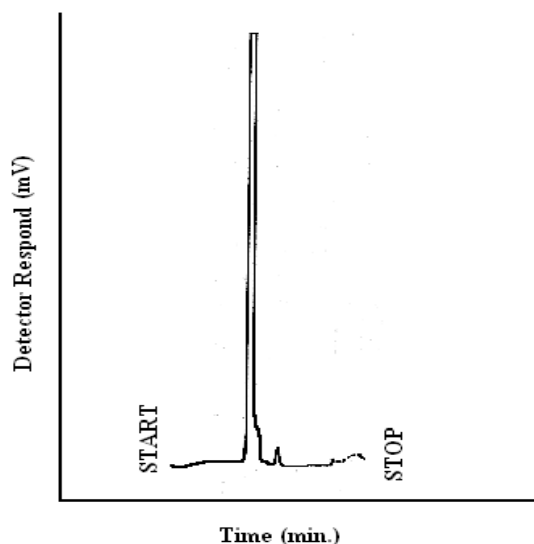


Figure (3.22): Chromatogram of PAHs mixture B on 20% PEG Condition oven temperature 110°C; F_c 25 ml/min and detector temperature 250°C, peak, naphthalene1, fluorine 2, phenanthrene 3, anthracene 4.

Table (3.7): Adjusted retention times (t'_R / minute) for mixture A on 20% N-(*n*-butyloxy-4'-bezoyloxy)-4'-benzylidene}-4-butyl aniline (4d)

Temp.°C Comp.	Retention Time (t'_R /min.)								
	100°C	110°C	120°C	130°C	140°C	150°C	160°C	170°C	180°C
o -cresol	2.326	2.483	2.315	2.265	2.197	2.034	1.913	1.771	1.369
p-cresol	7.203	7.430	7.161	6.810	6.482	6.157	5.703	5.208	4.930
m-cresol	9.398	9.817	8.170	7.742	7.443	6.907	6.329	5.762	4.352

Table (3.8): Adjusted retention times (t'_R / minute) for mixture B on 20% N-(*n*-butyloxy-4'-bezoyloxy)-4'-benzylidene}-4-butyl aniline (4d)

Temp.°C Comp.	Retention Time (t'_R /min.)								
	100°C	110°C	120°C	130°C	140°C	150°C	160°C	170°C	180°C
Naphthalene	9.528	9.186	9.315	9.048	8.743	8.362	7.989	7.546	7.029
Fluorene	11.471	10.942	11.613	11.247	10.788	10.254	10.105	9.453	9.048
Phenanthrene	15.428	14.656	15.792	15.124	14.247	13.938	13.153	12.668	11.749
Anthracene	16.898	16.146	17.472	16.694	15.839	15.178	14.793	14.268	13.314

Better separation was obtained at the temperature 120°C, this related to the higher order of the liquid crystal stationary phase which makes it easier for molecules of substances are retained stronger and stay longer in the column. As the temperature increase the retention time decrease this arise as the fact that with increase in temperature the order of a liquid crystal decreases which result in a smaller influence of substances which molecules are of the shape hindering their interaction with the structure of liquid crystals of lower order.

The order of elution's of cresol isomers (mixture A) was *ortho*, *para* and *meta*, this could be explained to the ability of the nitrogen atom of imine group to form inter molecular hydrogen bonding.

The elution of PAHs (mixture B) were naphthalene, fluorine, phenanthrene and anthracene. Chang et al. reported that the elution patterns of PAHs were almost consistent with their L/B (length to breadth) ratio⁽⁶⁰⁾ and their boiling point.

Resolution R_s is the term used to describe the degree of separation of successive solute peaks. The chromatograms used to obtain the resolution R_s of mixture A and B on column **4d** using⁽⁶¹⁾:

$$R_s = 2(t'_{RB} - t'_{RA})/(w_A + w_B) \quad \dots \quad 3.3$$

Where t'_{RA} and t'_{RB} are the retention times of peaks 1 and 2 and w_A and w_B are the widths of the peaks at the baseline. The R_s values for the two mixtures on column **4d** are listed in Tables (3.9) and (3.10).

Table (3.9): Resolution R_s for mixture A on 4d.

Temp.°C \ Comp.	Resolution R_s								
	100°C	110°C	120°C	130°C	140°C	150°C	160°C	170°C	180°C
<i>p</i> -cresol/ <i>o</i> -cresol	1.35	1.37	1.35	1.15	1.19	1.14	1.15	0.95	0.99
<i>m</i> -cresol/ <i>p</i> -cresol	0.48	0.52	0.22	0.19	0.21	0.16	0.13	0.12	0.09

Table (3.10): Resolution R_s for mixture B on 4d.

Temp.°C \ Comp.	Resolution R_s								
	100°C	110°C	120°C	130°C	140°C	150°C	160°C	170°C	180°C
Flu./Naph.	0.52	0.28	0.54	0.52	0.48	0.44	0.50	0.45	0.47
Phen./Flu.	0.70	0.66	0.74	0.68	0.61	0.65	0.54	0.57	0.48
Anth./Phen	0.49	0.50	0.56	0.53	0.53	0.41	0.55	0.54	0.52

The separation is also dependent on the relative retention characteristics of the solute characteristics of the solute components α , often called the selectivity factor⁽⁶²⁾.

$$\alpha = V'_B/V'_A \quad \dots 3.4$$

where V'_A , V'_B are the adjusted specific retention volumes of solute components A and B respectively.

The selectivity factor was calculated for each adjacent peaks. Tables (3.11) and (3.12) show the values of the selectivity factor for mixtures A and B respectively.

Table (3.11): Selectivity factor (α) for mixture A on 4_d.

Temp.°C Comp.	Selectivity factor α								
	100°C	110°C	120°C	130°C	140°C	150°C	160°C	170°C	180°C
<i>p</i> -cresol/ <i>o</i> -cresol	3.29	2.99	3.09	3.00	2.98	3.02	2.98	2.94	3.59
<i>m</i> -cresol/ <i>p</i> -cresol	1.30	1.31	1.14	1.13	1.14	1.12	1.10	1.10	1.08

Table (3.12): Selectivity factor (α) for mixture B on 4_d.

Temp.°C Comp.	Selectivity factor α								
	100°C	110°C	120°C	130°C	140°C	150°C	160°C	170°C	180°C
Flu./Naph.	1.23	1.19	1.24	1.24	1.23	1.22	1.27	1.26	1.28
Phen./Flu.	1.34	1.33	1.35	1.34	1.37	1.35	1.30	1.34	1.29
Anth./Phen	1.09	1.10	1.11	1.10	1.13	1.04	1.15	1.17	1.23

The best selectivity factors were obtained at the temperature of 15°C above the formation of the nematic mesophase, i.e. at 120°C. This has been attributed to the nematic lattice layer are ordered in its optimum structural configuration

system. This mesophase represent the actual nematic phase planes compared to that at higher temperature, in which its properties are closer to the isotropic liquids phase than to the solid state. This phenomenon has also been noticed previously⁽¹⁷⁾.

In order to assess the performance and separation efficiency of column it is necessary to determine the effective plate number N_{eff} of column, which is defined by equation 3.2⁽⁶³⁾. The plate number shows a maximum at temperature 120°C, we therefore consider this temperature to be the optimum.

The N_{eff} value of 4d column for mixtures A and B are listed in Tables (3.13) and (3.14), respectively.

Table (3.13): the effective plate number (N_{eff}) for mixture A on 4_d.

Temp.°C Comp.	N_{eff}								
	100°C	110°C	120°C	130°C	140°C	150°C	160°C	170°C	180°C
o-cresol	295	395	304	243	214	183	161	139	98
p-cresol	491	613	484	473	416	393	326	290	249
m-cresol	2512	3144	2057	1658	1575	1253	1001	968	716

Table (3.14): The effective plate number (N_{eff}) for mixture B on 4_d.

Temp.°C Comp.	N_{eff}								
	100°C	110°C	120°C	130°C	140°C	150°C	160°C	170°C	180°C
Naphthalene	4531	5399	7814	3638	1907	1747	1258	911	653
Fluorene	1244	975	1597	1197	1099	750	724	635	510
Phenanthrene	3808	2838	4922	3020	2254	1838	1635	1307	1126
Anthracene	18274	16682	30527	17827	11142	10233	7143	5086	3499

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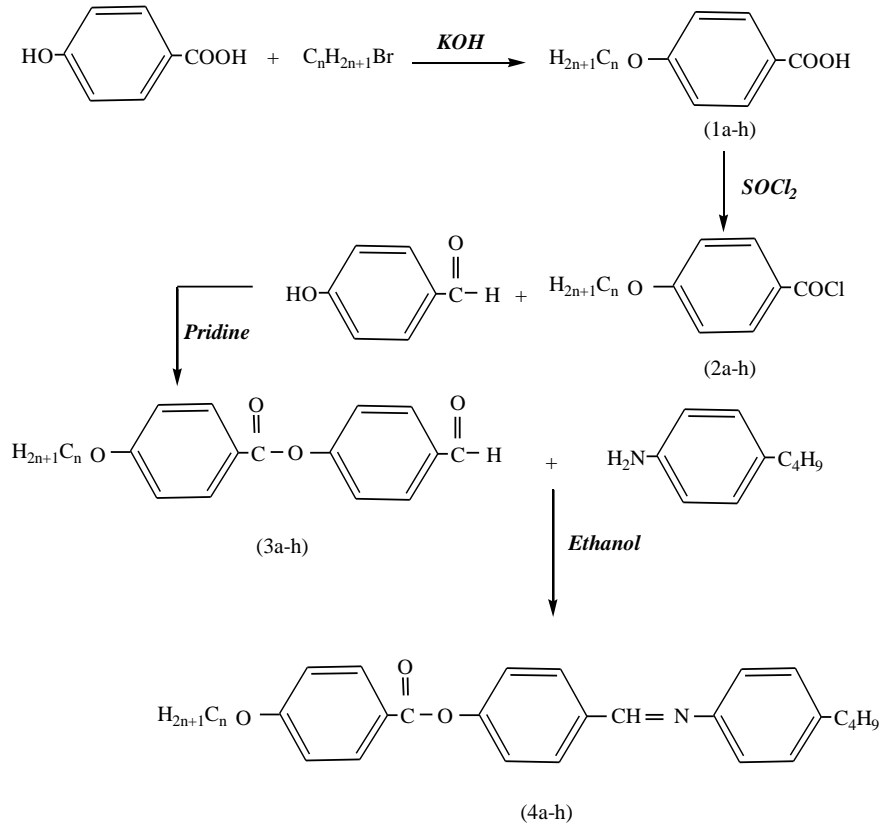
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الخلاصة

تتضمن الأطروحة تحضير المركبات البلورات السائلة N-{(n-alkoxy-4'-bezoyloxy)-4'-benzylidene}-4-butyl aniline (4a-h)

اعتماداً على المخطط ادناه:



a : n = 1
b : n = 2
c : n = 3
d : n = 4
e : n = 5
f : n = 6
g : n = 7
h : n = 8

تم تشخيص المركبات المحضرة بالطرائق الطيفية والمتمثلة بطيف الأشعة تحت الحمراء وطيف الرنين النووي المغناطيسي للبروتون والكاربون وطيف الكتلة وكذلك تحليل العناصر. كذلك تم دراسة الخواص البلورية السائلة المحضرة باستخدام مسعر المسح التفاضلي ومجهر الضوء المستقطب المزود بمنصة تسخين. تمت دراسة علاقة التركيب الجزيئي بالحالة الميزومورفية والاستقرار الحراري، كذلك تأثير وجود مجموعة الالكوكسي.

تم استخدام المركبات (4d) كطور ثابت في كروماتوغرافيا الغاز لفصل هايدروكربونات اروماتية .

تم تعبئة عمود الكروماتوغرافيا وذلك بتحميل المادة البلورية السائلة المحضرة على الساند الصلب نوع كروموسورب المغسول حامضياً نوع بنسبة ٢٠%.

تمت دراسة التأثيرات والاستخلاص لكروماتوغرافيا الغاز – السائل للهايدروكربونات على مدى من درجات الحرارة للطور البلوري السائل الثابت ولكل عمود حيث استخدمت المديات ١٠٠ - ١٨٠ مئوية للعمود. تم اختيار ظروف الفصل للأعمدة للهايدروكربونات وذلك من حساب كفاءة العمود وكفاءة التحليل ومعامل الانتقائية. ولوحظ ان قيم هذه الدوال تكون على احسنها على مدى الطور البلوري السائل النيماتي.



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

تحضير وتشخيص مواد بلورية سائلة واستخدام البعض منها كطور
ثابت لفصل ايزومرات هايدروكاربونية في كروماتوغرافيا الغاز

رسالة
مقدمة الى كلية العلوم- جامعة النهرين
وهي جزء من متطلبات نيل درجة الماجستير في علوم الكيمياء

من قبل
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