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 Reintizer[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.

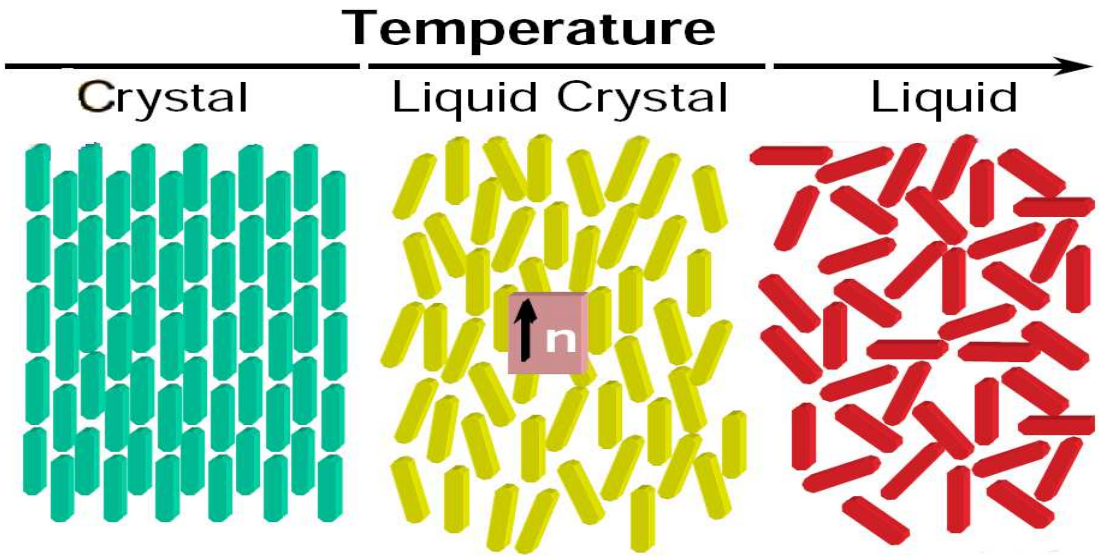
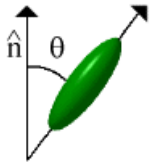


Figure (1.1): Alignment of the molecules for solid, liquid crystal and liquid phases.

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:

$$S = (1/2)\ (3\cos^2\theta - 1)$$



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].

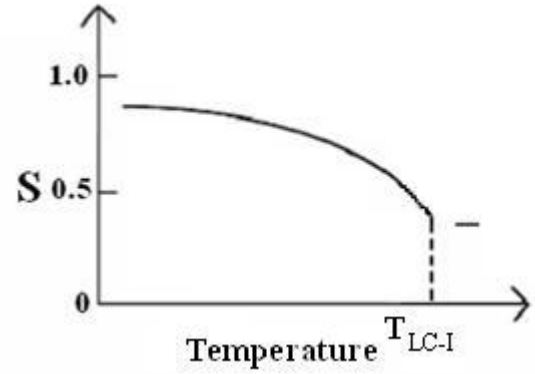


Figure (1.2): Typical temperature dependence of the liquid crystals order parameter with temperature. T_{LC-I} is the liquid crystal-isotropic transition temperature [1].

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 Characterization of Liquid Crystals

The following parameters describe the liquid crystalline structure:

- ***Orientational Order***
- ***Positional Order***
- ***Bond Orientational Order***

Each of these parameters describes the extent to which the liquid crystal sample is ordered, as shown in Figure (1.3) [3]. *Orientational order* (Figure 1.3 a) represents a measure of the tendency of the molecules to align along the director on a long-range basis. *Positional order* (Figure 1.3 b) refers to the extent to which an average molecule or group of molecules shows translational symmetry of lattice translation vectors (as crystalline material showed). A third type of order is *Bond Orientational Order* (Figure 1.3 c). A bond in the present context is not a chemical bond but a line in space joining the centers of nearest neighbor molecules without requiring a regular spacing along that line, when the orientation of these bonds is preserved over a long-range, then a system possesses bond orientational order.

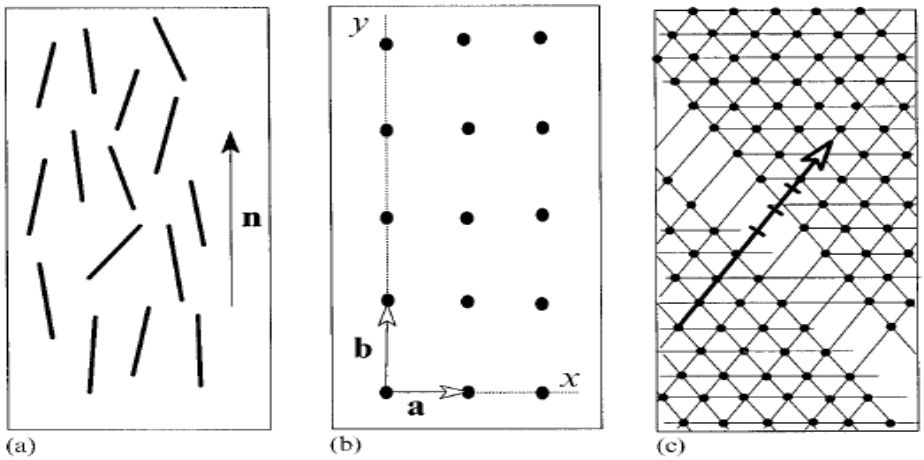


Figure (1.3): Schematic representation of the three basic types of order (a) Orientational order parallel to the direction n. (b) Positional order in two dimensions with lattice vectors a and b, and (c) Bond orientational order [3].

1.3 Liquid Crystal Phases

Most liquid crystal compounds exhibit *polymorphism*, or a condition where more than one phase is observed in the liquid crystalline state. The term *mesophase* is used to describe the "subphases" of liquid crystal materials. Mesophases can be characterized by the type of ordering that is present and they are formed by changing the amount of order in the sample, either by imposing order in only one or two dimensions, or by allowing the molecules to have a degree of translational motion [8].

Liquid crystal mesophases can be divided into two classes; *lyotropic*, and *thermotropic*. Lyotropic mesophases are concentration and solvent dependent. Solutions of biomolecules such as proteins and DNA and sufficiently concentrated solutions of surfactants can form an interesting class of liquid crystals. Since the phase behavior is more easily induced by changes in concentration, these are referred to as lyotropic liquid crystals. Representative

examples are synthetic poly-peptides, precipitated metal oxides, and rigid polymers in appropriate solvents [3,9].

Lyotropic liquid crystal mesophases were first studied by Onsager [10] and Flory [11]. These phases are formed by amphiphilic molecules [12]. Amphiphilic compounds are characterized by the presence of two groups, which have different solubility, in the same molecule. The first group is hydrophilic which consists of a polar head attached to the second group, the non-polar chain (lipophilic), (Figure 1.4a), and are often known as *surfactants* [13,14]. An example of such a system is a solution of soap in water. A typical soap molecule consists of a polar head and one or more hydrocarbon tails. When a sufficient number of such molecules are dissolved in a solvent, the lowest free energy state is a state in which the hydrocarbon tails segregate to shield themselves from the polar water environment. This leads to the formation of aggregates of molecules. Molecules in such aggregates, called micelles, are not covalently bonded and can assume several different geometries depending on the thermodynamic conditions and chemical nature of molecules. These aggregates can be rod-like or disk-like which can be orientationally and/or positionally ordered to exhibit a wide range of liquid crystalline phases [3,15]. Typical simple phases of amphiphilic materials are shown in Figure (1.4).

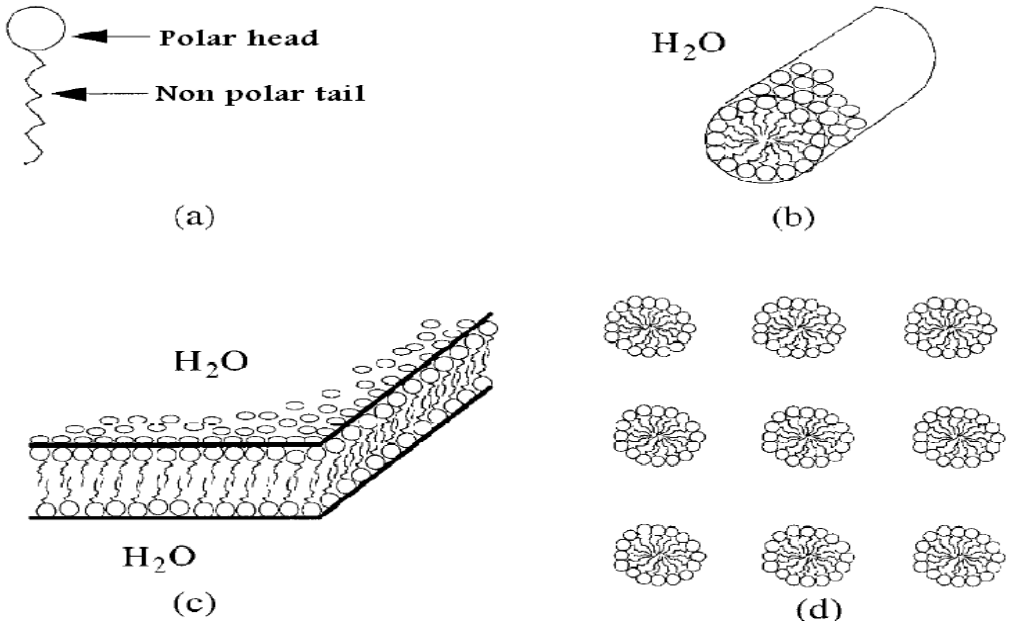


Figure (1.4):Schematic patterns of (a) A micelle, (b) an example of rod - like phase, (c) a slice of bilayer structure(an example of lamellar phase), and (d) a cubic phase formed by spherical aggregates[4].

Transitions in thermotropic phases are initiated by changes in temperature, while those to lyotropic phases can also be initiated by changes in concentration [16].Most thermotropic liquid crystals will have an isotropic phases at high temperature. That is, heating will eventually drive them into a conventional liquid phase characterized by random and isotropic molecular ordering, and fluid-like flow behavior. Under other conditions, (lower temperature for example), a liquid crystal might exhibit one or more phases with significant anisotropic orientational structure and long-range orientational order while still having an ability to flow.

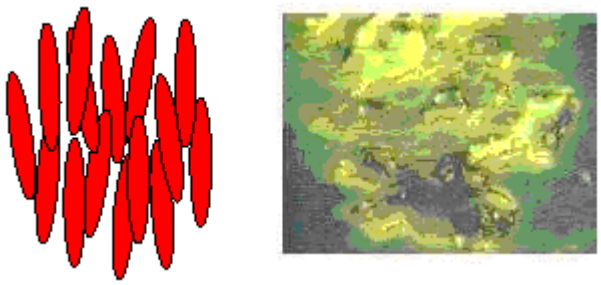
A thermotropic liquid crystalline phase occurs in some substances at a temperature region between the solid and liquid states [1]. It is formed by heating a solid or cooling an isotopic liquid, or by heating or cooling a thermodynamically stable mesophases [17].

Thermotropic liquid crystals can be classified into two groups as enantiotropic and monotropic. Enantiotropic liquid crystals, reach the liquid crystalline state by either lowering the temperature of the liquid or rising the temperature of the solid, but in monotropic, the liquid crystals either increase in the solid's temperature or decrease in the liquid's temperature, but not both [6,7].

Thermotropic liquid crystal phases fall into four different categories: nematic, chiral nematic, smectic, and discotic [7, 18], and these phases differ from each other in the type and extent of order and the symmetry that they possess.

1.3.1 Nematic Liquid Crystal Phases

The simplest liquid crystalline phase is the nematic (N) phase. (Nematic from the Greek word nematos meaning "thread") [19] .In nematic liquid crystals the molecules have no positional order, but they tend to point in the same direction, along the director. As seen in liquids, the molecules in nematic phase have long-range orientational order, but lack positional order and bond orientational order [9,20] as shown in Figure (1.5). The nematic phases are close to liquid phase. The arrangement of the nematic can be controlled with applied electric fields. Nematics are used commonly, with the devices having the twisted nematic geometry [3].



(a) **(b)**

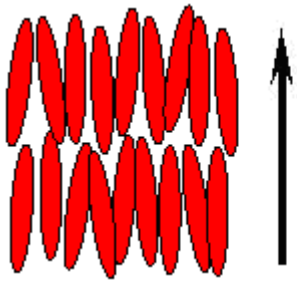
Figure (1.5): (a) Molecular arrangement of nematic phase, and (b) a photo of a nematic liquid crystal under crossed-polarizing microscope [3].

1.3.2 Smectic Liquid Crystal Phases

The word "smectic" is derived from the Greek word *smectos* meaning soap. This ambiguous origin is explained by the fact that the thick, slippery substance often found at the bottom of a soap dish is actually a type of smectic liquid crystal. The smectic state is another distinct mesophase of liquid crystal substances. Molecules in this phase show a degree of translational order not present in the nematic. In the smectic state, the molecules maintain the general orientational order of nematics, but also tend to align themselves in layers or planes. Motion is restricted within these planes. The increased order means that the smectic state is more "solid-like" than the nematic [1,19].

The smectics can be classified into three types, smectic A, C, and B. These phases have one common property in that they have a layered structure, so they have partial translational ordering which makes smectics more viscous than other phases [21].

In the smectic A mesophase, the director is perpendicular to the smectic plane (Figure 1.6) and the layers are fluid, and there is a high probability of the inter-layer diffusion when compared to smectic C. In smectic C phase the director is at a constant tilt angle with respect to the layer normal as shown in Figure (1.6). As in smectic A, phase layers are fluid but there is a lower probability of the inter-layer diffusion. The smectic B mesophase (similar to smectic A mesophase) orients with the director perpendicular to the smectic plane, but the molecules are arranged into a network of hexagons within the layer. In contrast to smectic A and C phases, layers are not fluid any more; hence there are three dimensional positional (and possibly even orientational) orders. These phases are called crystal mesophases, and are in fact nearly as ordered as solid crystals (although they still exhibit fluid-like flow). However the mechanical properties of smectic B phases are quite different from the solids, so smectic B phase may be a plastic crystal, indeed [22, 23].



Molecular arrangement of Smectic A

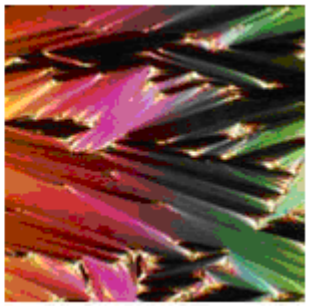
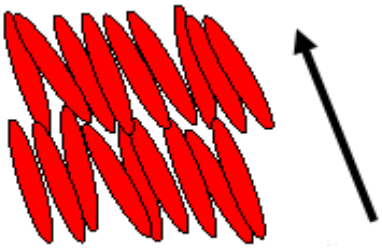


Photo of the smectic A phase under crossed polarizing microscope



Molecular arrangement of Smectic C

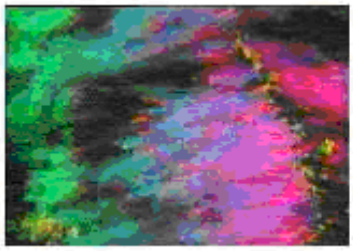


Photo of the smectic C phase under crossed polarizing microscope

Figure (1.6): Molecular arrangement of some representative examples of smectic phase[3].

1.3.3 Chiral Nematic Liquid Crystal Phases

The chiral nematic, (or cholesteric), liquid crystal phase is typically composed of nematic mesogenic molecules containing a chiral center which produces intermolecular forces that favor alignment between molecules at a slight angle to one another. This leads to the formation of a structure which can be visualized as a stack of very thin two-dimensional nematic like layers. This phase exhibits a twisting of the molecules along the director, with the molecular axis perpendicular to the director [15]. The finite twist angle between adjacent molecules is due to their asymmetric packing, which results in a longer range chiral order. The directors actually form in a continuous helical pattern about the layer normal as illustrated by the black arrow in the Figure (1.7). The black arrow represents director orientation in the succession of layers along the stack. The chiral pitch refers to the distance (along the director) over which the

mesogens undergo a full 360^{o} twist (but note that the structure repeats itself every half pitch). The pitch may be varied by adjusting temperature or adding other molecules to the LC fluid. For many types of liquid crystals, the pitch is on the same order as the wavelength of visible light. This causes these systems to exhibit unique optical properties, such as selective reflection. These properties are exploited in a number of optical applications [2,4].

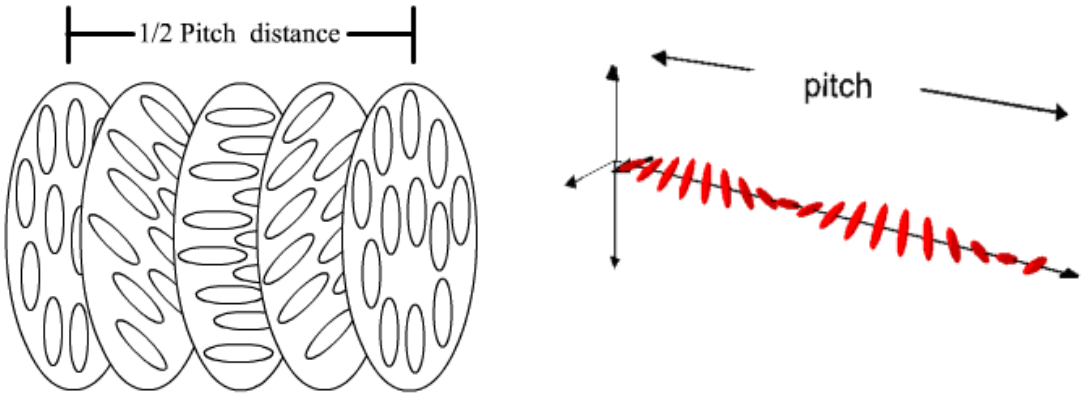


Figure (1.7): Chiral nematic phase[2].

1.3.4 Discotic Liquid Crystal Phases

The liquid crystalline phases formed by disk shaped molecules are referred to as the discotic phases. A second type of mesogenic structure was first synthesized and identified in 1977 [4]. The first series of discotic compounds are the hexa-substituted benzene derivatives which are shown in Figure 1.8, and synthesized by Chandrasekhar et al. [24] .

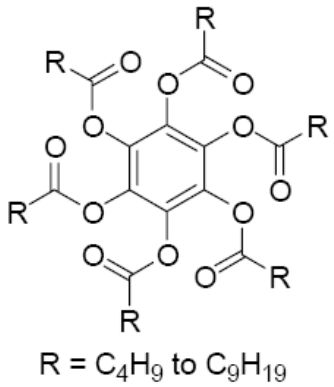


Figure (1.8): Molecular structure of the first discovered series of discotic compounds.

Structurally they generally form either nematic or columnar phases. Liquid crystal phases formed by discotic molecules fall into three different categories: discotic nematic, discotic chiral nematic, and columnar. The discotic nematic is similar in structure to the calamitic nematic, although in this case the short axes of the molecules tend to lie parallel. The same holds for the discotic chiral nematic phases. Columnar phases are equivalent to the smectic phases. The simplest columnar phase consists of stacked disks; this phase is characterized by the short axis of the molecule aligning parallel to the director. The structure of the columnar phase has an orientational order within the columns, but no positional order along the columns. The columns themselves are arranged with positional order and form a two-dimensional array which is either a rectangular or hexagonal lattice as shown in Figure (1.9) [25, 26].

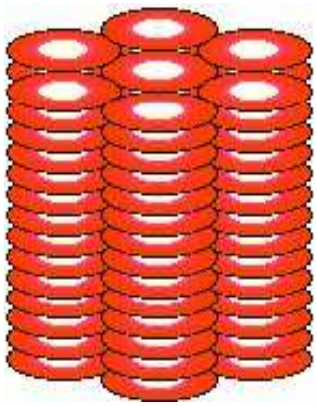
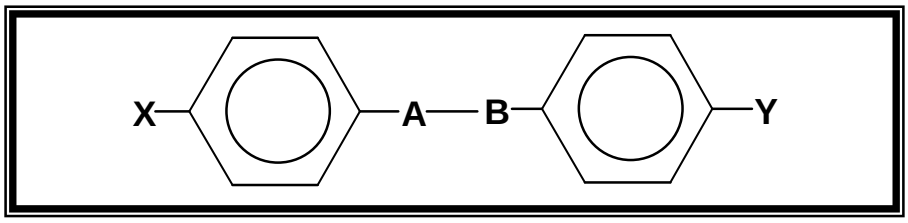


Figure (1.9): Columnar discotic phase [4].

1.4 Structural Features of Liquid Crystals

Organic compounds that form mesophase upon melting are characterized by being long, narrow, linear molecules. Both permanent dipoles and polarizable moieties are required [27].

The vast majority of liquid crystalline substances are based on the following structure:



They Possess:-

1) Two or more aromatic rings, usually benzene ring. The majority of liquid crystal molecular structures have two para linked aromatic rings. They are highly polarizable, planer, and rigid [28].
2) One or more bridging groups, A-B that bind the rings together. Suitable linking groups (A-B), which preserve the linearity of molecule and by being unsaturated also extend conjugation between two rings are [29]:

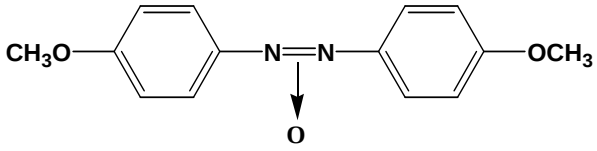
(-C ≡ C- , -CH = N- , -N=N-, -C – O- , …etc)
O
||

3) Terminal groups, X and Y: The terminal substituents are important factors that affect the anisotropy of molecular interactions. Normally they control both the nature and the type of mesophases. If terminal substituent groups are of high polarizability they favor the formation of less order mesophases, i.e.,

nematic mesophase, such as nitro, cyano and methoxy groups which strongly promote nematic properties. On the other hand, terminal groups which contribute strongly to the resultant dipole acting across the molecular long axis promote smectic properties [30]. The thermal stability of the mesophase formed (difference between the isotropic transition and melting temperatures) depends in large measure on stable structural, steric, and electronic effects, in the central and terminal groups [10].

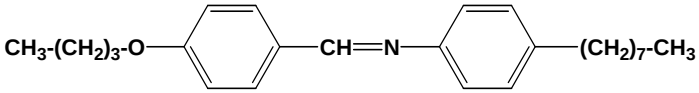
Some illustrative compound structures of nematic [1], smectic [2], cholesteric [3], and discotic [4] are shown below.

Nematic:



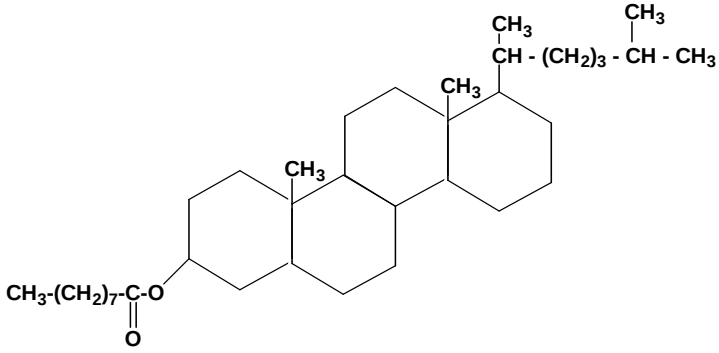
p-azoxyanisole [1]

Smectic:



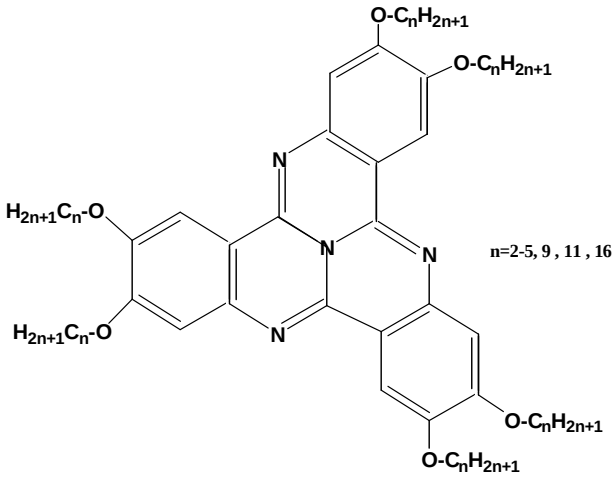
N-(p-butoxyphenylidene)-4-octylaniline [2]

Cholesteric:



Cholesteroyl nonanoate [3]

Discotic:



2,3,7,8,12,13-alkoxytricycloquinazoline [4]

1.5 The Liquid Crystals Applications

Liquid crystal compounds have been found to have a variety of uses. The most common application of liquid crystal is liquid crystal displays, which rely on the optical properties of certain liquid crystalline molecules in the presence or absence of an electric field [(1)]. More important and practical applications have been developed in such diverse areas as medicine and electronics [(27)]. Chiral nematic (cholesteric) liquid crystals reflect light with a wavelength equal to the pitch [(14)]. Because the pitch is dependent upon temperature, the color reflected also is dependent upon temperature. Liquid crystals make it possible to accurately gauge temperature just by looking at the color of the thermometer [(31)]. The medical applications include detection of breast cancer, location of the placenta, blood flow patterns in extremities of the humane anatomy, and observation of skin temperature changes following blockage of the sympathetic nervous system [(27)]. There is also an interest in using the liquid crystals in chromatography as stationary phases. A large number of new liquid crystal compounds have been prepared which have specific properties for different applications in diverse fields [(9)].

1.6 Liquid Crystals as Stationary Phases in Gas Chromatography (GC)

A search for better stationary phases, including highly selective ones, is an important trend of chromatography development. Among the stationary phases under investigations are liquid crystalline stationary phases (LCSPs). Liquid crystals were studied as stationary phases mostly for gas chromatography (GC) [(32-36)]. Recently, studies on the use of liquid crystals in liquid chromatography have come out [(37- 44)]. The separation of components of

mixtures occurs on the basis of the different interactions between liquid crystalline stationary phases and molecules of different geometric shapes. In some cases, very small differences in the shapes of molecules of compounds being separated suffice to obtain their good separation. At the same time, the separation of components of mixtures difficult to separate on conventional stationary phases whose separation ability is associated with polarity or non polarity of interacting molecules of chromatographed substances and stationary phases is obtained.

Thermotropic liquid crystals have been of interest for some time as stationary phase in gas chromatography for resolving closely related, rigid solute isomers [45]. Liquid crystals were used as gas chromatography stationary phases for the first time by Kelker [46,47] and Dewar [48]. The liquid crystalline stationary phases added some unique selectivity to chromatographic separations of rigid planar molecules like polycyclic aromatic hydrocarbons (PAHs). Liquid crystalline stationary phases are useful in separating close boiling isomers which are very difficult or impossible to separate on classical stationary phases. These interesting properties are due to the rod-like shape and the order arrangement of their molecules within the mesophase. When used in the appropriate temperature range, these liquid crystalline groups retain their orientation with respect to each other with their elongated molecular axes aligned in a parallel configuration.

The smectic phase exhibits a layered structure similar to the C_{18} structure in reversed phase liquid chromatography. Liquid crystal layers have successfully been applied to PAHs [49-58], and volatile aroma compounds [59-65], as well as to other organic pollutants like polychlorinated biphenyls (PCBs), dibenzodioxins (PCDDs), and dibenzofurans (PCDFs) [66-70]. The high temperature nematic liquid crystals, which provide separation on the basis of molecular geometry, are used in gas chromatography for the separations of

isomers such as: disubstituted benzenes [71-81], steroid epimers [82], methoxy substituted quinines [83], and PAHs [49,84-92]. Analytical applications of liquid crystals as stationary phases were reviewed by Witkiewicz [32,33,93].

Habboush et al.[94] studied the interaction and elution characteristics of C_5-C_9 normal, branched and cyclic alkanes using liquid crystalline stationary phases at different column temperatures of 60-100°C for *p*-(n-hexyloxy)phenyl *p'*-methoxybenzoate and 90-150°C for *p*-pentyloxyphenyl *p'*-ethoxyazoxybenzoate as stationary phases. The liquid crystal loading was **(**20**%** w/w) on 80-100 mesh Chromosorb W/AW DMCS.

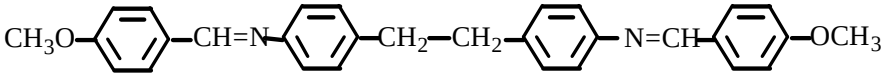
Sojak et al. [95] examined regularities and irregularities in the values of retention time of chromatographed substances, and affecting the selectivity of separation, with regard to the relationship: retention of a chromatographed substance-structure of a liquid crystal. They measured retentions of 49 branched alkynes C5-C13 on squalane and a liquid crystal: 4-*n*-pentylacetophenone-*O*-(4-*n*-pentyloxybenzoyl)oxime (PBO) were compared. The selectivity of a liquid crystal for isomers of *n*-alkynes increased with a shift of the triple bond from the centre to the end of the carbon chain. With a decrease in the length-to-width ratio of molecules of alkynes and with an increase in the screening of the triple bond, their retention indices on PBO decrease in comparison with squalane (SQ); ΔI^{PBO-SQ}.

Budzinski et al.[96] identified 12 dimethylphenanthrenes isomers and 25 trimethylphenanthrenes isomers, in crude oils and rock extracts; using GC on smectic liquid crystalline phase. The retention behavior of these alkylated phenanthrenes was related to molecular shape considerations, length to breadth ratio, dihedral angle and substitution pattern.

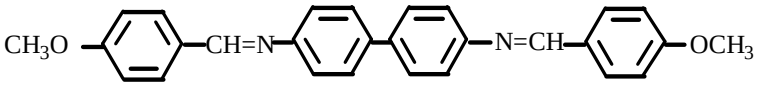
In the first period of investigations on LCSPs monomeric liquid crystals of relatively small molecular weight and of relatively narrow mesophase ranges were dealt with. Despite their good separation properties, the stationary phases

were not widely used. One of the reasons for it was the considerable volatility of LCSPs making their stability unsatisfactory.

With the wider use of capillary columns, the high stability of LCSPs was required within the wide range of temperatures where the mesophase should occur. One of the practical limitations of liquid crystals is the narrow nematic temperature region which limits the effective application of temperature programming [45]. Among such LCSPs are, first of all, monomeric liquid crystals of large molecular weight and liquid crystalline polymers [97]. Inspite of the general tendency to obtain monomers of large molecular weights, liquid crystals of relatively small molecular weights and of high melting temperatures, were synthesized [5,6] [63].



[5]



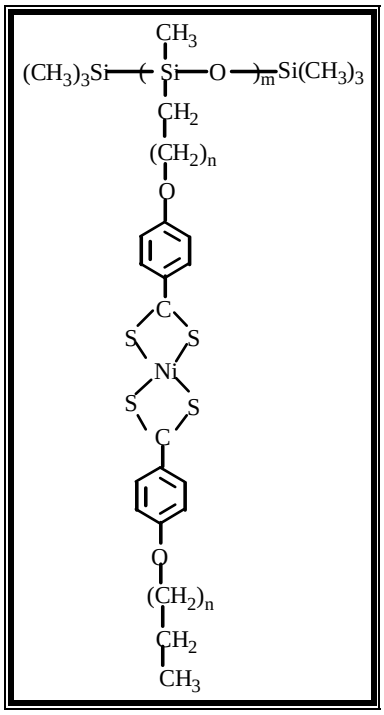
[6]

On monomeric LCSP: 4,4/-biphenylene-bis(4-*n*butyloxy-benzoate) placed in a capillary column, 12 PAHs present in both standard mixture and a mixture derived from coal tar were successfully separated [97]. Composite mixtures of vegetable origin (e.g. volatile oils) are difficult to separate. Therefore, highly selective stationary phases, including liquid crystalline nematic and cholesteric ones, were used for their separation with good results [59,61,62,64,98-101].Some liquid crystals, used for the separation of components of volatile oils, could be used supercooled [62]. Although the good separation of components of some mixtures is possible in the solid state of LCSP in its supercooled mesophase and also in the range of the isotropic liquid, the best

chromatographic effects are generally obtained within the temperature range of the stable mesophase. Some monomeric LCSPs, of high molecular weights, have been found to contribute to the separation of high boiling compounds at temperatures corresponding to the solid of a liquid crystal [102].

A lot of attention was traditionally paid to the separation of disubstituted benzene isomers. These isomers can be successfully separated on a great number of liquid crystals, both nematic and smectic [102,103]. Methylnaphthalenes (MN) and dimethylnaphthalenes (DMN) were more difficult to separate, but some pairs of these isomers were successfully separated, namely 1,2- and 2,6-DMN, 2,6- and 2,3-DMN as well as 1-MN and 2-MN [104]. Liquid crystals, with a relatively wide range of the mesophase (e.g. 116–191.5 °C), belonging to a group of nitroazo compounds, made the separation of different compounds possible in a short time [102]. Among them were benzene alkylderivatives, position isomers of alkanes, *cis* and *trans* isomers and numerous components of volatile oils. The separations obtained were much better than those obtained using the conventional phases SE 30 and Carbowax 20M.

Monomeric liquid crystals containing transition metals in organic complexes were described by Hudson and Maitlis [105]. Among monomeric liquid crystals, azo- and azoxy-compounds [36,106–108] and their derivatives [97,108] are still being synthesized. Their complexes with metals such as copper were also described [106]. The synthesis of polymeric liquid crystals where complexes zinc (II) and nickel (II) with 4-(dec-9′-en-1′-oxy)dithio-benzoate [109] were bound to the polysiloxane chain. The formula of such a liquid crystal is given in [7]. The nickel (II) complex showed particularly good properties. Thirteen PAHs from naphthalene to pyrene were separated on it in a capillary column 12m long within a temperature range of 150–190 ◦C. It turned out that the smectic phase of complex liquid crystals was as useful for the separation of PAHs as commonly used nematic phases.



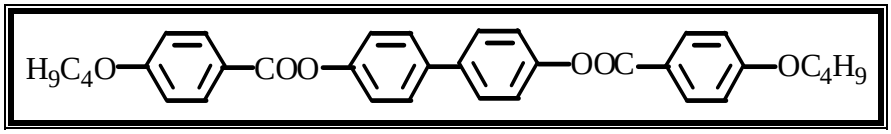
[7]

Recently, liquid crystalline moieties have been grafted onto polymethylsiloxane polymers to overcome the narrow mesophase temperature ranges of some liquid crystals [63,108,110]. The bonding of polysiloxanes with liquid crystalline compounds produced substances with interesting characteristics as stationary phases [76].

Berset et al.[111] have used a prototype smectic liquid crystalline polysiloxane as stationary phase in GC for the separation of 7 PCBs and 16 PAH compounds. The separation efficiency on the smectic phase was much higher for both groups compared to a non-polar stationary phase column of the DB-5 type. Moreover non-ortho substituted (coplanar) PCBs were well separated from the mono-ortho and di-ortho PCBs and appeared as a late eluting group. Finally the smectic column was very useful for qualitative analysis of PAHs.

Very often polymers with liquid crystalline properties have a polysiloxane backbone [56,57,112-114]. Among the polymeric liquid crystals were

the ones in which molecules possessing alkoxyl groups [97] [8] and crown ethers [57,113,115-117] [9] were bound to the polysiloxane chain.



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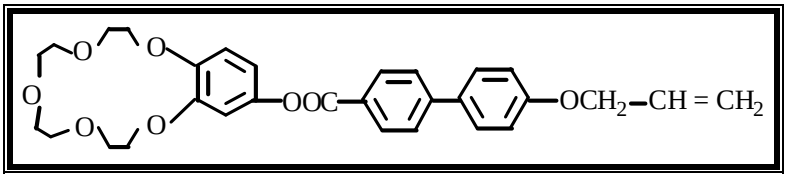


[9]

Naikwadi et al.[113] have used a new side chain liquid crystalline polysiloxane (SCLCP) having a wide liquid crystalline range of 140°C to 315°C as a stationary phase in capillary column gas chromatography. A series of new (SCLCPs) was synthesized using olefins containing 2,6-disubstituted naphthalene. The olefins were attached to a hydromethylpolysiloxane backbone by a hydrosilylation reaction using a platinum catalyst. These columns had a high thermal stability, efficiency and isomer specificity for the separation of isomeric polychlorinated dibenzo-*p*-dioxins, PAHs and pesticides were demonstrated as examples.

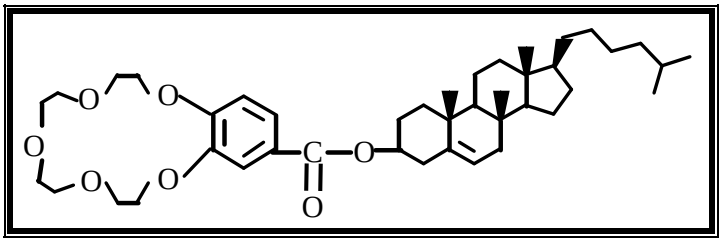
An analysis of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans presented a very difficult problem. The side chain liquid crystalline polysiloxane polymer of the smectic and nematic mesophases and of the transition temperature to the isotropic liquid 270 ◦C guaranteed the separation of some isomers of (PCDDs) and (PCDFs) better than the commercial conventional phases: HP-5MS and RTX-5MS, for example: 1,2,3,4-TeCDD vs. 2,3,7,8-TeCDD and 1,2,3,4,7,8-HxCDD vs. 1,2,3,6,7,8-HxCDD and the same substituted chlorine number compounds 1,2,3,4,6,7,8-HpCDF vs. 1,2,3,4,6,7,8-HpCDD and 1,2,3,4,6,7,8,9-OCDD vs. 1,2,3,4,6,7,8,9-

OCDF had a higher resolution than HP-5MS and RTX-5MS as suggested by the column makers [118].

Jing et al. [116] have used a side-chain liquid crystalline polysiloxane containing crown ethers for the chromatographic separation of both di- and tri-substituted benzene isomers as well as enantiomers [119].

New liquid crystalline biphenyl carboxylate ester polysiloxanes, which possessed wide smectic temperature ranges and high thermal stabilities, have also been reported [77,98,120].

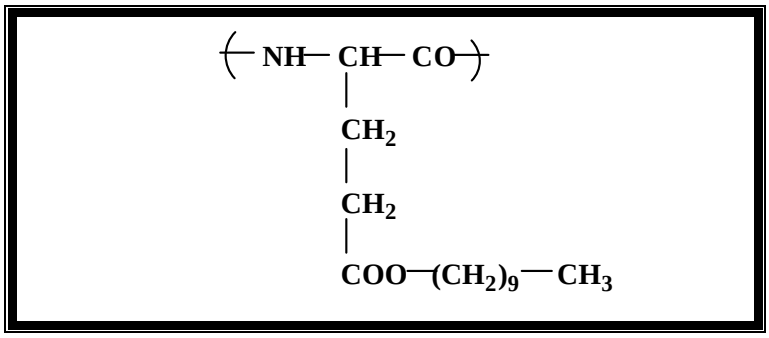
The LCSP whose molecule contained a cholesterol fragment [119] [10] was also obtained.



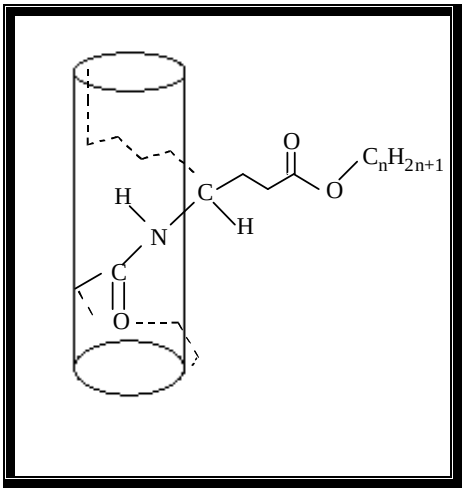
[10]

Relatively little attention was paid to cholesteric liquid crystalline stationary phases. However, polymeric cholesterics of the wide mesophase range were obtained, e.g. from 25 to 180 ºC and from 54 to 190 ºC [121]. These stationary phases were useful for the separation of isomers of alkanes from C8 to C20, poly-aromatic and aromatic hydrocarbons, volatile aromatic compounds as well as *cis* and *trans* isomers of some chemical compounds.

Liquid crystals with a polyglutamine skeleton were noteworthy among polymers with no polysiloxane skeleton. Decyl- and *n*-hexadecyl groups (11 and 12) were connected with this skeleton. These liquid crystals were chiral cholesterics of the mesophase range equal to 150 ºC [121].



[11]



[12]

Judeinstein et al. [98] have described the synthesis, analytical performances, thermodynamic and surface properties of two new liquid crystals substituted with poly(ethylene oxide) chains. The first of them was *N*,*N*′-diphenyl-[4-{2,3,4-tri[2-(2-methoxyethoxy)ethoxy]benzylidene}imine] piperidine **(**LC_1**)** and the second was 2-hydroxy-3-methyl-4-{4-[2-(2-butoxyethoxy)ethoxy]}4′-{4-[2-(2-butoxyethoxy)ethoxy]styryl} azobenzene (LC_2). The nematic ranges of the two liquid crystals, determined by differential scanning calorimetry (DSC), and GC. The analytical and thermodynamic studies of LC_1 and LC_2 in the solid, nematic and liquid state were done using a series of appropriate solutes. Analytical studies showed that the phenols, and derivative isomers separation on the stationary phase in the solid and in the liquid state were generally poor. The good separations of certain isomers observed in the nematic state, the increased discrimination with

respect to the shape of molecules led, however, to remarkable analytical performances.

The separation ability of *cis* and *trans* isomers was shown by quite a lot of LCSPs such as 2-[4′-(4-*trans*-pentylcyclohexyl)biphenyl]-2-(4-isothiocyanatophenyl)ethane on which *cis* and *trans* isomers of alkylcyclohexylbenzenes were separated [122].

Alfred and Gunter [123] studied the correlation between gas chromatography (GC) and infrared (IR) spectroscopic behavior in nematic phases. A slight change was observed in the slope of the specific retention volume (log Vg°) vs. inverse temperature (T^{-1}) functions. IR measurements were performed in order to check this effect by an independent technique, by observing the temperature dependence of the position of the OH band of 2-octanol, which was dissolved in the nematic phase. This position of the OH band was used as an indicator of intermolecular interactions and was compared with the log Vg° data.

Inverse gas chromatography (IGC) has been used to investigate the physicochemical properties of such liquid crystals [124,125]. While the dynamic method that the measurements recorded under the correct conditions could give accurate equilibrium thermodynamic information [126,127]. Price et al.[128] have described measurements on a number of low molar mass and polymeric liquid crystals that contain the same mesogenic groups. Transition temperatures for the mesophases have been measured and the supercooled region of hexyloxycyanobiphenyl studied, revealing some differences from the stable mesophase. Activity coefficients and interaction parameters for a range of probes have been measured and allowed determining the nature and origin of the thermodynamic interactions in the systems and how this fundamental

information can be used in designing more efficient stationary phases for analytical gas chromatography.

Comprehensive two-dimensional gas chromatography may be used when one-dimensional gas chromatography fails to resolve coeluting substances [129,130]. Danielsson et al.[131] have measured the trace amount of polychlorinated dibenzo-p-dioxins, dibenzofurans, and poly chlorinated biphenyls in food by using comprehensive two-dimensional gas chromatography. It was used with different column combinations for separating the target analytes. For the first dimension, non polar DB-XLB and VF-1 columns were used, and for the second dimension, an LC-50 liquid crystalline column with unique selectivity for planar compounds. The total toxic equivalence (TEQ) data obtained using DB-XLB x LC-50 were in good agreement with the results obtained by the GC–HRMS laboratories. While the data obtained with the VF-1 x LC-50 combination was also good, but the PCDD/F concentrations were sometimes overestimated due to matrix interferences.

Matisova et al.[132] have studied the dependence of the properties of liquid crystals on the film thickness and surface quality of capillary columns. Glass capillary columns were coated with {2-methyl-4-(trans-4-n-propyl-cyclohexylcarbonyloxy)benzoic acid-[4-n-heptyloxy-phenylester]} as the liquid phase, in different film thicknesses. The columns were tested using substances of different structures and polarities. It was verified that the capacity factors, retention indices and selectivity significantly depended on the thickness of the liquid crystalline stationary phase film and the quality of the tube, particularly in the case of columns with thin films. Transition temperatures of the liquid crystal were also dependent on these two factors.

The mixture of a liquid crystal with conventional stationary phase increased the efficiency of the column by improving the homogeneity of the stationary phase film upon the wall of a capillary column [133-137]. Janini and

Filfil [138], who mixed the liquid crystal with the conventional phase Dexsil 300 in the ratio of 23:77, gave an example of such a stationary phase. They used the phase in a packed column for separating four pentacyclic aromatic hydrocarbons: benzo(k)fluoranthene, benzo(e)pyrene, perylene and benzo(a)pyrene. Gorczynska [139] mixed LCSP called *N*,*N*′-di(*p*-butoxy-benzylidene)-α, α′-di-*p*-toluidine (BBBT) homogenously with the phase SE-30, carbochemical products (carbazole and anthracene oil) containing polycyclic aromatic hydrocarbons were separated. The good separation of PAHs, including phenanthrene and anthracene, was obtained using a packed glass column 1.9m long. The column was filled with a mixture of 3% BBBT phase and 2% SE-30 phase on Chromosorb G/AW.

The mixture of two liquid crystals can also prove advantageous [79,140-142]. Grushka and Solsky [143] tried to expand the temperature range of the mesophase using a mixed phase capable of forming an eutectic mixture. The thermodynamic properties of binary mixtures of liquid crystals have been studied by Differential Scanning Calorimetry (DSC) [140,141]. Grushka and Solsky [144] have also pointed out changes in the height equivalent of a theoretical plate ,H, as a function of changes in the temperature of the nematic crystal.

Boudah et al.[79] have studied the thermal and chromatographic properties of an equimolecular mixture of two liquid crystals (LC_a, LC_b). DSC showed that the clearing temperature of the mixture (LC_{a+b}) was an intermediate between the corresponding temperatures for the individual liquid crystals. The melting temperature was lower than the corresponding temperatures for the separate liquid crystals. Polarizing microscopy showed that the liquid crystal phase of the mixture (LC_{a+b}) was nematic. The analytical performance of the mixed liquid crystal was investigated using of different kinds of solute (PAHs, phenols, and volatile aroma compounds). It seemed that the behavior of the

nematic mixture was the same as that of a pure nematic liquid crystal. When separations were performed with the mixture the more elongated isomer (para for positional isomers) was the most retained solute [79].

1.7 Physico – Chemical Studies of Liquid Crystalline Stationary Phases (LCSPs)

The ordering of the liquid crystal structure is known to be of decisive importance in the separation of components of mixtures by distinguishing the shape of their molecules. However, investigations on the effect of other physico-chemical properties of liquid crystals on their behavior as stationary phases in a chromatographic column are still necessary. The results of such investigations should facilitate a search for liquid crystals of good separation properties and of such physico-chemical properties as to meet the general requirements set for stationary phases best. It is also important to learn more about the relationships between general physico-chemical properties of liquid crystals and their separation ability. The results of such investigations of LCSPs properties, were based on inverse gas chromatography (IGC) [124 -128,145] and conventional methods of examining liquid crystals, e.g. DSC, NMR and FTIR [93].

The selectivity of liquid crystals in relation to substances of different molecular shape can be determined by the dependence of the selectivity coefficient (α) of test substances on temperature: $\ln \alpha = f(1/T)$ [146]. The shape selectivity of 4-octoxyphenyl-4-pentoxybenzoate was thus examined in relation to polar xylene isomers and non-polar stereoisomers of dimethylcyclohexane and decalin [76,146]. Considering their small polarity, saturated cyclic compounds were found to be better for determining the selectivity of LCSPs connected with

the shape of molecules of chromatographed substances than more polar xylene isomers. On the basis of the dependence: ln $\alpha = -\Delta (\Delta G_{a,b})/(RT)$, it is possible to determine quantitatively differences of partial molar free energies of the substances **a** and **b** chromatographed on liquid crystals. Using the equation: $\Delta G = \Delta H - T\,\Delta S$, from the slope of straight lines ln $\alpha = f(1/T)$ for each pair of isomers, $\Delta (\Delta H_{a,b}/R)$ was calculated. In the case of chromatographic process 4-octoxyphenyl-4-pentoxybenzoate, these values were for *o*- and *p*-xylene =−2.11, for *p*- and *m*-xylene =−2.73, for *cis*- and *trans*-1,2-dimethylcyclohexane =−2.93 and for *cis*- and *trans*-decalin =−3.34, respectively [(146)]. The retention of isomers of chromatographed substances considerably depends on the type of the mesophase of the liquid crystalline stationary phase. It results from the fact that the type of mesophase affects the diffusion of isomers of the chromatographed substance to a different degree. Medina [(147)] studied the influence of the type of mesophase of the liquid crystalline stationary phase on the diffusion of xylene isomers on 4,4′-bis(heptyloxy)azoxybenzene (BHOAB) as stationary phase deposited on glass beads. The order of elution of xylene isomers was typical of liquid crystalline stationary phases *meta*, *para* and *ortho*. However, the diffusion coefficients in the smectic, nematic and isotropic phases decreased in the order *p*-xylene, *o*-xylene and *m*-xylene. The diffusion coefficient of *p*-xylene compared to *m*- and *o*-xylene was disproportionately larger in the smectic phase than in the other phases. Medina concluded, from the comparison of the values of diffusion coefficients of xylene isomers with their polarity, the length to width ratio and the molar volume that the diffusion coefficient of *para*-isomer was larger than *m*- and *o*-isomers was associated with its smaller polarity and the larger molecule length to width ratio than that of the other isomers. The described behavior of *p*- xylene isomers could account for its larger retention on liquid crystalline stationary phases than that of the *m*-xylene isomer. The retention on

conventional stationary phases is reversed and attributed to their boiling points. A clearly great difference in the activation energy of the diffusion of xylene isomers in smectic and nematic mesophases as well as in isotropic liquid resulted from the ordered structure of a smectic and a nematic mesophases, and from the disorder of the isotropic liquid. Molar diffusion coefficients of selected PAHs in the side chain liquid crystalline polymer determined by gas chromatography confirm the influence of the shape of molecules on its behavior in nematic and isotropic phases [145]. The non-planar *o*-terphenyl diffused more easily in the nematic phase of this liquid crystal than planar fluorene. In the isotropic phase molar diffusion coefficients for fluorene and *o*-terphenyl did not differ much. Activation energies of the diffusion of naphthalene with length to breadth L/B = 1.24 and that of fluorene with L/B = 1.52 in the isotropic phase did not differ much and were (32 and 30 kJ/mol), respectively, whereas in the ordered nematic phase they were clearly larger and different for naphthalene (40 kJ/mol) and for fluorene (68 kJ/mol).

The separation effect of components of mixtures on LCSPs was associated with the different energy of the interactions of the components of these mixtures with liquid crystals. Therefore, the determination of these interactions in different systems can contribute to a better knowledge of the nature of liquid crystal-chromatographed substance interactions. The effect of steric factors on the separation of *m*- and *p*-xylene isomers on liquid crystals: *p*-azoxyanisole (PAA) and 4-methoxy-benzylidene-4-butylaniline (MBBA) was presented [148]. The ratio of dissolution activity factors of *m*-xylene to *p*-xylene was smaller than unity and in practice it did not change in the isotropic phase while it was larger than unity in the nematic phase and depended on the structure of a liquid crystal.

The diffusion and the dissolution of chromatographed substances in stationary phases were determined by the mass transfer resistance which affects

the efficiency of chromatographic columns [93]. The efficiencies of columns with liquid crystalline stationary phases were generally lower than those of columns with conventional stationary phases. Therefore, it can be advisable to mix liquid crystalline stationary phases with conventional phases. It was shown by examining the mixtures of 4-propoxy-4/-ethoxyazoxybenzene (PEAB) with polymethylhydrogen siloxane (PMHS) in capillary columns [149]. Xylene isomers were chromatographed on these phases. With the suitable mixture ratio, the good separation of LCSPs and the small mass transfer resistance of the conventional stationary phase resulted in the optimal separation of the components of the mixture. The mixture of PEAB and PMHS in the ratio of 83:17 showed good separation properties. Little attention was paid to the effect of polarity of LCSPs on their separation properties. It was justifiable as the effect of polarity of LCSPs on obtaining the separation of components of mixtures was smaller than the effect of the ordered structure of the stationary phase. The effect of polarity should not be neglected, though, because in some cases it could be positive and might improve the separation of components of mixtures.

The retention time of chromatographed substances was known to depend on the temperature of a liquid crystal, practically on its phase state where it was at a given temperature. It contributed to determining the phase transition temperatures of liquid crystals. The phase transition temperatures determined by IGC and DSC were usually in agreement; it was shown, for example, for two liquid crystals containing external and internal nitro groups [102]. The results of determining temperatures of phase transitions for cholesteric [121] and nematic liquid crystals [98] by DSC and IGC were also compared. The phase transition temperatures measured by these methods were different by 5%.

The wide range of the mesophase was a very useful property of liquid crystalline stationary phases. The examination of properties of LCSPs,

including polymers, by inverse gas chromatography [128,150–152] made it possible not only to determine phase transition temperatures of liquid crystals but also to study and compare properties of mesophases in stable and supercooled states [128].

1.8 The Separation Mechanisms on LCSPs

The chromatographic separation of compounds of mixtures using most of the conventional stationary phases was associated with the polarity of these phases and with the polarity and polarizability of the chromatographed substances as well as the subsequent intermolecular interactions [93].

The mechanism of the chromatographic separation on LCSPs was mostly connected with the differentiation of the structure of molecules of chromatographed substances. The differentiation of the structure of molecules of chromatographed substances resulted from the ordering of the liquid crystal structure and depended on the type of mesophase and thermodynamic effects of dissolution of solutes in LCSP [80]. In the case of nematic liquid crystals, the best separations were obtained at the lowest temperatures of their existence, usually slightly above the melting point, but also below it, in the supercooled mesophase. The efficiencies of columns with LCSPs were generally lower than those of the columns with conventional stationary phases and, therefore, the mixture of a liquid crystal with the conventional stationary phase (e.g. the silicon one) can be advantageous [149].

In such systems both stationary phases interact with chromatographed substances independently, according to different mechanisms the liquid crystal by the ordered structure and the conventional stationary phase by polarity. This system can show better properties than the liquid crystal itself as regards the separation taking place according to two different mechanisms. With a certain

composition of the mixture being separated, disadvantageous effects of separation cannot be excluded. In such conditions, the good separation was obtained in a shorter time than during the separation in the mesophase range. Small differences in the structure of molecules of liquid crystals related to terminal or lateral position of the same functional group ($–NO_2$) were also found to affect not only the range of their mesophase but also their separation properties [102]. The properties of LCSP below its melting point (as the supercooled phase) were different depending on whether this phase was heated from the temperature below the melting point or cooled from the temperature higher than the melting point. It was shown by Betts et al.[60] that the separation of some aromatic components of volatile oils within the temperature range of 120 – 175 ºC on *N*,*N*′- bis(*p*-methoxy-benzylidene)- α, ά-bi-*p*-toluidine (BMBT), with the melting temperature of 179 ºC. The authors claimed that different mechanisms of the separation of components of mixtures were possible and that they were dependent on the thermal history of LCSP.

The mesophase of the liquid crystal existing after its melting can be supercooled when the temperature of a column decreases. The stability of the supercooled mesophase depends on the kind of liquid crystal and on the support on which it is deposited. The separation in the supercooled mesophase takes place according to the same mechanism as in the conventional mesophase at stronger mass transfer resistances in the supercooled phase [93].

The effects of the separation of components of mixtures, including isomers, on LCSPs at temperatures below their melting points, in the solid, similar to the effects of the separation within the temperature mesophase range were difficult to explain. The explanation given by Betts et al.[60] seemed very probable. The chromatographed solute moving down in the chromatographic column can produce locally a liquid eutectic mixture with a liquid crystal. If the liquid crystal has been previously heated above the melting point, it can then

retain the ordered structure of the mesophase after being cooled below the melting point and solidified. Such ordering does not occur in a liquid crystal which has not been molten earlier. Therefore, the interaction of the liquid crystal melted earlier with the chromatographed substance in the eutectic mixture can be stronger than that of the liquid crystal which has not been molten [60]. It appears that the separation of components of the same mixture can be different and take place according to different mechanisms related to the thermal history of a chromatographic column [93]. Considering the separation properties of LCSPs, the interactions in the chromatographic system, connected with polarity, cannot be completely omitted although they are not largely compared with the separation mechanism resulting from the ordered structure of these stationary phases [60,63,146]. It is noticeable in the case of separating *m*- and *p*-xylene isomers. The isomers on the conventional stationary phases, if separated, were eluted in the order *para* and *meta*, whereas on LCSPs they were eluted in the order *meta* and *para* [146,147]. The two isomers were very frequently used to assess the separation abilities of LCSPs. However, according to Krupčik et al. [146] the use of saturated cyclic compounds for assessing the selectivity of LCSPs was better than the use of xylene. It was justified by the fact that the polarity of cyclic compounds was smaller than that of xylenes and the influence of their polarity on the selectivity of the separation could be minimized.

With a view to obtaining stationary phases of the wide temperature range of the mesophase, of high stability in columns and of good separation properties, attention was paid to polymeric liquid crystals, including those in the form of complexes with transition metal ions (e.g. copper(II), zinc(II), nickel(II)) [109]. The separation was connected with both their ordered structure and the ability of exchanging organic ligands of a liquid crystal with organic substances, e.g. PAHs. The separation on these LCSPs was complex and in the

case of mixtures whose components could interact with LCSPs according to both mechanisms the separations obtained be good.

The different separation of the same mixtures in different types of the mesophase of liquid crystals (smectic, nematic, isotropic) could be related to different diffusion coefficients of the same substances in individual types of mesophase [147]. Rogalska et al. [153] have studied different interactions of chromatographed substances with different states of the liquid crystal *N*,*N*′-diphenyl-[4-(2,3,4-tri(2-methoxyethoxy)ethoxy)benzylidene) imine] piperidine by partial molar excess enthalpy and entropy in the case of the nematic and the isotropic liquid. Their values were much higher in the mesophase than in the isotropic liquid. It resulted from the different interaction of molecules of solutes with the ordered and disordered structures of a liquid crystal.

1.9 The Factors Affecting the Separation of Mixtures in LCSPs

1.9.1 The Kind of Liquid Crystal Phase

In LCSPs, the more ordered phase (i.e., smectic over nematic) provides greater shape selectivity. A possible explanation of this 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, and 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 [154,155].

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 and improved resolution than those of smectics, due to greater diffusion in the former and, thus, higher efficiency. and the smectics with a low degree of ordering of the mesophase (S_A, S_C) have better separation properties than those of a high degree of ordering (S_B). However, improved selectivity has been achieved using smectic phases [156-158].

1.9.2 Molecular Structure of the Liquid Crystal and the Chromatographed Substances

A fact of intermolecular interactions between the liquid crystal and the chromatographed substances is important for the understanding of the phenomena taking place in the chromatographic column [155]. The structure of the molecules and their polarity and polarizability effect, as well as, the solubility of the chromatographed substances in the liquid crystal plays an important influence on the separation.

The process of dissolution was dominated in the column during chromatography on a liquid crystal. However, as liquid crystals were usually phases of medium polarity [159], the mechanism of the retention of the substances chromatographed on them was accompanied by adsorption. Nevertheless, the contribution of adsorption to the total retention was usually much smaller than of dissolution. The properties of the liquid crystal stationary

phases depended both on the structure of the main chain of the molecule and on the terminal substituents which strongly affect the polarity of the molecules. However, an equally important or even greater effect on the chromatographic properties of liquid crystals was 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 [160]. The direct quantitative correlation between the retention of the chromatographed substances and their molecular structure was studied [161]. It was generally assumed that the ratio of the length to the smallest transverse dimension of the molecule, (L/D) (shape factor), was a decisive quantity for the retention of chromatographed substance on liquid crystal stationary phases.

1.9.3 The Effect of the Support

The effect of solid support activity on the chromatographic properties of stationary phase has long been a subject of a controversy. 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 were 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 [162]. The selectivity of the system depended strongly on the kind of support used and on the amount of the liquid crystal deposited on it [163]. The selectivity also depended on the thickness of the liquid crystal layered on the column wall and the character of the wall surface [164]. The

reproducibility and reliability of the retention data were better when the surface of the column wall was inactive and the thickness of the liquid crystal layer was relatively thick [132].

The interaction of the support surface with the liquid crystal stationary phase may give specific effects. One of these is lowering the melting point of the liquid crystal by 7ºC owing to its contact with silanized surface [165]. The lowering of the melting point was 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 was not related to the kind of substance chromatographed but depended on the kind and amount of the liquid crystal deposited on the support and was a feature of the liquid crystal–solid support interactions [166]. In order to explain the variation of retention data with percentage loading and the type of solid support used, Korol [167] studied squalane (non polar) and oxydipropionitrile (strongly polar) as stationary phases. He invoked an argument that the stationary phase was present on the solid support in two types of configurations, a film on the surface and a bulk liquid in the pores. With low percentage loading, most of the stationary phase was present as a surface film and solute retention was largely due to the adsorption on the gas-liquid interface, and on the gas-solid support surface interface. As the amount of liquid phase increased the support pores were filled and solute solubility in the bulk predominated the retention process. Unlike isotropic phases, liquid crystals exhibited a macro structure which strongly depended on the properties of the surface over which the mesophase was deposited. It was therefore, expected that the effect of solid support would be even more dramatic with such a phase.

Vernon and Rayanakorn [168], investigated the solid support effect and the polarity of LCSP in GC. They found that, when polar stationary phases were

used, the main cause of retention data variation was gas-liquid interfacial adsorption, support activity being eliminated if the solid support surface was sufficiently covered by these phases. For non polar stationary phase, with percent loading less than 5% (w/w) a solid support effect would exist so the high percentage loading would be recommended.

Another factor that affected on the separation of mixtures was heat treatment [137]. The properties of the system were affected by the conditions under which the column filling was heat treated. During heating, a redistribution of the liquid crystal on the support took place and as a result the properties of the system were changed [169]. In some instances conditioning at high temperatures led to a more advantageous ordering of the liquid crystals in the column. Therefore, if this treatment was not long enough or was conducted at an insufficiently high temperature, sometimes the selectivity of the column may change in the course of its use [162]. The occurrence of this phenomenon was related to the kind of liquid crystal used and the properties of the surface on which it was deposited.

1.10 Aim of the Work

The effect of the liquid crystal technology can be observed in many areas of science, engineering and also in device technology. Applications are still being discovered and they will continue to produce solutions to many different problems in different branches.

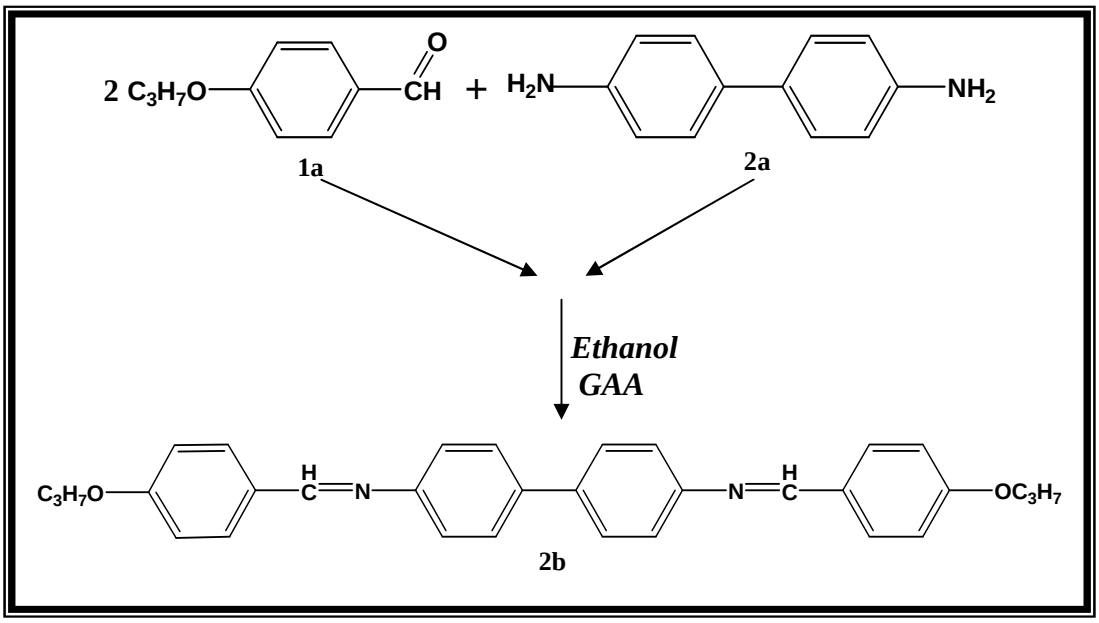
Gas chromatography separation technique is one of the importance techniques in modern chemical analysis in different fields. Recently, liquid crystalline compounds as new stationary phases in gas liquid chromatography have been widely used, so the aims of this work are:

1- Preparation and characterization two liquid crystal compounds containing benzene and heterocyclic rings, and use them as stationary phases.
2- Coating these compounds on inert solid support and pack them in GC columns.
3- Studying the interactions and elution characteristics of PAHs, alcohols, and positional isomers by determination their chromatographic parameters.
4- Comparing the separation characteristics of the prepared stationary phases at different coating ratios.
5- Using the gas-liquid chromatography for the investigation of the thermodynamics and physical properties of solutes in liquid crystals.

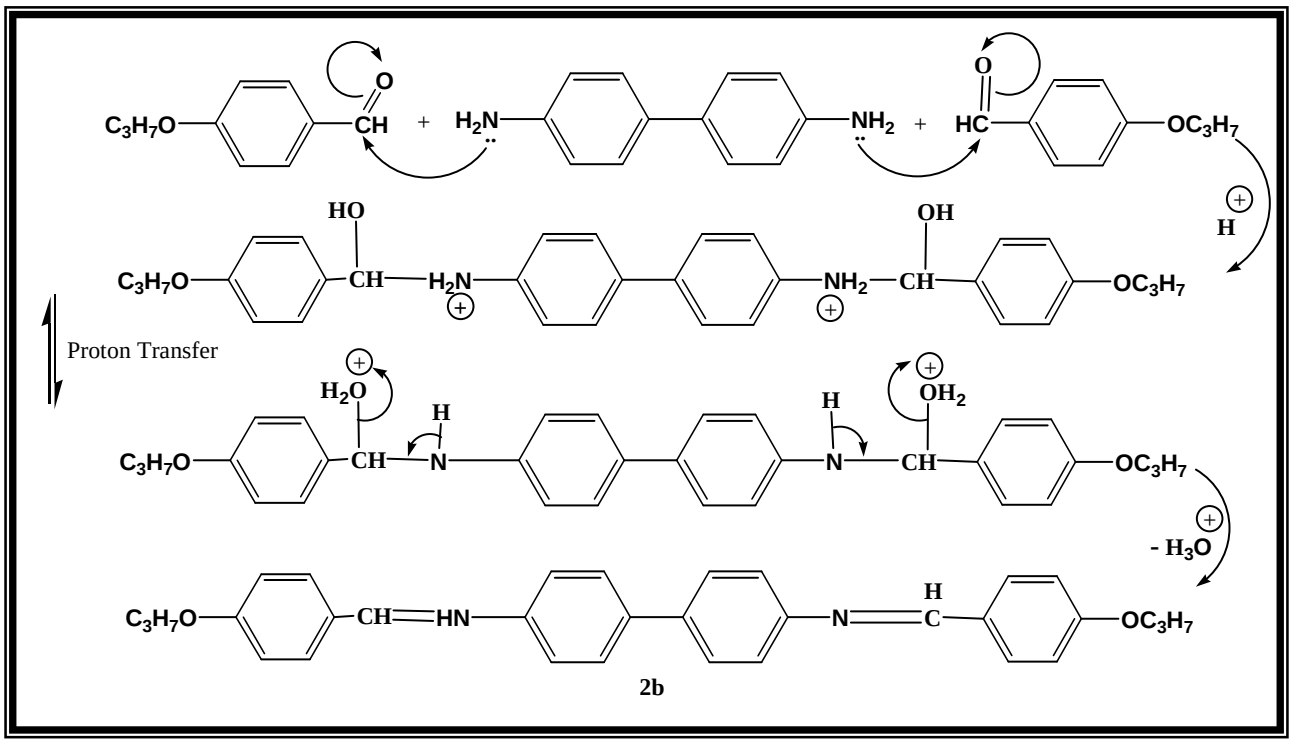
Chapter Three
Results and Discussion

3.1 Preparation and Characterization of 4,4′-bis-(4-propoxybenzylideneamino)biphenyl (2_b)

Compound ($\mathbf{2_b}$) was prepared by the condensation reaction between 4-propoxybenzaldehyde ($\mathbf{1_a}$) and 4,4′-Diaminobiphenyl ($\mathbf{2_a}$) in boiling absolute ethanol, and glacial acetic acid as a catalyst.



The Schiff base mechanism of this reaction may be outlined as shown in the following scheme (3.1) [174].



Scheme (3.1): Mechanism for the formation of compound (2_b).

The synthesized compound was identified by FTIR, ^{1}HNMR, and CHN elemental analysis. The characteristic bands of 4,4/-bis-(4-propoxybenzylideneamino)biphenyl **(2_b)** are shown in Figure (3.1). The appearance of bands at 2960, 2943, and 2876 cm^{-1} may be assigned to the asymmetrical and symmetrical stretching of C–H aliphatic, respectively. The C=N bond appeared at 1625 cm^{-1}. The appearance of typical absorption of C=C stretching in benzene rings was at 1609, 1589, and 1517 cm^{-1}. The C–O–C bond showed asymmetrical and symmetrical bands at 1248 and 1162 cm^{-1}. The C–H bending of the para di-substituted benzene appeared clearly at 836 cm^{-1}.

The ^{1}HNMR spectrum of compound **(2_b)** is shown in Figure (3.2) with the following features ($CDCl_3$, ppm): two pairs of doublet at δ 6.98 - 7.03 and 7.41 - 7.43 could be attributed to the eight protons of the biphenyl ring. While the other multiple band at δ 7.58 - 7.68 suggesting the attribution of the eight protons of the alkoxy phenyl rings which have different substituents at position 1 and 4.

The spectrum also showed a triplet at δ 4.00 - 4.07 that could be assigned to the four protons of (O–CH_2) groups, the shift in the value of the group was due to the α- substitution (O– group). The multiple signal at δ 1.79 - 1.91 was assigned to the four protons of the (CH_2) group between (–CH_3) and (OCH_2–) and the triplet signal at δ 1.06 - 1.11 was assigned to the six protons of lateral (–CH_3) groups. While the proton of the (N=CH) group appeared at δ 8.45 as a sharp singlet signal. The signal at δ 7.28 may be due to the solvent.

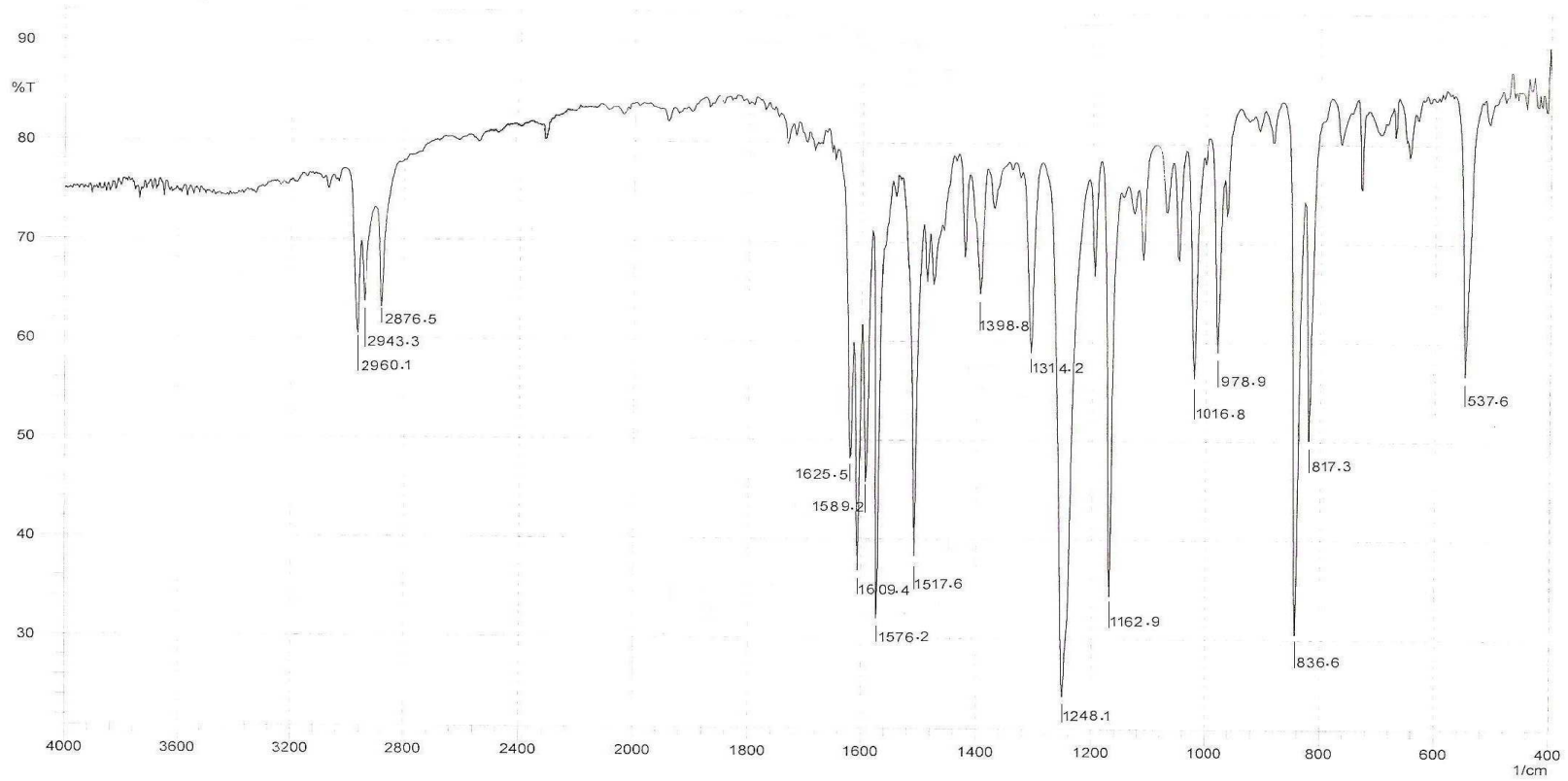
CHN analysis for compound (**2_b**) was performed, and the results are listed in the Table (3.1).

Table (3.1): Elemental analysis of the compound 4,4′-bis-(4-propoxy benzylideneamino)biphenyl (2_b).

Element % / Estimation	C %	H %	N %
Theoretical	80.67	6.72	5.88
Experimental *	81.06	7.11	6.12
Relative Error%	+0.48	+5.80	+4.08

* Represents the average value of two measurements.

It was found that the relative error values between the experimental and theoretical estimations of the presence of C, H, and N percentage in the compound (**2_b**) were acceptable and ranged from (+ 0.48 – +5.80).



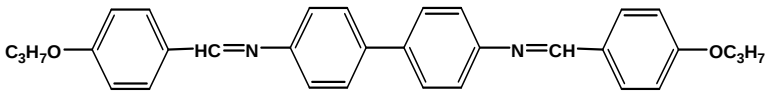
Melting point:(246 – 253) ^{o}C	
Yield: (90 – 95) %	

Figure (3.1): FTIR spectrum of 4,4′-bis-(4-propoxybenzylideneamino)biphenyl (2_b).

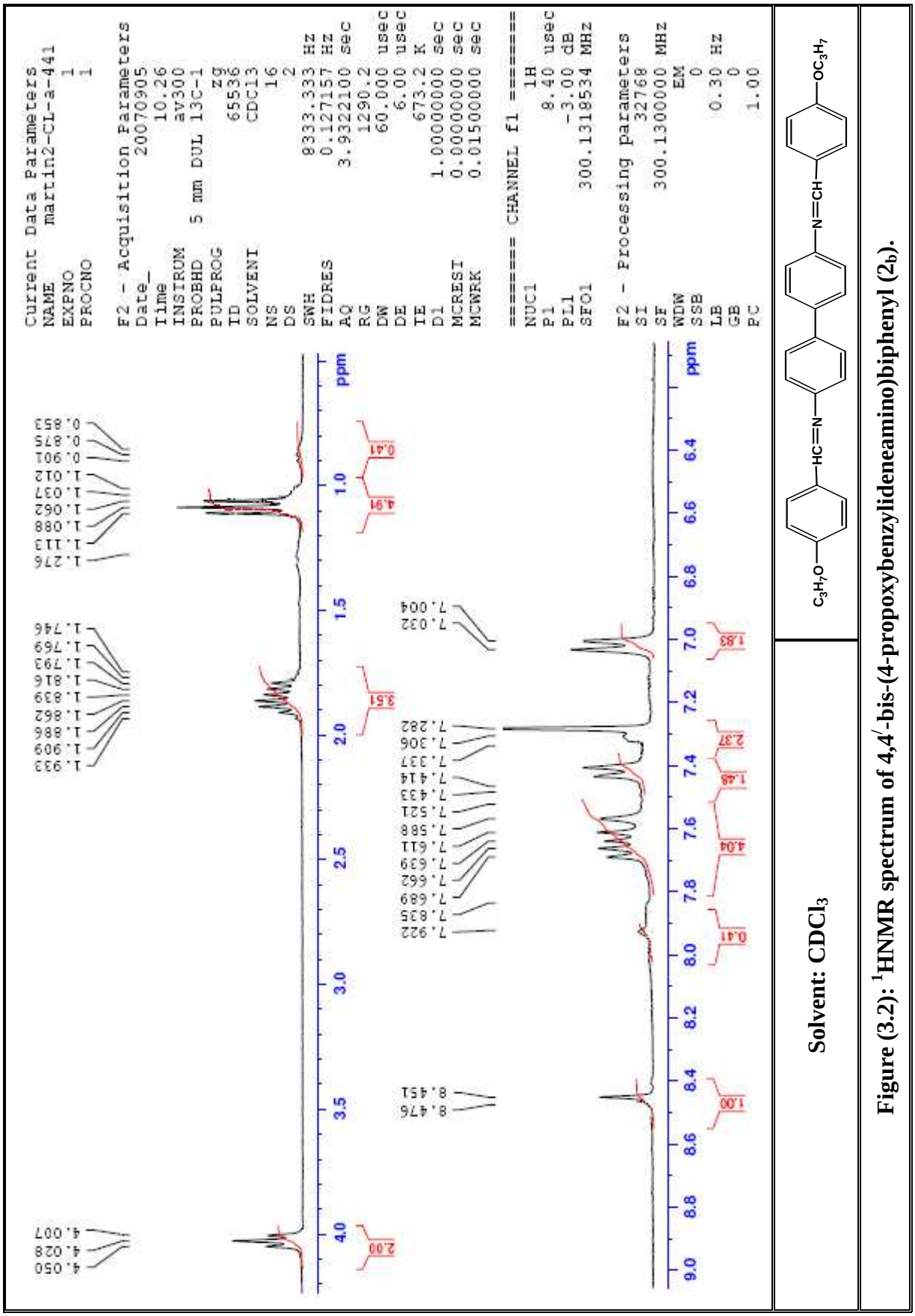


Figure (3.2): ^{1}HNMR spectrum of 4,4′-bis-(4-propoxybenzylideneamino)biphenyl (2_b).

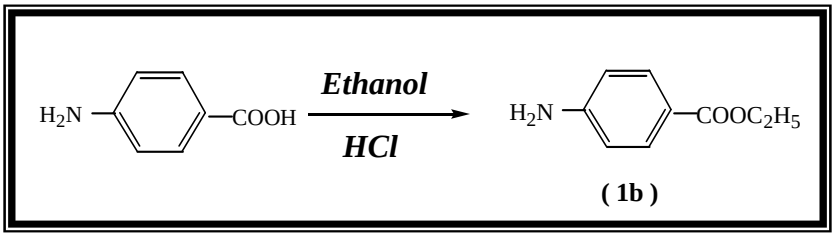
3.2 Preparation and Characterization of 2,5-bis-[4-(4´-propoxybenzylideneamino)phenyl] 1,3,4-oxadiazole (1f)

The route adopted for the synthesis of compound (1_f) was given in scheme (2.2).

4-propoxybenzaldehyde ($\mathbf{1_a}$) was prepared by the reaction of n-propyl bromide with 4-hydroxybenzaldehyde in the presence of sodium hydroxide, the mechanism of the reaction was nucleophilic substitution reaction.

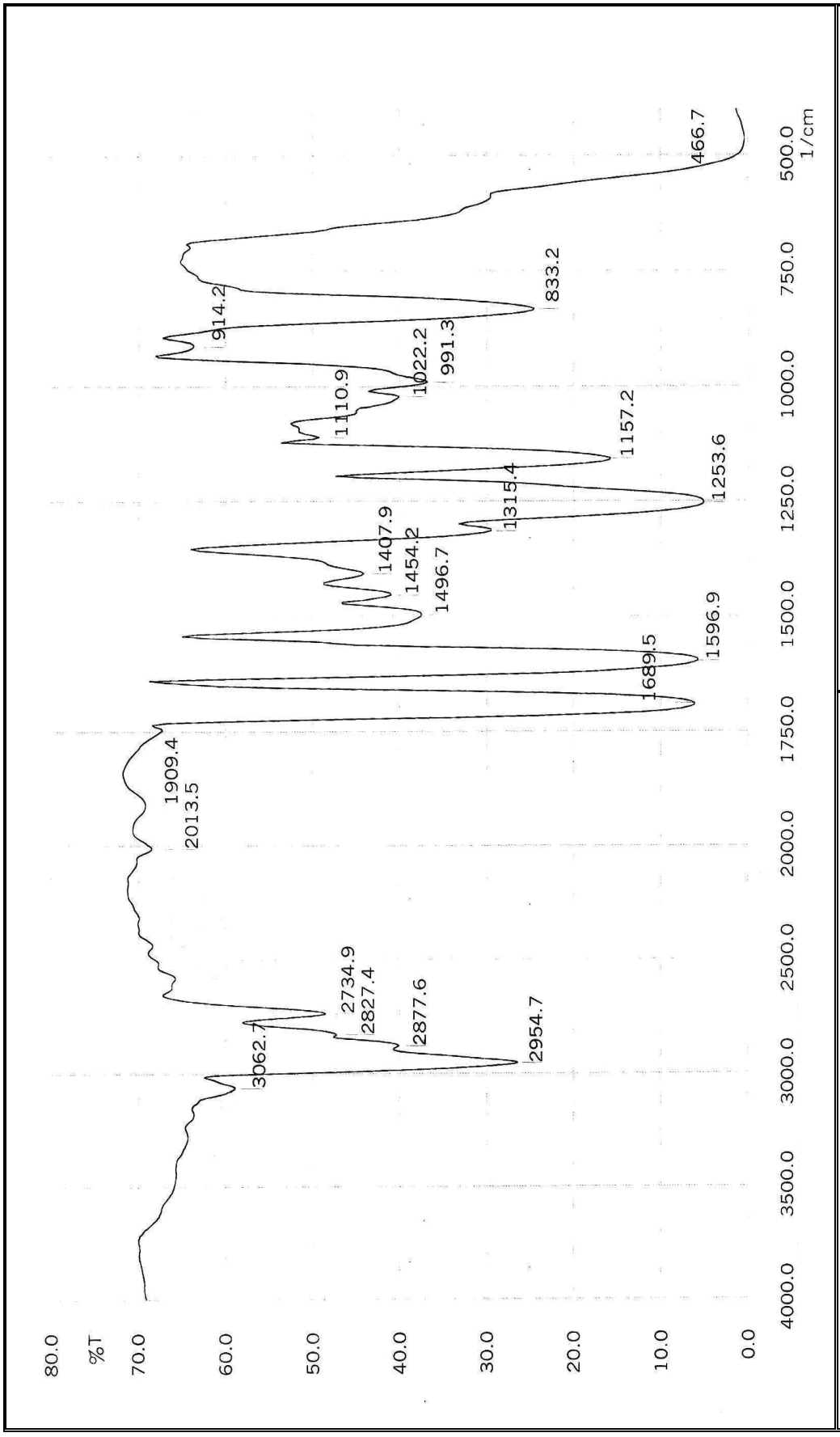
The compound was identified by FTIR spectroscopy. Figure (3.3) shows the FTIR spectrum of ($\mathbf{1_a}$) which showed the characteristic absorption bands at 3062 cm^{-1} that could be attributed to C–H aromatic stretching, and bands at 2954 cm^{-1} and 2877 cm^{-1} were due to aliphatic C–H asymmetrical and symmetrical stretching, respectively. The carbonyl of the aldehyde appeared at 1689 cm^{-1} while the bands at 1596 cm^{-1} and 1496 cm^{-1} are due to the ring C–C skeletal stretching .The C–H bending of the para di-substituted benzene appeared at 833 cm^{-1}.

Ethyl-4-amino benzoate ($\mathbf{1_b}$) was prepared by the condensation reaction of 4-aminobenzoic acid with HCL saturated ethanol



(1b)

The melting point of the compound was (86-88) ºC, while the reported melting point was (88-90) ºC [170].



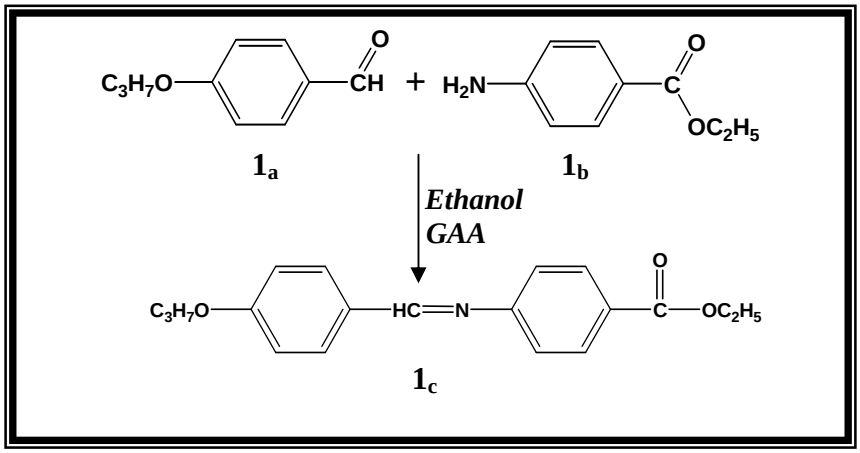
C_3H_7O

Yield: (85 – 90)%

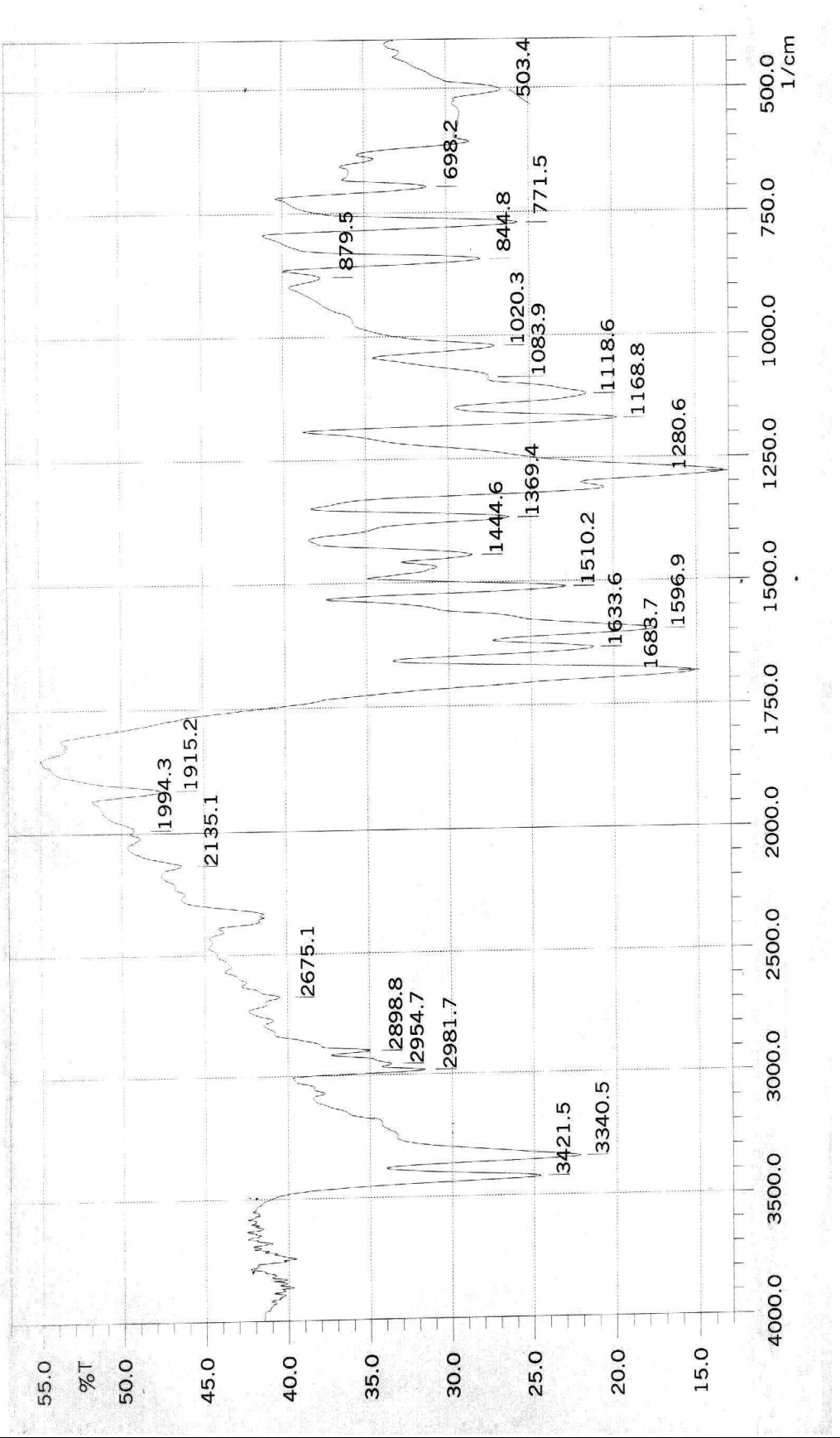
Figure (3.3): FTIR spectrum of 4-propoxybenzaldehyde (1a).

The compound (**1_b**) was also identified by FTIR spectroscopy. Figure (3.4) shows the FTIR spectrum of (**1_b**) using KBr disc which showed the characteristic absorption bands at 3421 cm^{-1} and 3340 cm^{-1} that could be attributed to NH_2 asymmetrical and symmetrical stretching, respectively, and bands at 2981, 2954 and 2898 cm^{-1} due to aliphatic C–H asymmetrical and symmetrical stretching, respectively. The carbonyl of the ester appeared at 1683 cm^{-1} while the C–O stretching of the ester appeared at 1280 cm^{-1}.The C–H bending of the para di-substituted benzene appeared at 844 cm^{-1}.

The 4(4/-propoxybenzylideneamino)ethylbenzoate **(1_c)** was prepared by the condensation reaction between (**1_a**) and (**1_b**) in boiling alcohol.

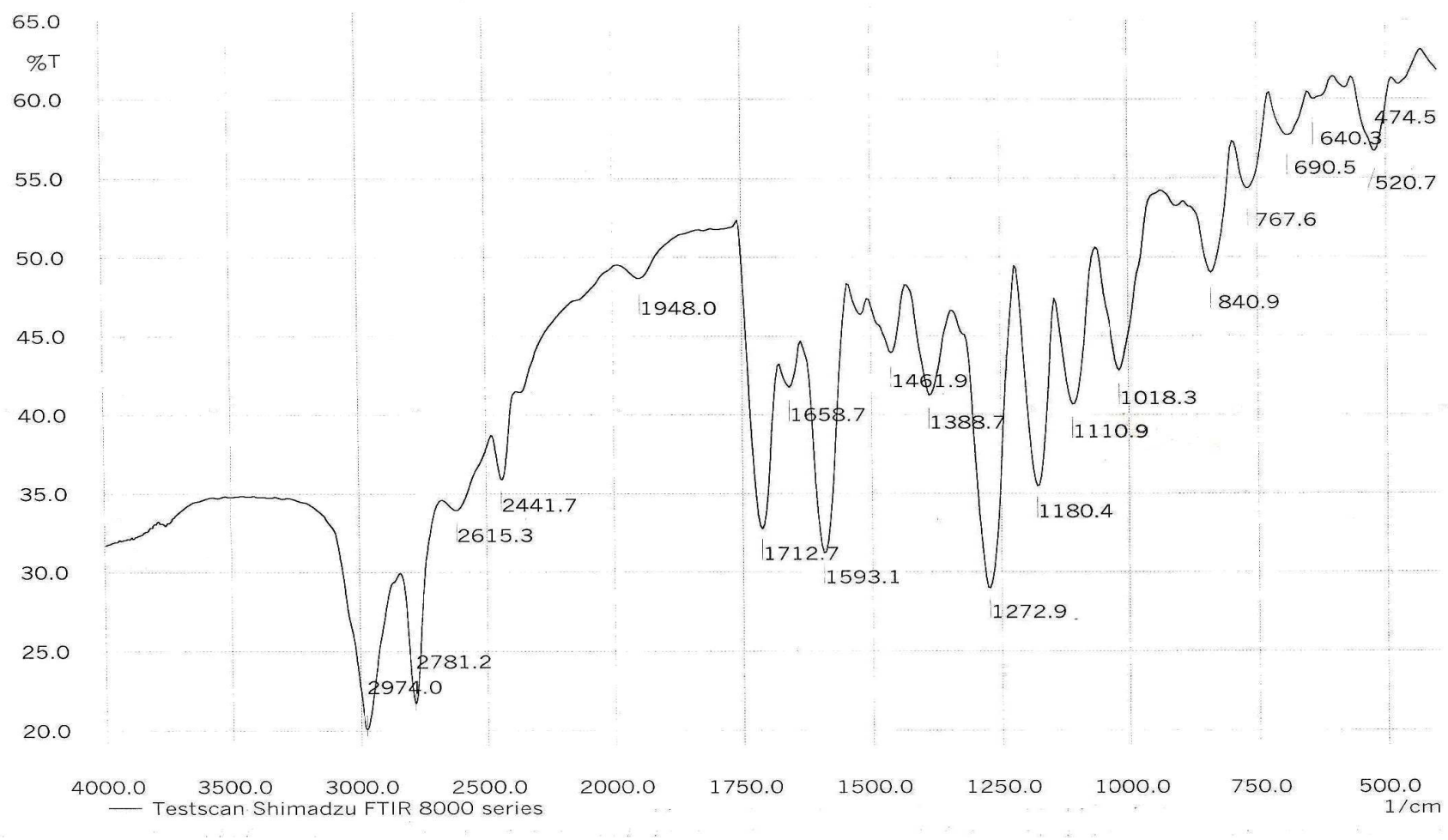


The melting point of this compound (**1_c**) was (66-68) ºC [155]. Figure (3.5) shows the FTIR spectrum for compound (**1_c**). The spectrum shows the disappearance of the NH_2 bands and the appearance of band at 1658 cm^{-1} for C=N stretching. The band at 1712 cm^{-1} represents the carbonyl of the ester.



Melting point:(86 – 88) °C
Yield: (70 – 75) %

Figure (3.4): FTIR spectrum of ethyl 4-aminobenzoate (1_b).



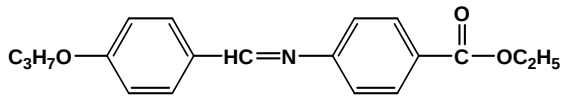
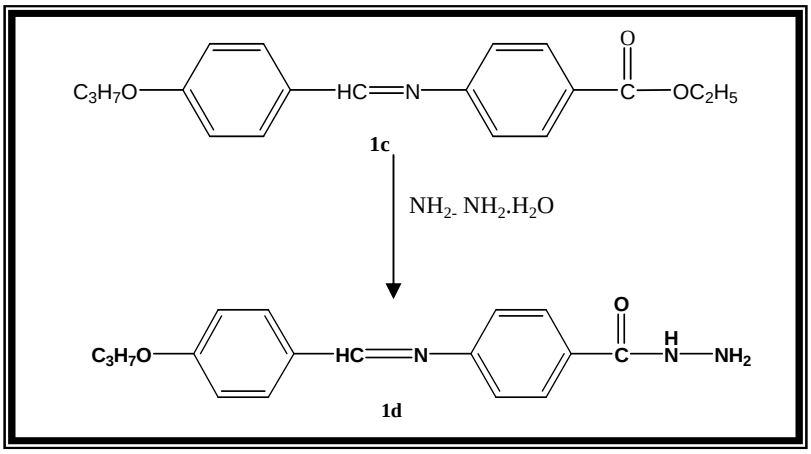
Melting point: (66 -68) ^{o}C	
Yield: (90 – 95)%	

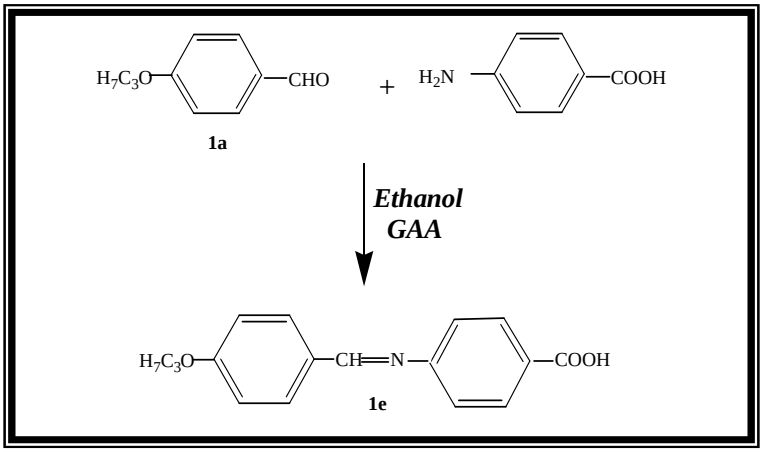
Figure (3.5): FTIR spectrum of 4(4$^{/}$-propoxybenzaylideneamino) ethylbenzoate (1c).

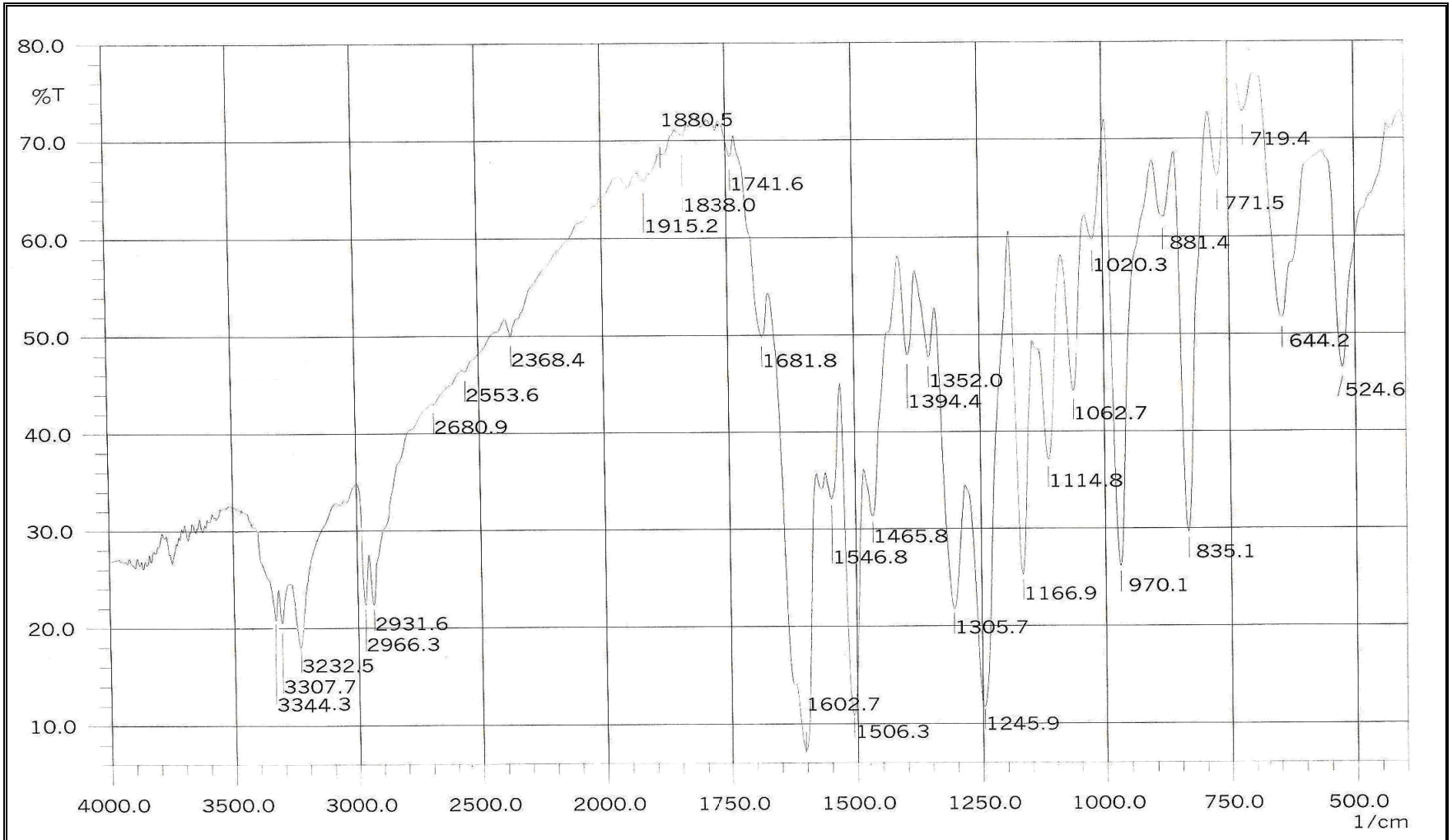
4-(4´-propoxybenzylideneamino)phenyl acid hydrazide **(1_d)** was prepared by the condensation of (**1_c**) with excess hydrazine hydrate in the presence of ethanol as solvent. The melting point of the compound (**1_d**) was (129-131) ºC.



The product was verified by FTIR spectral data. The spectrum is shown in Figure (3.6). The appearance of bands at 3344 cm^{-1}, 3307 cm^{-1} and 3232 cm^{-1} were due to N–H_2 and N–H stretching, respectively. A new stretching band appeared at 1681 cm^{-1} which could be attributed to C = O stretching of amide group (amide I) and a band at 1546 cm^{-1} due to N–H bending (amide II).

4-(4´-propoxybenzylideneamino) benzoic acid (**1_e**) was prepared by the condensation reaction between 4-propoxybenzaldehyde (**1_a**) and 4-aminobenzoic acid in boiling absolute ethanol.





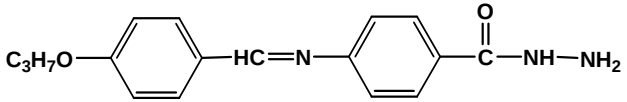
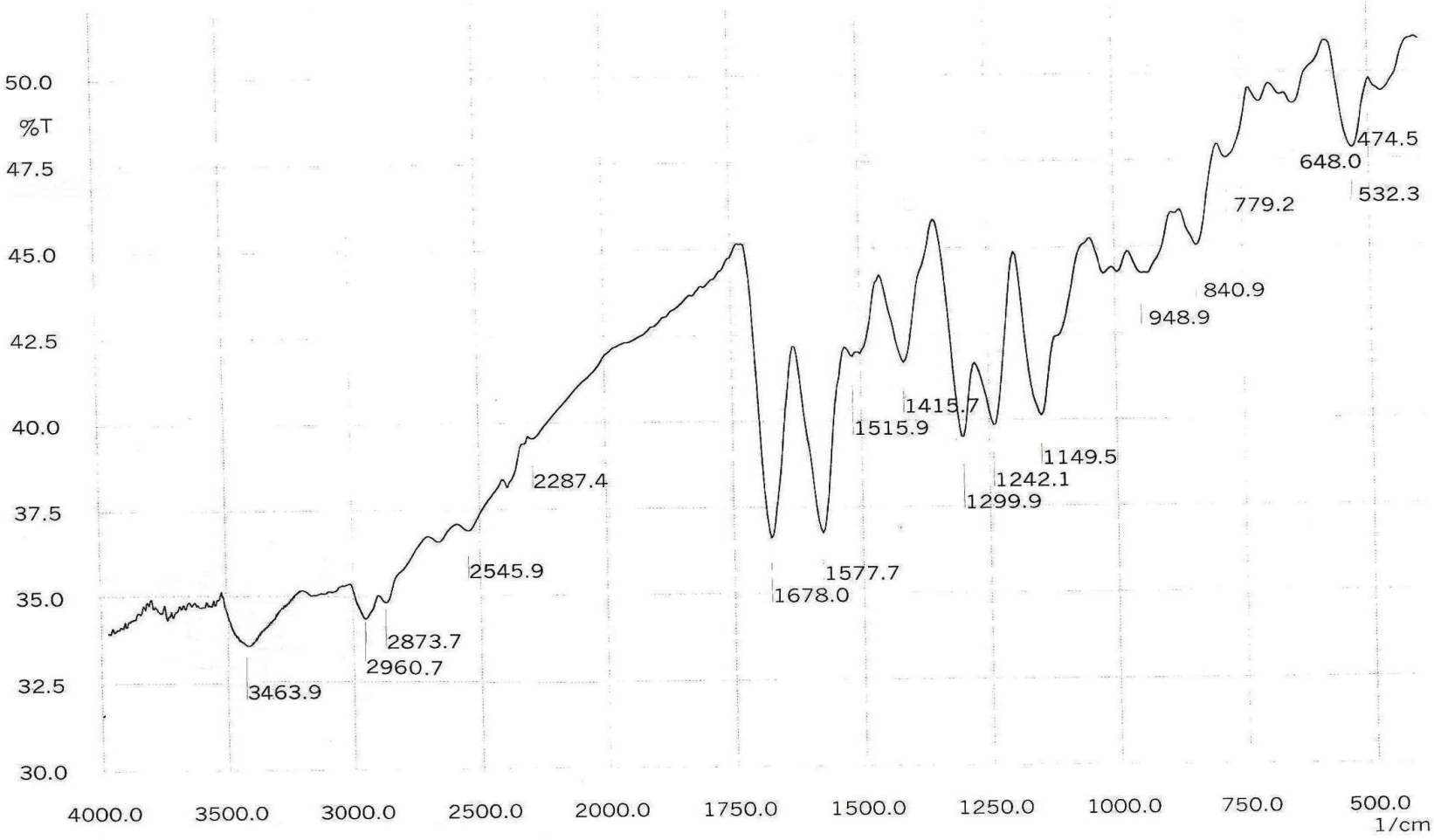
Melting point: (129 – 131) ^{o}C	
Yield: (85 – 90) %	

Figure (3.6): FTIR spectrum of 4-(4´-propoxybenzylideneamino)phenyl acid hydrazide (1_d).

The melting point of the compound was (181-183) ºC. The compound was verified using FTIR, as shown in Figure (3.7). The spectrum shows an absorption band for the O–H stretching at 3463 cm^{-1}. The band at 1678 cm^{-1} represents the stretching of C=O, while the band at 1577 cm^{-1} could be attributed to the stretching of C=C and C=N. The band at 2960 and 2873 cm^{-1} assigned to the asymmetrical and symmetrical stretching C–H aliphatic, respectively. The bending of the C–H aromatic appeared clearly at 840 cm^{-1}.



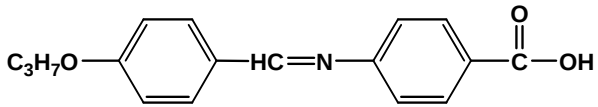
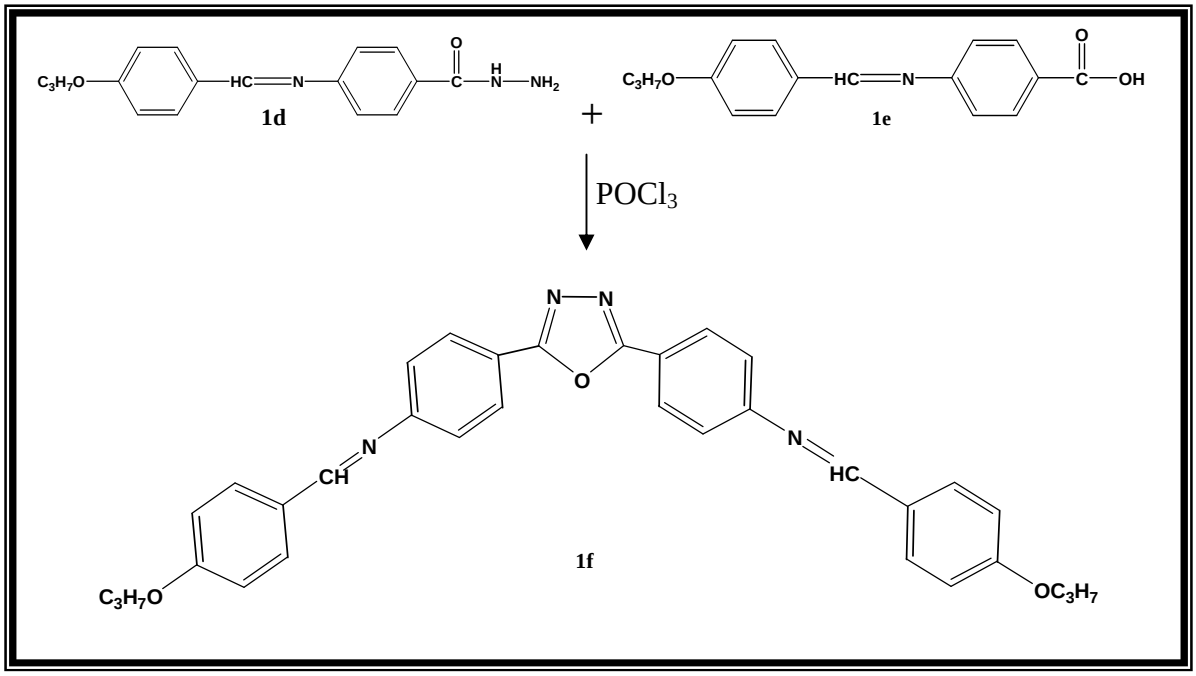
Melting point: (181 – 183) ^{o}C	
Yield: (90 – 95) %	

Figure (3.7): FTIR spectrum of 4-(4´-propoxybenzylideneamino)benzoic acid (1_e).

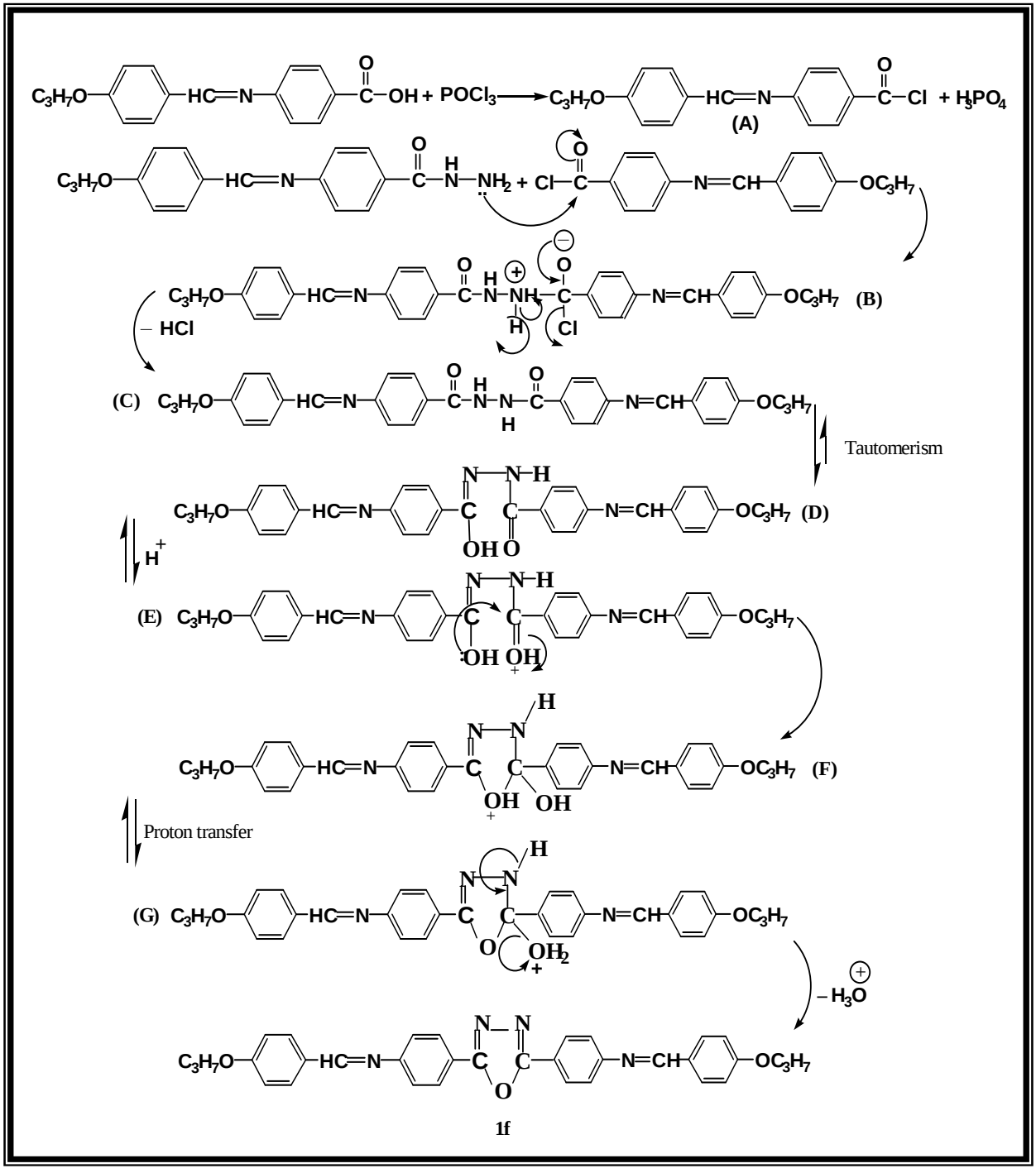
Compound 2,5-bis-[4-(4′-propoxybenzylideneamino)phenyl]1,3,4-oxadiazole (**1_f**) was synthesized by refluxing compound (**1_d**) and 4-(4′-propoxybenzylideneamino)benzoic acid (**1_e**) in phosphorous oxychloride ($POCl_3$).



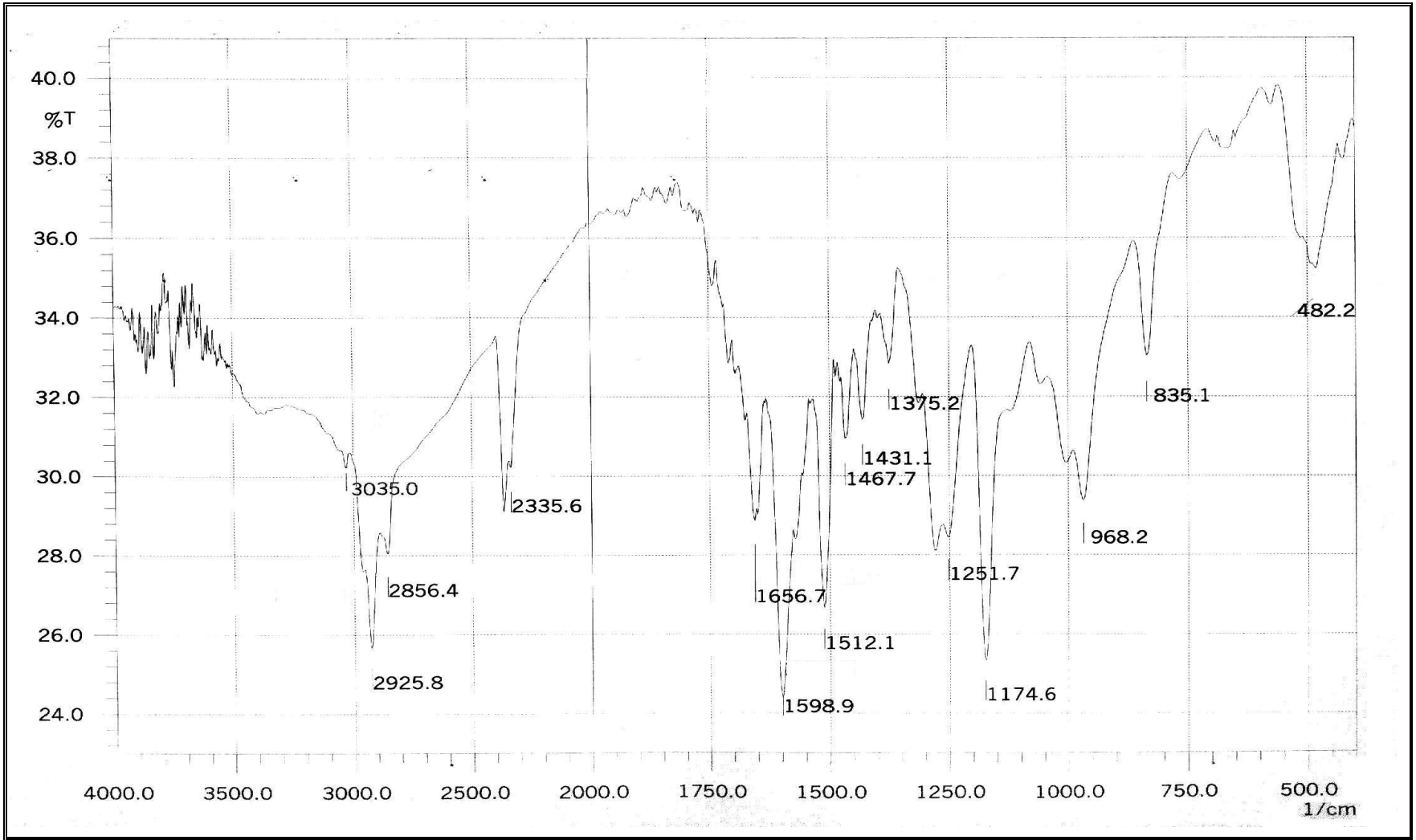
The suggested mechanism of this reaction is outlined in scheme (3.2). The reaction was initiated by the conversion of acid to the acid chloride (A), to increase its electophilicity, followed by a nucleophilic attack of the most nucleophilic nitrogen of acid hydrazide on the carbonyl of the acid chloride in a nucleophilic substitution reaction to keto form intermediate (C) which tautomerised to enol form (D). The enol form (D) in acidic medium was converted to (E). The later intermediate suffered from internal nucleophilic attack by the oxygen atom of the hydroxide to form the oxadiazole ring (**1_f**).

The structure of this compound was elucidated by FTIR, ^{1}HNMR, and CHN elemental analysis. The FTIR spectrum of this compound is shown in Figure (3.8). The spectrum revealed the disappearance of absorption band of N–H, $N–H_2$, and O–H. The appearance of typical absorption of C=N

stretching at 1656 cm^{-1}. Band at 3035 cm^{-1} represented the C–H aromatic and at 2925 and 2856 cm^{-1} assigned to the asymmetrical and symmetrical stretching C–H aliphatic. The C–O–C bond showed asymmetrical and symmetrical bands at 1251 and 1174 cm^{-1}, respectively. The bending of the C–H aromatic appeared clearly at 835 cm^{-1}.



Scheme (3.2): Mechanism of the formation reactions of the compound (1_f).



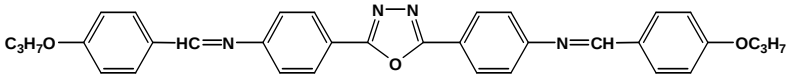
Melting point: (143 – 151) ^{o}C	
Yield: (75 – 80) %	

Figure (3.8): FTIR spectrum of 2,5-bis-[4-(4$^{/}$-propoxybenzylideneamino)phenyl]1,3,4-oxadiazole (1_f).

The ^{1}HNMR spectrum of compound 2,5-bis-[4-(4′-propoxybenzylideneamino)phenyl]1,3,4-oxadiazole (**1_f**) was shown in Figure (3.9). The following characteristics chemical shifts ($CDCl_3$ as a solvent, ppm) appeared: two pairs of doublet at δ 6.97 - 7.04 and 7.82 - 7.86 that could be attributed to the eight protons of the phenyl attached to the oxadiazole ring. While the other doublet of doublet at δ 8.11 - 8.21 suggesting the attribution of the eight protons of the alkoxy phenyl ring which had different substituents at position 1 and 4.

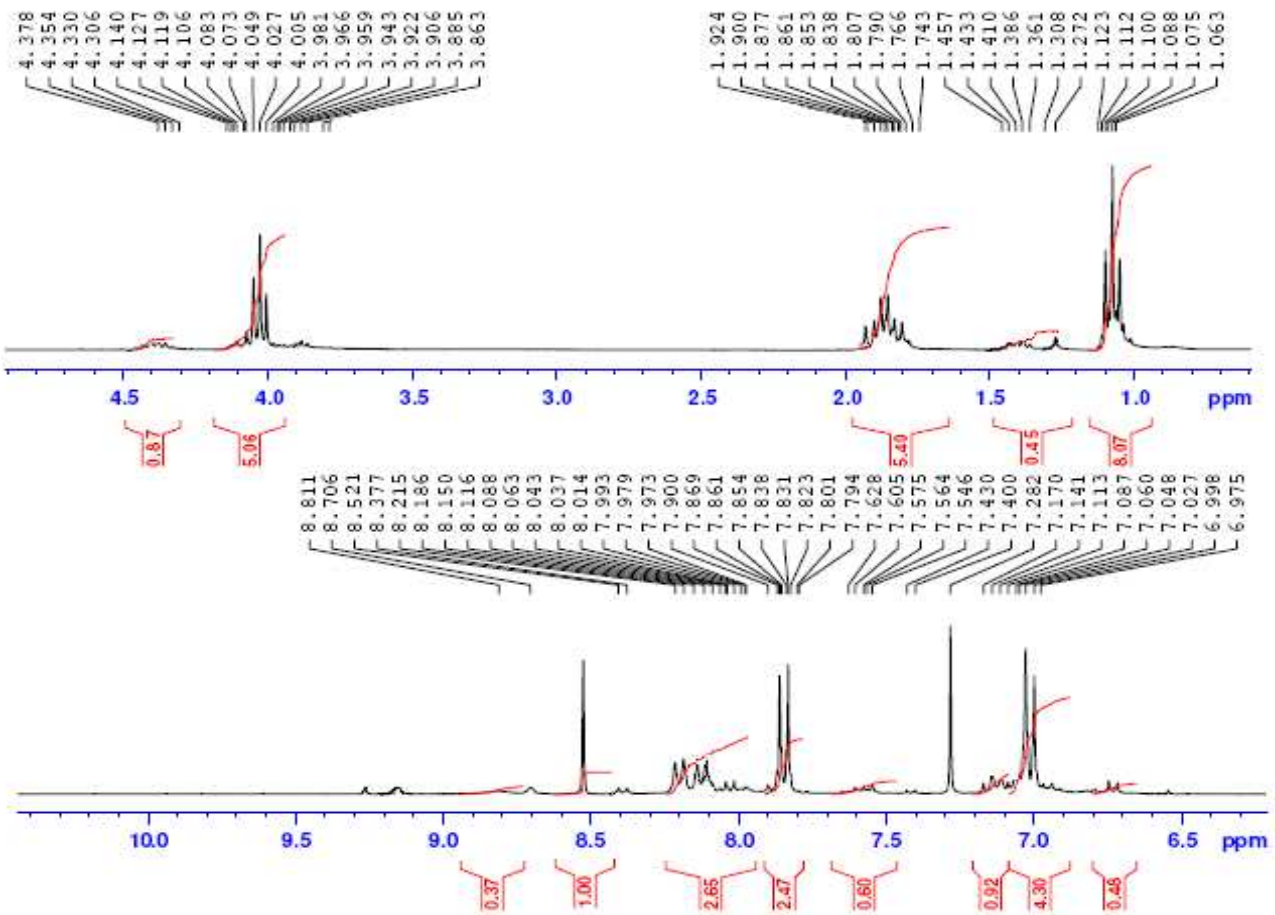
The spectrum also showed a triplet at δ 4.02 - 4.07 that could be assigned to the four protons of (O–CH_2) group, the shift in the value of the group was due to the α- substitution (O– group). The multiple signal at δ 1.80 - 1.92 was assigned to the four protons of the (CH_2) group between (–CH_3) and (OCH_2–). The triplet signal at δ 1.06 - 1.11 was assigned to the six protons of lateral (–CH_3) group. While the proton of the (N=CH) group appeared at δ 8.52 as a sharp singlet signal. The signal at δ 7.28 may be due to the solvent.

CHN elemental analysis was performed and the results are listed in Table (3.2).

Table(3.2):Elemental analysis of 2,5-bis-[4-(4′-propoxybenzylideneamino) phenyl]1,3,4-oxadiazole (1_f).

Element % / Estimation	C %	H %	N %
Theoretical	75.00	5.88	10.29
Experimental *	74.42	5.50	10.54
Relative Error%	- 0.77	- 6.46	+2.43

* Represents the average value of two measurements.



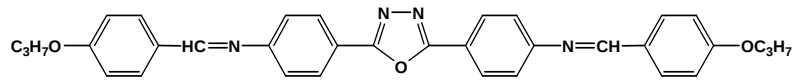
Solvent: $CDCl_3$	

Figure (3.9): ^{1}HNMR spectrum of 2,5-bis-[4-(4$^/$-propoxybenzylideneamino)phenyl]1,3,4-oxadiazole (1_f).

The percentages of the theoretical estimation of the C, H, and N present in 2,5-bis-[4-(4′-propoxybenzylideneamino)phenyl]1,3,4-oxadiazole (**1$_f$**) were 75.00, 5.88, and 10.29, respectively. While the experimental percentages were 74.42, 5.50, and 10.54, respectively. The relative errors between the theoretical and experimental measurements were - 0.77, - 6.46, and +2.43, respectively. From the relative error values it may be said that a good agreement is between theoretical and experimental measurements, although the relative error of the H is relatively high due to its small ratio.

3.3 Liquid Crystalline Properties of the Synthesized Compounds

Liquid crystalline properties of the two synthesized compounds 4,4′-bis-(4-propoxybenzylideneamino)biphenyl (2_b), and 2,5-bis-[4-(4′-propoxy benzylideneamino)phenyl]1,3,4-oxadiazole (1_f) were examined by DSC, and hot-stage polarizing microscope.

3.3.1 Liquid Crystalline Properties of 4,4′-bis-(4-propoxybenzylideneamino)biphenyl (2_b)

The thermal behavior of this compound was shown in DSC thermogram Figure (3.10), and exhibited a peak that represented an actual transition temperature from solid crystal phase to nematic liquid crystalline phase (C → N), at 246 ºC.

The nature of mesophase formed by 4,4′-bis-(4-propoxybenzylideneamino)biphenyl (2_b) was studied by hot-stage polarizing microscope. This compound in its liquid crystalline phase at 246 ºC showed Sheller-nematic texture Figure (3.11), which indicated that the mesophase formed by this compound was nematic. This texture was persisted through heating the sample to > 300 ºC.

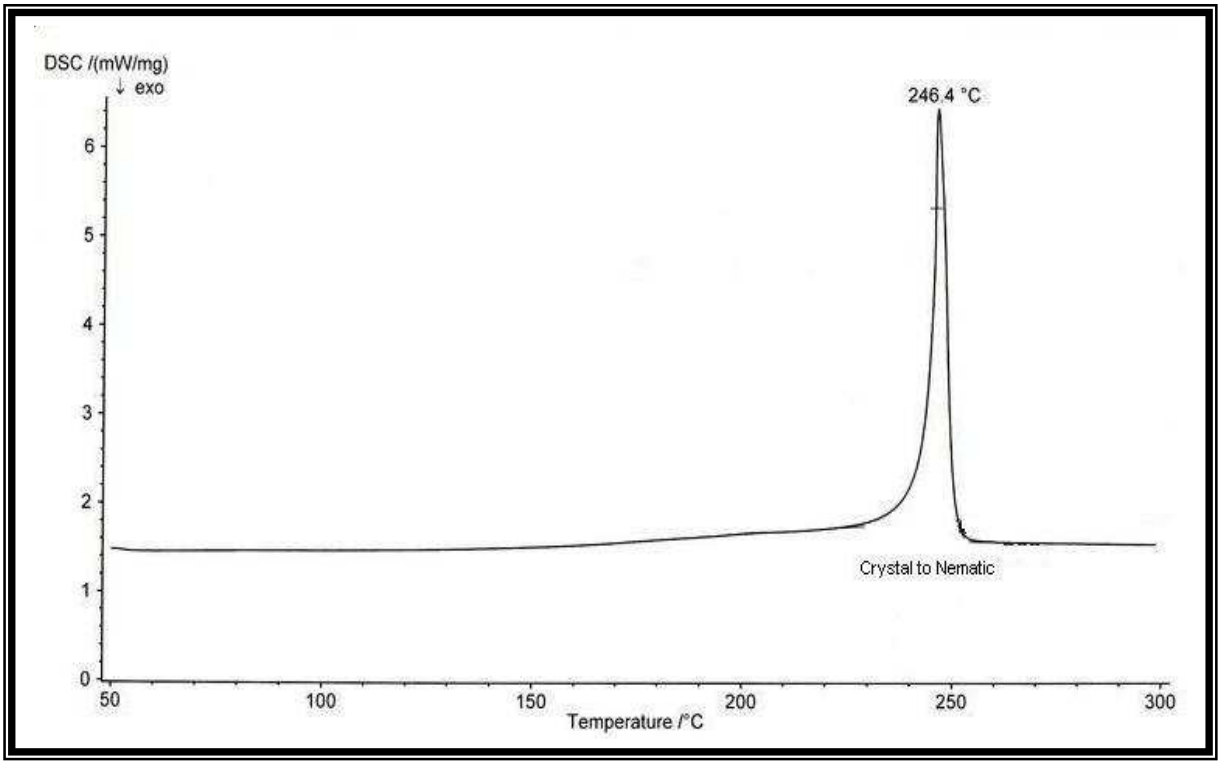


Figure (3.10): DSC thermogram of 4,4′-bis-(4-propoxybenzylideneamino)biphenyl (2_b).

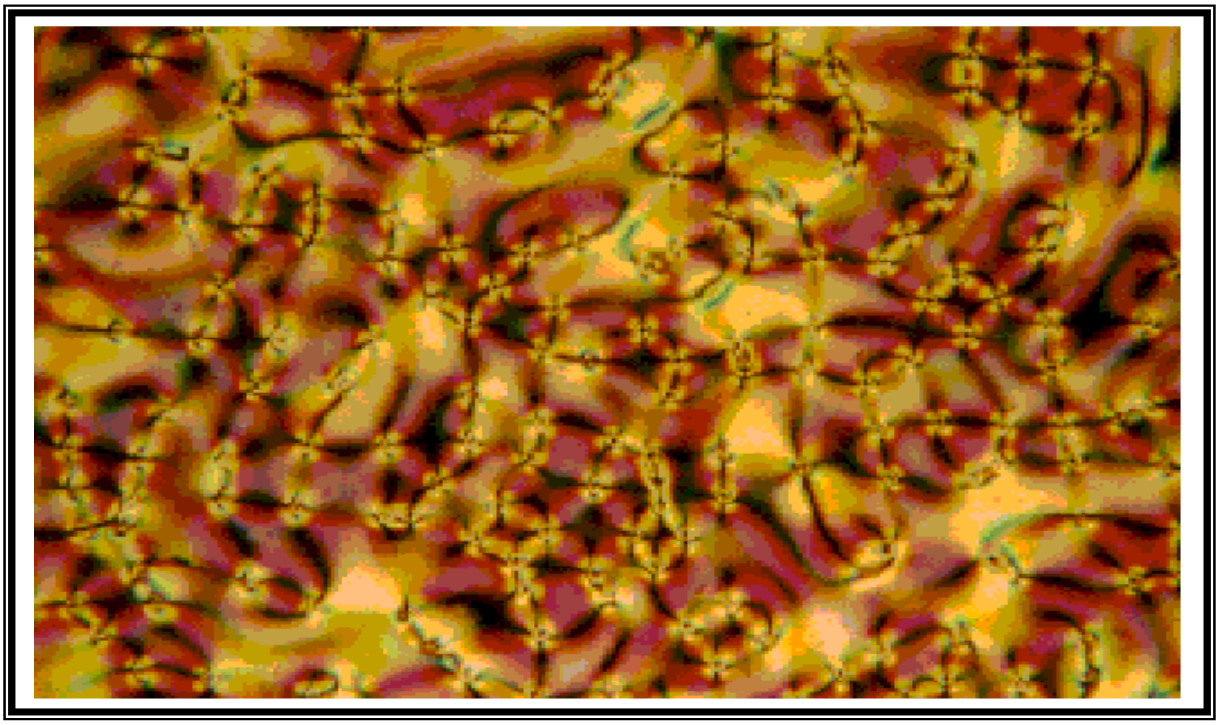


Figure (3.11): Nematic texture of model 4,4′-bis-(4-propoxybenzylideneamino)biphenyl (2_b) at 246 °C.

3.3.2 Liquid Crystalline Properties of 2,5-bis-[4-(4/-propoxybenzylideneamino)phenyl]1,3,4-oxadiazole (1_f)

The DSC thermogram of compound (1_f) is shown in Figure (3.12), which shows two peaks. The first one represented the transition temperature from crystalline phase to crystalline phase (C → C), in both these phases the molecules were tilted with respect to the layer by approximately 25 to 30°, due to molecular tilt [(4)]. The molecular arrangement within a plane appeared at 106 ºC. The second peak was attributed to the transition from solid crystalline phase to nematic liquid crystalline phase (C → N), occurred at 143 ºC. The presence of oxadiazole ring in compound (1_f) cause a change in liquid crystalline properties and the mesophase range of the compound.

The optical observation under the hot-stage polarizing microscope of 2,5-bis-[4-(4/-propoxybenzylideneamino)phenyl]1,3,4-oxadiazole (1_f) revealed that this compound displayed a nematic mesophase of typical thread-like texture at its liquid crystalline temperature range i.e. above 143 ºC (Figure 3.13). On further heating these threads shrinked to form nematic droplets near liquid isotropic transition temperature as shown in Figure (3.14). No liquid isotropic phase has been observed through heating of the compound to a temperature more than 300 ºC.

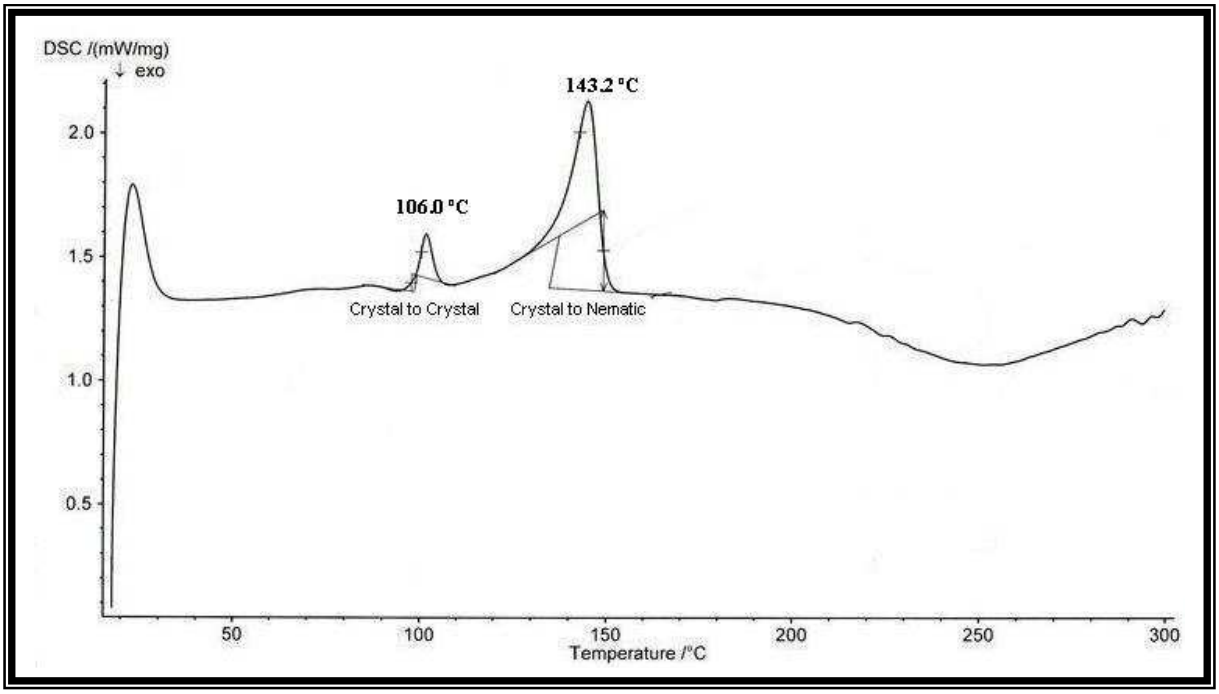


Figure (3.12): DSC thermogram of 2,5-bis-[4-(4′-propoxybenzylideneamino)phenyl] 1,3,4-oxadiazole (1_f).

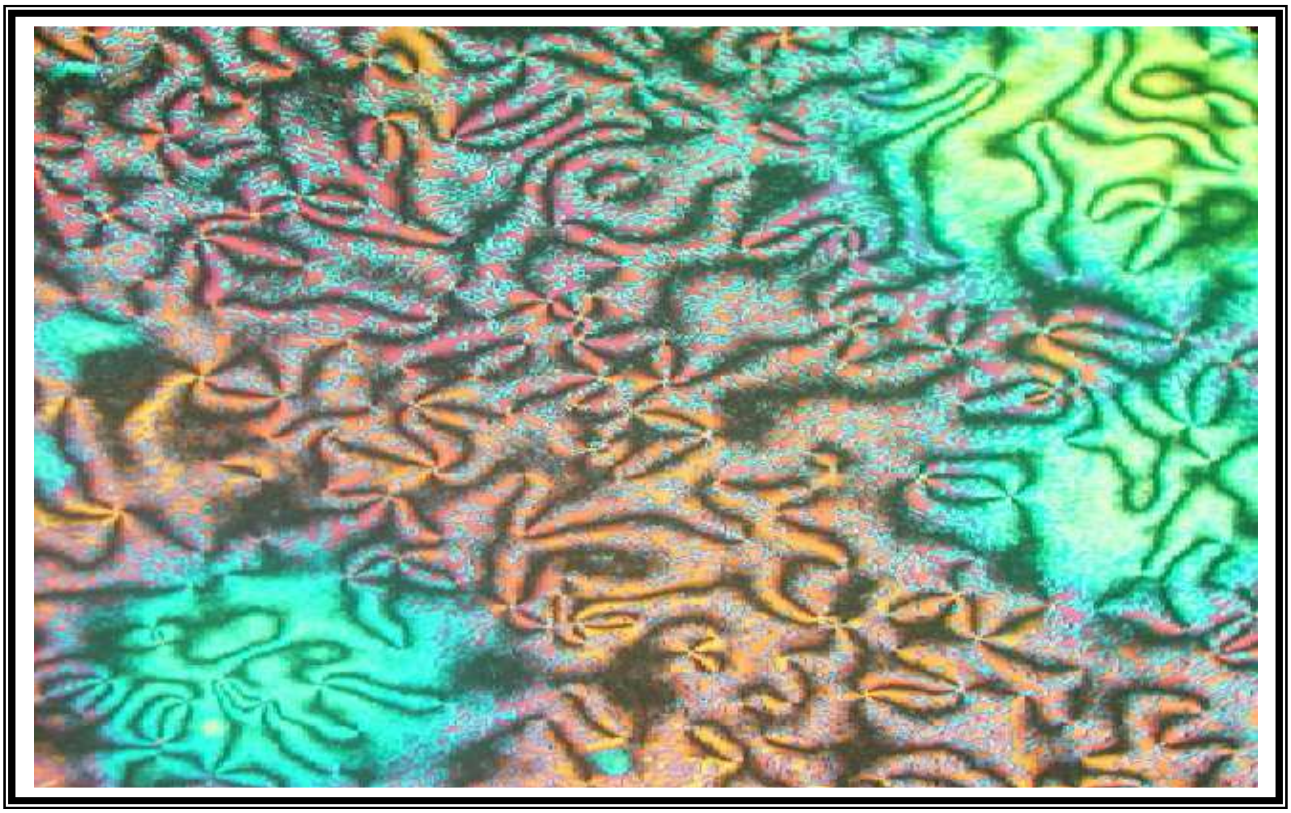


Figure (3.13): Tread-like nematic texture of model 2,5-bis-[4-(4′-propoxybenzylidene amino)phenyl]1,3,4-oxadiazole (1_f) at 143 °C.

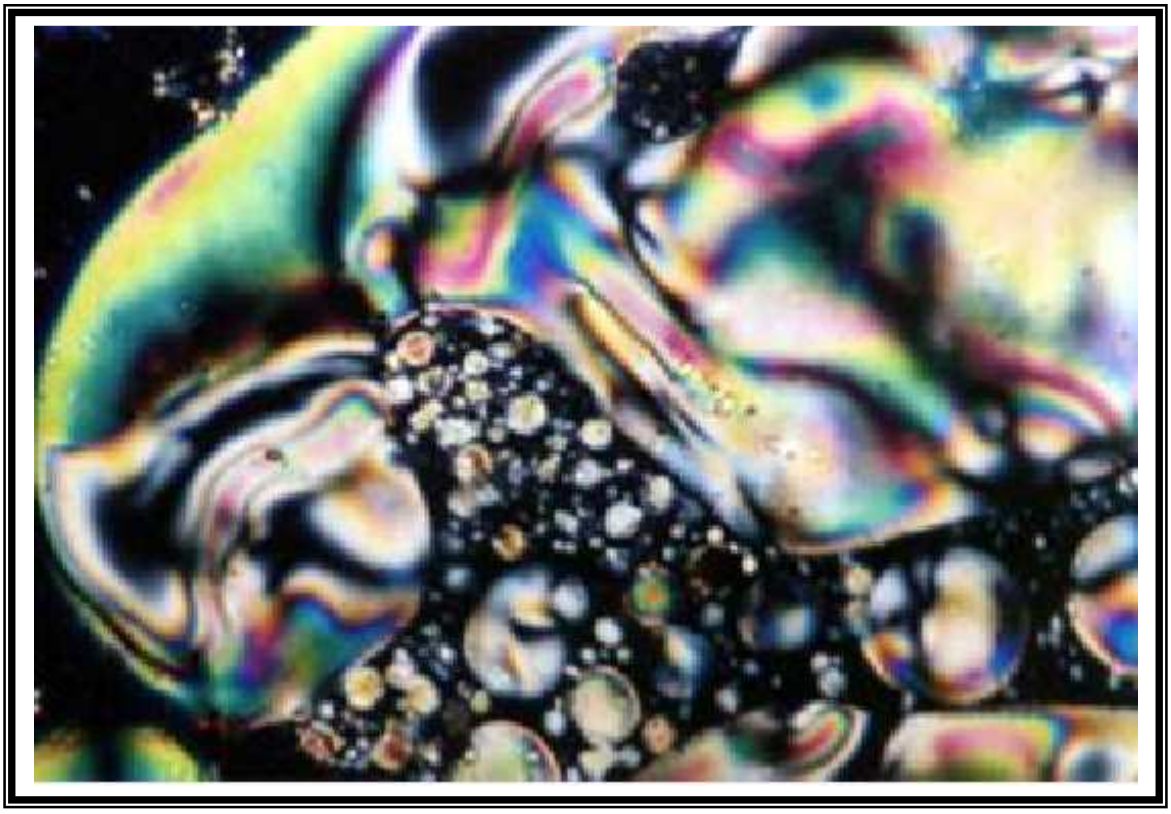


Figure (3.14): Nematic droplets texture of model 2,5-bis-[4-(4′-propoxybenzylidene amino)phenyl]1,3,4-oxadiazole (1_f) at 250 °C.

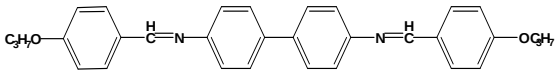
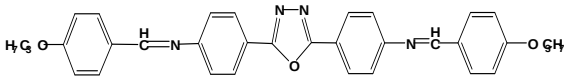
3.4 The Liquid Crystals Stationary Phases

3.4.1 Column Packing

The stationary phases were prepared by coating each of the prepared liquid crystals on the chromosorb W/HP, 100-120 mesh size, solid support. The effect of solid support activity on the chromatographic properties of stationary phase has long been a subject of controversy [166]. In practice, retention times are affected by the amount of liquid phase and the type and treatment of the solid support. So, the use of the chromosorb W/HP, the most inert solid support, is to decrease its influence on the chromatographic properties of the stationary phase [166].

The reason for choosing these two liquid crystals was to study the influence of entering hetero aromatic system like 1,3,4-oxadiazole ring on the chromatographic properties of traditional aromatic systems. In this work, three stationary phases were used, two of them were liquid crystals, and the third one was polyethylene glycol (PEG) or carbowax column as standard column to compare the liquid crystals and conventional columns. Table (3.3) lists the chemical names, structural formula, phase transition, and maximum analysis temperature of the stationary phases.

Table (3.3): Stationary phases used in this work.

Chemical name of the stationary phase	Structural formula	Phase Transition	Max. analysis Temp.°C
4,4′-bis-(4-propoxybenzylideneamino)biphenyl (2_b)		C → LC(N) = 246 LC(N) → I > 350	320
2,5-bis-[4-(4′-propoxybenzylideneamino)phenyl]1,3,4-oxadiazole (1_f)		C → C = 106 C → LC(N) = 143 LC(N) → I > 350	280
Polyethylene glycol (PEG) or Carbowax 20-M	$HO\text{-}(\text{-}CH_2CH_2O)_n\text{-}H$	-----	240

The slurry was prepared by dissolving the liquid crystal in chloroform and mixing it with the solid support using a stirrer to homogenize the mixture. The stirring continued for 24 hours to ensure complete homogeneity and uniform coating. The solvent was then evaporated, and the resulting stationary phase was dried at 100 ºC for two hours.

Different coating percentages (1%, 3%, and 20%) were used to study the influence of the loading percentage on stationary phase characteristics and families of analytes that can be separated.

Column packing was not the only a critical factor, but it represents one of the most important aspects affecting the quality of the chromatographic system. The stationary phase was packed into a stainless steal column, by inserting the glass wool at end of column that was connected to a vacuum pump to prevent the loss of the stationary phase out of the column. The plastic funnel was fixed on the top of the other end. The prepared stationary phase was added into the column through the funnel, and the purpose of using the hand vibrator was to reduce the porosity between particles of stationary phase and to eliminate all dead spaces in the column and to make sure that the column was completely full.

The prepared columns were conditioned for 48 hours by maintaining each column at (10-15) ºC above the maximum temperature at which the column was used, with a stream of nitrogen gas passing through the column. The exit end of the column should be left disconnected from the detector, to avoid the detector contamination. This column conditioning was vital to discard the remaining solvent, humidity, and any other volatiles.

3.4.2 Column Performance Evaluation

The performance for each of the newly prepared columns has been tested. This was done by choosing the optimum flow rate of the carrier gas, class of compounds that can be analyzed through the prepared column, efficiency and selectivity of column.

The retention time (t_R) was affected by several factors such as column length, nature and type of stationary phase, how well the column was packed, the velocity of carrier gas, the pressure as well as the nature of the analyzed compounds. The adjusted retention time (t'_R), was calculated by measuring the time of unretained species (t_m), and subtracting it from the retention time (t_R) to get the corrects time of the analyte spent in the column.

$$\mathbf{t'_R = t_R - t_m} \qquad \text{.....} \quad \mathbf{3.1}\ ^{(175)}$$

A related measure of the column efficiency was the effective plate number ($N_{eff.}$) of a column. The $N_{eff.}$ was calculated using the following equation [175]:

$$\mathbf{N_{eff} = 16\ (t'_R/w_b)^2} \qquad \text{.....} \quad \mathbf{3.2}$$

where t'_R is the adjusted retention time, and w_b is the peak width at base-line.

A better measure of the efficiency of a chromatographic system is resolution (R_s). It is defined as the degree of separation between two neighboring bands or adjacent peaks.

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

where t'_{RA} and t'_{RB} are the adjusted retention times of two adjacent peaks and W_A and W_B are the widths of the peaks at the baseline.

Another useful measure of separation ability of two analytes was the ratio of their partition coefficient on a given column. This ratio is called the column selectivity or more generally, the separation factor.

$$\mathbf{\alpha = V'_B/V'_A} \qquad \text{.....} \quad \mathbf{3.4}$$

where $V'_{A,}$ and V'_{B} are the adjusted retention volumes for A and B solutes components, respectively. A large α means a more selective column, and better resolution.

3.4.3 4,4/-bis-(4-propoxybenzylideneamino)biphenyl (2_b) as Stationary Phase

3.4.3.1 20% Loading of (2_b) as Stationary Phase

The compound (2_b) was packed in GC column as stationary phase, with 20% loading percentage as suggested by previous studies [94,155,176]. The prepared column was used to analyze:

i) Mixture of Poly Aromatic Hydrocarbons (PAHs); naphthalene, acenaphthene, phenanthrene, anthracene, and pyrene as an example of high boiling point compounds, and also as pollutants; in addition to that some of them are considered as carcinogens or mutagens. Therefore, the analysis of PAHs in environmental samples has become an important topic.
ii) Mixture of o, m, p- xylene as an example of positional isomers.
iii) Mixture of alcohols, methanol, ethanol, 2-propanol, 1-propanol, as an example of low boiling point compounds.

Methanol, ethanol, 2-propanol, and 1-propanol were first injected through the column individually. Figure (3.15) shows the chromatogram of each analyte at 200 ºC column temperature, flow rate 20 mL/minute, and N_2 as a carrier gas with pressure of 20 psi. The t_R of methanol, ethanol, 2-propanol, and 1-propanol were 1.44, 3.12, 6.50, and 9.50 minute respectively. This means that the elutions of alcohols depend on their boiling point.

The mixture of alcohols, diluted with hexane, was injected through the 20% (2_b) column at different column temperatures from (140-320) ºC.

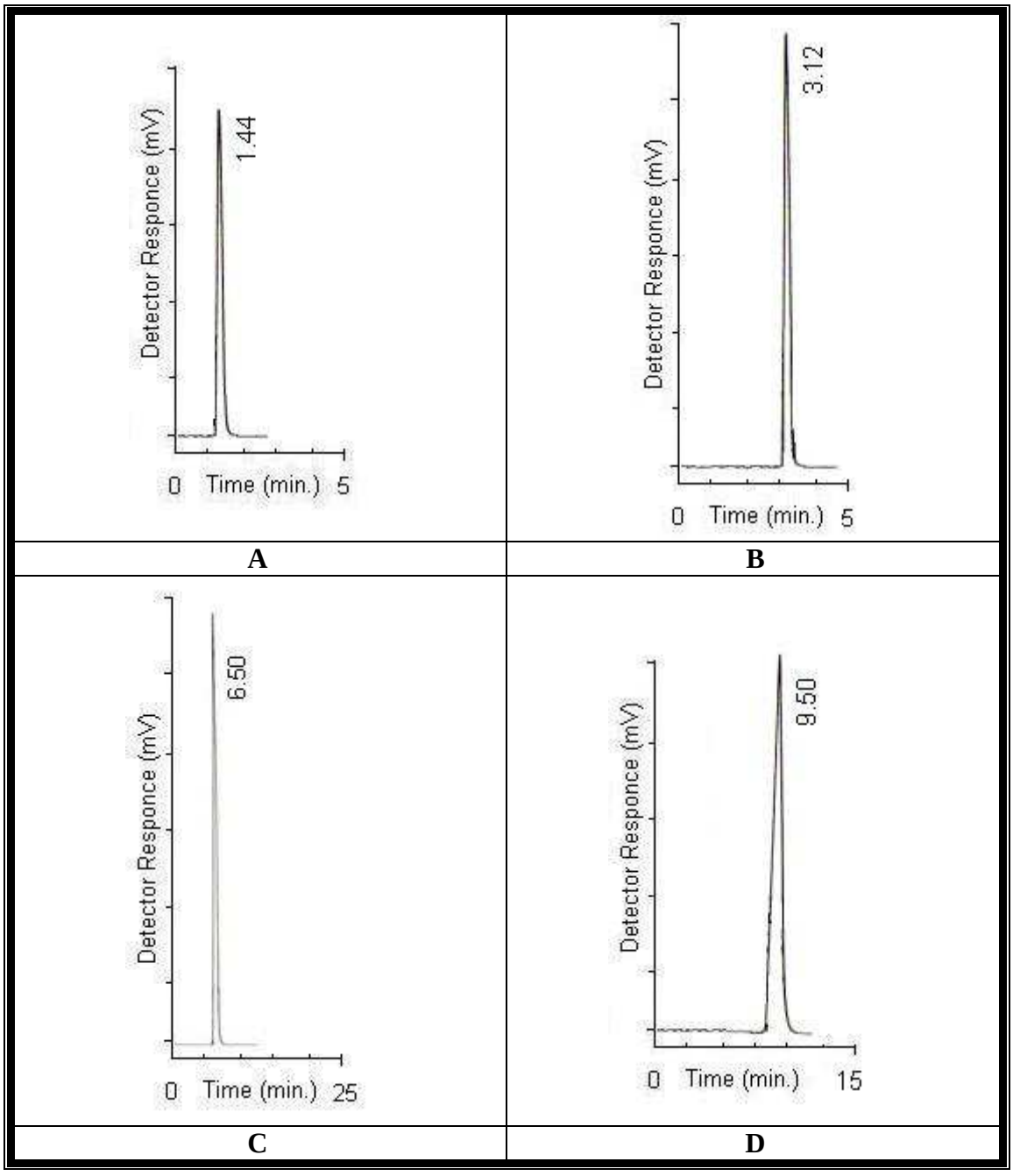


Figure (3.15): Chromatogram of A) methanol, B) ethanol, C) 2-propanol, and D) 1-propanol in 20% (2_b) column. Conditions: column temperature 200 ºC; detector temperature 320 ºC; injector temperature 300 ºC; flow rate: 20 mL/min.; injection volume: 1µL; and carrier gas N_2 with pressure 20 psi.

The chromatograms showed that the best separation took place at column temperature of 180 ºC as shown in Figure (3.16).

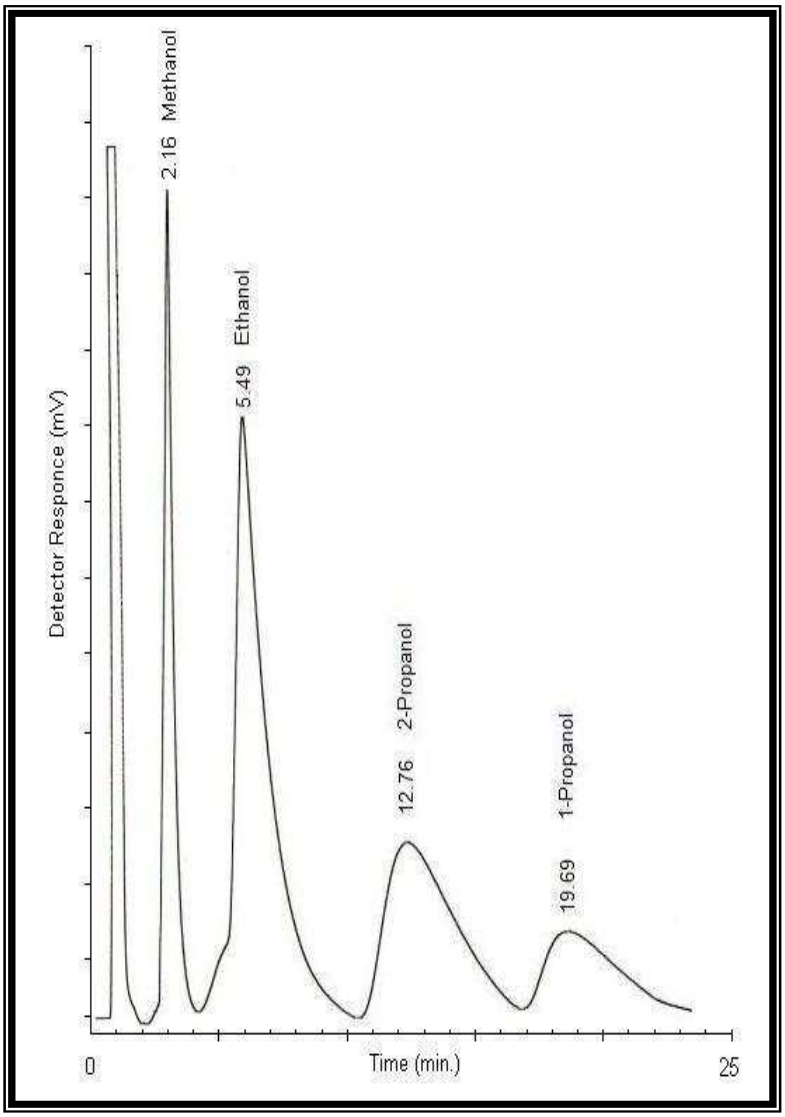


Figure (3.16): Chromatogram of mixture of alcohols in 20% (2_b) column. Conditions: column temperature 180 ºC; detector temperature 320 ºC; injector temperature 300 ºC; flow rate: 20 mL/min.; injection volume: 1µL; and carrier gas N_2 with pressure 20 psi.

Table (3.4) listed the adjusted retention times (t'_R), measured for each analyte in the mixture at a temperature range (140-320) ºC.

Table (3.4): Adjusted retention times (t'_R) for mixture of alcohols on 20% 4,4′-bis-(4-propoxybenzylideneamino)biphenyl (2_b) column.

Compound	Adjusted retention time (t'_R) min. at temp.ºC										
	140	**160**	**170**	**180**	**190**	**200**	**220**	**250**	**270**	**290**	**320**
Methanol	2.58	1.51	1.24	1.07	0.89	0.74	0.40	0.00	0.00	0.00	0.00
Ethanol	12.00	5.80	5.34	4.40	3.25	2.45	1.30	0.39	0.24	0.00	0.00
2- Propanol	38.79	18.86	14.47	11.67	8.17	5.86	2.98	1.06	0.63	0.35	0.21
1- Propanol	57.30	30.65	23.01	18.60	12.47	8.77	4.37	1.51	0.86	0.35	0.21

A related measure of system efficiency was the effective plate number of the column ($N_{eff.}$). The $N_{eff.}$ of 20% (2_b) column for each compound are listed in Table (3.5).

Table (3.5): The effective plate number (N_{eff}) for mixture of alcohols on 20% (2_b) column.

Compound	The effective plate number ($N_{eff.}$) at temp. ºC										
	140	**160**	**170**	**180**	**190**	**200**	**220**	**250**	**270**	**290**	**320**
Methanol	87.68	107.39	102.52	80.90	55.97	48.54	36.60	----	----	----	----
Ethanol	76.13	81.44	96.00	89.46	96.18	92.37	52.12	33.93	24.88	----	----
2- Propanol	68.52	78.96	100.97	96.24	98.67	73.19	56.92	38.45	27.89	21.08	17.29
1- Propanol	52.72	69.61	86.76	193.16	100.73	75.34	53.16	42.98	35.11	21.08	17.29

----- was not measured.

Resolution (R_s) was the term used to describe the degree of separation of successive solute peaks. The R_s values are listed in Table (3.6).

Table (3.6): Resolution (R_s) for mixture of alcohols on 20% (2_b) column.

Compound Pair	Resolution (R_s) at temp. °C										
	140	160	170	180	190	200	220	250	270	290	320
Etha./Meth.	2.13	2.19	2.76	1.87	1.57	1.48	1.45	-----	-----	-----	-----
2-Prop/Etha.	1.78	2.28	2.30	1.90	1.85	1.42	1.41	0.84	0.75	-----	-----
1-Pro/2- Prop	0.64	0.97	1.05	1.21	1.04	0.72	0.63	0.50	0.33	-----	-----

----- was not measured.

The separation also depends on the partition coefficients of the solute components in the column. The separation factor (α) was calculated for each two adjacent peaks. Table (3.7), shows the values of separation factor of alcoholic mixture.

Table (3.7): Separation factor (α) for mixture of alcohols on 20% (2_b) column.

Compound Pair	Separation factor (α) at temp. °C										
	140	160	170	180	190	200	220	250	270	290	320
Etha./Meth.	4.65	3.84	4.31	4.11	3.65	3.31	3.25	-----	-----	-----	----
2-Prop/Etha.	3.23	3.25	2.71	2.65	2.51	2.39	2.29	2.71	2.63	-----	-----
1-Pro/2- Prop	1.48	1.63	1.59	1.60	1.52	1.50	1.47	1.42	1.37	-----	-----

----- was not measured.

In the mixture of alcohols, 2-proanol and 1-propanol were much difficult to separate than any other pairs in the mixture. Although the values of R_s and α for the ethanol/methanol, and 2-propanol/ethanol pairs at 160 and 170°C were

much better than the values of R_s and α at 180 ºC, but these values of 1-propanol/2-propanol at 160 and 170 ºC were not acceptable as a good resolution like the values of R_s and α at 180 ºC. So, the best separation was obtained at 180 ºC. The separation achieved below the mesophase range (246-350 ºC), due to the supercooling phenomenon. This phenomenon occurs with many organic compounds, when the compound is heated and cooled without attention to the cooling rate [166]. Wasik and Chesler [177], have been reported the use of nematic liquid crystal below its normal solid-nematic transition temperature by about 65 ºC. The evidence of supercooling is changing the optimum temperature of alcohols separation, when the column cooling with fast cooling rate. It is found when the cooling rate was vary, the best separation occurred at different temperatures like 160 and 170 ºC.

In order to make a comparison with the separation on the conventional column, the separation of alcohols was done on PEG column. The chromatogram showed only two peaks at the optimized conditions, and no separation was obtained between methanol and ethanol, and 2-propanol and 1-propanol pairs. This work showed the importance of liquid crystal as a stationary phase. Figure (3.17) shows the separation of alcohols mixture on column PEG.

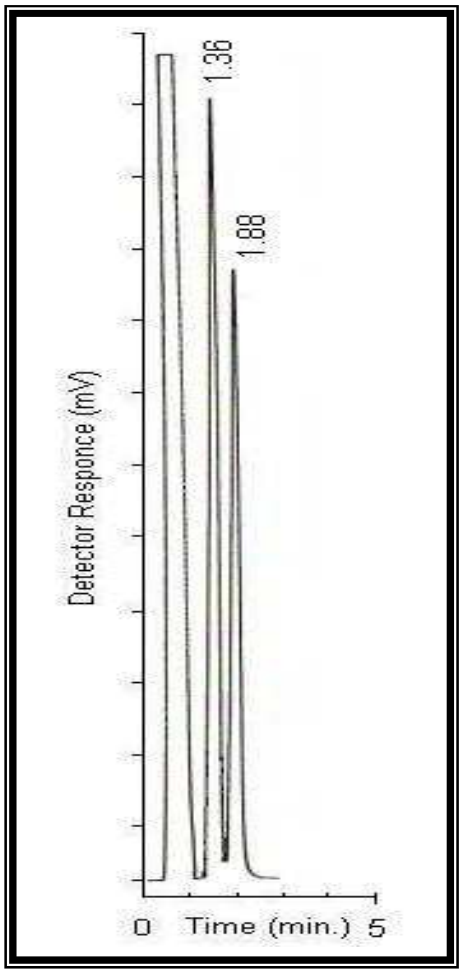


Figure (3.17): Chromatogram of mixture of alcohols in PEG column. Conditions: column temperature 180 ºC; detector temperature 320 ºC; injector temperature 300 ºC; flow rate: 20 mL/min.; injection volume: 1µL; and carrier gas N_2 with pressure 20 psi.

The 20% (2_b) column was also used to analyze positional isomers; o, m, p-xylene. Figure (3.18) shows the chromatograms and the retention times of p, m, and o-xylene were 7.34, 7.51, and 8.63 minute, respectively. The separation took place at a crystal range of liquid crystal compound, so the order of elution was according to their boiling points, p, m, and o-xylene, not to their structure.

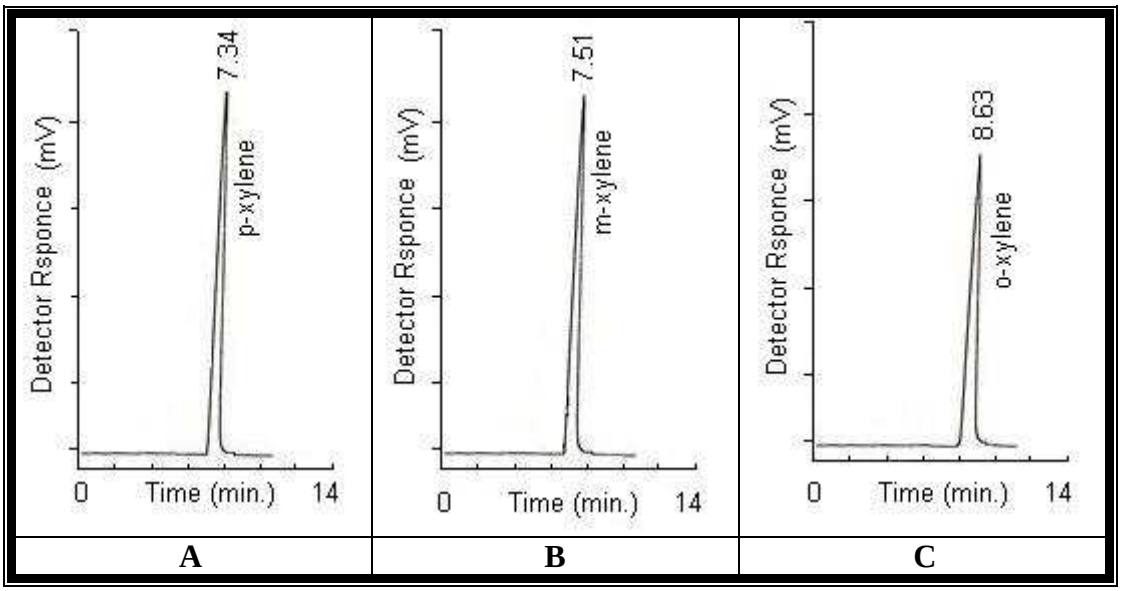


Figure (3.18): Chromatogram of A) p-xylene, B) m-xylene, and C) o-xylene in 20% (2_b) column. Conditions: column temperature 70 ºC; detector temperature 250 ºC; injector temperature 130 ºC; flow rate: 20 mL/min.; injection volume: 0.5 µL; and carrier gas N_2 with pressure 20 psi.

Mixture of xylene isomers diluted with hexane was injected through (2_b) column at different temperatures (50, 70, 110, 130, and 140) ºC. There was no separation between the three isomers at 140, 130, and 110 ºC. Although at 70, and 50 ºC, there was a separation between o-xylene and the two other isomers, however at 50 ºC the separation was the best as shown in Figure (3.19). The R_s and α value at 50 ºC were 1.15, and 1.21, respectively.

Many parameters were changed like the flow rate, temperature of column, injector, and detector, sensitivity of the instrument, and constituents ratio of isomers, to get a better separation between m, and p-xylene isomer, but all attempts did not succeed.

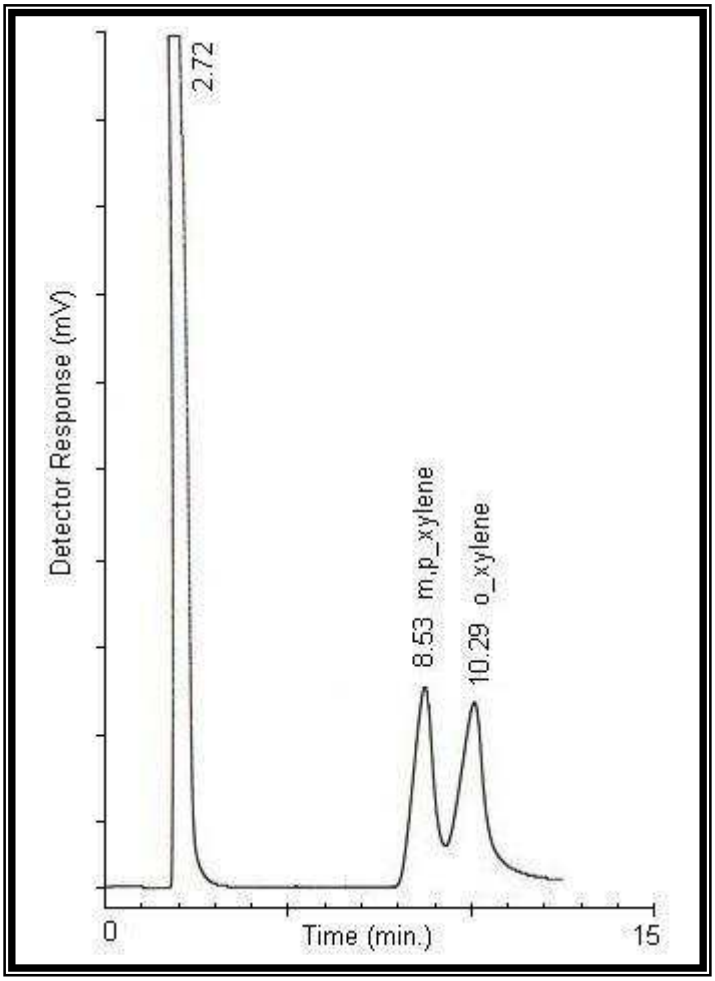


Figure (3.19): Chromatogram of mixture of xylene isomers in 20% (2_b) column. Conditions: column temperature 50 ºC; detector temperature 200 ºC; injector temperature 70 ºC; flow rate: 20 mL/min.; injection volume: 0.5 µL; and carrier gas N_2 with pressure 20 psi.

The 20% (2_b) column was also used to analyze PAHs. Naphthalene, having the lower boiling point among PAHs, was injected through the column. The t_R of naphthalene at optimum conditions (column temperature 350 ºC, detector temperature 300 ºC, and injector temperature 310 ºC), was 8.54 minute. Other PAHs such as acenaphthene, and phenanthrene after 90 minute run, were not eluted; therefore, decreasing the ratio of coating was attempted.

3.4.3.2 3% Loading of (2_b) as Stationary Phase

The compound (2_b), was coated on the solid support with 3%, to improve its ability to analyze the PAH compounds.

The PAHs, naphthalene, acenaphthene, phenanthrene, and anthracene, were dissolved in hexane, and injected through the column individually, as shown in Figure (3.20).

The elution of PAHs was in the trend naphthalene, acenaphthene, phenanthrene and anthracene. The elution patterns of PAHs were almost consistent with their L/B (length to breadth) ratio [93] and their boiling point.

The analysis of PAHs mixture was performed on 3% loading column at the temperature range (180-280) ºC, as shown in Figure (3.21).

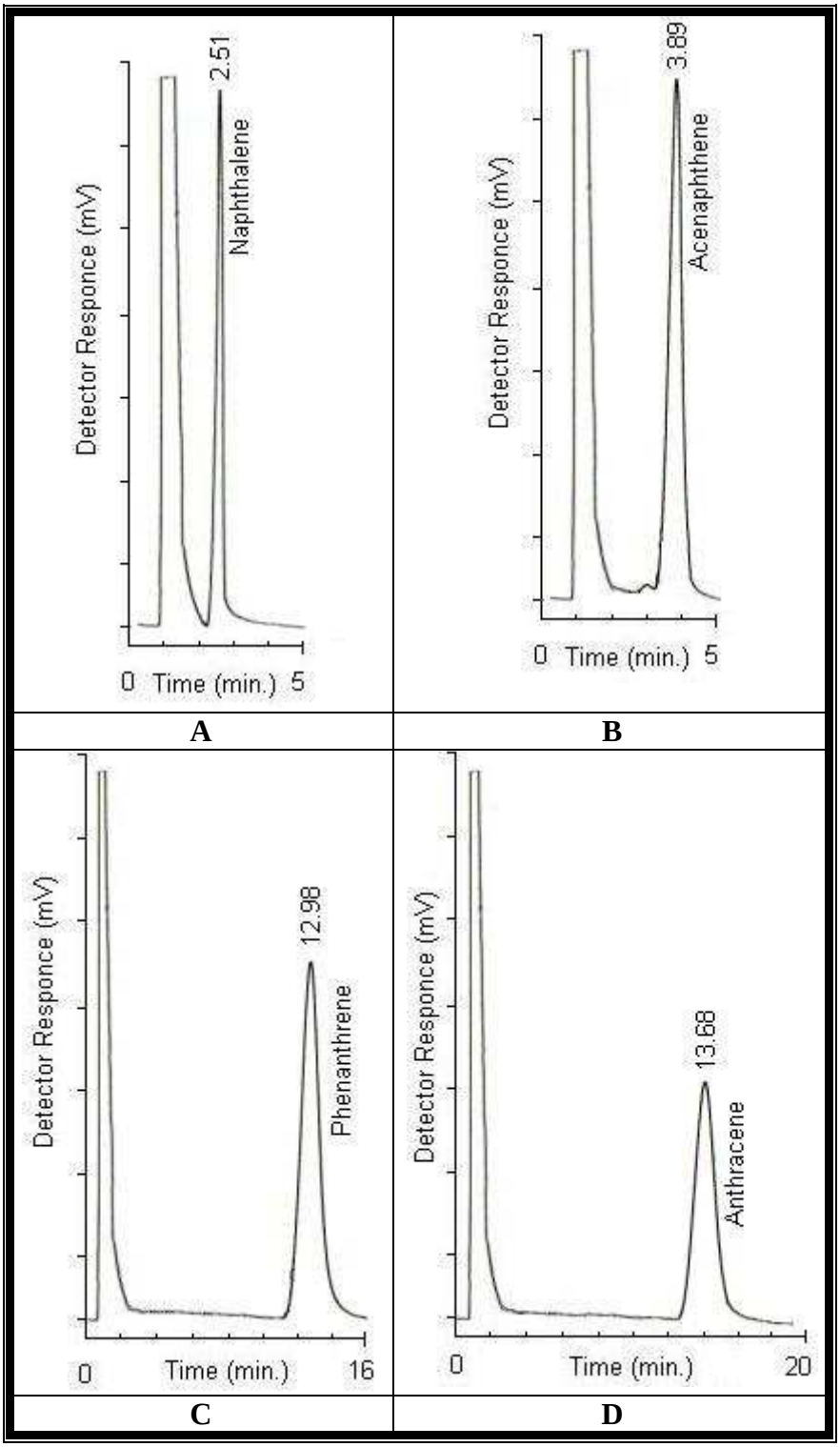


Figure (3.20): Chromatogram of A) naphthalene, B) acenaphthene, C) phenanthrene, and D) anthracene in 3% (2_b) column. Conditions: column temperature 220 ºC; detector temperature 300 ºC; injector temperature 280 ºC; flow rate: 20 mL/min.; injection volume: 0.5 µL; and carrier gas N_2 with pressure 24 psi.

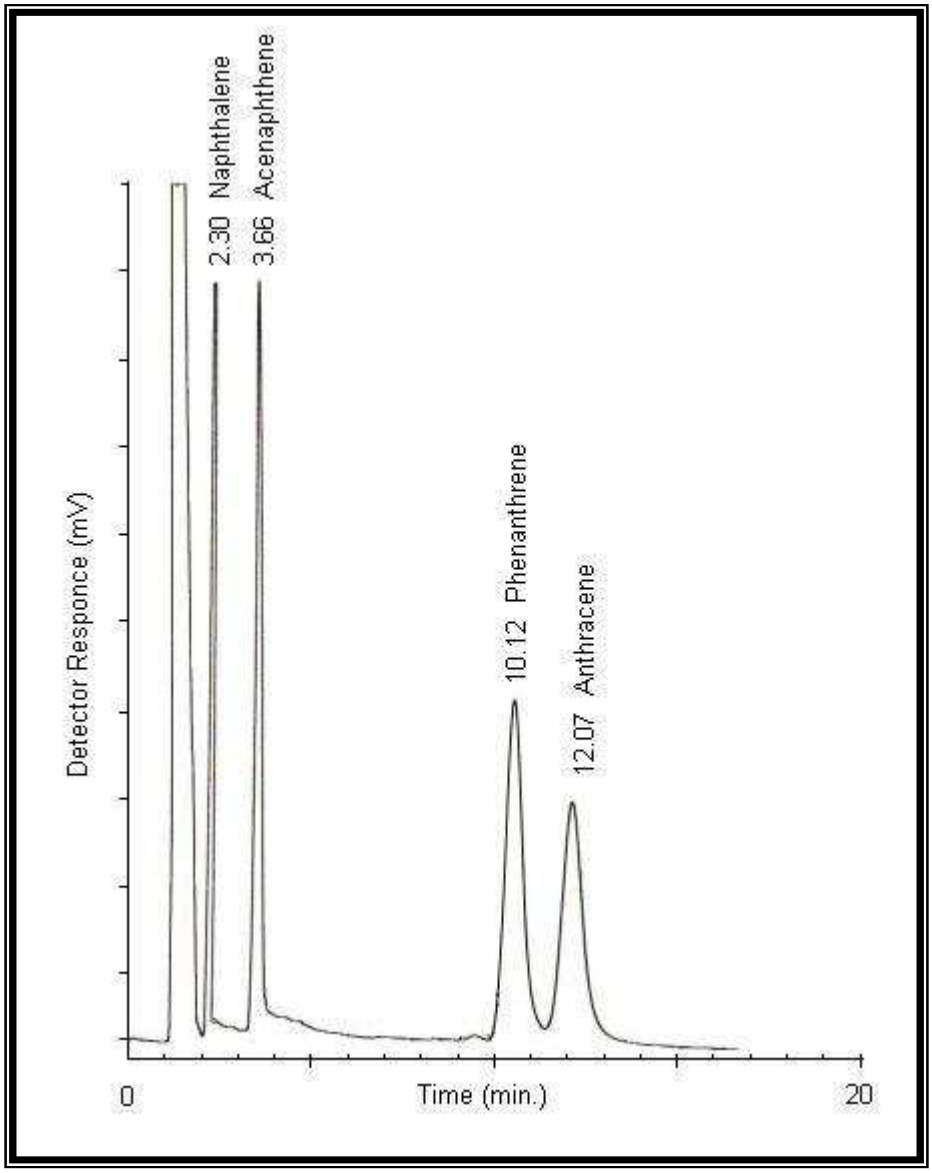


Figure (3.21): Chromatogram of PAHs mixture using 3% (2_b) column. Conditions: column temperature 240 ºC; detector temperature 300 ºC; injector temperature 280 ºC; flow rate: 20 mL/min.; injection volume: 1 µL; and carrier gas N_2 with pressure 24 psi.

The adjusted retention time (t'_R) of each compound in the mixture was measured at different column temperatures. The data of $t'_{R.s}$ are listed in Table (3.8).

Table (3.8): Adjusted retention times (t'_R) for mixture of PAHs on 3% (2_b) column.

Compound	Adjusted Retention Time (t'_R) min. at temp. °C				
	180	220	240	260	280
Naphthalene	1.29	0.66	0.68	0.51	0.45
Acenaphthene	5.65	2.42	2.04	1.46	1.54
Phenanthrene	33.27	11.33	8.50	5.59	4.26
Anthracene	33.27	12.98	10.45	6.73	4.93

The t'_R values showed that the separation took place at all temperatures, except at 180 °C, when the t'_R was the same for phenanthrene, and anthracene, and also it was found that as the temperature increased the retention time decrease. This arises from the fact that with an increase in temperature the order of a liquid crystal decreases, so the interaction between the molecules of substances and the structure of liquid crystal will decrease. The $N_{eff.}$, R_s, and α values of the mixture constituents at different temperatures were calculated, to determine at which temperature best resolution can be achieved. Table (3.9) shows the $N_{eff.}$ of the column (2_b) for each analyte at different temperatures.

Table (3.9): The effective plate number (N_{eff}) for mixture of PAHs on 3% (2_b) column..

Compound	The effective plate number ($N_{eff.}$) at temp. °C				
	180	220	240	260	280
Naphthalene	30.66	54.45	118.37	104.04	100.00
Acenaphthene	107.20	205.79	289.00	176.17	249.48
Phenanthrene	126.39	633.92	874.10	453.49	646.83
Anthracene	126.39	516.16	1193.39	621.30	710.15

The plate number values show maximum at temperatures 220, and 240 ºC, so we can expect that a good separation achieved at these two temperatures.

In order to assess the performance and separation efficiency of column it was necessary to determine the R_s and α. The R_s and α values for PAHs mixture are listed in Tables (3.10), and (3.11), respectively.

Table (3.10): Resolution (R_s) for mixture of PAHs on 3% (2_b) column.

Compound Pair	Resolution (R_s) at temp. ºC				
	180	220	240	260	280
Acena./Napht	2.80	3.45	3.73	2.97	3.82
Phen./Acena.	3.17	7.12	7.74	5.54	5.13
Anth./Phen.	-----	0.81	1.63	1.07	0.95

----- was not measured.

The results in Table (3.10), indicated that the resolution between naphthalene, acenaphthene, and phenanthrene were possible at all temperatures with acceptable values ranged from (2.80 - 7.74), while the separation between phenanthrene, and anthracene (structural isomers), was difficult at 180, 220, 260, and 280 ºC, however, at temperature of 240 ºC gave an acceptable value (R_s = 1.63).

Table (3.11): Separation factor (α) for mixture of PAHs on 3% (2_b) column.

Compound Pair	Separation factor (α) at temp. ºC				
	180	220	240	260	280
Acena./Napht	4.38	3.67	3.00	2.86	3.42
Phen./Acena.	5.89	4.68	4.17	3.83	2.77
Anth./Phen.	-----	1.14	1.23	1.20	1.16

----- was not measured.

The separation factor (α) values in Table (3.11) for PAHs were acceptable, at all temperatures especially, at 180, 220, and 240 ºC, but at 180 ºC three PAHs can be separated, while at 220 and 240 ºC four PAHs can be separated.

A better separation was obtained at the temperature of 240 ºC. This means that the higher order of the liquid crystal stationary phase happened at this temperature which made molecules of substances interact with the stationary phase and retained longer in the column. The separation achieved in temperature below the solid-nematic transition temperature, due to the supercooling phenomenon. It is found when the loading ratio decreases, the shift in mesophase range due to the supercooling phenomenon, have been smaller.

Other PAHs, like pyrene, benzo[e] pyrene, and benzo[a] pyrene, which have a higher boiling point, were injected through the (2_b) column. These compounds retained through the column for a long time, so the decreasing of loading percentage was suggested.

A mixture of aliphatic alcohols; methanol, ethanol, 2-propanol, and 1-propanol was injected through the 3% (2_b) column, individually. The retention times of the constituents of alcohols mixture at column temperature 120 ºC were 0.73, 0.75, 0.79, and 0.85, respectively. The mixture of the alcohols was injected through the column, and it gave only one peak at 0.86 minute.

Xylene isomers mixture was also injected in the prepared column, and only one peak of the mixture was also obtained, so we can conclude that the separation of alcohols and xylene isomers were difficult at 3% loading.

3.4.3.3 1% Loading of (2_b) as Stationary Phase

A 1% loading ratio (2_b) stationary phase was coated on chromosorb W/HP, to study the influence of decreasing coating percentage on the chromatographic performance in the separation of PAHs.

A prepared mixture of PAHs containing naphthalene, acenaphthene, phenanthrene, anthracene, and Pyrene was analyzed. After column conditioning, the mixture was injected at different temperatures. Figure (3.22) represents the chromatogram of PAHs mixture at column temperatures of 240 ºC.

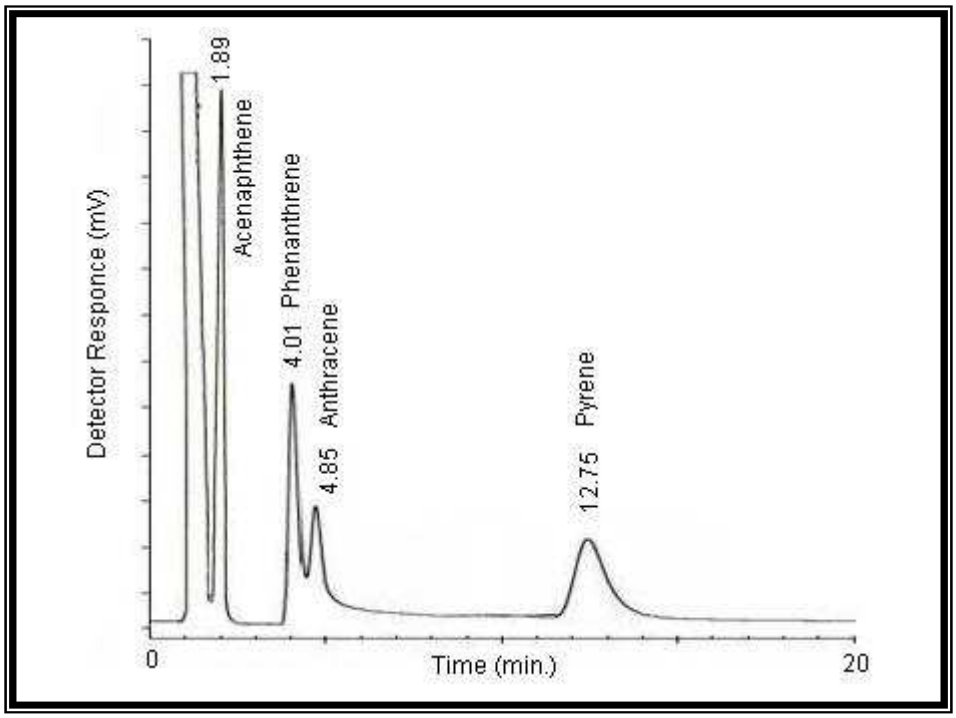


Figure (3.22): Chromatogram of PAHs mixture in 1% (2_b) column. Conditions: column temperature 240 ºC; detector temperature 300 ºC; injector temperature 280 ºC; flow rate: 20 mL/min.; injection volume: 1 µL; and carrier gas N_2 with pressure 35 psi.

The adjusted retention time for each compound was measured at temperatures range from (180-280) ºC. Table (3.12) summarized the obtained results. Naphthalene was eluted with solvent at all temperatures. Acenaphthene had t'_R

1.20 minute at 180 ºC, and when the temperature increased the retention time decreased, and was eluted with solvent at 260 ºC. The t'_R values of phenanthrene ranged from (7.32-1.45) minute through that range of temperatures. While the t'_R values of anthracene (the structural isomer of phenanthrene), were ranged from (8.70 - 1.73) minute. Pyrene had a relatively high t'_R at 180 ºC, and made the analysis time very long. From the above, it can be concluded that four compounds of the mixture can be separated, at temperatures 180, 200, 220, and 240 ºC, but with different efficiency.

Table (3.12): Adjusted retention times (t'_R) for mixture of PAHs on 1% (2_b) column.

Compound	Adjusted Retention Time (t'_R) min. at temp. ºC					
	180	**200**	**220**	**240**	**260**	**280**
Naphthalene	0.00	0.00	0.00	0.00	0.00	0.00
Acenaphthene	1.20	0.74	0.62	0.50	0.00	0.00
Phenanthrene	7.32	4.19	3.05	2.62	2.05	1.45
Anthracene	8.70	4.92	3.78	3.46	2.57	1.73
Pyrene	37.54	19.06	11.88	11.36	7.77	5.11

In order to assess the performance and separation efficiency of the column, it was necessary to determine the effective plate number ($N_{eff.}$) of the column, resolution (R_s), and separation factor (α) between each two adjacent peaks in the mixture, and these values are listed in Tables (3.13), (3.14), and(3.15), respectively.

Table (3.13): The effective plate number (N_{eff}) for mixture of PAHs on 1% (2_b) column.

Compound	The effective plate number (N_{eff}) at temp. °C					
	180	200	220	240	260	280
Naphthalene	0.00	0.00	0.00	0.00	0.00	0.00
Acenaphthene	36.92	17.38	16.53	25.00	0.00	0.00
Phenanthrene	376.00	339.21	287.11	305.08	222.28	173.76
Anthracene	315.24	320.08	357.21	414.24	314.15	207.84
Pyrene	724.17	564.10	328.97	603.30	485.87	243.46

Table (3.14): Resolution (R_s) for mixture of PAHs on 1% (2_b) column.

Compound Pair	Resolution (R_s) at temp. °C					
	180	200	220	240	260	280
Acen./Napht.	-----	-----	-----	-----	-----	-----
Phen./Acen.	5.32	4.26	3.65	4.24	-----	-----
Anth./Phen.	0.80	0.73	0.96	1.31	0.92	0..61
Pyre./Anth.	7.65	6.56	4.74	6.25	5.23	3.78

----- was not measured.

Table (3.15): Separation factor (α) for mixture of PAHs on 1% (2_b) column.

Compound Pair	Separation factor (α) at temp. °C					
	180	200	220	240	260	280
Acen./Napht.	-----	-----	-----	-----	-----	-----
Phen./Acen.	6.10	5.66	4.92	5.24	-----	-----
Anth./Phen.	1.19	1.17	1.24	1.32	1.25	1.19
Pyre./Anth.	4.31	3.87	3.14	3.28	3.02	2.95

----- was not measured.

The values of R_s, and α for the acenaphthene / naphthalene pair can not be measured, because naphthalene was eluted with solvent i.e. no separation between the two components. Phenanthrene / acenaphthene pair had acceptable values from 180 to 240 ºC. While at 260, and 280 ºC, acenaphthene started to elute with a solvent, so R_s, and α values can not be measured. Anthracene and phenanthrene analytes have close boiling point values, so the values of R_s, and α of this pair, determined at what temperature the acceptable separation, can take place. The temperature 240 ºC had the large value of R_s, and α. Pyrene and anthracene pair gave excellent values of R_s, and α at all temperatures. So, the best separation between the four components of the mixture can be performed at 240 ºC. The supercooling phenomenon in 1% coating ratio, cause a shift in mesophase range below its normal range, that recorded by DSC and hot-stage polarizing microscope.

A comparison between the three ratios of loading (2_b) as stationary phase was done, and it was found that a high loading ratio (20%), just low boiling point alcohols could be separated. Positional isomers (xylene isomers), at temperatures below the mesophase range temperatures, can be separated o-xylene from m, and p-xylene. At 3% loading, the PAHs that had boiling point between (200-350) ºC, could be separated, while those having boiling points between (250-405) ºC, could be only separated at 1% coating ratio. The separation between the structural isomers (phenanthrene, and anthracene) was better at 3% than at 1% coating ratio.

3.4.4 2,5-bis-[4-(4/-propoxybenzylideneamino)phenyl] 1,3,4-oxadiazole (1_f) as Stationary Phase

3.4.4.1 3% Loading of (1_f) as Stationary Phase

The compound (1_f) was coated on the chromosorb W/HP with a coating ratio of 3%. After the column conditioning, naphthalene, acenaphthene, acenaphthylene, phenanthrene, anthracene, and pyrene were injected through the prepared column. The retention times of the analytes at 240 ºC were 1.13, 2.19, 2.25, 9.75, and 9.86, respectively, while pyrene retained through the column even after 40 minute run.

Acenaphthene / acenaphthylene, and phenanthrene / anthracene pairs had close retention times, so each of these two pairs was injected individually to determine the possibility of their separation. It was found that the separation between them was difficult, so two mixtures of PAHs were prepared. Mixture (A) contained naphthalene, acenaphthene, phenanthrene, and pyrene, while mixture (B) contained naphthalene, acenaphthylene, anthracene, and pyrene.

The analysis of mixture (A) is shown in Figure (3.23), while that of mixture (B) is shown in Figure (3.24).

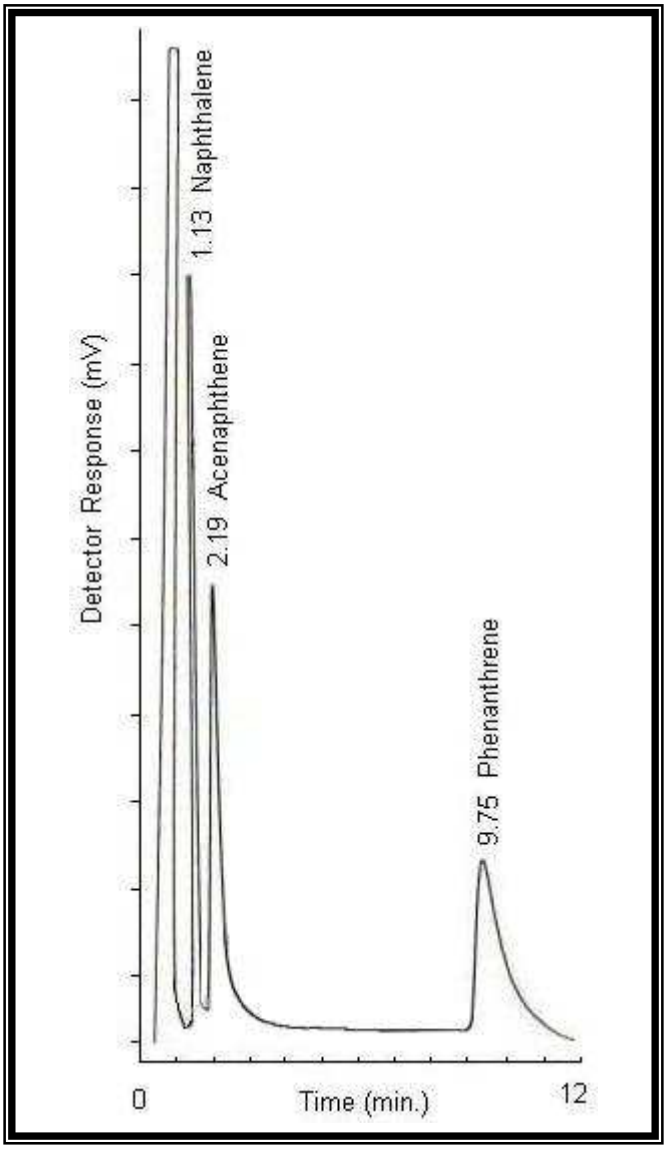


Figure (3.23): Chromatogram of mixture (A) with 3% (1_f) column. Conditions: column temperature 240 ºC; detector temperature 300 ºC; injector temperature 280 ºC; flow rate: 20 mL/min.; injection volume: 1 µL; and carrier gas N_2 with pressure 24 psi.

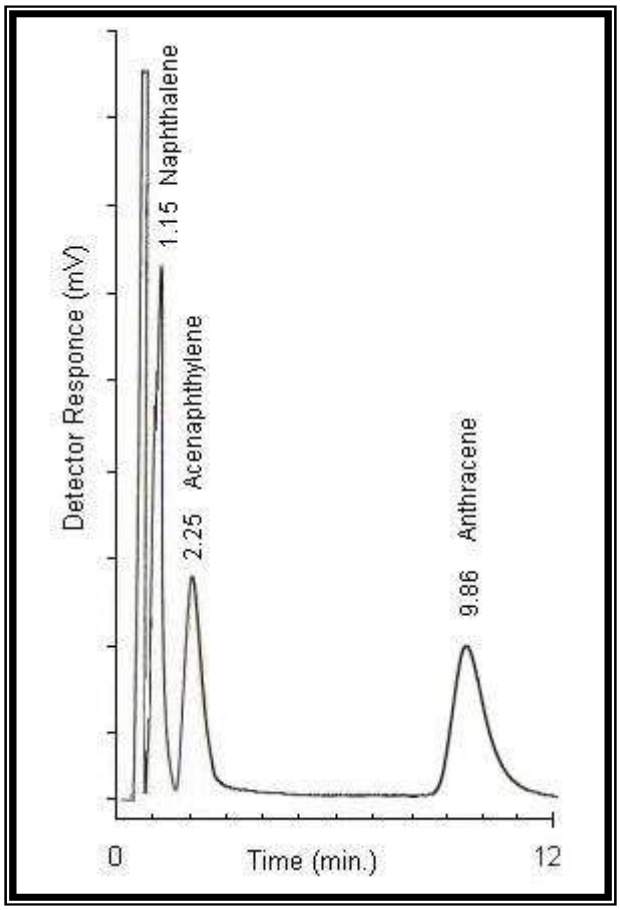


Figure (3.24): Chromatogram of mixture (B) with 3% (1_f) column. Conditions: column temperature 240 ºC; detector temperature 300 ºC; injector temperature 280 ºC; flow rate: 20 mL/min.; injection volume: 1 µL; and carrier gas N_2 with pressure 24 psi.

The adjusted retention times (t'_R) are listed in Tables (3.16), and (3.17). The results showed that the t'_R of naphthalene were 4.88, and 4.86 minute in mixture (A), and (B), respectively, and decreased until elute with a solvent at 260, and 280 ºC. Acenaphthene and acenaphthylene were also eluted with a solvent at 260, and 280 ºC. Phenanthrene and Anthracene had t'_R very large at 170, and 200 ºC, beyond 200 ºC the time decreased to 40 minute. Pyrene was eluted from the column at temperatures 260, and 280 ºC, i.e. pyrene could be separated only from phenanthrene in mixture (A), and from anthracene in

mixture (B). Another behavior of the column was a large jump of the t_R values of the analyte, when the temperature increased.

Table (3.16): Adjusted retention times (t'_R) for mixture (A) of PAHs on 3% 2,5-bis-[4-(4/-propoxybenzylideneamino)phenyl]1,3,4-oxadiazole (1_f) column.

Compound	Adjusted Retention Time (t'_R) min. at temp. °C					
	170	200	220	240	260	280
Naphthalene	4.88	2.94	1.04	0.42	0.00	0.00
Acenaphthene	22.05	12.32	3.86	1.48	0.00	0.00
Phenanthrene	123.81	50.58	27.48	9.04	2.74	1.51
Pyrene	-----	-----	-----	-----	24.96	5.71

----- Retained through column for a long time.

Table (3.17): Adjusted retention times (t'_R) for mixture (B) of PAHs on 3% (1_f) column.

Compound	Adjusted Retention Time (t'_R) min. at temp. °C					
	170	200	220	240	260	280
Naphthalene	4.86	2.95	1.05	0.44	0.00	0.00
Acenaphthylene	23.35	13.31	4.69	1.54	0.00	0.00
Anthracene	125.83	51.43	28.23	9.15	3.64	1.57
Pyrene	-----	-----	-----	-----	25.24	5.91

----- Retained through column for a long time.

The efficiency, resolution and selectivity of the prepared column were examined by calculating, the $N_{eff.}$, R_s, and α of each compound in the mixtures at different temperatures. Tables (3.18) and (3.19), indicate that the high values of the effective theoretical plate number of plat were present at temperatures 200, 220, and 240 °C.

Table (3.18): The effective plate number (N_{eff}) for mixture (A) of PAHs on 3% (1_f) column.

Compound	The effective plate number (N_{eff}) at temp. °C					
	170	200	220	240	260	280
Naphthalene	173.95	108.31	29.96	27.56	0.00	0.00
Acenaphthene	81.00	56.61	95.49	82.95	0.00	0.00
Phenanthrene	222.51	448.82	774.40	412.68	82.04	54.26
Pyrene	-----	-----	-----	-----	216.21	835.87

Table (3.19): The effective plate number (N_{eff}) for mixture (B) of PAHs on 3% (1_f).

Compound	The effective plate number (N_{eff}) at temp. °C					
	170	200	220	240	260	280
Naphthalene	182.25	96.69	26.23	13.44	0.00	0.00
Acenaphthylene	66.54	45.42	43.33	28.69	0.00	0.00
Anthracene	276.85	1049.56	686.42	303.76	96.78	72.02
Pyrene	-----	-----	-----	-----	168.63	705.53

Tables (3.20 – 3.23), show the values of R_s, and α for mixture (A) and (B) of PAHs using 3% (1_f) column.

Table (3.20): Resolution (R_s) for mixture (A) of PAHs on 3% (1_f) column.

Compound Pair	Resolution (R_s) at temp. °C					
	170	200	220	240	260	280
Acen./Naphth	3.03	2.44	2.41	2.19	-----	-----
Phen./Acen.	4.73	4.75	8.54	6.12	-----	-----
Pyre./Phen.	-----	-----	-----	-----	5.56	5.22

----- was not measured.

Table (3.21): Selectivity factor (α) for mixture (A) of PAHs on 3% (1_f) column.

Compound Pair	Separation factor (α) at temp. °C					
	170	200	220	240	260	280
Acen./Naphth	4.52	4.19	3.71	3.52	-----	-----
Phen./Acen.	5.61	4.11	7.12	6.11	-----	-----
Pyre./Phen.	-----	-----	-----	-----	9.11	3.78

----- was not measured.

Table (3.22): Resolution (R_s) for mixture (B) of PAHs on 3% (1_f) column.

Compound Pair	Resolution (R_s) at temp. °C					
	170	200	220	240	260	280
Aceny./Naphth	2.87	2.28	1.98	1.35	-----	-----
Anth./Aceny.	4.92	5.35	6.58	4.68	-----	-----
Pyre./ Anth.	-----	-----	-----	-----	4.67	5.33

----- was not measured.

Table (3.23): Selectivity factor (α) for mixture (B) of PAHs on 3% (1_f) column.

Compound Pair	Separation factor (α) at temp. °C					
	170	200	220	240	260	280
Aceny./Naphth	4.80	4.51	4.47	3.50	-----	-----
Anth../Aceny.	5.39	3.86	6.02	5.94	-----	-----
Pyre./ Anth.	-----	-----	-----	-----	23.59	3.76

----- was not measured.

From the above tables, the values of R_s, and α were acceptable for the separation of naphthalene, acenaphthene, and phenanthrene in mixture (A), and naphthalene, acenaphthylene, and anthracene in mixture (B) at 200, 220, and 240 ºC, especially at 220 ºC.

A better separation was obtained at the temperature of 220 ºC, this is related to the fact that the higher order of this liquid crystal (mesophase range 143-350 ºC), occurred at these temperature, which made the analytes more interactive with the stationary phase. As the temperature increased the retention time decreased this arose as the fact that with increasing the temperature the order of the liquid crystal decreased which made the interaction of analytes with the structure of liquid crystal decrease.

The separation of phenanthrene and anthracene from pyrene in mixture (A) and (B), respectively, were better at 260 ºC, but at 280 ºC the results were also acceptable. In addition, the time of analysis was very short as compared with the analysis at 260 ºC.

3.4.4.2 1% Loading of (1_f) as Stationary Phase

The (1_f) stationary phase was prepared with 1% loading percentage, to study the chromatographic performances of the prepared stationary phase. Mixture of PAHs injected through the 1% of (1_f) column which contained naphthalene, acenaphthene, phenanthrene, and Pyrene was analyzed. Figure (3.25) shows the chromatogram of PAHs at column temperature of 240 ºC.

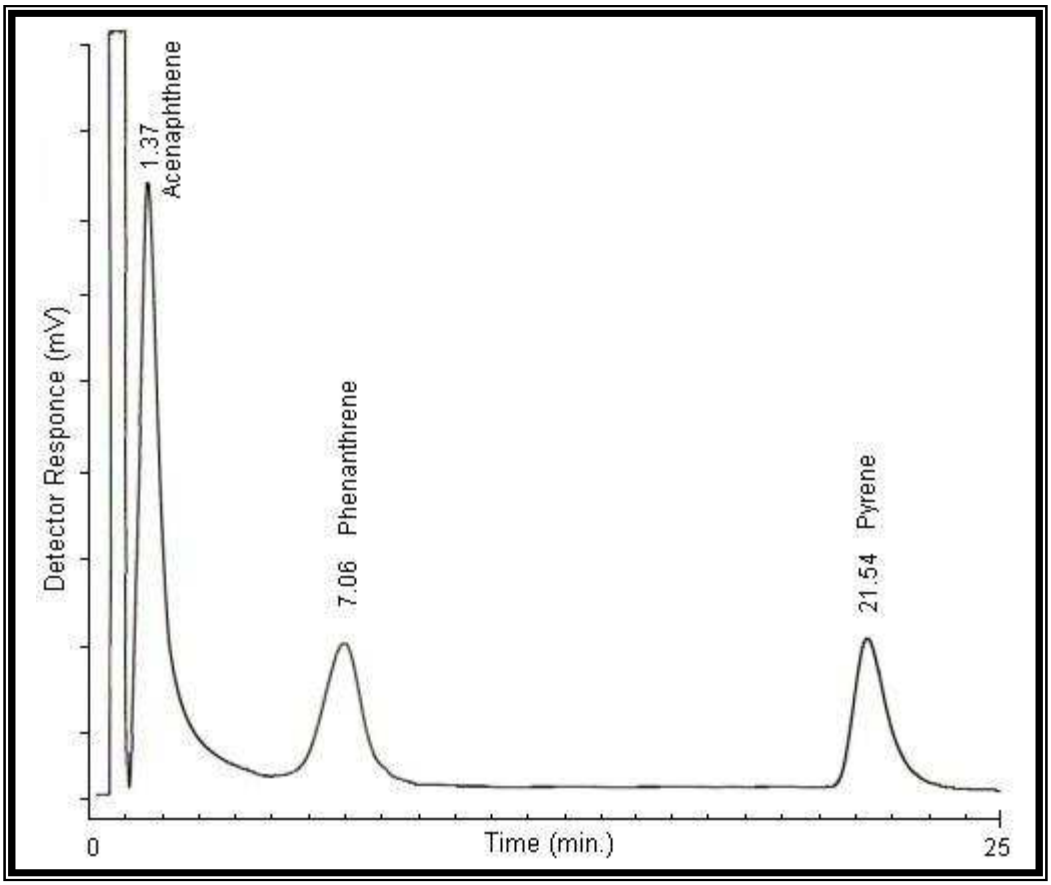


Figure (3.25): Chromatogram of PAHs mixture in 1% (1_f) column. Conditions: column temperature 240 ºC; detector temperature 300 ºC; injector temperature 280 ºC; flow rate: 20 mL/min.; injection volume: 1 µL; and carrier gas N_2 with pressure 24 psi.

Table (3.24) shows the t'_R values of these compounds measured at temperature range (200-280) ºC.

Table (3.24): Adjusted retention times (t'_R) for mixture of PAHs on 1% (1_f) column.

Compound	Adjusted retention times (t'_R) at temp. ºC				
	200	220	240	260	280
Naphthalene	1.25	0.00	0.00	0.00	0.00
Acenaphthene	6.13	2.12	0.70	0.00	0.00
Phenanthrene	37.05	18.81	6.39	1.98	0.95
Pyrene	-----	61.89	20.87	6.80	2.70

Naphthalene, acenaphthene, and phenanthrene can be separated at 200 ºC, while pyrene retained through the column for more than 70 minute. Starting from 220 ºC, naphthalene was eluted with a solvent, and acenaphthene, phenanthrene, and pyrene could be separated at 220 and 240 ºC. The retention times of PAH compounds at 240 ºC were much smaller than that at 220 ºC. Acenaphthene was eluted with a solvent at 260 ºC, and phenanthrene and pyrene could be separated at 260, and 280 ºC.

The efficiency of the prepared column was examined by measuring $N_{eff.}$, R_s, and α values of analytes at temperature range (200-280) ºC as shown in Tables (3.25-3.27).

Table (3.25): The effective plate number (N_{eff}) for mixture of PAHs on 1% (1_f) column.

Compound	The effective plate number (N_{eff}) at temp. ºC				
	200	220	240	260	280
Naphthalene	30.19	0.00	0.00	0.00	0.00
Acenaphthene	15.64	10.63	4.00	0.00	0.00
Phenanthrene	217.89	109.20	113.42	51.84	34.18
Pyrene	-----	3165.60	1580.25	634.29	385.59

Table (3.26): Resolution (R_s) for mixture of PAHs on 1% (1_f) column.

Compound Pair	Resolution (R_s) at temp. ºC				
	200	220	240	260	280
Acen./Naph.	1.37	-----	-----	-----	-----
Phen./Acen.	3.80	3.41	2.99	-----	-----
Pyre./Phen.	-----	7.43	6.44	4.42	3.18

----- was not measured.

Table (3.27): Separation factor (α) for mixture of PAHs on 1% (1_f) column.

Compound Pair	Separation factor (α) at temp. ºC				
	200	220	240	260	280
Acen./Naph.	4.90	-----	-----	-----	-----
Phen./Acen.	6.04	11.18	9.13	-----	-----
Pyre./Phen.	-----	3.35	3.27	3.43	2.84

----- was not measured.

The values of $N_{eff.}$, R_s, and α were acceptable at 200 ºC. The above parameters were satisfactory for separation of acenaphthene, phenanthrene, and pyrene at 220 and 240 ºC, especially at 220 ºC, but the elution times of these components were very long. The separation of phenanthrene and pyrene at 260 ºC had a good efficiency than the separation of these compounds at 280 ºC.

From the above, we can conclude that the best separation of naphthalene, acenaphthene, and phenanthrene took place at 200 ºC, but with a long time of elution. The best separation of acenaphthene, phenanthrene, and pyrene was achieved at 220 ºC, and these analytes can be separated in a short time at 240 ºC, but with acceptable values of efficiency parameters.

From the comparison between 3% and 1% of loading for (1_f) as stationary phase, it was found that the separation of naphthalene, acenaphthene, and phenanthrene was achieved at 170, 200, 220, and 240 ºC with 3% (1_f), while the separation of these compounds occurred at 200 ºC, with long time of elution through the column loaded with 1% of stationary phase.

The separation of acenaphthene, phenanthrene, and pyrene with 3% of (1_f) did not take place at any temperatures, while the separation of these analytes occurred at 220 and 240 ºC through the 1% loading.

The small differences in the structure of the two liquid crystal molecules (the presence of oxadiazole ring in 1_f compound), were found to effect not only on the range of their mesophase, but also to their separation properties [93]. Comparison was done between the two prepared liquid crystals. The (2_b) liquid crystal compound had the ability to separate the two structural isomers (phenanthrene and anthracene), while (1_f) could not be used to separate these two analytes. The retention times of PAHs using (2_b) column decreased normally with the increasing temperature, while with (1_f) column the temperature increase was the result of a large drop in retention time values. These two facts make us propose, that the separation mechanisms in these two stationary phases were differing. The separation mechanism in (2_b) column might be, due to L/B ratio (length to breadth), while in (1_f) column the separation took place according to the boiling point of the analytes.

The stationary phase (2_b) with the loading percentage 1% was used to separate acenaphthene, phenanthrene, anthracene, and pyrene, while naphthalene eluted with solvent. The (1_f) stationary phase could be used to separate naphthalene, acenaphthene, and phenanthrene at 200 ºC, and to separate acenaphthene, phenanthrene, and pyrene at 220, and 240 ºC.

The coated ratio of 3% (2_b) could be used to analyze naphthalene, acenaphthene, phenanthrene, and anthracene, while pyrene retained for a long time. Naphthalene, acenaphthene, and phenanthrene could be separated with 3% coating of (1_f) column at 170, 200, 220, and 240 ºC. Phenanthrene and pyrene could be separated at high temperatures of 260 and 280 ºC.

A mixture of alcohols could be separated at a high ratio of loading (20%) of (2_b) compound. Since (1_f) compound had a low solubility in most solvents, so the preparation of high loading percentage was difficult.

The mixture of PAH compounds was done on the PEG column, to make a comparison between the liquid crystal columns and conventional columns.

The mixture of PAHs contained naphthalene, acenaphthene, phenanthrene, and pyrene was injected through the column at column temperature of 200 ºC as shown in Figure (3.26).

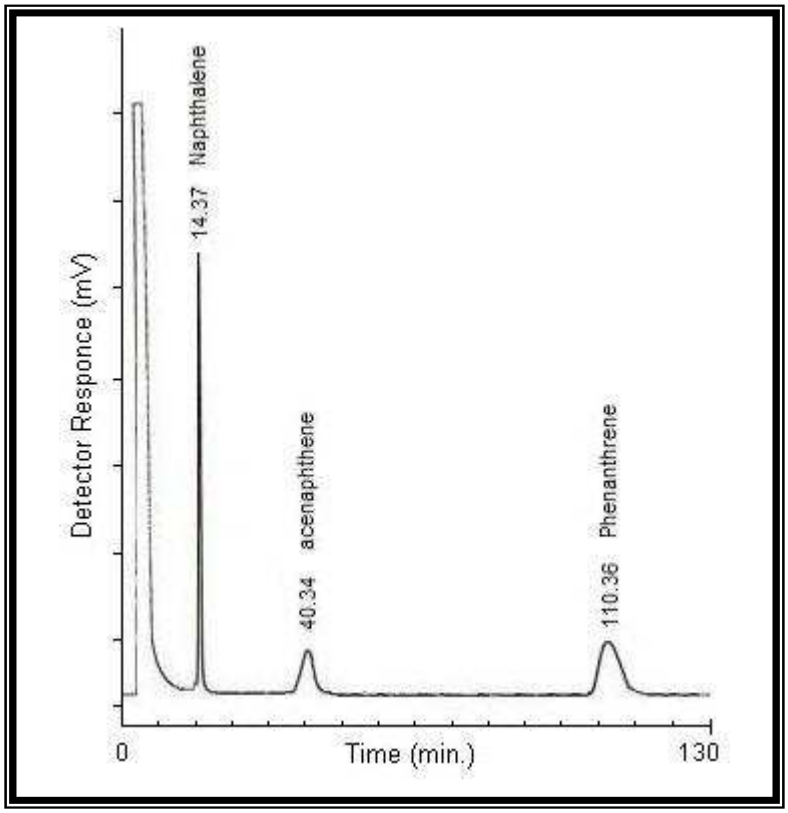


Figure (3.26): Chromatogram of PAHs mixture in PEG column. Conditions: column temperature 200 ºC; detector temperature 300 ºC; injector temperature 280 ºC; flow rate: 20 mL/min.; injection volume: 1 µL; and carrier gas N_2 with pressure 24 psi.

The above chromatogram shows that the t_R of naphthalene, acenaphthene, and phenanthrene was 14.37, 40.34, and 110.36 minute respectively, while pyrene retained for more than 130 minute through the column.

A comparison between the prepared liquid crystals as stationary phases and PEG column was made and it is found that the analysis time of PAHs through the prepared columns was shorter than that with PEG column; therefore, the prepared stationary phases were more practical than PEG column for the separation of PAH compounds.

3.5 Thermodynamics Study of the Analyzed Solutes on Prepared LCSPs

Gas-Liquid chromatography is an effective method for the investigation of the properties of solvents and the behavior of solutes in liquid crystals, in which one component is at infinite dilution [94]. The special texture of the liquid crystal compounds leads to the specific solvent behavior with respect to other stationary phases. This behavior depends upon the specific molecular interaction (time or volume) on these liquid crystal compounds.

The thermodynamic functions of the dissolution of a solute in the stationary phase can be calculated based on its specific retention volume (Vg°), the volume of carrier gas at S.T.P. per gram of stationary phase required to elute the solute. This is related to the solute retention time, t_R, by [178 - 182]

$$Vg^{\circ} = \frac{(t_R - t_M)F'J}{W} \quad \text{..... 3.5}$$

Where t_M is the retention time of the unretained species, F' is the carrier flow rate corrected to S.T.P., J is the correction for gas compressibility and W the mass of stationary phase (liquid crystal) in the column. F' can be calculated from the measured flow rate, F, obtained at laboratory conditions and corrected for the laboratory temperature, T, and atmospheric pressure, p_A, as well as for water vapor pressure, p_w, in the flow meter using Literature constants [180, 181].

$$F' = F \cdot \left(\frac{273.15}{T}\right) \cdot \left(\frac{760}{p_A}\right) \cdot \left[1 - \left(\frac{p_w}{p_A}\right)\right] \quad \text{..... 3.6}$$

The corrected flow rate was found to be 17.75 mL/min, when we used flow rate 20 mL/min. under the experimental conditions mentioned above.

The correction factor for gas compressibility is given in terms of the column inlet and outlet pressures, p_i and p_o respectively by [152,182]:

$$J = \frac{3}{2}\left[\frac{(p_i/p_o)^2 - 1}{(p_i/p_o)^3 - 1}\right] \quad \ldots\ldots 3.7$$

The p_i was recorded from the outlet gauge of the N_2 bottle, and p_o corrected by soap bubble flow meter. The (J) was found to be 0.764 which was calculated from equation (3.7).The data of Vg° are listed in Tables (3.28) – (3.32), at different column temperatures and for different analytes.

Table (3.28): Specific retention volumes (Vg°) for mixture of alcohols on 20% 4,4′-bis-(4-propoxybenzylideneamino)biphenyl (2_b) column.

Compound	Specific retention volume (Vg°) mL.g^{-1} at temp. °C										
	140	160	170	180	190	200	220	250	270	290	320
Methanol	43.74	25.60	21.02	18.14	15.10	12.55	6.78	0.00	0.00	0.00	0.00
Ethanol	203.45	98.33	90.53	74.60	55.10	41.54	22.04	6.61	4.07	0.00	0.00
2- Propanol	657.65	319.75	245.32	197.85	138.51	99.35	50.52	17.97	10.68	5.93	3.56
1- Propanol	971.46	519.64	390.11	315.34	211.42	148.96	74.09	25.60	14.58	5.93	3.56

Table (3.29): Specific retention volumes (Vg°) for mixture of PAHs on 3% (2_b) column.

Compound	Specific retention volume (Vg°) mL.g^{-1} at temp. °C				
	180	220	240	260	280
Naphthalene	145.81	74.60	76.86	57.64	50.86
Acenaphthene	638.60	273.53	230.58	165.02	174.06
Phenanthrene	3760.42	1280.60	960.73	631.82	481.50
Anthracene	3760.42	1467.10	1181.14	760.67	557.23

Table (3.30): Specific retention volumes (Vg°) for mixture of PAHs on 1% (2_b) column.

Compound	Specific retention volume (Vg°) mL.g^{-1} at temp. °C					
	180	200	220	240	260	280
Naphthalene	0.00	0.00	0.00	0.00	0.00	0.00
Acenaphthene	406.90	250.92	210.23	169.54	0.00	0.00
Phenanthrene	2482.08	1420.75	1034.20	888.40	695.12	491.67
Anthracene	2950.02	1668.28	1281.73	1173.22	871.44	586.61
Pyrene	12729.15	6462.91	4028.30	3851.97	2634.67	1732.71

Table (3.31): Specific retention volumes (Vg°) for mixture of PAHs on 3% 2,5-bis-[4-(4′-propoxybenzylideneamino)phenyl]1,3,4-oxadiazole (1_f) column.

Compound	Specific retention volume (Vg°) mL.g^{-1} at temp. °C					
	170	200	220	240	260	280
Naphthalene	551.59	332.31	117.55	47.47	0.00	0.00
Acenaphthene	2492.31	1392.53	436.30	167.28	0.00	0.00
Phenanthrene	13994.24	5717.06	3106.06	1021.79	309.70	170.68
Pyrene	-----	-----	-----	-----	2821.23	645.40

----- Retained through column for a long time.

Table (3.32): Specific retention volumes (Vg°) for mixture of PAHs on 1% (1_f) column.

Compound	Specific retention volume (Vg°) mL.g^{-1} at temp. °C				
	200	220	240	260	280
Naphthalene	423.85	0.00	0.00	0.00	0.00
Acenaphthene	2078.56	718.85	237.36	0.00	0.00
Phenanthrene	12562.91	6378.09	2166.72	671.38	322.13
Pyrene	-----	20985.66	7076.60	2305.74	915.52

The Specific retention volumes (Vg°) of each compound were found to decrease with increasing temperature. This may be attributed to the fact that with an increase in temperature the order of a liquid crystal decreases, so the interaction between the molecules of substances and the structure of liquid crystal will decrease.

It was shown by Everett [183] that, at infinite dilution, Vg° could be related to the thermodynamics of the analyte – stationary phase interaction. It is also readily shown that Vg° is related to the Gibbs energy of solution of the probe in the stationary phase by [128, 166]:

$$\Delta G = - RT \ln Vg° = \Delta H - T\Delta S \quad \ldots\ldots (3.8)$$

by dividing equation (3.8) on -RT, we get equation (3.9).

$$\ln Vg° = - \Delta H / RT + \Delta S / R \quad \ldots\ldots\ldots (3.9)$$

Plots of the ln Vg° against the reciprocal absolute temperatures in (Kelvin) for the prepared columns at different coating ratios are shown in Figures (3.27) – (3.31).

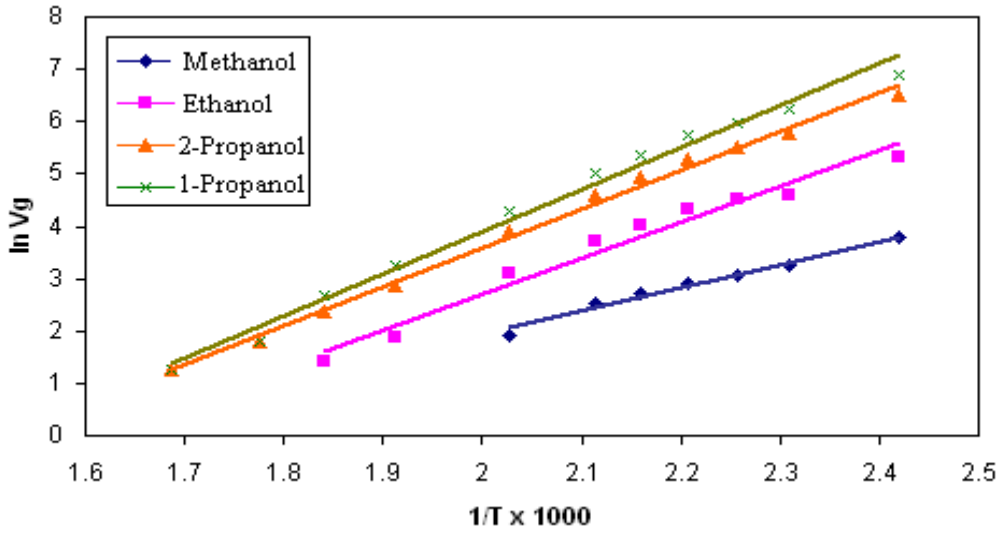


Figure (3.27): Natural logarithm of specific retention volume (lnVg°) versus reciprocal absolute temperature for mixture of alcohols on 20% 4,4′-bis-(4-propoxybenzylideneamino)biphenyl (2_b) column.

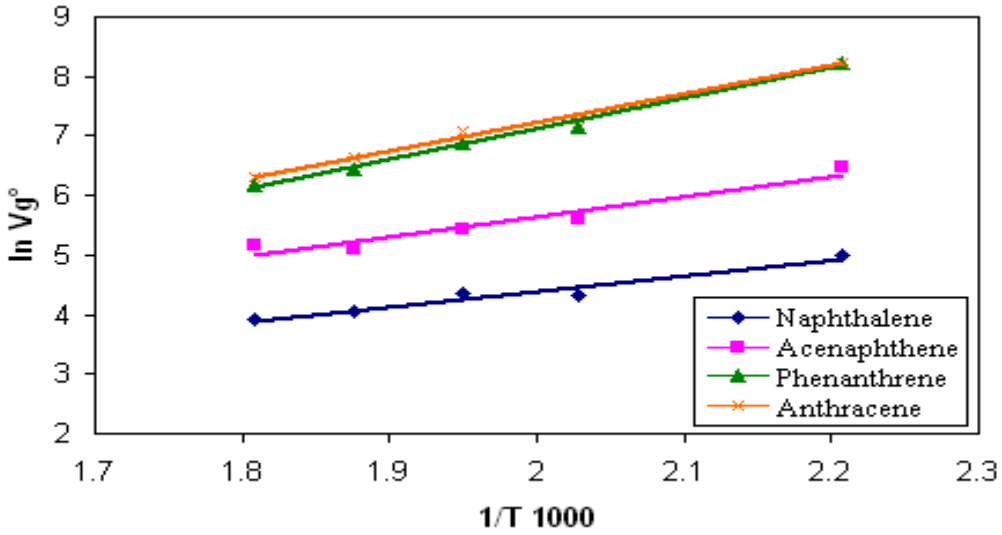


Figure (3.28): Natural logarithm of specific retention volume (lnVg°) versus reciprocal absolute temperature for mixture of PAHs on 3% (2_b) column.

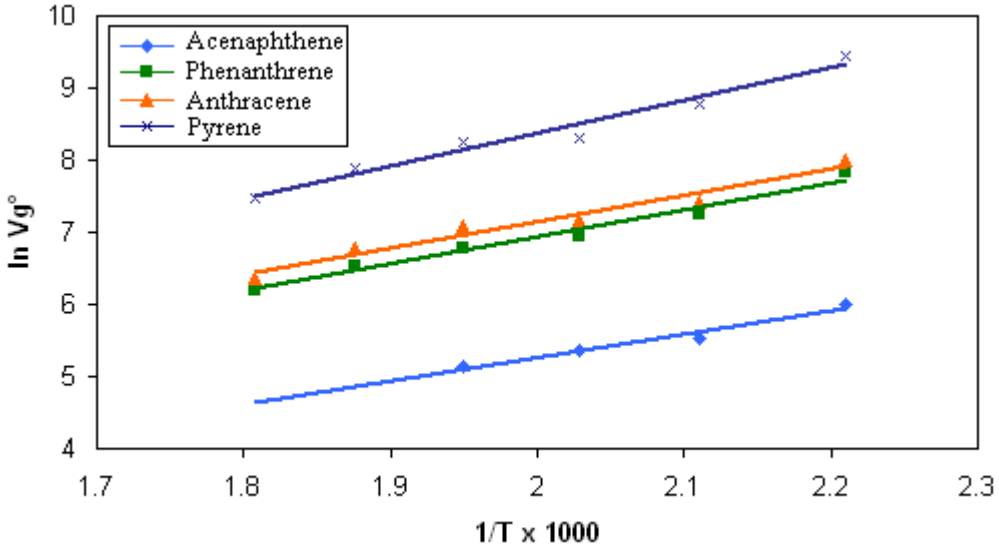


Figure (3.29): Natural logarithm of specific retention volume (lnVg°) versus reciprocal absolute temperature for mixture of PAHs on 1% (2_b) column.

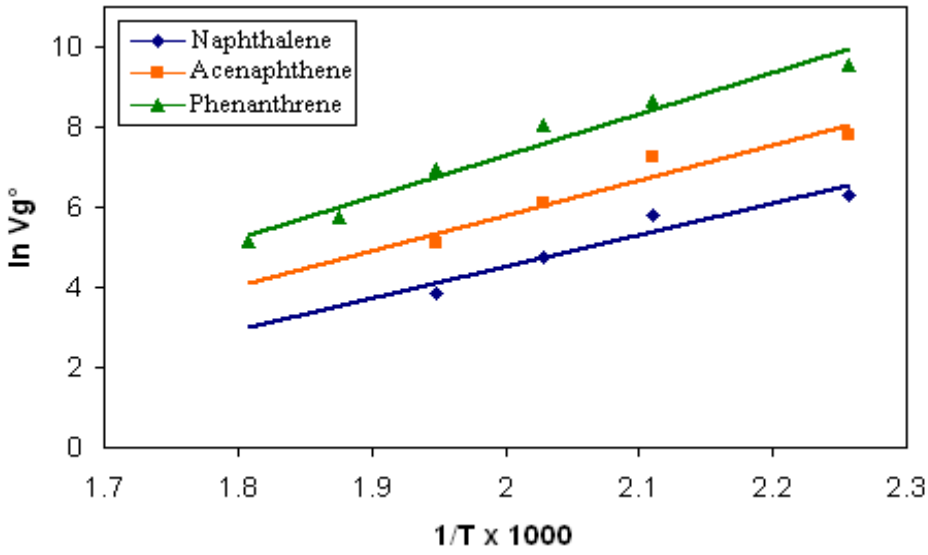


Figure (3.30): Natural logarithm of specific retention volume (lnVg°) versus reciprocal absolute temperature for mixture of PAHs on 3% 2,5-bis-[4-(4′-propoxybenzylideneamino)phenyl]1,3,4-oxadiazole (1_f) column.

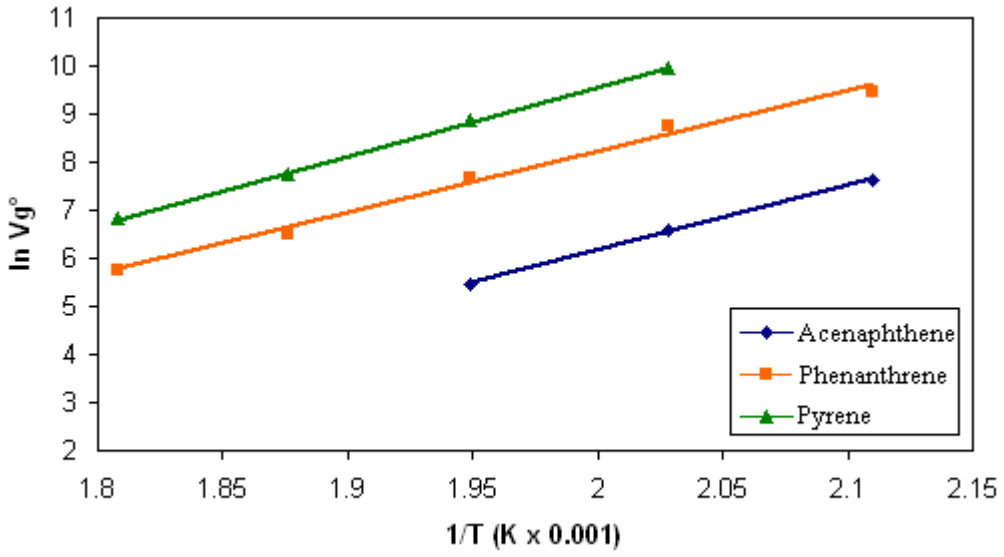


Figure (3.31): Natural logarithm of specific retention volume (lnVg°) versus reciprocal absolute temperature for mixture of PAHs on 1% (1_f) column.

Enthalpies and entropies for the interaction process between each analyte and stationary phase can be measured from the slope and intercept of each analyte in the prepared columns as shown in Tables (3.33) – (3.37).

Table (3.33): Enthalpy (ΔH), entropy (ΔS), and linear equation for mixture of alcohols on 20% 4,4/-bis-(4-propoxybenzylidene amino)biphenyl (2_b) column.

Compounds	Linear Equation Y=aX + b *	ΔH (kJ.mol^{-1})	ΔS (J.mol^{-1}.K^{-1})
Methanol	Y= 4453.49 X – 6.98	-37.03	-58.05
Ethanol	Y= 6815.38 X – 10.92	-56.66	-90.83
2-Propanol	Y= 7405.68 X – 11.21	-61.57	-93.24
1-Propanol	Y= 8009.40 X – 12.13	-66.59	-100.81

*** Where (Y) is lnVg°, (a) is – ΔH / R, (X) is 1/T, and (b) is + ΔS / R.**

Table (3.34): Enthalpy (ΔH), entropy (ΔS), and linear equation for mixture of PAHs on 3% (2_b) column.

Compounds	Linear Equation Y=aX + b *	ΔH (kJ.mol^{-1})	ΔS (J.mol^{-1}.K^{-1})
Naphthalene	Y= 2566.51X - 0.74	-21.34	-6.19
Acenaphthene	Y= 3428.90 X - 1.21	-28.51	-10.08
Phenanthrene	Y= 5139.00 X - 3.17	-42.73	-26.32
Anthracene	Y= 4732.83 X - 2.23	-39.35	-18.58

*** Where (Y) is lnVg°, (a) is – ΔH / R, (X) is 1/T, and (b) is + ΔS / R.**

Table (3.35): Enthalpy (ΔH), entropy (ΔS), and linear equation for mixture of PAHs on 1% (2_b) column.

Compounds	Linear Equation Y=aX + b *	ΔH (kJ.mol^{-1})	ΔS (J.mol^{-1}.K^{-1})
Acenaphthene	Y= 3292.72 X -1.32	-27.38	-11.02
Phenanthrene	Y= 3749.35 X - 0.56	-31.17	-4.67
Anthracene	Y= 3641.22 X -0.14	-30.27	-1.17
Pyrene	Y= 4559.69 X -0.75	-37.91	-6.25

*** Where (Y) is lnVg°, (a) is – ΔH / R, (X) is 1/T, and (b) is + ΔS / R.**

Table (3.36): Enthalpy (ΔH), entropy (ΔS), and linear equation for mixture of PAHs on 3% 2,5-bis-[4-(4′-propoxybenzylideneamino) phenyl]1,3,4-oxadiazole (1_f) column.

Compounds	Linear Equation Y=aX + b *	ΔH (kJ.mol^{-1})	ΔS (J.mol^{-1}.K^{-1})
Naphthalene	Y= 7949.37 X -11.39	-66.09	-94.74
Acenaphthene	Y= 8795.00 X - 11.78	-73.12	-97.95
Phenanthrene	Y= 10276.11 X - 13.26	-85.44	-110.23

*** Where (Y) is lnVg°, (a) is – ΔH / R, (X) is 1/T, and (b) is + ΔS / R.**

Table (3.37): Enthalpy (ΔH), entropy (ΔS), and linear equation for mixture of PAHs on 3% (1_f) column.

Compounds	Linear Equation Y=aX + b *	ΔH (kJ.mol^{-1})	ΔS (J.mol^{-1}.K^{-1})
Acenaphthene	Y= 13474.77 X - 20.78	-112.03	-172.74
Phenanthrene	Y= 12660.53 X - 13.48	-105.26	-112.04
Pyrene	Y= 14339.14 X -19.50	-119.22	-162.10

*** Where (Y) is lnVg°, (a) is – ΔH / R, (X) is 1/T, and (b) is + ΔS / R.**

The ΔS of the solutions describe the change in entropy. The analytes suffers from transferring from the gas phase to the infinitely dilute solution. Large, negative values indicate a large restriction on analyte movement in the infinitely dilute solutions but strong interactions between analyte and liquid crystal would also lower this entropy [128].

Tables (3.38) – (3.42) list the values of the Gibbs free energy (ΔG) calculated according to equation (3.8).

Table (3.38): The Gibbs free energy for mixture of alcohols on 20% 4,4′-bis-(4-propoxybenzylidene amino)biphenyl (2_b) column.

Compound	ΔG (kj.mol^{-1}) at temp. °C										
	140	160	170	180	190	200	220	250	270	290	320
Methanol	-12.98	-11.68	-١١.22	-10.92	-10.45	-9.95	-7.85	0.00	0.00	0.00	0.00
Ethanol	-18.26	-16.52	-16.60	-16.25	-15.44	-14.66	-12.68	-8.21	-6.34	0.00	0.00
2- Propanol	-22.29	-20.77	-20.27	-19.92	-18.99	-18.09	-16.08	-12.56	-10.70	-8.33	-6.26
1- Propanol	-23.63	-22.52	-21.98	-21.68	-20.62	-19.68	-17.65	-14.10	-12.10	-8.33	-6.26

Table (3.39): The Gibbs free energy for mixture of PAHs on 3% (2_b) column.

Compound	ΔG (kj.mol^{-1}) at temp. °C				
	180	220	240	260	280
Naphthalene	-18.76	-17.67	-18.51	-17.95	-18.07
Acenaphthene	-24.33	-22.99	- 23.20	-22.64	-23.72
Phenanthrene	-31.00	-29.35	-29.30	-28.58	-28.41
Anthracene	-31.00	-29.88	-30.15	-29.38	-29.06

Table (3.40): The Gibbs free energy for mixture of PAHs on 1% (2_b) column.

Compound	ΔG (kj.mol^{-1}) at temp. °C					
	180	200	220	240	260	280
Acenaphthene	-22.64	-21.75	-21.93	-21.88	-----	-----
Phenanthrene	-29.45	-28.55	-28.46	-28.96	-28.98	-28.51
Anthracene	-30.09	-29.18	-29.35	-30.15	-30.00	-29.29
Pyrene	-35.59	-34.49	-34.49	-35.23	-34.92	-34.30

----- was not measured.

Table (3.41): The Gibbs free energy for mixture of PAHs on 3% 2,5-bis-[4-(4/-propoxybenzylideneamino) phenyl]1,3,4-oxadiazole (1_f) column.

Compound	ΔG (kj.mol^{-1}) at temp. °C					
	170	200	220	240	260	280
Naphthalene	-23.24	-22.85	-19.55	-16.46	-----	------
Acenaphthene	-28.80	-28.47	-24.92	-21.84	-----	-----
Phenanthrene	-35.17	-34.02	-32.95	-29.56	-25.44	-23.63

----- was not measured.

Table (3.42): The Gibbs free energy for mixture of PAHs on 1% (1_f) column.

Compound	ΔG (kj.mol^{-1}) at temp. °C				
	200	220	240	260	280
Acenaphthene	-30.04	-26.97	-23.33	-----	-----
Phenanthrene	-37.12	-35.91	-32.76	-28.85	-26.53
Pyrene	-----	-40.78	-37.79	-34.30	-31.36

----- was not measured.

All calculated free energies for the two coated liquid crystal compounds had negative values. These results demonstrated that the dissolvation process with these liquid crystal compounds were spontaneous [(94)]. In addition, these values negatively decreased as temperature increased which indicates the decrease in the order of solute molecules with nematic lattices with the increasing temperature.

The activity coefficient is a fundamental thermodynamic property of solution as it gives a measure of the deviation from Raoult's law for a particular liquid mixture [(155)]. Knowledge of the activity coefficient at infinite dilution (γ^{∞})

is important since solution behavior is clearly expressed at infinite dilution. The solute activity coefficient (γ^{∞}) can be obtained from the specific retention volume using the equation [94,181,184]:

$$\gamma^{\infty} = 273.15 \times R / P^{o}_{2} M V g° \quad ..... 3.10$$

where M, is the molecular mass of the stationary phase (liquid crystal) and P^{o}_{2} is the vapor pressure of the pure solute, and R = 8.314 $J.K^{-1}.mol^{-1}$. The solute vapor pressures were calculated from the Antoine's equation [94, 98, 166]:

$$\text{Log } P^{o}_{2} = A - B/ (T + C) \quad ..... 3.11$$

where A, B, and C are Antoine's coefficients and T, is column temperature in Celsius, and P^{o}_{2} the pressure in mm Hg. The values of A, B, and C for the analytes are listed in Table (3.43).

Table (3.43): The Antoine's coefficients of the analytes.

Analytes	Antoine's coefficients		
	A	B	C
Methanol	8.07	1574.99	238.87
Ethanol	8.21	1652.05	231.48
2-Propanol	8.12	1580.92	219.62
1-Propanol	7.62	1375.14	193.01
Naphthalene	7.01	1733.71	201.86
Acenaphthene	7.25	1998.72	202.74
Phenanthrene	6.61	1591.40	138.50
Anthracene	7.01	1812.20	174.60
Pyrene	7.04	1904.13	160.32

The data of γ^{∞} values are listed in Tables (3.44) – (3.48).

Table (3.44): The solute activity coefficient at infinite dilution (γ^{∞}) for mixture of alcohols on 20% 4,4′-bis-(4-propoxybenzylideneamino)biphenyl (2_b) column.

Compound	Solute activity coefficient at infinite dilution (γ^{∞}) at temp. °C										
	140	160	170	180	190	200	220	250	270	290	320
Methanol	0.0994	0.1051	0.1025	0.0961	0.0944	0.0936	0.1209	-----	-----	-----	-----
Ethanol	0.0301	0.0370	0.0315	0.0304	0.0330	0.0355	0.0453	0.0894	0.1060	-----	-----
2- Propanol	0.0103	0.0124	0.0127	0.0125	0.0142	0.0161	0.0213	0.0353	0.0432	0.0582	0.0651
1- Propanol	0.0119	0.0130	0.0135	0.0133	0.0158	0.0182	0.0248	0.0427	0.0550	0.1020	0.1154

----- was not measured.

Table (3.45): The solute activity coefficient at infinite dilution (γ^{∞}) for mixture of PAHs on 3% (2_b) column.

Compound	Solute activity coefficient at infinite dilution (γ^{∞}) at temp. °C				
	180	220	240	260	280
Naphthalene	0.8307	0.6026	0.3811	0.3436	0.2720
Acenaphthene	0.5311	0.3975	0.2883	0.2571	0.1614
Phenanthrene	0.2308	0.1878	0.1458	0.1364	0.1154
Anthracene	0.1203	0.0936	0.0698	0.0682	0.0610

Table (3.46): The solute activity coefficient at infinite dilution (γ^{∞}) for mixture of PAHs on 1% (2_b) column.

Compound	Solute activity coefficient at infinite dilution (γ^{∞}) at temp. °C					
	180	200	220	240	260	280
Naphthalene	-----	-----	-----	-----	-----	-----
Acenaphthene	0.8336	0.7440	0.5172	0.3922	-----	-----
Phenanthrene	0.3497	0.3096	0.2325	0.1577	0.1240	0.1130
Anthracene	0.1534	0.1447	0.1071	0.0703	0.0595	0.0580
Pyrene	0.1018	0.0981	0.0830	0.0488	0.0423	0.0401

----- was not measured.

Table (3.47): The solute activity coefficient at infinite dilution (γ^{∞}) for mixture of PAHs on 3% 2,5-bis-[4-(4′-propoxybenzylideneamino)phenyl]1,3,4-oxadiazole (1_f) column.

Compound	Solute activity coefficient at infinite dilution (γ^{∞}) at temp. °C					
	170	200	220	240	260	280
Naphthalene	0.2545	0.1896	0.3346	0.5399	-----	-----
Acenaphthene	0.1644	0.1173	0.2180	0.3478	-----	-----
Phenanthrene	0.0791	0.0673	0.0677	0.1200	0.2435	0.2847
Pyrene	-----	-----	-----	-----	0.0346	0.0942

----- was not measured.

Table (3.48): The solute activity coefficient at infinite dilution (γ^{∞}) for mixture of PAHs on 1% (1_f) column.

Compound	Solute activity coefficient at infinite dilution (γ^{∞}) at temp. °C				
	200	220	240	260	280
Naphthalene	0.1486	-----	-----	-----	-----
Acenaphthene	0.0786	0.1323	0.2451	-----	-----
Phenanthrene	0.0306	0.0330	0.0566	0.1123	0.1509
Pyrene	-----	0.0139	0.0232	0.0423	0.0664

----- was not measured.

The values of the activity coefficients **(γ^{∞})** were < 1, which indicates a negative deviation of the solutions from ideality. Low values of activity coefficients are the result of strong interactions between the solutes and/or little restriction of the analytes molecule in solution.

3.6 Conclusions

Two liquid crystal compounds, 4,4´-bis-(4-propoxybenzylidene amino)biphenyl (2_b), and 2,5-bis-[4-(4´-propoxybenzylideneamino) phenyl] 1,3,4-oxadiazole (1_f) were synthesized and their properties were examined. These compounds were used as stationary phases in gas chromatography for the separation some PAHs, alcohols, and xylene isomers.

The two liquid crystal compounds (2_b,1_f), have nematic liquid crystal properties with a wide mesophase range which is a useful property to be considered as stationary phases in gas chromatography. The 2_b compound has mesophase range of (246-350 ºC) and (143-350 ºC) that of 1_f . The oxadiazole ring in (1_f) has changed the crystal-nematic liquid crystal transition temperature from 246 ºC in (2_b) to 143 ºC in (1_f).

Chromosorb W/HP, was used as an inert solid support to be coated with the proposed stationary phases 2_b and 1_f.

The best separation of alcohols was performed with 20% coating of (2_b) at 180 ºC, which is below the mesophase range (246-350 ºC). This may be attributed to the supercooling phenomenon. The supercooling state was obtained by changing the optimum temperature during alcohols separation. The column was cooled with fast cooling rate. It was found that when the cooling rate was varied, the optimum separation occurred at different temperatures like 160 and 170 ºC. The separation of xylene isomers has been obtained at 50 ºC in which the liquid crystal was in the solid phase. Even at temperature higher than 350 ºC, the PAHs retained at the column for a long time (more than 90 minute), except naphthalene which was eluted at 8.54 minute.

Mixture PAHs that contained naphthalene, acenaphthene, phenanthrene, and anthracene, has been separated with 3% (2_b) column at 240 ºC. The separation was achieved in temperature below the solid-nematic transition temperature, due to the supercooling phenomenon. It was found that when the

loading ratio decreased, mesophase range was experienced a small shift due to the supercooling phenomenon. However, PAHs mixture has been separated with a good chromatographic performance. The analysis time of PAH compounds was performed in less than 15 minute. Naphthalene was eluted at the beginning with 2.30 minute, and last compounds anthracene was eluted at 12.07 minute, with well resolved peaks. Pyrene was not eluted from the column.

We were unable to separate alcohols as well as xylene isomers mixtures using this loading percentage.

The decreasing of the loading percentage of (2_b) to 1% has caused naphthalene to elute with solvent peak at 1.33 minute. The high boiling point (pyrene), start to elute at 37.54 minute. A mixture of acenaphthene, phenanthrene, anthracene, and pyrene has been separated with high efficiency at 240 ºC in 14 minute. The supercooling phenomenon in 1%, also caused a shift in mesophase range below its normal range.

The separation between the structural isomers (phenanthrene, and anthracene), was better at 3% than that of 1% coating ratio, with resolution of 1.63 and 1.23, respectively.

A 3% coating of (1_f) was used to separate naphthalene, acenaphthene, and phenanthrene mixture at 220 ºC, however, at 240 ºC the separation with acceptable values and with short analysis time. Separation was obtained at 220 and 240 ºC, may be related to the fact that the higher order of this liquid crystal (mesophase range 143-350 ºC), occurred at these temperatures. This made interaction of the analytes more efficient with the stationary phase. As the temperature of the column increased the retention time decreased may be due to the fact that with increasing the temperature the order of the liquid crystal decreased and made the interaction of analytes with the structure of liquid crystal decreased.

It has been noted also that decreasing of coating ratio to 1% of (1_f) made the separation of naphthalene, acenaphthene, and phenanthrene occurred just at 200 ºC, while the separation of acenaphthene, phenanthrene, and pyrene occurred at 220 and 240 ºC.

The presence of oxadiazole ring in (1_f) compared to (2_b) has effected not only the range of their mesophase, but also their separation properties. The (2_b) liquid crystal compound has the ability to separate the two structural isomers (phenanthrene and anthracene), while (1_f) could not be used to separate them.

The retention times of PAHs using (2_b) column have decrease normally with increasing temperature, while with (1_f) column a temperature increase, was the result of a large drop in retention time values. The separation mechanism in (2_b) column might be due to L/B ratio, while in (1_f) column the separation took place according to the boiling point of the analytes. In addition, the supercooling phenomenon has been noticed in (2_b), and not in (1_f) compound.

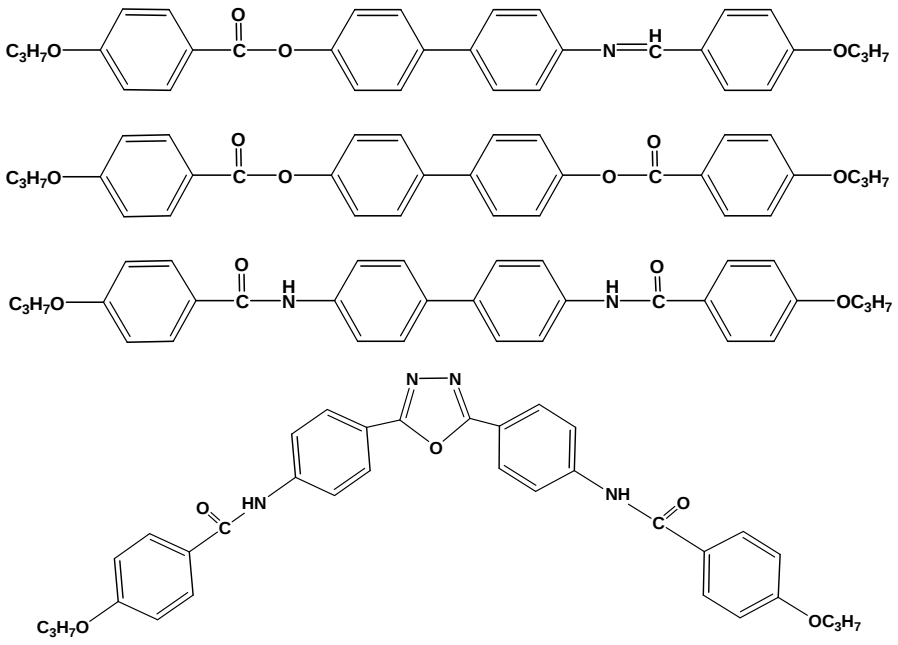
Columns coated with (2_b,1_f) have shown better chromatographic performance than that of PEG commercial column with respected to the analytes separated in this work.

The calculated Gibbs free energies (ΔG) for the two coated liquid crystal columns have negative values. These results demonstrated that the dissolvation process of the analytes with these liquid crystal compounds were spontaneous. The values of the activity coefficients **(γ^{∞})** were < 1, which indicated a negative deviation of the solutions from ideality.

3.7 Suggestions for Future Work

In the light of the present study, the following suggestions may be considered to expand the field of the work.

1. Studing the ability of the prepared stationary phases to separate different kinds of compounds like poly chlorinated biphenyls (PCBs), volatile aroma compounds, and cis and trans isomers such as cis and trans stilbene.
2. Coating the prepared stationary phases at lower ratios such as 0.5% and 0.1% to separate high boiling point PAHs like benzo[a] Pyrene, benzo[e] Pyrene, and chrysene.
3. Using mixed liquid crystal compounds as stationary phases to increase the range of the mesophase of these liquid crystals, and change the characteristic and selectivity of separation.
4. Studying the ability of using the synthesized liquid crystals as normal stationary phases in HPLC by chemical bonding to the support instead of coating.
5. Synthesizing a new kind of liquid crystals and characterizing their chromatographic behaviors. Such as the following examples:



Chapter Two
Experimental Part

2.1 Chemicals

All chemicals in this study are presented in Table (2.1), and were used directly as received from their mentioned suppliers, without any further purification:

Table (2.1): Chemicals and their manufactures.

Chemicals	Manufactured by, Country
4-aminobenzoic acid	BDH, England
Ammonium chloride	BDH, England
Chloroform	Fluka, Switzerland
4,4′ Diaminobiphenyl	Fluka, Switzerland
Diethyl ether	BDH, England
Ethanol (absolute)	BDH, England
Glacial acetic acid	Fluka, Switzerland
Hydrazine hydrate	BDH, England
Hydrobromic acid	Merck, Germany
Hydrochloric acid	Merck, Germany
4-Hydroxybenzaldehyde	Fluka, Switzerland
Magnesium sulfate	Merck Germany
Phosphorous oxychloride ($POCl_3$)	Fluka, Switzerland
Potassium hydroxide	BDH, England
1-Propanol	BDH, England
Sodium bicarbonate	BDH, England
Sodium carbonate	Fluka, Switzerland
Sodium hydroxide	Fluka, Switzerland
Sulphuric acid	Fluka, Switzerland

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.

- ***Proton Nuclear Magnetic Resonance Spectrometer (^{1}HNMR)***

^{1}H spectra were recorded on Brüker ultra shield instrument operating on 300 MHz with TMS as an internal standard in the AL al-Bayt University, Mafraq, Jordan.

- ***Elemental Analysis (EA)***

The elemental analysis of the prepared compounds were made using Euro Vector, model EA 3000 A, to estimate the amount of Carbon, Hydrogen, and Nitrogen. These analyses were carried out in the AL al-Bayt University, Mafraq, Jordan.

- ***Differential Scanning Calorimeter (DSC)***

All DSC measurements were made with a METTLER TOLEDO STAR^e DSC 822 in unsealed aluminum pans in a dry nitrogen atmosphere with heating rate of 20ºC per minute. These analyses were carried out in the University of Jordan, Amman, Jordan.

- ***Hot-stage Polarizing Microscope***

The optical behavior observations were made using MEIJI microscope equipped with METTLER FP80 hot stage and central processor controller, and connected with SONY color video camera. These analyses were carried out in the University of Jordan, Amman, Jordan.

- ***Melting Points***

The melting points of the prepared compounds were recorded on hot stage Gallen kamp melting point apparatus (U.K).

- ***Gas Chromatograph (GC)***

The gas chromatograph used in this work was Varian 3300, (USA), which has been equipped with flame ionization detector (FID). These analyses were carried out in the University of Jordan, Amman, Jordan.

- ***Rotary Evaporator***

The rotary evaporator used in evaporating processes of organic solvents, was Büchi RE 120 (Switzerland).

- ***Vibrator***

Vibrator type Burgess, V 74, 50 Hz (USA) was used in packing the columns.

- ***Ultrasonicator***

Ultrasonic type Elma, LC200H (Germany), was used to mix the slurry in the preparation of the stationary phases.

- ***Vacuum Pump***

Vacuum pump type Edwards, 50 Hz, was used for packing the columns, made by Edwards high vacuum, (U.K).

- ***Columns***

The dimensions of the stainless steal columns were 2.0 m in length, and 2.0 mm internal diameter (i.d). Obtained locally.

- ***Hydrodynamics Syringe***

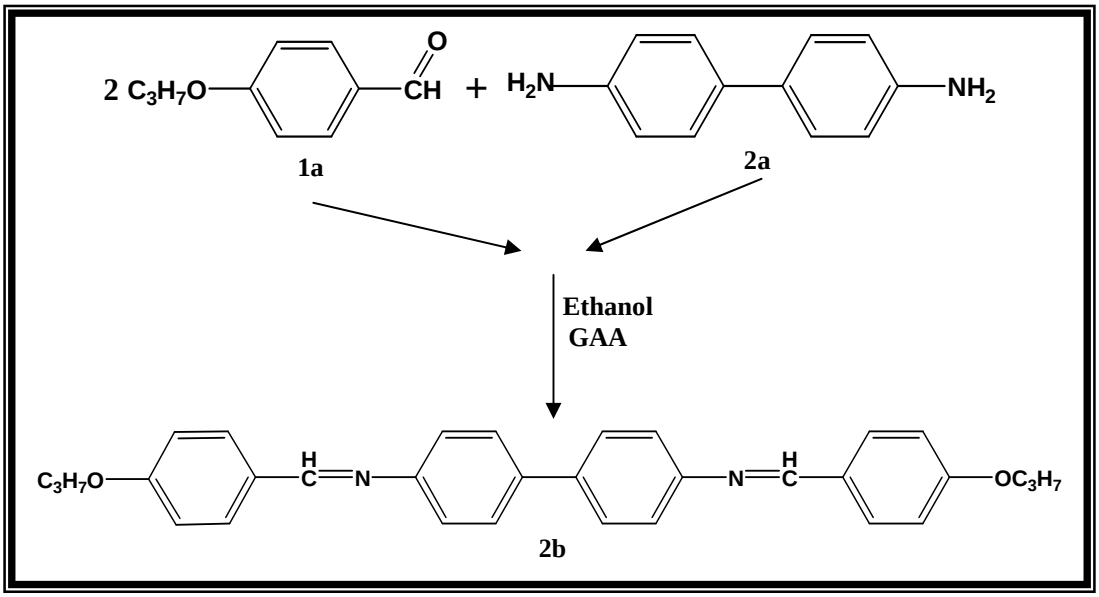
Samples were injected using a calibrated 10 µL hydrodynamics syringe type Hamilton, (USA).

- ***Flow meter***

The flow rates of the carrier gas have been measured using soap bubble flow-meter.

2.3 Preparation Procedures

2.3.1 Preparation of 4,4′-bis-(4-propoxybenzylidene amino)biphenyl (2_b)

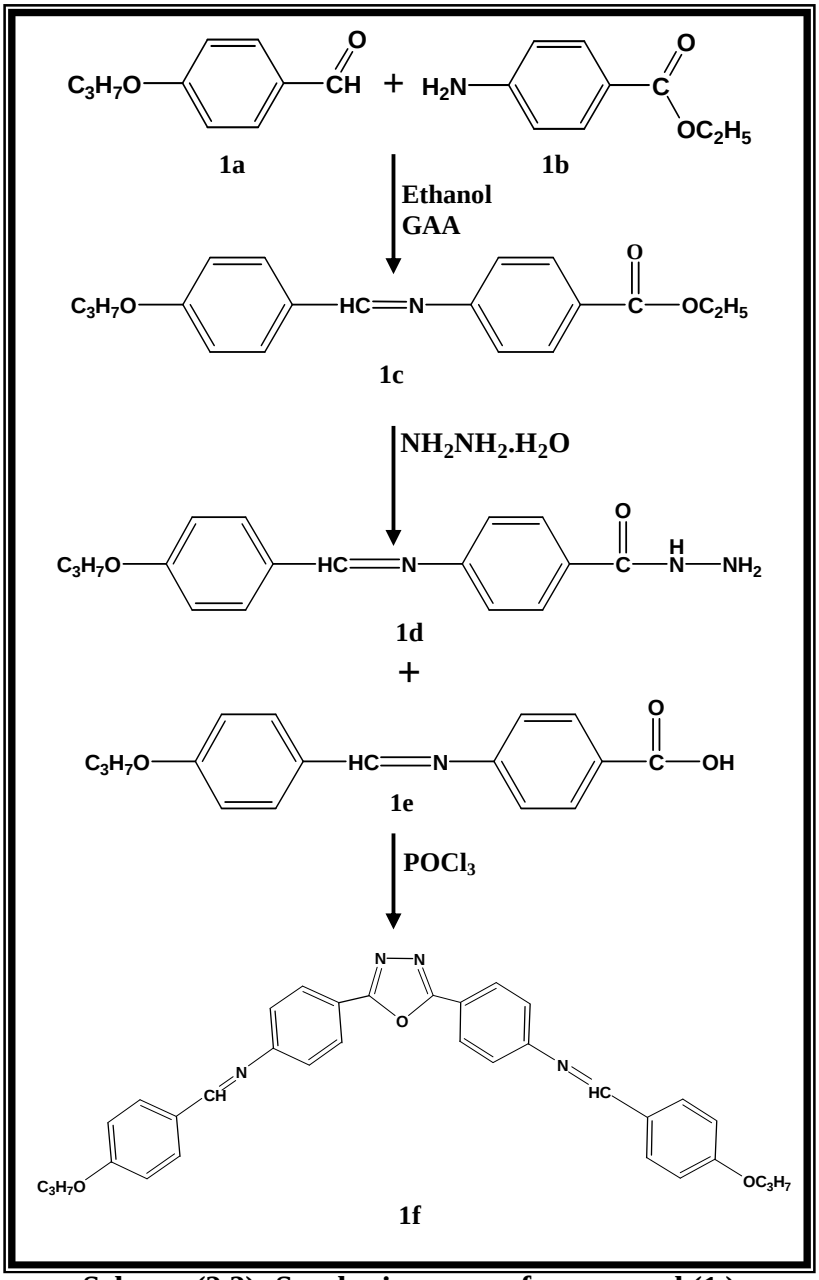


Scheme (2.1): Synthesis of compound (2_b).

The compound was prepared by the condensation reaction between 4-propoxybenzaldehyde (**1_a**) (3.28g, 20 mmol) and 4,4/ Diaminobiphenyl (**2_a**) (1.84g, 10 mmol) in boiling absolute ethanol (20mL), and two drops of glacial acetic acid were added. After reflux for 3 hours, the solid product was filtered and dried. Recrystallization from Ethanol gave yellow crystals 95% yield. The compound was identified by FTIR, ^{1}HNMR, and CHN analysis.

2.3.2 Preparation of 2,5-bis-[4-(4´-propoxybenzy lideneamino)phenyl]1,3,4-oxadiazole (1_f)

This compound was prepared as shown in the scheme (2.2) and as described below:- [155]



Scheme (2.2): Synthesis routes of compound (1_f).

2.3.2.1 Preparation of n-Propylbromide

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-propanol 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 or for 5 hours. During this period the formation of n-propylbromide 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-propyl bromide [170].

2.3.2.2 Preparation of 4-propoxybenzaldehyde (1_a)

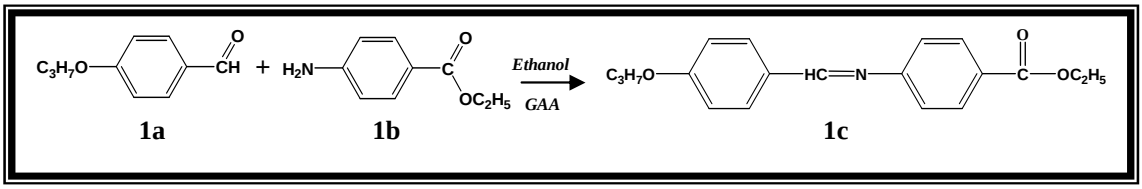
To a solution of (4.87 g, 0.087mol) potassium hydroxide in 50 mL of absolute ethanol, (10.61g, 0.087 mol) of 4-hydroxybenzaldehyde and (0.13 mol) of n-propyl bromide were added, the mixture was refluxed for 6 hours, and potassium bromide was precipitated. A 50 mL of water and 50 mL of diethyl ether were added. The mixture was extracted, and the organic phase was washed with 25 mL of water and 25 mL of 10% sodium hydroxide solution. Then the organic layer was also washed with 25 mL of water. The organic layer was dried by adding magnesium sulphate. The solution was filtered then evaporated the solvent to yield 4-propoxybenzaldehyde (**1_a**) (85 – 90) % [171].

2.3.2.3 Preparation of ethyl-4-aminobenzoate (1_b)

This compound was prepared according to the method described in the literature [170], as follows:

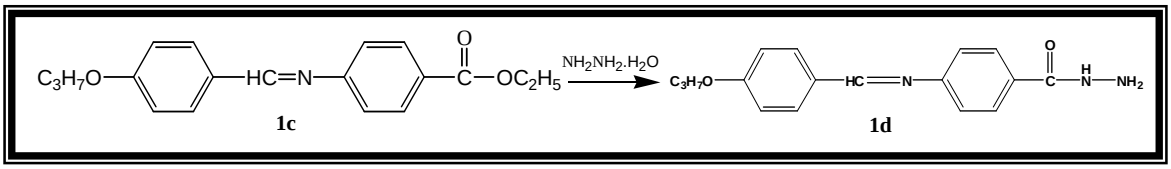
Dry hydrogen chloride, (which was prepared by the reaction of conc. H_2SO_4 with fused ammonium chloride in a Kipp's apparatus), was passed through 80 mL of absolute ethanol in a 250 mL conical flask equipped with a two-holed cork and wash-bottle tubes until saturation. The solution was transferred to a 250 mL round bottomed flask, (12g, 0.08 mol) of 4-aminobenzoic acid was introduced, and the mixture was refluxed for 2 hours. The hot solution was poured into crushed ice and water. Sodium carbonate was added to the clear solution until neutralized to litmus. The precipitated ester was filtered off and dried. The yield of ethyl-4-aminobenzoate (**1_b**), (m.p.= 86 – 88 ^oC) was (70 – 75) %.

2.3.2.4 Preparation of 4(4´-propoxybenzylidene amino) ethylbenzoate (1_c)



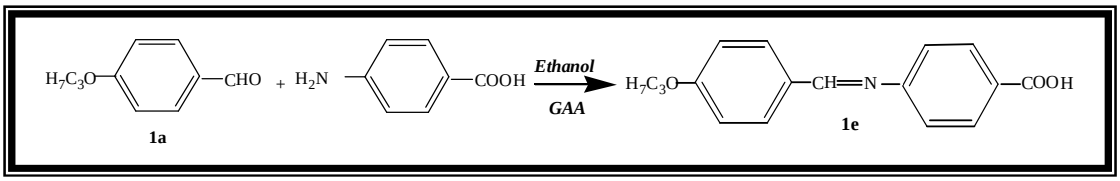
Compound (**1_c**) was prepared by the condensation reaction between 4-propoxybenzaldehyde (**1_a**) (1.64g, 0.01 mol) and ethyl 4-aminobenzoate (**1_b**) (1.65g, 0.01mol) in boiling absolute ethanol (20mL), two drops of glacial acetic acid were added. After reflux for 3 hours, the solid product was filtered and dried. Recrystallization from ethanol gave pale yellow crystals 95% yield, (m.p.= 66 – 68 ^oC).

2.3.2.5 Preparation of 4-(4´-propoxybenzylidene amino) phenyl acid hydrazide (1_d)



Fifteen milliliters of hydrazine hydrate was added to a 4(4′-propoxybenzaylideneamino)ethylbenzoate (**1_c**) (1.55g, 5mmol). The mixture was refluxed for 4 hours, then 30 mL of ethanol abs. was added and the reflux continued over night. The ethanol was distilled off and the mixture was cooled to room temperature. The obtained solid was filtered, and washed with cold water. Recrystallization from ethanol yielded 90%, (m.p.= 129 – 131 ºC) of **1_d**.

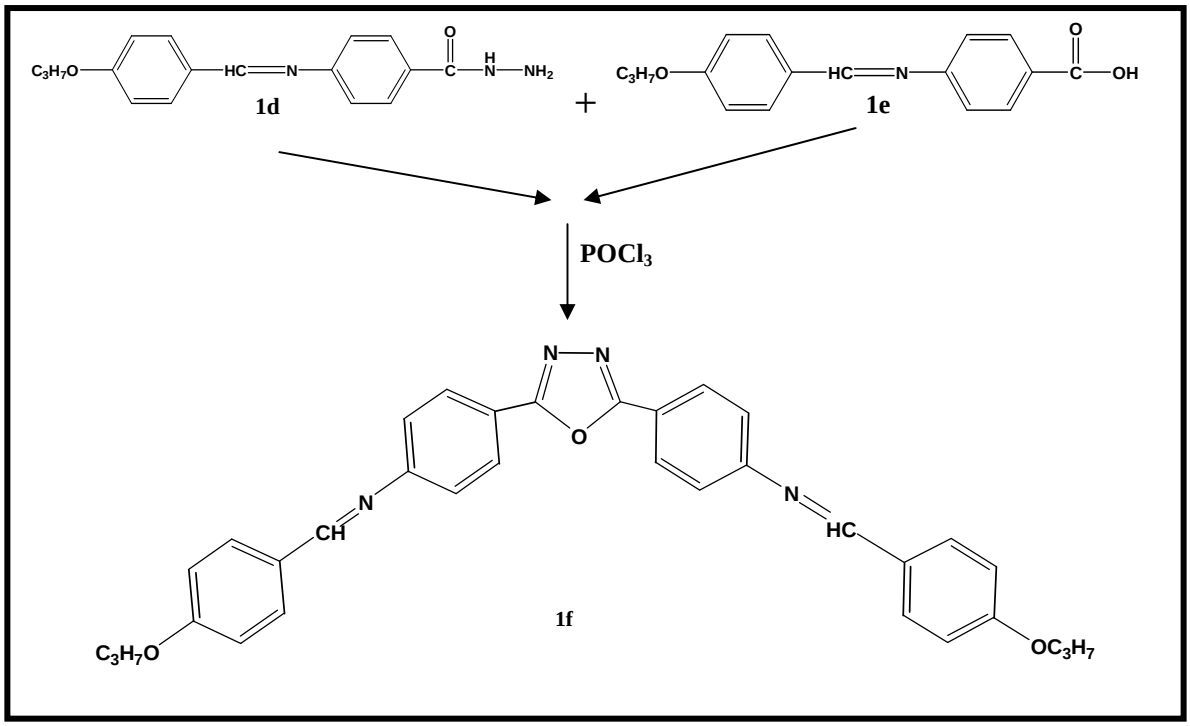
2.3.2.6 Preparation of 4-(4´-propoxybenzylidene amino) benzoic acid (1e)



This compound was prepared by the condensation reaction between 4-propoxybenzaldehyde (**1_a**) (1.64g, 10 mmol) and 4-aminobenzoic acid (1.37g, 10 mmol) in boiling absolute ethanol (20mL), two drops of glacial acetic acid were added. After reflux for 3 hours, the solid product was filtered and dried. Recrystallization from ethanol gave yellow crystals 95% yield, (m.p. = 181 – 183 ºC) of **1_e**.

All the above compounds were identified by FTIR spectrum.

2.3.2.7 Preparation of 2,5-bis-[4-(4´-propoxybenzyl ideneamino)phenyl]1,3,4-oxadiazole (1f)



A (1.58g, 5 mmol) of 4-(4´-propoxybenzylideneamino)phenyl acid hydrazide (**1_d**) and (1.415g, 5 mmol) of 4-(4´-propoxybenzylidene amino)benzoic acid (**1_e**) with 5mL $POCl_3$ were refluxed for 24 hours. The cold mixture was poured on crushed ice and made basic by adding $NaHCO_3$ solution. The resulting solid was filtered, dried and recrystallized from chloroform to give orange crystals with yield of (75 – 80) %. The oxadiazole (**1_f**) was identified by using FTIR, ^{1}HNMR, and CHN analysis.

2.4 Stationary phases preparation

The stationary phases were prepared by coating each of the liquid crystal compounds on chromosorb W/HP 100 – 120 mesh size, solid support. Different weights of the liquid crystal compounds (0.04, 0.12, and 0.80 g) and (3.96, 3.88, and 3.20 g) of the solid support were used, to prepare liquid crystal stationary phase with coating percentage 1%, 3%, and 20% respectively. 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 24 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 100ºC for 2 hours [155].

2.5 Packing and Conditioning Process

The stainless steal columns were packed by 1%, 3%, and 20% (loading percent) of the two different liquid crystal stationary phases (**2_b,1_f**). The methodology of packing process is described below [155].

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, they were added into 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. At the completion of the packing process, a glass wool was then inserted at the other end of the column.

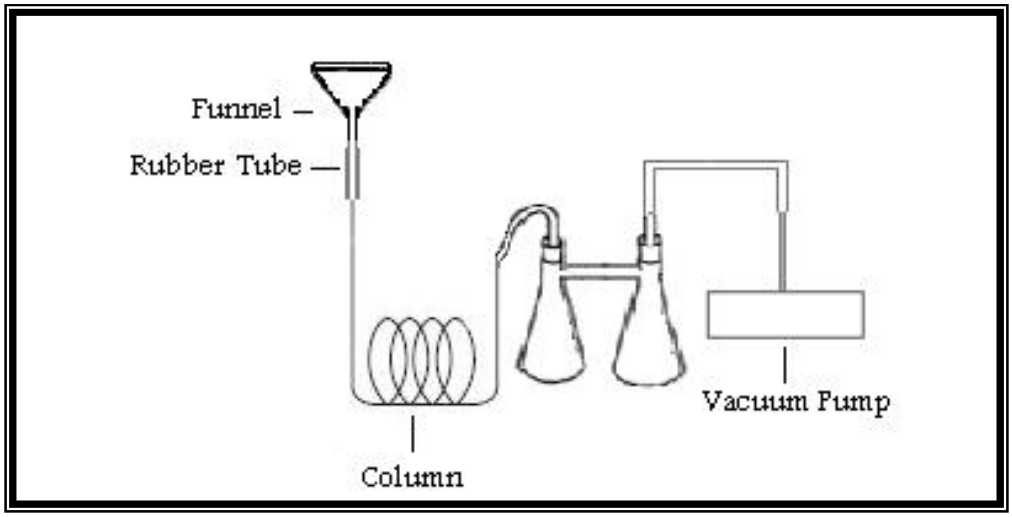


Figure (2.1): Packing assembly layout.

The prepared columns were conditioned as follows: the column was maintained at (10–15ºC) 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 [172,173].

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 20ºC 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.

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List of Abbreviations

δ	**Chemical shift**
γ^{∞}	**Solute activity coefficient at infinite dilution**
C	**Crystalline phase**
DMN	**Dimethyl naphthalene**
DSC	**Differential Scanning Calorimetry**
I	**Isotropic liquid**
IGC	**Inverse gas chromatography**
GC	**gas chromatography**
GAA	**glacial acetic acid**
LCSPs	**liquid crystalline stationary phases**
MN	**Methylnaphthalenes**
N	**Nematic phase**
PAHs	**polycyclic aromatic hydrocarbons**
PCBs	**polychlorinated biphenyls**
PCDDs	**polychlorinated dibenzodioxins**
PCDFs	**polychlorinated dibenzofurans**
PEG	**polyethylene glycol**
SCLCP	**side chain liquid crystalline polysiloxane**
TMS	**Tetra methyl silane**

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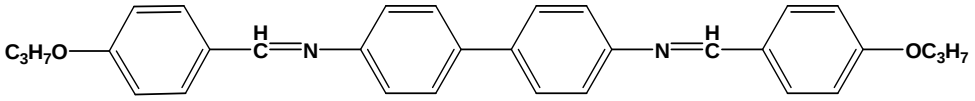
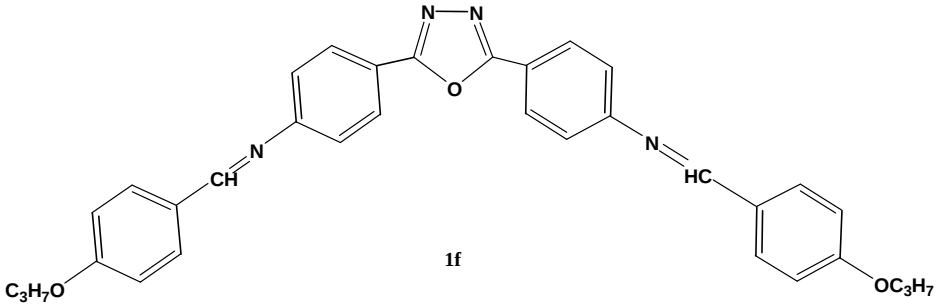
Summary

This work involves the preparation of two liquid crystalline compounds, 4,4´-bis-(4-propoxybenzylidene amino)biphenyl (2_b), and 2,5-bis-[4-(4´-propoxybenzylideneamino)phenyl]1,3,4-oxadiazole (1_f).



2 b



1f

The prepared compounds were characterized qualitatively by using FTIR, ^{1}HNMR, and elemental analysis (EA). The liquid crystalline properties of the synthesized compounds were verified using hot-stage polarizing microscope and differential scanning calorimetry (DSC).

The prepared liquid crystal compounds have a wide mesophase range that gives useful properties to these compounds as stationary phases in Gas Chromatography (GC). Compounds (2_b) and (1_f) were prepared to be used as stationary phases by loading them separately on chromosorb W/HP 100 – 120 mesh size, as solid support with different loading ratios (1%, 3%, and 20%). The prepared stationary

phases were packed through the stainless steal columns, and tested for separation of poly aromatic hydrocarbons PAHs (naphthalene, acenaphthene, acenaphthylene, phenanthrene, anthracene, and pyrene), alcohols (methanol, ethanol, 2-propanol, and 1- propanol), and positional isomers (o, m, and p-xylene).

A chromatographic study of the interaction and elution characteristics of the studied analytes through the prepared columns was carried out at different column temperatures of, 140-320 ºC for 4,4´-bis-(4-propoxybenzylideneamino)biphenyl (2_b) and 170-280 ºC for 2,5-bis-[4-(4´-propoxybenzylideneamino) phenyl]1,3,4-oxadiazole (1_f).

The best chromatographic conditions, efficiency, and selectivity of the columns for separation of PAHs, alcohols, and positional isomers were characterized by measuring the effective plate number of column ($N_{eff.}$), resolution (R_s), and separation factor (α). It was found that the supercooling phenomenon has occurred with 2_b column, which made a decrease in solid-nematic transition temperature. The best separation of alcohols was obtained at 180 ºC through 20% 2_b column. PAHs could be separated through 3% and 1% 2_b column at 240 ºC.

The best chromatographic performance for separation of PAHs using 1_f column was achieved at 220 ºC. This was related to the fact that the higher order of this liquid crystal occurred at these temperatures, which made the analytes interact more with the stationary phase.

Specific retention volumes (Vg°) were calculated to study the thermodynamic behaviors of the analytes (solutes) on the liquid

crystal stationary phases LCSPs (solution). From the plots of ln Vg° ($mL.g^{-1}$) versus 1/T (K^{-1}), the enthalpy (ΔH) and entropy (ΔS) of the solutions were measured. Gibbs free energy (ΔG) of the separated analytes at different temperatures was calculated. These values showed that the dissolution of the analytes on LCSPs were spontaneous.

The study also included measurements of the activity coefficients at infinite dilution (γ^{∞}). These values were < 1, which indicates a negative deviation of the solutions from ideality.

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A thesis
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BY

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Supervisor certification

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We the examining committees, certify that we read this thesis and examined the student ***Martin George Shlemon***, in its contents and that, according to our opinion, is accepted as a thesis for the degree of Doctor of philosophy, in chemistry.

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جمهورية العراق
وزارة التعليم العالي والبحث العلمي
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تحضير ودراسة خواص مركبات بلورية سائلة كأطوار ثابتة في كروماتوغرافيا الغاز

رسالة
مقدمة الى كلية العلوم - جامعة النهرين
وهي جزء من متطلبات نيل درجة الدكتوراه فلسفة في الكيميـاء

من قبل
مارتن جورج شليمون
بكالوريوس ٢٠٠٠ (جامعة النهرين)
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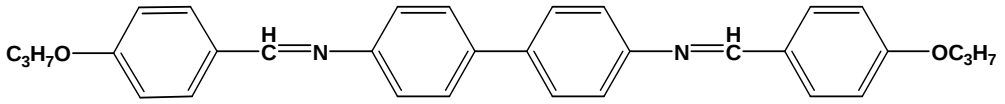
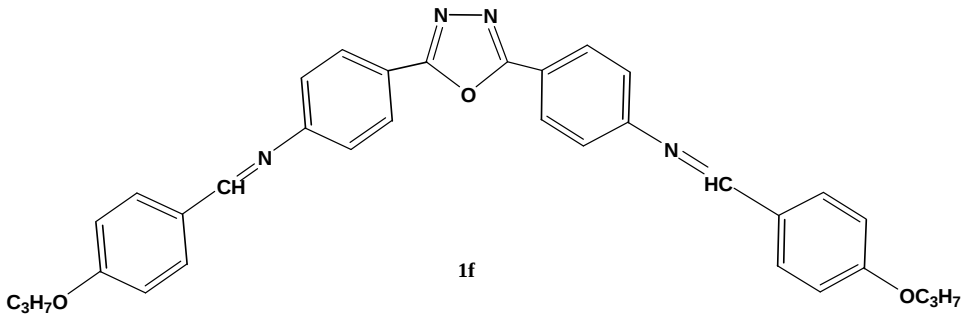
ايار ٢٠٠٨ جمادى الاولى ١٤٢٩

الخلاصة

تتضمن الأطروحة تحضير المركبات البلورية السائلة ٤،٤/ - بس- (٤- بروبوكسي بنزيليدين امينو)باي فنيل (2_b) ، و ٥،٢- بس- [٤-(٤/بروبوكسي بنزيليدين امينو)فنيل] ١،٣،٤ اوكسادايازول (1_f).



2 b



1f

تم تشخيص المركبات المحضرة، نوعياً بأستخدام الطرائق الطيفية والمتمثلة بطيف الاشعة تحت الحمراء FTIR ، طيف الرنين النووي المغناطيسي $HNMR^1$، وبأستخدام تحليل العناصر لكل من الكاربون، الهيدروجين والنيتروجين. كذلك تم دراسة الخواص البلورية السائلة للمركبات المحضرة بأستخدام مسعر المسح التفاضلي و مجهر الضوء المستقطب المزود بمنصة تسخين، ولقد لوحظ ان هذه المركبات لها مدى ميزومورفي واسع مما يعطيها اهمية في أستخدامها كأطوار ثابته في كروماتوغرافيا الغاز.

لقد تم أستخدم المركبين 2_b و 1_f كأطوار ثابته بتحميلها على الساند الصلب كروموسورب وبنسب تحميل مختلفة (١%، ٣%، ٢٠%). تم تعبئة الاطوار الثابته في أعمده فولاذية، وأستخدمت في فصل الهيدروكاربونات الاروماتية (النفثالين، اسينافثين، اسينافثيلين، فينانثرين،انثراسين، والبايرين)، الكحولات (ميثانول، ايثانول، ٢- بروبانول، و ١- بروبانول)، وكذلك الايزومرات (اورثو، ميتا، بارا- زايلين). تم دراسة الخواص الكروماتوغرافيه للاعمدة المحضرة في درجات حرارة مختلفة، حيث أستخدمت المديات (١٤٠-٣٢٠) درجه مئوية للمركب 2_b و (١٧٠-٢٨٠) درجه مئوية للمركب 1_f . تم أختبار ظروف الفصل للأعمده وذلك من خلال حساب عدد الصفائح المؤثرة في العامود و معامل الفصل، ولقد لوحظ حدوث ظاهرة الطبخ الحراري بالنسبة للطور الثابت 2_b مما سبب أنخفاض في درجة الانتقال الحراري من

الطور الصلب الى النيماتي، لذلك تم فصل الكحولات عند درجة الحرارة ١٨٠ درجه مئوية خلال العامود ٢٠% 2_b، وعند درجة الحرارة ٢٤٠ درجه مئوية تم فصل الهيدروكاربونات الاروماتية في العامودين ١% و ٣% 2_b. اما بالنسبة الى العامود 1_f فقد تم الحصول على افضل فصل للهيدروكاربونات الاروماتية عند درجة الحرارة ٢٢٠ درجه مئوية.

كذلك تم حساب حجم الاحتجاز النوعي لكل من المواد المراد فصلها وفي كلا العامودين، وذلك لدراسة الخصائص الديناميكية الحرارية لهذه المواد في المركبات البلورية السائلة المحضرة كأطوار ثابته. لقد تم رسم اللوغاريتم الطبيعي لهذه الدالة مع مقلوب درجة الحرارة، وذلك لحساب الانثالبي (ΔH) والانتروبي (ΔS) لهذه المواد. تم ايضا حساب طاقة كبس الحرة (ΔG)، وقد لوحظ ان جميع القيم كانت سالبة مما يدل على ان عملية أذابة المحاليل في المركبات البلورية السائلة المستخدمة كأطوار ثابتة تحدث بصورة تلقائية.

في هذه الدراسة تم حساب معامل الفعالية للمحاليل المراد فصلها وتحت ظروف التخفيف المتناهي، وكانت هذه القيم أصغر من واحد، مما يدل على أن هذه المحاليل تنحرف سلبياً عن سلوك المحاليل التي تعتبر كمحاليل مثالية.