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College of Education For Pure Science
Ibn Al-Haitham
Department of Chemistry

Synthesis, Characterization and Study of Liquid Crystalline Properties of Some New Derivatives Containing Pyrazole ring

A thesis
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بسم الله الرحمن الرحيم

فأما الزبد فيذهب جفاء وأما
ما ينفع الناس فيمكث في الأرض

صدق الله العظيم

الرعد ١٧

Supervisor certification

I certify that this thesis was prepared under my supervision at the Department of Chemistry, College of Education for Pure Science (Ibn-Al-Haitham) University of Baghdad, as a partial fulfillment of the requirements for the Degree of Master of Science in Chemistry.

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We, the examining committee, certify that we have read this thesis and examined the student (**Alaa Nashme Kurdi**) in its contents and that, in our opinion; it is adequate with " excellent " standing as a thesis for the Degree of Master of Science in Chemistry .

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This work is

Dedicated

To

My Family

Alaa

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Abstract

The present work involves the synthesis and investigation of liquid crystalline behaviors for newly prepared derivatives containing pyrazole ring, as following:

1- Synthesis and identification of pyrazole compounds $[XII\text{-}XVIII]_{a,b}$ using the following steps:

   a. Compounds $[I]_{a,b}$, were synthesized via the reaction of 1,4-phenylenediamine or benzidine, chloro acetic acid with sodium acetate in ethanol as a solvent.

   b. Synthesis of compounds $[II]_{a,b}$ by refluxing compounds $[I]_{a,b}$ and methanol (MeOH) in H_2SO_4 .

   c. Synthesis of acid hydrazide $[III]_{a,b}$ by the reaction of compounds $[II]_{a,b}$ and hydrazine hydrate in ethanol as a solvent.

   d. The reaction of acid hydrazine $[III]_{a,b}$ with substituted acetophenone$[IV]_n$ to synthesized substituted acetophenone hydrazones$[V\text{-}XI]_{a,b}$.

   e. Synthesis of 4-formylpyrazole derivatives $[XII\text{-}XVIII]_{a,b}$ via cyclisation of substituted acetophenone hydrazones$[V\text{-}XI]_{a,b}$ with Vilsmeier-Haack reagent DMF/$POCl_3$.

2- The synthesized compounds were characterized by spectral data.

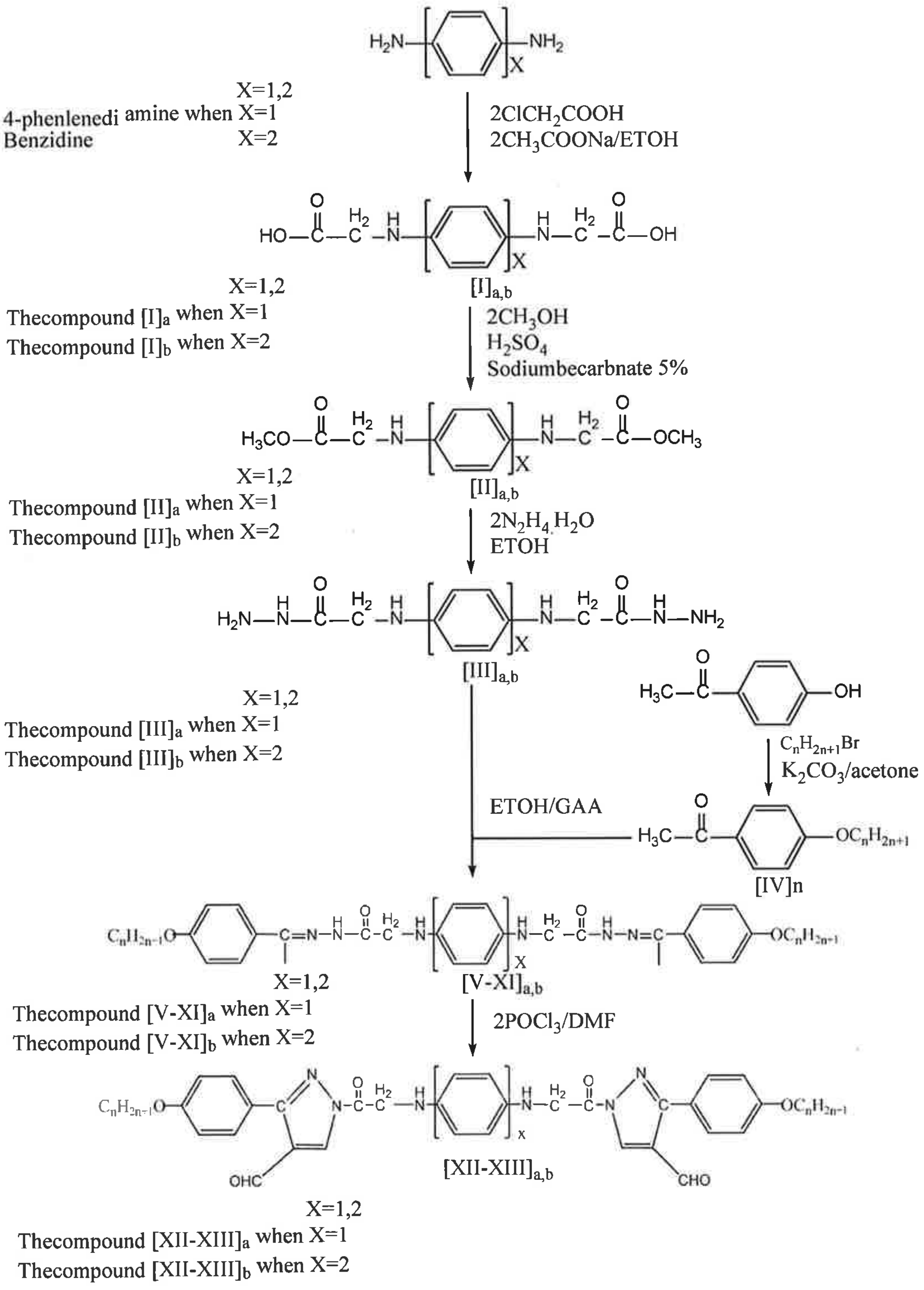
3- Study of liquid crystal behaviour using Differential scanning calorametry (DSC) and polarized optical microscope (POM) of the synthesized compounds showed the following

a. The compounds [V-VIII]$_a$ displayed enantiotropic nematic phase only while compounds [IX]$_a$, [X]$_a$ showed enantiotropic dimorphism SmB and N nematic phases , and [XI]$_a$ displayed enantiotropic smectic C phase and nematic phase.

b. The compounds [V-VIII]$_b$ displayed enantiotropic nematic phase only and compound [IX]$_b$ display enantiotropic dimorphism smectic A phase besides to nematic phase, but compound [X]$_b$ showed smectic B only . Compound [XI]$_b$ showed smectic A phase only

c. The compounds [XII-XV]$_a$ showed no liquid crystals behavior or change from solid crystalline state to the isotropic liquid. The compounds [XVI-XVIII]$_a$ exhibited enantiotropic nematic phases only.

d. The compound [XII]$_b$ showed no liquid crystals behavior or change from the solid crystalline state to the isotropic liquid on the other hand the compounds [XIII-XVIII]$_b$ showed enantiotropic dimorphism smectic B phase in addition to nematic phase. The present work summarized by the following Scheme (I).



n=1,2,3,5,6,7,8

Scheme(1)

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Chapter Two: Experimental part

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List of Scheme

List of abbreviations	
Abs.	Absolute
asym	Asymmetry
cm^{-1}	Centimeter of Wave number
δ	Chemical shift
Conc.	Concentration
^{o}C	Degree centigrade
Cr	Crystal phase
d	Doublet
DMF	N,N-dimethyl formamide
DMSO-d_6	Dimethyl sulfoxide deuterated
DSC	Differential Scanning Calorimetry
FT-IF	Fourier Transform Infrared
Gm	Gram
GAA	Glacial acetic acid
^{1}HNMR	Proton Nuclear Magnetic Resonance
I	Isotropic
L C	Liquid crystalline
mp	Melting Point
mL	Milliliter
M	Molarity
ND	Nematic discotic
N	Nematic phase
OPM	Optical Polarized Microscopy
ppm	Part per million
Sm	Smectic phase

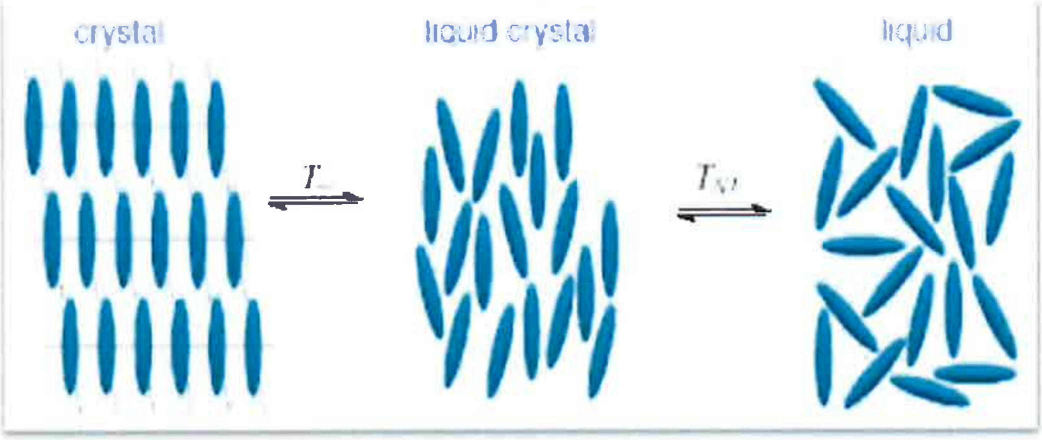
s	Singlet
sym	Symmetry
TBHP	Tert-Butyl hydroperoxid
TMS	Trimethylsilan
PTSA	Toluenesulfonic acid
t	Triplet

Chapter One
Introduction

1 Liquid crystal

1.1 Introduction

Liquid crystal is a state of matter which have properties of those conventional liquid and crystals (1). For instance, liquid crystals flow like liquid and oriented in crystals, Figure (1-1). There are different phases of liquid crystals which have been distinguished using many optical properties. Under polarized optical microscope, Liquid crystal have many types of textures depending on the orientation of substance(1).



Figure(1-1) state of matter.

The Austrian botanical physiologist Friedrich Reinitzer(2), reported the physico-chemical properties of different compounds of cholesterol which now belong to the type of substance known as cholesteric liquid crystals. The workers observed the color of cholesterol compounds effects on cooling just above the freezing point, however not associated it as a new phenomenon. Reinitzer observed the color modify in a substance cholesteryl benzoate were not the most peculiar feature. He noticed that the cholesteryl benzoate does not melt in the same manner as many derivatives, it has two melting points. In 145.5 °C it melts to give a cloudy liquid, while at 178.5 °C melts again and the cloudy liquid becomes clear (2)

In 1889 Otto Lehmann(3) used the expression "liquid crystals" to describe this state. In 1922 Friedl(4), used the term mesophase (from the Greek word meso, meaning “in between” the crystal and liquid phases).

1.2 Liquid crystal phases

Liquid crystalline materials are generally divided into two categories: The lyotropic mesophases and thermotropic (5), Figure (1-2).

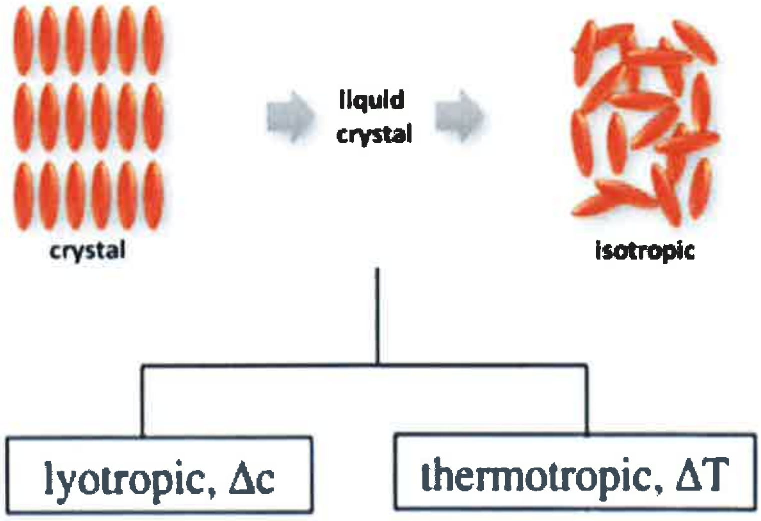


Figure (1-2): Placement of the liquid crystal phases within the general scheme.

1.2.1 Lyotropic liquid crystals

This type of liquid crystals have two or many substance which show liquid crystals behavior in different concentration. Solvent in this phase plays important role to prevent the system from turning back to the liquid state.

The substance which have two parts in same molecule named amphiphilic substance. These compounds can display lyotropic type. A lyotropic liquid crystals as soap and cell membranes Figure(1-3)(6).

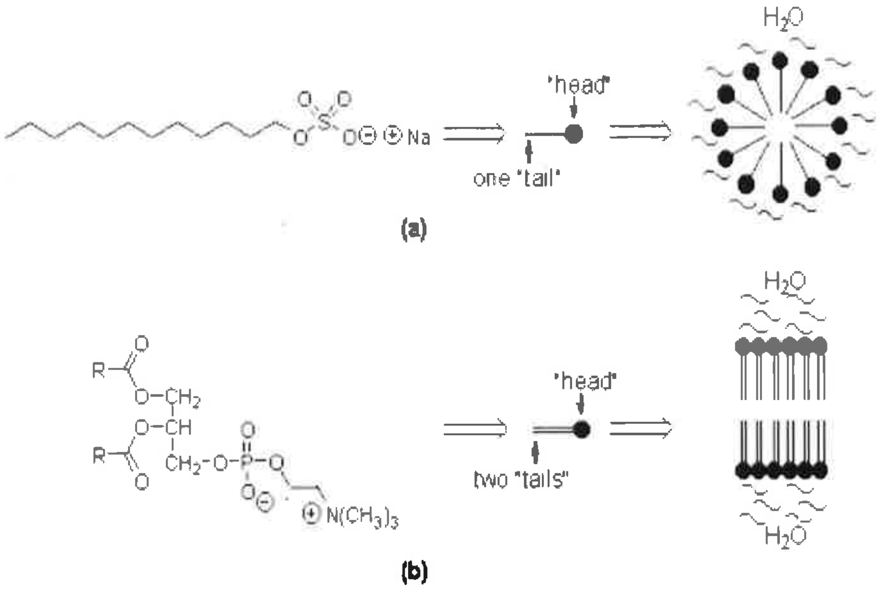
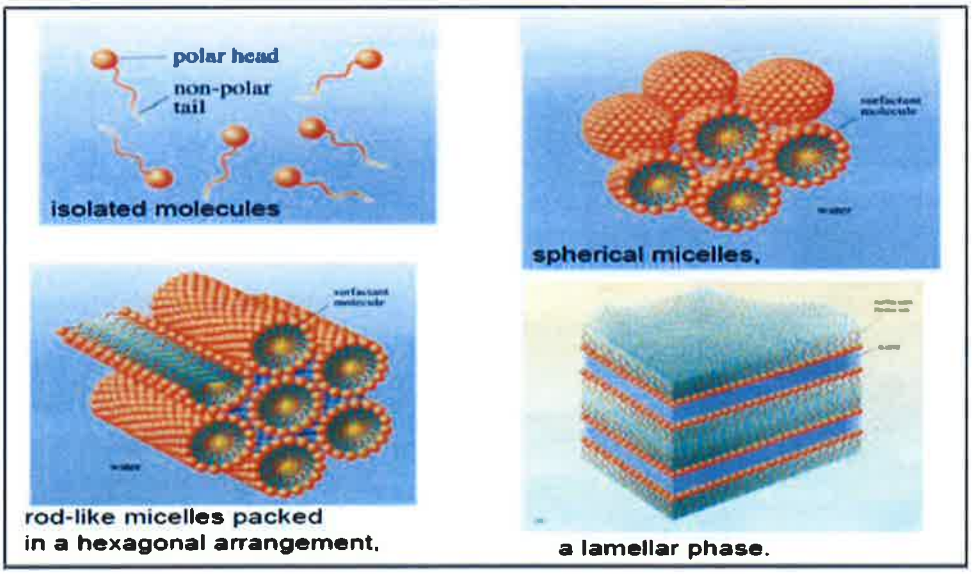


Figure (1-3): (a) Soap shape micelles (b) a phospholipids (lecitine) as bilayer arrangement.

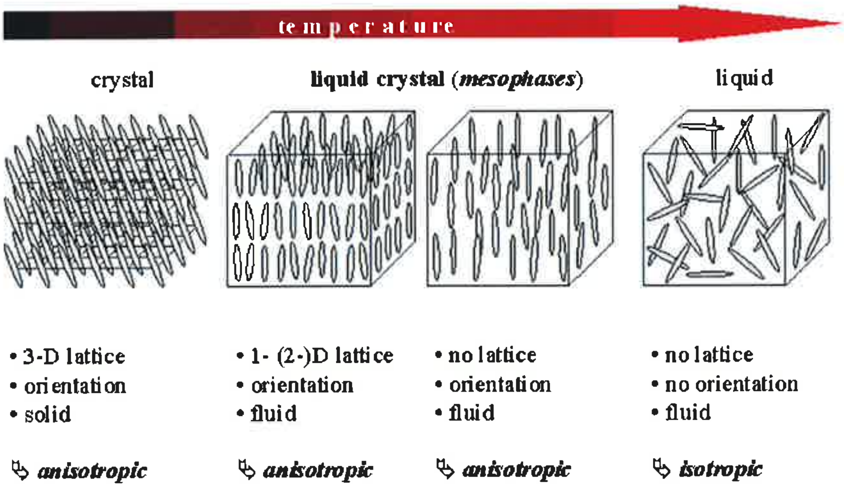
When the amphiphiles as cylinders form the major shape of hexagonal columnar , which oriented into a roughly hexagonal lattice. This is named the middle soap phase. At still higher concentration, a lamellar phase can be form, where in extended sheets of amphiphiles are separated via water as thin layers. Also in this type can form a cubic phase in addition to lamellar phases Figure (1-4)(7).



Figure(1-4): Lyotropic Types

1.2.2. Thermotropic liquid crystals

This phase of liquid crystals appear in a range of temperatures. At high temperatures, thermal force breaks the delicate cooperative direction of the LC phase and pushing the substance into a conventional isotropic phase. While at low temperature, the LC materials will form a conventional solid crystal.(8,9) Figure (1-5) shows the changes in phases of thermotropic LC with temperature changing.(10)



Figure(1-5):Solid, liquid crystals and isotropic liquid phase.

1.2,2.1.Calamitic liquid crystals

The materials of liquid crystal which have elongated shape is called calamitic or rod like LCs(11). In this kind of LC the length (l) is greater than the molecular breadth (b) as shown in the Figure (1-6).

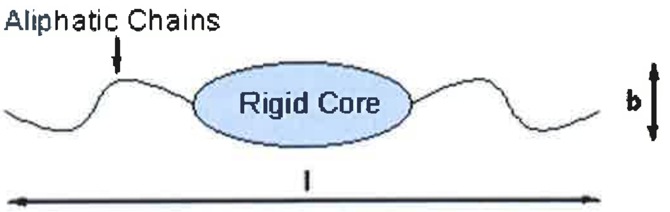


Figure (1-6): The calamitic liquid crystals(length(l) >> breadth(b)).

The calamitic liquid crystals are divided to the three types:

-Nematic phase

-Cholesteric phase

-Smectic phase

i) Nematic phase

The nematic phase is the common liquid crystal phases. The nematic word means thread which comes from Greek: nema. When the substance in the calamitic shaped have no direction, which arrange parallel to the long axes(12),they are called nematic. That means, the substance like flow of the liquid, also order of position. The direction of director is called vector ***n*(*r*)**. The uniaxial in this phase have one longer axis that's appear as rod, Figure (1-7).(13)

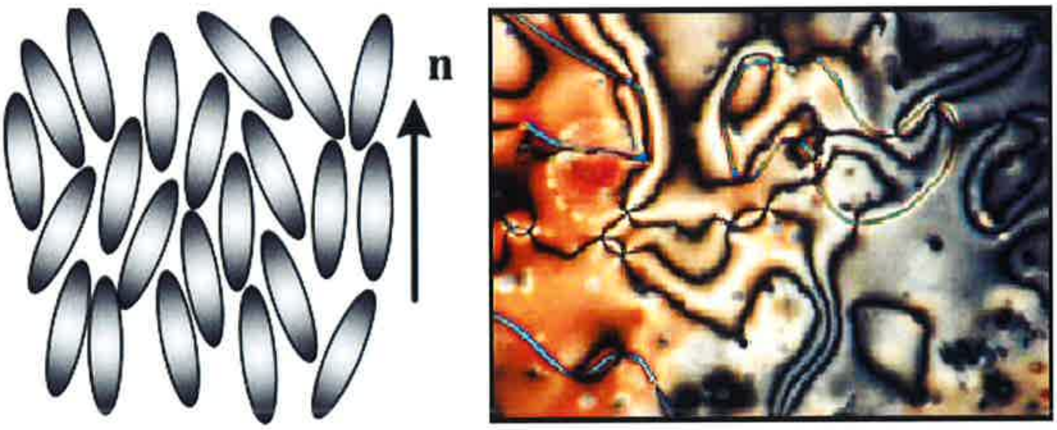


Figure **(1-7):** Nematic phase.

The nematics have fluidity like to the ordinary isotropic phase and can be aligned via electric field or an external magnetic. They also have the optical properties of uniaxial crystals, and for this can, they have been used in liquid-crystal displays (LCD) (14). The molecules in a nematic rotate around their long axes. The behave optically as a uniaxial material and the sign of the director has no physical significance(15)

ii) Cholesteric phases (chiral nematic)

The chiral nematic phase is named the cholesteric phase for first showed for cholesterol compounds. The chiral compounds can give same a phase. This phase display a twisting of the compounds perpendicular to the director with axis parallel to the director. Twist angle between the molecules makes chiral order(16,17). When liquid crystal substance twist 360° the distance means pitch(p), Figure (1-8).

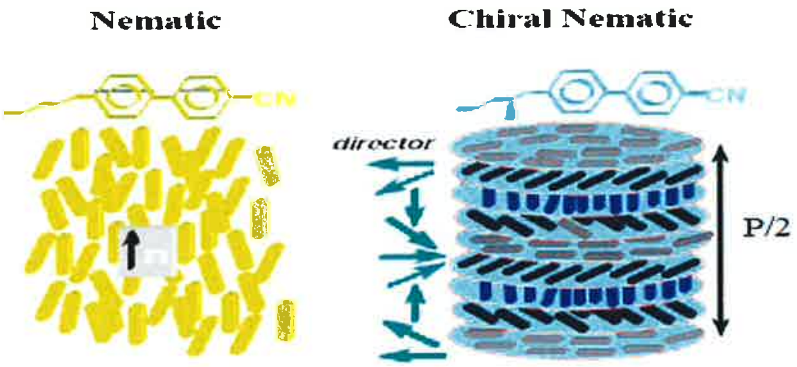


Figure (1-8): cholesteric phase

The chiral pitch p, is altered with temperature, then the pitch of a given material to be tuned accordingly. The direction pitch in some liquid crystal systems is in the same order as wavelength of light. Therefore, properties such as Bragg reflection have been employed in many optical applications.(18,19)

iii) Smectic phase

The word smectic originates from the Greek word "Smectic" which means having similar properties to those for soap. This seemingly have a wide 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. In this phase the compounds have a degree of translational arrange differ from those in the nematic. The smectic phase has two dimensional orderand the layers of the substance are flexible in this phase.

The smectic liquid crystals containing many types of phases that differs in the ordered of layer. When order is high, this means the smectic state is like a solid. A number of different classes of smectics have been recognized as smectic –(A,B,C,D,E, F, G, H, I), SmA, SmB, SmC, ……, respectively. When the layer structure are parallel to to the plane, this formed smectic A (SmA). These are optically uniaxial and hence homeotropic texture watched on light crossed polarizes. The focal conic texture or baton nets may be gives(20-24).

The smectic C (SmC) is closely related to SmA phase but SmC is a tilt. The difference between the two phases are tilt of the layers to the long of axes in the molecule, Figure (1-9).

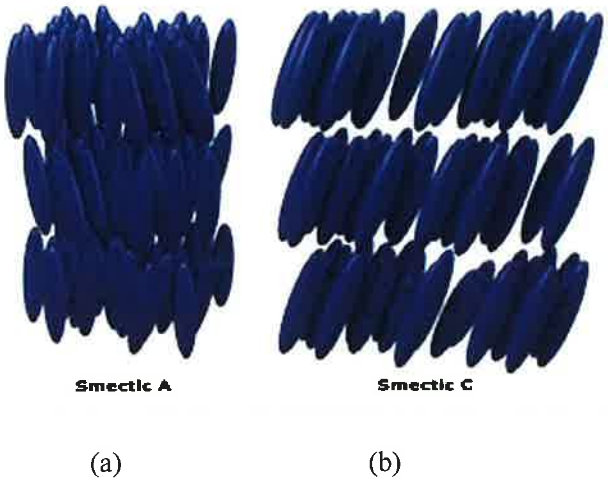
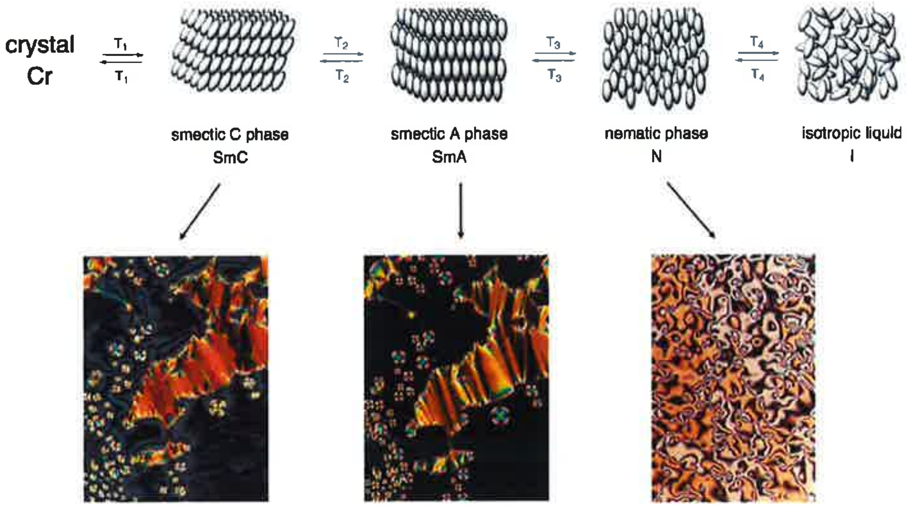


Figure (1-9): Molecular arrangement (a) the SmA phase, and (b) the SmC phase.

In this phase, the molecules are tilted layers and the textures of the system is characterized as biaxial , Figure (1-10).



Figure(1-10) Textures of liquid crystal.

1.2.2.2. Discotic liquid crystals

Nematic texture is formed in many types of mesophases and different degrees of organization. It can be divided into two types mesophases:

a. Nematic discotic b. Columnar.

a. Nematic discotic phase

The least arrangement mesophase is the Nematic discotic (ND)$^{(25)}$,where the molecules have only orientational order being aligned on average with the director this shown as Figure (1-11). The order is no positional in this phase.

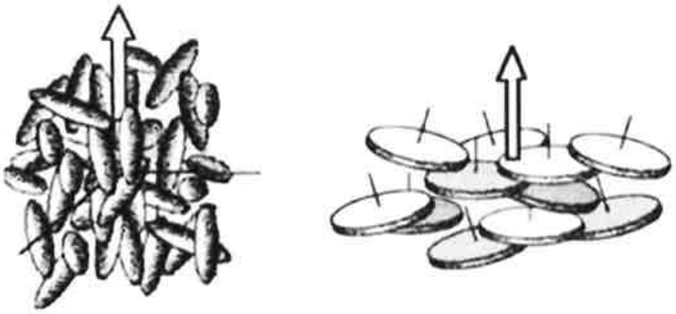


Figure (1-11) Nematic discotic phase.

b. Columnar phase

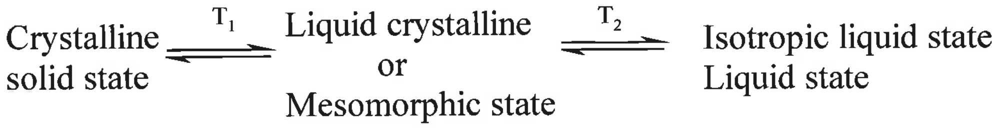
The columnar phase is a class of mesophases in which molecules assemble into cylindrical structures to act as mesogens. Originally, these kinds of liquid crystals were called discotic liquid crystals(26) because the structure of discotic is similar to columnar phase as shown in Figure (1-12).

Figure (1-12) discotic columnar phase.

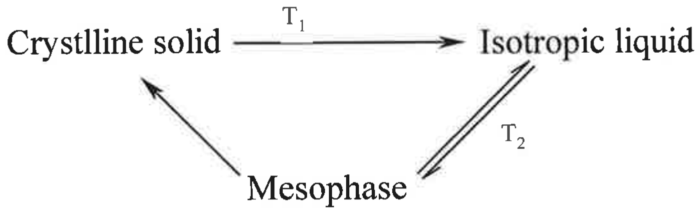
1.3 Order of appearance

Thermotropic liquid crystals can be classified into three types:

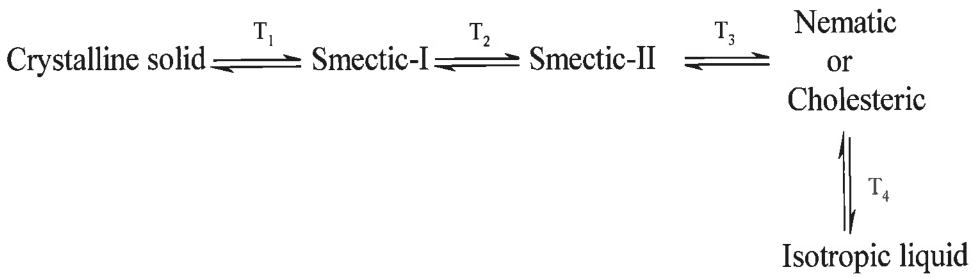
1. **Enantiotropic liquid crystals**: this can be changed into the liquid crystalline state by heating and cooling .



2. **Monotropic liquid crystals**: this can only be changed into the liquid crystalline state by cooling.



3. **Polymorphism liquid crystals:** different types of substances that display smectic mesophase structure only or exclusively nematic mesophase structure. While some display two types of mesophase, smectic and nematic. This phenomenon is known as polymorphism Figure (1-13).



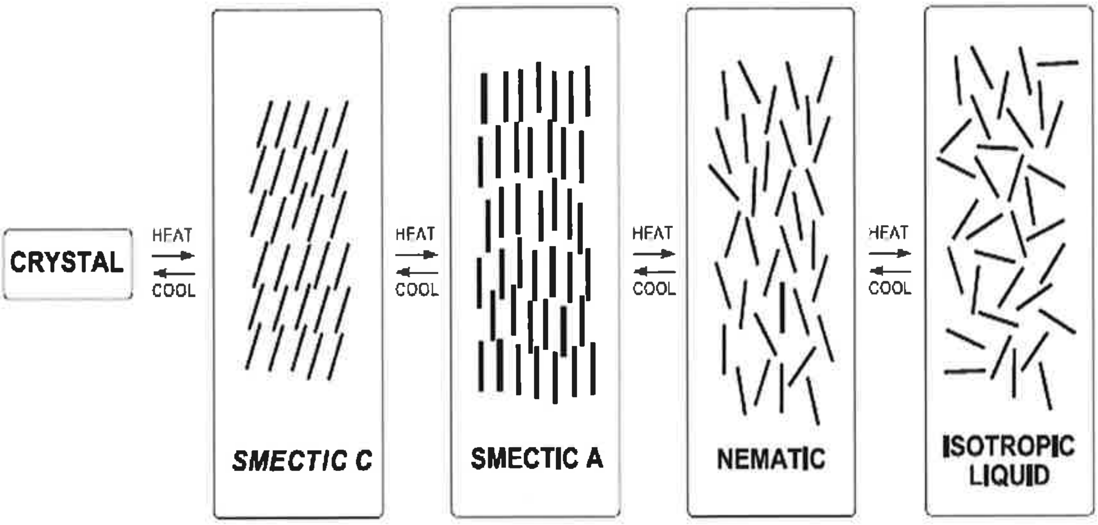
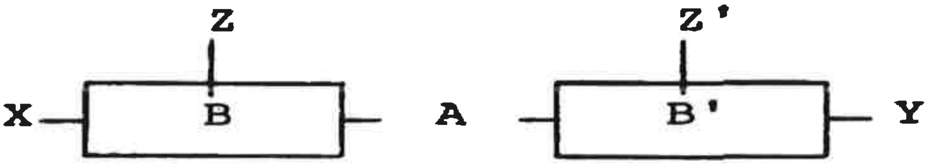


Figure (1-13): liquid crystal phases.

1.4 General structural of liquid crystals

Liquid crystal phases can be exhibited by molecules having different molecular shapes. The structure of molecules may be formed as rod shape, it is now named calamatic, which is recently found in discotic liquid crystal phases as disc like molecules. The typical structure of calamatic liquid crystal molecule [27] is shown in Figure(1-14).



Figure(1-14) general molecular structure of Liquid crystal.

X and Y are terminal groups as (C_nH_{2n+1} , OC_nH_{2n+1} , Br, Cl, F, CN).

A is a linking group as (-CH_2CH_2- , -CH=CH- , -CH=N- , -N=N-).

B and B' are two(or more) ring systems.

Z and Z' are lateral group.

1.5 Application of liquid crystals

liquid crystals have a wide range of application particularly in display due to their optical properties with or without electric field. In display device the thick of liquid crystal layer is 4 µm between the two polarizers that are at 90° oriented to each other. The liquid crystal alignment is chosen for this is twisted phase(14).

This twisted phase allow the light to pass through the first and then the second polarizer. When an electric field applied to the LC layer, the molecule align in parallel to the electric field redirection light, the first and second polarizer is absorbed light polarized and when raise voltage, loses transparency in the device. The electric field may be make a pixel switch. LCD device employ the same technique, used color filters to make red, green, and blue pixels(14).

In ferroelectric LCDs used chiral smectic phase, that modulators switching light . Used same precept to manufacture many liquid crystal with optical devices(28). The filters LC can made the in a electro optical devices(29), for example hyper spectral imaging.

The liquid crystal thermometers can made from thermo tropic LC whose pitch change with temperature, the color material is change will as change the pitch. Color liquid crystal can used on many aquarium in addition to baths(30). Many substance of LC change the color, for this in industry used liquid crystal sheets also in map heat flow. In the semiconductor industry can used liquid crystal in flow type.

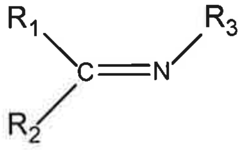
Gas chromatography has a great importance in the modern chemical analysis and physico-chemical investigation. The first use of liquid crystals as stationary phases in gas liquid chromatography is described by Kelker and Fresenius in 1963(31), the use of liquid crystals especially nematic as stationary phase in gas liquid chromatography (GLC) has gained a great interest, for example the separation of m- and p-xylen, which has been difficult to separate is separated by nematic stationary phase by GLC chromatography.

Liquid crystal can be used in liquid crystal lasers in the lasing medium as a replacement to the external mirrors. Emission can made via the liquid crystals with dielectric structure (32,33). Moreover, liquid crystals polymer can used as adhesive that applied to windows which are electrically switched between clear and opaque modes.

Different fluids, for instance, soapy water, are in fact liquid crystals. Many types of liquid crystals can be formed depending on the concentration of soap in water (34).

1.6. Schiff bases

The first preparation of Schiff bases was reported in 1864 by Hugo Schiff. Schiff bases are formed when a primary amine reacts with an aldehyde or a ketone under specific conditions. Structurally, Schiff base are the compounds containing azomethine group (-HC=N-) [1]. Schiff bases are of the most widely used organic compounds. They are used as pigments and dyes, catalysts, intermediates in organic synthesis, and as polymer stabilizers . Schiff bases have also been shown to exhibit a broad range of biological activities. Imine or azomethine groups are present in various natural, natural-derived, and non-natural compounds(35). They are also used as liquid crystals , in analytical ,medical and polymer chemistry (36-39).



[1]

R^1, R3 = alkyl , aryl

R^2 = H, alkyl, aryl

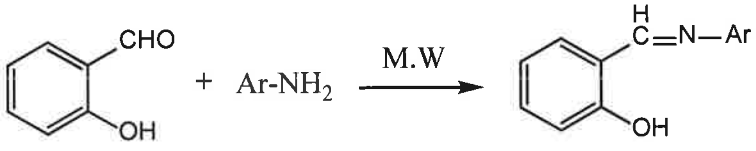
1.6.1.Synthesis of Schiff bases

Different methods for the synthesis of imines have been described The classical synthesis reported by Schiff involves the condensation products of ketones (or) aldehydes with primary amines. Formation of Schiff base generally takes place under acid or base catalysis or with heat(40). Schiff bases can be synthesized from an aliphatic or aromatic amine and a carbonyl compound by nucleophilic addition forming a hemiaminal, followed by dehydration to generate an imine(41).

In the past 12 years a number of innovations and new techniques have been reported, including solvent-free/clay/microwave irradiation, solid-state synthesis and silica/ultrasound irradiation. Among these innovations, microwave irradiation has been extensively used due to its operational simplicity, enhanced reaction rates, and great selectivity. Microwave irradiation is less environmentally problematic than other methods and another feature of this technique is that the reactions achieve high efficiency in a shorter period of time (35).

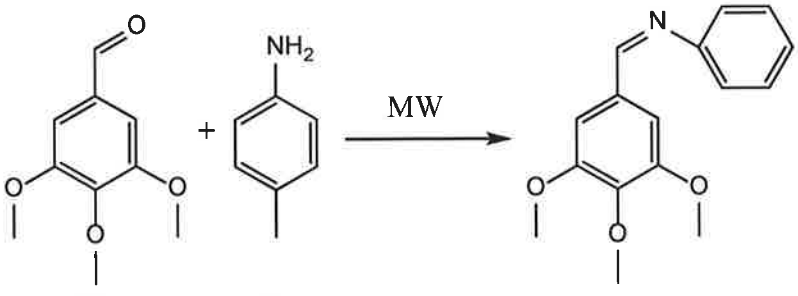
Many workers synthesis Schiff bases as below:

Yang *et al.*(42) developed a microwave-assisted preparation method of Schiff base[4] *via* efficient condensation of salicylaldehyde [2] and aryl amines [3] without solvent, which is described in high yield as well as environment friendly reaction in organic synthesis.



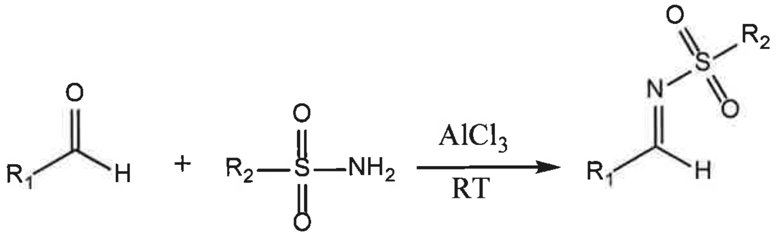
[2] [3] [4]

Yang and Sun (43) reported the synthesis of (*E*)-4-methyl-N-(3,4,5-trimethoxybenzylidene) benzenamine [7] by reacting compound [5]with 4-methyl aniline [6] under microwave irradiation.



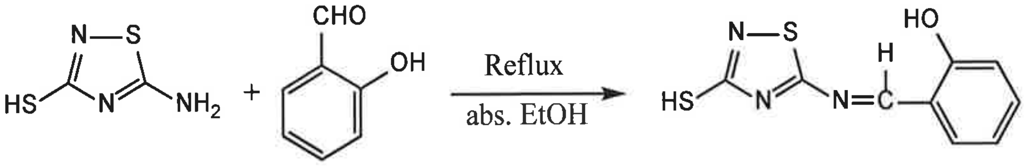
[5] [6] [7]

N-Sulfonyl aldimines [10] are powerful synthetic intermediates in organic synthesis and industrial application. Sharghi, at el(44) were prepared expeditiously under solvent-free conditions by the reaction between different aromatic aldehydes [8] and sulfonamides [9] in the presence of $AlCl_3$.



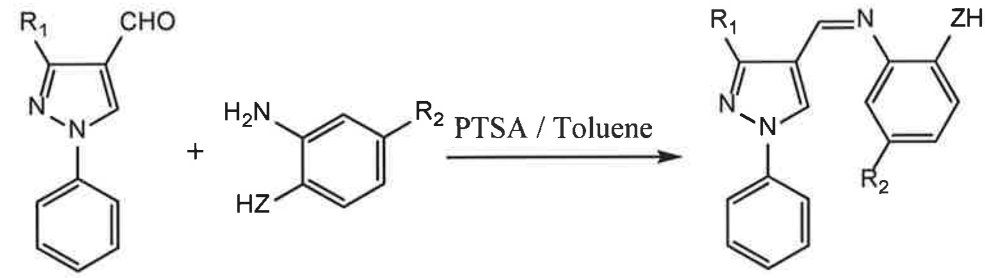
[8] [9] [10]

AL-Shimary (45) reported Schiff bases [12] derived from the reaction of 5-amino-3- mercapto-1,2,4-thiadiazole [11] with salicyaldehyde [2] in ethanol solvent



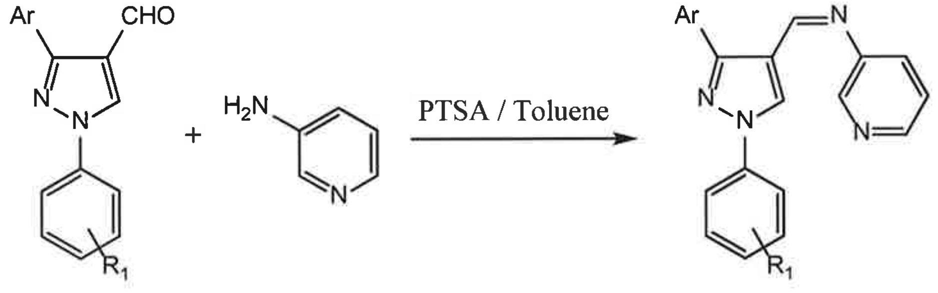
[11] [2] [12]

Also , Praveen et al.(46) synthesized Schiff bases of pyrazole [15] from reacting 4-formyl pyrazole[13] with aromatic amine [14] using P-Toluenesulfonic acid (PTSA) in toluene as a catalyst.

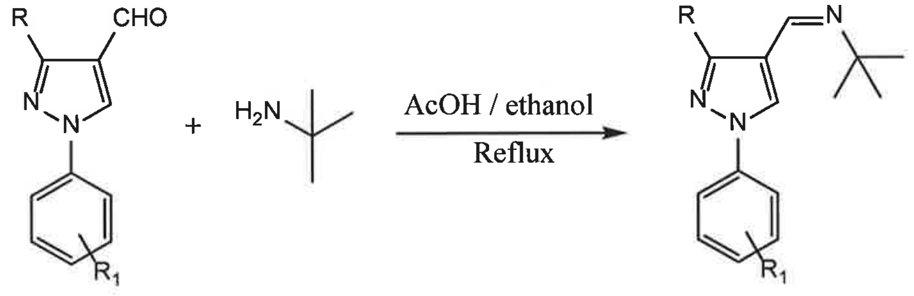


[13] [14] [15]

Argade (47) synthesized azomethine compounds [18] and[21] using condensation reactions of 4-formyl pyrazoles [16]and[19] with hetero-aromatic amine[17] as well as aliphatic amines[20] as below.

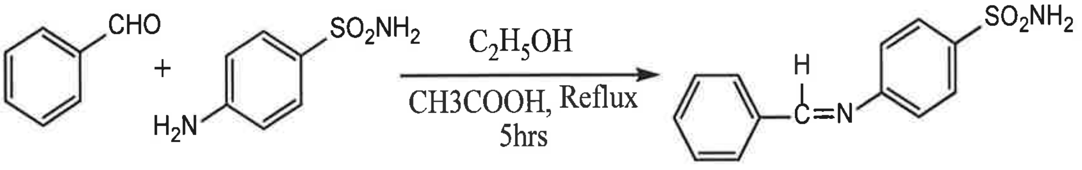


[16] [17] [18]



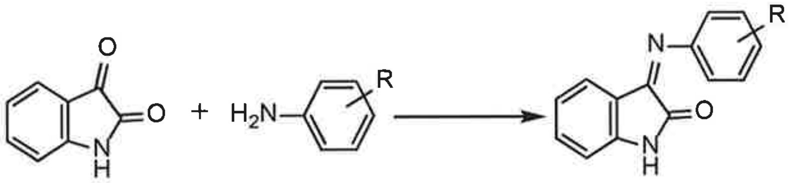
[19] [20] [21]

Kumar *et al.*$^{(48)}$ synthesized better antimicrobial compound using benzaldehyd [22] with aromatic amine [23] for the formation of Schiff base [24] in presences of alcohol and acidic reagent.



[22] [23] [24]

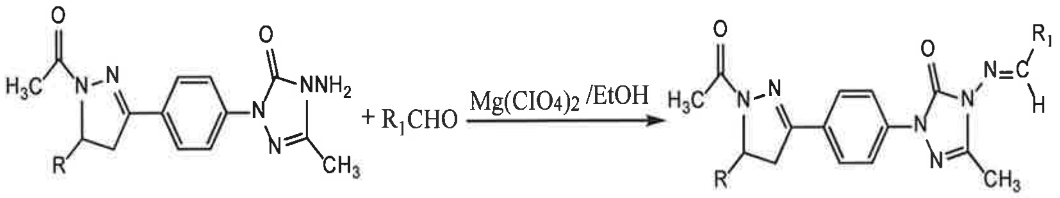
Kriza *et al.*$^{(49)}$ Developed a synthetic approach for obtaining Schiff bases [27] *via* condensation reactions between isatin [25] and various amines [26].



[25] [26] [27]

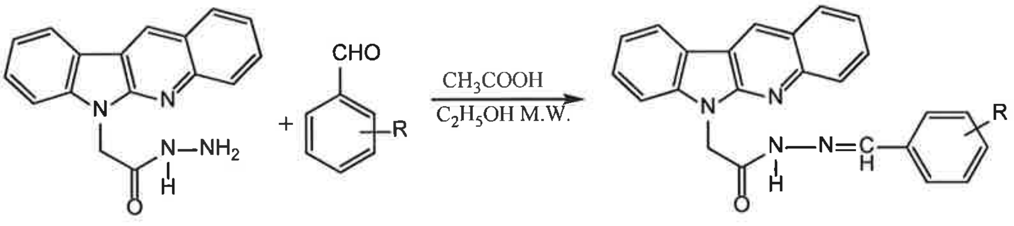
R=H,2-OCH_3,4-OCH_3

In addition, synthesis of Schiff bases[30] from reacting 4-amino-2-aryl-3-oxo-1,2,4-triazoles [28] with aldehyde [29] under $Mg(ClO_4)_2$ as a catalyst in ethanol as a solvent was performed $^{(50)}$.



[28] [29] [30]

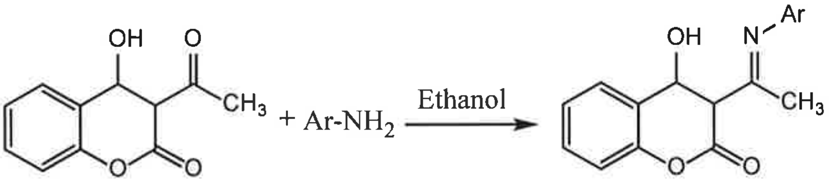
Pai and Waghmode (51) used microwave promoted synthesis of Schiff bases of indolo [2, 3-b] quinoxaline [33] by the reaction of acid hydrazide [31] with different aldehydes[32] in ethanol and glacial acetic acid GAA. Microwave assisted synthesis has not only reduced the reaction time drastically but also gave excellent yields of Schiff bases



[31] [32] [33]

R=H, 3-NO_2, Furfural, 4-CH_3, 2-OH, 4-OH, 4-$N(CH_3)_2$, 2-Cl, 3-OCH_3, 4-OCH_3

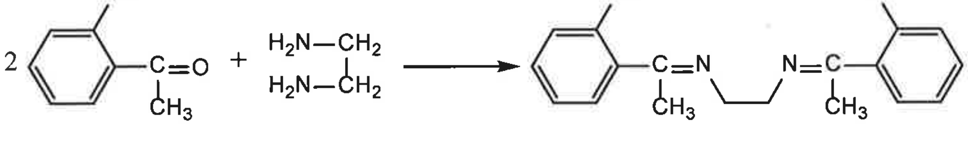
Girgaonkar and Shirodker (52) synthesized Schiff base 4-hydroxy-3-(1-(arylimino)ethyl)chromen-2- ones [36], by condensation of 3-acetyl-4-hydroxychromen-2-one [34] with primary aromatic amines [35] in ethanol as a solvent.



[34] [35] [36]

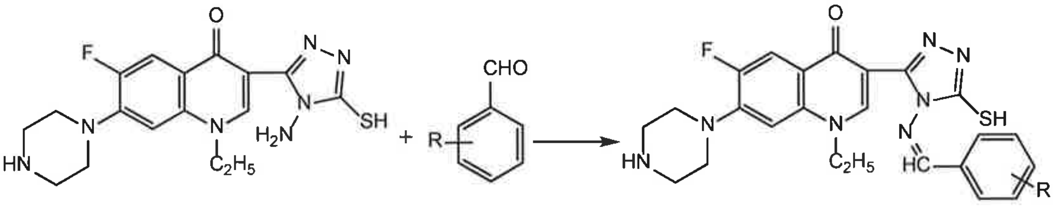
Ar=Phenyl, Toluyl, 4-chloroPhenyl, 4-anisyl

Hamil, et al.(53) synthesized a new Schiff base 2-[2-(E)-(2-hydroxyphenyl) ethylidene]aminoethyl) ethanimidoyl] phenyl [39], via the reaction of two mole of 2-hydroxyacetophenone [37] with ethylene-diamine [38].



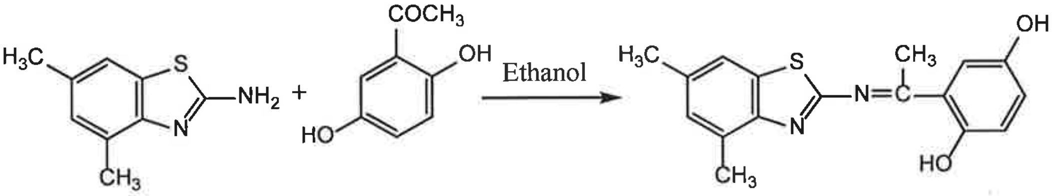
[37] [38] [39]

Also, 3-Substituted-4-amino-5-mercapto-1, 2, 4-triazole [42] was obtained in an excellent yield in a single step by the condensation of compound [40] with substituted aldehyde [41] (54).



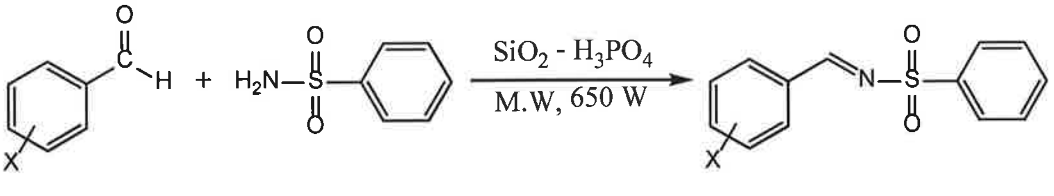
[40] [41] [42]

Kulkarni, et al (55) synthesized Schiff bases [45] by the condensation of 2-amino-4,6-dimethyl benzothiazole [43] with 2,5-dihydroxy acetophenone [44] in ethanol



[43] [44] [45]

N-[(*E*)-phenylmethylidene]-benzenesulfonamide derivatives [48] were synthesized by the reaction of aldehyde [46] with sulfonamide [47] using solid SiO_2-H_3PO_4 catalyst under solvent free conditions using microwave irradiation (56).

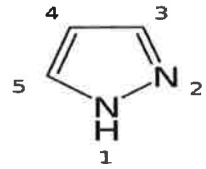


[46] [47] [48]

X= H, 3-Br, 4-Br, 2-Cl, 4-Cl, 2-F, 4-OCH_3 , 4-CH_3 , 4-NO_2

1.7.pyrazole

Pyrazole is an organic compound with the formula of $C_3H_4N_2$. It is a heterocycle characterized by a 5-membered ring of three carbon atoms and two adjacent nitrogen atoms (57).



Pyrazole

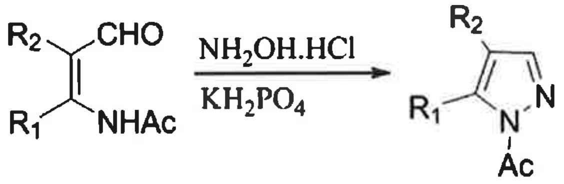
The term pyrazole was given to this class of compounds by the German Chemist Ludwig Knorr in 1883 (58). In a classical method developed by German chemist Hans von Pechmann in 1898(59).

Pyrazoles are useful in organic synthesis. They are one of the most studied groups of compounds among the azole family. Indeed, a huge variety of synthesis methods and synthetic analogues have been reported over the years. The presence of the pyrazole nucleus in different structures leads to diversified applications in different areas such as technology, medicine and agriculture(60).

1.7.1.Synthesis of pyrazole derivatives

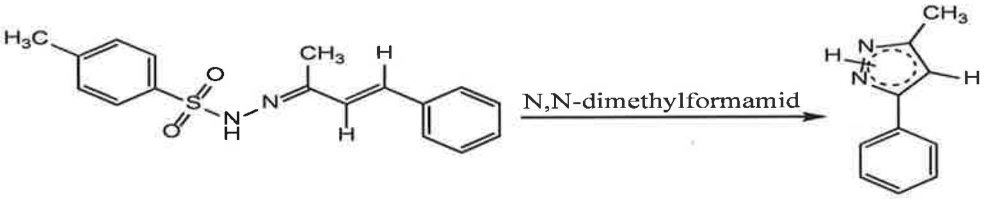
Many methods describe the synthesis of pyrazole derivatives as below:

One-pot synthesis of pyrazoles [50] has been accomplished by the reaction of β-formyl enamides [49] with hydroxylamine hydrochloride catalyzed by potassium dihydrogen phosphate in acidic medium (61).



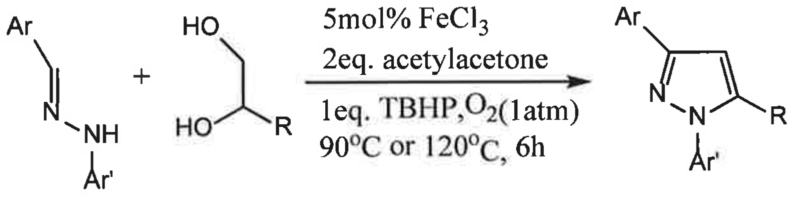
[49] [50]

A novel pyrazole derivatives[52] were synthesized from tosylhydrazone [51] exploiting microwave activation coupled with solvent free reaction conditions (62).



[51] [52]

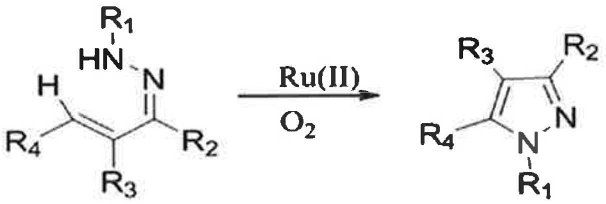
Synthesis of 1,3- and 1,3,5-substituted pyrazoles[55] from regioselective reaction of diarylhydrazones [53] and vicinal diols [54] in iron-catalyzed (63).



[53] [54] [55]

R=H,CH_3

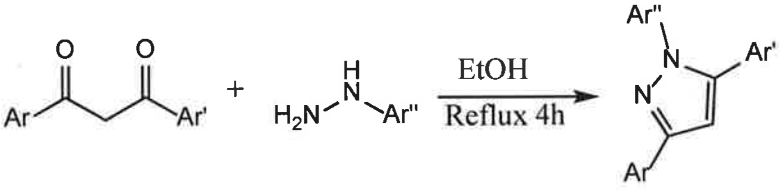
Also, a ruthenium (II)-catalyzed intramolecular oxidative (C=N) coupling method for the facile synthesis of a tri- and tetra-substituted pyrazoles [57]. Oxygen gas was employed as an oxidant in this transformation and the reaction demonstrated excellent reactivity (64).



[56] [57]

R_1=Aryl R_2,R_3,R_4=H, Aryl , Alkenyl

In addition to synthesized 1-aryl-3,5-bisarylpyrazoles[60] via reaction of 1,3-diketone[58] and arylhydrazines[59] with complementary regioselectivity at position 3 and 5 (65).



[58] [59] [60]

Ar = 4-ClC_6H_4

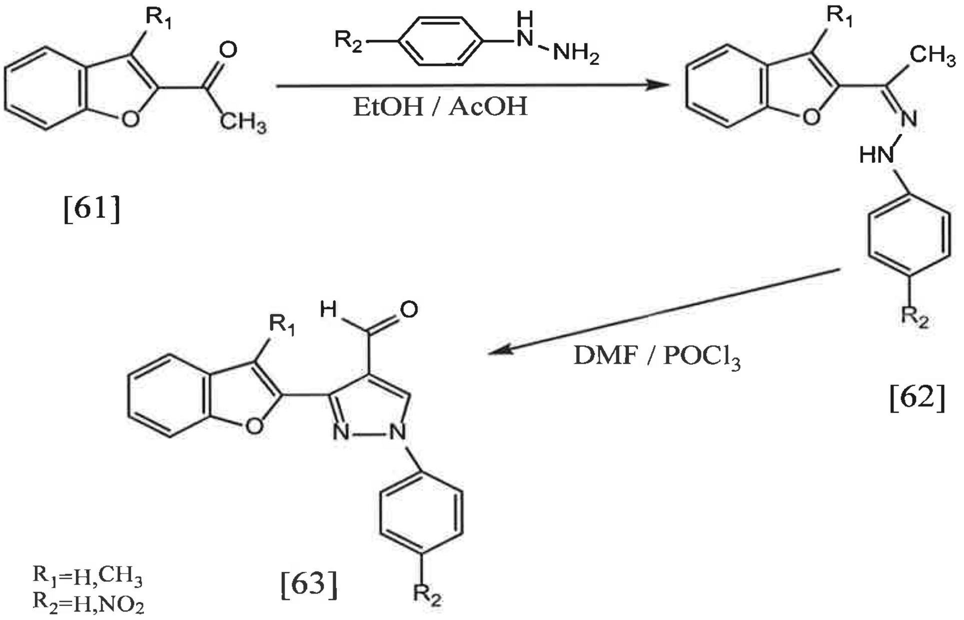
Ar'', Ar' = C_6H_5

Vilsmeier–Haack reaction

The Vilsmeier Haack reagent, a halomethylenium salt formed from phosphorus oxychloride ($POCl_3$) and N,N-dimethylformamide (DMF), has attracted the attention of synthetic organic chemists since its discovery in 1927. The Vilsmeier Haack reaction is a mild method for the introduction of formyl group in various activated aromatic and heteroaromatic compounds. The Vilsmeier Haack reagent is also utilized for synthesis of many heterocyclic derivatives (66).

Many researchers synthesized pyrazole derivatives using Vilsmeier–Haack reaction as below:

Rajput and Girase(66) converted 2-acetyl benzofurans [61] into benzofuran phenyl hydrozone [62] via reaction with phenyl hydrazine in ethanol and acetic acid. The intermediate phenyl hydrazone [62] was cyclized to product pyrazoles derivatives [63] when subjected to Vilsmeier-Haack reaction conditions.



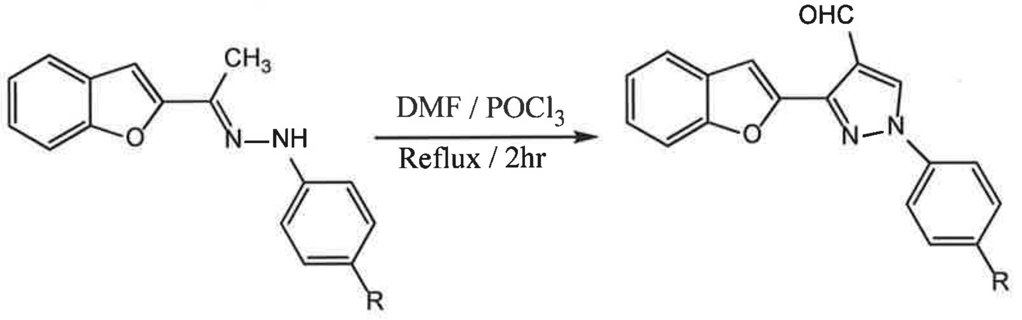
[61]

[62]

[63]

R_1=H,CH_3
R_2=H,NO_2

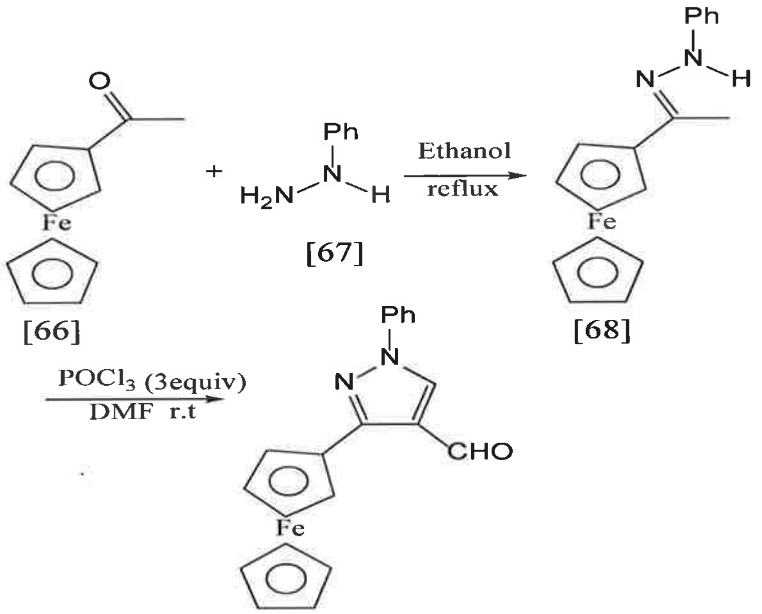
Also, Goudarshivannanavar et al.(67) reported the reaction of 2-acetyl benzofurohydrozones [64] with Vilsmeier-Haack reagent then via formylation to produce 3-(benzofuran-2-yl)-1-(substituted phenyl)- 1*H*-pyrazole-4-carbaldehyde [65] .



R=H,CH_3,OCH_3,Cl,F,Br

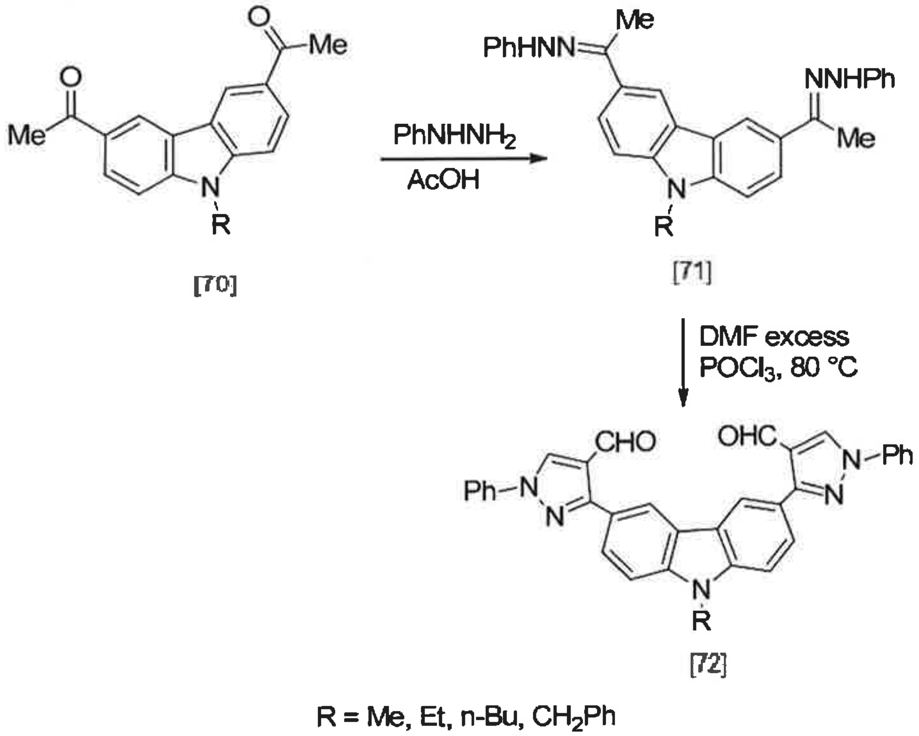
[64] [65]

Condensation of acetylferrocene [66] and phenyl hydrazine [67] then intramolecular cyclization of the intermediate hydrazone [68] under Vilsmeier-Haack conditions to produce 1*H*-3-ferrocenyl-1-phenyl pyrazole-4- carboxaldehyde [69] were reported by Damljanovic et al.(68)



[66] [67] [68] [69]

Ramu, and Rajagopal (69) have reported the synthesis of 3,6-di(pyrazol-4-yl) carbazoles [72]. The reaction of the Vilsmeier reagent with hydrazones of diacetylcarbazoles [71] yielded the corresponding pyrazole dicarbaldehydes [72] in good yields.



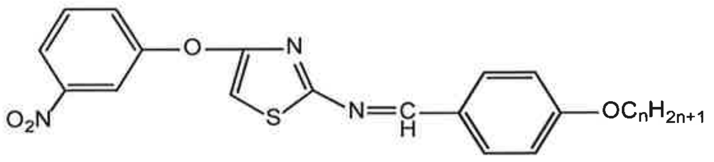
1.8. Liquid crystal compounds containing heterocyclic rings

Many liquid-crystalline substance containing heterocyclic units has been synthesized over many years. This research area has grown in recent years for substantial synthetic methodologies. When the thermotropic materials containing heterocyclic as core units, this lead to importance to their ability to impart lateral and longitudinal dipoles combined with changes in the molecular shape. Moreover, presence heteroatoms may influence considerable changes in the liquid-crystalline phases as well as in the physical properties of the showed phases, this is because of the heteroatoms (S, O, and N) that are more polarizable than carbon.

Many researchers reported that five-membered heterocyclic display mesophases and the presence of a heteroatom can influence the mesomorphic behavior, due to the electronegativity difference presented in relation to carbon or through changes in geometry of compounds. The heterocyclic compounds are used due to their large dipolar moment. The five membered ring with disubstituted is not linear also this infulance of linearity, don't formed the mesophases. However, studied the relation between structural of five membered heterocyclics unity and liquid crystals properties (70).

In recent years the research synthesized liquid crystals that have heterocyclic due the development new mesogenic compounds which has attracted their attention. There are many types of heterocyclic liquid crystals such as compounds containing 1,3,4-oxadiazole and 1,3,4-thiadiazole moiety. The later compounds were very useful in producing of stable thermotropic smectic and nematic phases than the 1,3,4-oxadiazole substance. Moreover, recently research have investigated the influence of length the alkoxy or alkyl chain , cores of mesogenic and hetero ring on liquid crystal behavior (71).

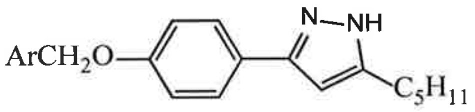
Murza et al. (72) prepared new liquid crystalline azomethines with thiazole moiety [73] showed nematic mesomorphism. The study showed the correlation between the geometric parameters and liquid crystalline properties.



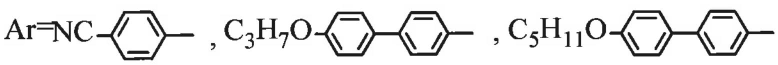
[73]

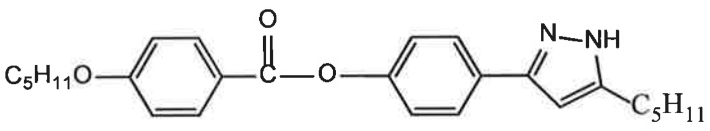
n=1-8

Also, U. Kauhanka and M. Kauhanka.(73) synthesized and reported new liquid crystalline for compounds 3-aryl-5-alkyl-1H-pyrazoles with ether [74] and ester[75]. They also discussed the influences of core heterocycle type and bridging group on the mesomorphic properties for the synthesized compounds.



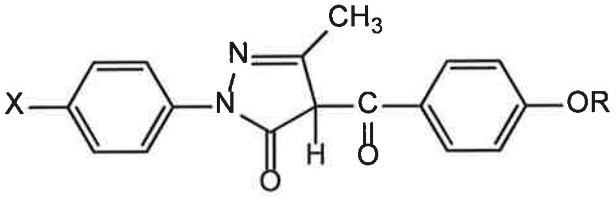
[74]





[75]

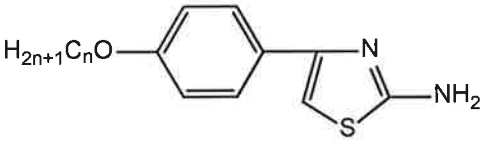
Thaker, et al.(74) synthesized and studied liquid crystalline properties of two new homologous series of calamitic liquid crystals containing a substituted pyrazole ring 4-(4-n-alkoxybenzoyl)-5-methyl-2-(phenyl or 4- methyl phenyl) -2,4- dihydro -3H- pyrazole -3-one [76]. Both series show liquid crystalline properties from the heptyl homologue. Middle members of Series-A and Series-B exhibit nemetogenic behavior while higher homologues exhibit smectogenic behavior only (75).



[76]

Where, X= H or CH_3; R= C_nH_{2n+1}, n = 2 to 8, 10, 12, 14, 16, 18

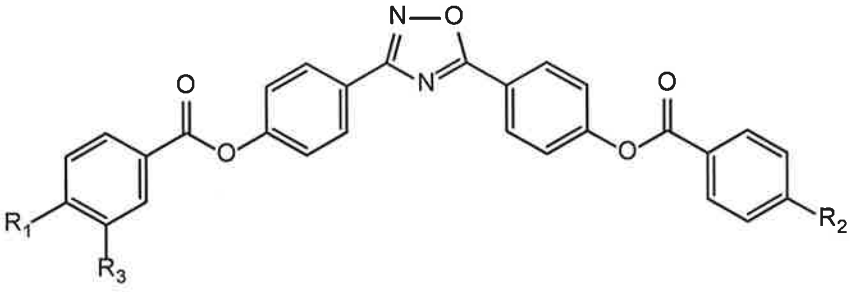
Karam, et al. (76) synthesized amino compounds with 1,3-thiazole $[73]_n$. All compounds $[77]_n$ displayed enantiotropic mesomorphism. The compounds$[77]_n$ (when n=1-5 $_n$) display enantiotropic nemetic mesophase while the compounds of series $[77]_n$ (when n=6-8) displayed an anantiotropic smectic C and nematic phases.



[77]

n=1-8

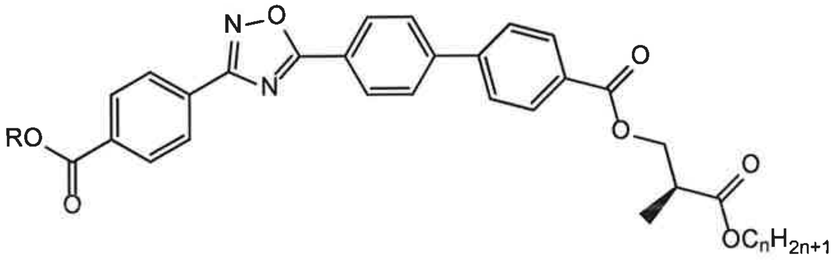
Shanker et al.(75) synthesized and studied liquid crystalline properties for compounds containing 1,2,4 –oxadiazole ring [78], these compounds showed the nematic phase.



[78]

$R^1 = C_4H_9, C_5H_{11}, C_6H_{13}$
$R^2 = OC_6H_{13}$, $R^3 = H$

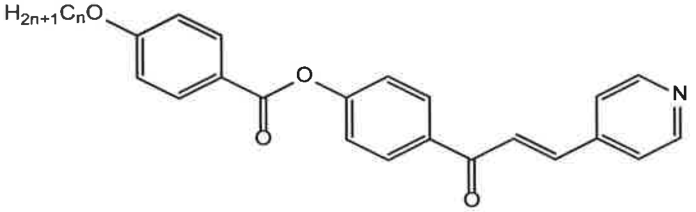
Also, Subrao et al. (77) synthesized and studied liquid crystalline properties for compounds containing 1,2,4 –oxadiazole ring [79]. These compounds showed the semactic SmA phase only when $R=PhCH_2$ but showed SmA and SmC* phases when $R=C_{12}H_{25}$.



[79]

$R=PhCH_2, C_{12}H_{25}$
n=8,9,10,12

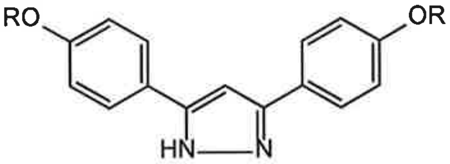
Lim et al. (78) synthesized compounds containing pyridyl ring[80]. The decyloxy compound not displayed LC, but *n*-dodecyloxy to *n*-hexadecyloxy compounds showed Sm A phase.



[80]

n≥ 12

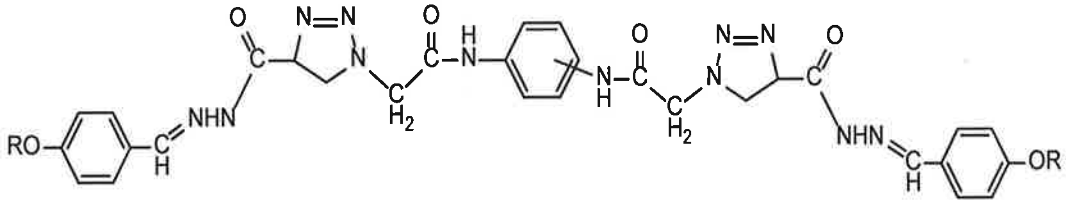
Al-Karawi, et al.(79) synthesized and studied mesomorphism behavior of pyrazoles compounds 3,5-bis[4-(n-alkoxy)phenyl]-1H-pyrazole (where, n-alkoxy: $O(CH_2)_nH$, n = 6,7,8,9 or 10)[81]. The studies showed that all of these compounds of the pyrazole derivatives are liquid crystal materials.



[81]

$R=C_nH_{2n+1}$ n=6,7,8,9,10

In addition synthesis and investigation of liquid crystalline, properties for 1,2,3-triazolederivatives [82] via cycloaddition reaction derived from 3-phenylenediamine or 4-phenylenediamine (80).

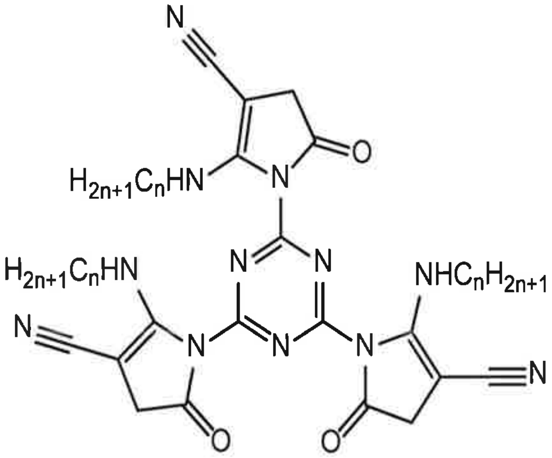


[82]

$R=C_nH_{2n+1}$

n=1,2,3,5,6,7,8

Recently, Karam et al.(81) synthesized and investigated the mesomorphic properties for new series of triazine-core[83]. The formation of mesomorphic properties was found to be dependent on the number of methylene unit in alkyl side chains.



[83]

n=3,4,5,6,7,8

The aim of the work

This work including the synthesis, structural characterisation and studying of liquid crystal behaviour for two series containing pyrazole ring. This contains:

-Synthesis and characterization of new compounds containing pyrazole ring derived from 1,4-phenilinediamine and benzidine compounds.

- Study the effect of heterocyclic on the liquid crystal behavior of synthesis derivatives.

- Study the effect of rigid core, imine linkage and alkoxy as a terminal group in synthesized derivatives on the liquid crystal behaviors.

Chapter Two

Experimental Part

2. Chemicals and techniques

2.1 Chemicals

The chemicals and solvents used in present work and supplies companies are listed in Table (2-1).

Table(2-1) Chemicals used in this work and their suppliers

Company supplied	**compound**	**Purity %**
Aldrich	Benzidine	98
	1-Bromo (ethane,propane,pentane ,hexane,heptane ,octane)	99
	chloro acetic acid	99
	Ethyl acetate	90
	Hydrazine hydrate	80
	1-Iodo methane	99.5
	Iodine	99.9
	4-phenlenedi amine	99.9
	Phosphorus oxychloride ($POCl_3$)	99
	Sodium acetate	99.9
BDH	N,N-Dimethylformamide (DMF)	99
	4-Hydroxy acetophenone	99
Fluka	Acetone	99.5
	Methanol	99.9

GPR	Anhydrous potassium carbonate	99
Merck	Diethyl Ether	99.5
	Dimethyl sulphoxide (DMSO)	99
	glacial acetic acid	98
	Sodium bicarbonate	98
Riedel–deHean	Benzene	99.5
	Hydrochloric acid	37
	Sulfuric acid	98
Scharlau	Absolute ethanol	99.9

2.2. Techniques

2.2.1.Spectroscopy

a) Fourier transform infra-red spectrophotometer (FTIR)

The spectra of FTIR were measurement using SHIMADAZU (IR Affinity-1) FTIR spectroscopy at College of Education for Pure Science (Ibn-Al-Haitham), University of Baghdad; and to FTIR-600 spectrometer, (UK) at College of Education for pure Science (Ibn- Al-Haitham)\ Central Service Laboratory, University of Baghdad.

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

^{1}HNMR spectra were measurement using Ultra Shield 300 MHz, Bruker, Switzerland, at University of Tehran, Center Lab (Islamic Republic of Iran). The measurement were in ppm(δ), DMSO as a solvent and TMS as internal standard.

c) Mass spectroscopy:

The mass spectral of measurement were done using: Agilent Technology(HP). MS model:5973Network Mass Selective Detector. Ion source electron Impact (El) was 70ev. Ion source temperature was230^{o}C at University of Sanfati Sharif-Tehran /Iran.

2.2.2. Melting point measurements

Uncorrected melting points were determined using hot-stage, Gallen Kamp melting point apparatus.

2.2.3. Hot stage polarizing microscopy

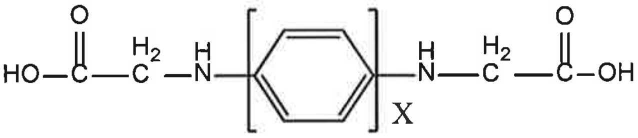
The texture as while as transition temperatures were recorded via polarized optical microscope model Leica DM2500 M, College of Education for Pure Science (Ibn-Al-Haitham)\ Central Service Laboratory, University of Baghdad.

2.2.4. Differential scanning calorametry (DSC)

The differential scanning calorametry DSC measurements were determined using STAPT-1000LINSIS, German origin, average heat rate 5^{o}C/minute, College of Education for Pure Science (Ibn-Al-Haitham)\ Central Service Laboratory, University of Baghdad.

2.3.Synthetic procedures

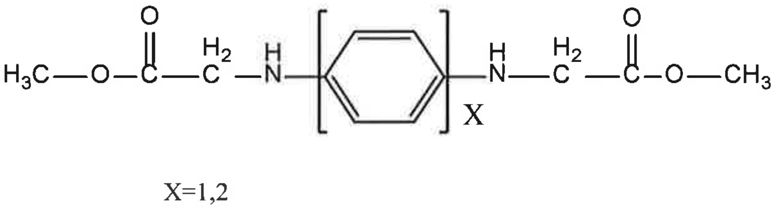
2.3.1. Preparation of 2,2'-(1,4-phenylene bis (azanediyl)) di acetic acid [I]$_a$ and 2,2'-([1,1'-biphenyl]-4,4'-diylbis(azanediyl))diacetic acid [I]$_b$(82)



[I]$_{a,b}$

A mixture of 1,4-phenylenediamine (0.108gm , 0.001 mol) or benzidine (0.184gm, 0.001mol), chloro acetic acid (0.188 gm ,0.002mol) with sodium acetate(0.16gm , 0.002mol) in ethanol(5mL) was prepared. The mixture was refluxed for 4 hrs. The mixture was then Cooled and ice water added. After the mixture was filtered and acidified using 10%HCl. After adding ethyl acetate, the organic layer was separated, dried and recrystallized. The nomenclature, structural formula, molecular formula, yield, melting point and color of these compounds are listed in Table (2-2).

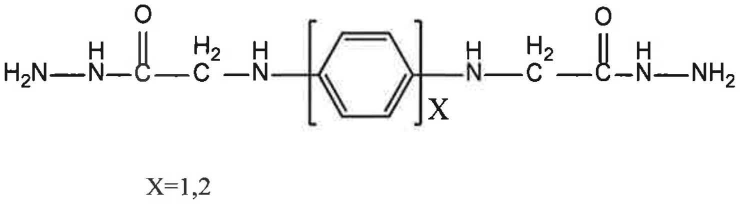
2.3.2. Preparation of di methyl 2,2'-(1,4-phenylene bis (azanediyl)) diacetate[II]$_a$ and di methyl 2,2'-([1,1'-bi phenyl]-4,4'-diyl bis (azanediyl)) di acetate[II]$_b$(83)



[II]$_{a,b}$

To 200 mL of absolute methanol 55.158gm (0.246mol) of compound [I]$_a$ or 73.8gm (0.246mol) of compound [I]$_b$ and (5.4mL) of Conc. H_2SO_4 wasadded. The mixture was refluxed for 6hrs, cooled then solution of sodium bicarbnate 5% was added. After that precipat was filtered then washed with water and ethanol was for recrystallized. The nomenclature, structural formula, molecular formula, yield, melting point and color are summarized in Table (2-2).

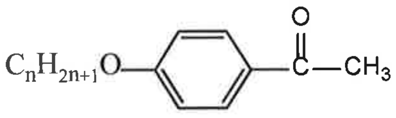
2.3.3. Synthesis 2,2'-(1,4-phenylene bis (azanediyl))di(acetohydrazide) [III]$_a$ and 2,2' -([1,1' – biphenyl] - 4,4' - diyl bis (azanediyl)) di (acetohydrazide) [III]$_b$(82)



[III]$_{a,b}$

To compound [II]$_a$ (1.5gm , 0.006mol) or compound [II]$_b$ (1.97gm , 0.006mol), 3mL of hydrazine hydrate (80%) and absolute ethanol 5mL were added. The mixture was refluxed for 3hrs and left to cool at room temperature; then dried and recrystallized by ethanol. The nomenclature,structural formula, molecular formula, yield, melting point and color of these compound are summarized in Table(2-2).

2.3.4.General procedure of prepared 4-n-alkoxyacetophenone[IV]$_n$ (78)

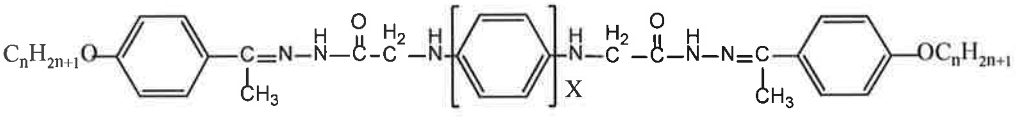


n=1,2,3,5,6,7,8

[IV]$_n$

A mixture of 4-hydroxyacetophenone (0.204gm , 0.0015mol) and anhydrous potassium carbonate (0.8gm , 0.012mol) was dissolved in 20mL of acetone. After that, n-alkylbromide (0.004mol) was added and the mixture was refluxed overnight. After word, the mixture was poured onto ice water. The mixture was extracted by ethyl acetate and the organic phase was removed after that and evaporated to yield 4-n-alkoxyacetophenone. The nomenclature, structural formula, molecular formula, yield, melting point and color of these compounds are listed in Table (2-3).

2.3.5.Synthesis of 2,2'-(1,4-phenylenebis(azanediyl))bis(N'-(1-(4-alkoxyphenyl)ethylidene)acetohydrazide)[V-XI]$_a$ and 2,2'-([1,1'-bi phenyl]-4,4'-diyl bis (azanediyl)) bis (N'-((E)-1-(4-alkoxyphenyl) ethylidene) acetohydrazide) [V-XI]$_b$



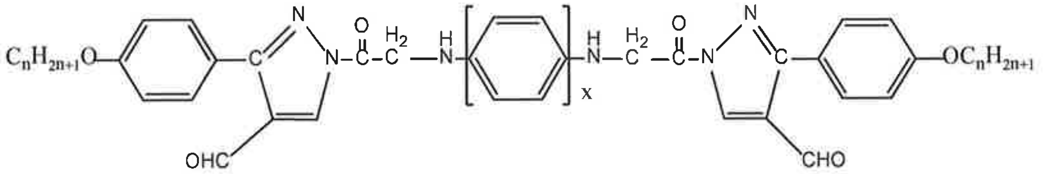
X=1,2

n=1,2,3,5,6,7,8

[V-XI]$_{a,b}$

Acid hydrazide $[III]_a$ or $[III]_b$ (0.001mol),4-alkoxy acetophenone $[IV]_n$ (0.002mol), 5mL of absolute ethanol and some drops from glacial acetic acid (GAA) were mixed. The solution was heated for 4-5hrs then cooled after that filtered and recrystallized from ethanol to give the compounds $[V\text{-}XI]_a$ and $[V\text{-}XI]_b$. The nomenclature, structural formula, molecular formula, yield, melting point and color for derivatives $[V\text{-}XI]_a$, $[V\text{-}XI]_b$ summarized in Table (2-4) and (2-5), respectively.

2.3.6. Synthesis of 1,1'-(2,2'-(1,4-phenylene bis (azanediyl)) bis (acetyl)) bis (3-(4-alkoxyphenyl)-1H-pyrazole-4-carbaldehyde) $[XII\text{-}XVIII]_a$ and 1,1'-(2,2'-([1,1'-biphenyl]-4,4'-diyl bis (azanediyl)) bis (acetyl)) bis (3-(4-ethoxyphenyl)-1H-pyrazole-4-carbaldehyde) $[XII\text{-}XVIII]_b$



X=1,2

n=1,2,3,5,6,7,8

$[XII\text{-}XVIII]_{a,b}$

The derivatives $[V\text{-}XI]_a$ or $[V\text{-}XI]_b$ (0.01mole) were added to a mixture of Vilsmeier-Haack reagent (prepared by drop wise addition of 6mL of phosphorus oxychloride $POCl_3$ and 50mL of dimethyl formamid DMF in ice cooled). The reaction mixture was refluxed for 6 hrs. After that the mixture was cooled and poured onto ice cold water. Following, the solution was neutralized using sodium bicarbonate than was filtered to obtained the products. The nomenclature, structural formula, molecular formula, yield, melting point and color for derivatives$[XII\text{-}XVIII]_a$, $[XII\text{-}XVIII]_b$ were summarized in Tables (2-6) and(2-7), respectively.

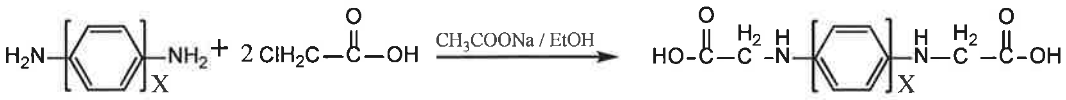
Chapter Three

Results & Discussion

3. Results and discussion

3.1. Preparation and characterization of 2,2'-(1,4-phenylene bis (azanediyl))diacetic acid[I]$_a$ and 2,2'-([1,1'-biphenyl]-4,4'-diyl bis (azanediyl))diacetic acid [I]$_b$

The substances [I]$_{a,b}$ prepared via the reaction of 1,4-phenylenediamine or benzidine and two moles of chloro acetic acid in ethanol and sodium acetate.


X=1,2

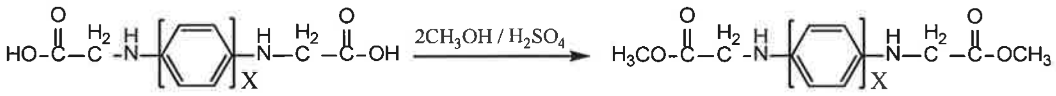
[I]$_{a,b}$

The compounds [I]$_{a,b}$ were characterized using melting points measurements and FTIR spectroscopy.

The spectra of FTIR for compounds [I]$_a$ and [I]$_b$ showed disappearance of stretching bands of NH_2 groups of starting materials and showed absorption of stretching bands at 3404-2596 cm^{-1} , 3363-2590 cm^{-1} of OH groups,3404 cm^{-1} (interference with OH group),3186 cm^{-1} for NH groups in addition to C=O (carboxylic groups) at (1728) cm^{-1} , (1712) cm^{-1} , respectively. Figures (3-1) and (3-2) show the data of FTIR spectra for [I]$_a$ and [I]$_b$ respectively.

3.2. Preparation and Characterization of di methyl 2,2'-(1,4-phenylene bis (azanediyl)) diacetate[II]$_a$ di methyl 2,2'-([1,1'-bi phenyl]-4,4'-diyl bis (azanediyl)) di acetate[II]$_b$

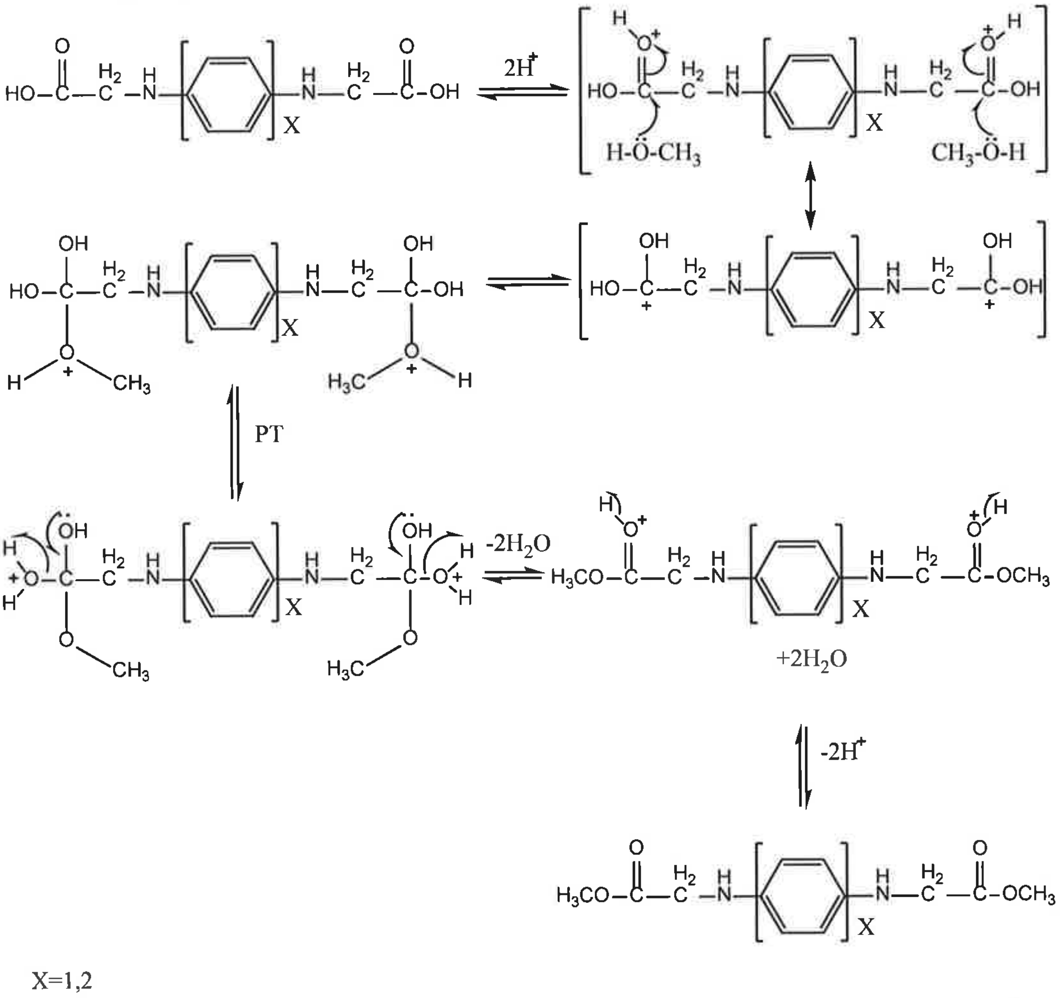
The reaction of compound [I]$_a$ or [I]$_b$ and two moles of methanol with H_2SO_4 produced substance [II]$_a$ or [II]$_b$


[I]$_{a,b}$

[II]$_{a,b}$

X=1,2

The mechanism(84) for synthesize of these compounds is shown Scheme (3-1) below:

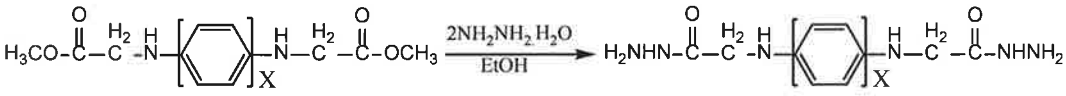


Scheme(3-1): The mechanism for synthesized $[II]_{a,b}$

Compounds $[II]_{a,b}$ identified via melting points and FTIR spectroscopy. The data spectral of FTIR displayed disappearance of stretching band of C=O and OH groups for carboxylic acid$[I]_{a,b}$. They also showed bands at (1735)cm^{-1}, (1728) cm^{-1} for C=O (ester groups) and C-O groups at (1253)cm^{-1}, (1261)cm^{-1}, respectively. Figures (3-3) , (3-4) show FTIR spectra for substances $[II]_a$ and $[II]_b$,respectively .

3.3. Synthesis and Characterization of 2,2'-(1,4-phenylene bis (azanediyl)) di (acetohydrazide) [III]$_a$ and 2,2'-([1,1'-biphenyl]-4,4'-diyl bis (azanediyl)) di (acetohydrazide) [III]$_b$

The derivatives [III]$_{a,b}$ synthesized by the reaction of [II]$_a$ or [II]$_b$ with two moles of hydrazine hydrate (80%) and ethanol .


[II]$_{a,b}$ [III]$_{a,b}$

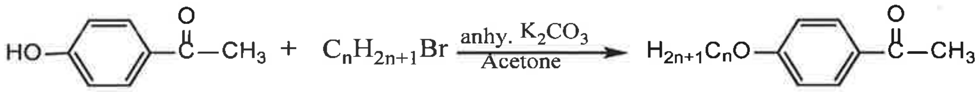
X=1,2

The acid hydrazide compounds [III]$_{a,b}$ identified via melting points and FTIR spectroscopy .

The spectra of FTIR of [III]$_{a,b}$ displayed disappearance of stretching band of C=O for ester groups for compounds [II]$_{a,b}$ and appearance of asymmetric and symmetric bands for NH_2 and NH groups in (3311-3197)cm^{-1}, (3332-3180)cm^{-1} and bands at (1662)cm^{-1} , (1664) cm^{-1} to C=O (amide groups), respectively. Figures (3-5) and (3-6) show FTIR spectra for compounds [III]$_a$ and [III]$_b$, respectively.

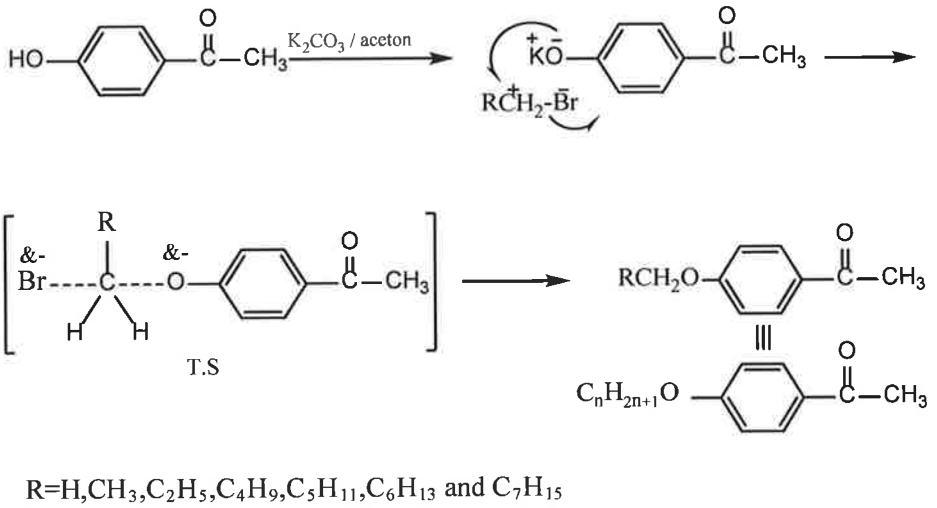
3.4. Preparation and characterization 4-n-alkoxyacetophenone [IV]$_n$$^{(85)}$

The compounds [IV]$_n$ were preparation from the reaction of 4-hydroxyacetophenone with n-alkylbromide and anhydrous potassium carbonate in acetone.


[IV]$_n$

n= 1,2,3,5,6,7,8

The mechanism(85) for synthesized compounds is illustrated in Scheme (3-2) below:



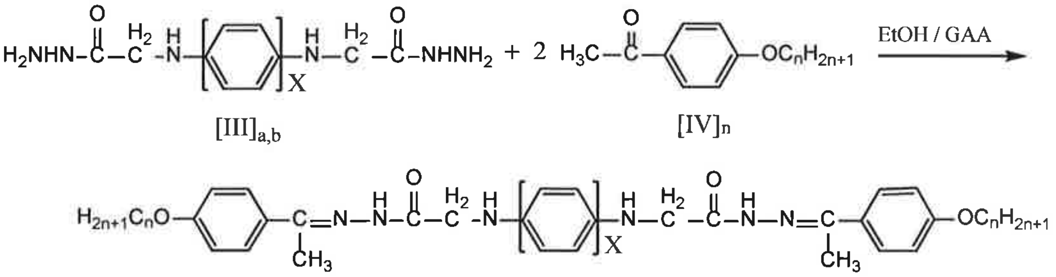
$R=H, CH_3, C_2H_5, C_4H_9, C_5H_{11}, C_6H_{13}$ and C_7H_{15}

Scheme (3-2): The mechanism for synthesized compounds $[IV]_n$

The compounds $[IV]_n$ were characterized using FTIR spectroscopy . The FTIR spectra for these compounds showed the disappearance of a absorption stretching band of OH group of 4-hydroxyacetophenone and the appearance absorption stretching bands of C-O groups of 4-n-alkoxyacetophenone $[IV]_n$ in the region (1225-1259) cm^{-1}. The data of FTIR for [IV]n were summarized in Table (3-1), Figures (3- 7) and (3-8). The FTIR spectra for compounds $[IV]_5$ and $[IV]_7$, respectively.

3.5. Synthesis and characterization of 2,2'-(1,4-phenylene bis (azanediyl)) bis (N'-(1-(4-n-alkoxyphenyl)ethylidene) acetohydrazide) $[V\text{-}XI]_a$ and 2,2'-([1,1'-bi phenyl]-4,4'-diyl bis (azanediyl)) bis (N'-((E)-1-(4-n-alkoxyphenyl) ethylidene) acetohydrazide) $[V\text{-}XI]_b$

The Schiff bases compounds $[V\text{-}XI]_a$ and $[V\text{-}XI]_b$ were synthesized from the reaction of acid hydrazide $[III]_a$ or $[III]_b$ and two moles of 4-n-alkoxyacetophenone$[IV]_n$ and some drops of glacial acetic acid (GAA) in solvent as ethanol.



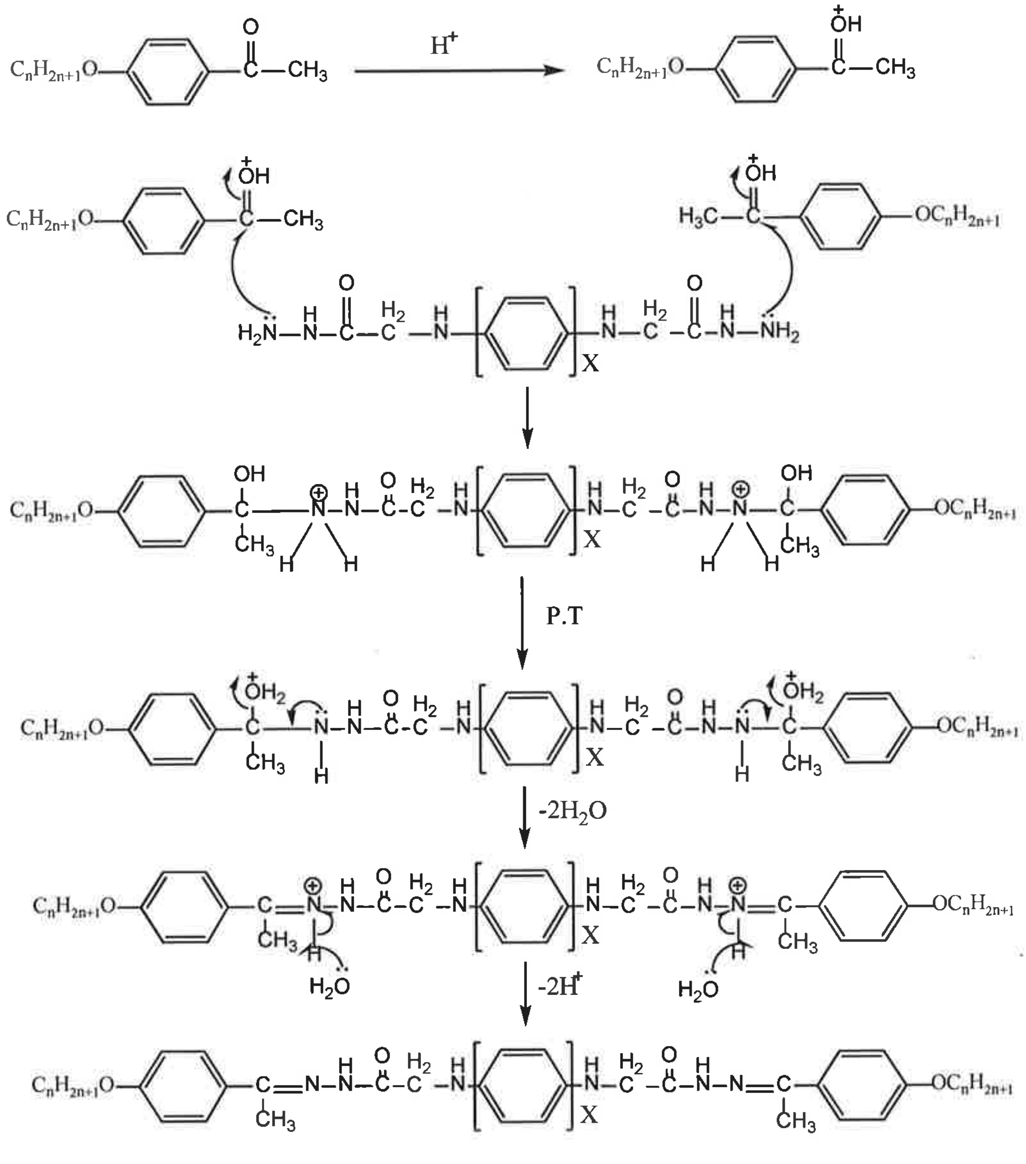
$[V\text{-}XI]_{a,b}$

X=1,2 n=1,2,3,5,6,7,8

compounds $[V\text{-}XI]_a$ when X=1

compounds $[V\text{-}XI]_b$ when X=2

The mechanism(86) for synthesized compounds is shown in Scheme (3-3) below:



X=1,2

n =1,2,3,5,6,7,8

Scheme (3-3) The mechanism for synthesized compounds $[V\text{-}XI]_{a,b}$

Synthesized derivative compounds were characterized these via FTIR and ^{1}HNMR spectroscopy.

The FTIR data for derivatives $[V\text{-}XI]_{a,b}$ displayed disappearance of stretching bands of NH_2 groups of $[III]_{a,b}$ and C=O(ketone) for 4-n-alkoxyacetophenone$[IV]_n$ and appear bands of (C=N) group in (1635-1610) cm^{-1} and (1630-1620) cm^{-1} ,respectively. Also, appear bands of NH groups in (3390-3290) cm^{-1} and (3373-3310) cm^{-1} ,respectively. Also showed stretching bands of carbonyl groups (C=O amid) in the region (1670-1660) cm^{-1} and (1674-1664) cm^{-1} ,respectively. Figures (3-9) ,(3-10) for compounds $[V]_a$, $[X]_a$ and Figures (3-11) ,(3-12) for compounds $[VII]_b$,$[VIII]_b$, respectively.

The values of FTIR of derivatives$[V\text{-}XI]_a$ and $[V\text{-}XI]_{a,b}$ are summarized in Tables (3-2) and (3-3) ,respectively.

The spctrum of ^{1}HNMR (in DMSO-d6) for $[VII]_a$ Figure (3-13) displayed a singlet signal at δ 10.33 ppm of two protons of NH of (-CO NH -)groups, a singlet signal at δ 9.80 ppm of two protons of NH of ($-NHCH_2-$) groups, signals at δ (7.84-6.84) ppm for twelve aromatic protons, signal at δ 3.99ppm for four protons of OCH_2 groups , signals at δ (3.51) ppm for protons of ($-CH_2-$) groups , a singlet signal at δ 2.28 ppm for six protons of two CH_3 groups and triplet signal at δ (1.76-0.85)ppm of six protons of two CH_3 groups($-CH_2\underline{CH_3}$).

The ^{1}HNMR (in DMSO-d6) for $[X]_a$ Figure (3-14) showed a singlet signal at δ 10.37 ppm of two protons of NH of (-CO NH -)groups, a singlet signal at δ 7.92 ppm of two protons of NH of ($-NHCH_2-$) groups, signals at δ (7.91-6.84) ppm for twelve aromatic protons, triplet signal at δ (4.06-4.04) ppm of four protons of ($-OCH_2-$) groups , signal at δ 3.72 ppm for four protons of ($-CH_2-$)of ($-NH\underline{CH_2}-$) groups, signals at region δ (1.70-1.11) ppm for twenty protons of ($-OCH_2\ \underline{(C_5H_{10})}CH_3$) groups ,a singlet signal at δ 2.47 ppm for six protons of two CH_3 groups and triplet signal at δ (0.88-0.86) ppm of six protons of two CH_3 ($-CH_2\underline{CH_3}$). 2.47

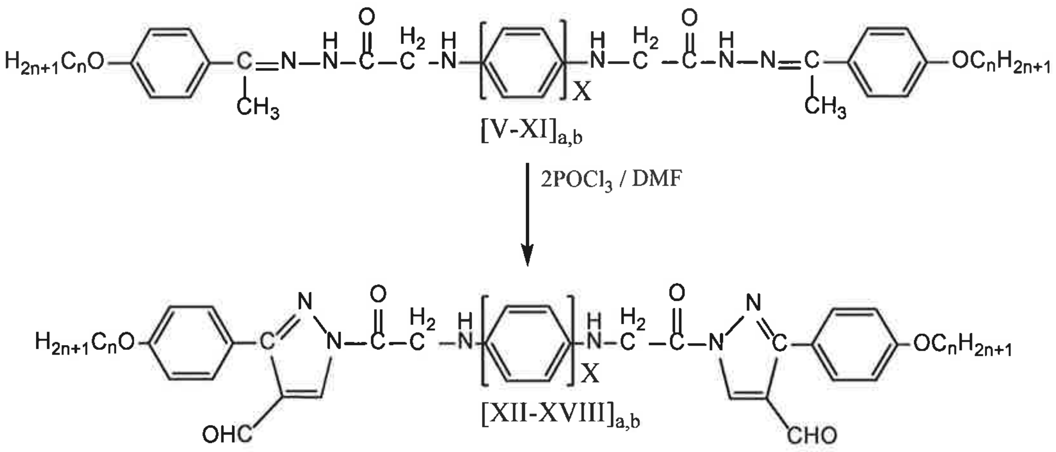
^{1}HNMR (in DMSO-d6) of $[XI]_a$, Figure (3-15), displayed a singlet signal at δ 10.37 ppm of two protons of NH of (-CO NH -), a singlet signal at δ 8.41 ppm for two protons of NH of (-NH$\underline{CH_2}$-), signals in δ (7.92-6.84) ppm for twelve aromatic protons, triplet signal at δ (4.06-4.03) ppm of four protons of (-OCH_2-) groups , signal at δ 3.75 ppm for four protons of (-CH_2-)of (-NH$\underline{CH_2}$-), signals at region δ (1.7-1.11) ppm for twenty four protons for (-OCH_2 (C_6H_{12})CH_3) groups ,a singlet signal at δ 2.54 ppm for six protons of two CH_3 groups and triplet signal at δ (0.88-0.85) ppm for six protons of two CH_3 groups(-$CH_2\underline{CH_3}$).

The ^{1}HNMR spectrum (in DMSO-d6) for $[VIII]_b$, Figure (3-16), displayed a singlet signal at δ 10.41 ppm of two protons of NH of (-CO NH -), a singlet signal at δ 7.70 ppm of two protons of NH of (-$NHCH_2$-), signals in δ (7.84-6.85) ppm of sixteen aromatic protons, signals at δ (4.05) ppm of four protons of (-O$\underline{CH_2}$-) groups , signal at δ 2.47ppm of four protons of (-CH_2-)of (-NH$\underline{CH_2}$-) groups, many signals at δ (2.27 -1.35) ppm of twelve protons of (-$OCH_2\underline{(CH_2)_3}$ CH_3), a singlet signal at δ 2.09 ppm for six protons for two CH_3 , signals at region δ (1.24 -0.90) ppm for six protons for (-$OCH_2(CH_2)_3$ $\underline{CH_3}$).

Mass spectrum for $[VII]_b$, Figure(3-17), showed many peaks may be to related the formation of compound $[VII]_b$.

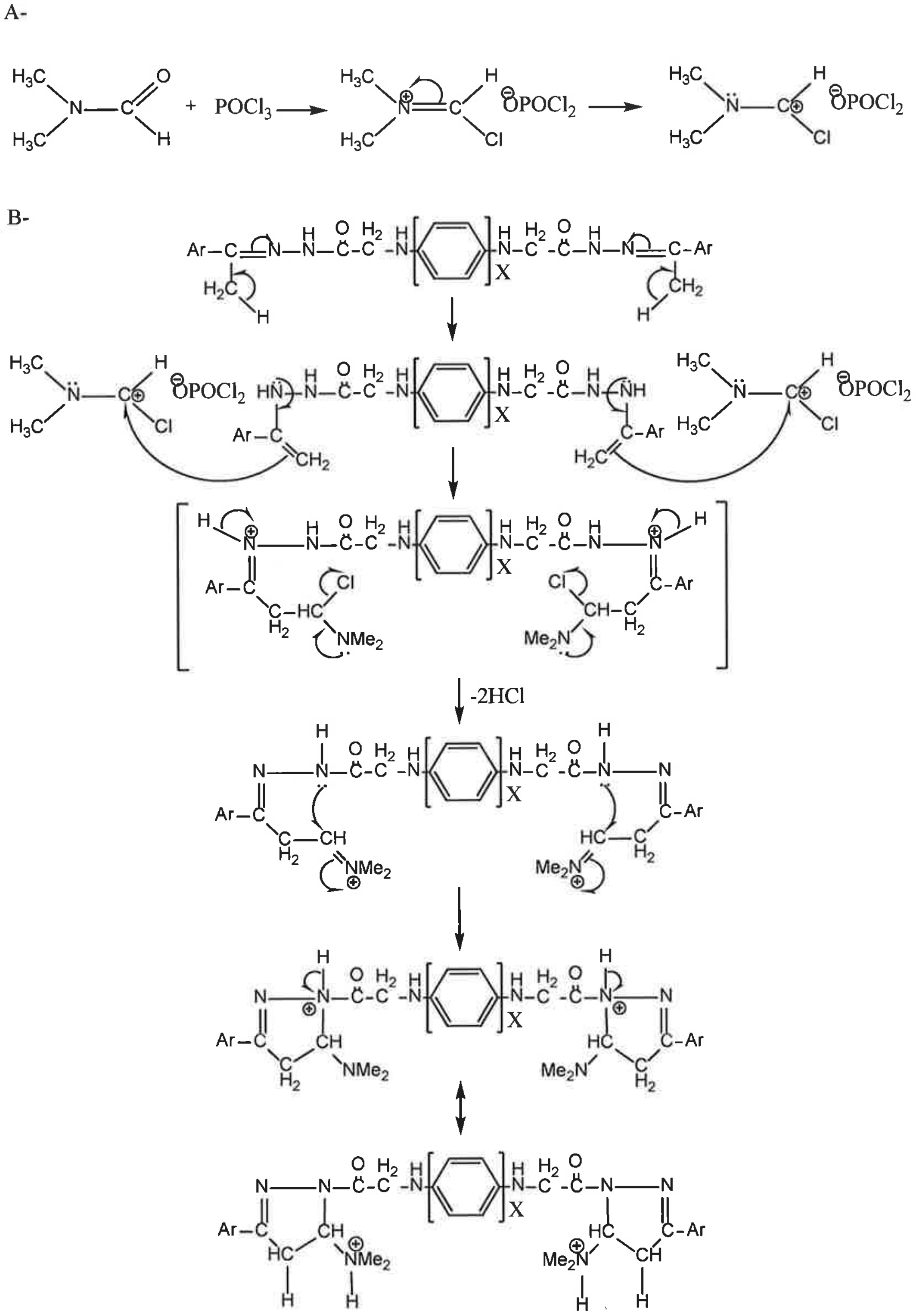
3.6. Synthesis and characterization of 1,1'-(2,2'-(1,4-phenylene bis (azanediyl)) bis (acetyl)) bis (3-(4-n-alkoxyphenyl)-1H-pyrazole-4-carbaldehyde) $[XII\text{-}XVIII]_a$ and 1,1'-(2,2'-([1,1'-biphenyl]-4,4'-diyl bis (azanediyl)) bis (acetyl)) bis (3-(4-n-alkoxyphenyl)-1H-pyrazole-4-carbaldehyde) $[XII\text{-}XVIII]_b$

Synthesized 4-formyl pyrazole derivatives $[XII\text{-}XVIII]_{a,b}$ via cyclisation substituted acetophenone hydrazones $[V\text{-}XI]_a$ or $[V\text{-}XI]_b$ with Vilsmeier-Haack reagent DMF/$POCl_3$

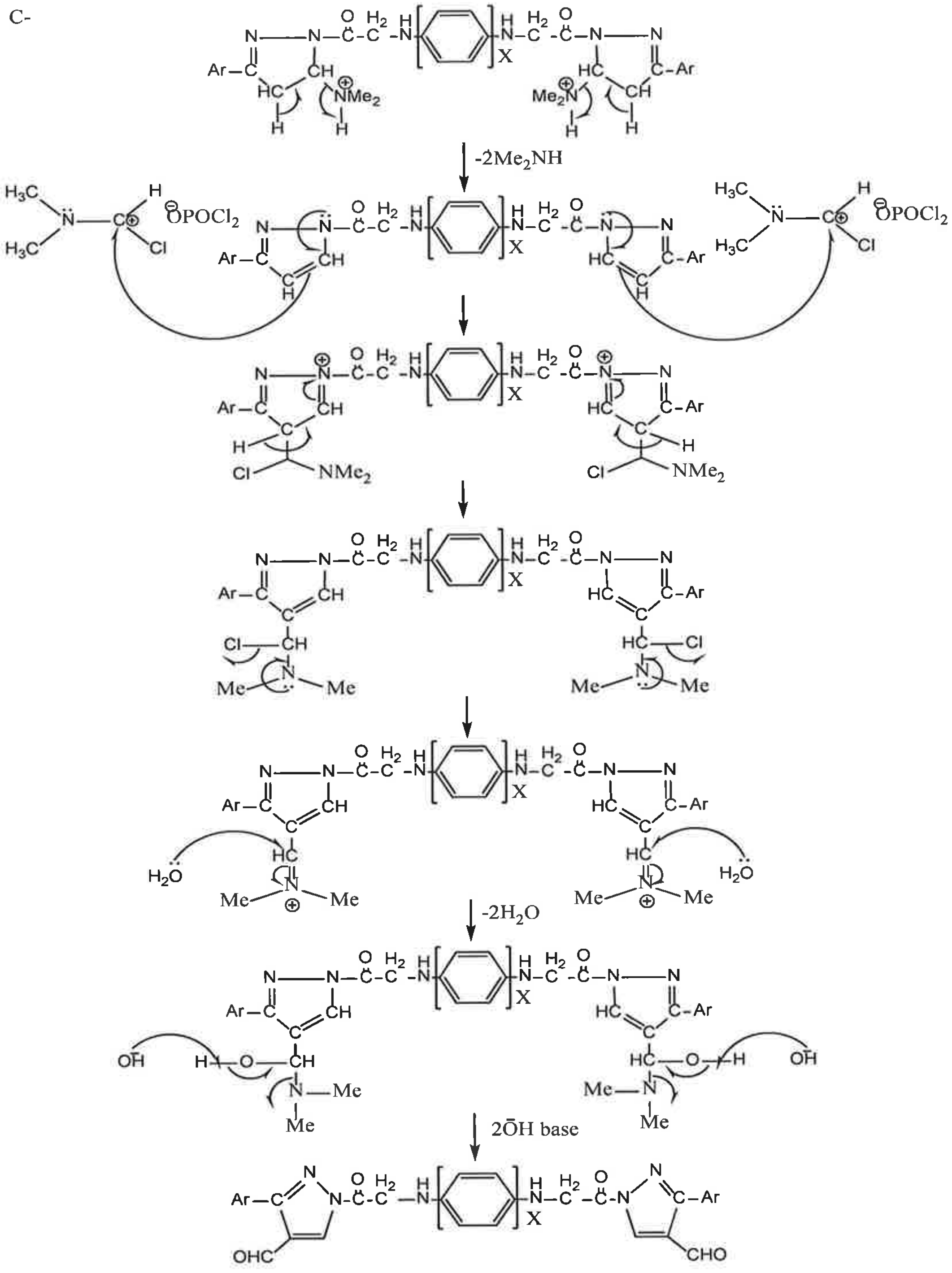


X=1,2 n=1,2,3,5,6,7,8

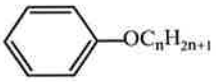
The Scheme(3-4) shows the mechanism reaction[87]



C-



X=1,2



n=1,2,3,5,6,7,8

Scheme (3-4): The mechanism for synthesized compounds[XII-XVIII]$_{a,b}$

The 4-formyl pyrazole derivatives [XII-XVIII]$_{a,b}$ were characterized via FTIR, ^{1}HNMR in addition to mass spectroscopy (for compound [XVI]$_a$) .

The data FTIR for these compounds showed disappearance of stretching bands of Schiff bases groups for starting materials [V-XI]$_{a,b}$ also appearance bands in region (1708-1674) cm^{-1} and (1695-1690) cm^{-1} assigned to C=O aldehyde groups and absorption bands at region (1649-1630) cm^{-1} and (1649-1630) cm^{-1} for C=N groups of pyrazole rings$^{(88)}$, respectively. This is a good evidence for cyclization of pyrazole ring. The FTIR data for [XII-XVIII]$_a$, [XII-XVIII]$_b$ were summarized in Tables (3-4) and (3-5) ,respectively. Figures (3-18),(3-19) for compounds [XII]$_a$, [XV]$_a$ and (3-20), (3-21) for compounds [XIII]$_b$, [XV]$_b$, respectively.

The ^{1}HNMR spectrum for [XII]$_a$ (in DMSO-d6), Figure (3-22), showed a singlet signal at δ 9.92 ppm of two protons for CH of (-CHO, a singlet signal at δ 8.63ppm of two protons NH for (-NH$\underline{CH_2}$-) , signals at δ (7.93-6.83) ppm of twelve aromatic protons and two protons of pyrazole rings$^{(89)}$. A singlet signal at δ 3.81 ppm for six protons of OCH_3 groups , a singlet signal at δ 2.93ppm for four protons of (-CH_2-) groups were also observed.

The ^{1}HNMR spectrum for [XV]$_a$ (in DMSO-d6), Figure (3-23), showed a singlet signal at δ 12.62 ppm for two protons NH for (-$NHCH_2$-), a singlet signal at δ 9.87 ppm for two protons of CH of (-CHO -) groups, signals at δ (8.07-6.77) ppm for twelve aromatic protons and two protons of pyrazole rings, triplat signal at δ (4.09-3.98) ppm of four protons for OCH_2, a singlet signal at δ 2.95ppm for four protons of (-CH_2-), signals at (1.7 -1.24) ppm for twelve protons of (-$\underline{CH_2}$-)$_3$ groups and triplet signal at δ (0.91-0.89)ppm of six protons of CH_3.

Mass spectrum for [XVI]$_a$, Figure(3-24), showed many peaks that can be to formed from pyrazol ring.

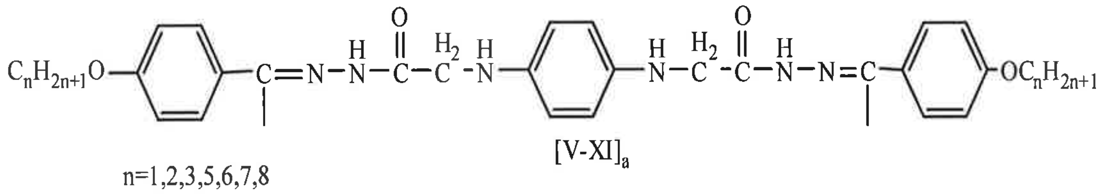
The ^{1}HNMR spectrum of [XIV]$_b$ (in DMSO-d6 as a solvent), Figure (3-25), appeared a singlet signal at δ 10.28 ppm of two protons for CH of (CHO), a singlet signal at δ 9.82ppm of two protons NH for ($-\underline{NH}CH_2-$), signals at δ (8.30-6.77) ppm of sixteen aromatic protons and two protons for pyrazole rings, triplat signal at δ (4.05-3.95) ppm of four protons of ($-O\underline{CH_2}-$) , a singlet signal at δ 2.95ppm of four protons for ($-\underline{CH_2}N-$), signals at (2.09 -1.72) ppm of four protons for ($-OCH_2\underline{CH_2}CH_3$) and triplet signal at δ (1.24-0.86)ppm of six protons of ($-OCH_2CH_2\underline{CH_3}$).

The ^{1}HNMR spectrum of [XVII]$_b$ (in DMSO-d6 as a solvent), Figure (3-26), displayed a singlet signal at δ 10.30 ppm of two protons of CH for(CHO), a singlet signal at δ 8.20ppm of two protons NH for ($-\underline{NH}CH_2-$) , signals at δ (7.92-6.84) ppm of sixteen aromatic protons and two protons for pyrazole rings, triplat signal at δ (4.08-3.98) ppm of four protons for($-O\underline{CH_2}-$) , a singlet signal at δ 3.12ppm of four protons for ($-N\underline{CH_2}-$), signals at (2.95 -1.23) ppm of twenty protons for ($-OCH_2\underline{(CH_2)}_5CH_3$) groups and triplet signal at δ(0.88-0.85)ppm of six protons of groups ($-OCH_2(CH_2)_5\underline{CH_3}$).

3.7. Liquid crystalline properties

The transition phase temperatures and mesophase type (texture identity) of all compounds were investigated by using hot-stage polarizing optical microscopy (POM) and by differential scanning calorimetry (DSC). Phase identification was made by comparing the observed textures with those reported in the literature(90,91).

3.7.1. The mesomorphic properties of Schiff bases [V-XI]$_a$



[V-XI]$_a$

The transition phase temperatures and phase assignment of series [V-XI]$_a$ are summarized in Table (3-6). The derivatives [V-VIII]$_a$ displayed enantiotropic nematic phase only as in Figures (3-27) and (3-28) for compounds[V]$_a$ and[VII]$_a$, respectively, the DSC thermogram for [V]$_a$ as in Figure (3-29). While the compounds [IX]$_a$ and [X]$_a$ showed enantiotropic dimorphism SmB phase besides to N phase as in Figures (3-30) of smectic B phase for compounds [IX]$_a$. The Figure (3-31)shows nematic texture for compound [X]$_a$. In addition, compound [XI]$_a$ showed enantiotropic smectic C phase and nematic phase as Figure (3-32) of textures smectic C phase for compound [XI]$_a$. The Schiff bases [V-VIII]$_a$ with n= 1-3,5 showed nematogenic behavior, while the compounds [IX-XI]$_a$ with n=6-8 exhibited dimorphism Smectic(Sm) and nematic(N).

Gray and Goodby (92) were explain this results in expression of ratio of terminal/lateral (t/l) interaction forces. If the ratio is high, the substances tend to show nematic phase, while , if the ratio is low the substance tend to display smectic phase.

A plot of the transition temperature against the number (n) of carbon atoms in the alkoxy chain for compounds $[V\text{-}XI]_a$ is shown in Figure (3-33). The geometry of the compounds$[V\text{-}XI]_a$ is shown in Figure (3-34).

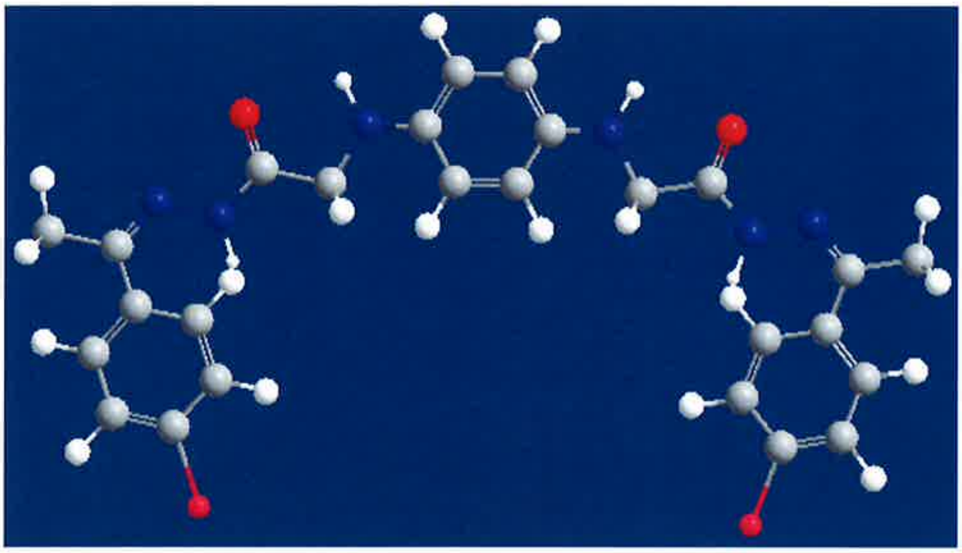
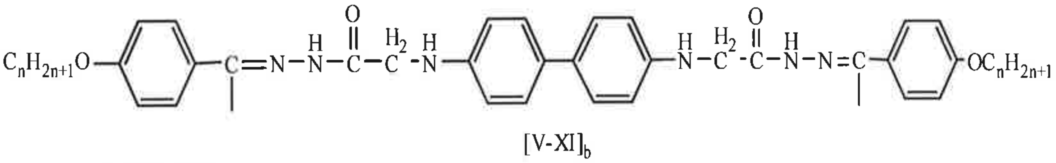


Figure (3-34): 3D structure of $[V\text{-}XI]_a$

3.7.2. The mesomorphic properties of Schiff bases [V-XI]$_b$



[V-XI]$_b$

n=1,2,3,5,6,7,8

The phase transition temperatures of Schiff bases [V-XI]$_b$ is summarized in Table (3-7). Compounds [V-VIII]$_b$ displayed enantiotropic nematic phase only as in Figure (3-35) for compound[VI]$_b$. The compound [IX]$_b$ showed enantiotropic dimorphism smectic A phase besides to nematic phase as Figure (3-36) for texture smectic A phase of compound [IX]$_b$. But the compound [X]$_b$ showed SmB phase only as in Figures (3-37) and (3-38) for texture of smectic B phase and DSC thermogram , respectively.. In addition to the compound [XI]$_b$ display SmA phase only as Figures(3-39) and (3-40) for texture of smectic A phase and DSC therrmogram, respectively. The geometry of these compounds is in Figure (3-41).

The transition temperature versus the number (n) of carbon atoms in the alkoxy chain for compounds [V-XI]$_b$ were plotted in Figure (3-42). The homologous series shows nematogenic and smectogenic behavior with good thermal stability when n=7,8.

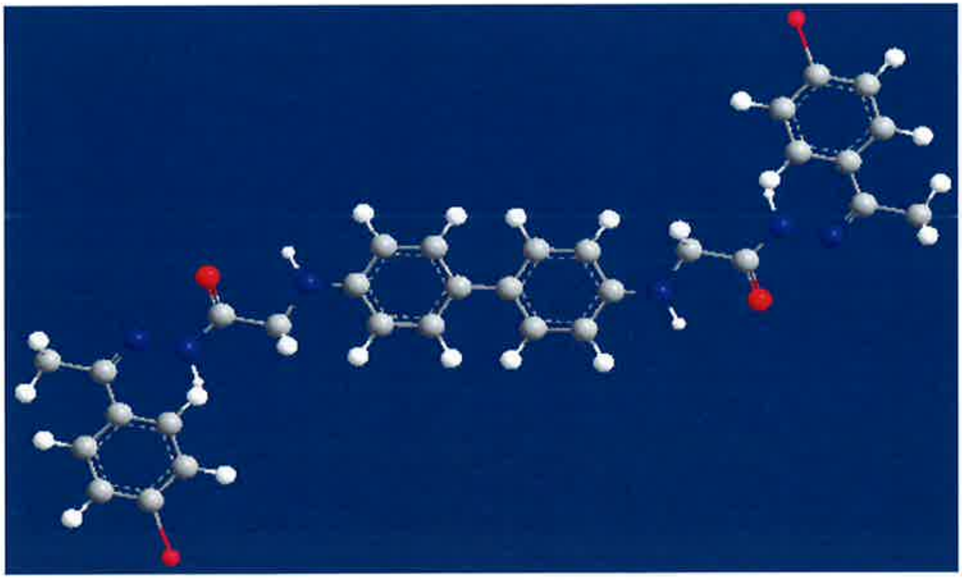
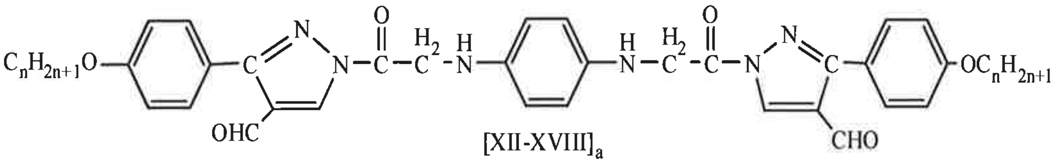


Figure (3-41) 3D structure for compounds [V-XI]$_b$

3.7.3. The mesomorphic properties of [XII-XVIII]$_a$



[XII-XVIII]$_a$

n=1,2,3,5,6,7,8

The phase transitions temperatures for compounds [XII-XVIII]$_a$ are summarized in Table (3-8).

The derivatives [XII-XV]$_a$ did not reveal any liquid crystalline behavior but simpl changes from the solid crystalline state to the isotropic liquid.

The compounds [XVI-XVIII]$_a$ gave enantiotropic nematic phases only, as shown Figures (3-43),(3-44) and (3-45),respactivaly. The geometry of the compounds [XII-XVIII]$_a$ is in Figure (3-46).

The transition temperature versus the number (n) of carbon atoms in the alkoxy chain for compounds [XII-XVIII]$_a$ were plotted, in Figure (3-47). The regular odd-even effect of both the crysral to nematic and nematic to isotropic transition can be clearly seen in this Figure. The homologous series shows nematogenic behavior with good thermal stability when n=6.

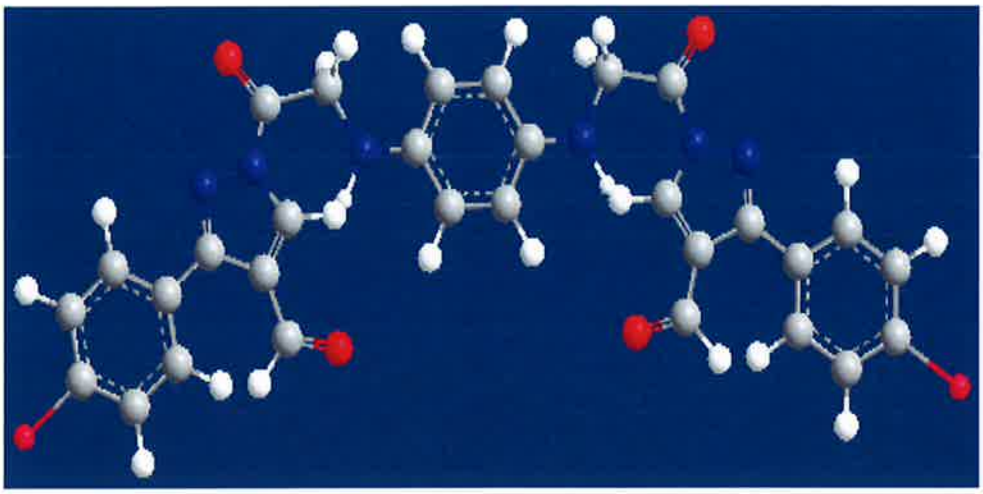
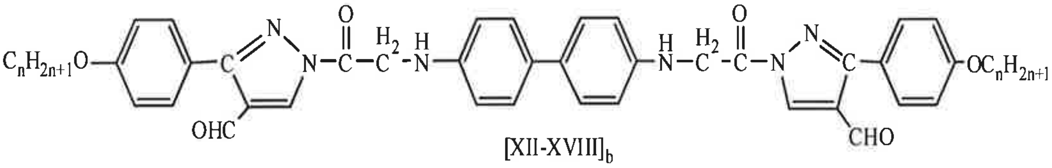


Figure (3-46) Three dimensional structure for derivatives [XII-XVIII]$_a$

3.7.4. The mesomorphic properties of [XII-XVIII]$_b$



n=1,2,3,5,6,7,8

The phase transition temperatures of compounds [XII-XVIII]$_b$ were summarized in Table (3-9). The compound [XII]$_b$ did not show any liquid crystalline behavior, but simple changes from the solid crystalline state to the isotropic liquid. On the other hand, the compounds [XIII-XVIII]$_b$ showed enantiotropic dimorphism SmB phase besides to N phase as in Figure (3-48) for texture of smectic B phase of compound [XIV]$_b$. The nematic phase texture for compound [XVI]$_b$ is shown in Figure (3-49). In addition to Figure (3-50) for nematic phase for compound [XVIII]$_b$. The geometry of the compounds [XII-XVIII]$_b$ is shown in Figure (3-51).

The transition temperature versus the number (n) of carbon atoms in the alkoxy chain for compounds [XII-XVIII]$_b$ were plotted in Figure (3-52). The odd-even effect of the crysral to smectic B, smectic B to mematic and nematic to isotropic transition can be clearly seen in this Figure when the n=5-8.

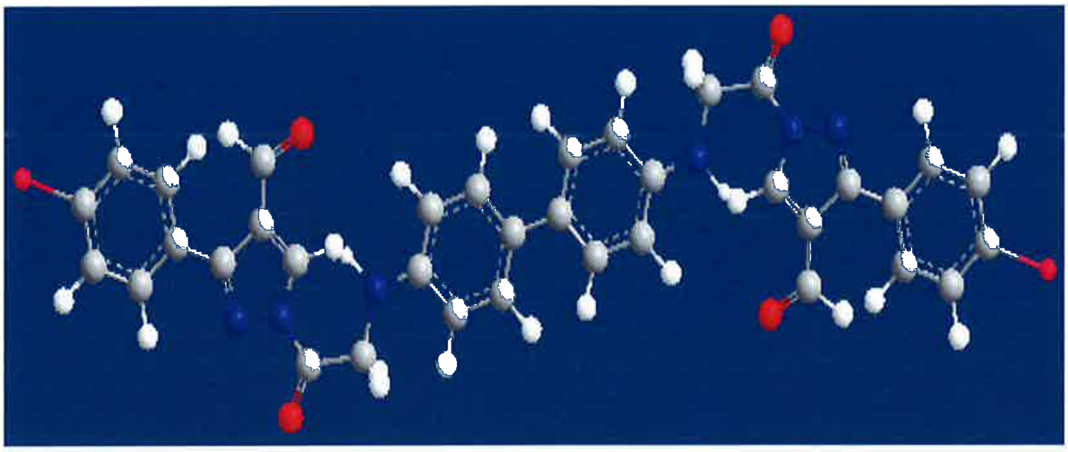
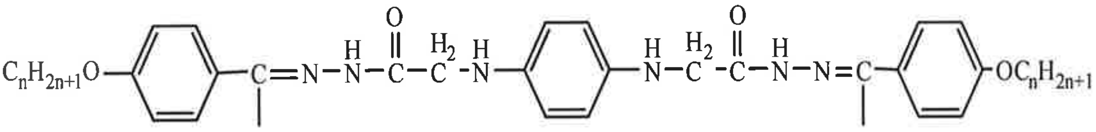


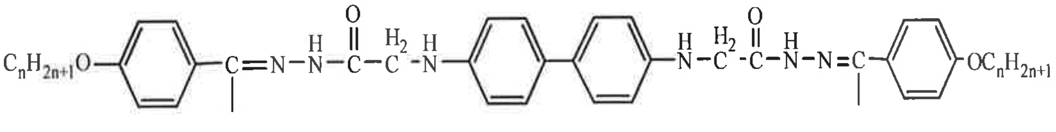
Figure (3-51) 3D structure for derivatives [XII-XVIII]$_b$

In this study, comparison between the homologous series $[V\text{-}XI]_a$ and series $[V\text{-}XI]_b$ revealed many findings.



$[V\text{-}XI]_a$

n=1,2,3,5,6,7,8

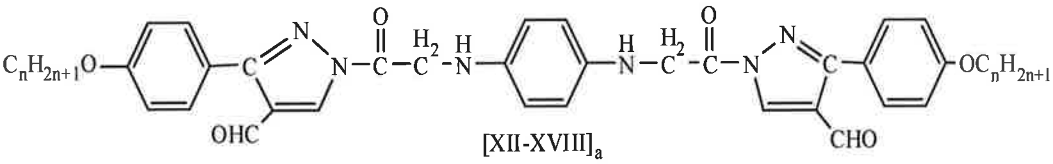


$[V\text{-}XI]_b$

n=1,2,3,5,6,7,8

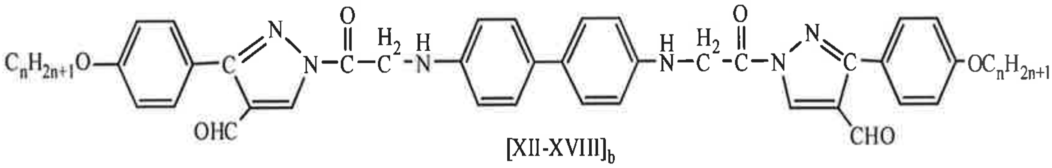
We found that both of the homologous series $[V\text{-}XI]_{a,b}$ showed different types of nematogenic and smectogenic behavior in addition to the series $[V\text{-}XI]_a$ which gave mesomorphic transitions N-I at lower temperatures than series $[V\text{-}XI]_b$.

Also, when compared between the homologous series $[XII\text{-}XVIII]_a$ and series $[XII\text{-}XVIII]_b$.



$[XII\text{-}XVIII]_a$

n=1,2,3,5,6,7,8



$[XII\text{-}XVIII]_b$

n=1,2,3,5,6,7,8

The compounds[XII]$_{a,b}$ didn't show any liquid crystalline behavior, but simply changes from the solid crystalline state to the isotropic liquid this result may be attributed to the shorter of alkoxy chain (when n=1). In addition, the compounds [XIII-XV]$_{a}$ showed no liquid crystalline behavior while the homologous series [XIII-XV]$_{b}$ gave enantiotropic nematic phase for compound [XIII]$_{b}$ and enantiotropic nematogenic and smectogenic behavior for compounds [XIV]$_{b}$,[XV]$_{b}$.

The compounds [XVI-XVIII]$_{a}$ showed only enantiotropic nematogenic behavior but the compounds[XVI-XVIII]$_{b}$ showed enantiotropic dimorphism SmB phase in addition to N phase. The above structures of derivatives[V-XI]$_{a,b}$ and the derivatives [XII-XVIII]$_{a,b}$ appear that have the same structure but different in rigid core, the compounds [V-XI]$_{a}$ and [XII-XVIII]$_{a}$ containing phenyl core but the compounds [V-XI]$_{b}$ and [XII-XVIII]$_{b}$ containing biphenyl core. The biphenyl system is fairly rigid and if the individual biphenyl rings are near planer, conjugative interactions in the molecule will be enhanced$^{(93)}$.

Thus the monophenyl compounds [V-XI]$_{a}$ and [XII-XVIII]$_{a}$ gave mesomorphic transitions N-I at lower temperatures in comparison with the homologues containing two aromatic rings compounds[V-XI]$_{b}$ and [XII-XVIII]$_{b}$,respactivaly. It means that the increasing of the aromatic rings on the core structures of a liquid crystal compounds can largely effect on the transition temperature of that particular compounds$^{(94)}$.

Conclusions

According to the obtained result from this study, the following conclusions can be drawn:

1- Synthesis of new pyrazole derivatives derived from 1,4-phenylenediamine or benzdine. The FTIR, ^{1}HNMR, and mass data gave a good evidence for the formation derivatives.

2- Studying the liquid crystalline behaviors of synthesized derivatives gave:

a) Schiff bases $[\text{V-XI}]_{a,b}$ with different alkoxy terminal groups which showed different types of mesomorphic phases. This behavior may by related to geometry of structure and interaction forces in compounds.

b) The compounds containing pyrazole ring $[\text{XII-XV}]_a$ did not display liquid crystal behavior, but the compounds $[\text{XVI-XVIII}]_a$ exhibit enantiotropic nematic phases. Also, derivatives $[\text{XII}]_b$ showed no liquid crystalline behavior, but the compounds $[\text{XIII-XVIII}]_b$ showed mesomorphases behavior smectic B phase besides nematic phase and study the influence of the terminal groups in addition to the geometry of the molecules on mesophases properties.

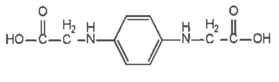
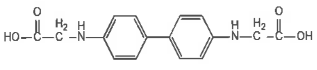
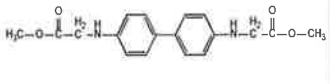
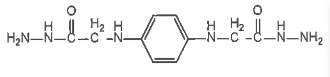
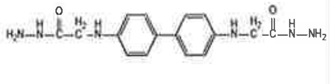
Suggestion for future work

1. Synthesis and determine the liquid crystalline properties of new pyrazole derivatives derived from 1,2-phenylenediamine or 1,3-phenylenediamine

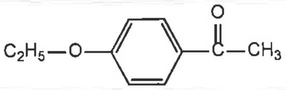
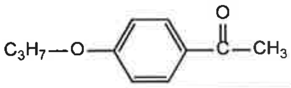
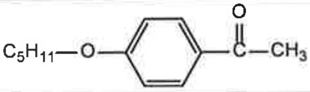
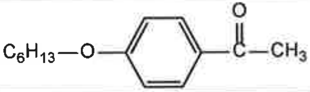
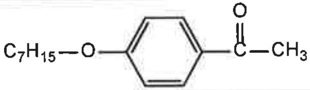
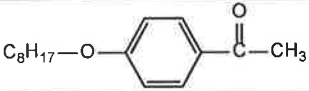
2. Synthesis and determine liquid crystalline behavior of new Schiff bases dervived from 4-formylpyrazole derivatives with different aromatic amines.

Tables

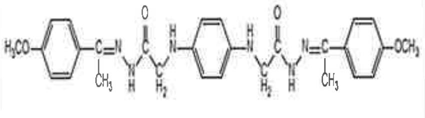
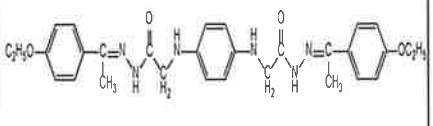
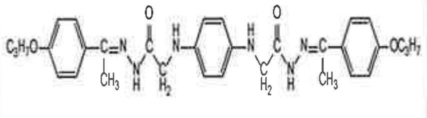
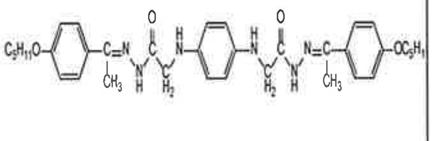
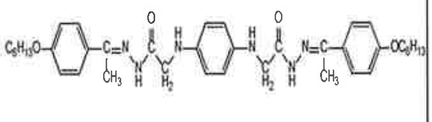
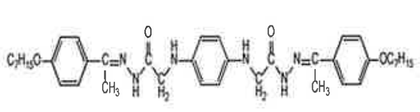
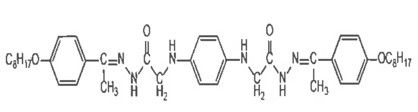
Table(2-2): The nomenclature, structural formula, molecular formula, yield, melting point and color of compounds [I-III]$_{a,b}$

Comp. No.	Nomenclature	Structural formula	Molecular formula	Yield %	M. P ^{0}C	Color
[I]$_a$	2,2'-(1,4-phenylenebis(azanediyl))diacetic acid[I]$_a$		$C_{10}H_{12}N_2O_4$	65 %	98-100°	brown
[I]$_b$	2,2'-([1,1'-biphenyl]-4,4'-diylbis(azanediyl))diacetic acid		$C_{16}H_{16}N_2O_4$	68%	>300°	brown
[II]$_a$	dimethyl 2,2'-(1,4-phenylene bis (azanediyl)) diacetate		$C_{12}H_{16}N_2O_4$	80%	>300°	dark brown
[II]$_b$	dimethyl 2,2'-([1,1'-biphenyl]-4,4'-diylbis(azanediyl))diacetate		$C_{18}H_{20}N_2O_4$	70%	145°	brown
[III]$_a$	2,2'-(1,4-phenylenebis(azanediyl))di(acetohydrazide)		$C_{10}H_{16}N_6O_2$	85 %	Gummy	dark brown
[III]$_b$	2,2'-([1,1'-biphenyl]-4,4'-diylbis(azanediyl))di(acetohydrazide)		$C_{16}H_{20}N_6O_2$	75%	165	brown

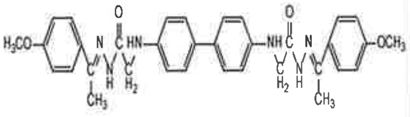
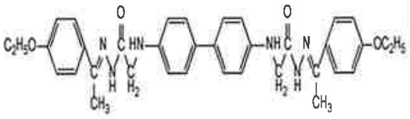
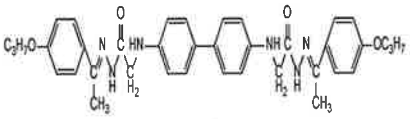
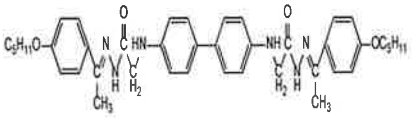
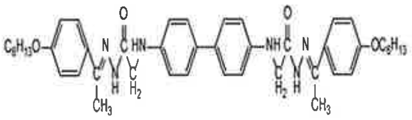
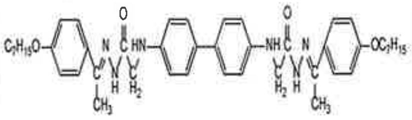
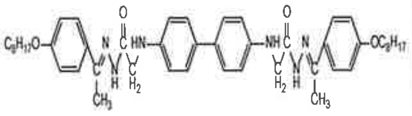
Table(2-3): The nomenclature, structural formula, molecular formula, yield, melting point and color of compounds $[IV]_n$

Comp. No.	Nomenclature	Structural formula	Molecular formula	Yield %	M. P ^0C	Color
$[IV]_1$	1-(4-methoxyphenyl) ethan-1-one		$C_9H_{10}O_2$	78	32-34	brown
$[IV]_2$	1-(4-ethoxyphenyl) ethan-1-one		$C_{10}H_{12}O_2$	70	Oily	brown
$[IV]_3$	1-(4-propoxyphenyl)ethan-1-one		$C_{11}H_{14}O_2$	77	Oily	brown
$[IV]_5$	1-(4-(pentyloxy)phenyl) ethan-1-one		$C_{13}H_{18}O_2$	72	28-30	brown
$[IV]_6$	1-(4-(hexyloxy)phenyl) ethan-1-one		$C_{14}H_{20}O_2$	74	Oily	brown
$[IV]_7$	1-(4-(heptyloxy)phenyl) ethan-1-one		$C_{15}H_{22}O_2$	78	40-42	brown
$[IV]_8$	1-(4-(octyloxy)phenyl) ethan-1-one		$C_{16}H_{24}O_2$	70	Oily	brown

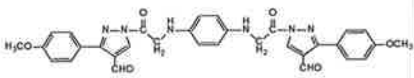
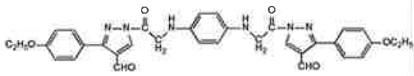
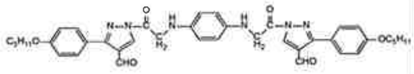
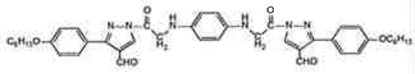
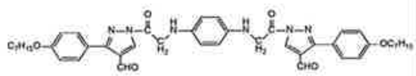
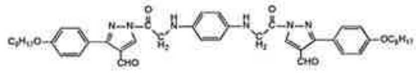
Table(2-4): The nomenclature, structural formula, molecular formula, yield, melting point and color of compounds [V-XI]$_a$

Comp . No.	Nomenclature	Structural formula	Molecular formula	Yield %	M. P ^{0}C	Color
[V]$_a$	2,2'-(1,4-phenylenebis(azanediyl))bis(N'-((E)-1-(4-methoxyphenyl)ethylidene)acetohydrazide)		$C_{28}H_{32}N_6O_4$	75	156-158	brown
[VI]$_a$	2,2'-(1,4-phenylenebis(azanediyl))bis(N'-((E)-1-(4-ethoxyphenyl) ethylidene)acetohydrazide)		$C_{30}H_{36}N_6O_4$	73	162-164	brown
[VII]$_a$	2,2'-(1,4-phenylenebis(azanediyl))bis(N'-((E)-1-(4-propoxyphenyl) ethylidene)acetohydrazide)		$C_{32}H_{40}N_6O_4$	70	158-160	brown
[VIII]$_a$	2,2'-(1,4-phenylenebis(azanediyl))bis(N'-((E)-1-(4-(pentyloxy)phenyl)ethylidene)acetohydrazide)		$C_{36}H_{48}N_6O_4$	69	150-152	brown
[IX]$_a$	2,2'-(1,4-phenylenebis(azanediyl))bis(N'-((E)-1-(4-(hexyloxy)phenyl)ethylidene)acetohydrazide)		$C_{38}H_{52}N_6O_4$	75	143-145	brown
[X]$_a$	2,2'-(1,4-phenylenebis(azanediyl))bis(N'-((E)-1-(4-(heptyloxy)phenyl)ethylidene)acetohydrazide)		$C_{40}H_{56}N_6O_4$	70	218-220	brown
[XI]$_a$	2,2'-(1,4-phenylenebis(azanediyl))bis(N'-((E)-1-(4-(octyloxy)phenyl)ethylidene)acetohydrazide)		$C_{42}H_{60}N_6O_4$	73	248-250	brown

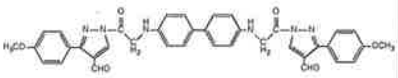
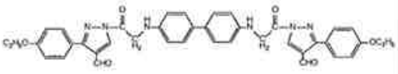
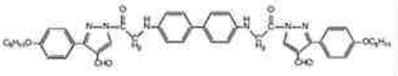
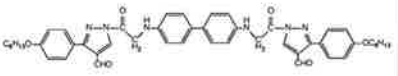
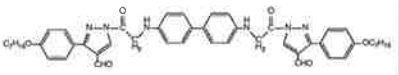
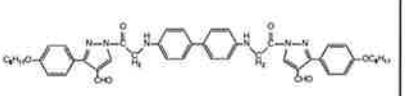
Table(2-5): The nomenclature, structural formula, molecular formula, yield, melting point and color of compounds [V-XI]$_b$

Comp. No.	Nomenclature	Structural formula	Molecular formula	Yield %	M. P ^{0}C	Color
[V]$_b$	2,2'-([1,1'-biphenyl]-4,4'-diylbis(azanediyl))bis(N'-((E)-4-methoxybenzylidene)acetohydrazide)		$C_{32}H_{32}N_6O_4$	65	59-61	brown
[VI]$_b$	2,2'-([1,1'-biphenyl]-4,4'-diylbis(azanediyl))bis(N'-((E)-4-ethoxybenzylidene)acetohydrazide)		$C_{34}H_{36}N_6O_4$	67	76-78	brown
[VII]$_b$	2,2'-([1,1'-biphenyl]-4,4'-diylbis(azanediyl))bis(N'-((E)-4-propoxybenzylidene)acetohydrazide)		$C_{36}H_{40}N_6O_4$	63	148-150	brown
[VIII]$_b$	2,2'-([1,1'-biphenyl]-4,4'-diylbis(azanediyl))bis(N'-((E)-4-(pentyloxy)benzylidene)acetohydrazide)		$C_{40}H_{48}N_6O_4$	70	>300 °	brown
[IX]$_b$	2,2'-([1,1'-biphenyl]-4,4'-diylbis(azanediyl))bis(N'-((E)-4-(hexyloxy)benzylidene)acetohydrazide)		$C_{42}H_{52}N_6O_4$	66	132-135	brown
[X]$_b$	2,2'-([1,1'-biphenyl]-4,4'-diylbis(azanediyl))bis(N'-((E)-4-(heptyloxy)benzylidene)acetohydrazide)		$C_{44}H_{56}N_6O_4$	68	150-152	brown
[XI]$_b$	2,2'-([1,1'-biphenyl]-4,4'-diylbis(azanediyl))bis(N'-((E)-4-(octyloxy)benzylidene)acetohydrazide)		$C_{46}H_{60}N_6O_4$	73	138-140	brown

Table(2-6): The nomenclature, structural formula, molecular formula, yield, melting point and color of compounds $[\text{XII-XVIII}]_a$

Comp. No.	Nomenclature	Structural formula	Molecular formula	Yield %	M. P ^0C	Color
$[\text{XII}]_a$	1,1'-(2,2'-(1,4-phenylenebis(azanediyl))bis(acetyl))bis(3-(4-methoxyphenyl)-1H-pyrazole-4-carbaldehyde)		$C_{32}H_{28}N_6O_6$	70	83-85	brown
$[\text{XIII}]_a$	1,1'-(2,2'-(1,4-phenylenebis(azanediyl))bis(acetyl))bis(3-(4-ethoxyphenyl)-1H-pyrazole-4-carbaldehyde)		$C_{34}H_{32}N_6O_6$	68	102-104	brown
$[\text{XIV}]_a$	1,1'-(2,2'-(1,4-phenylenebis(azanediyl))bis(acetyl))bis(3-(4-propoxyphenyl)-1H-pyrazole-4-carbaldehyde)		$C_{36}H_{36}N_6O_6$	65	95-97	brown
$[\text{XV}]_a$	1,1'-(2,2'-(1,4-phenylenebis(azanediyl))bis(acetyl))bis(3-(4-(pentyloxy)phenyl)-1H-pyrazole-4-carbaldehyde)		$C_{40}H_{44}N_6O_6$	73	120-122	dark brown
$[\text{XVI}]_a$	1,1'-(2,2'-(1,4-phenylenebis(azanediyl))bis(acetyl))bis(3-(4-(hexyloxy)phenyl)-1H-pyrazole-4-carbaldehyde)		$C_{42}H_{48}N_6O_6$	77	180-182	dark brown
$[\text{XVII}]_a$	1,1'-(2,2'-(1,4-phenylenebis(azanediyl))bis(acetyl))bis(3-(4-(heptyloxy)phenyl)-1H-pyrazole-4-carbaldehyde)		$C_{44}H_{52}N_6O_6$	68	200-202	dark brown
$[\text{XVIII}]_a$	1,1'-(2,2'-(1,4-phenylenebis(azanediyl))bis(acetyl))bis(3-(4-(octyloxy)phenyl)-1H-pyrazole-4-carbaldehyde)		$C_{46}H_{56}N_6O_6$	65	158-160	dark brown

Table(2-7): The nomenclature, structural formula, molecular formula, yield, melting point and color of compounds [XII-XVIII]$_b$

Comp. No.	Nomenclature	Structural formula	Molecular formula	Yield %	M. P ^{0}C	Color
[XII]$_b$	1,1'-(2,2'-([1,1'-biphenyl]-4,4'-diylbis(azanediyl))bis(acetyl))bis(3-(4-methoxyphenyl)-1H-pyrazole-4-carbaldehyde)		$C_{38}H_{32}N_6O_6$	63	>300 °	dark brown
[XIII]$_b$	1,1'-(2,2'-([1,1'-biphenyl]-4,4'-diylbis(azanediyl))bis(acetyl))bis(3-(4-ethoxyphenyl)-1H-pyrazole-4-carbaldehyde)		$C_{40}H_{36}N_6O_6$	60	134-136	dark brown
[XIV]$_b$	1,1'-(2,2'-([1,1'-biphenyl]-4,4'-diylbis(azanediyl))bis(acetyl))bis(3-(4-propoxyphenyl)-1H-pyrazole-4-carbaldehyde)		$C_{42}H_{40}N_6O_6$	65	65-67	brown
[XV]$_b$	1,1'-(2,2'-([1,1'-biphenyl]-4,4'-diylbis(azanediyl))bis(acetyl))bis(3-(4-(pentyloxy)phenyl)-1H-pyrazole-4-carbaldehyde)		$C_{46}H_{48}N_6O_6$	72	90-92	dark brown
[XVI]$_b$	1,1'-(2,2'-([1,1'-biphenyl]-4,4'-diylbis(azanediyl))bis(acetyl))bis(3-(4-(hexyloxy)phenyl)-1H-pyrazole-4-carbaldehyde)		$C_{48}H_{52}N_6O_6$	72	118-120	dark brown
[XVII]$_b$	1,1'-(2,2'-([1,1'-biphenyl]-4,4'-diylbis(azanediyl))bis(acetyl))bis(3-(4-(heptyloxy)phenyl)-1H-pyrazole-4-carbaldehyde)		$C_{50}H_{56}N_6O_6$	67	98-100	dark brown
[XVIII]$_b$	1,1'-(2,2'-([1,1'-biphenyl]-4,4'-diylbis(azanediyl))bis(acetyl))bis(3-(4-(octyloxy)phenyl)-1H-pyrazole-4-carbaldehyde)		$C_{52}H_{60}N_6O_6$	69	150-152	dark brown

Table(3-1):FTIR absorption bands of $[IV]_n$

Comp. No.	**Characteristic bands FTIR spectra(cm^{-1})**				
	υ (C -H) aromatic	**υ (C- H) aliphatic**	**υ (C=O) keto**	**υ (C=C) aromatic**	**υ (C-O) ether**
$[IV]_1$	3045	2964-2843	1672	1600	1225
$[IV]_2$	3050	2983-2885	1668	1598	1249
$[IV]_3$	3060	2966-2877	1674	1597	1251
$[IV]_5$	3040	2960-2868	1676	1600	1259
$[IV]_6$	3055	2931-2862	1670	1597	1249 lit(78)
$[IV]_7$	3047	2945-2852	1672	1600	1244 lit(78)
$[IV]_8$	3060	2954-2854	1676	1598	1253 lit(78)

Table(3-2): FTIR absorbtion bands of [V-XI]$_a$

Comp. No.	Characteristic bands FTIR spectra(cm^{-1})					
	υ (N-H)	υ (C- H) aromatic	υ (C- H) aliphatic	υ (C=O) amid	υ (C=N)	υ (C=C) aromatic
[V]$_a$	3390	3010	2956-2837	1660	1635	1593
[VI]$_a$	3354	3025	2962-2850	1664	1626	1598
[VII]$_a$	3300	3045	2962-2873	1670	1625	1593
[VIII]$_a$	3340	3060	2935-2866	1666	1615	1593
[IX]$_a$	3300	3035	2931-2862	1670	1610	1598
[X]$_a$	3290	3050	2927-2858	1670	1615	1597
[XI]$_a$	3330	3040	2924-2858	1670	1610	1597

Table(3-3): FTIR absorption bands of [V-XI]$_b$

Comp. No.	Characteristic bands FTIR spectra(cm^{-1})					
	υ (N-H)	υ (C- H) aromatic	υ (C- H) aliphatic	υ (C=O) amid	υ (C=N)	υ (C=C) aromatic
[V]$_b$	3356	3010	2960-2850	1664	1630	1604
[VI]$_b$	3350	3028	2966-2885	1665	1620	1604
[VII]$_b$	3310	3030	2966-2877	1670	1620	1597
[VIII]$_b$	3325	3015	2943-2866	1666	1620	1593
[IX]$_b$	3373	3020	2931-2866	1674	1630	1600
[X]$_b$	3371	3010	2927-2854	1674	1625	1599
[XI]$_b$	3370	3018	2924-2854	1670	1620	1600

Table(3-4):Characteristics FTIR absorption bands of $[XII-XVIII]_a$

Comp. No.	Characteristic bands FTIR spectra(cm^{-1})						
	υ (N-H)	υ (C- H) aromatic	υ (C- H) aliphatic	υ (C=O) alde	υ (C=O) amide	υ (C=N) endocyclic	υ (C=C) aromatic
$[XII]_a$	3390	3008	2935-2835	1674	1664	1645	1606
$[XIII]_a$	3335	3035	2980-2883	1680	1666	1635	1598
$[XIV]_a$	3360	3060	2958-2858	1695	1665	1649	1597
$[XV]_a$	3340	3040	2927-2866	1701	1670	1640	1600
$[XVI]_a$	3330	3045	2927-2862	1708	1670	1630	1597
$[XVII]_a$	3320	3060	2924-2858	1705	1670	1635	1597
$[XVIII]_a$	3335	3040	2930-2860	1698	1666	1642	1600

Table(3-5):Characteristics FTIR absorption bands of $[XII-XVIII]_a$

Comp. No.	Characteristic bands FTIR spectra(cm^{-1})						
	υ (N-H)	υ (C- H) aromatic	υ (C- H) aliphatic	υ (C=O) alde	υ (C=O) amide	υ (C=N) endocyclic	υ (C=C) aromatic
$[XII]_b$	3400	3016	2951-2850	1695	1665	1649	1598
$[XIII]_b$	3410	3035	2985-2885	1690	1678	1631	1597
$[XIV]_b$	3410	3010	2962-2880	1690	1662	1630	1608
$[XV]_b$	3410	3020	2958-2870	1693	1662	1640	1604
$[XVI]_b$	3409	3039	2931-2858	1690	1660	1631	1604
$[XVII]_b$	3400	3066	2954-2858	1695	1662	1630	1600
$[XVIII]_b$	3405	3062	2927-2854	1690	1674	1630	1602

Table(3-6):Phase transition temperatures of series[V-XI]$_a$

Comp. No.	Phase transition temperatures
[V]$_a$	$\mathrm{cr} \underset{150}{\overset{195}{\rightleftharpoons}} \mathrm{N} \overset{253}{\rightleftharpoons} \mathrm{I}$
[VI]$_a$	$\mathrm{cr} \overset{175}{\rightleftharpoons} \mathrm{N} \overset{205}{\rightleftharpoons} \mathrm{I}$
[VII]$_a$	$\mathrm{cr} \overset{120}{\rightleftharpoons} \mathrm{N} \overset{180}{\rightleftharpoons} \mathrm{I}$
[VIII]$_a$	$\mathrm{cr} \overset{150}{\rightleftharpoons} \mathrm{N} \overset{195}{\rightleftharpoons} \mathrm{I}$
[IX]$_a$	$\mathrm{cr} \overset{110}{\rightleftharpoons} \mathrm{SmB} \overset{135}{\rightleftharpoons} \mathrm{N} \overset{160}{\rightleftharpoons} \mathrm{I}$
[X]$_a$	$\mathrm{cr} \overset{155}{\rightleftharpoons} \mathrm{SmB} \overset{185}{\rightleftharpoons} \mathrm{N} \overset{210}{\rightleftharpoons} \mathrm{I}$
[XI]$_a$	$\mathrm{cr} \overset{140}{\rightleftharpoons} \mathrm{SmC} \overset{175}{\rightleftharpoons} \mathrm{N} \overset{200}{\rightleftharpoons} \mathrm{I}$

Cr, crystalline phase;SmB smectic B phase ;SmC smecticC phase; N, nematic phase; I, isotropic liquid

Table(3-7):Phase transition temperatures of series$[V\text{-}XI]_b$

Comp. No.	Phase transition temperatures
$[V]_b$	$cr \xrightleftharpoons{210} N \xrightleftharpoons{265} I$
$[VI]_b$	$cr \xrightleftharpoons{190} N \xrightleftharpoons{220} I$
$[VII]_b$	$cr \xrightleftharpoons{125} N \xrightleftharpoons{190} I$
$[VIII]_b$	$cr \xrightleftharpoons{175} N \xrightleftharpoons{205} I$
$[IX]_b$	$cr \xrightleftharpoons{120} SmA \xrightleftharpoons{145} N \xrightleftharpoons{170} I$
$[X]_b$	$cr \xrightarrow{101} SmB \xrightarrow{233} I$
$[XI]_b$	$cr \xrightarrow{100} SmA \xrightarrow{244} I$

Cr, crystalline phase; SmA smectic A phase; SmB smecticB phase; N, nematic phase; I, isotropic liquid

Table(3-8):Phase transition temperatures of series[XII-XVIII]$_a$

Comp. No.	Phase transition temperatures
[XII]$_a$	$\text{cr} \xrightleftharpoons{95} \text{I}$
[XIII]$_a$	$\text{cr} \xrightleftharpoons{115} \text{I}$
[XIV]$_a$	$\text{cr} \xrightleftharpoons{100} \text{I}$
[XV]$_a$	$\text{cr} \xrightleftharpoons{125} \text{I}$
[XVI]$_a$	$\text{cr} \xrightleftharpoons{120} \text{N} \xrightleftharpoons{145} \text{I}$
[XVII]$_a$	$\text{cr} \xrightleftharpoons{90} \text{N} \xrightleftharpoons{110} \text{I}$
[XVIII]$_a$	$\text{cr} \xrightleftharpoons{115} \text{N} \xrightleftharpoons{130} \text{I}$

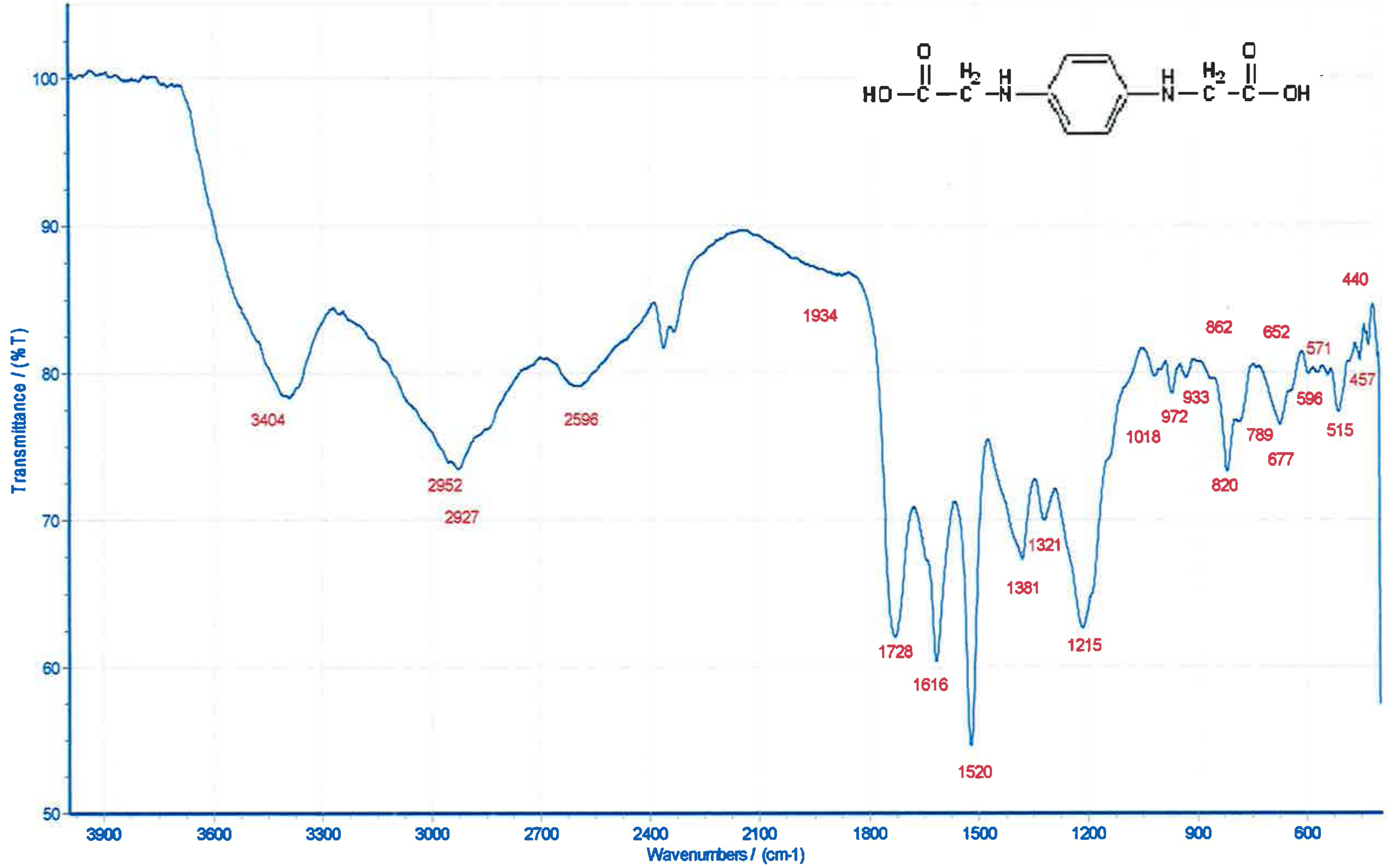
Cr, crystalline phase; N, nematic phase; I, isotropic liquid

Table(3-9):Phase transition temperatures of series$[\mathrm{XII}\text{-}\mathrm{XVIII}]_b$

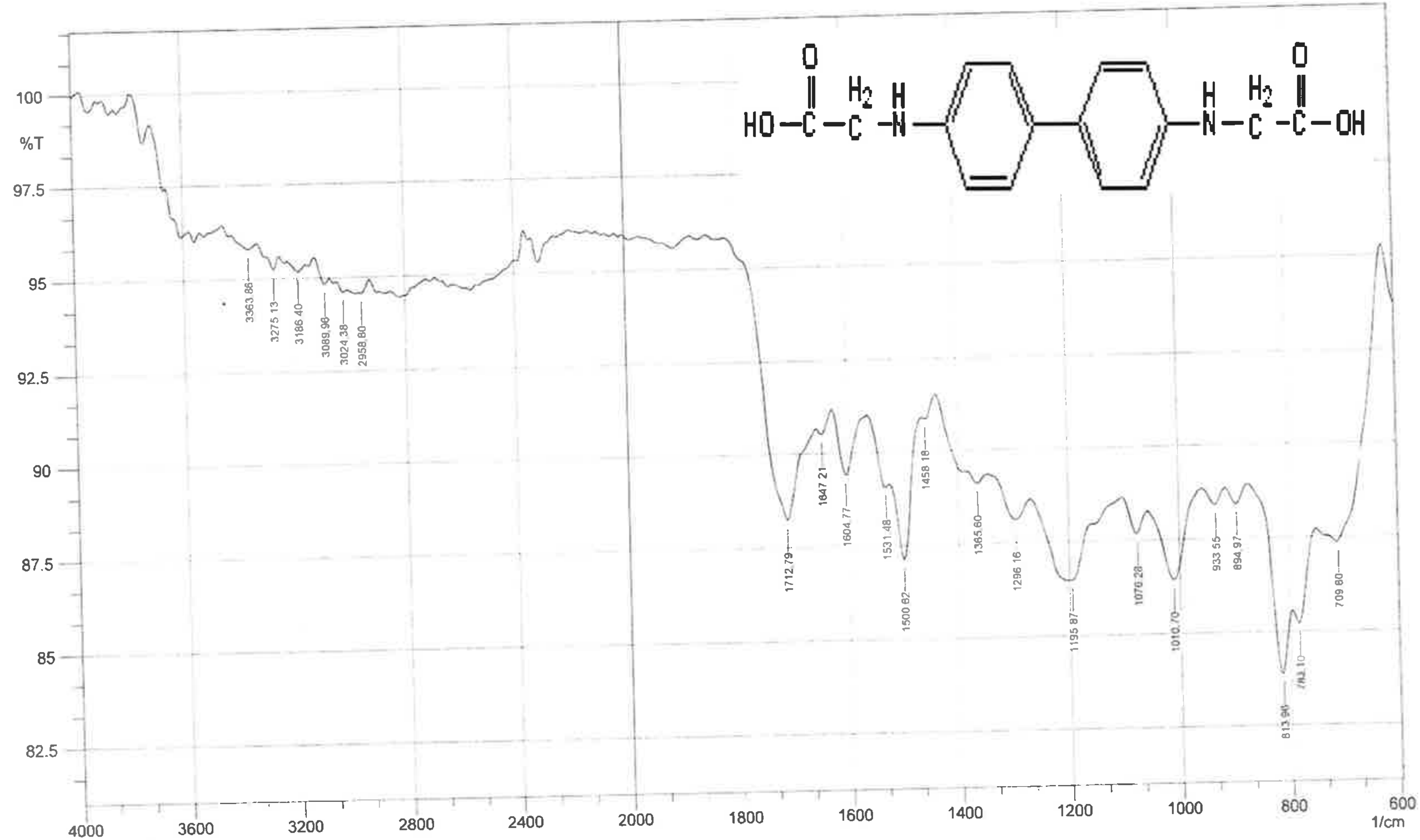
Comp. No.	Phase transition temperatures
$[\mathrm{XII}]_b$	$\mathrm{cr} \overset{285}{\rightleftharpoons} \mathrm{I}$
$[\mathrm{XIII}]_b$	$\mathrm{cr} \overset{140}{\rightleftharpoons} \mathrm{N} \overset{160}{\rightleftharpoons} \mathrm{I}$
$[\mathrm{XIV}]_b$	$\mathrm{cr} \overset{75}{\rightleftharpoons} \mathrm{SmB} \overset{90}{\rightleftharpoons} \mathrm{N} \overset{110}{\rightleftharpoons} \mathrm{I}$
$[\mathrm{XV}]_b$	$\mathrm{cr} \overset{85}{\rightleftharpoons} \mathrm{SmB} \overset{105}{\rightleftharpoons} \mathrm{N} \overset{120}{\rightleftharpoons} \mathrm{I}$
$[\mathrm{XVI}]_b$	$\mathrm{cr} \overset{120}{\rightleftharpoons} \mathrm{SmB} \overset{135}{\rightleftharpoons} \mathrm{N} \overset{150}{\rightleftharpoons} \mathrm{I}$
$[\mathrm{XVII}]_b$	$\mathrm{cr} \overset{80}{\rightleftharpoons} \mathrm{SmB} \overset{100}{\rightleftharpoons} \mathrm{N} \overset{125}{\rightleftharpoons} \mathrm{I}$
$[\mathrm{XVIII}]_b$	$\mathrm{cr} \overset{105}{\rightleftharpoons} \mathrm{SmB} \overset{125}{\rightleftharpoons} \mathrm{N} \overset{145}{\rightleftharpoons} \mathrm{I}$

Cr, crystalline phase;SmB, smectic B phase; N, nematic phase; I, isotropic liquid

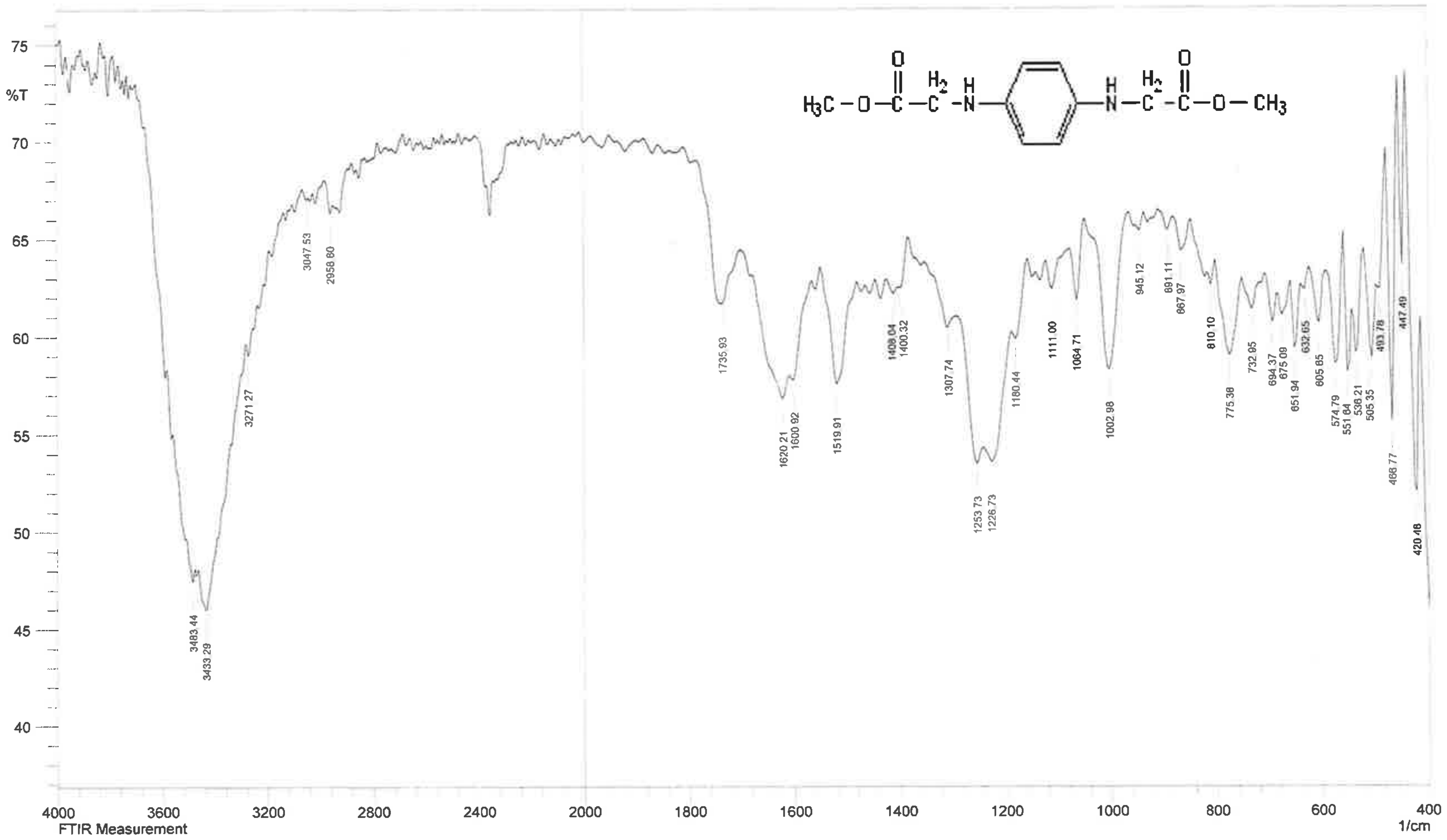
Figures



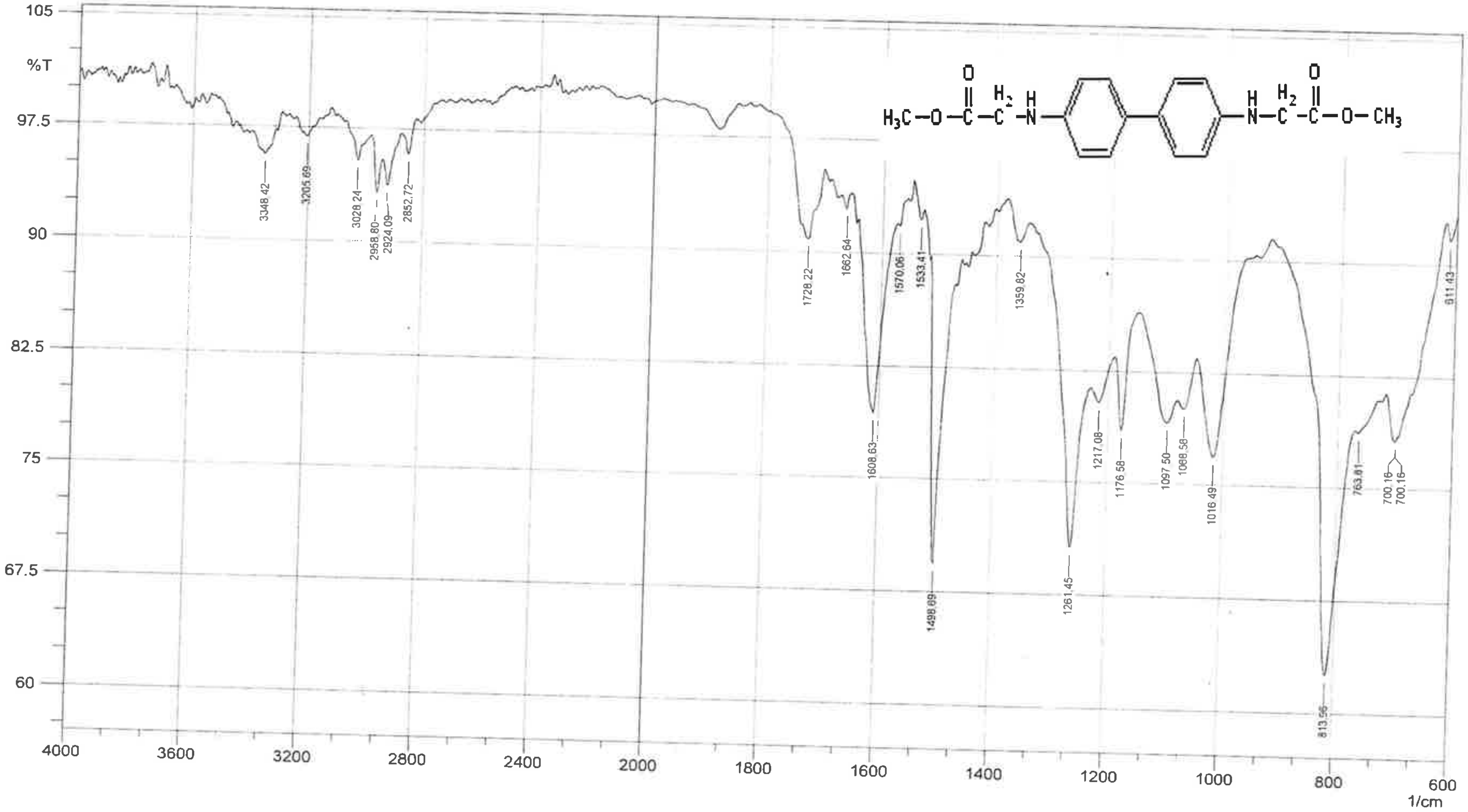
Figure(3-1) : FTIR spectrum for compound [I]a



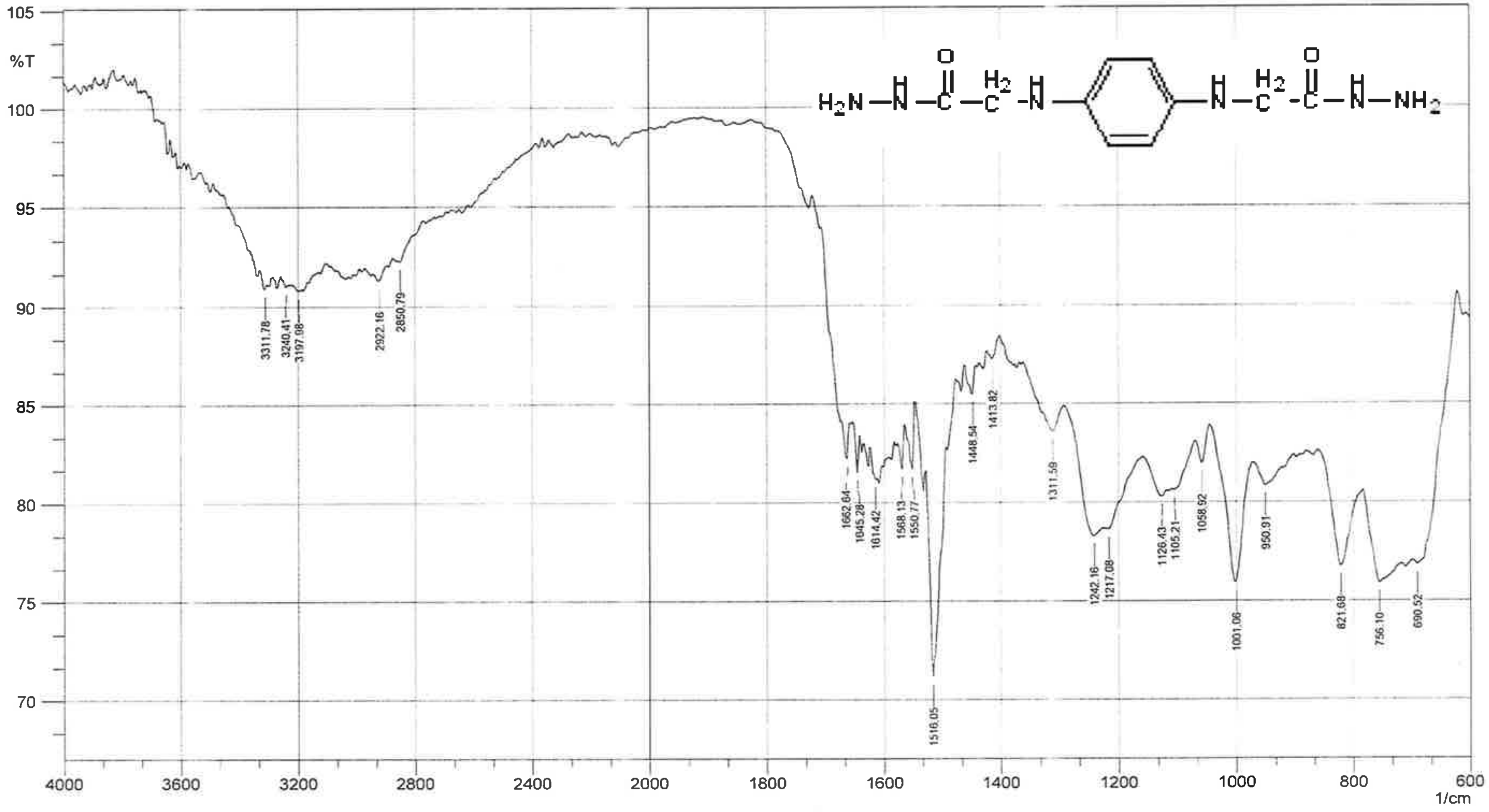
Figure(3-2) :FTIR spectrum for compound $[I]_b$



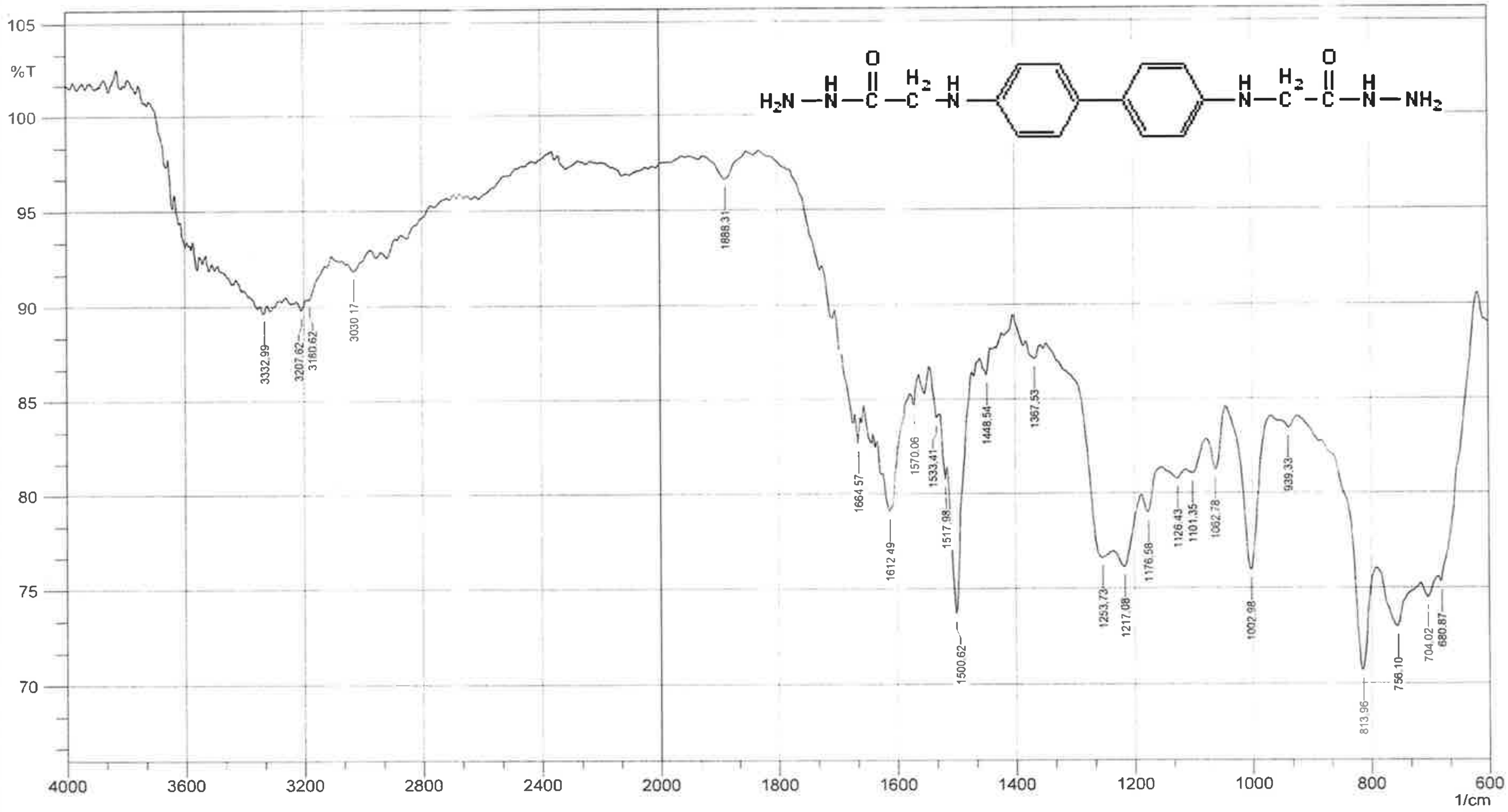
Figure(3-3):FTIR spectrum for compound [II]$_a$



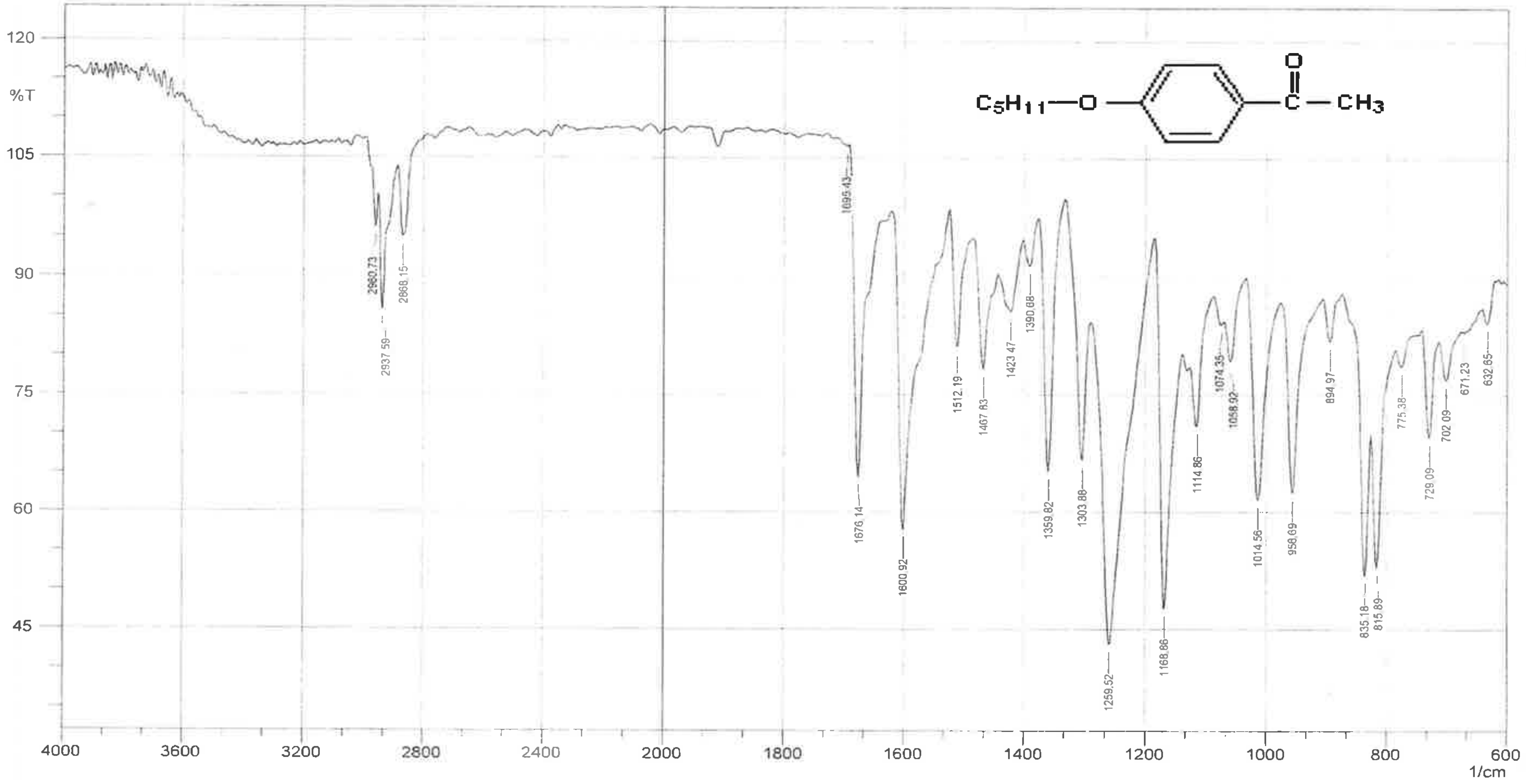
Figure(3-4):FTIR spectrum for compound $[II]_b$



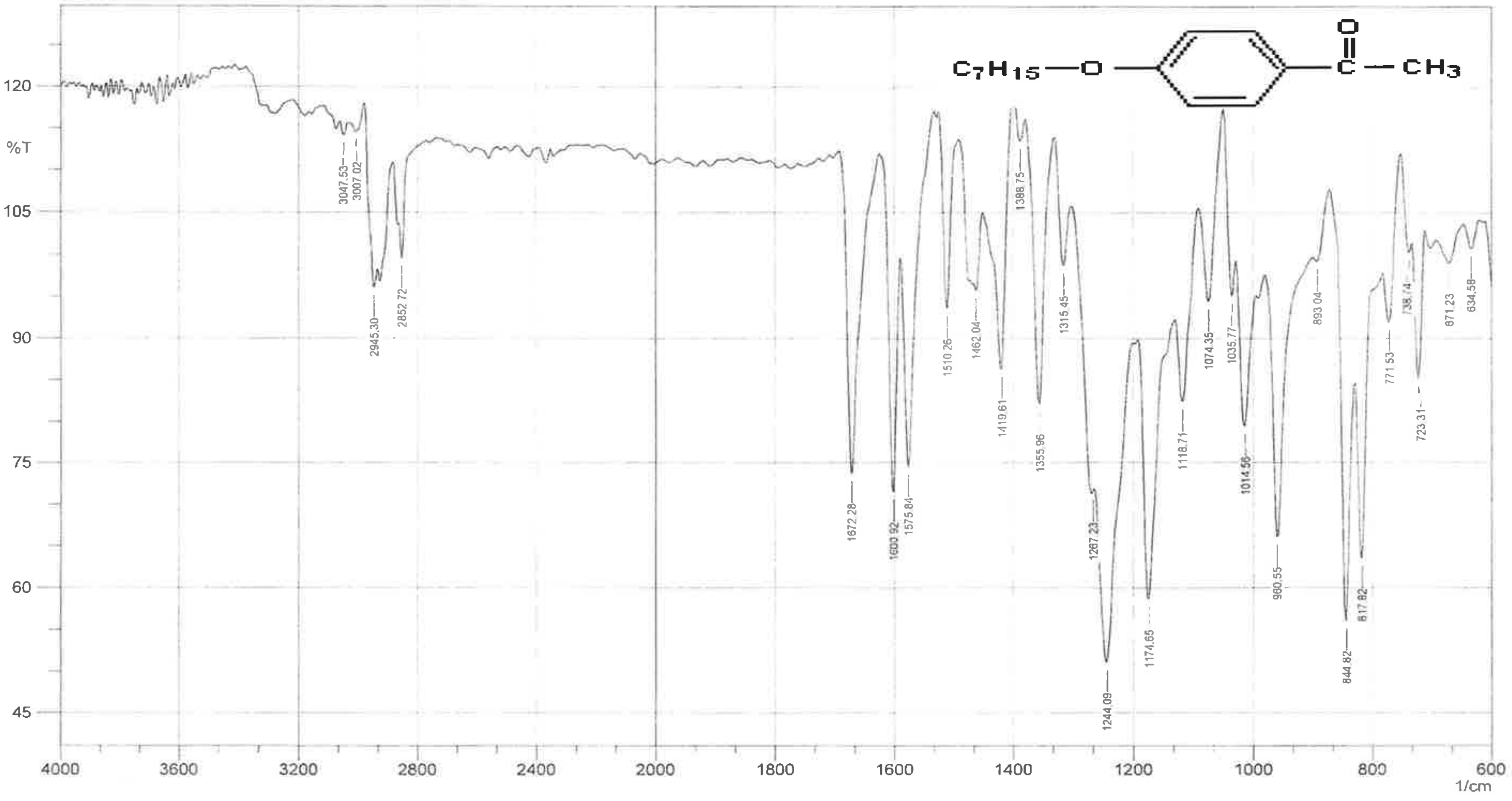
Figure(3-5):FTIR spectrum for compound [III]a



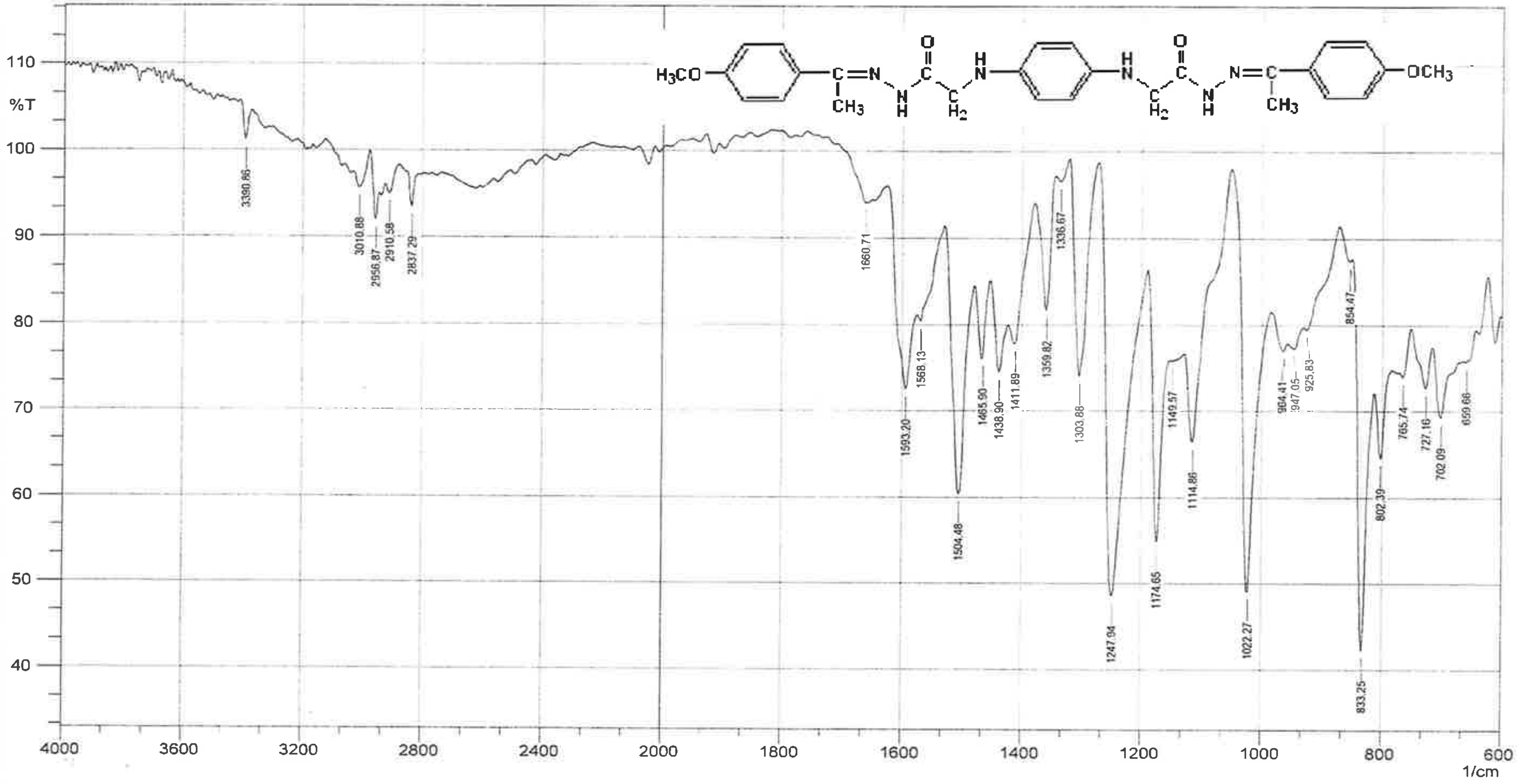
Figure(3-6):FTIR spectrum for compound [III]$_b$



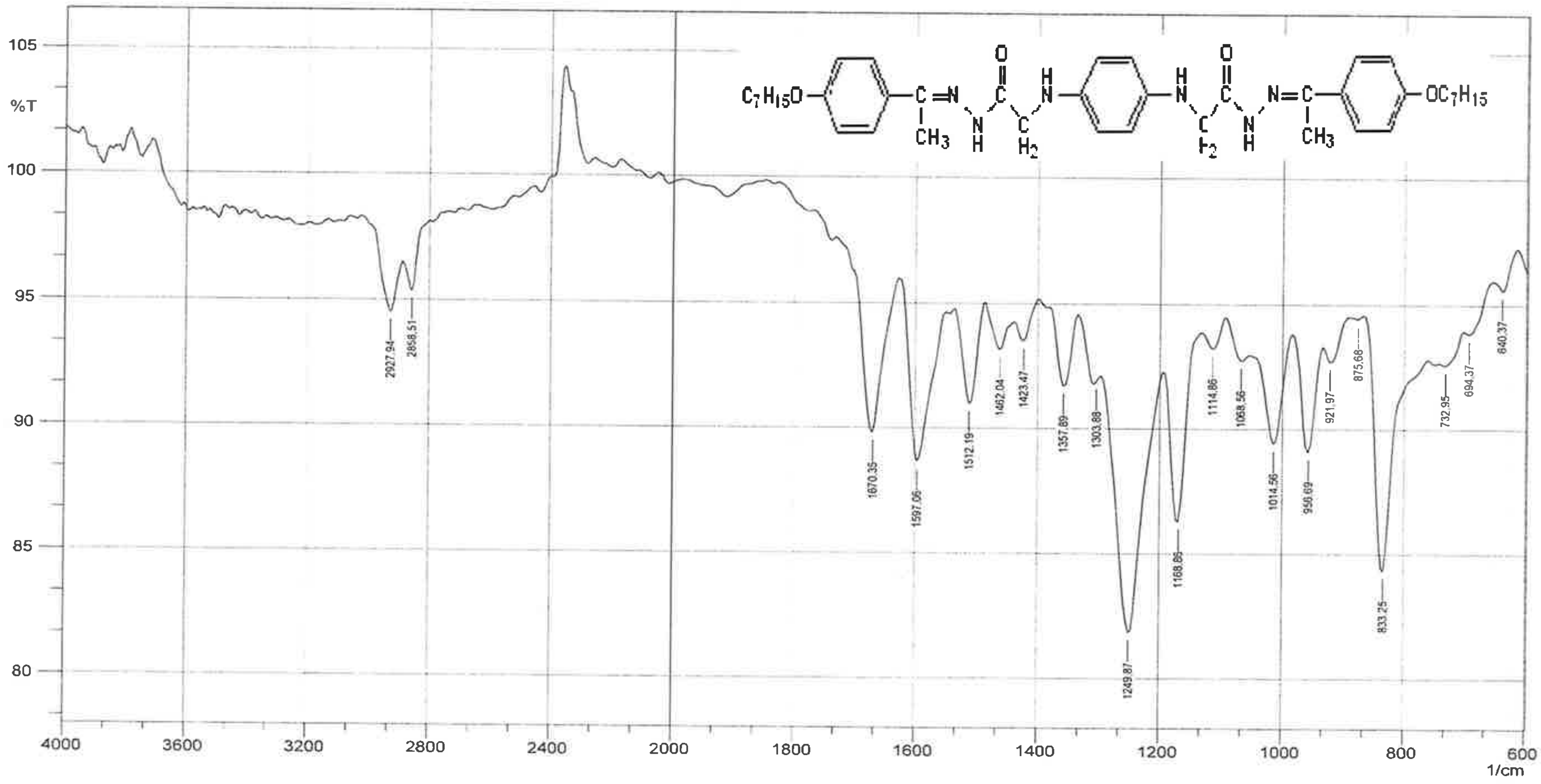
Figure(3-7):FTIR spectrum for compound [IV]$_5$



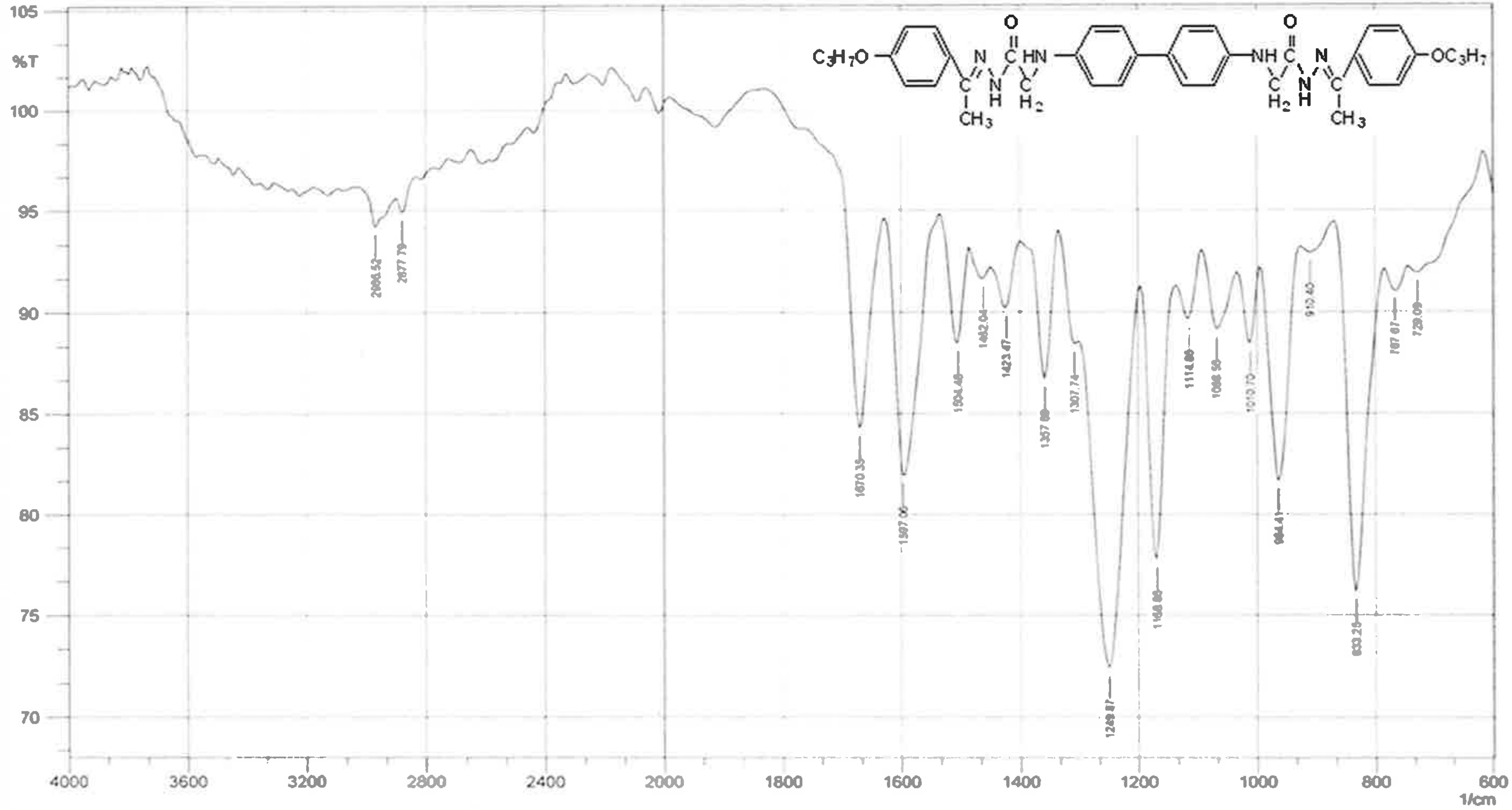
Figure(3-8):FTIR spectrum for compound $[IV]_7$



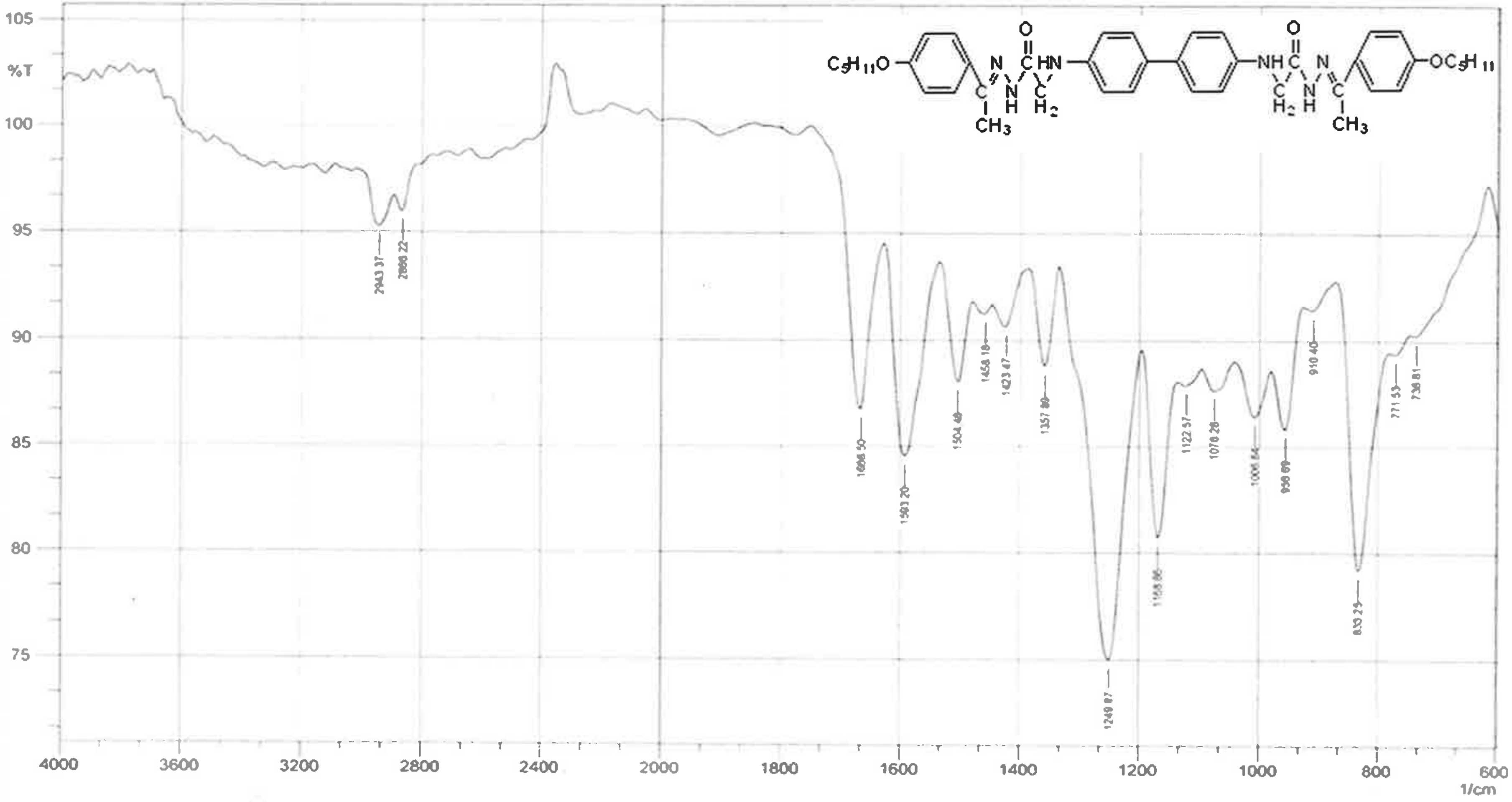
Figure(3-9):FTIR spectrum for compound [V]$_a$



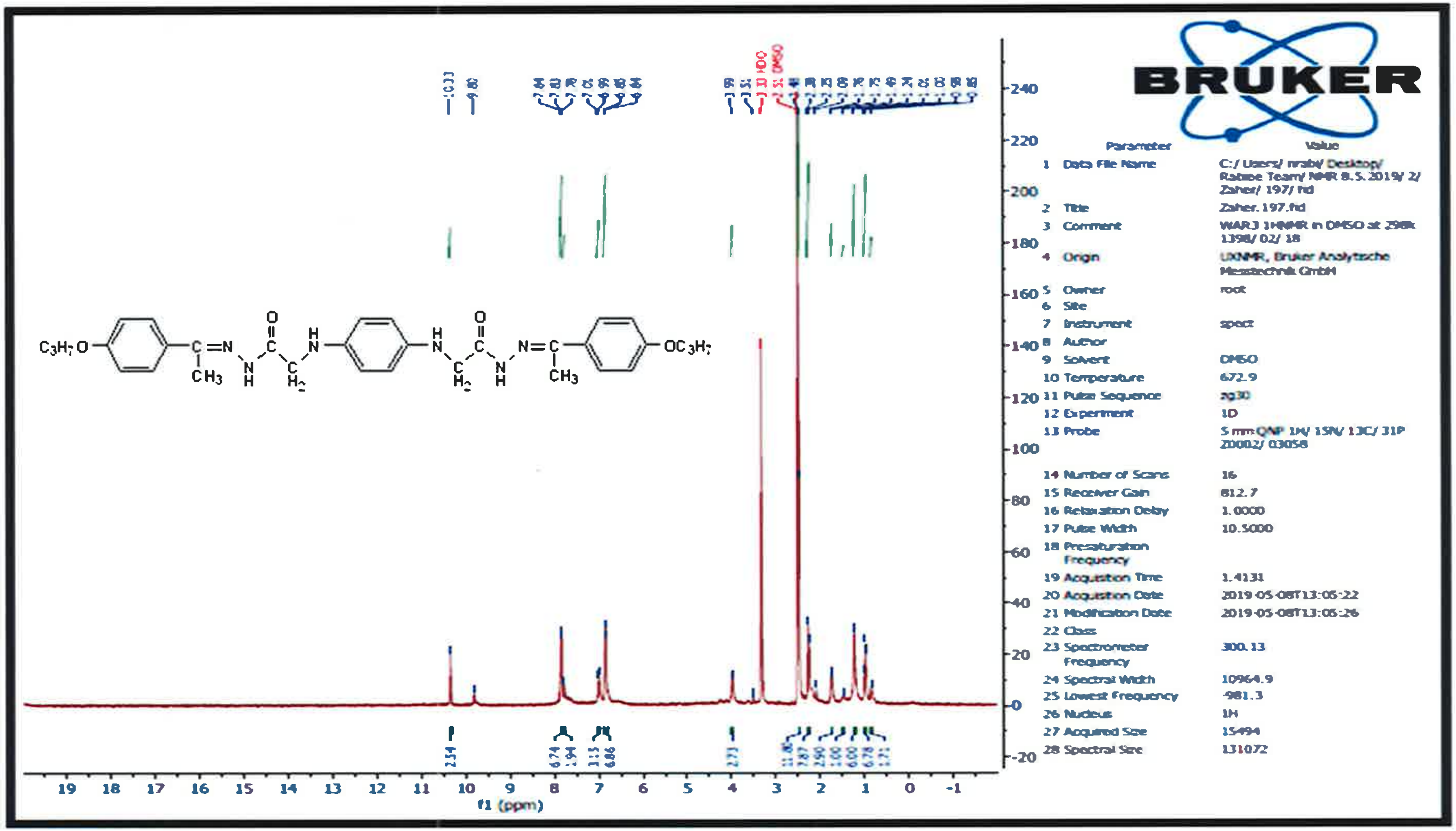
Figure(3-10):FTIR spectrum for compound $[X]_a$



Figure(3-11): FTIR spectrum for compound [VII]$_b$



Figure(3-12): FTIR spectrum for compound $[VIII]_b$



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5	Owner	root
6	Site	
7	Instrument	spect
8	Author	
9	Solvent	DMSO
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19	Acquisition Time	1.4131
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21	Modification Date	2019-05-08T13:05:26
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23	Spectrometer Frequency	300.13
24	Spectral Width	10964.9
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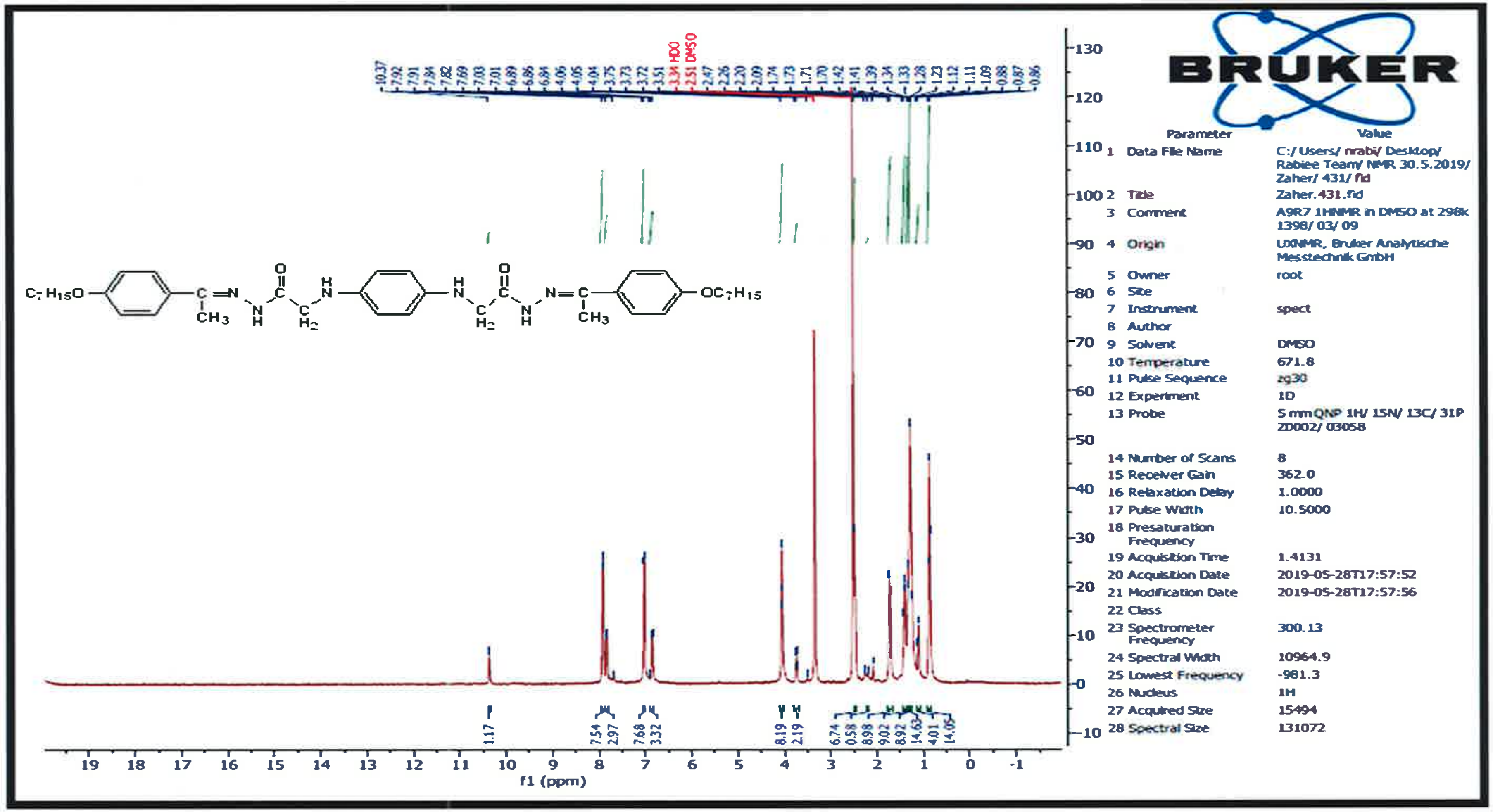
Figure(3-13):^{1}HNMR spectrum for compound $[VII]_a$



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6	Site	
7	Instrument	spect
8	Author	
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20	Acquisition Date	2019-05-28T17:57:52
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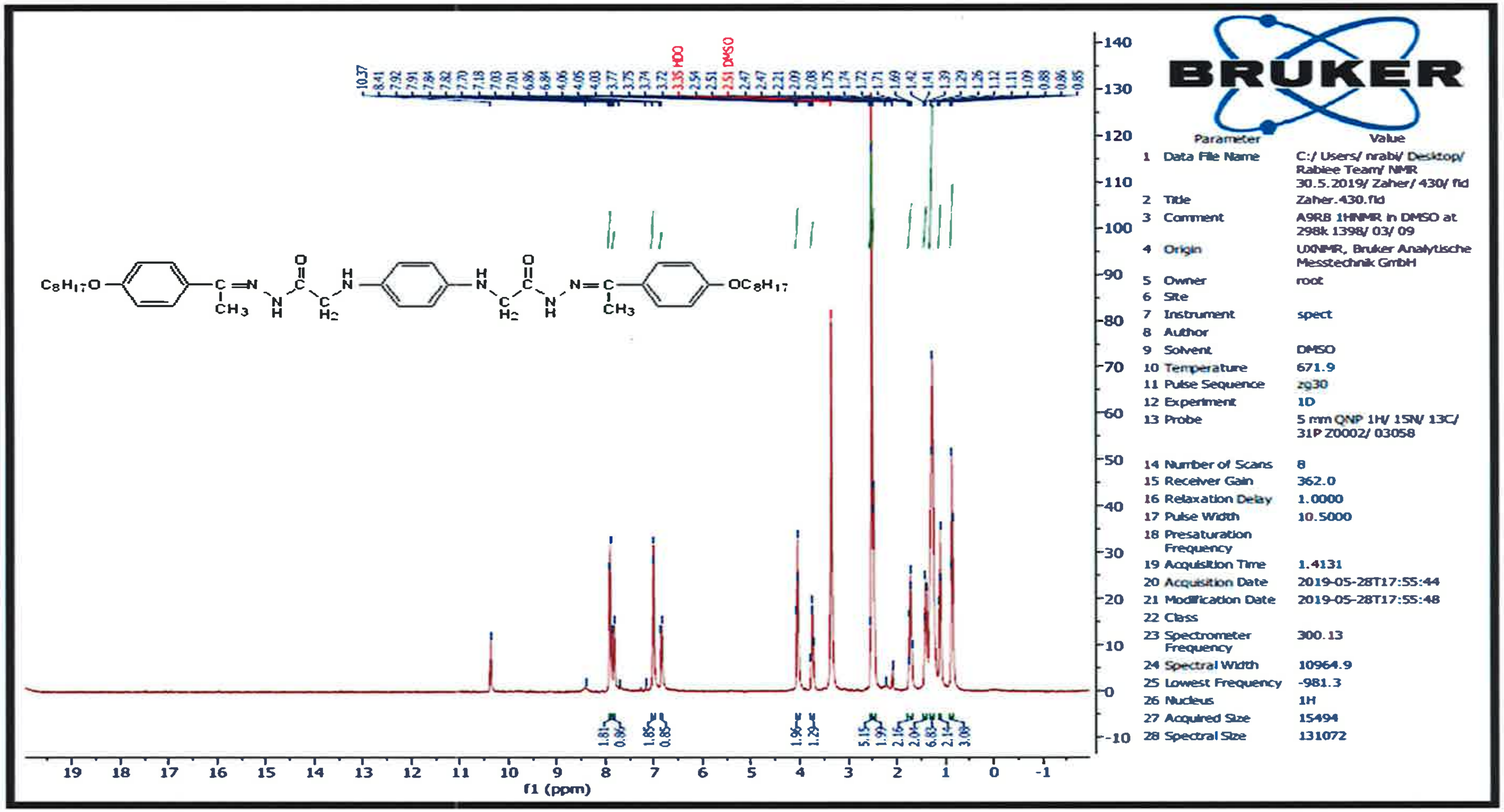
24	Spectral Width	10964.9
25	Lowest Frequency	-981.3
26	Nucleus	1H
27	Acquired Size	15494
28	Spectral Size	131072

Figure(3-14): ^{1}HNMR spectrum for compound $[X]_a$



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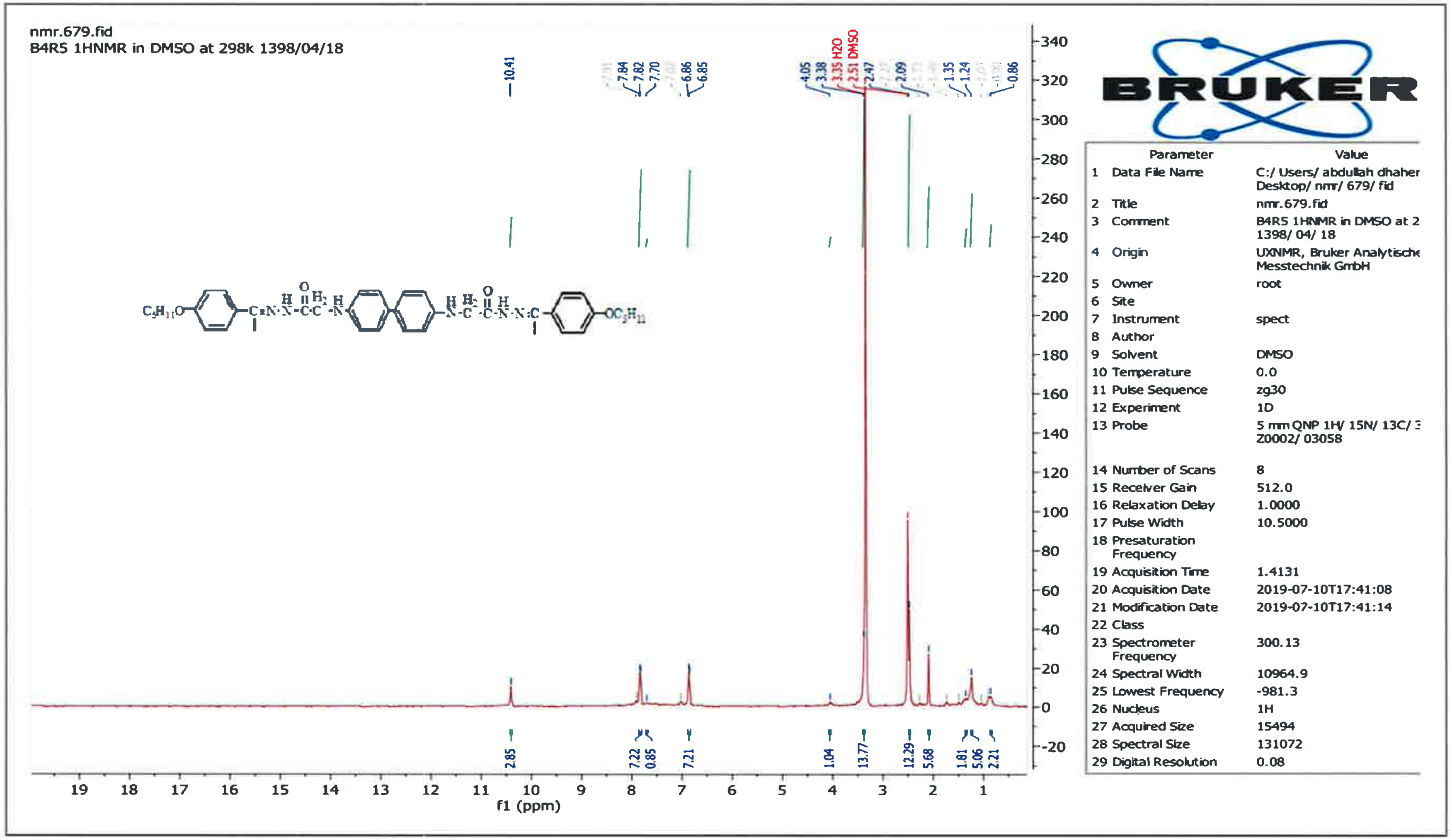
4	Origin	UXNMR, Bruker Analytische Messtechnik GmbH
5	Owner	root
6	Site	
7	Instrument	spect
8	Author	
9	Solvent	DMSO
10	Temperature	671.9
11	Pulse Sequence	zg30
12	Experiment	1D
13	Probe	5 mm QNP 1H/ 15N/ 13C/ 31P Z0002/ 03058
14	Number of Scans	8
15	Receiver Gain	362.0
16	Relaxation Delay	1.0000
17	Pulse Width	10.5000
18	Presaturation Frequency	
19	Acquisition Time	1.4131
20	Acquisition Date	2019-05-28T17:55:44
21	Modification Date	2019-05-28T17:55:48
22	Class	
23	Spectrometer Frequency	300.13
24	Spectral Width	10964.9
25	Lowest Frequency	-981.3
26	Nucleus	1H
27	Acquired Size	15494
28	Spectral Size	131072

Figure(3-15): ^{1}HNMR spectrum for compound $[XI]_a$



	Parameter	Value
1	Data File Name	C:/ Users/ abdullah dhaher Desktop/ nmr/ 679/ fid
2	Title	nmr.679.fid
3	Comment	B4R5 1HNMR in DMSO at 2 1398/ 04/ 18
4	Origin	UXNMR, Bruker Analytische Messtechnik GmbH
5	Owner	root
6	Site	
7	Instrument	spect
8	Author	
9	Solvent	DMSO
10	Temperature	0.0
11	Pulse Sequence	zg30
12	Experiment	1D
13	Probe	5 mm QNP 1H/ 15N/ 13C/ 3 Z0002/ 03058
14	Number of Scans	8
15	Receiver Gain	512.0
16	Relaxation Delay	1.0000
17	Pulse Width	10.5000
18	Presaturation Frequency	
19	Acquisition Time	1.4131
20	Acquisition Date	2019-07-10T17:41:08
21	Modification Date	2019-07-10T17:41:14
22	Class	
23	Spectrometer Frequency	300.13
24	Spectral Width	10964.9
25	Lowest Frequency	-981.3
26	Nucleus	1H
27	Acquired Size	15494
28	Spectral Size	131072
29	Digital Resolution	0.08

Figure(3-16): The ^{1}HNMR spectrum for compound [VIII]$_b$

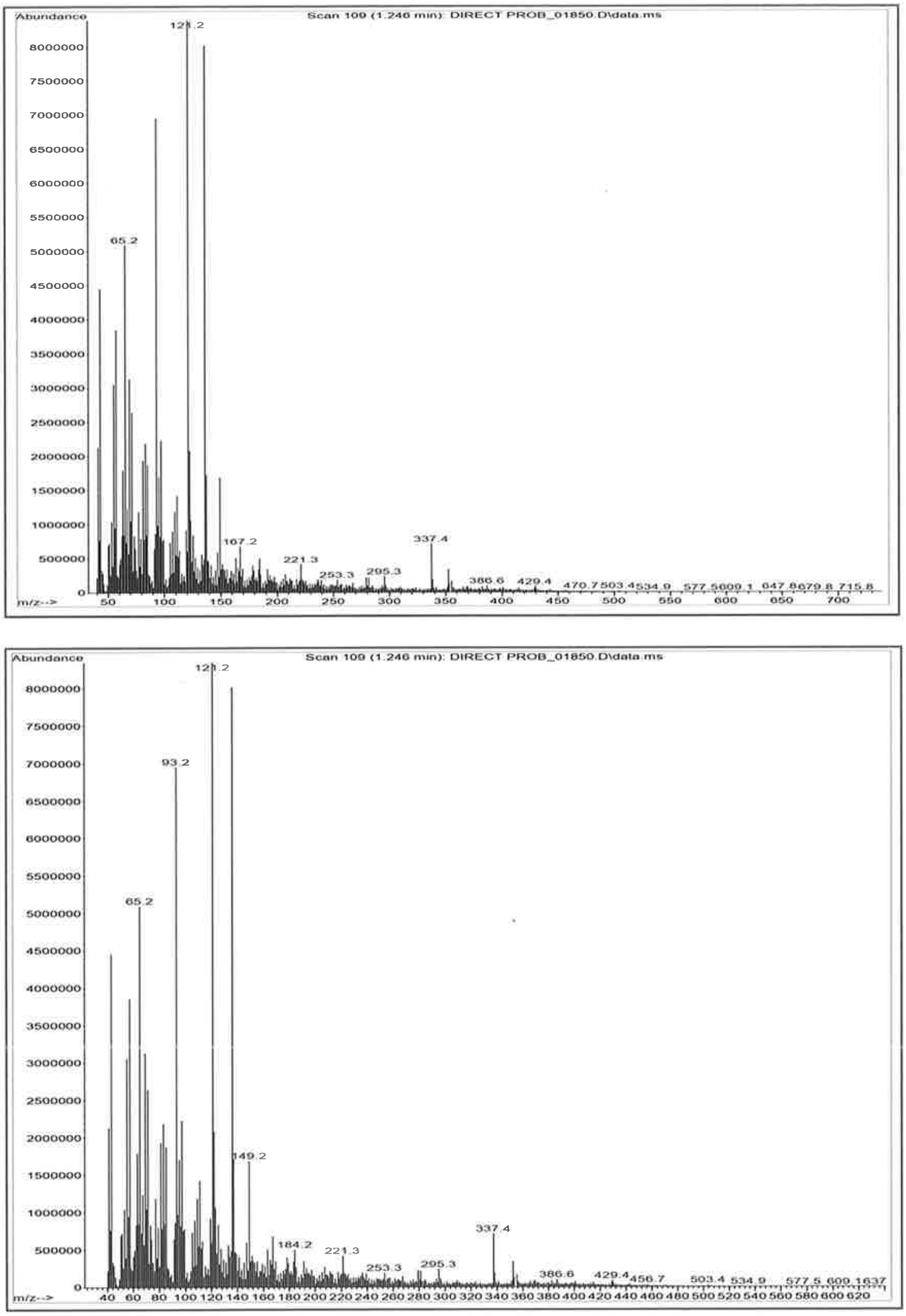
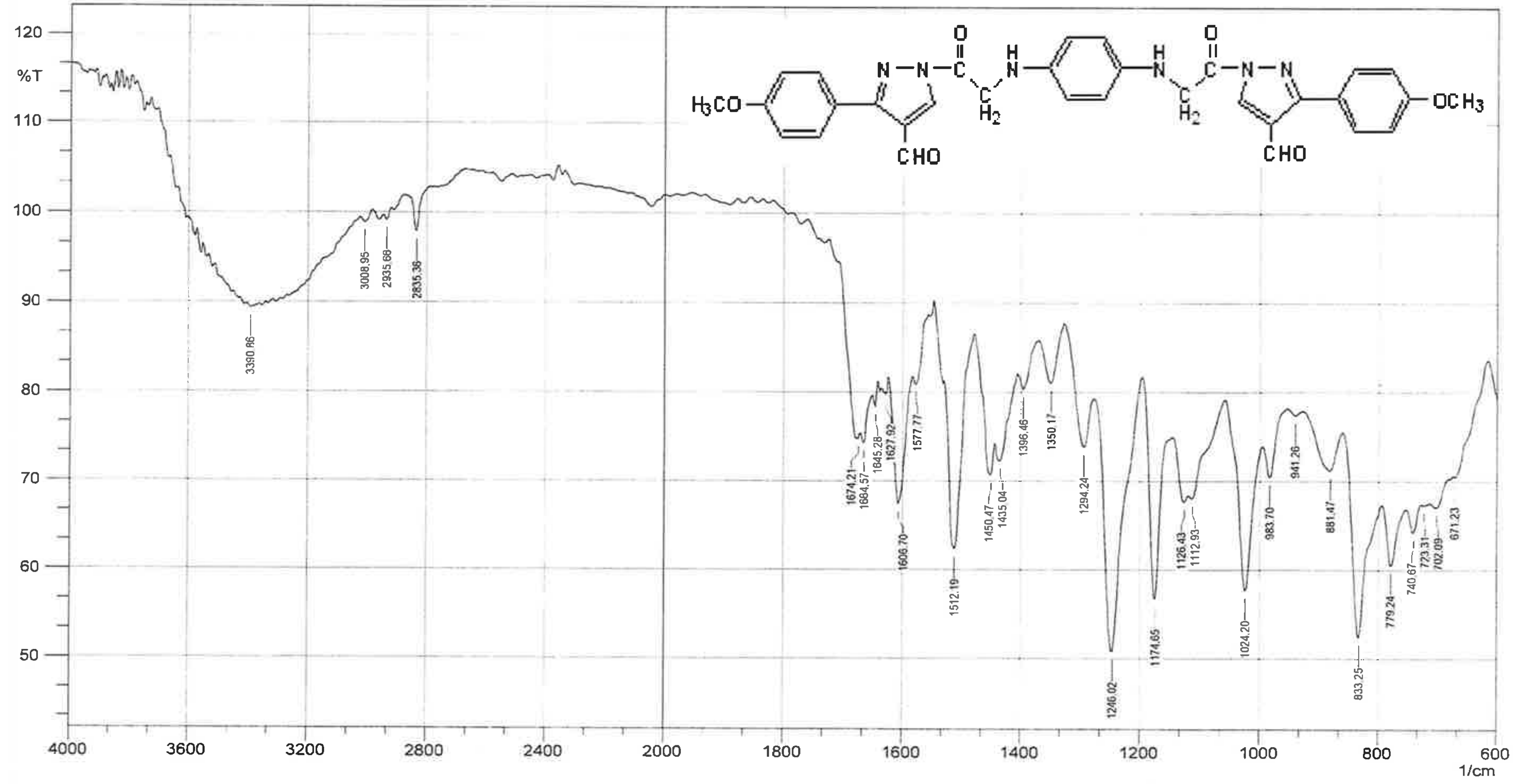
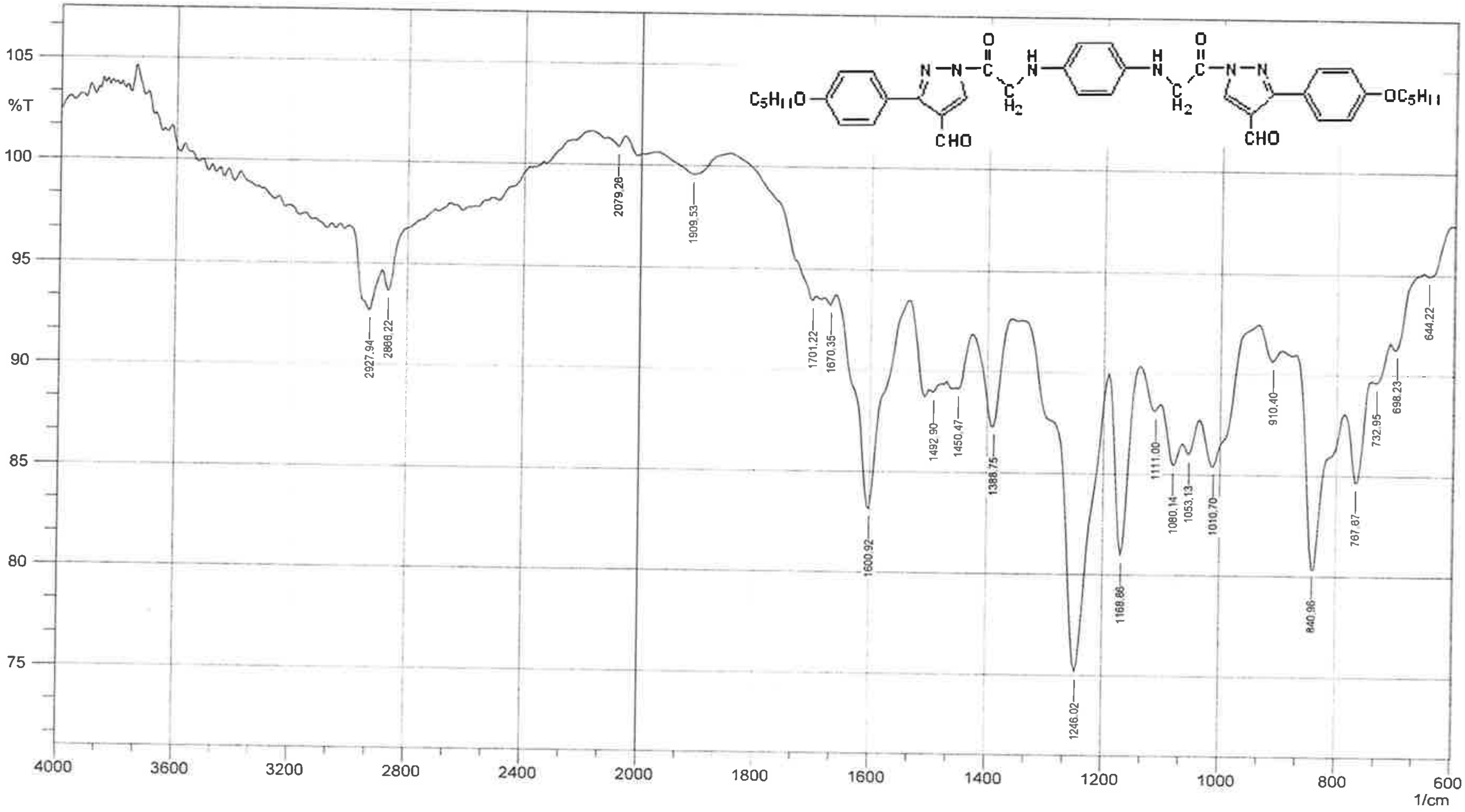


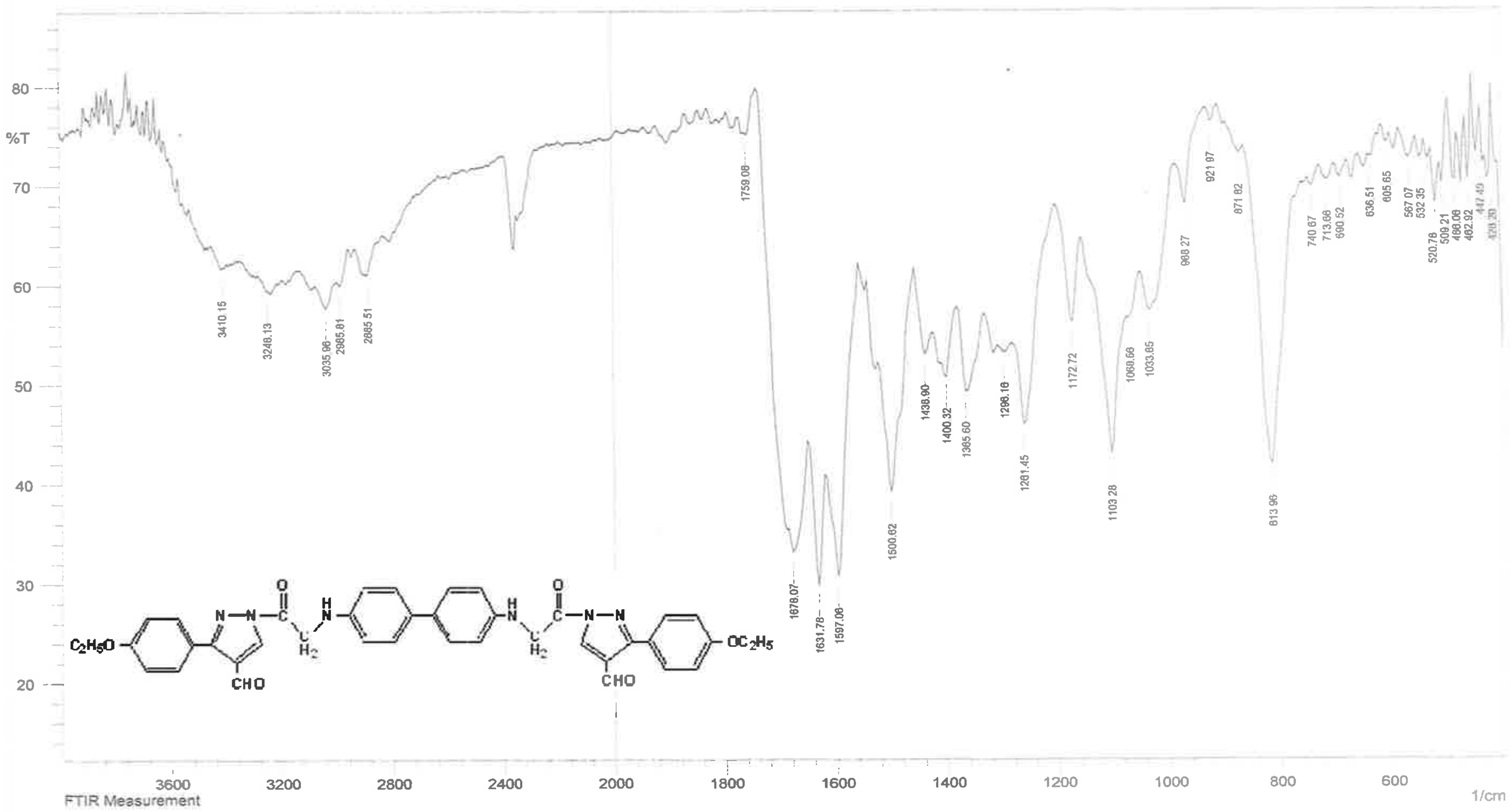
Figure (3-17): The mass spectrum of compound [VII]$_b$



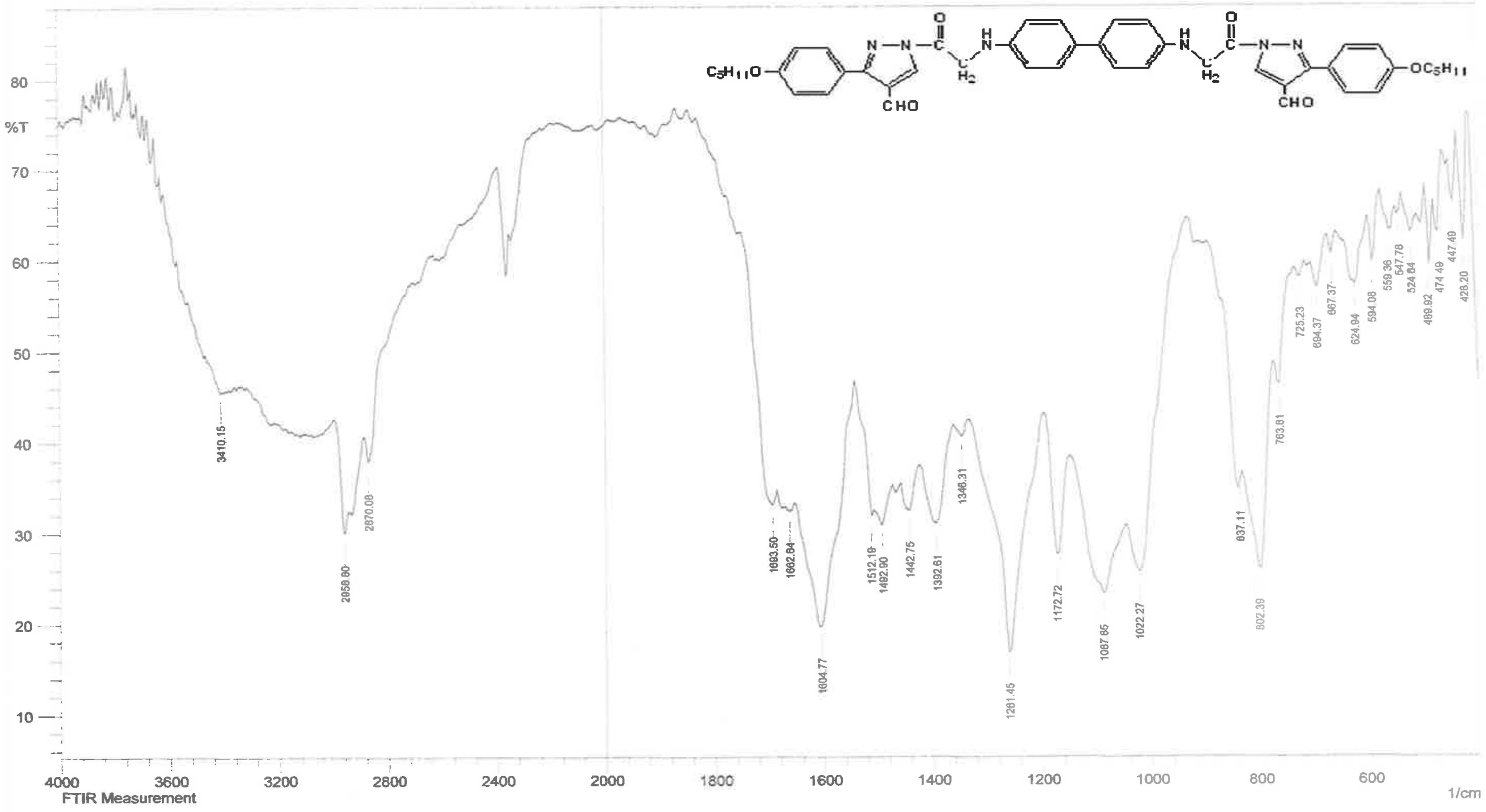
Fgiure(3-18):FTIR spectrum for compound [XII]$_a$



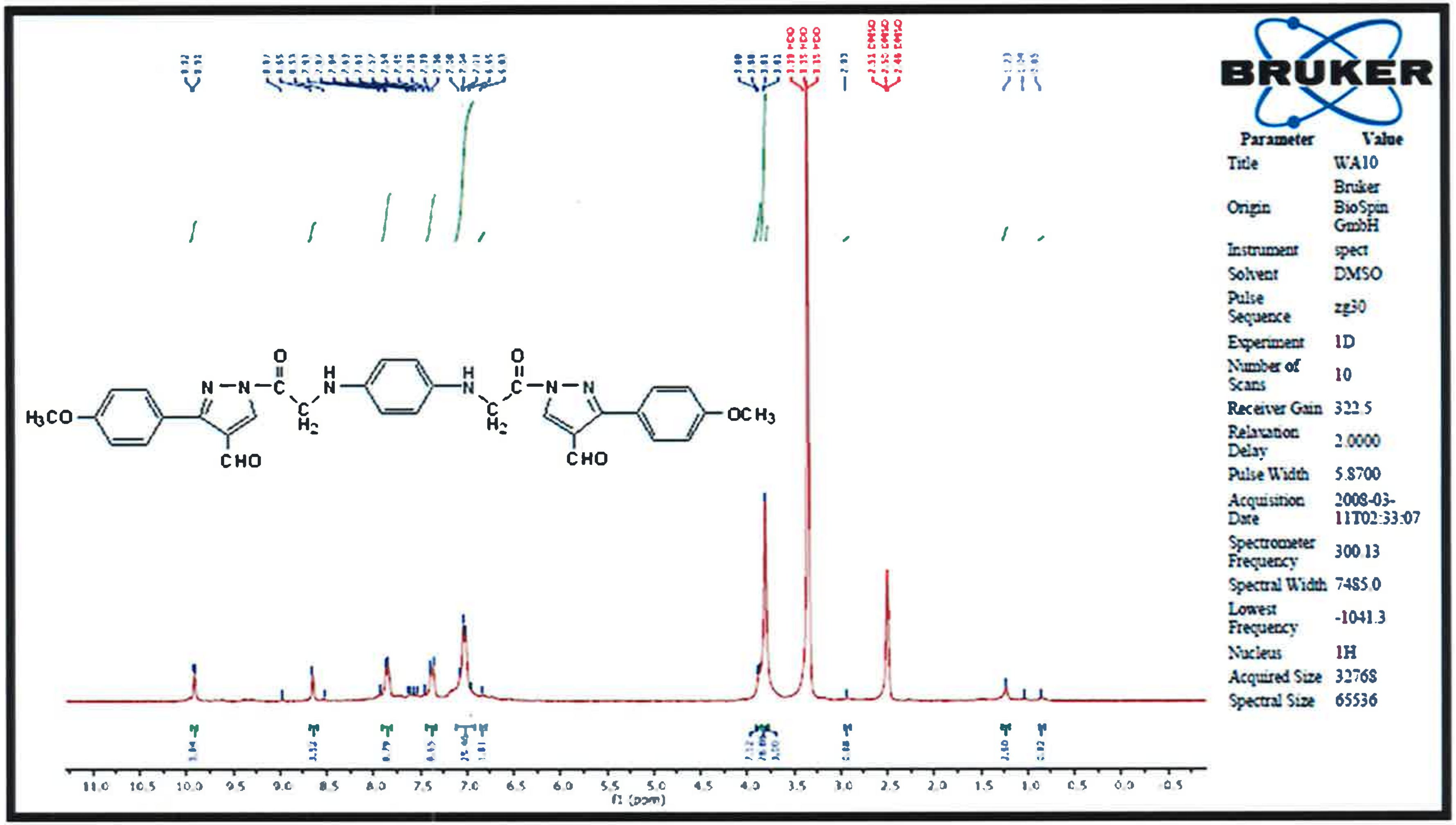
Figure(3-19):FTIR spectrum for compound $[XV]_a$



Figure(3-20): FTIR spectrum for compound [XIII]$_b$

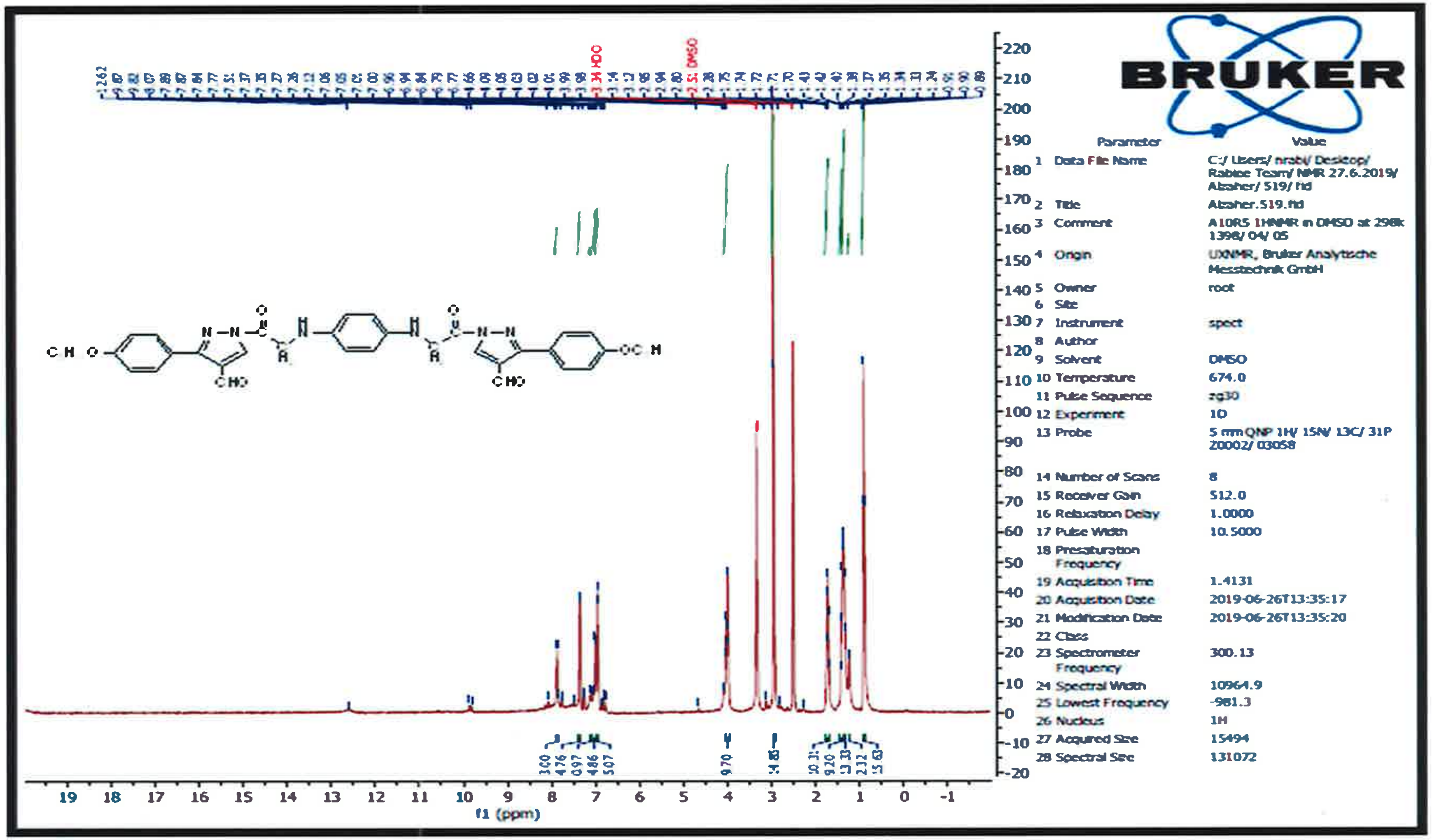


Figure(3-21):FTIR spectrum for compound $[XV]_b$



Parameter	Value
Title	WA10
Origin	Bruker BioSpin GmbH
Instrument	spect
Solvent	DMSO
Pulse Sequence	zg30
Experiment	1D
Number of Scans	10
Receiver Gain	322.5
Relaxation Delay	2.0000
Pulse Width	5.8700
Acquisition Date	2008-03-11T02:33:07
Spectrometer Frequency	300.13
Spectral Width	7485.0
Lowest Frequency	-1041.3
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

Figure(3-22): ^{1}HNMR spectrum for compound $[XII]_a$



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4	Origin	UXNMR, Bruker Analytische Messtechnik GmbH
5	Owner	root
6	Site	
7	Instrument	spect
8	Author	
9	Solvent	DMSO
10	Temperature	674.0
11	Pulse Sequence	zg30
12	Experiment	1D
13	Probe	5 mm QNP 1H/ 15N/ 13C/ 31P Z0002/ 03058
14	Number of Scans	8
15	Receiver Gain	512.0
16	Relaxation Delay	1.0000
17	Pulse Width	10.5000
18	Presaturation Frequency	
19	Acquisition Time	1.4131
20	Acquisition Date	2019-06-26T13:35:17
21	Modification Date	2019-06-26T13:35:20
22	Class	
23	Spectrometer Frequency	300.13
24	Spectral Width	10964.9
25	Lowest Frequency	-981.3
26	Nucleus	1H
27	Acquired Size	15494
28	Spectral Size	131072

Figure(3-23): ^{1}HNMR specrtrum for compound [XV]$_a$

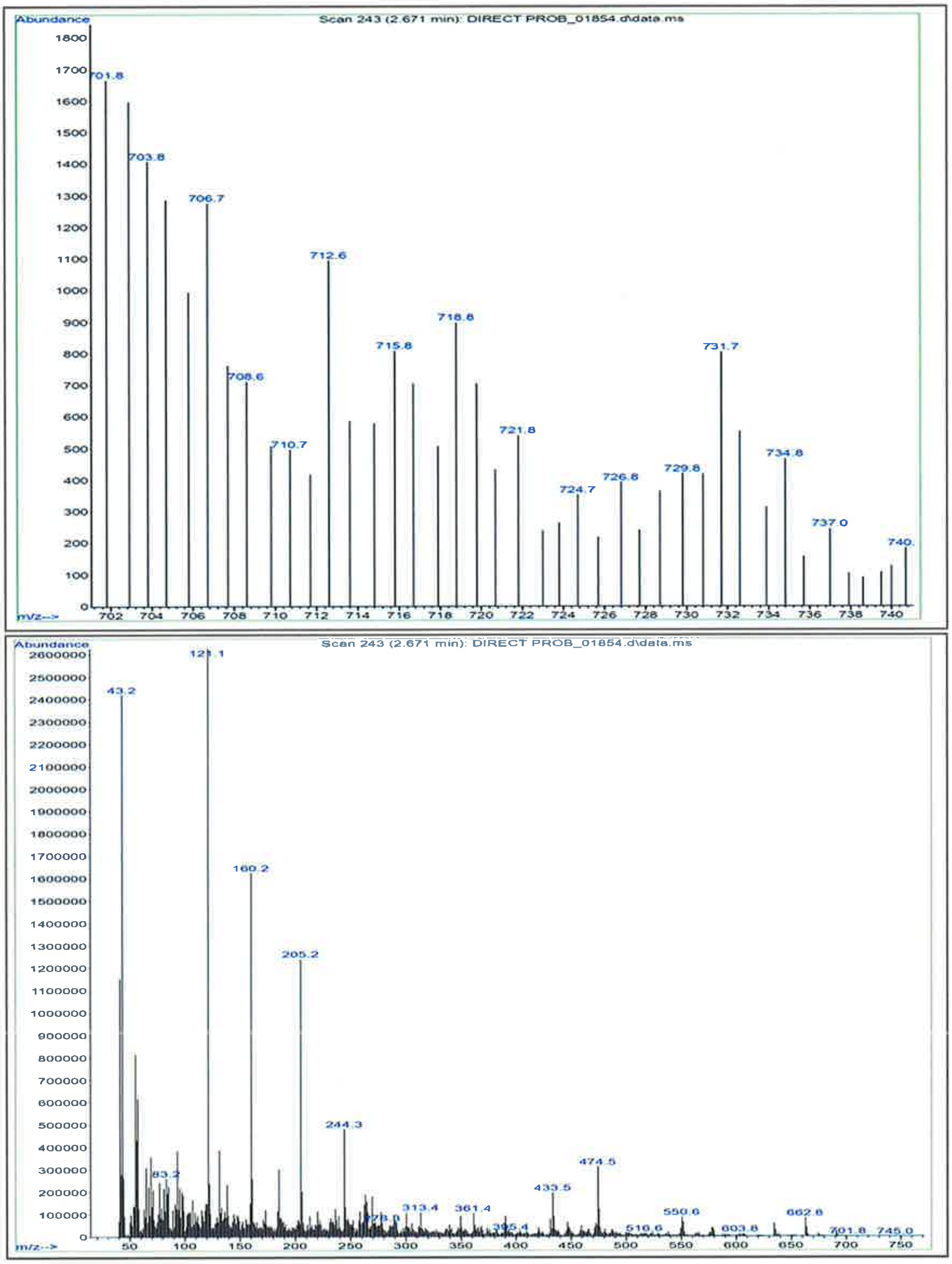
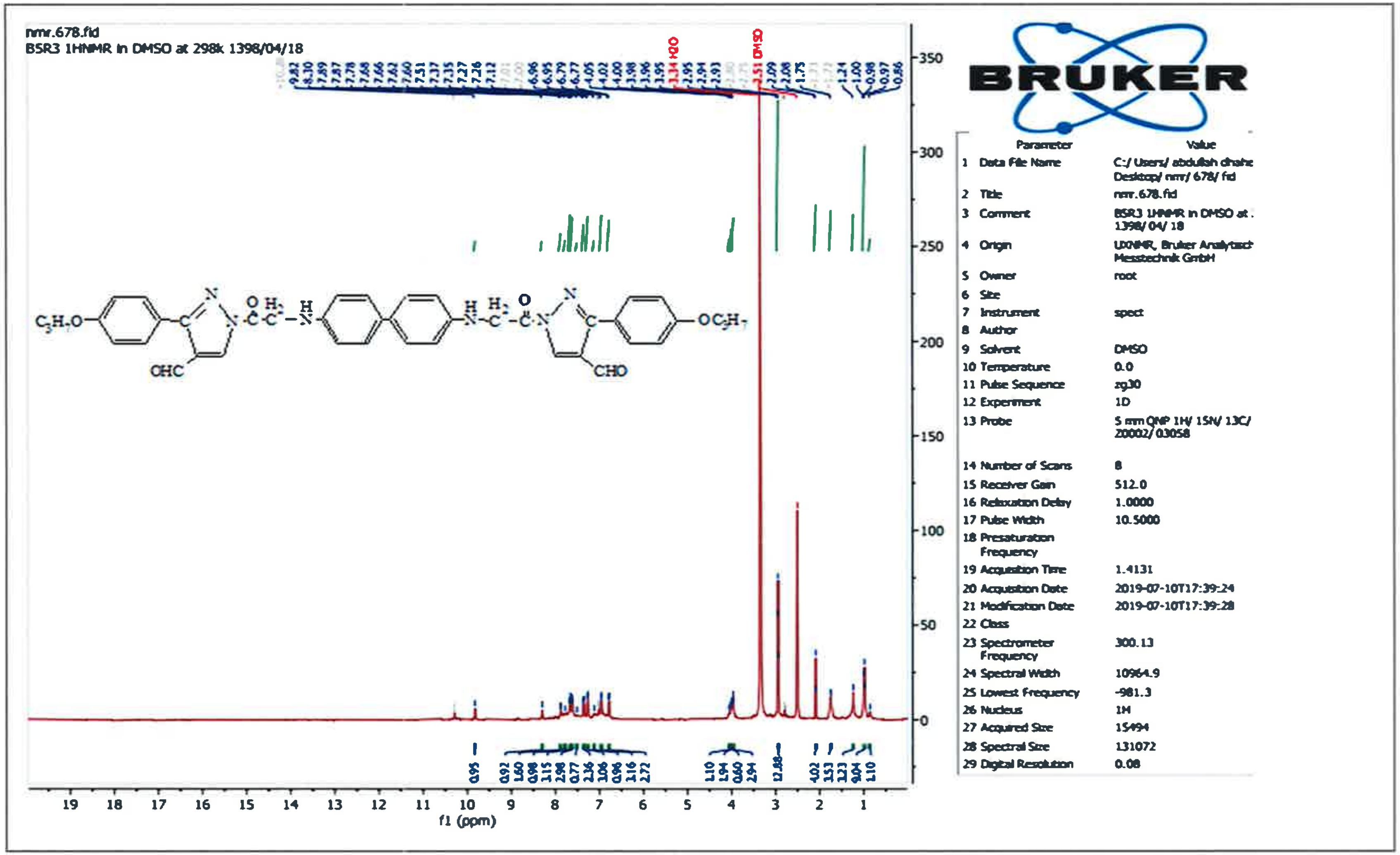


Figure (3-24): The mass spectrum of compound $[XVI]_a$



	Parameter	Value
1	Data File Name	C:/ Users/ abdullah dhahe Desktop/ nmr/ 678/ fid
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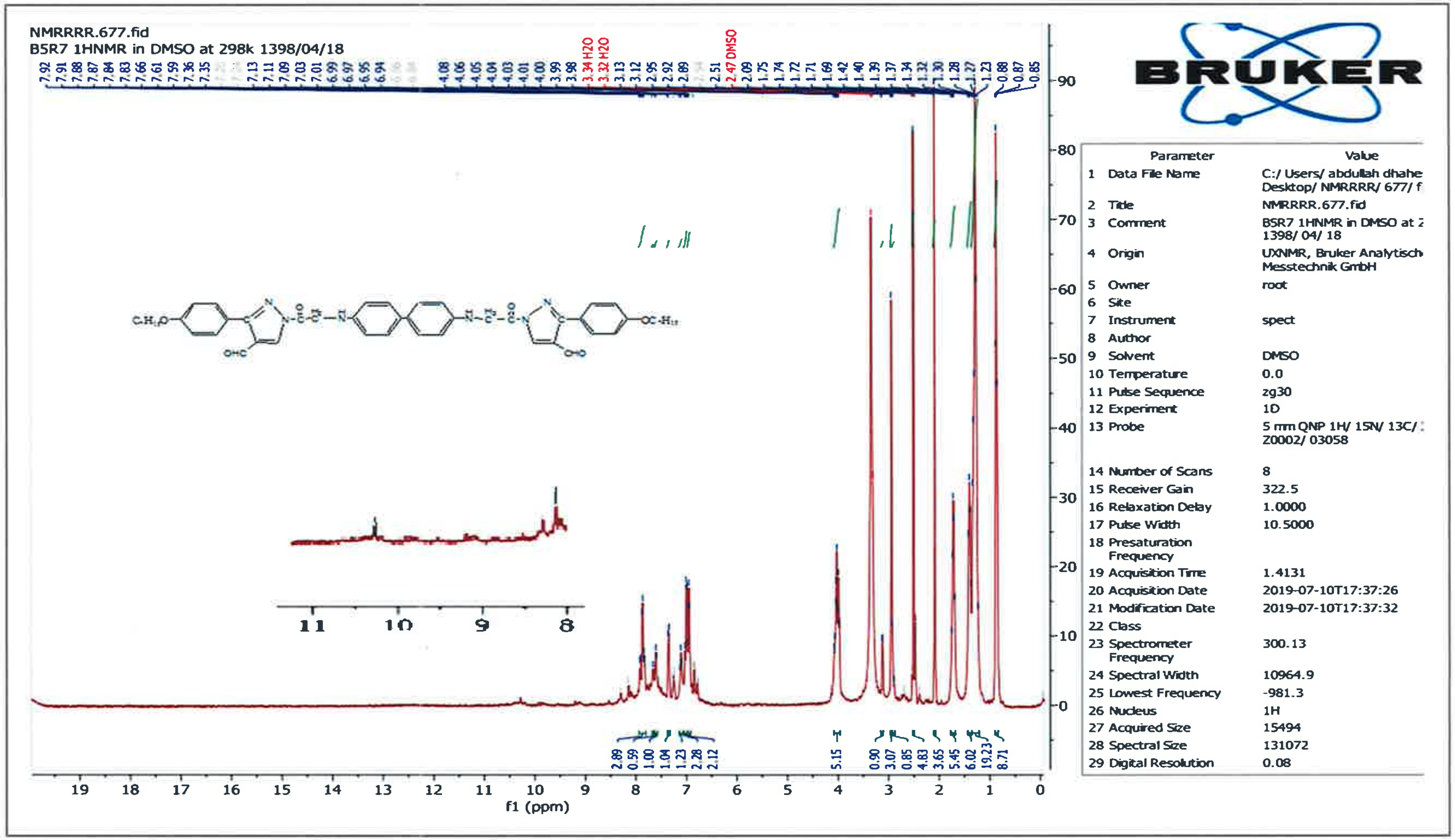
4	Origin	UXNMR, Bruker Analytisch Messtechnik GmbH
5	Owner	root
6	Site	
7	Instrument	spect
8	Author	
9	Solvent	DMSO
10	Temperature	0.0
11	Pulse Sequence	zg30
12	Experiment	1D
13	Probe	5 mm QNP 1H/ 15N/ 13C/ Z0002/ 03058
14	Number of Scans	8
15	Receiver Gain	512.0
16	Relaxation Delay	1.0000
17	Pulse Width	10.5000
18	Presaturation Frequency	
19	Acquisition Time	1.4131
20	Acquisition Date	2019-07-10T17:39:24
21	Modification Date	2019-07-10T17:39:28
22	Class	
23	Spectrometer Frequency	300.13
24	Spectral Width	10964.9
25	Lowest Frequency	-981.3
26	Nucleus	1H
27	Acquired Size	15494
28	Spectral Size	131072
29	Digital Resolution	0.08

Figure(3-25):The ^{1}HNMR spectrum for compound $[XIV]_b$



	Parameter	Value
1	Data File Name	C:/ Users/ abdullah dhahe Desktop/ NMRRRR/ 677/ f
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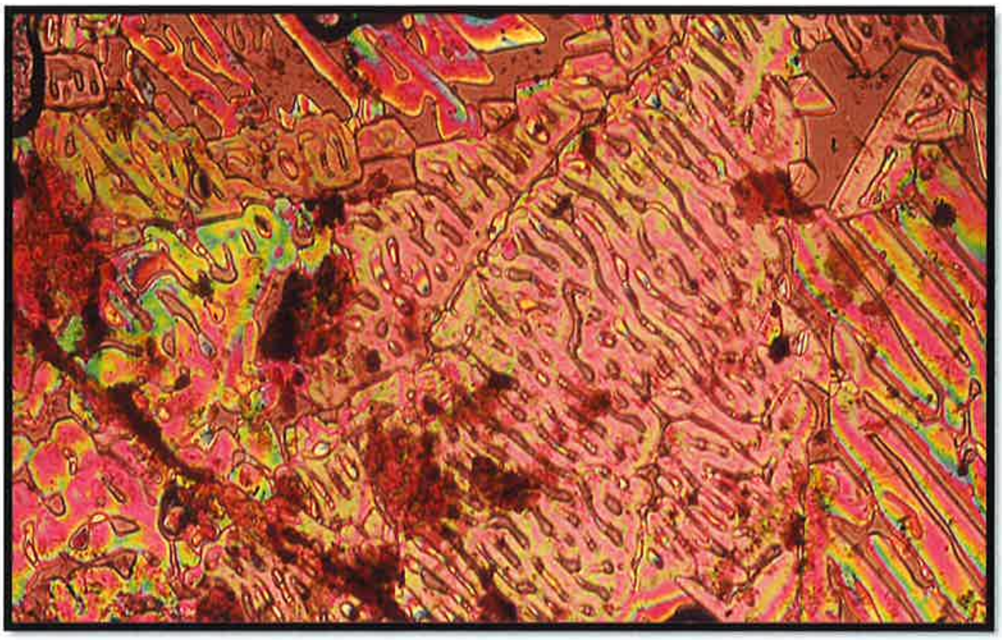
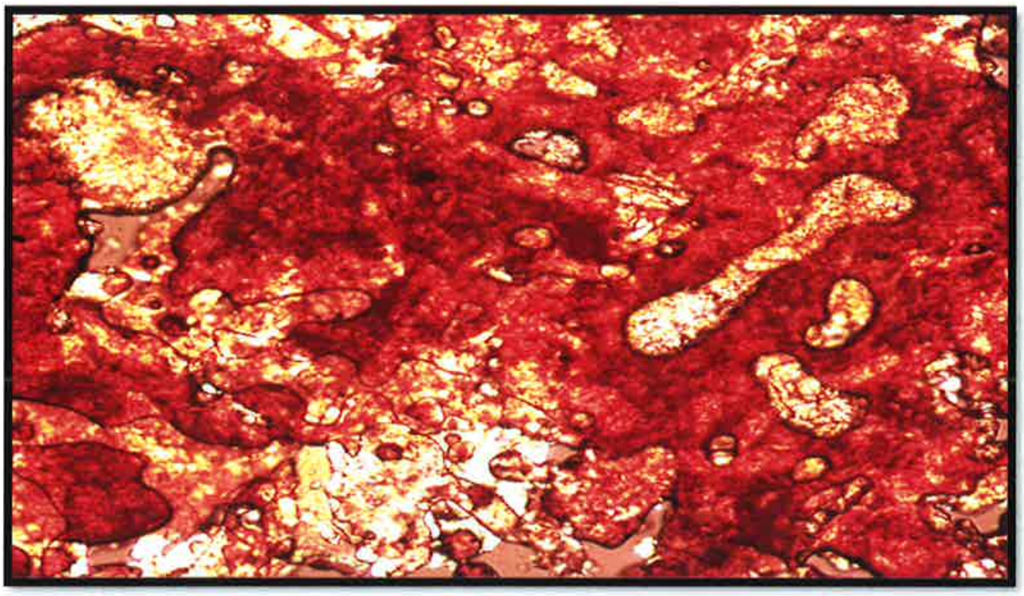
4	Origin	UXNMR, Bruker Analytisch Messtechnik GmbH
5	Owner	root
6	Site	
7	Instrument	spect
8	Author	
9	Solvent	DMSO
10	Temperature	0.0
11	Pulse Sequence	zg30
12	Experiment	1D
13	Probe	5 mm QNP 1H/ 15N/ 13C/ Z0002/ 03058
14	Number of Scans	8
15	Receiver Gain	322.5
16	Relaxation Delay	1.0000
17	Pulse Width	10.5000
18	Presaturation Frequency	
19	Acquisition Time	1.4131
20	Acquisition Date	2019-07-10T17:37:26
21	Modification Date	2019-07-10T17:37:32
22	Class	
23	Spectrometer Frequency	300.13
24	Spectral Width	10964.9
25	Lowest Frequency	-981.3
26	Nucleus	1H
27	Acquired Size	15494
28	Spectral Size	131072
29	Digital Resolution	0.08

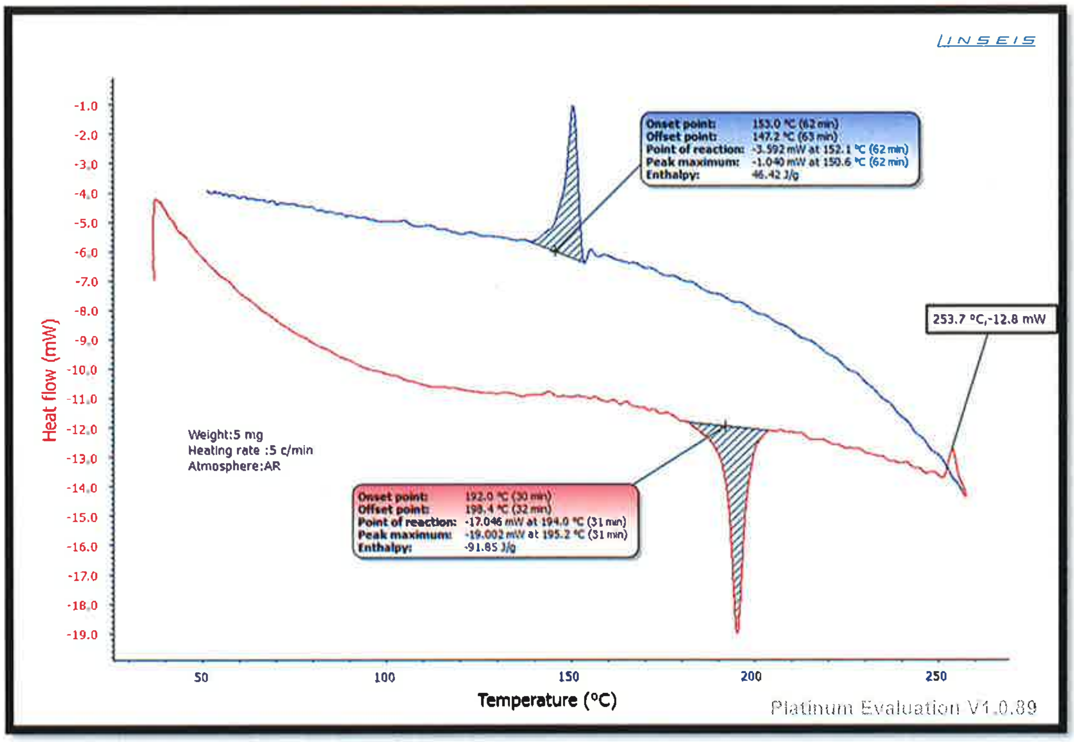
Figure(3-26): The ^{1}HNMR spectrum for compound $[XVII]_b$



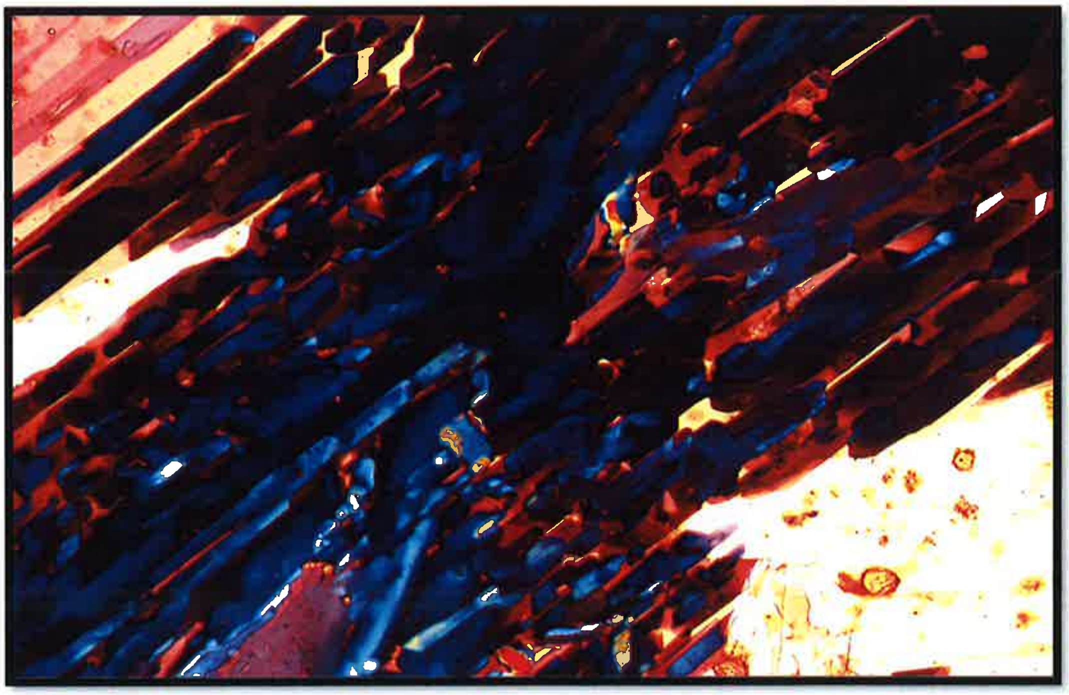
Figure(3- 27):Cross polarizing optical textures of nematic phase for compound $[V]_a$ at 203°C



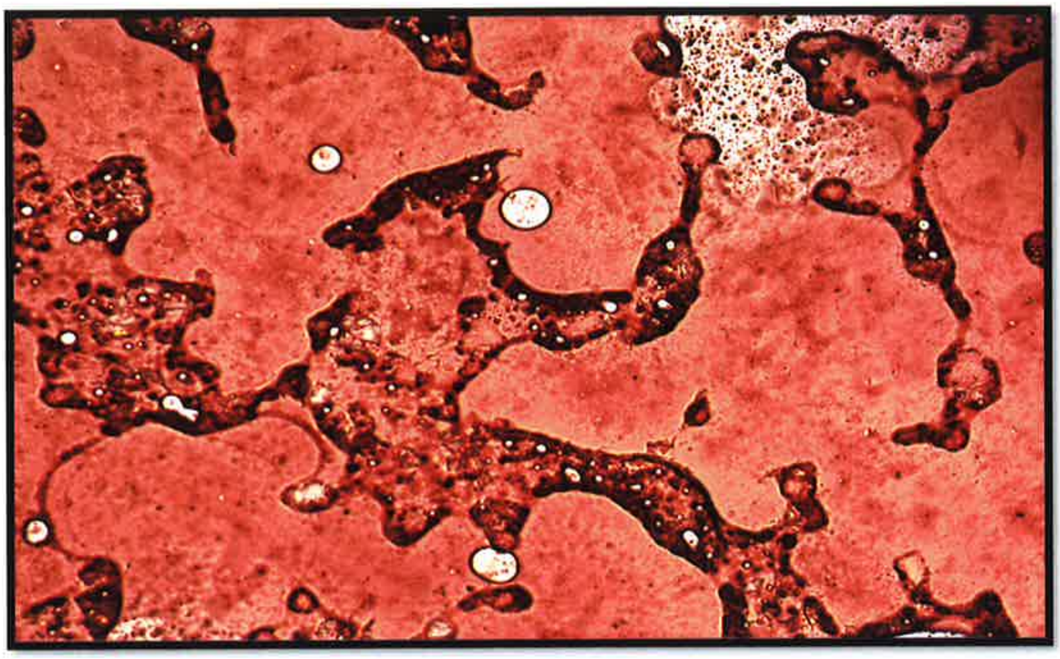
Figure(3-28): Cross polarizing optical textures of nematic thread-like texture for compound $[VII]_a$ at 130 °C



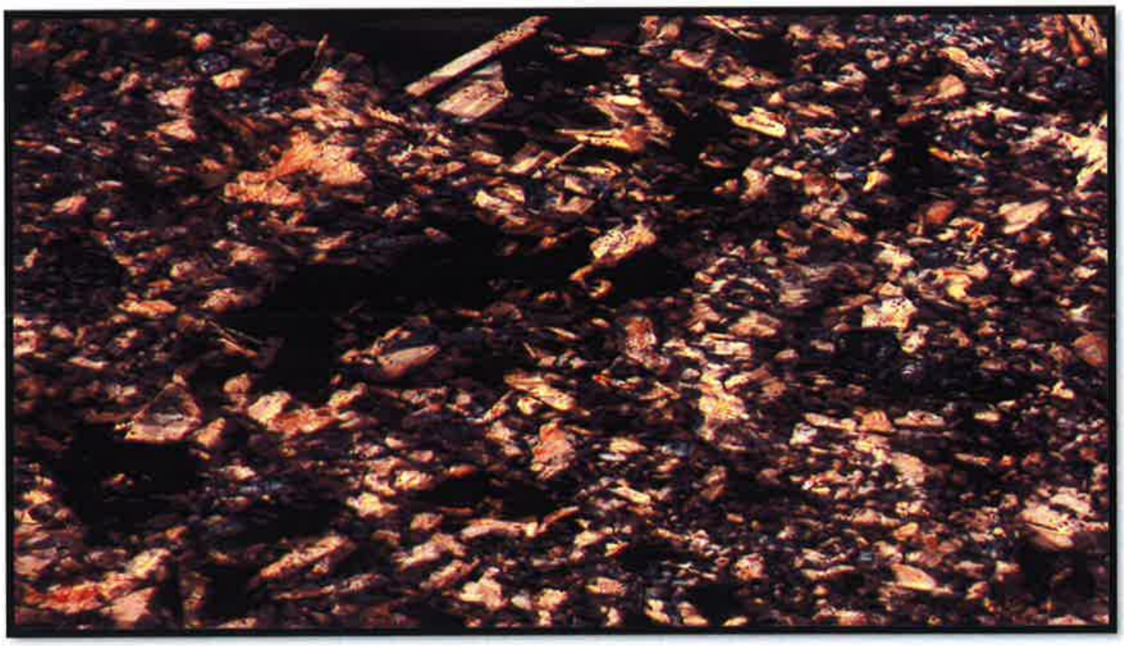
Figure(3-29): DSC thermogram for compound $[V]_a$



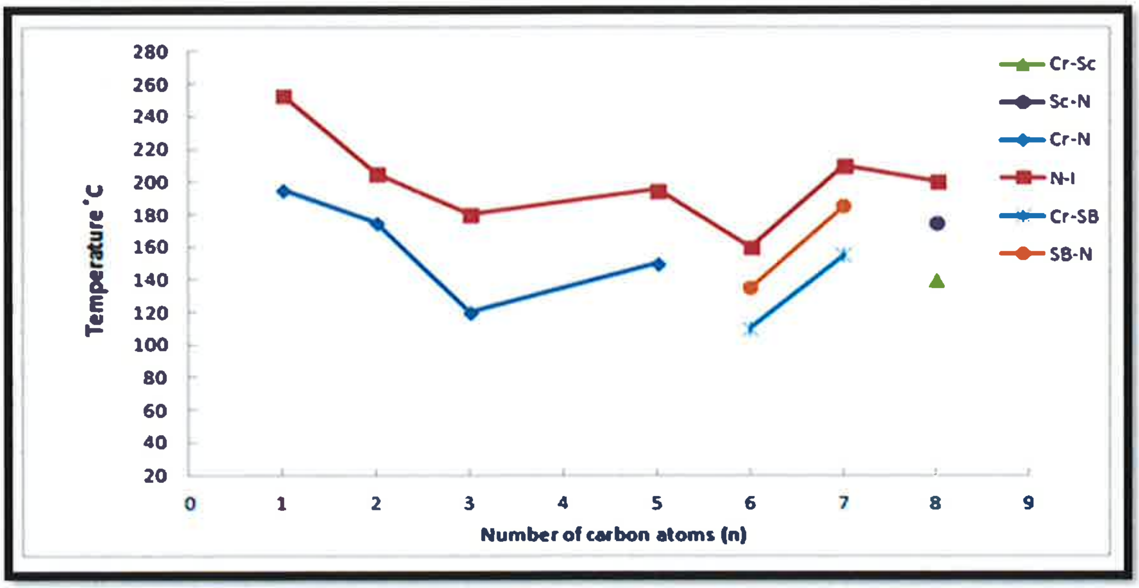
Figure(3- 30) : Cross polarizing optical textures of smectic B phase for compound $[IX]_a$ at 120°C



Figure(3-31): Cross polarizing optical textures of nematic thread-like texture for compound $[X]_a$ at 200 °C

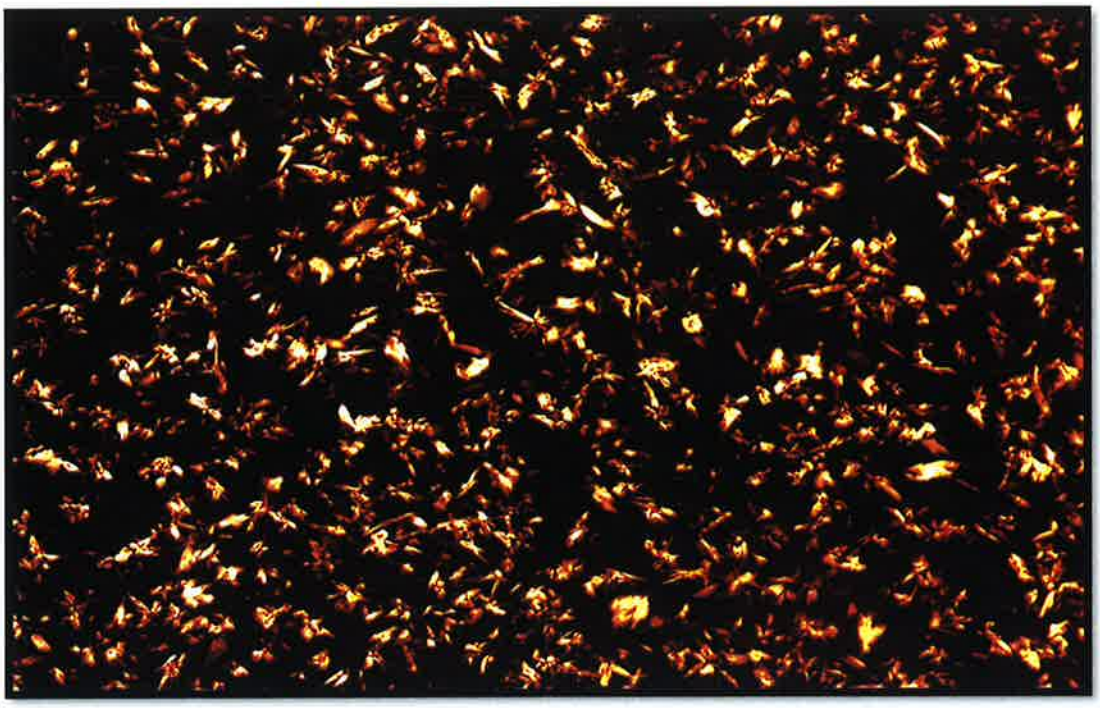


Figure(3-32): Cross polarizing optical textures of smectic C phase of compound $[XI]_a$ at 160 °C

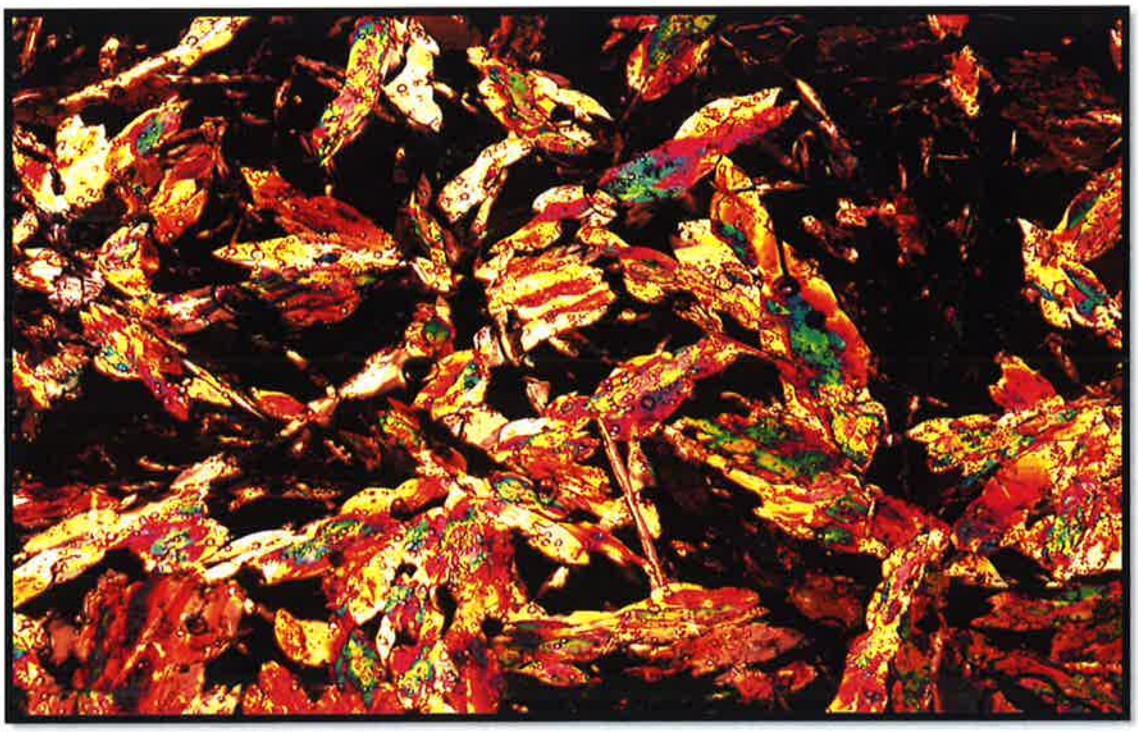


Figure(3-33): Dependence of transition temperatures on the increasing number of carbon atoms (*n*) in the terminal alkoxy chains for the $[V\text{-}XI]_a$ series compounds

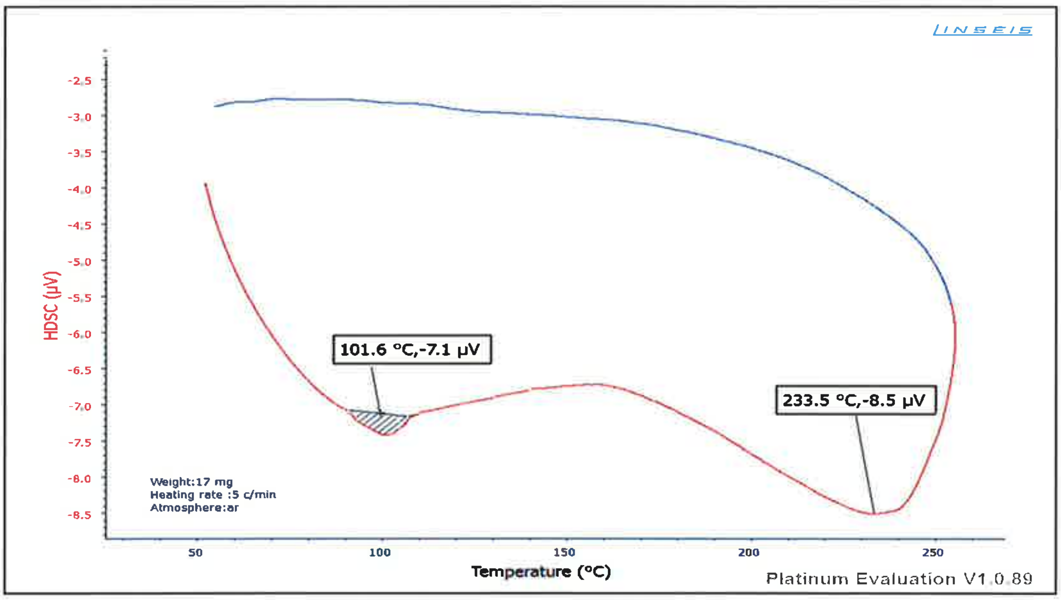
Figure(3-35): Cross polarizing optical textures of nematic texture for compound $[VI]_b$ at 200 °C



Figure(3-36) : Cross polarizing optical textures of smectic A phase for compound $[IX]_b$ at 130 °C



Figure(3-37) : Cross polarizing optical textures of smectic B phase for compound$[X]_b$ at 185°C



Figure(3-38): DSC thermogram for compound $[X]_b$

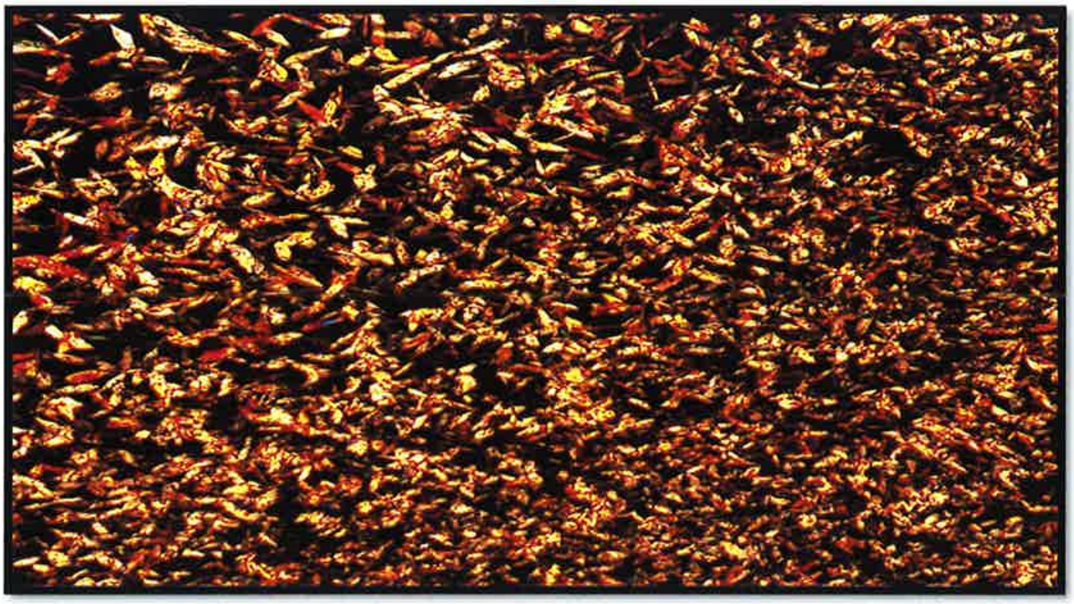
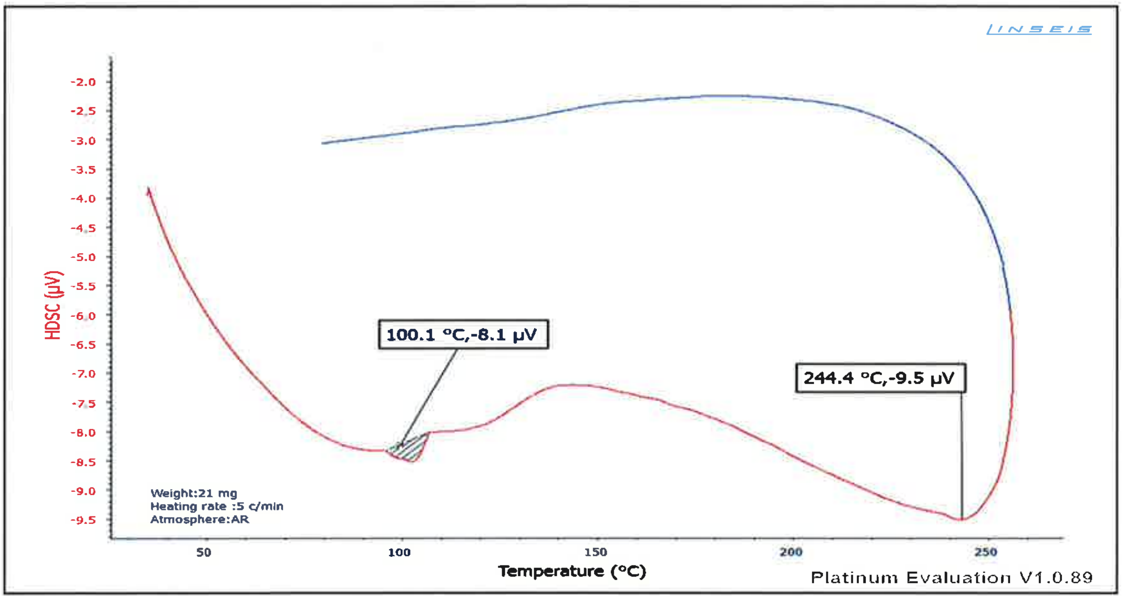
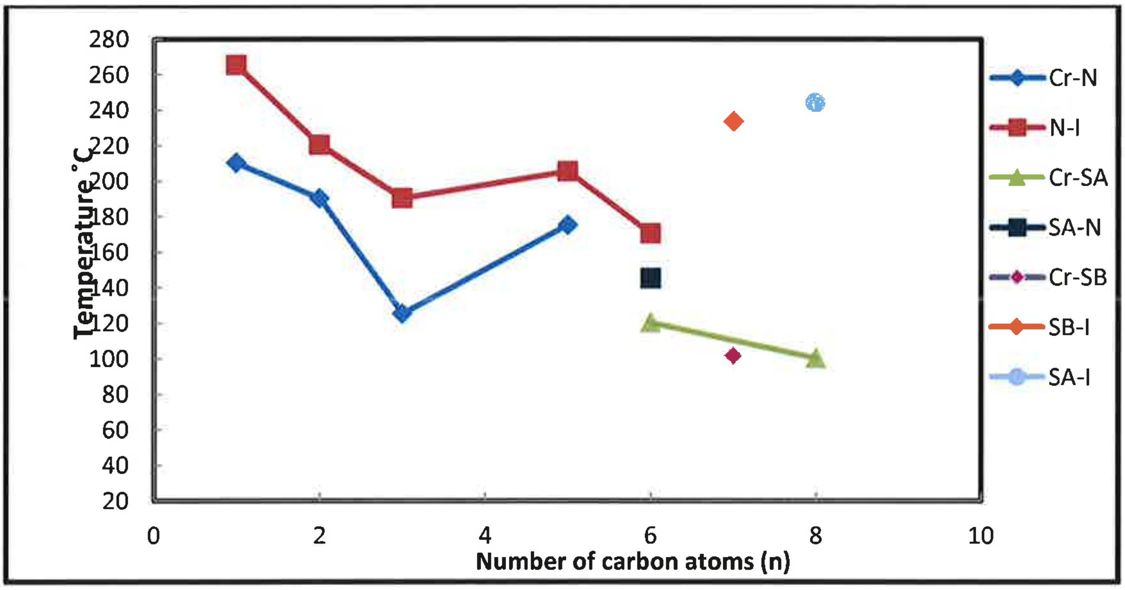


Figure (3-39) : Cross polarizing optical textures of smectic A phase for compound$[XI]_b$ at 140 °C



Figure(3-40): DSC therrmogram for compound $[XI]_b$



Figure(3-42): Dependence of transition temperatures on the increasing number of carbon atoms (*n*) in the terminal alkoxy chains for the $[V\text{-}XI]_b$ series compounds

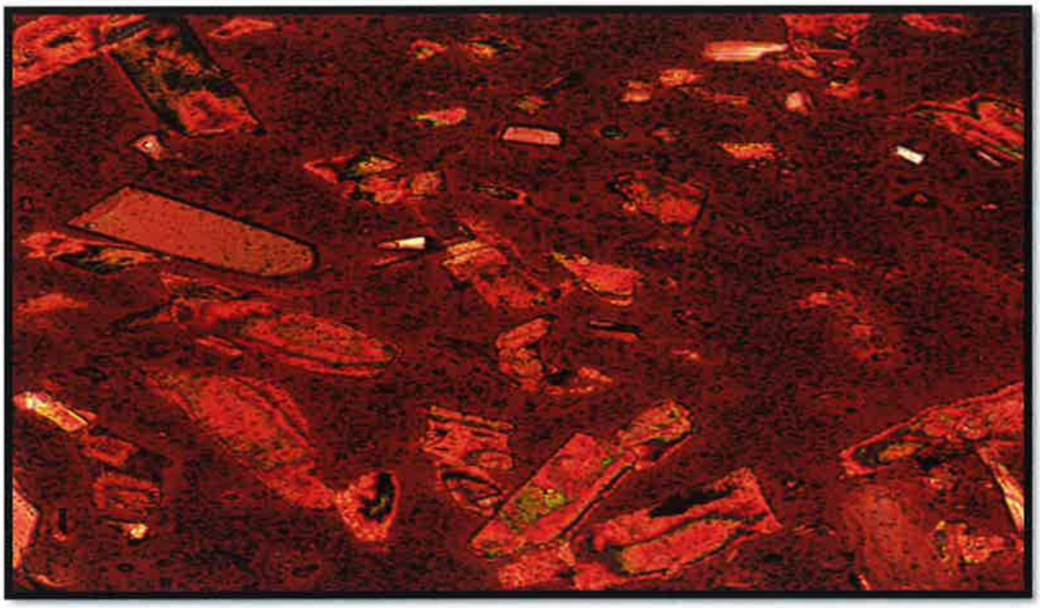


Figure (3-43): Cross polarizing optical textures of nematic phase for compound $[XVI]_a$ at 135 °C

Figure (3-44): Cross polarizing optical textures of droplets nematic phase for compound $[XVII]_a$ at 95 °C

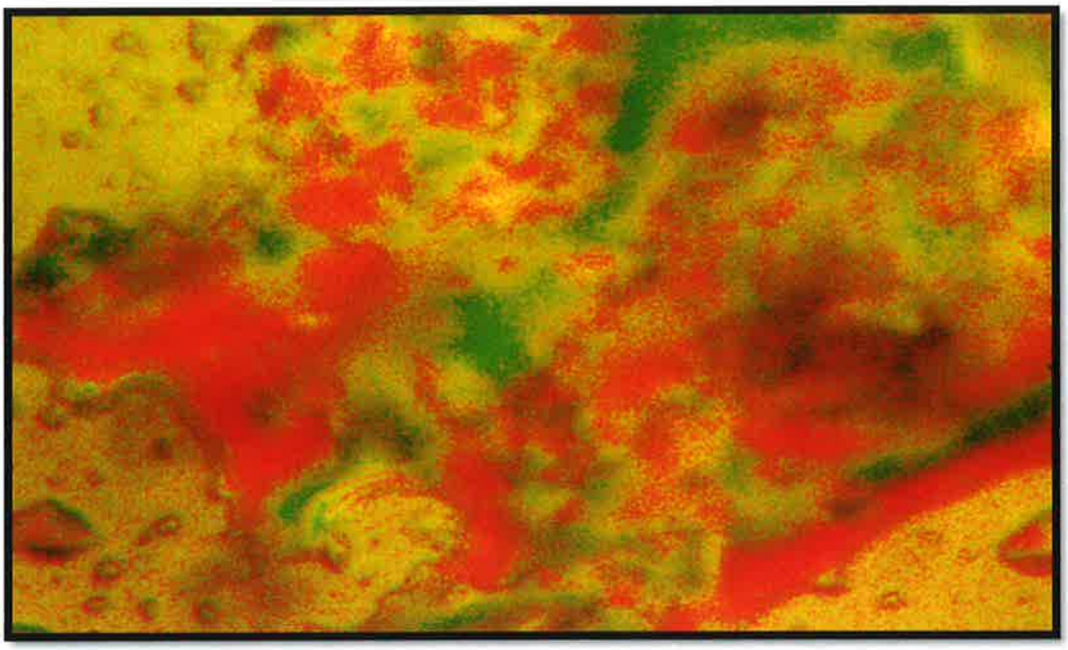
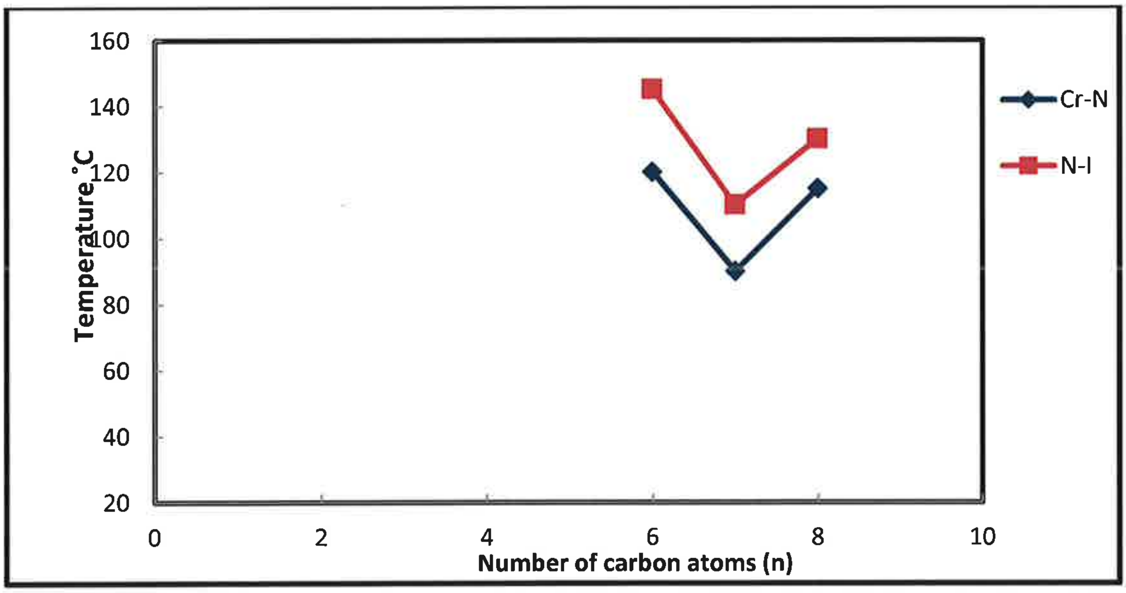


Figure (3-45): Cross polarizing optical textures of nematic phase for compound $[XVIII]_a$ at 125 °C



Figure(3-47): Dependence of transition temperatures on the increasing number of carbon atoms (*n*) in the terminal alkoxy chains for the $[XII\text{-}XVIII]_a$ series compounds

Figure (3-48): Cross polarizing optical textures of smectic B phase for compound $[XIV]_b$ at 80 °C

Figure (3-49): Cross polarizing optical textures of nematic phase thread-like texture for compound $[XVI]_b$ at 145 °C

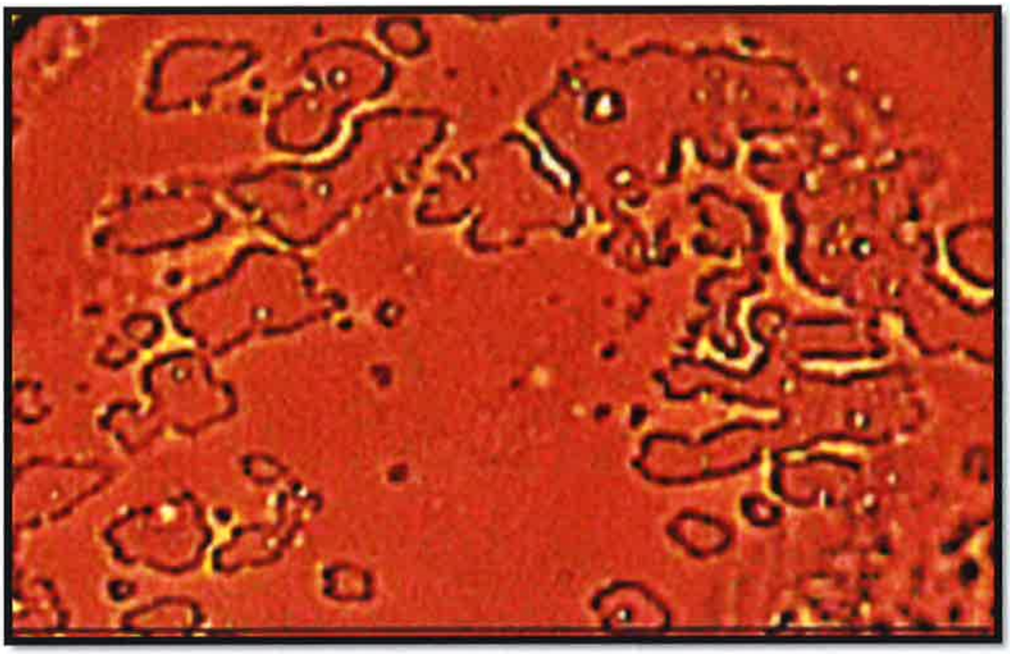
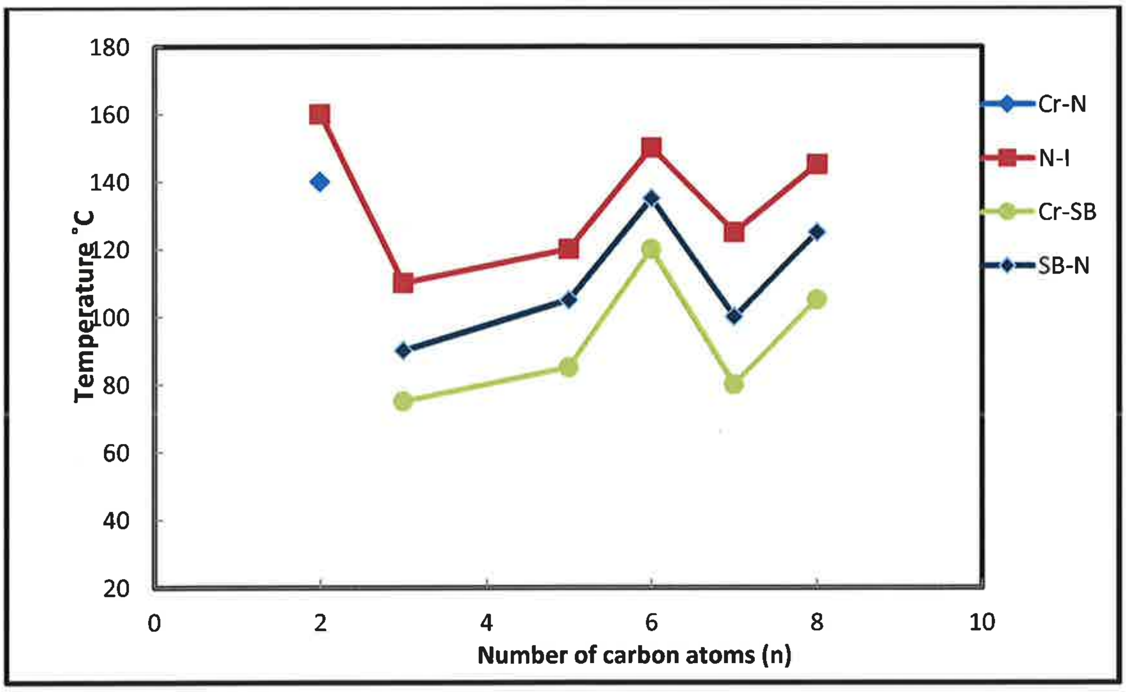


Figure (3-50): Cross polarizing optical textures of nematic phase thread-like texture for compound [XVIII]$_b$ at 130 °C



Figure(3-52): Dependence of transition temperatures on the increasing number of carbon atoms (*n*) in the terminal alkoxy chains of [XII-XVIII]$_b$ series compounds

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الخلاصة

هذا العمل يتضمن تحضير و تشخيص و دراسة خصائص البلورات السائله لبعض المشتقات الجديده التي تحتوي على حلقة البايرازول كالاتي.

1- تخليق وتشخيص مشتقات بايرازول جديده $[XII\text{-}XVIII]_{a,b}$ كما في الخطوات الاتيه:

أ- تخليق مركبات $[I]_{a,b}$ ،هذه المركبات خلقت بواسطة تفاعل 1,4- فنلين ثنائي الامين او البنزدين مع كلوروحامض الخليك و خلات الصوديوم في الايثانول كمذيب.

ب- مركبات الاسترات $[II]_{a,b}$ تحضر بواسطة تفاعل تصعيد للمركبات $[I]_{a,b}$ مع الميثانول بوجود H_2SO_4 كعامل مساعد.

ت- حضرت مركبات حامض الهايدرازايد $[III]_{a,b}$ بواسطة تفاعل مركبات الاسترات $[II]_{a,b}$ مع الهايدرازين المائي في الايثانول.

ث- تفاعل مركبات حامض الهايدرازايد $[III]_{a,b}$ مع معوض الاسيتوفينون $[IV]_n$ لتحضير هيدرازونات معوض الاسيتوفينون $[V\text{-}XI]_{a,b}$.

ج- حضرت مشتقات 4-فورمل بايرازول $[XII\text{-}XVIII]_{a,b}$ بواسطة تخليق هيدراونات معوض الاسيتوفينون $[V\text{-}XI]_{a,b}$ مع كاشف فليسماير- هوك $DMF/POCl_3$.

2- المركبات المحضره تم تشخيصها بواسطة بياناتها الطيفيه ، طيف الاشعة تحت الحمراء FTIR ،طيف الرنين النووي المغناطيسي ^1HNMR و مطيافية الكتله (للبعض).

3- دراسة خصائص البلورات السائله (بواسطة مسعر المسح التفاضلي DSC ومجهرالضوء المستقطب) للمركبات المحضره اظهرت:

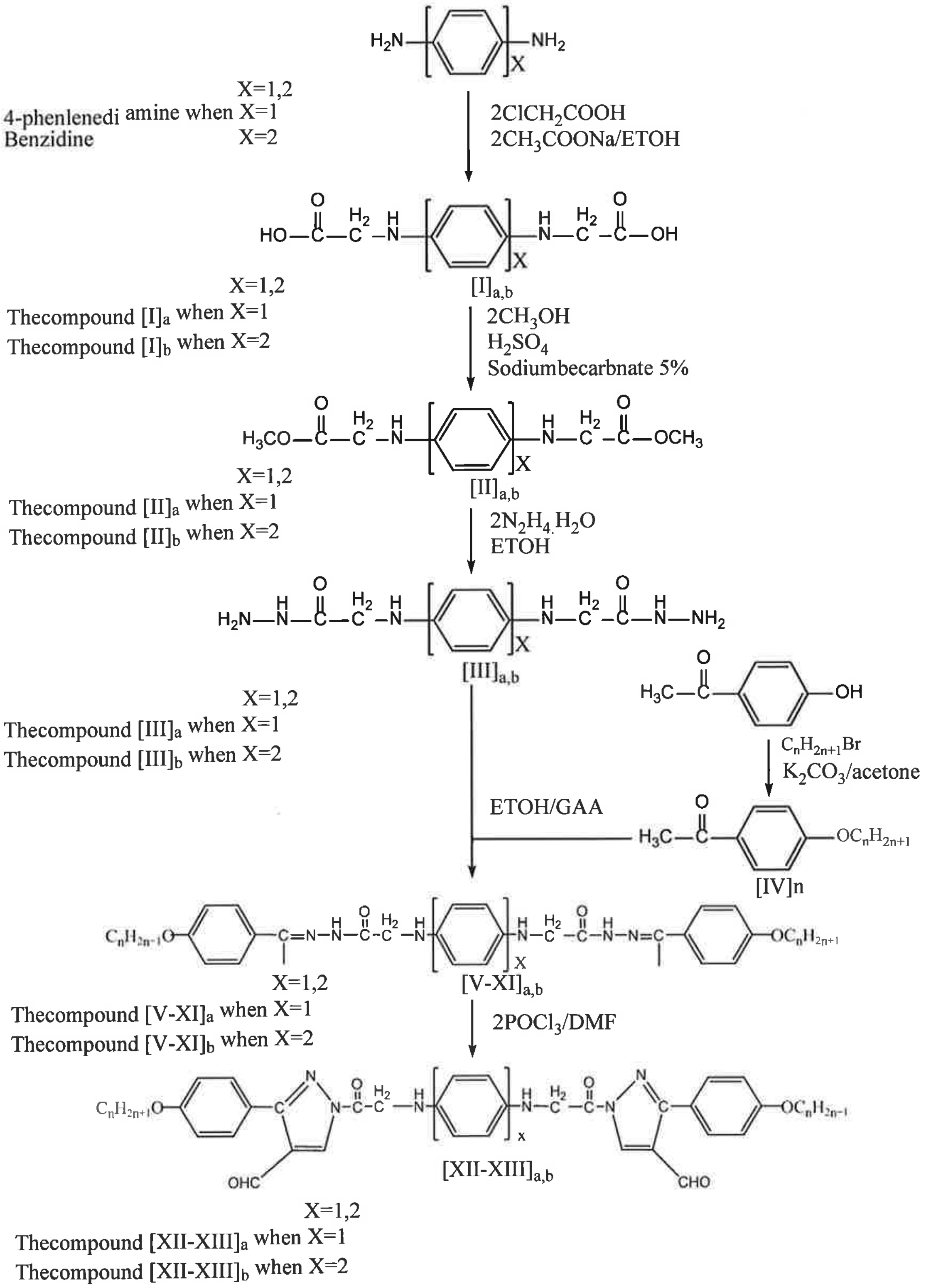
أ- المركبات $[V\text{-}VIII]_a$ اظهرت طور نيماتي انعكاسي فقط بينما المركبات $[IX]_a$ و $[X]_a$ اظهر اطوار متعدده انعكاسيه سمكتيه نوع B وطور نيماتي اضافة الى ذالك المركب $[XI]_a$ اظهر طور انعكاسي سمكتي C و طور نيماتي.

ب- المركبات $[V\text{-}VIII]_b$ اظهرت طور انعكاسي نيماتي فقط و المركب $[IX]_b$ اظهر اطوار متعدده انعكاسيه سمكتيه A بالاضافه الى الطور النيماتي، بينما المركب $[X]_b$ اظهر طور سمكتي نوع B فقط. اضافة الى المركب$[XI]_b$ اظهر طور سمكتي A فقط.

ت- المركبات $[XII\text{-}XV]_a$ لم تظهر اي سلوك بلوري سائل، لكن تتغير من حالة البلورات الصلبه الى السائل المماثل. بينما المركبات$[XVI\text{-}XVIII]_a$ اظهرت اطوار نيماتيه انعكاسيه فقط.

ث- المركب $[XII]_b$ لم يظهر اي سلوك بلوري سائل، تغير من حالة البلورات الصلبه الى السائل المماثل. بينما المركبات$[XIII\text{-}XVIII]_b$ اظهرت اطور متعدده انعكاسيه سمكتيه B بالاضافه الى الطور النيماتي.

هذا العمل يمكن تلخيصه بالمخطط (I) الاتيه:



n=1,2,3,5,6,7,8

Scheme(1)

جمهورية العراق

وزارة التعليم العالي والبحث العلمي
جامعة بغداد

كلية التربية للعلوم الصرفة/ إبن الهيثم

قسم الكيمياء

تحضير ، تشخيص ودراسة الخصائص البلورية السائلة لبعض المشتقات الجديدة التي تحتوي على حلقة البايرازول

رساله مقدمة الى

مجلس كلية التربية للعلوم الصرفة/ ابن الهيثم- جامعة بغداد كجزء من
متطلبات نيل درجة ماجستيرعلوم في الكيمياء

من قبل

علاء نشمي كردي

بكالوريوس تربية في الكيمياء/ كلية التربية للعلوم الصرفة / ابن الهيثم- جامعة بغداد 2016

بأشراف

أ. م. د. نسرين حسين كرم

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