Republic of Iraq
Ministry of Higher Education
& Scientific Research
University of Baghdad/
College of Education for
Pure science–Ibn AL–Haitham
Chemistry Department

Synthesis ,Characterization and Study of Liquid crystalline Behavior of New thiazolidin-4-one and 1,3,4-oxadiazole Compounds

A Thesis

Submitted to the Council of College of Education For Pure science–Ibn AL–Haitham, University of Baghdad In Partial Fulfillment of the Requirements for the Degree of Master of Science in Chemistry

By

Alaa Kadim Shanshal

B.Sc.College Of Education For Pure science–Ibn AL–Haitham,University of Baghdad in (2002-2003)

Supervised by

Asst.Prof. Dr. Nisreen Hussain Karam

1439 A.H **2017 A.D**

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This is dedicated

To

my father

Alaa Kadim

ACKNOWLEDGMENT

"O Allah to you belongs all praise, you are the light of the heavens and the earth and all that is within them. To you belongs all praise, you are the lord of the heavens and the earth and all that is within them. To you belongs all praise, and the kingdom of the heavens and the earth and all that is within them, and the prayer and peace upon the master of the mankind our beloved messenger of Allah "Muhammad" and his pure progeny: companions and all those who follow his way in charity to Judgment Day."

I wish to express my sincere gratitude and great appreciation to my Supervisors Asst.Prof. Dr. Nisreen H. Karam for her guidance and her encouragement throughout this work.

Sincere thanks are also to the Dean of the College of Education/ Ibn Al-Haitham. I express my thanks to the Head of the Chemistry Department and the staff, also I would like to thank Asst. Prof. Dr. Najwa Issac Abdulla for assistance.

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My thanks to all my professors in the department of chemistry and to the staff members of College of Education for pure science _Ibn_AL_Haitham.

Finally, I am deeply indebted to my family for their support and patience during the years of my study.

Alaa

2017

Abstract

This work includes synthesis , characterization and study the liquid crystalline behavior of some new compounds containing heterocyclic, as follows :

Synthesize two series containing thiazolidin-4-one ring ,were synthesized by converted resorcinol or hydroquinone to a corresponding compounds [I] and [II] by refluxing with chloracetyl chloride, then the result compounds reacted with 4-hydroxybenzylaldehyde to produce dialdehyde compounds [III] and [IV] . The later compounds reaction with different aromatic amines to synthesized the Schiff bases compounds [V-VII] and [VIII-X] .After that reaction of Schiff bases compounds with thioglycolic acid to synthesized the bent and liner core mesogens containing thiazolidin-4-one ring [XI-XIII] and [XIV-XVI].

Also, synthesized the compound [XVII] from reacted the piperazine with chloracetyl chloride then the result compound reacted with 4-hydroxybenzylaldehyde to product dialdehyde compound [XVIII].

The ester compound[XIX] was prepared from estrfecation of cinnamic acid with methanol then the condensation of ester compound[XIX]with hydrazine hydrate to yield acid hydrazide compound [XX] , which were reacted with glysine in phosphorous oxychloride to yield (5-styryl-1,3,4-oxadiazol-2-yl) methanamine[XXI].

In addition , synthesized new Schiff base compounds [XXII-XXV] from reacted the1,3,4-oxadiazole compound [XXI] with different aromatic aldehydes, while reacted the oxadiazol compound[XXI]with dialdehyde compound [III] or [IV] to produce new Schiff bases compounds [XXVI] and [XXVII] , afterword the addition thioglycolic acid to the later compounds to give new thiazolidin-4-one derivatives [XXVIII] and [XXIX], respectively.

Finally, synthesized a new Schiff base compound[XXX] by reacted the oxadiazole compound [XXI] with dialdehyde compound[XVIII].

The synthesized compounds were characterized by FTIR , ^{1}HNMR, C.H.N analysis and mass spectroscopy (of some of them).

The study of liquid crystalline properties (by DSC and polarizing microscope) of the synthesized compounds showed:

All the schiff bases compounds [V-VII] showed liquid crystals phases, the compound [V]showed nematic phase, while the compound [VI] showed dimorphism smectic B (S_mB)and nematic phases , but the compound [VII] showed dimorphism enantiotropic smectic A phase (SmA) and nematic phases.

Also, All the schiff bases compounds [VIII-X] showed liquid crystals phases, the compound [VIII] showed enantiotropic smectic B (S_mB) only but the compound [IX] showed dimorphism smectic B (S_mB)and nematic phases, while the compound [X] showed dimorphism enantiotropic smectic A (SmA) and nematic phases.

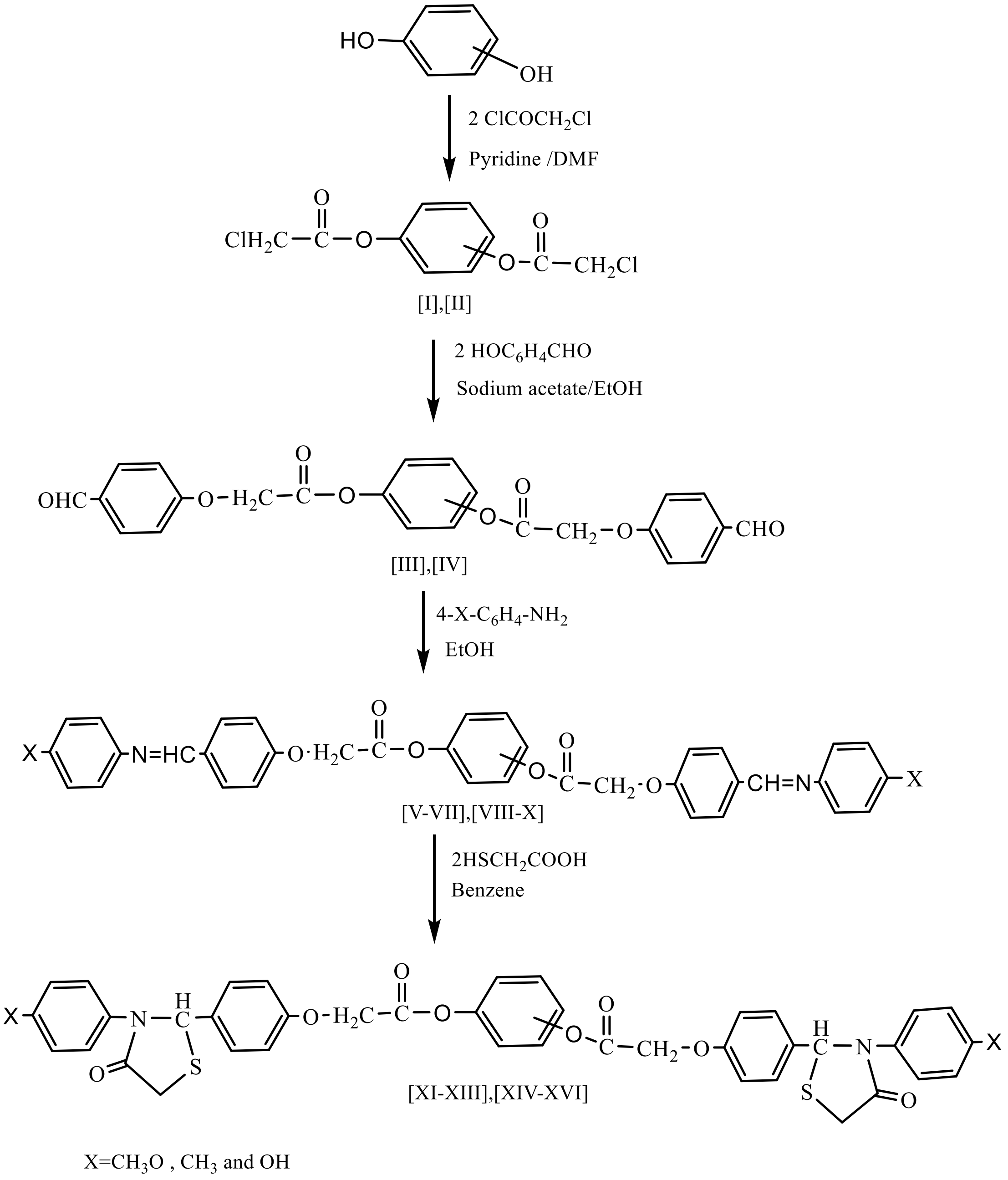
All thiazolidin-4-one derivatives[XI-XIII]and [XIV-XVI]didn’t showed any liquid crystals properties.

The Schiff bases compounds [XXII-XXV] showed liquid crystals behavior as follow : the compound [XXII] showed dimorphism enantiotropic smectic B (S_mB) and nematic phases ,also the compound [XXV] showed nematic phases ,while the compounds [XXIII]and[XXIV] didn’t show any mesomorphic behavior.

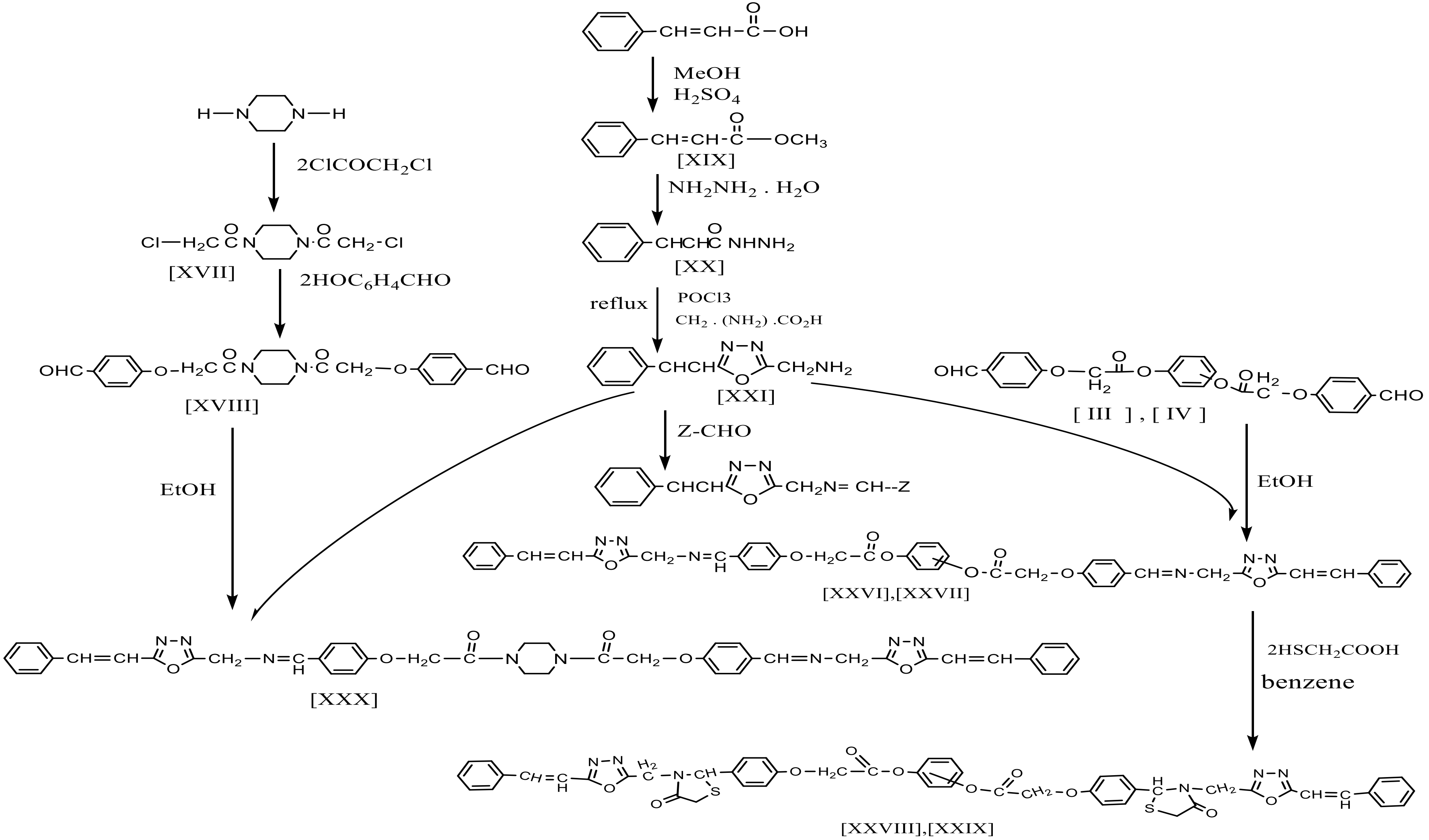
The compound [XXVIII] displayed a banana shape (nematic phase), but the compound [XXIX] didn’t showed any liquid crystals properties.

Finally, the compound [XXX] showed enantiotropic nematic phase.

This work can be summarized by the following , Schemes I and II :



Scheme I



$Z= C_6H_5$--CH=CH- ,--COOH ,4-CH_3O-C_6H_4- , 4-HO-C_6H_4--

Scheme II

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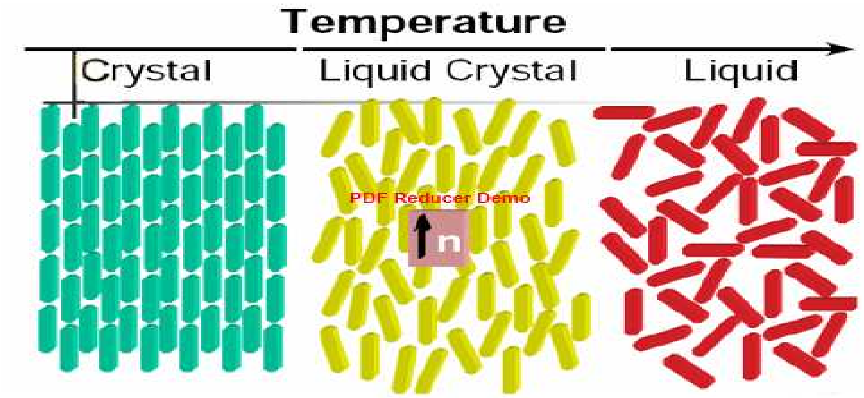
Chapter One

Introduction

1.1 Introduction to Liquid Crystals

Initially, there were thought to only be three major phases of matter while molecular order in most substances can be easily described by the previously established solid, liquid, and gas phases, some compounds have been discovered that, upon cooling or heating and cooling, display phases that are neither liquid nor crystalline, but rather new phases that exhibit properties of both. In 1888, an intermediate state of matter between the liquid and solid state was discovered by the Austrian botanist Friedrich Reinitzer (1). He observed two melting points while heating cholesteryl benzoate. The cloudy liquid he observed between the two melting points was the first recorded observation of liquid crystalline phase. Liquid crystals are a class of molecules that show phases that are intermediate between the crystalline solid and the isotropic liquid as Figure(1-1) .

The Liquid Crystals would display unique properties, such as strange colored patterns due to the compound’s birefringent properties(2). While observation of these properties would continue over the next few decades, their properties would not be taken advantage of until the 1960s. At this time, liquid crystals had been discovered to be compelling candidates for use in display technology.



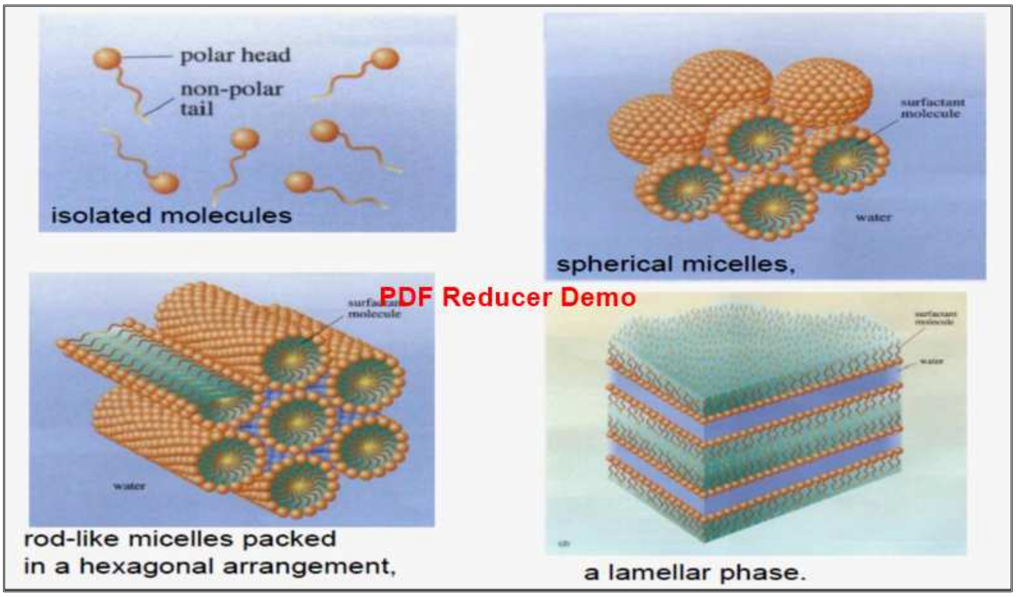
Figure(1-1):Liquid crystals phase

1.2-Classification of Liquid Crystals

Liquid crystals were divided into lyotropic phase in addition to the thermotropic phase. Both of these represented intermediate phases which include organic molecules.

1.2.1 Lyotropic liquid crystal phase

Lyotropic liquid crystal phase formation is dependent on the concentration of the liquid crystal molecule within a solution, such as in the case of micelles formed by amphiphilic detergent molecules dispersed in water(3) as Figure(1-2).



Figure(1-2):Types of lyotropic liquid crystals

1.2.2 Thermotropic liquid crystal

Thermotropic phases are those that occur in a certain temperature range. If the temperature is raised too high, thermal motion will destroy the delicate cooperative ordering of the LC phase, pushing the material into a conventional isotropic liquid phase as Figure(1-3).

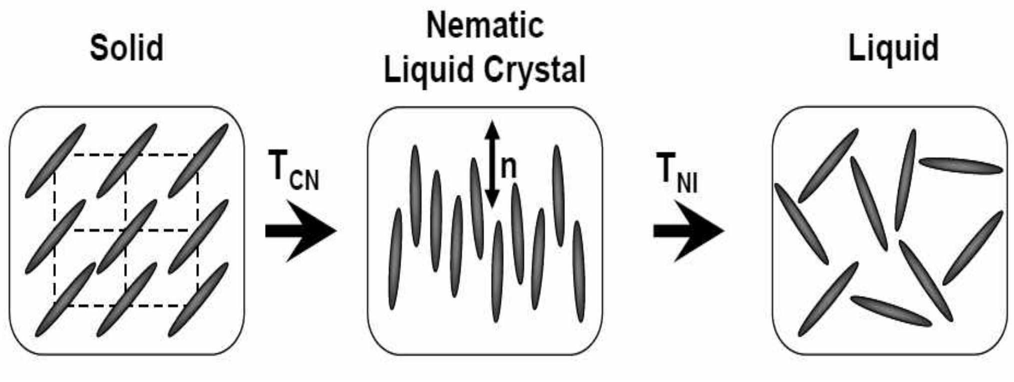


Figure (1-3) :Schematic representation of the molecules of a thermotropic liquid crystal represented the solid, nematic liquid crystal, and liquid phases.

Many liquid crystals have a similar rod-like (calamitic) or disc-like (discotic) shape.

1.2.2.1 Glamatic liquid crystals

Calamitic materials possess an inherent molecular anisotropy due to their rod-like shape. In a liquid crystal phase, unlike isotropic liquids, these molecules tend to align their long axes along a specific director, but still possess some freedom of movement within the phase as the result of the molecular length (l) being significantly greater than the molecular breadth (b), as depicted in the cartoon representation in Figure (1-4).

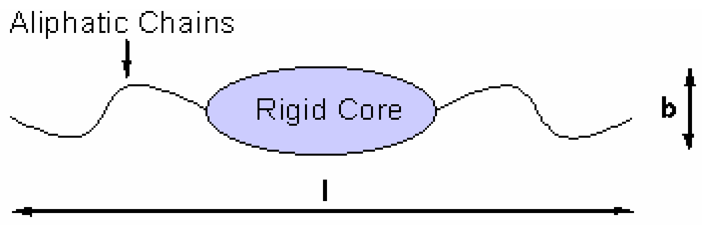


Figure (1-4): Schematic representation of calamitic liquid crystals, where .(length(l) >> breadth(b)

(calamitic liquid crystals) were further devided into three main classes, (nematic),(cholesteric) besides to the (semectic) liquid crystals(4).

i-Nematic phase

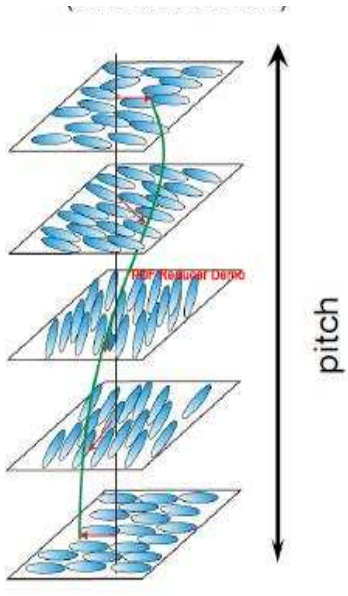
The nematic phase is characterized as a phase in which there is a lack of positional organization of molecules within the sample, but the optical axes of the molecules are oriented along a specific director(5). The molecules of a material within this phase are able to move freely within the sample, and are not bound to any specific layer unlike the smectic and some crystalline phases. Most, if not all,currently known nematic materials are uniaxial, and the directionality of this axis can be changed by an applied external electric field, making the nematic phase ideal for display applications Figure (1-5).

Figure(1-5): nematic phase

ii-cholestyric phase

The cholesteric phase is a nematic phase composed of chiral molecules, or induced by the presence of chiral molecules .As a consequence, the system acquires a helical ordering perpendicular to the long axis of the molecules(Figure 1-6). The helix may be right- or left-handed depending on the molecular chirality. The pitch is the distance after which the molecules have the same average orientation.

A special property of this phase is that light of a wavelength equal to the pitch is selectively reflected and circularly polarized.

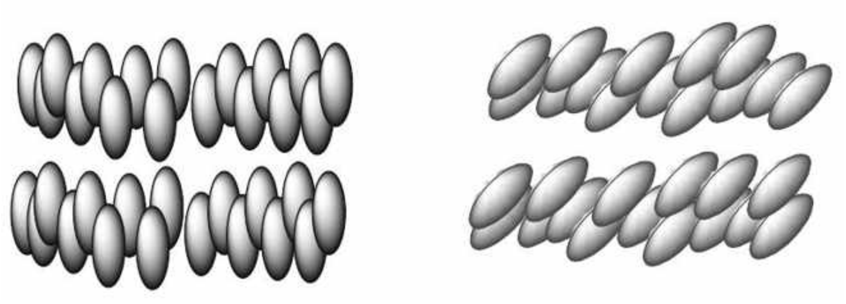


Figure(1-6): cholesteric phase

iii- Smectic phase

The smectic phase is defined by layered positional organization of molecules within the sample, as well as the optical axes of the molecules being aligned on average along a single director(6). In this phase, the molecules are generally organized in discrete layers, though they may be able to move past molecules within their same layer and even migrate between layers, depending on the structure of the specific smectic phase.

The alignment of molecules within these layers also delineates the type of smectic phase that is observed. For example, within the Smectic A (SmA) phase, the molecules are arranged in layers with the optical axes oriented on average perpendicular to the layer plane. In the Smectic C phase, however, the molecules within the layers are aligned on average at a tilted angle with respect to the normal along which the Smectic A phase aligns Figure(1-7). The alignment of the smectic B phase is similar to smectic A, however the molecules are positioned within each layer in a hexatic arrangemen$^{(7)}$.



Figure(1-7) :smectic A phase on the left and smectic C phase on the right

Many kinds of (smectic phases) have been detected. These types have been named ; smectic A, B, C, D, E, F, G, H, I, J, K, M, O, Q and X phases Figure (1-8)showed the structural identifications of each smectic phase and their molecular arrangement.

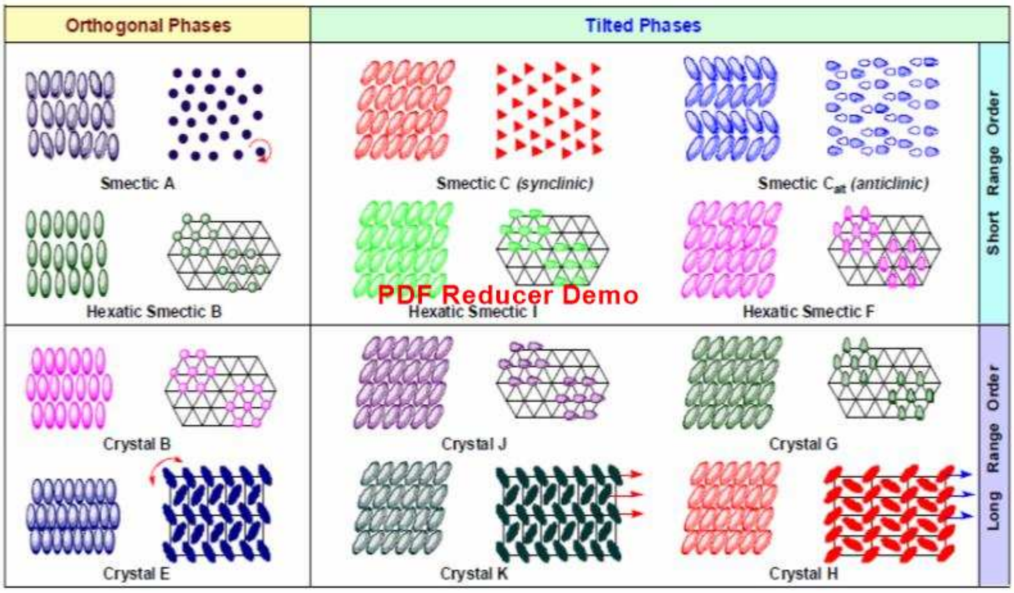


Figure (1-8): Various classes of smectic liquid crystals

1.2.2.2 Discotic Liquid crystals

Disk-shaped liquid crystals usually consist of an aromatic core with pendant flexible chains. In general discotic liquid crystalline phases are derived from this class of molecules (8) . This phase divided two principle mesophases are:

a. Nematic discotic phase (ND)

Nematic discotic phase is the least ordered mesophase (9),where the molecules have only orientational order being aligned on average with the director as illustrated in Figure (1-9). There is no positional order.

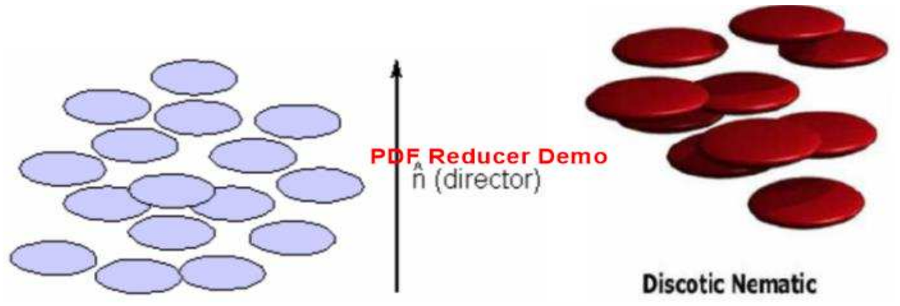


Figure (1-9): Schematic representation of the nematic discotic phase

b. columnar phase

In the columnar phase stacks of disk-like molecules are present Figure(1-10). The molecules in these columns can be arranged in a number of different ways, leading different columnar mesophases. The columns themselves maybe organized into rectangular or hexagonal arrays(10). The columns can be tilted or non-tilted and can such several variants are known(11,12).

Figure (1-10): Shematic representation of discotic columnar phase.

1.3-Order of appearance

Thermotropic liquid crystals can be classified into two types:

1-Enantiotropic liquid crystals:

This can be changed into the liquid crystalline state from heating and cooling

2-Monotropic liquid crystals:

Which can only be changed into the liquid crystalline state from cooling

3-Polymorphism liquid crystals:

Many Liquid crystalline substances which have exclusively smectic mesophase structure or exclusively nematic mesophase structure. But some can exist as both types of mesophase, smectic followed by nematic. This phenomenon is known as polymorphism(13) Figure (1-11)

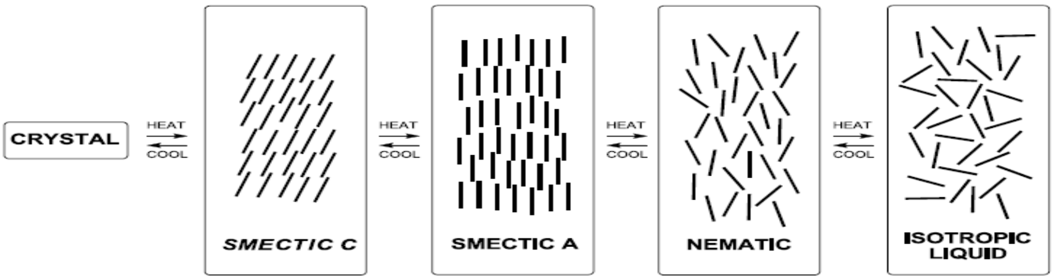
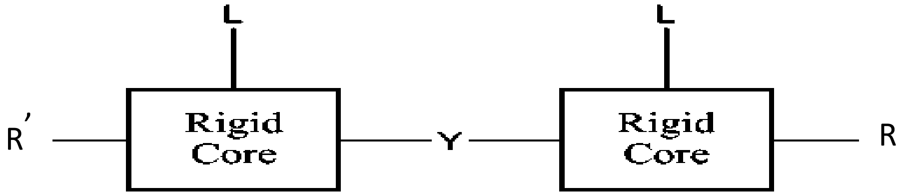


Figure (1-11): Schematical phase sequence of a liquid crystal

1.4 General structural of liquid crystals

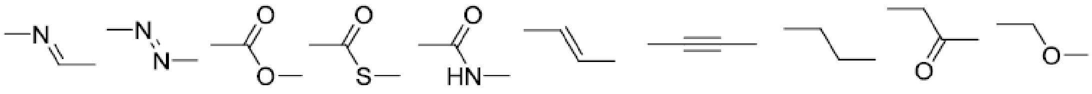
The majority of liquid-crystalline substances are based on the following structure Figure(1-12):



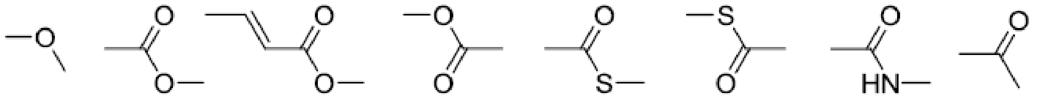
L = Lateral substituents
R, R' = Terminal aliphatic chains
Y=Central linkage

Figure(1-12): General structural of liquid crystals

The central linkage(14) as :



The terminal groups as:



1.5-Bent Liquid Crystals

The bent shaped mesogens(15)constituted of two mesogenic groups linked through a rigid group in such a way as not to be co-linear ,Figure (1-13). The mesogenic groups are mostly calamitic molecules consisting of aromatic rings also varied linking groups (Y, Y',X,X') between them, and a terminal group in para substituted of the aromatic rings .The two mesogenic types are connected to a rigid mainly six-member-aromatic ring and the angle middle the two calamitic mesogenic (bending angle) is around 120 degrees(16). This is noticed when connected (calamitic molecules)by 1,3disubstituted benzene ring.For this, the (non-linear shape)prepared from the meta-substituted of benzene ring .

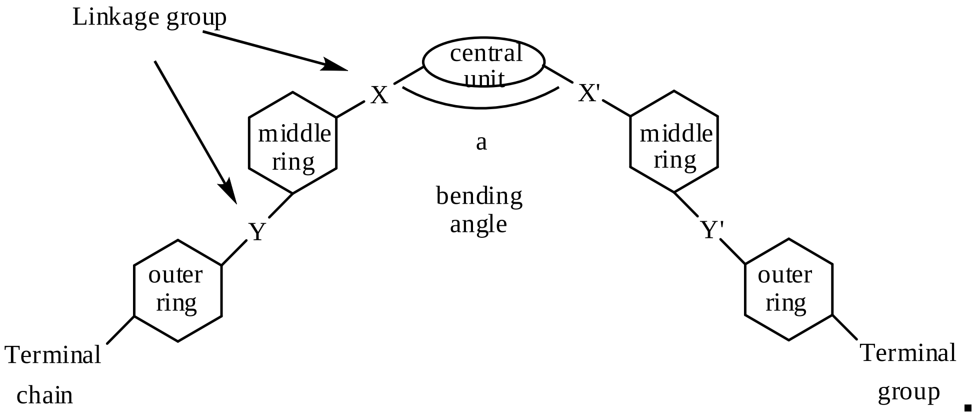


Figure (1-13) :General scheme of bent-shaped molecules

1.6 Application of Liquid Crystals

1.6.1 Display Application

The important properties of liquid crystals are that their orientation can easily be influenced by an electric field and by surfaces. These properties have led to their application in display devices such as LCDs. A frequently used class of liquid crystals are chiral and non-chiral cyanobiphenyls(17). Because of their chemical stability and suitable temperature range in which the liquid crystalline phase is present, they were for a long time used in LCDs. Nowadays in the current displays they have been replaced by halogenated aromatic and cycloaliphatic compounds because of their higher purity, lower viscosity and more balanced optical and dielectric properties.

1.6.2 Gas-liquid chromatography

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(18), 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.

1.6.3 Medical applications

Cholesteric liquid crystal mixtures have also been suggested for measuring body skin temperature, to outline tumors ,any inflammation or construction of the vessels will naturally affect the temperature of the skin: this will help in the location of inflammation, since the warmer areas will by outlined the color pattern (19).

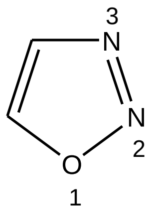
1.6.4. Other Applications

Thermotropic chiral LCs whose pitch varies strongly with temperature can be used as crude thermometers, since the color of the material will change as the pitch is changed. Liquid crystal color transitions are used on many aquarium and pool thermometers. Other liquid crystal materials change color when stretched or stressed. Thus, liquid crystal sheets are often used in industry to look for hot spots, map heat flow, measure stress distribution patterns, and so on.

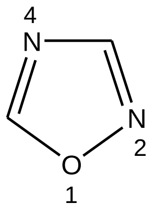
Liquid crystals are being used in many skin care products. The first, and probably most successful product in Eyzone. This incorporated very attractive coils of iridescent liquid crystals in a clear gel. It is probable that Vitamin A palmitate is mixed with the liquid crystal(20) .

1.7 oxadiazole

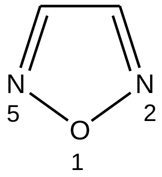
Oxadiazoles are five-membered ring compounds with three atoms one oxygen atom and two nitrogen atoms. The oxadiazole ring has four(21) isomers as shown below:



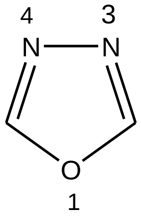
1,2,3-oxadiazole



1,2,4-oxadiazole



1,2,5-oxadiazole

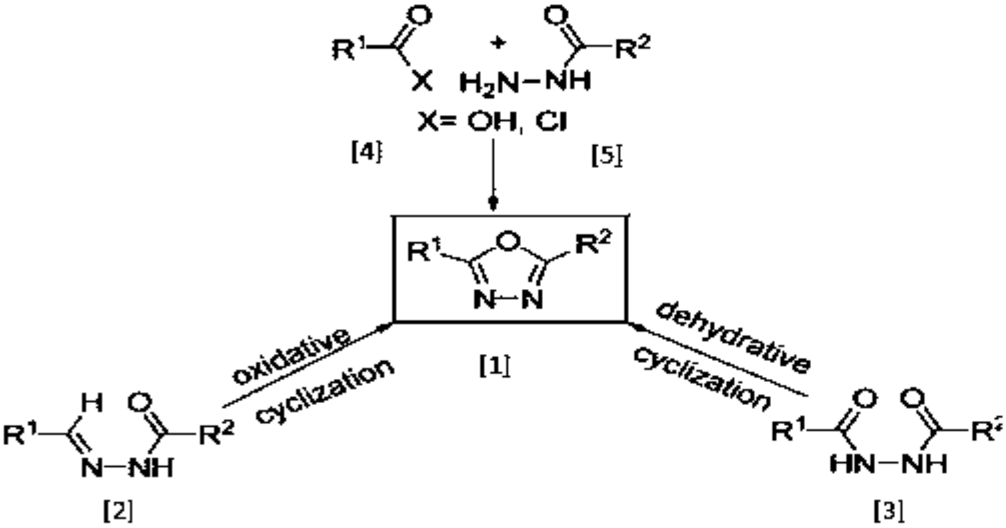


1,3,4-oxadiazole

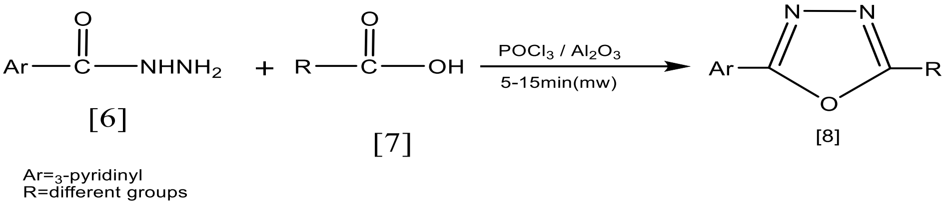
1,3,4-Oxadiazole is the most thermally stable isomer which has attracted special attention, this is primarily due to the large number of uses in many diverse areas, including drugs, scintillation materials, dyes(22) and surface active agents (23).

1.7.1 Synthesis of 1,3,4-oxadiazoles

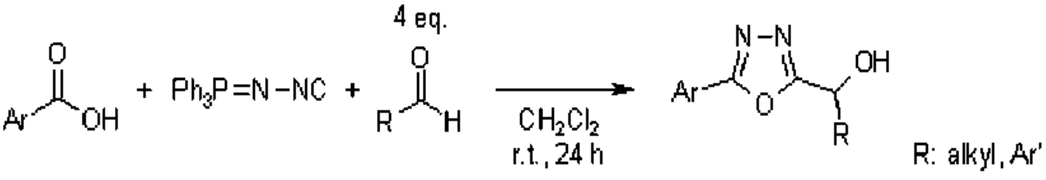
In the literature, the following methods for preparation of 1,3,4-oxadiazole[1] were reports : (a) oxidative cyclization of N-acylhydrazones[2] with various oxidizing agents(24) (b) cyclodehydration of 1,2-diacylhydrazines[3] with reagents such as thionyl chloride or phosphorus oxychloride(25) (c) direct reaction of carboxylic acids or acyl chlorides[4] with acid hydrazides[5] or hydrazines(26).



Carlson and Jorgensen(27),have synthesized a number of 2,5-disubstituted-1,3,4-oxadiazole [8] under microwave irradiation through the reaction of variable hydrazides[6] with different carboxylic acids[7] in the presence of phosphorous oxychloride and Al_2O_5

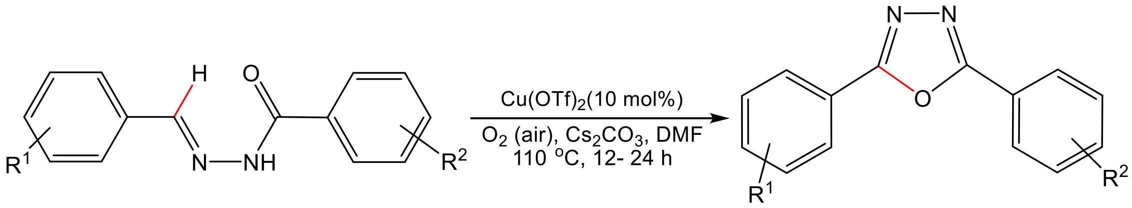


N-Isocyaniminotriphenylphosphorane[9],aldehydes, and benzoic acids undergo a onepot, three component reaction under mild conditions to afford 2aryl5hydroxyalkyl 1,3,4-oxadiazoles[10] in good yields(28).



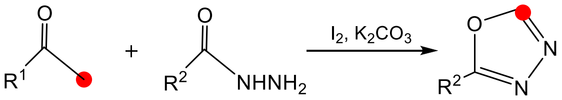
[9] [10]

Guin et. Al. (29) synthesized symmetrical and unsymmetrical 2,5-disubstituted [1,3,4]-oxadiazoles [12] through an imine C-H functionalization of N-arylidenearoylhydrazide [11] could be obtained in 85%isolated yield when performed in the presence of $Cu(OTf)_2$ (10 mol%), Cs2CO3 as the base, at 110 _C in N,N-dimethyl formamide DMF as a solvent under an air Atmosphere .



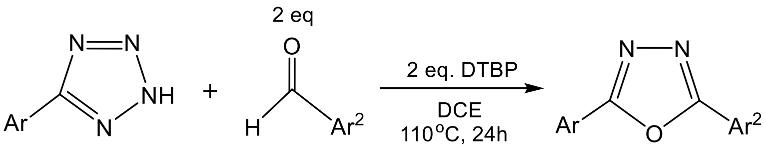
[11] [12]

Also , (30) 1,3,4-oxadiazoles were synthesized [15] by reaction methyl ketones[13] with hydrazides [14] in presence of iodine I_2 and potassium carbonate K_2CO_3 as a base .



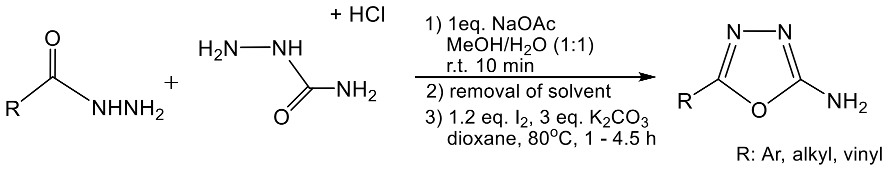
[13] [14] [15]

Also, Wang(31) et. al., used one pot to synthesize 2,5diaryl 1,3,4oxadiazoles[18]via reaction of aryl tetrazoles[16] with aromatic aldehydes[17], a 70% yield of [18] was obtained when the reaction was conducted in 1,2-dichloroethane DCE as a solvent and di-tert-butyl peroxide (DTBP, 2 equiv) as oxidant followed by thermal rearrangement.



[16] [17] [18]

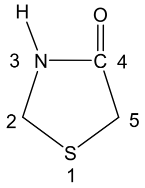
Recently, a transition metal free condensation of hydrazide[19] with semicarbazide[20]hydrochloride followed by I_2 mediated oxidative C-O bond formation provides 2amino substituted 1,3,4-oxadiazoles(32)[21] .



[19] [20] [21]

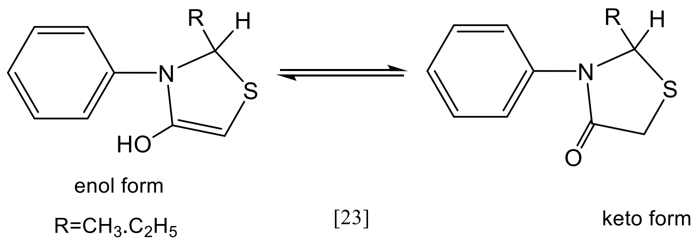
1.8 Thiazolidin-4-one

Thiazolidin-4-one [22] is an important five member heterocyclic compounds containing sulfur and nitrogen with carbonyl group at position (4)



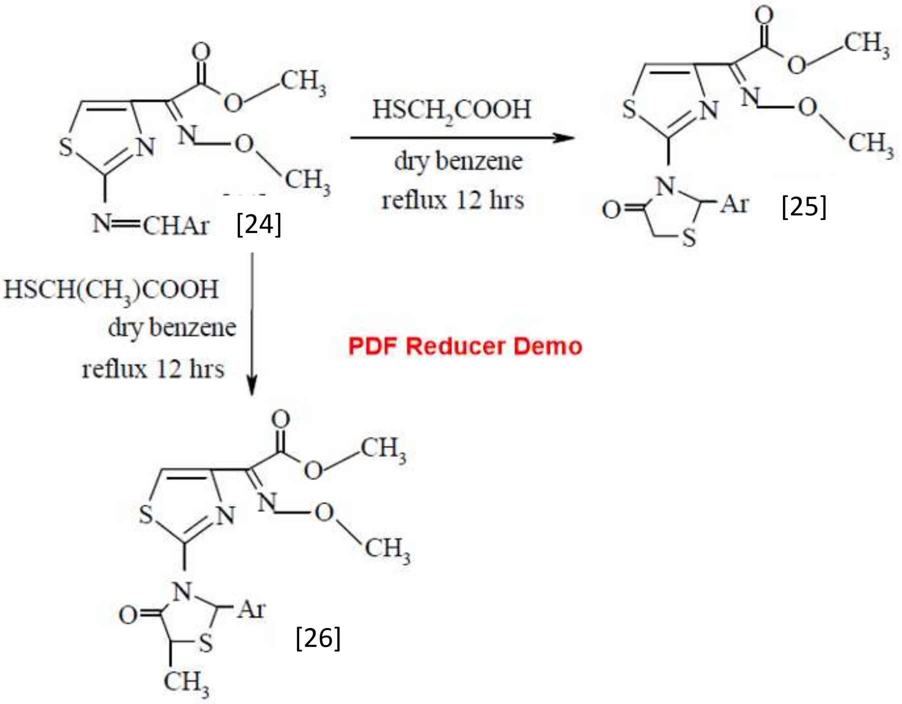
[22]

Thiazolidin-4-one has keto and enol tautmerisum [23](33,34).

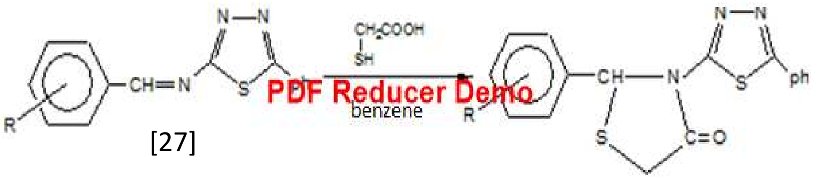


1.10 Synthesis of thiazolidin-4-one

Parekh et. al. (35), prepared thiazolidinones [25] and [26] by the reaction of 2-Benzalamino-4-(α-methoxyiminocarbomethoxymethyl)-thiazoles [24] with thioglycolic acid or 2- mercapto propanoic acid ، respectively in dry benzene .



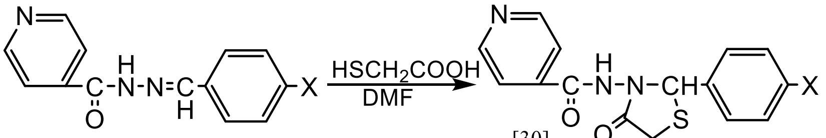
Also , thiazolidinone derivatives [28] were synthesized by refluxing equimolar amounts from the imine [27] with thioglycolic acid in dry benzene(36)



[27] [28]

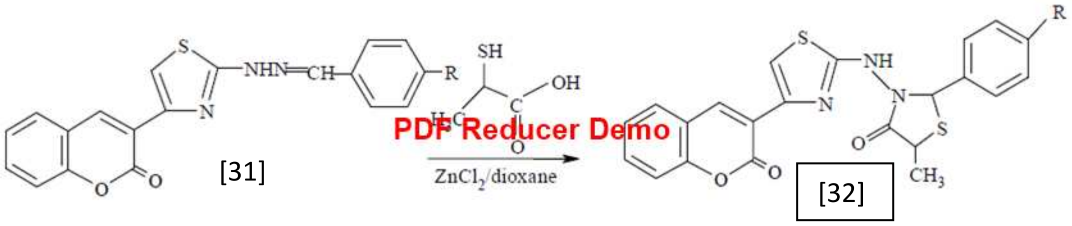
R=alkyl,aryl

While, Vinay(37) et.al, synthysized new derivatives of thiozolidinone[30] from reaction of 4-pyridyl semicarbazon of 4-substituted benzaldehyde compounds [29] with thioglycolic acid in DMF as a solvent.



[29] [30]

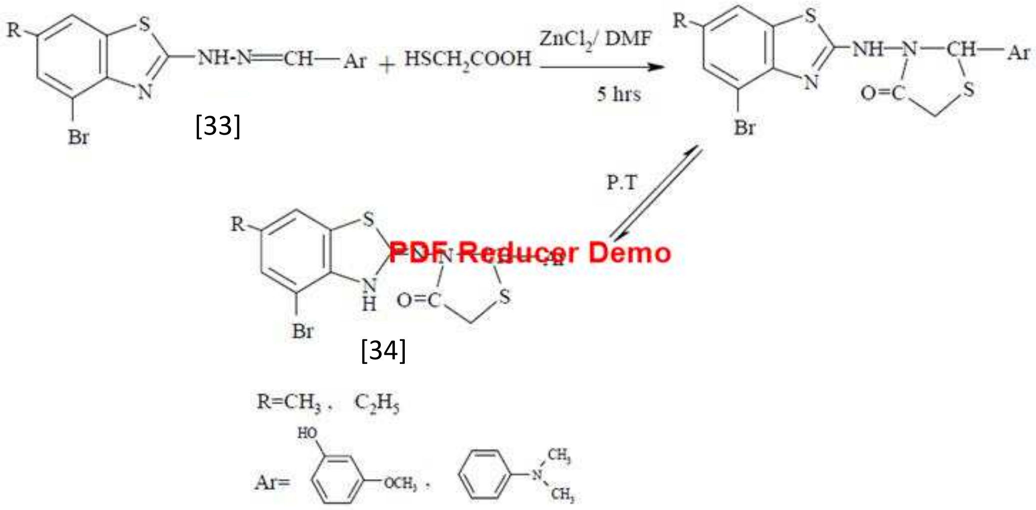
In addition , Deepthi and Manjunath (38),synthesized compounds of 3-[5`-methyl-2`-aryl-3`-(thiazol-2`` -yl amino) thiazolidin-4`-one] coumarins [32] from reaction of 3-[2`-(2``-arylidene hydrazinyl) thiazolyl] coumarin derivatives [31] with 2-mercapto propanoic acid in the presence of $ZnCl_2$ using dioxane as a solvent.



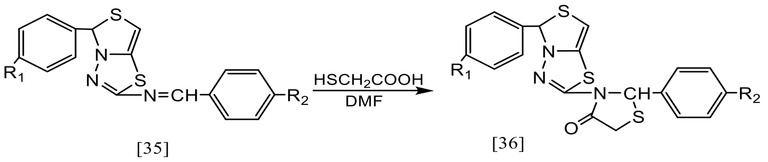
[31] [32]

R=H, 4-CH_3, 4-Cl, 4-OH , 4-F

On the other hand ,Bhagat et. al.(39) , synthesized 2-substitued phenyl -3- substituted benzothiazolyl-2-amino-yl-4-thiazolidinone [34] by the reaction of 4-bromo-6-methyl/ethyl-2-substituted benzyldine benzothiazolyl hydrazone [33] with thioglycolic acid using ZnCl2 in DMF.

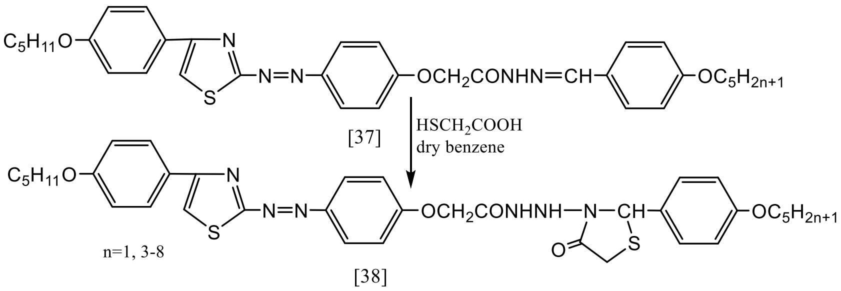


Also, Malipeddei$^{(40)}$ et.al, have been synthysized thiazolidinones[36] by cyclocondensation of Schiff bases of amino thiadiazole[35] with thioglycolic acid in DMF as a solvent.

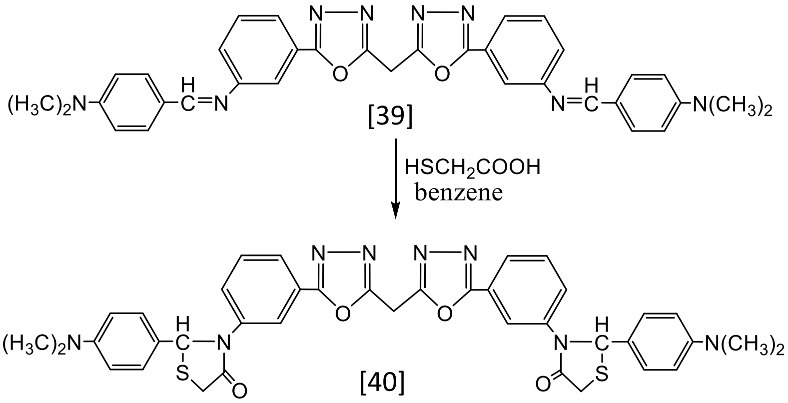


R_1 , R_2 = H and 4-CH_3

Also, two new series of Schiff bases [37] and their thiazolidin-4-one derivatives[38] were synthesized$^{(41)}$ by using thioglycolic acid a Acid and as a solvent.

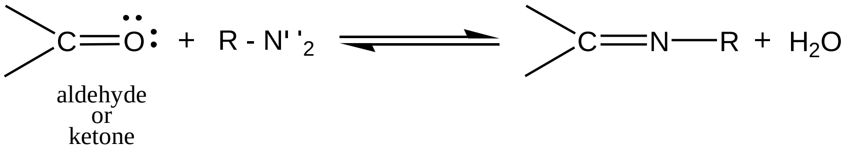


Synthesis of 3,3'-((methylenebis(1,3,4-oxadiazole-5,2-diyl))bis(3,1-phenylene))bis(2-(4-(dimethylamino)phenyl)thiazolidin-4-one)[40] by the reaction of Schiff bases[39] and thioglycolic acid in dry benzene (42).



1.9.1 Schiff's Bases:

The condensation of an aldehyde or ketone with primary amine is usually formed Schiff's bases according to the following equation (43,44).



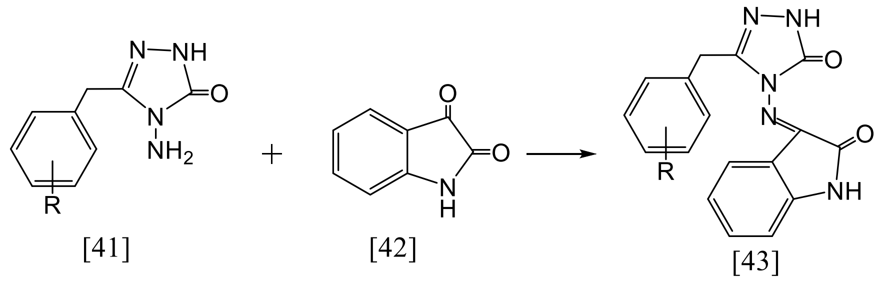
Schiff bases that contain aryl substitutes are substantially more stable and more readily synthesized, while those which are contain alkyl substituents are relatively unstable. The formation of Schiff bases fromaldehyde or ketone is a reversible reaction and generally takes place under acid or base catalysis upon heating.(44) In the Schiff bases synthesis a catalyst are usually required, in addition to the removal of the water as it is formed(45).

Schiff bases have been a great interest for many years(46) . They are also used to prepare super-conducting polymers(47) .

Schiff bases are reported to show a variety of interesting biological activities, including antibacterial (48), antifungal (49), antivirus (50), anticancer (51) and herbicide activities (52).

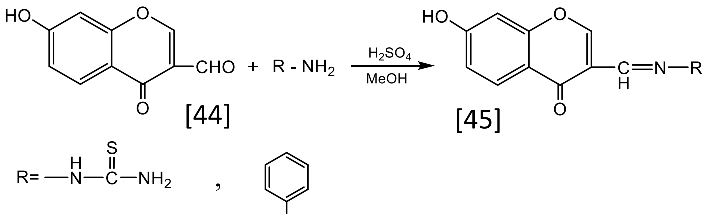
1.9.1 Synthesis of Schiff bases

the condensation between compounds [41] with isatin [42] results new Schiff bases [43] (53) .

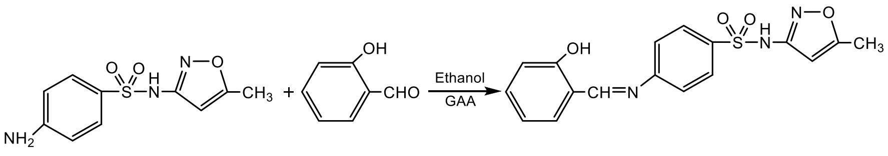


R= 2-F , 4-F

(2009) The Schiff bases compounds[45] were synthesized from the reaction of 7-hydroxy -3-formyl chormen4-one [44]and various amines by using H_2SO_4 as a catalyst in methanol as a solvent(54):

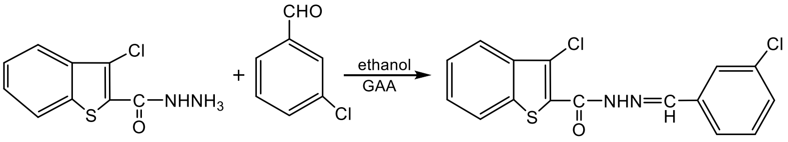


Hussain(55) et al synthesized of 4-[(2-hydroxy-benzylidene)-amino]-N-(5-methyl-isoxazol-3-yl)-benzene sulfonamide[48] via reaction of Sulphamethaxazole [46]with 2-hydroxybenzaldehyde [47] in ethanol and few drops of glacial acetic acid as a catalyst.



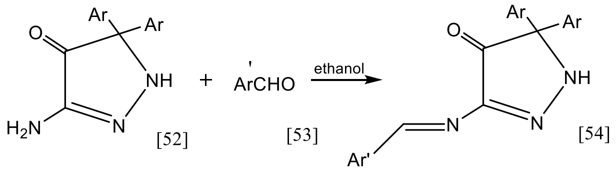
[46] [47] [48]

While , the Schiff base derivative [51] was synthesized from the reaction of 3-chloro benzo[b]thiophene-2-carbohydrazide [49]with 3-chloro benzaldehyde [50](56) in ethanol and glacial acetic acid GAA .



[49] [50] [51]

Also, Azab(57) et al reportted formation the Schiff's bases compounds [54] through condensation reactions between the amino pyrazolone derivatives [52] and the aldehyde [53] in ethanol as a solvent.



[52] [53] [54]

Ar' = C_6H_5, C_6H_4 - Cl -4

Ar = C_6H_4 - CH_3 -4, C_6H_4 -OCH_3 -4

1.13 .Liquid Crystal of Heterocyclic Compounds

Many factors responsible for appearing of (liquid crystal phases) such the structure of mesogen, geometry, polarizability, molecular conformation, length-to-breadth ratio also the number and the permanent dipole moments ' s location (58) .

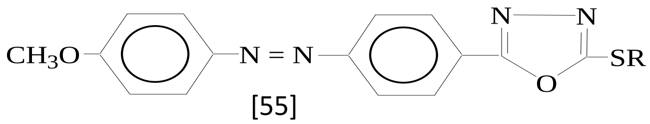
In the latterly years , study of mesomorphic heterocycles compounds as a result of their optical and photochemical properties(59) . The significance effects of the heterocyclic core on the properties of liquid crystals have been noticed in a series of review papers(60) . When heterocyclic liquid crystals having high dielectric biaxiality these compounds can be used in essential in technological devices as well as in other applications such as in optical information storage(61) . Usually heterocyclic mesogens are incorporated with heteroatoms , such as (N, O and S) causing the symmetry reduced in the overall molecule also the generation of a stronger polar induction. The polarity, polarizability and to a certain extent the geometry of a molecule can considerably change by the inclusion of the heteroatom, thus influencing the type of mesophase, the phase transition temperatures in addition of other properties(62) . Examples of liquid crystals with incorporated (heterocyclic rings) are thiophene(63) , benzoxazole(64) , pyridine (65)and oxadiazole(66) .

1.14 Liquid crystal compounds

Many series of liquid crystalline compounds containing heterocyclic rings have been synthesized because of their interesting properties ,the heteroatom causes considerable changes in chemical and physical properties and influences the type of liquid crystal phase, also phase transition temperatures and other properties of the mesogens(67).

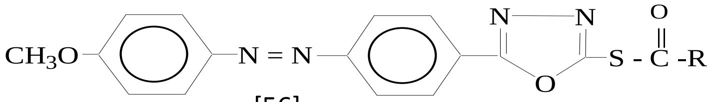
Many workers synthesized liquid crystals compounds as follow:

Al-Rujaiby(68)has synthesized and studied mesomorphic behavior of new azo compounds containing 1,3,4-oxadiazole unit, series[55] and series[56].



[55]

R=C_nH_{2n+1} , n= 1-8

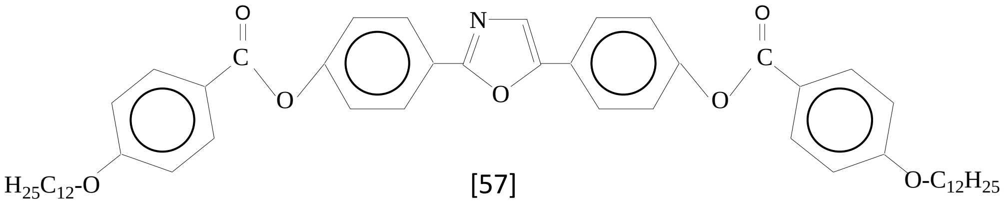


[56]

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

It has been found that all compounds of series [55] showed liquid crystalline behavior. The compounds with n=(1,3-5) showed only nematic phase, while the compounds with n=(2,6-8) showed nematic and smectic phases. The replacement of thioalkyl terminal substituent in series[55] by thiocarboxy group in series[56] were found to enhance the thermal stability of the mesophase and maintains the molecules in layer arrangement of smectic mesophase where takes place. All compounds of series [56] showed liquid crystalline properties.

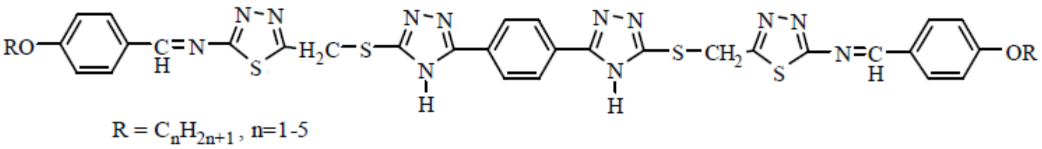
J.A. Olivares et.al ,(69). studied the liquid crystalline behaviors and optical studies of the nematic phase of an oxazole-derived bent-core liquid crystal[57].



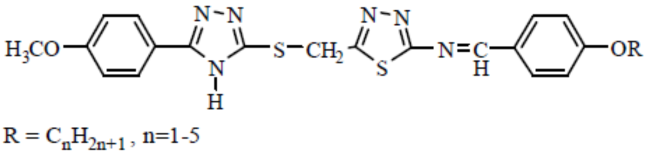
[57]

While , Rou'il(70)synthesized and characterized two novel series of new compounds containing (1,3,4-thiadiazole) in addition of (1,2,4-triazole) units [58] and [59]. The liquid crystalline properties of series

[58] showed nematic textures except compound n=3, while only the compounds n=1,3 in the series [59] showed the mesomorphic behavior (nematic and smectic phases) .

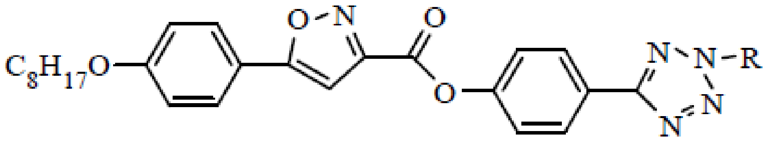


[58]



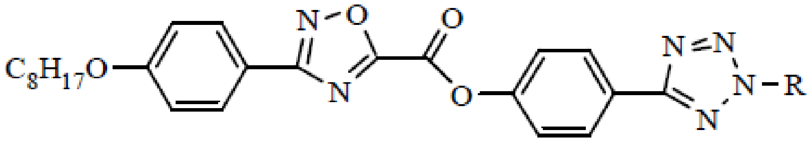
[59]

Furthermore , Dos Santos et. Al.(71), synthesized a new liquid crystalline heteroaromatic compounds with the five-membered isoxazole , tetrazole also1،2،4-oxadiazole rings . The compounds include the mesogenic units tetrazole together with isoxazole [60] showed (nematic as well as smectic C phases)، however the compounds containing tetrazole with 1,2,4-oxadiazole unit[61]presented (nematic, smectic C beside to smectic A mesophases) .



$R = C_nH_{2n+1}$; n = 6 , 8 , 10 , 12

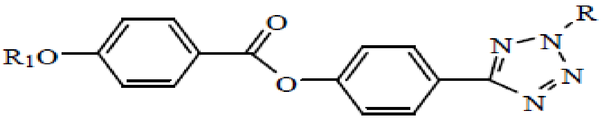
[60]



$R = C_nH_{2n+1}$; n = 6 , 8 , 10 , 12

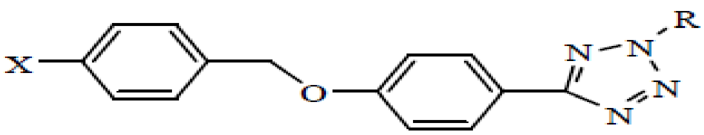
[61]

Tariq et.al. ,(73) synthesized and characterized of 4-[(2-alkyl)-2H-tetrazole-5-yl]phenyl-4-alkyloxybenzoates $[62]_{a-h}$ and 5-{4-(4-substituted) benzyloxy]phenyl}-2-alkyl-2H-tetrazoles $[63]_{a-e}$. The tetrazolyl benzoates compounds $[62]_{a-h}$ showed (nematic , smectic C addition to smectic A mesophases) . while tetrazoles compounds [63]a-e didn›t show any mesomorphic behavior mainly due to replacement of the carbonyl by a methylene group .



$[62]_{a-h}$

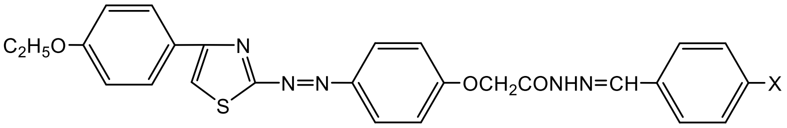
R_1 = n-hexyloxy , R = n-hexyl
R_1 = n-hexyloxy , R = n-heptyl
R_1 = n-hexyloxy , R = n-octyl
R_1 = n-heptyloxy , R = n-hyptyl
R_1 = n-octyloxy , R = n-octyl
R_1 = n-nonyloxy , R = n-nonyl
R_1 = n-decyloxy , R = decyl
R_1 = n-decyloxy , R = (S)-citronnelly1



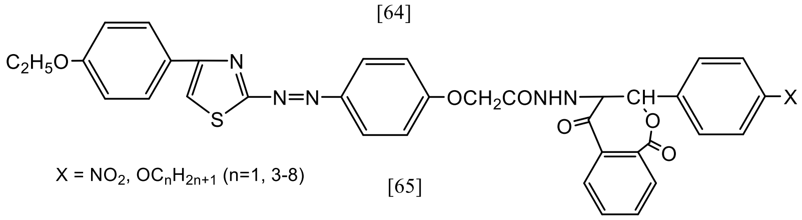
$[63]_{a-e}$

X = vinyl , R = n-nonyl
X = H , R = n-nonyl
X = F , R = n-nonyl
X = Br , R = n-nonyl
X = Br , R = (S)-citronnellyl

Al-Dujaili et.al. ,(67)synthesized and studied the liquid crystalline properties of two series [64] and [65] containing heterocyclic1,3-thiazole and 1,3-oxazepine-4-7-diones.



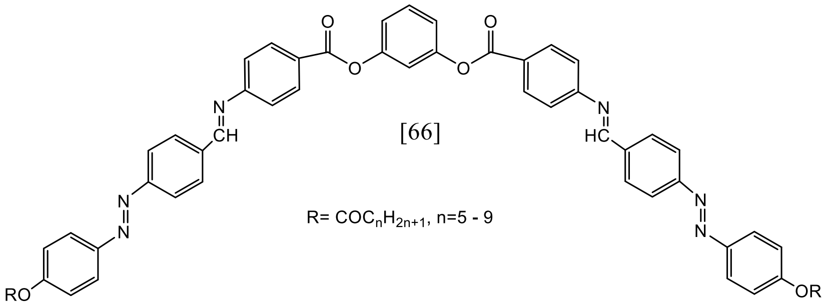
[64]



X = NO_2, OC_nH_{2n+1} (n=1, 3-8)

[65]

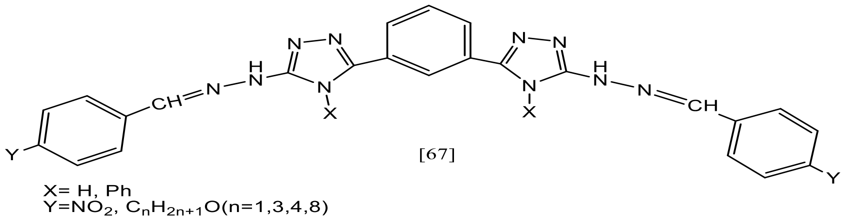
Also ,Ciobanu(75) et. al. , synthesized and investigated liquid crystalline behavior of symmetrical non liner liquid crystal containing 1,3- disubstituted benzene ring as a central core also consisting of different linkage groups to connect between the three aromatic rings beside to terminal alkyloxy chain containing 6 to 10 carbon atoms[66].All compounds appeared enantiotropic mosophases nematic and smectic phases.



[66]

R= COC_nH_{2n+1}, n=5 - 9

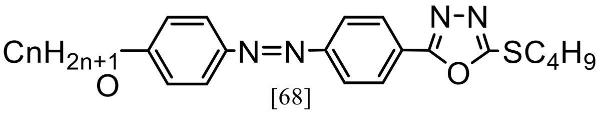
In addition to, synthesize and investigation of liquid crystalline properties of two series of bent core mesogen containing 1,2,4-traizole ring[67] derived from isophthalic acid(71).



[67]

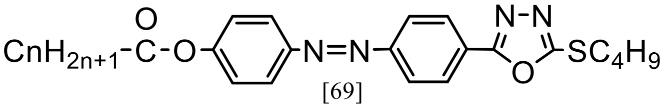
X= H, Ph
Y=NO_2, $C_nH_{2n+1}O$(n=1,3,4,8)

As while as, synthesized two new non symmetrical mesogenic homologous series of terminal substituent ether group series [68] and carboxy group series [69] incorporating azobenzene and 1,3,4-oxadiazole ring(68).



[68]

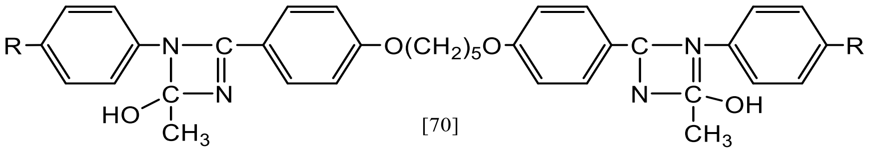
n= 1 -9 or 12



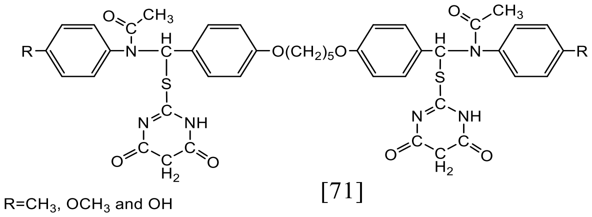
[69]

n= 1, 2, 3, 5 or 7

Also,It was synthesized and studied the liquid crystalline properties(69) of 1,3-diazetine derivatives [70] and pyrimidine compounds[71]. All the compounds with alkoxy tails form enantiotropic nematic phases but the compounds with alkyl tails do not form liquid crystals.

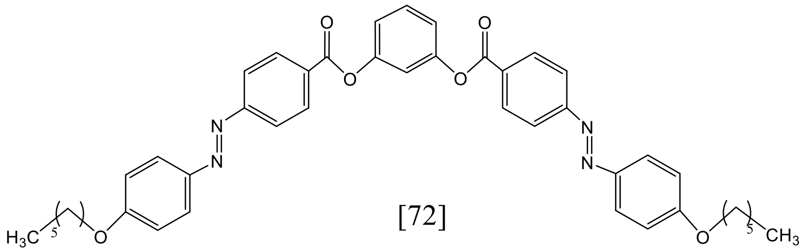


[70]



[71]

Recently , Yuvaraj et al(76)investigated the liquid crystalline and light-induced properties of resorcinol spacer based dimericazobenzene[72],this compound showed nematic and smectic A phases.



[72]

The Aim of the work

The aim of this work includes the following:

1- Synthesis and characterization of new Schiff bases derived from bis-acid hydrazide , and converting the resulted Schiff bases to the corresponding thiazolidin-4-ones.

2-Synthesis and characterization of new derivatives containing 1,3,4-oxadiazole ring.

3-Study of the effect of structure and geometry of the molecule on it's liquid crystalline properties.

4- Study the effect of the 1,3,4-oxadiazole ring , thiazolidin-4-ones ,imino linkage and the terminal group on liquid crystalline behavior of the synthesized compounds.

Chapter Two

Experimental Part

2. Chemicals and Techniques

2.1. Chemicals

The following chemicals in Table (2-1) were obtained from different companies.

Table (2-1) :listed liquid and solid chemicals used in this work

Name of material	Name of company	Purity %
Acetone	BDH	99
Anisaldehyde	Aldrich	97
Anisoyl chloride	Merck	99.5
Benzene	Riedal-deHaën	99.5
cinnamic acid	Aldrich	99
Diethyl ether	Fluka	99.5
N,N-Dimethylformamide (DMF)	Merck	99.5
Dimethyl sulphoxide (DMSO)	Aldrich	99.8
Ethanol (absolute)	GCC	99.8
Ethyl acetate	Aldrich	99
Glyoxilic acid	Aldrich	99
Hydrazine hydrate	Aldrich	80
4-hydroxy benzaldehyde	Aldrich	99
Hydroquinone	Aldrich	99
Hydrochloric acid	Riedal-deHaën	37
Methanol	Scharlau	99.8
piperazine	Aldrich	99

Pyridine	Merck	99.5
phosphorous oxychloride	Aldrich	99
Sodium bicarbonate	Scharlau	99.7
sodium acetate	Merck	99
Sulfuric acid	Aldrich	99
Thioglycolic acid	Aldrich	98
triethyl amine	Merck	99

2.2. Techniques

2.2.1. Spectroscopy

a) Fourier transform infra-red spectrophotometer (FTIR)

FTIR spectra were recorded by using potassium bromide discs on a SHIMADZU (IR Affinity-1) FTIR spectroscopy. College of Education for Pure Science (Ibn-Al-Haitham), University of Baghdad and FTIR-600 spectrometer,(UK).College of Education for Pure Science (Ibn-Al-Haitham)\ Central Service Laboratory , University of Baghdad .

b) Nuclear magnetic resonance spectrometer (^{1}HNMR)

1H-NMR spectra were carried out by company: Bruker ,500 MHz and were reported in ppm(δ), DMSO was used as a solvent with TMS as an internal standard, measurements were made at Central lab ,Tehran University.

c) Mass spectroscopy:

Mass spectrum was determined by scan110(1.257min):direct prob-013777.d, at Central lab ,Tehran University.

d) C.H.N analysis was determined by EuroEA 3000/Italy College of Education for Pure Science (Ibn-Al-Haitham)\ Central Service Laboratory , University of Baghdad ..

2.2.2. Melting points measurements

Uncorrected melting points were determined by using Stuart , SMP 10 , (UK) .

2.2.3. Thin layer chromatography(TLC)

The TLC was preformed on aluminum plate coated with layer of silica gel, supplied by Merck. The compounds were detected by iodine vapor.

2.2.4. Hot-stage polarizing microscopy

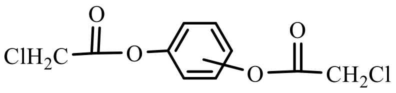
The transition temperatures and textures of the mesophases were determined using polarized optical microscope modelLeica DM2500 M ,College of Education for Pure Science (Ibn-Al-Haitham)\ Central Service Laboratory , University of Baghdad .

2.2.5. Differential scanning calorametry (DSC)

DSC measurements were recorded by the STAPT-1000LINSIS , German origin , heat rate was average 5 ^{0}C /minute , College of Education for Pure Science (Ibn-Al-Haitham)\ Central Service Laboratory , University of Baghdad .

2.3. Synthetic Methods

2.3.1 Preparation of 1,3-phenylene bis(2-chloroacetate) [I]and 1,4-phenylene bis(2-chloroacetate)[II] (79 , 80)



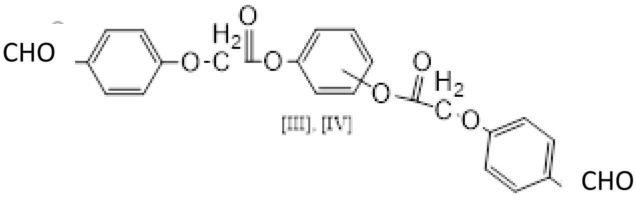
[I] , [II]

Chloracetyl chloride (0.002 mol) was slowly added to a stirred solution of resorcinol or hydroquinone (0.11 g ,0.001 mol) , pyridine 1 ml and DMF 2 ml at 0 ℃. Then, the reaction mixture was stirred for 3 hrs. at room temperature then, neutralized with saturated sodium bicarbonate solution. The precipitate was filtered and wash with water, dried and the residue was recrystallized from ethanol.

Data compound [I]: reddish color, Yield 70 %, m.p.= 66-68^{0}C

Data compound [II]: white color ,Yield 78 %, m.p.= 122-123^{0}C

2.3.2 Synthesis of1,3-phenylene bis(2-(4-formylphenoxy)acetate)[III] and1,4-phenylene bis(2-(4-formylphenoxy)acetate)[IV]

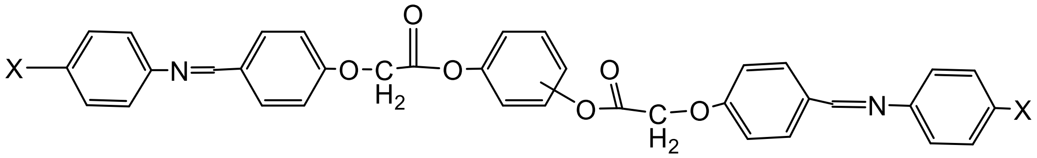


A mixture of compound [I] or [II](0.001mol) ,4-hydroxybenzylaldehyde (0.002 mol) and fused sodium acetate (0.246 g , 0.003 mol) in absolute ethanol 5 ml was refluxed for 4 hrs. , then cooled and poured into cold water . The precipitate was filtered and recrystallized by ethanol .

Data compound [III]: brown color , Yield 70 %, m.p = 86-88^{0}C

Data compound [IV]: dark brown color , Yield 68 %, m.p = 58-60^{0}C

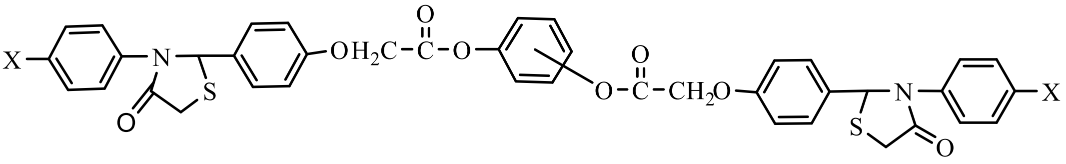
2.3.3 Synthesis of new Schiff bases compounds[V-VII] , [VIII- X]



[V - VII], [VIII - X]

A mixture of compound [III] or [IV] (0.001 mol) and different aromatic amines (0.002 mol) was dissolved in 5ml absolute ethanol , refluxed for 3-4 hrs. , and cooled to room temperature , The solid product was filtered to give a new Schiff basses . The physical properties are listed in Table(2-2).

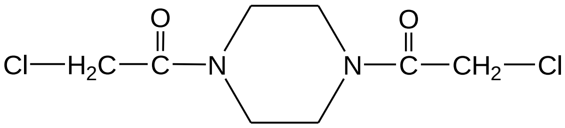
2.3.4 Synthesis of thiazolidin-4-one derivatives[XI-XIII] and [XIV-XVI]



[XI-XIII] , [XIV-XVI]

A mixture of Schiff bases [V-VII] or [VIII-X] (0.001mol) and thioglycolic acid (0.002 mol) was refluxed in dry benzene (3 ml) for 12 hrs . The solvent was evaporated and residue was neutralized with sodium bicarbonate solution then, the precipitate was filtered. The physical properties are listed in Table (2-2).

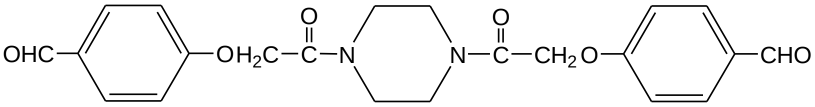
2.3.5 Preparation of 1,1'-(piperazine-1,4-diyl)bis(2-chloroethanone)[XVII]



[XVII]

A mixture of piperazine (0.001 mol , 0.086 g) and triethyl amine (1 ml) in 3 (ml) DMF , chloroacetyle chloride (0.002 mol , 0.226 g) was added drop-wise .The reaction mixture was stirred for 3 hrs. , at the end of the reaction the resulting mixture was poured onto ice water. The precipitate was filtered and washed with water several times , dried and recrystallized from acetone ,the color was yellow, yield percentage was 70 %, and the melting point was mp.=138^{0}C.

2.3.6 Synthesis of4,4'-(2,2'-(piperazine-1,4-diyl)bis(2-oxoethane-2,1-(diyl))bis(oxy)dibenzaldehyde[XVIII]



[XVIII]

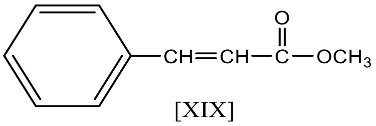
A mixture of compound [XVII] (0.001 mol) , 4- hydroxybenzylaldehyde (0,002 mol) and fused sodium acetate (0.246 g , 0.003 mol) in ethanol 5 ml was refluxed for 4 hrs . then cooled and poured into cold water , the resulting was filtered and recrystallized from ethanol. color off white, Yield 64 %,mp. = 104^{0}C.

Elemental analysis of compound [XXII]

Calc.:C%=64.390 ,H%=5.365 ,N%=6.829

Found: C%=65.206 ,H%=5.132 ,N%=7.412

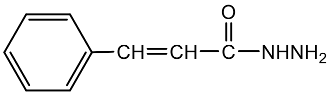
2.3.7 Preparation of Methyl 3-phenyl-2-propenoate[XIX] (81)



[XIX]

A mixture of cinnamic acid (36.408 g , 0.246 mol) in absolute methanol (100 ml) and sulfuric acid (3 ml) was refluxed for (6 hrs.) after cooling the mixture was washed with sodium bicarbonate solution , then washed with water several times dried and recrystallized from ethanol. Yield 80 % , m.p=36-38^{0}C.

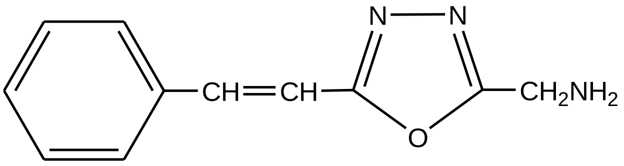
2.3.8 Preparation of 3-Phenyl-2-propenohydrazide[XX]



[XX]

A mixture of ester compound [XIX] (0.006 mol) and 80% hydrazine hydrate (3 ml) in absolute ethanol (5 ml) was refluxed for (3 hrs) . the mixture was cooled at room temperature(82) then solvent was evaporated and solid formed recrystallized from acetone. Yield 76 %, m.p115−117^{0}C.

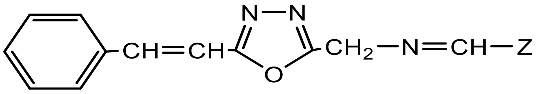
2.3.9 Synthesis of(5-styryl-1,3,4-oxadiazol-2-yl)methanamine[XXI]



[XXI]

Compound [XX](1.62g, 0.01 mol) and glysine(0.75g, 0.01 mol) were refluxed with phosphorous oxychloride (5mL) for 24 hrs. and the reaction mixture was then treated with ice water carefully and made basic by adding concentrated sodium bicarbonate solution. The resulting solid was filtered, dried and recrystallized by ethanol. dark brown color, Yield 65%,m.p = 166-168 ^{0}C.

2.3.10 Synthesis of new schiff bases compounds[XXII-XXV]$^{(83)}$



[XXII-XXV]

Z= C_6H_5--CH=CH- ,--COOH ,4-CH_3O-C_6H_4- , 4-HO-C_6H_4--

A mixture of compound (5-styryl-1,3,4-oxadiazol-2-yl)methanamine[XXI] (0.001mol) and different aldehydes (0.001mol)was dissolved in 5ml absolute ethanol and refluxed for 3-4 hrs . then cooled to room temperature , the solid product was filtered and recrystallized from ethyl acetate to give new Schiff basses. The physical properties are listed in Table (2-3).

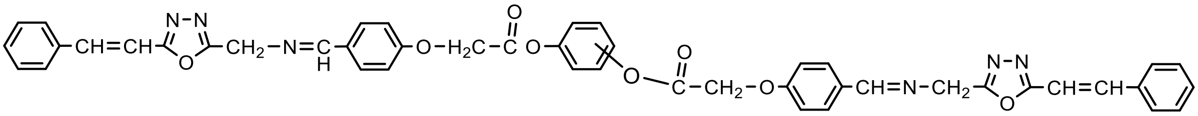
Elemental analysis of compound [XXII]

Calc.:C%=76.190,H%=5.396,N%=13.333

Found: C%=77.151,H%=5.093,N%=12.711

2.3.11 Synthesis of [XXVI] and[XXVII] 1,3-phenylene bis(2-(4-

1,3-phenylene bis(2-(4-((((5-styryl-1,3,4-oxadiazol-2-yl)methyl)imino)methyl)phenoxy)acetate[XXVI] And 1,4-phenylene bis(2-(4-((((5-styryl-1,3,4-oxadiazol-2-yl)methyl)imino)methyl)phenoxy)acetate (([XXVII]



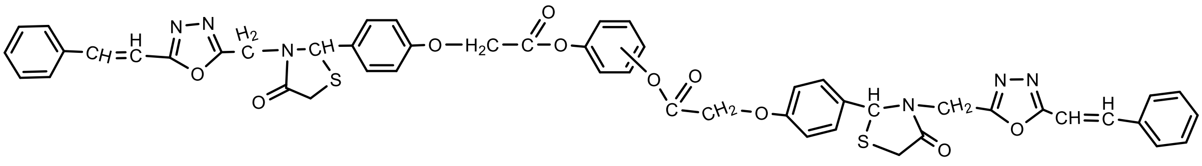
[XXVI],[XXVII]

These compounds were synthesized by using the same procedure given for synthesis compounds [V – VII] , [VIII – X], except using the compound[XXI] as aromatic amine,. the solid product was filtered and recrystallized from ethanol to give new Schiff basses .

Data compound [XXVI]: brown color , Yield 77 %, m.p = 118 0C

Data compound [XXVII]: brown color , Yield 70 %, m.p = 68-70 ^{0}C

2.3.12 Synthesis of1,3-phenylene bis(2-(4-(4-oxo-3-((5-styryl-1,3,4-oxadiazol-2-yl)methyl)thiazolidin-2-yl)phenoxy)acetate) [XXVIII] and 1,4-phenylene bis(2-(4-(4-oxo-3-((5-styryl-1,3,4-oxadiazol-2-yl)methyl)thiazolidin-2-yl)phenoxy)acetate) [XXIX](84)



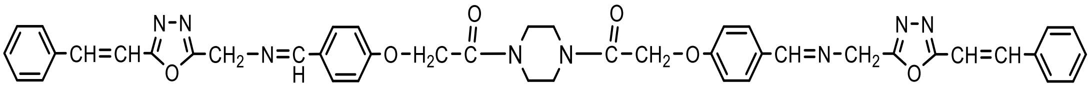
[XXVIII],[XXIX]

These compounds were synthesized by using the same procedure given for synthesis compounds [XI – XIII] and [XIV – XVI] except using the compounds[XXVI] and [XXVII] instead of compounds[V-VII] and [VIII-X]. The precipitate was recrystallized from acetone .

Data compound [XXVIII]: brown color , Yield 63 %, m.p = 125-127 ^{0}C

Data compound [XXIX]: brown color , Yield 65 %, m.p = $>^{300}$ ^{0}C

2.3.13 Synthesis of 1,1'-(piperazine-1,4-diyl)bis(2-(4-(((5-styryl-1,3,4-(oxadiazol-2-yl)methylimino)methyl)phenoxy)ethanone[XXX]



[XXX]

This compound was synthesized by using the same procedure given for synthesis compounds [XXVI] and [XXVII], except using the compound

[XVIII]instead of compounds[III] and [IV].The solid product was recrystallized from ethyl acetate to give new Schiff base browm color , Yield 71 %, m.p = (188-190) ^{0}C.

Table (2-2): The physical properties for the compounds[V-XVI]

Comp. No.	X	Nomenclature	Molecular formula	Yield %	M. P ^0C	Color
[V]	CH_3O	1,3-phenylene bis(2-(4-((4-methoxyphenylimino)methyl)phenoxy)acetate)	$C_{38}H_{32}N_2O_8$	85	212-214	golden
[VI]	CH_3	1,3-phenylene bis(2-(4-((p-tolylimino)methyl)phenoxy)acetate)	$C_{38}H_{32}N_2O_6$	87	203-205	Yellow
[VII]	OH	1,3-phenylene bis(2-(4-((4-hydroxyphenylimino)methyl)phenoxy)acetate)	$C_{36}H_{28}N_2O_8$	73	165-167	brown
[VIII]	CH_3O	1,4-phenylene bis(2-(4-((4-methoxyphenylimino)methyl)phenoxy)acetate)	$C_{38}H_{32}N_2O_8$	82	190-192	golden
[IX]	CH_3	1,4-phenylene bis(2-(4-((p-tolylimino)methyl)phenoxy)acetate)	$C_{38}H_{32}N_2O_6$	75	209-211	brown
[X]	OH	1,4-phenylene bis(2-(4-((4-hydroxyphenylimino)methyl)phenoxy)acetate)	$C_{36}H_{28}N_2O_8$	86	>300	dark brown
[XI]	CH_3O	1,3-phenylene bis(2-(4-(3-(4-methoxyphenyl)-4-oxothiazolidin-2-yl)phenoxy)acetate)	$C_{42}H_{36}N_2O_{10}S_2$	82	gummy	Pal yellow
[XII]	CH_3	1,3-phenylene bis(2-(4-(4-oxo-3-p-tolylthiazolidin-2-yl)phenoxy)acetate)	$C_{42}H_{36}N_2O_8S_2$	72	gummy	Pal yellow
[XIII]	OH	1,3-phenylene bis(2-(4-(3-(4-hydroxyphenyl)-4-oxothiazolidin-2-yl)phenoxy)acetate)	$C_{40}H_{32}N_2O_{10}S_2$	68	gummy	brown
[XIV]	CH_3O	1,4-phenylene bis(2-(4-(3-(4-methoxyphenyl)-4-oxothiazolidin-2-yl)phenoxy)acetate)	$C_{42}H_{36}N_2O_{10}S_2$	62	170-172	Off white
[XV]	CH_3	1,4-phenylene bis(2-(4-(4-oxo-3-p-tolylthiazolidin-2-yl)phenoxy)acetate)	$C_{42}H_{36}N_2O_8S_2$	67	gummy	brown
[XVI]	OH	1,4-phenylene bis(2-(4-(3-(4-hydroxyphenyl)-4-oxothiazolidin-2-yl)phenoxy)acetate)	$C_{40}H_{32}N_2O_{10}S_2$	74	133-135	brown

Table (2-3): The physical properties for the compounds[XXII-XXV]

Comp . No.	Z	Nomenclature	Molecular formula	Yield %	M. P °C	Color
XXII	-CH=CH-C_6H_4	3-phenyl-N-((5-styryl-1,3,4-oxadiazol-2-yl)methyl)prop-2-en-1-imine	$C_{20}H_{17}N_3O$	35	135	Darck brown
XXIII	-COOH	2-(((5-styryl-1,3,4-oxadiazol-2-yl)methyl)imino)acetic acid	$C_{13}H_{11}N_3O_3$	78	70	brown
XXIV	4-CH_3O—C_6H_4	1-(4-methoxyphenyl)-N-((5-styryl-1,3,4-oxadiazol-2-yl)methyl)methanimine	$C_{19}H_{17}N_3O_2$	69	139	brown
XXV	4-HO-C_6H_4	4-((((5-styryl-1,3,4-oxadiazol-2-yl)methyl)imino)methyl)phenol	$C_{18}H_{15}N_3O_2$	76	110	Darck brown

Chapter Three

Results

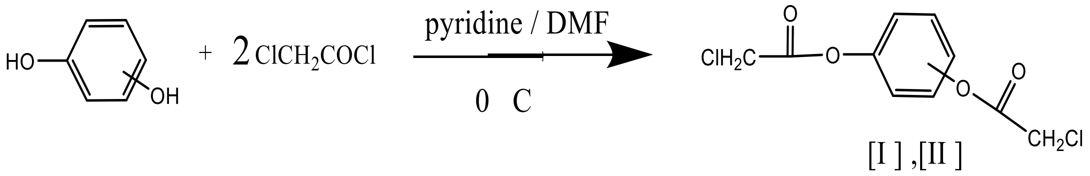
&

Discussion

3.1. Synthesis and Characterization

3.1.1. Preparation and Characterization of 1,3- phenylene bis(2-chloroacetate) [I] and 1,4-phenylene bis(2-chloroacetate) [II]

In order to obtain the compounds [I] and [II] ,we reacted resorcinol or hydroquinone with two moles of chloroacyl chloride in pyridine and DMF as a solvent .

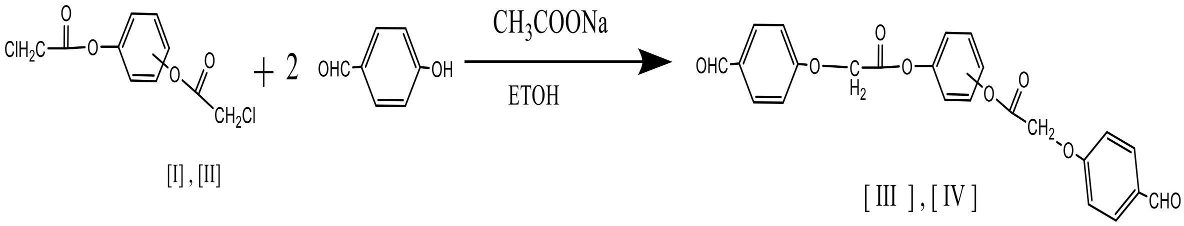


These compounds were identified by melting points and FTIR spectroscopy.

The FTIR spectra of these compounds as in Figure (3-1) for compound [I] showed disappearance bands of the υ OHgroups, which was observed in the starting materials and showed new absorption stretching bands at 1774 cm^{-1} and 1764cm^{-1} that are attributed to the C=O of ester groups(85) , respectively. Also, showed stretching band at 793cm^{-1} and 758 cm^{-1} for υ CH_2Cl ,respectively.

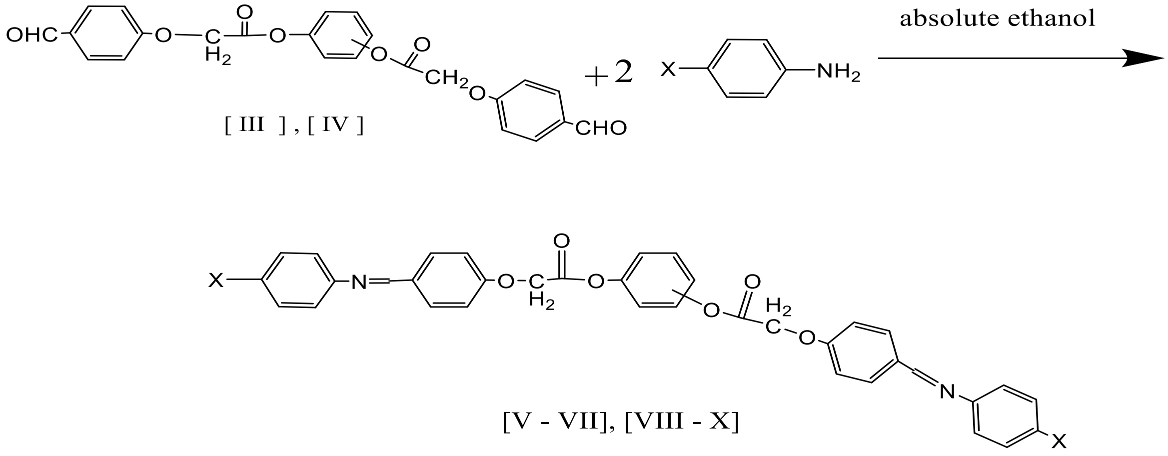
3.1.2 Synthesis of 1,3-phenylene bis(2-(4-formylphenoxy)acetate)[III] and 1,4-phenylene bis(2-(4-formylphenoxy)acetate)[IV]

The dialdehydes[III] and [IV] were synthesized by the reaction of two moles of 4-hydroxybenzaldehyde with one mole of compound [I] or compound [II] , using absolute ethanol as a solvent in CH_3COONa medium .



The FTIR spectra of these compounds [III] and [IV] showed a new stretching bands at 1686cm^{-1} and1668 cm^{-1}assigned to CHO groups , also showed a new stretching bands at 1215 cm^{-1} and1217 cm^{-1} for ether groups($-CH_2-O-$), as in Figure (3-2) and (3-3), respectively . While, The ^{1}HNMR spectrum (in DMSO-d_6 as a solvent) of compound [III], Figure(3-4) showed: a singlet signal at δ9.77 ppm for two protons of CHO groups, many signals in the region δ (6.17-7.75) ppm of twelve aromatic protons of benzene rings, a singlet signal at δ 3.45 ppm due to four protons of two (OCH_2CO)groups .

3.1.3. Synthesis and characterization of new Schiff base compounds[V-VII] and [VIII- X] :



These Schiff bases were synthesized by refluxing one mole of dialdehyde compounds [III] or [IV] and two moles of different amino compounds in absolute ethanol as a solvent .

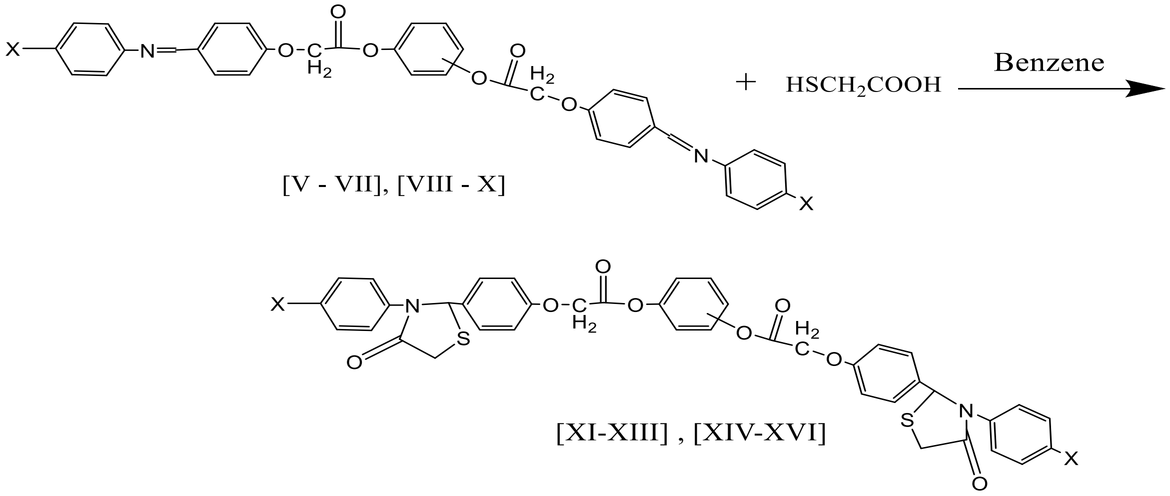
The structure of these schiff's bases **[**V-VII] and [VIII- X] were characterized by melting points , FTIR and ^{1}HNMR spectroscopy (for some of them) .

The FTIR spectrum showed the disappearance of absorption bands which due to NH_2 and CHO groups of the starting materials together with the appearance of new absorption stretching bands of C=N group in the region(1654–1651) cm^{-1} and (1645-1638) cm^{-1} Figure (3-5) and(3-6) display the FTIR spectrum for compound [V] and [X] , respectively .

The other data of functional groups which are characteristic of these compounds are given in Table(3-1) .

The ^{1}HMNR spectra of Schiff base compounds [V] and [IX] as in Figures (3-7) and (3-8) , respectively showed the following signals: twenty aromatic protons appeared as multiplet in the region δ (6.85-7.74) ppm and δ (6.54-7.75) ppm respectively , sharp singlet at δ (8.45) ppm and δ (8.59) ppm that could be attributed to azomethine protons , respectively . A sharp signal at δ 3.75 ppm is due to four protons of (OCH2CO) groups and six protons of two (CH3) terminal groups for compound [V]. while two protons of two (OCH_2CO) groups and six protons of two (CH_3) terminal groups for compound [IX] appear at δ 3.32 ppm and δ (2.29) ppm, respectively.

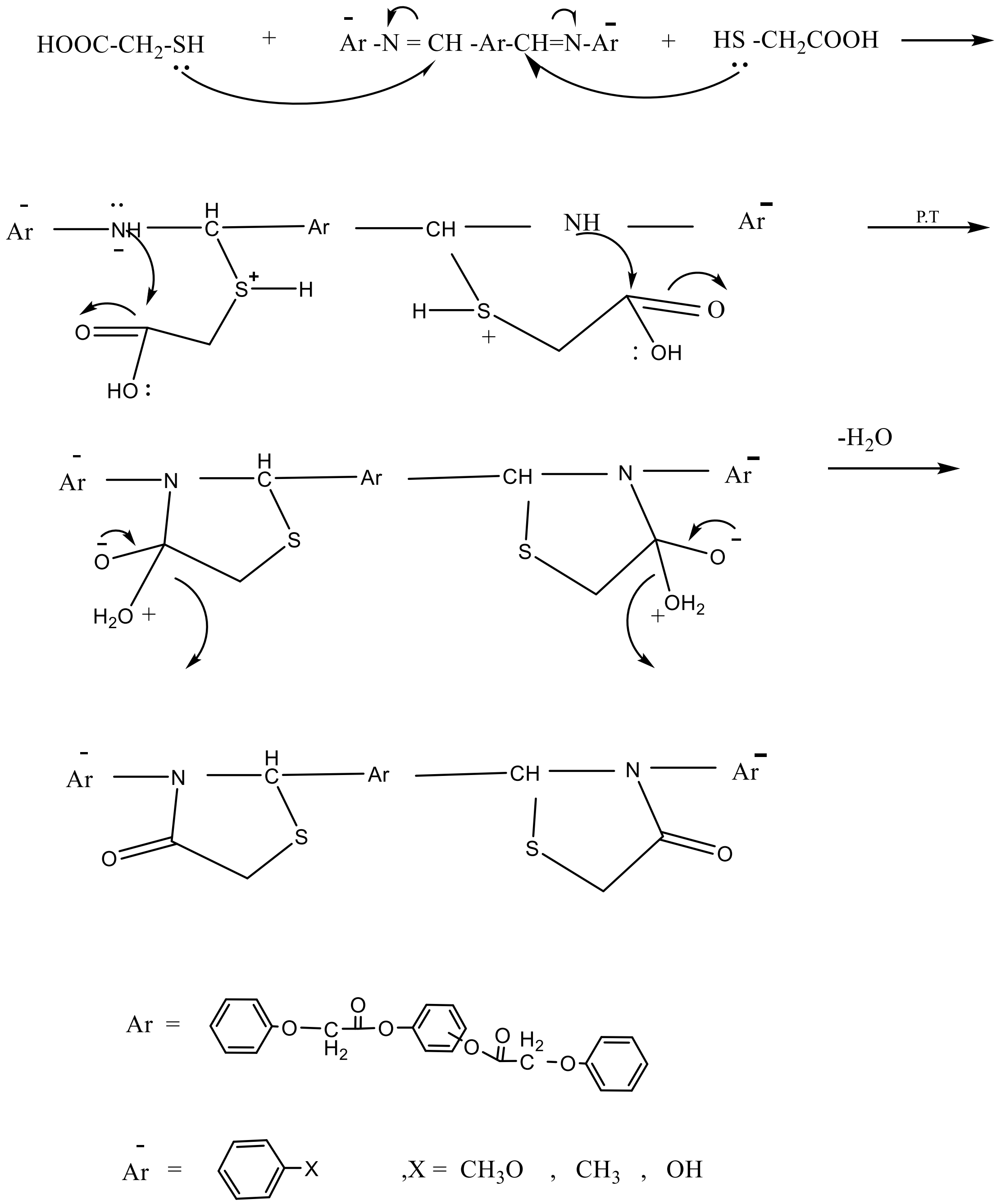
3.1.4 Synthesis and Characterization of Thiazolidine-4-one compounds [XI-XIII],[XIV-XVI]:



[V - VII], [VIII - X]

[XI-XIII] , [XIV-XVI]

Thiazolidine-4-one compounds [XI-XIII] and [XIV-XVI] were synthesized by the reaction of Schiff bases compounds [V-VII] and [VIII-X] with two moles of thioglycolic acid in dry benzene, respectively . The mechanism(86) for synthesized these compounds shown as in Scheme (3-1)



Scheme(3-1)

These compounds were characterized by their melting points, FTIR and ^{1}HNMR spectroscopy (for some of them) .

The FT-IR spectrum of compound [XII] as in Figure (3-9) showed the appearance of carbonyl group of the thiazoldinone(87) at (1651) cm^{-1} and (C-H) aliphatic band at (2958-2858) cm^{-1}, (C-H) aromatic(88) band at (3030) cm^{-1} , (C=C) aromatic at (1608) cm^{-1} and band at (964) cm^{-1} for (C-S)group.

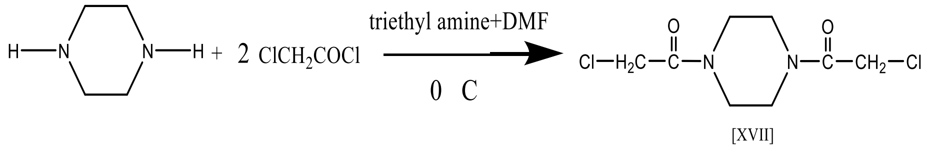
The ^{1}H-NMR spectrum of compound [XII] as in Figure (3-10), showed signal at δ (2.13) ppm for six protons of the two (CH_3) groups , a singlet was observed at δ 3.65 ppm for four protons of (O-CH_2CO) groups . Singlet signal appeared at δ 4.36 ppm due to four protons of two (H-5 thiazoldinon) . Also signals appear at δ(6.30-7.46)ppm for twenty aromatic protons of benzene rings as of two protons of two (H-2 thiazoldinon) .

The FT-IR spectrum of compound [XV] as in Figure (3-11) , showed The appearance of carbonyl group of the thiazolidinone in (1685) cm^{-1} and (C-H) aliphatic band at (2970-2830) cm^{-1}, (C-H) aromatic band at (3030) cm^{-1} , (C=C) aromatic at (1608) cm^{-1} and band at (997) cm^{-1} for (C-S) group.

The FT-IR absorption bands of thiazoldin-4-ones [XI-XVI] are listed in Table (3 -2) .

The ^{1}H-NMR spectrum of compound [XIV] Figure (3-12) showed signal at δ 3.65 ppm for six protons of the two (CH_3O) groups , a singlet was observed at δ3.72 ppm for four protons of (OCH_2CO) groups. Singlet signal appeared at δ 4.10ppm due to four protons of two(H-5 thiazolidinone) . Also ,multiplet signals appeared at δ (6.85-7.51)ppm for twenty aromatic protons of benzene rings and two protons of two (H-2 thiazolidinone) .

3.1. 5 Preparation and characterization of 1,1'-(piperazine-1,4-diyl)bis(2-chloroethanone)[XVII]

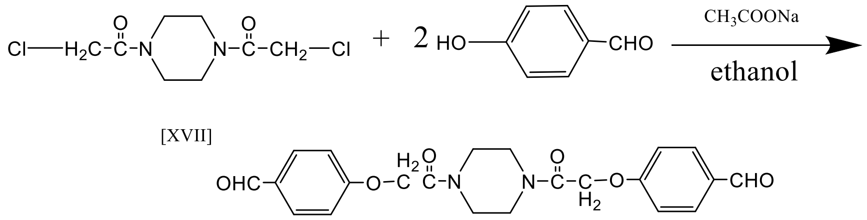


[XVII]

The compound [XVII] was prepared from the reaction of piperazine with two moles of chloroacetyle chloride in triethyl amine (TEA) and DMF as a solvent .

The structure of the compound [XVII] has been characterized by FTIR spectroscopy. The FTIR spectrum for compound[XVII], Figure (3-13) showed the disappearance of absorption stretching bands of N-H groups in starting material of (piperazine) together with the appearance of new stretching bands at 1637 $cm^{-1}$of C=O group, CH-aromatic at 3037 cm^{-1} , CH-aliphatic at (2991 – 2864) cm^{-1}.

3.1. 6 Synthesized and characterization of 4,4'-(2,2'-(piperazine-1,4-diyl)bis(2-oxoethane-2,1-diyl))bis(oxy)dibenzaldehyde[XVIII]



[XVIII]

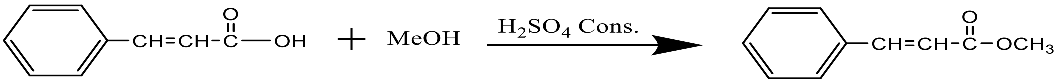
The compound [XVIII] was synthesized from the reaction of compound [XVII] with two moles of 4-hydroxybenzaldehyde and CH_3COONa in absolute ethanol as a solvent .

The structure of the compound [XVIII] has been characterized by FTIR and ^{1}HNMR spectroscopy .

The FTIR spectrum for compound [XVIII] as in Figure (3-14) showed : (C=O) group at 1668 cm^{-1} , C=C-Ar group at 1600 cm^{-1} , CH-aromatic at 3169 cm^{-1} and CH-aliphatic at (2966-2862)cm^{-1}.

The ^{1}HNMR spectrum Figure (3-15) for compound [XVIII], showed : singlet signal at δ (9.77)ppm for two protons of CHO groups , signals in regions δ (6.90 – 7.75) ppm for eight protons of aromatic rings , signal in δ 4.78 ppm for four protons of (O-CH$_2$ =O) groups , finally singlet signal at δ (2.06)ppm for protons of piperazine ring .

3.1.7 Preparation and Characterization of Methyl 3-phenyl-2-propenoate[XIX] (79)

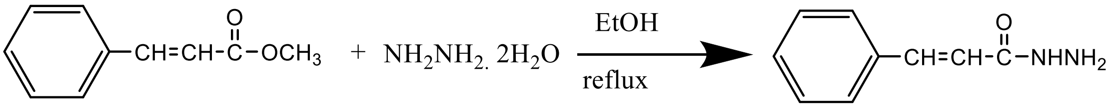


[XIX]

The ester compound [XIX] was prepared from the reaction of cinnamic acid with methanol in conc. H$_2$SO$_4$ (as a catalyst). This compound was characterized by melting point and FTIR spectrum.

The FTIR spectrum for compound [XIX] as in Figure (3-16) showed the disappearance of absorption stretching bands of O-H and C=O groups of (carboxylic moiety) in starting materials together with the appearance of a new stretching band at (1716) cm^{-1} assigned to C=O group of ester moiety.

3. 1.8 Preparation and Characterization of 3-Phenyl-2-propenohydrazide[XX]



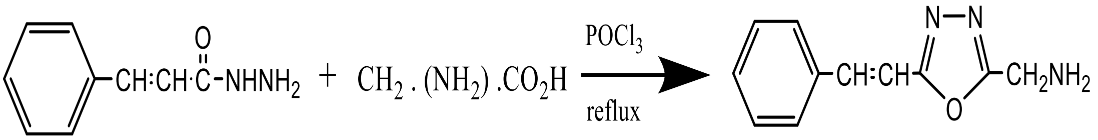
[XIX] [XX]

The condensation of one mole of ester compound [XIX] with one mole of 80% hydrazine hydrate in ethanol produced the acid hydrazide [XX] .

The structure of the compound [XX] has been characterized by melting point and FTIR spectrum .

The FT-IR spectrum as in Figure (3-17), for hydrazide compound [XX] showed disappearance of absorption streching bands due to ester group with the appearance of the characteristic absorption bands in the regions (3311-3200) cm-1 due to asymmetric and symmetric stretching vibration of the (NH2 and NH) groups, the FT-IR spectrum also showed the appearance of absorption band at (1643) cm^{-1} due to the stretching vibration of the carbonyl group.

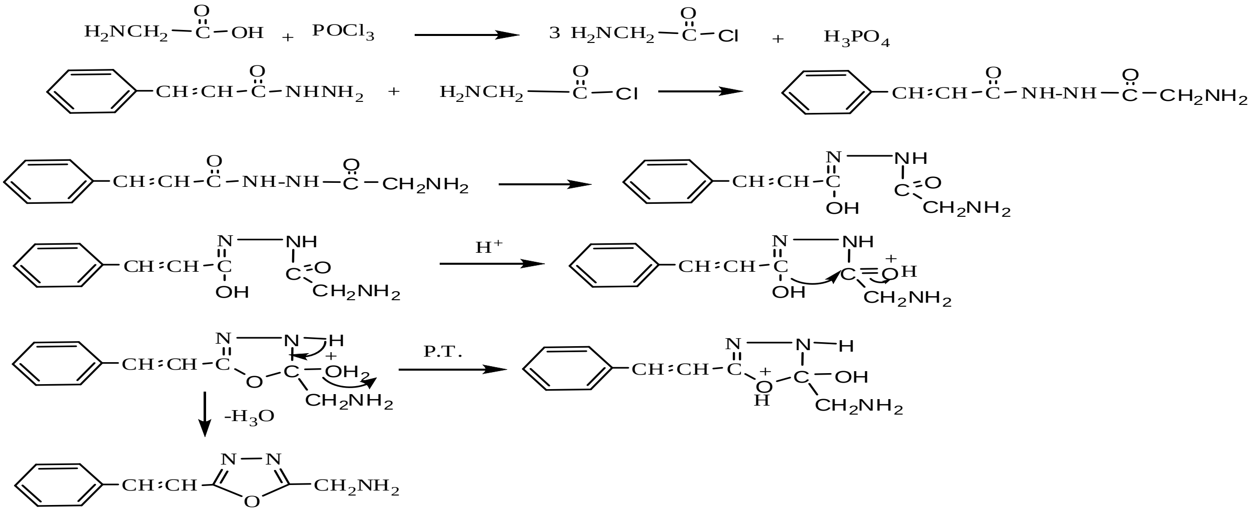
3.1.9 Synthesis and Characterization of(5-styryl-1,3,4-oxadiazol-2-yl)methanamine[XXI]



[XX] [XXI]

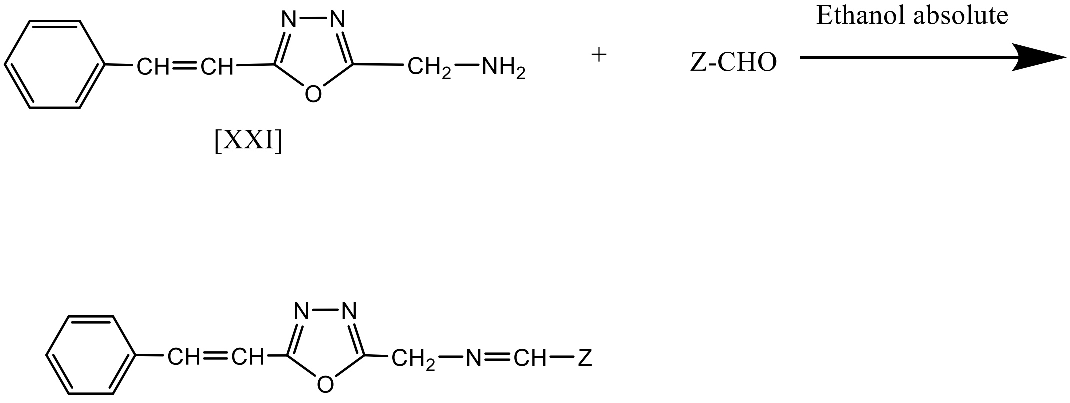
The acidhydrazide[XX] and glysine compound could be smoothly cyclidehydrated by boilig in phosphorus oxychloride $POCl_3$ to produce the 1,3,4-oxadiazol compound[XXI].This compound characterized by FTIR spectroscopy .

The FTIR spectrum for this compound showed disappearance of absorption stretching bands for starting materials and appearance of new absorption stretching band at 1637cm^{-1}due to υ C=N group for oxadiazol ring as in Figure (3-18). The mechanism(89) of dehydration in the presence of $POCl_3$ is depicted in the following steps Scheme (3-2):



Scheme (3-2):The mechanism steps for formation of compound [XXI].

3.1.10 Synthesis and Characterization of new schiff base compounds[XXII-XXV] :



[XXI]

[XXII-XXV]

Z = C_6H_5-CH=CH , -COOH , 4- CH_3O-C_6H_4- , 4-HO-C_6H_4-

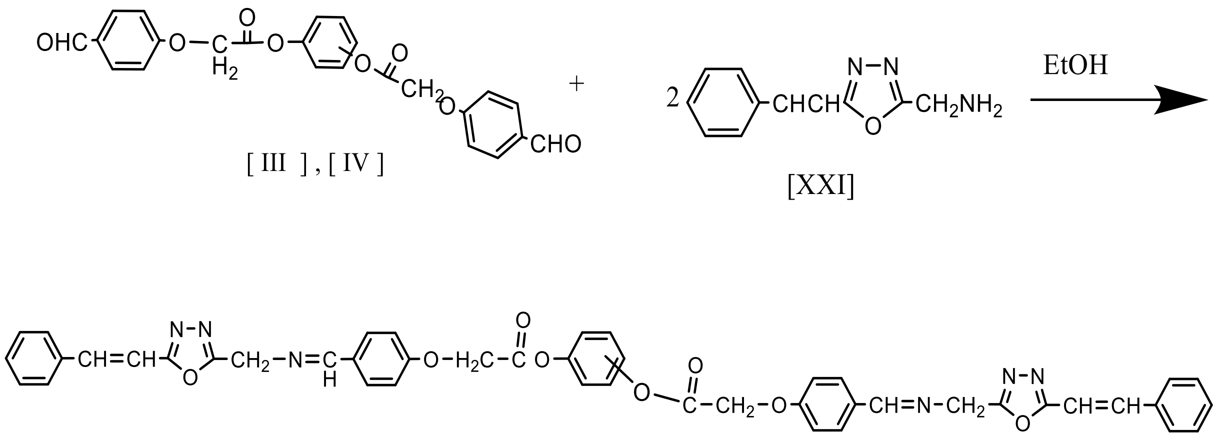
New Schiff base compounds [XXII- XXV] can be synthesized from the reaction of 1,3,4-oxadiazol compound[XXI] with different aromatic aldehydes . The structure of these schiff's bases [XXII-XXV] were characterized by FTIR , and ^{1}HNMR spectroscopy for compound[XXV] .

The FTIR spectrum showed the disappearance of absorption bands due to NH_2 and CHO groups of the starting materials together with the appearance of new absorption stretching bands of C=N groups in the region(1647 – 1626) cm^{-1} as in Figure (3-19) for compound [XXV]

The other data of functional groups which are characteristic of these compounds are given in Table (3-3) .

^{1}HMNR spectrum of Schiff base compound [XXV] as in Figure (3-20) showed the following signals: multiplet signals appeared in the region δ (6.93-8.19)ppm for nine aromatic protons , a signal at δ (8.56) ppm for proton of azomethine group ,also sharp signal at δ 9.79 ppm is due to proton of hydroxyl group$^{(90)}$ and signals at δ(4.07-4.26)ppm that could be attributed to the protons of (-CH=CH-) group. Finally signal appeared at δ 3.99 ppm due to two protons of (CH_2N) group.

3.1.11 Synthesis and Characterization of new schiff bases compounds [XXVI] and [XXVII]



[III] , [IV]

[XXI]

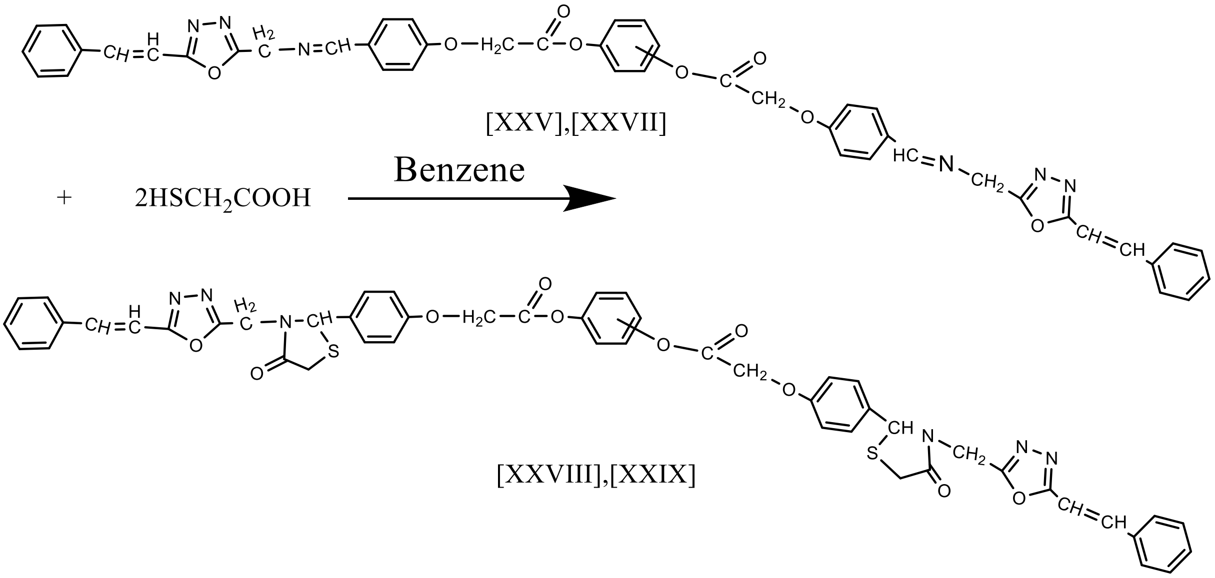
[XXVI],[XXVII]

New Schiff base compounds [XXVI] and [XXVII] were synthesized from the reaction of two moles of 1,3,4-oxadiazol compound[XXI] with dialdehyde compound [III] or [IV] , respectively. These Schiff bases were characterized by melting points , FTIR and 1HNMR spectroscopy.

The characteristic FTIR spectra of these compounds showed the disappearance of absorption bands due to NH_2 and CHO for stretching bands of starting material together with the appearance of stretching bands at 1645cm^{-1} and 1651cm^{-1} assignable to C=N groups ,respectively as in Figure (3-21)and (3-22) for compounds [XXVI] and [XXVII] ,respectively .

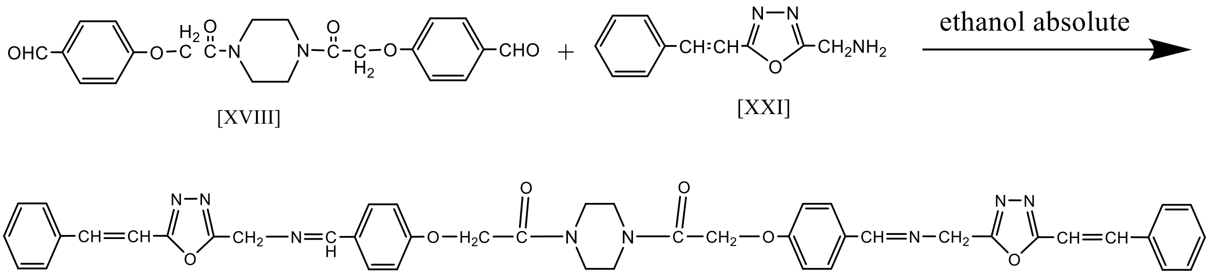
The ^{1}HNMR spectrum (in DMSO-d_6 as a solvent) for compound [XXVI]as Figure (3-23) showed: a singlet signals at δ8.53 ppm for two protons of azomethine (N=CH) groups , multiplet signals appear at δ (6.40-7.75)ppm for twenty two aromatic protons of benzene rings, signals at δ(5.41-6.33) ppm that could be attributed to the four protons of two(-CH=CH-) groups. Also singlet signal appear at δ 3.51 ppm due to four protons of two (OCH_2CO) groups and signal appear at δ2.7 ppm for four protons of two(CH_2N) groups.

3.1.12 Synthesis and characterization of thiazolidin-4-one compounds [XXVIII] and [XXIX]



synthesized new thiazolidin-4-one derivatives [XXIII] and [XXIX] by added two moles of thioglycolic acid to one mole of Schiff bases [XXV] and [XXVII] in dry benzene as a solvent. The FTIR spectra for these compounds as in Figure (3-24) for compound[XXVIII] showed the disappearance of a stretching band of imine group and the appearance of a stretching band of carbonyl group of thiazolidinone moiety(91) at 1674 $cm^{-1}$and 1655 cm^{-1} also C-S groups at 997 $cm^{-1}$and 968 cm^{-1},respectively. Figure (3-25) showed mass fragments for compound [XXIX] .

3 -1 .13 Synthesis and Characterization of 1,1'-(piperazine-1,4-diyl)bis(2-(4-(((5-styryl-1,3,4-oxadiazol-2-yl)methylimino)methyl)phenoxy)ethanone[XXX]



[XVIII] [XXI]

[XXX]

New Schiff base compound [XXX] synthesized from the reaction of two moles of 1,3,4-oxadiazol compound[XXI] with dialdehyde compound [XVIII] in ethanol as a solvent . This Schiff base compound was characterized by FTIR spectroscopy and mass spectroscopy.

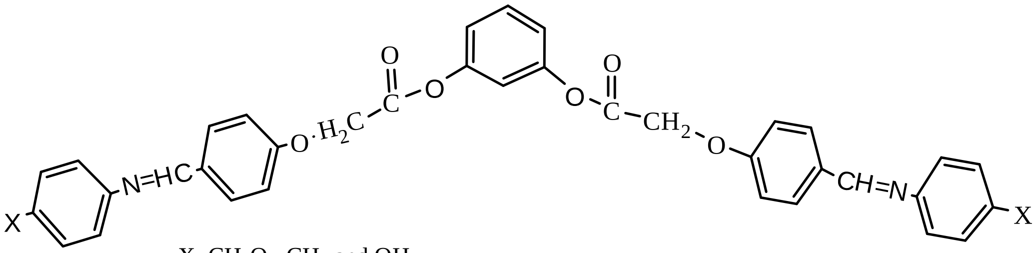
The FTIR spectrum ,Figure (3-26) showed the disappearance of absorption bands due to NH_2 and CHO groups of the starting materials together with the appearance of new absorption stretching band of C=N group at (1651) cm^{-1} ,c=c-aromatic(1600) cm^{-1} .

Figure (3- 27) showed the mass spectrum of compound [XXX] that has the molecular weight =928 .

3.2. Liquid Crystalline Properties of the Synthesized Compounds

The transition temperatures and mesophase type (texture identity) of all compounds were investigated by hot-stage polarized optical microscopy (POM) and some of them by differential scanning calorimetry (DSC).

3.2.1. Mesomorphic Properties of compounds [V-VII]and [VIII-X]:



X=CH_3O , CH_3 and OH

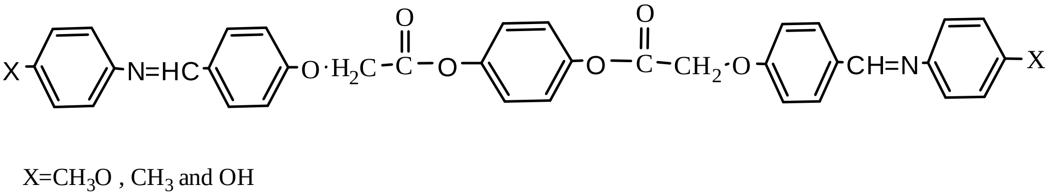
[V-VII]

All the schiff bases compounds [V-VII] showed liquid crystals phases. The compound [V]showed droplets nematic texture under POM because the methoxy groups have a higher polarizability, this could be explained in term of terminal/lateral(t/l)interactionforces ratio, because the methoxy chain led to a higher ratio of t/l interaction forces and when this ratio is high, compound tend to give less ordered mesophases (nematic mesophase)(90) as shown in Figure (3-28) ,while the Figure(3-29) showed DSC thermogram for this compound.

The compound [VI] showed dimorphism smectic B (S_mB)and nematic phases , but the compound [VII] showed dimorphism enantiotropic smectic A phase (SmA) and nematic phases. The DSC thermogram for compound [VI] as in Figure (3-30).

The phase transition temperatures for compounds [V-VII] were listed in Table (3-4).

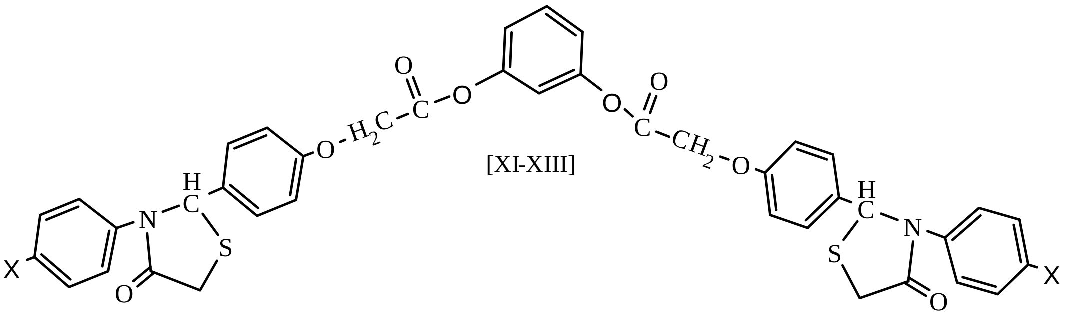
3.2.2. Mesomorphic Properties of compounds [VIII-X]:



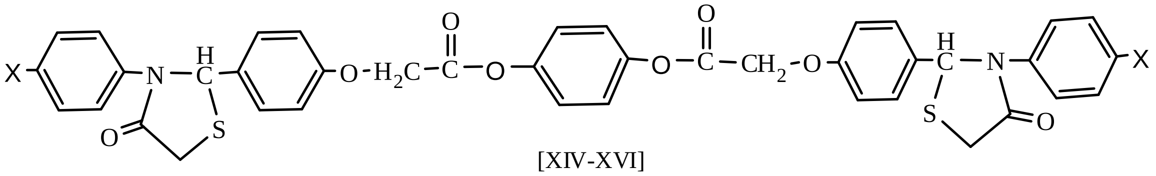
[VIII-X]

The compound [VIII] showed enantiotropic smectic B (S_mB) only but the compound [IX] showed dimorphism enantiotropic smectic B (S_mB)and nematic phases,while the compound [X] showed dimorphism enantiotropic smectic A (SmA) and nematic phases .The Figures (3-31) and (3-32) display the optical textures of smecticB phase and DSC thermogram for compound [VIII] ,respectively ,while the Figure (3-33) showed the optical texture of smectic A phase for compound [IX] . The phase transition temperatures for compounds [VIII-X] were listed in Table (3-4).

3.2.3. Mesomorphic Properties of thiazolidin-4-one derivatives [XI-XIII] and [XIV-XVI] compounds :



[XI-XIII]



[XIV-XVI]

X=CH_3O , CH_3 and OH

All thiazolidin-4-one derivatives[XI-XIII]and [XIV-XVI] didn’t showed any liquid crystalline properties but simply changes from the crystalline solid state to the isotropic liquid .This could be attributed to the presence of thiazolidin-4-one rings which is affect in two ways , firstly by increasing the breadth of this molecule and secondly reducing in the planarity of the molecules. However , the literature survey did not report any mesomorphic of 4-thiazolidinones compounds , (this is represented in three dimensional structures of series [XI-XIII]and [XIV-XVI])as in Figures (3-34) and (3-35), respectively . For this reason, thiazolidin-4-one derivatives[XI-XIII]and [XIV-XVI]didn’t show any liquid crystalline properties. The phase transition temperatures of thiazolidin-4-one derivatives [XI-XIII] and [XIV-XVI]were listed in Table (3-5).

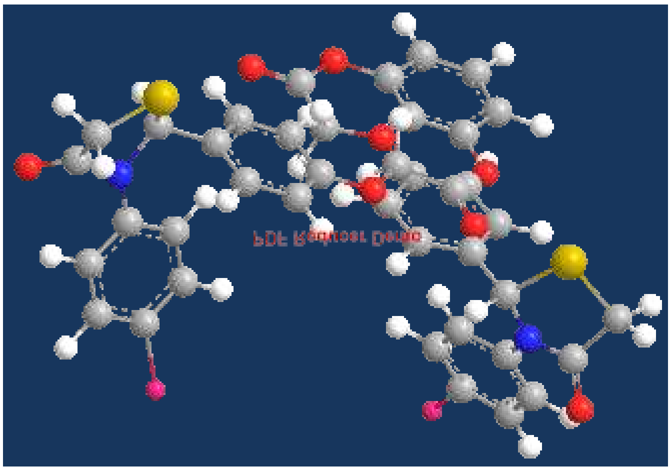


Figure (3-34) :Three dimensional structures of compounds [XI-XIII]

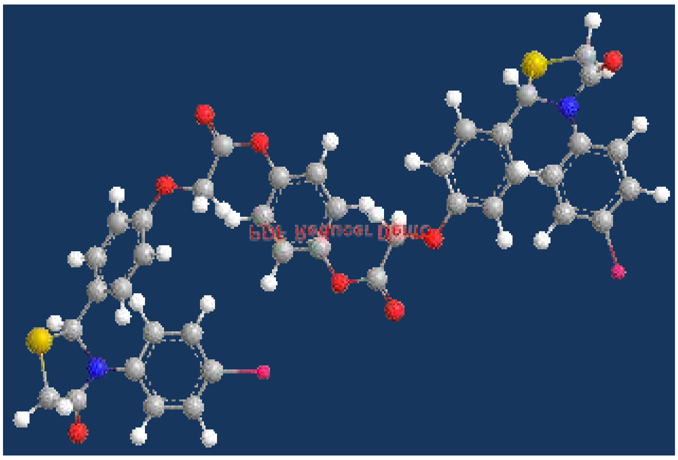
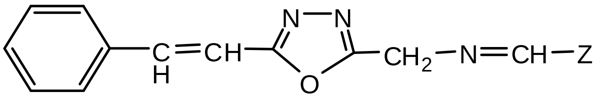


Figure (3-35) :Three dimensional structures of compounds [XIV-XVI]

3.2.4. Mesomorphic Properties of Schiff bases compounds [XXII-XXV]



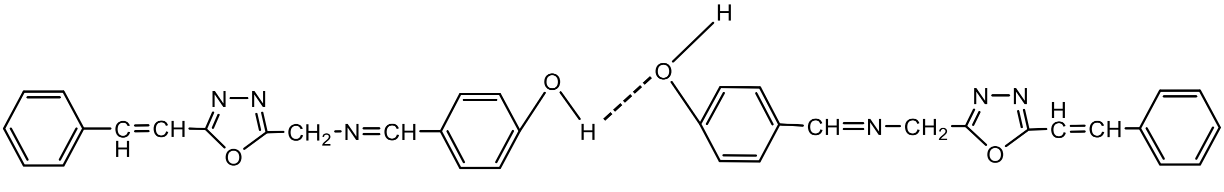
Z=C_6H_5-CH=CH-, -COOH, 4-CH_3O-C_6H_4-, 4-HO-C_6H_4-

[XXII-XXV]

When studying liquid crystalline properties for Schiff bases compounds [XXII-XXV] we found that the compound [XXII] showed dimorphism enantiotropic smectic B (SmB)and nematic phases as in Figures(3-36) and (3-37) for dendritic texture (91) and droplets nematic phases for compound [XXII],respectively , this behavior can attributed to the presence of (C_6H_5-CH=CH-) group in the compound [XXII] and this increasing the rigidity and polarizability of the core and extending the molecular length(92), for this reason the compound [XXII] appears liquid crystals mesophese. While the compounds [XXIII] and [XXIV]didn’t show any mesomorphic behavior but changing from crystals to isotropic liquid.

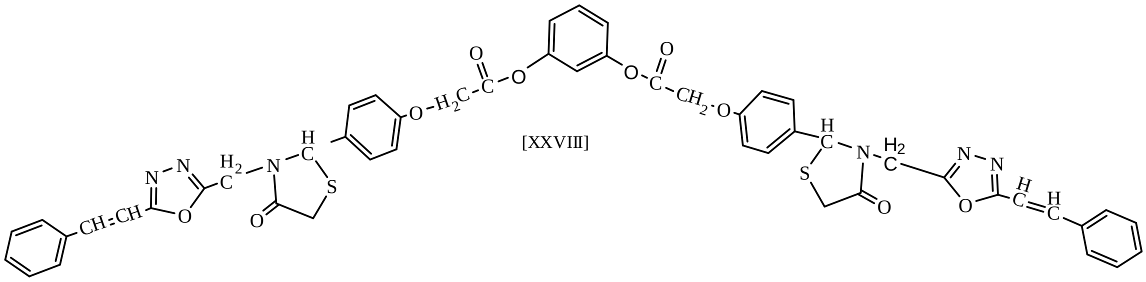
In addition to above the compound [XXV] showed enantiotropic nematic phase.

In this study the compound [XXV] showed nematic phase .This can be attributed to the presence of OH group as a terminal group which could form intermolecular hydrogen bonding(13)as shown in Figure (3-38), for this reason the compound [XXV] favor nematic mesophase. The transition temperatures for Schiff bases compounds[XXII-XXV] are summarized in Table(3-6)

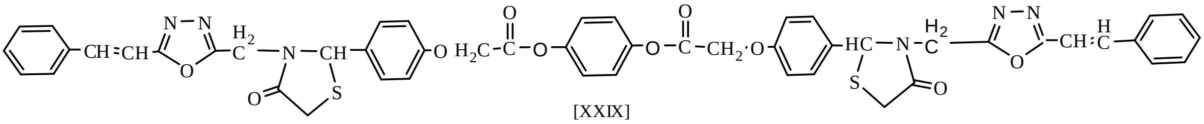


Figure**(3-38) :**Hydrogen bonding formation for compound [XXV]

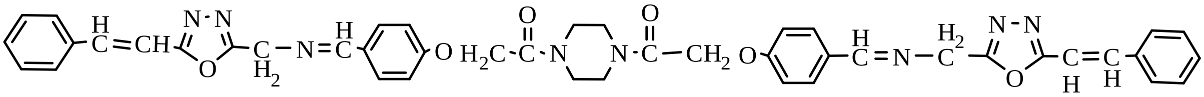
3.2.5. Mesomorphic Properties of thiazolidin-4-one compounds [XXVIII], [XXIX] and compound[XXX].



[XXVIII]



[XXIX]

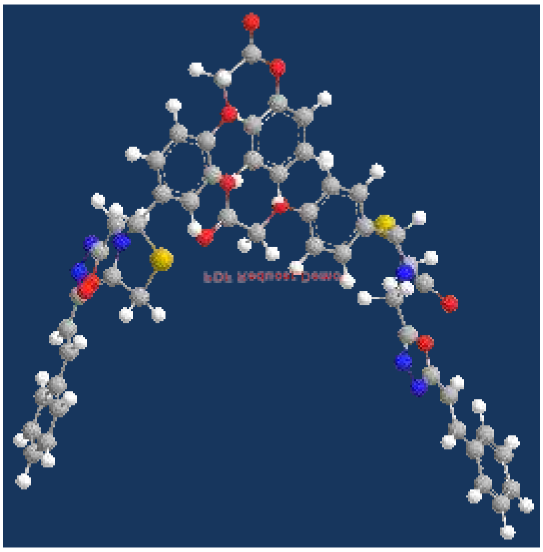


[XXX]

The compound [XXVIII] displayed a banana shape (nematic phase) , but the compound [XXIX] didn’t showed any liquid crystalline properties but simply changes from the crystalline solid state to the isotropic liquid.

In this work when compared between the compounds [XXVIII] and [XXIX] we found that the compound [XXVIII] displayed a banana shape (nematic phase) ,this is maybe related to presence of oxadiazole ring and geometric structure because this compound containing 1,3 disubstituted benzene ring as bent core mesogene(this is represented in three dimensional) as in figure(3-39). This behavior can't be observed in compound [XXIX] which contained planner center core (1,4 disubstituted benzene ring) for this reason the compound[XXIX] didn't show any liquid crystalline properties.

Finally, under the polarized optical microscopy the compound [XXX] showed enantiotropic nematic phases. The transition temperatures for these compounds are listed in Table(3-6).



Figure(3-39) : Three dimension structure of compound [XXVIII]

Conclusions

The conclusions for this work can be draw -:

1-Synthesis of different types of new compounds derived from resorcinol , hydroquinone or piperazine and study the liquid crystalline properties of these new compounds , as follows:

a) New bent and linear core mesogens [V-VII] and [VIII-X] derived from resorcinol and hydroquinone containing imine linkage and different terminal groups these compounds exhibited liquid crystalline properties (nematic and smectic phases) .

b) New compounds containing thiazolidin-4-one ring [XI-XIII] and [XIV-XVI] didn’t show any liquid crystalline mesophase .

c) Schiff bases compounds[XXII-XXV] containing 1,3,4-oxadiazole ring

, the compounds [XXII] and [XXIII] showed liquid crystalline properties, while the compounds [XXIV]and[XXV] didn’t show any mesomorphic behavior.

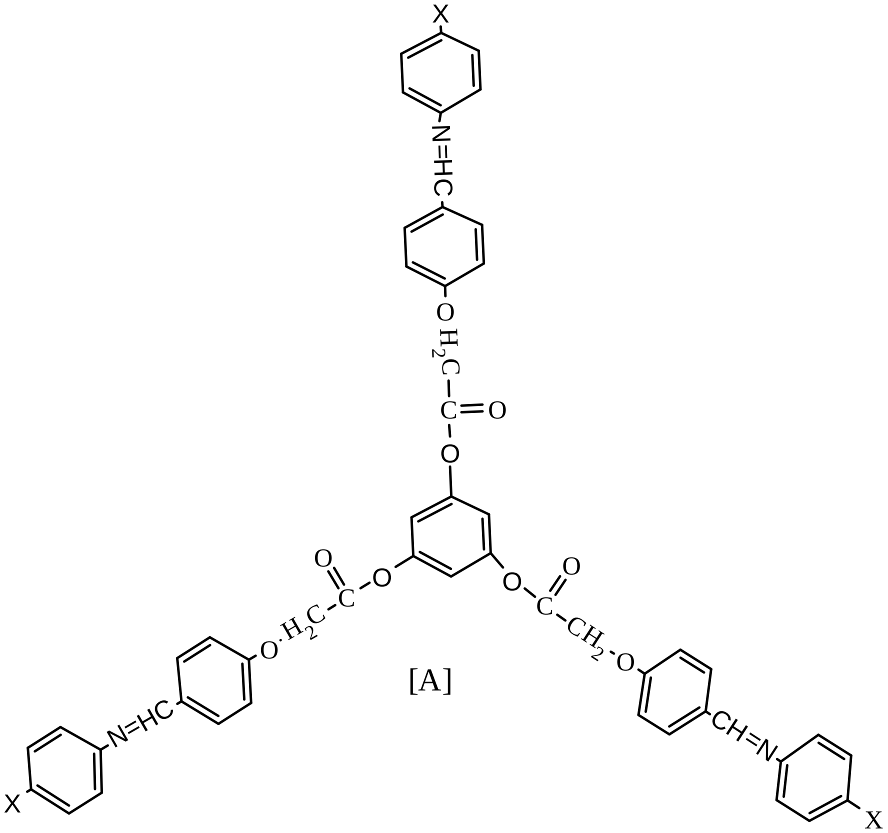
d) The new thiazolidin-4-one derivatives [XXVIII] and [XXIX],the compound [XXVIII] displayed nematic phase, but the compound [XXIX] didn’t showed any liquid crystalline properties. Also new Schiff base compound [XXX] derived from piperazine containing oxadiazole ring showed enantiotropic nematic phase.

2-The spectroscopy data gave a good evidence for the formation of the synthesized compounds .

Suggestion for Future Work

1. Synthesis and study the liquid crystalline behavior of new compounds derived from 1,3,5 –tri hydroxy benzene with imine linkage[A]. These new compounds might exhibit discotic mesomorphic properties .

2. Synthesis and study the liquid crystalline properties of new compounds containing heterocyclic units derived from compound[A] .



[A]

X= different substitute

Figures

Table (3-1):Characteristics FTIR absorption bands of compounds[V-X]

Comp. No.	Characteristic bands FTIR spectra(cm^{-1})					
	Ʋ(O-H)	Ʋ(C-H) aromatic	Ʋ(C-H) aliphatic	Ʋ(C=O) ester	Ʋ(C=N)	Ʋ (C=C) aromatic
[V]	_	3003	2970-2841	1741	1653	1606
[VI]	_	3026	2970-2866	1732	1654	1604
[VII]	3415	3070	2966-2858	1707	1651	1604
[VIII]	_	3005	2972-2839	1720	1645	1606
[IX]	_	3026	2978-2866	1730	1640	1606
[X]	3415	3051	2981-2823	1714	1638	1608

Table (3 -2):Characteristics FTIR absorption bands of thiazoldin-4-ones [XI-XVI]

Comp. No.	Characteristic bands FTIR spectra(cm^{-1})				
	Ʋ(C-H) aromatic	Ʋ(C-H) aliphatic	Ʋ(C=O) thiazoldinone	Ʋ(C=C) aromatic	Ʋ(C-S)
[XI]	3095	2962-2833	1662	1603	950
[XII]	3030	2958-2858	1678	1608	964
[XIII]	3068	2962-2806	1678	1604	993
[XIV]	3010	2956-2837	1654	1600	970
[XV]	3030	2970-2830	1685	1608	997
[XVI]	3010	2966-2852	1681	1600	995

Comp. No.	Characteristic bands FTIR spectra(cm^{-1})				
	Ʋ(C-H) aromatic	Ʋ(C-H) aliphatic	Ʋ(C=N) exo	Ʋ (C=C) aromatic	Other group
[XXII]	3059	2962-2850	1626	1601	_
[XXIII]	3035	_	1635	1605	Ʋ COOH 1734
[XXIV]	3012	2926-2850	1630	1600	_
[XXV]	3057	2980-2821	1647	1597	Ʋ OH 3363

Table (3-3):Characteristics FTIR absorption bands of compounds[XXII-XXV]

Table (3-4): Phase transition temperatures (°C) of Schiff bases compounds[V-X]

Comp. No.	Transition Temperatures (°C)
[V]	$\text{Cr} \xrightarrow{201} \text{N} \xrightarrow{224} \text{I}$
[VI]	$\text{Cr} \xrightarrow{202} \text{SmB} \xrightarrow{217} \text{N} \xrightarrow{228} \text{I}$
[VII]	$\text{Cr} \xrightleftharpoons{150} \text{SmA} \xrightleftharpoons{185} \text{N} \xrightleftharpoons{209} \text{I}$
[VIII]	$\text{Cr} \xrightleftharpoons[229]{200} \text{SmB} \xrightleftharpoons{235} \text{I}$
[IX]	$\text{Cr} \xrightleftharpoons{175} \text{SmB} \xrightleftharpoons{220} \text{N} \xrightleftharpoons{233} \text{I}$
[X]	$\text{Cr} \xrightleftharpoons{120} \text{SmA} \xrightleftharpoons{160} \text{N} \xrightleftharpoons{200} \text{I}$

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

Table (3-5): Phase transition temperatures (^oC) of thiazolidin-4-one derivatives [XI-XIII] and[XIV-XVI] .

Comp. No.	**Transition Temperatures (^oC)**
[XI]	$\mathrm{Cr} \xrightarrow{170} \mathrm{I}$
[XII]	$\mathrm{Cr} \xrightarrow{150} \mathrm{I}$
[XIII]	$\mathrm{Cr} \xrightarrow{160} \mathrm{I}$
[XIV]	$\mathrm{Cr} \xrightarrow{179} \mathrm{I}$
[XV]	$\mathrm{Cr} \xrightarrow{165} \mathrm{I}$
[XVI]	$\mathrm{Cr} \xrightarrow{140} \mathrm{I}$

Cr, crystalline phase ; I, isotropic liquid

Table (3-6): Phase transition temperatures (^{o}C) of Schiff bases compounds [XXII-XXV] ,thiazolidin-4-one compounds [XXVIII] , [XXIX] and compoumd[XXX].

Comp. No.	**Transition Temperatures (^{o}C)**
[XXII]	$\mathrm{Cr} \overset{185}{\rightleftharpoons} \mathrm{SmB} \overset{210}{\rightleftharpoons} \mathrm{N} \overset{230}{\rightleftharpoons} \mathrm{I}$
[XXIII]	$\mathrm{Cr} \xrightarrow{79} \mathrm{I}$
[XXIV]	$\mathrm{Cr} \xrightarrow{145} \mathrm{I}$
[XXV]	$\mathrm{Cr} \overset{95}{\rightleftharpoons} \mathrm{N} \overset{120}{\rightleftharpoons} \mathrm{I}$
[XXVIII]	$\mathrm{Cr} \overset{110}{\rightleftharpoons} \mathrm{N} \overset{175}{\rightleftharpoons} \mathrm{I}$
[XXIX]	$\mathrm{Cr} \xrightarrow{310} \mathrm{I}$
[XXX]	$\mathrm{Cr} \overset{115}{\rightleftharpoons} \mathrm{N} \overset{160}{\rightleftharpoons} \mathrm{I}$

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

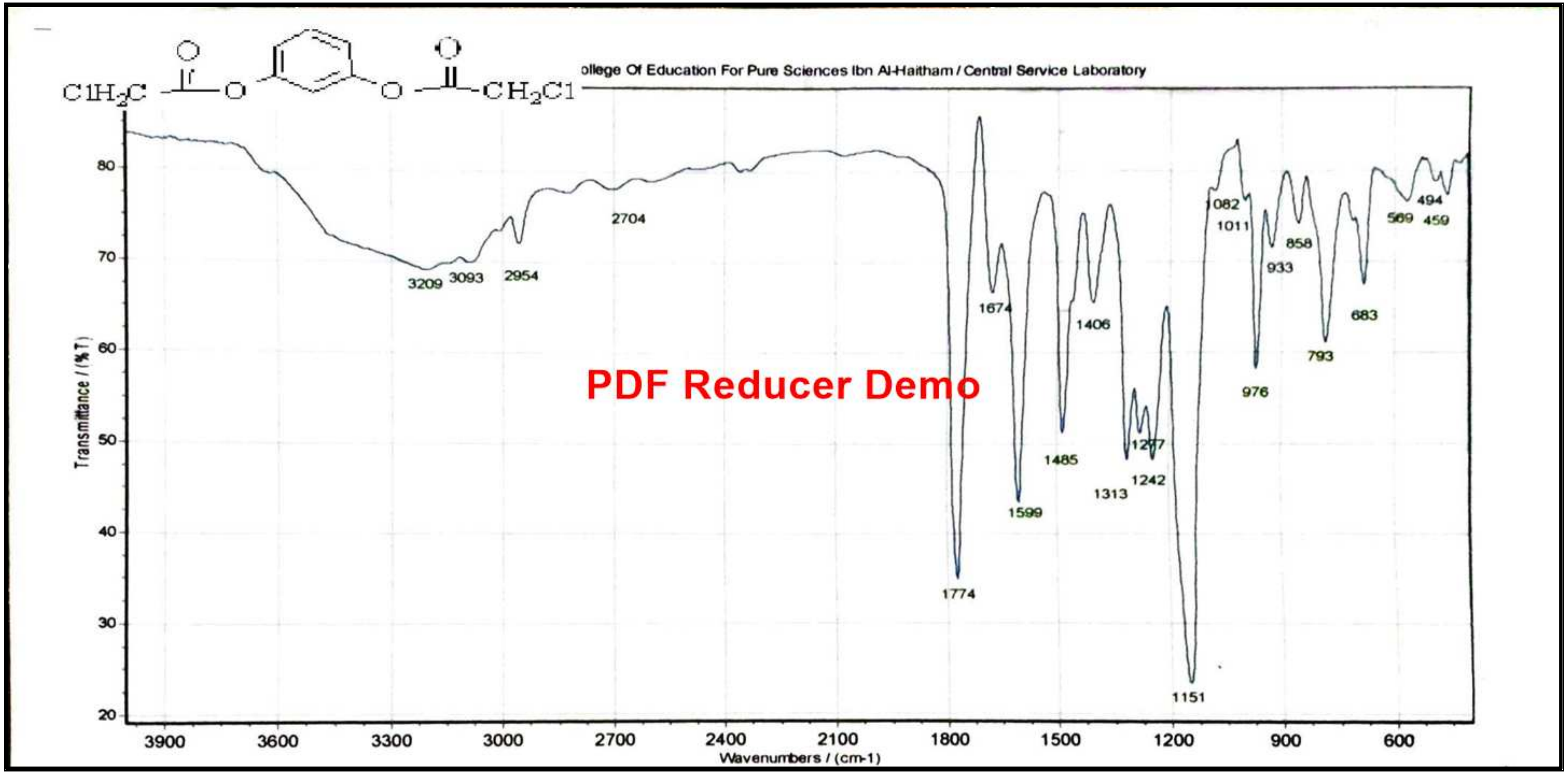


Figure (3 - 1) : FTIR spectrum for compound[I]

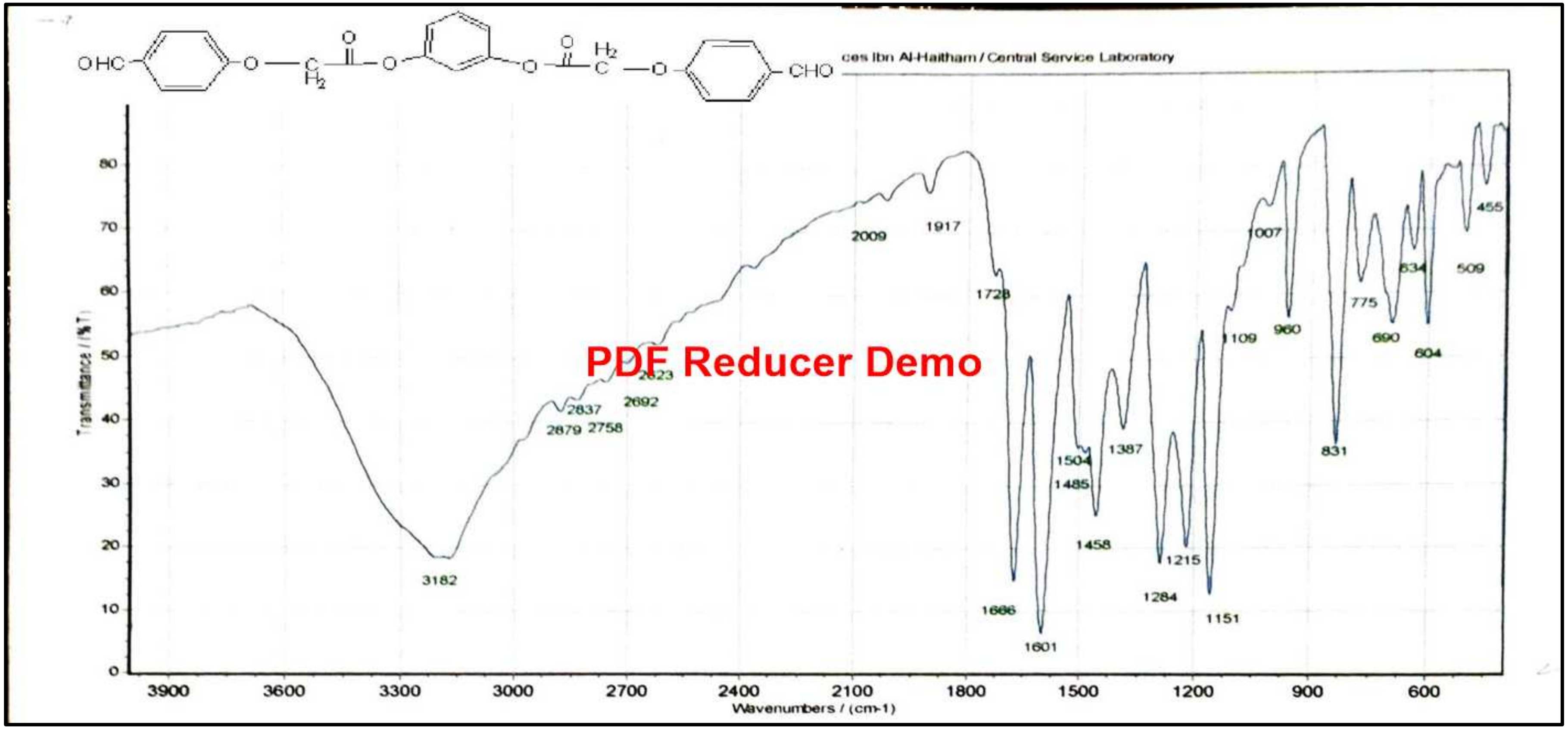


FIGURE (3 - 2) : FTIR spectrum for compound[III]

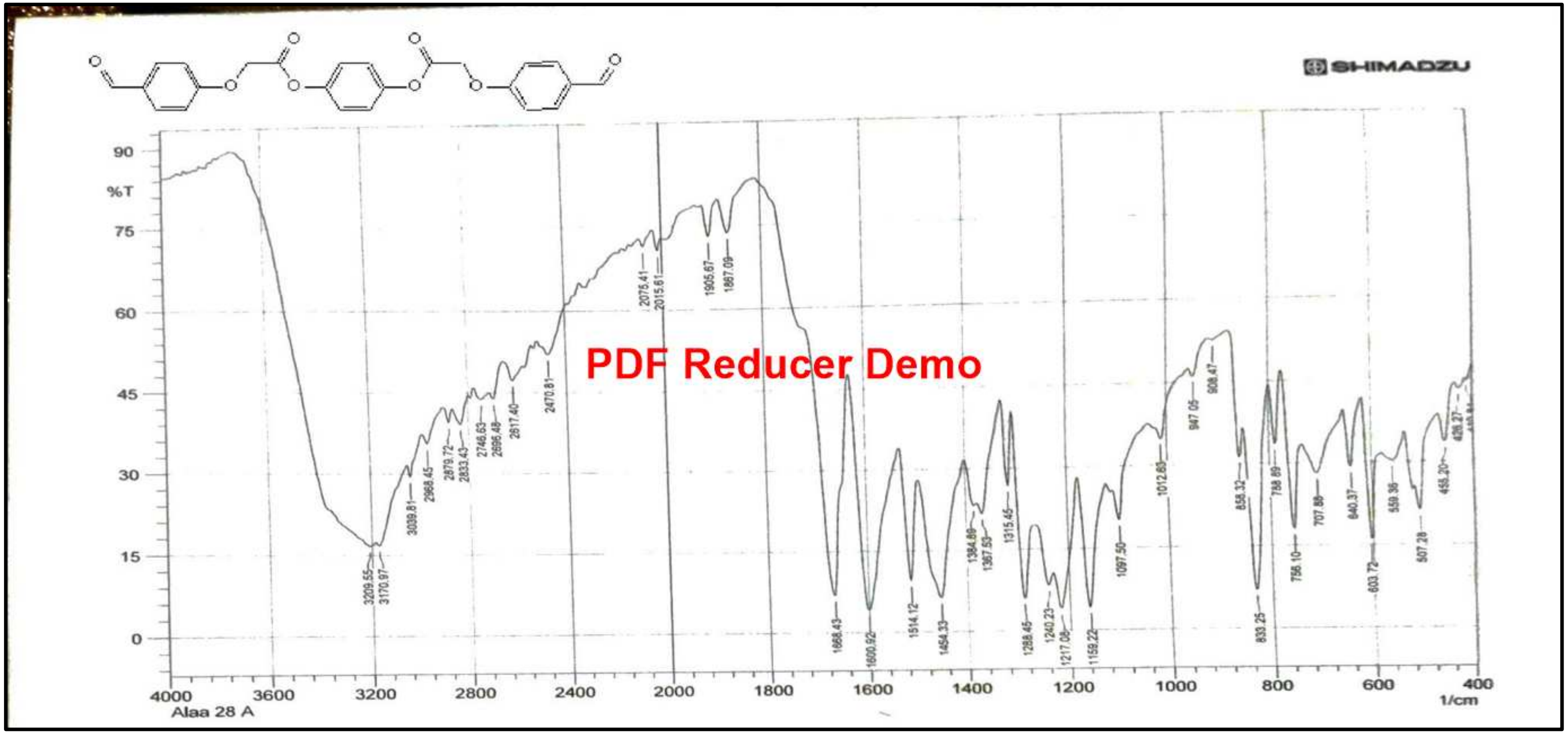
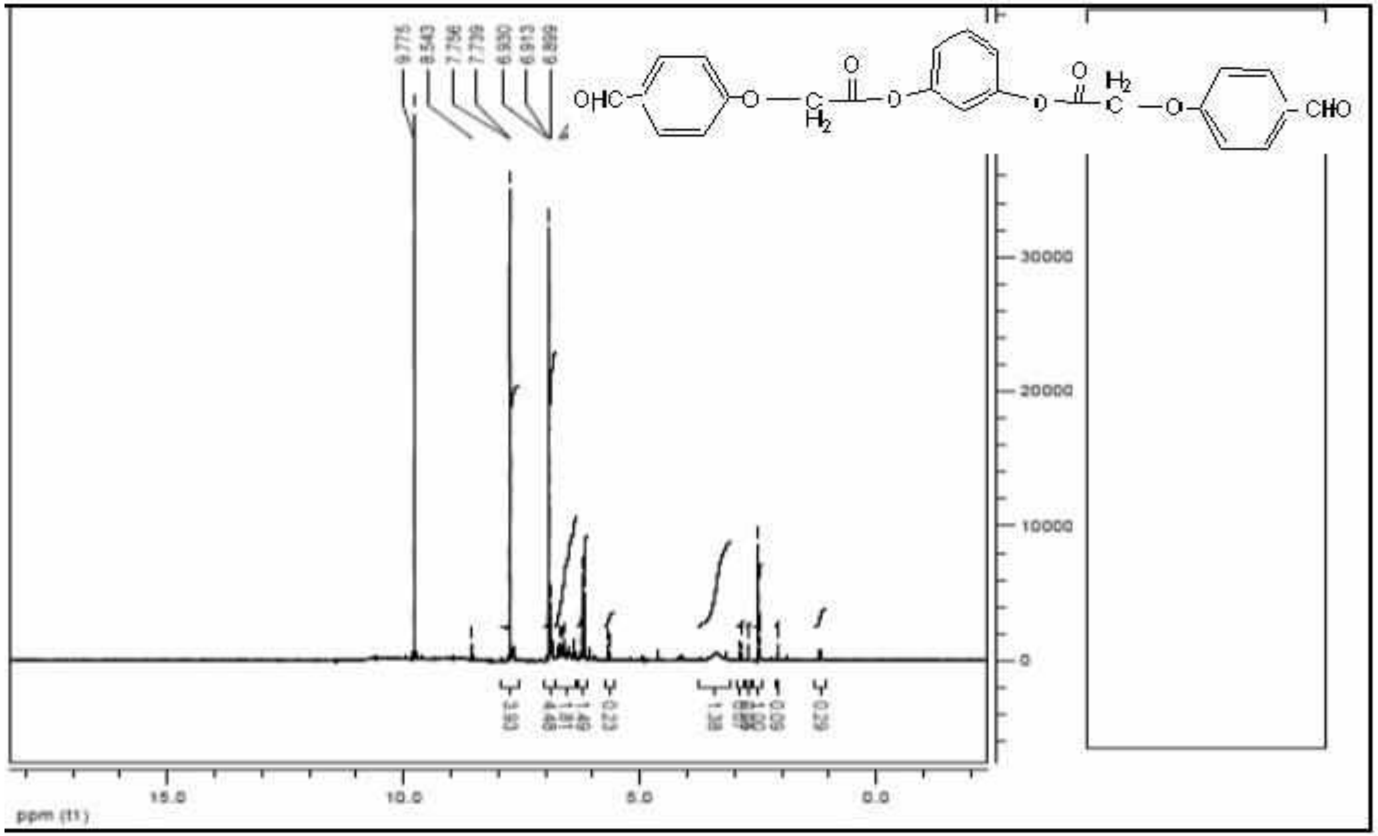


FIGURE (3 - 3) : FTIR spectrum for compound[IV]



Figure(3-4):1H-NMR spectrum for compound [III]

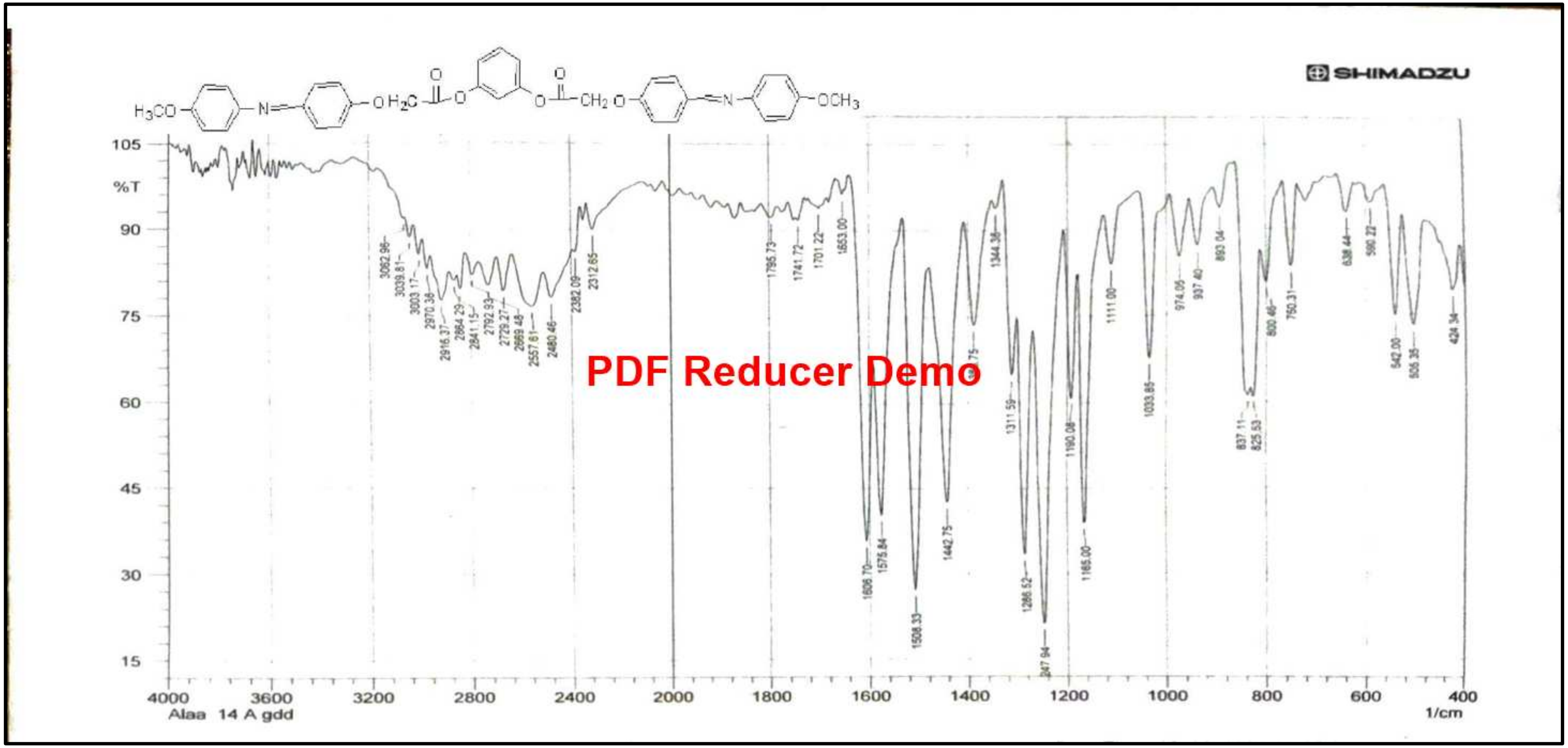


Figure (3 - 5) : FTIR spectrum for compound[V]

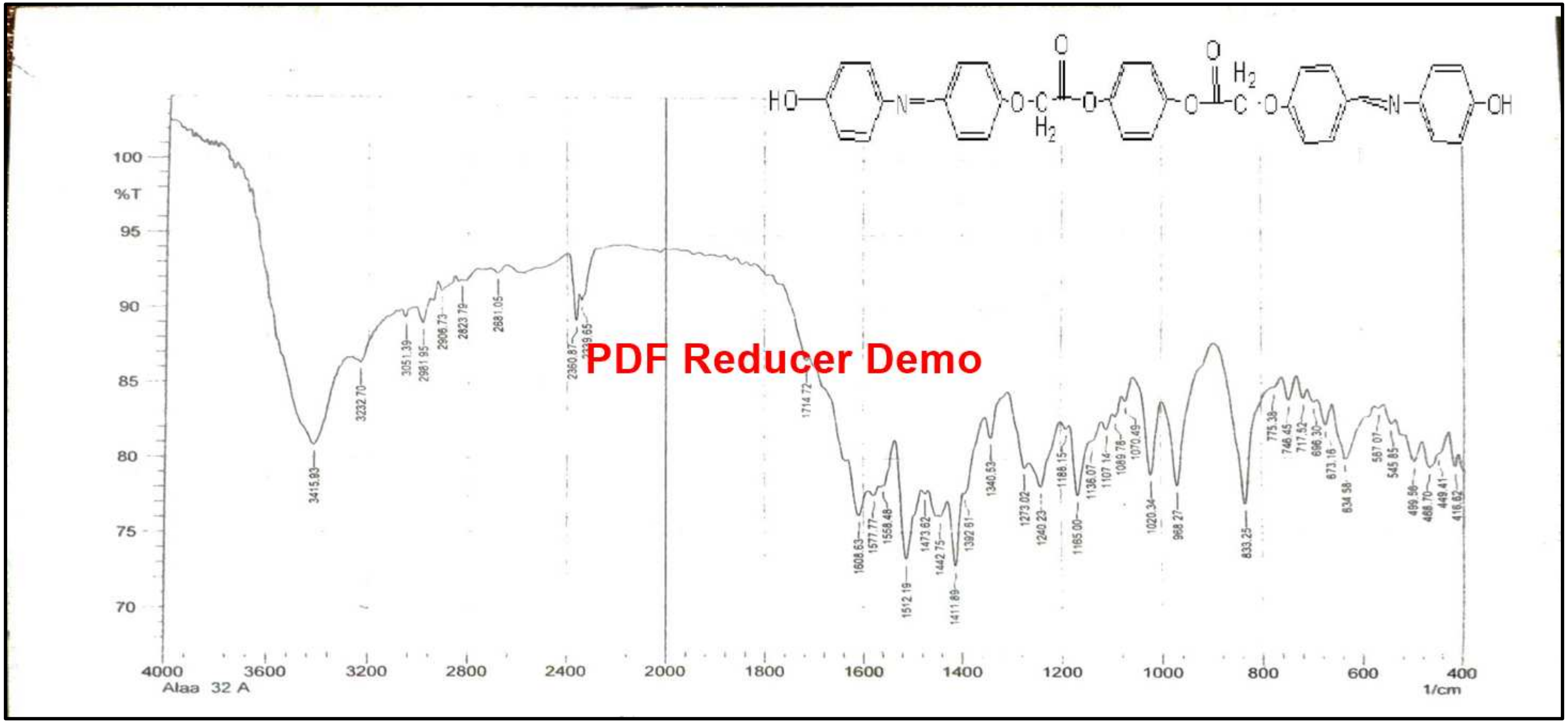
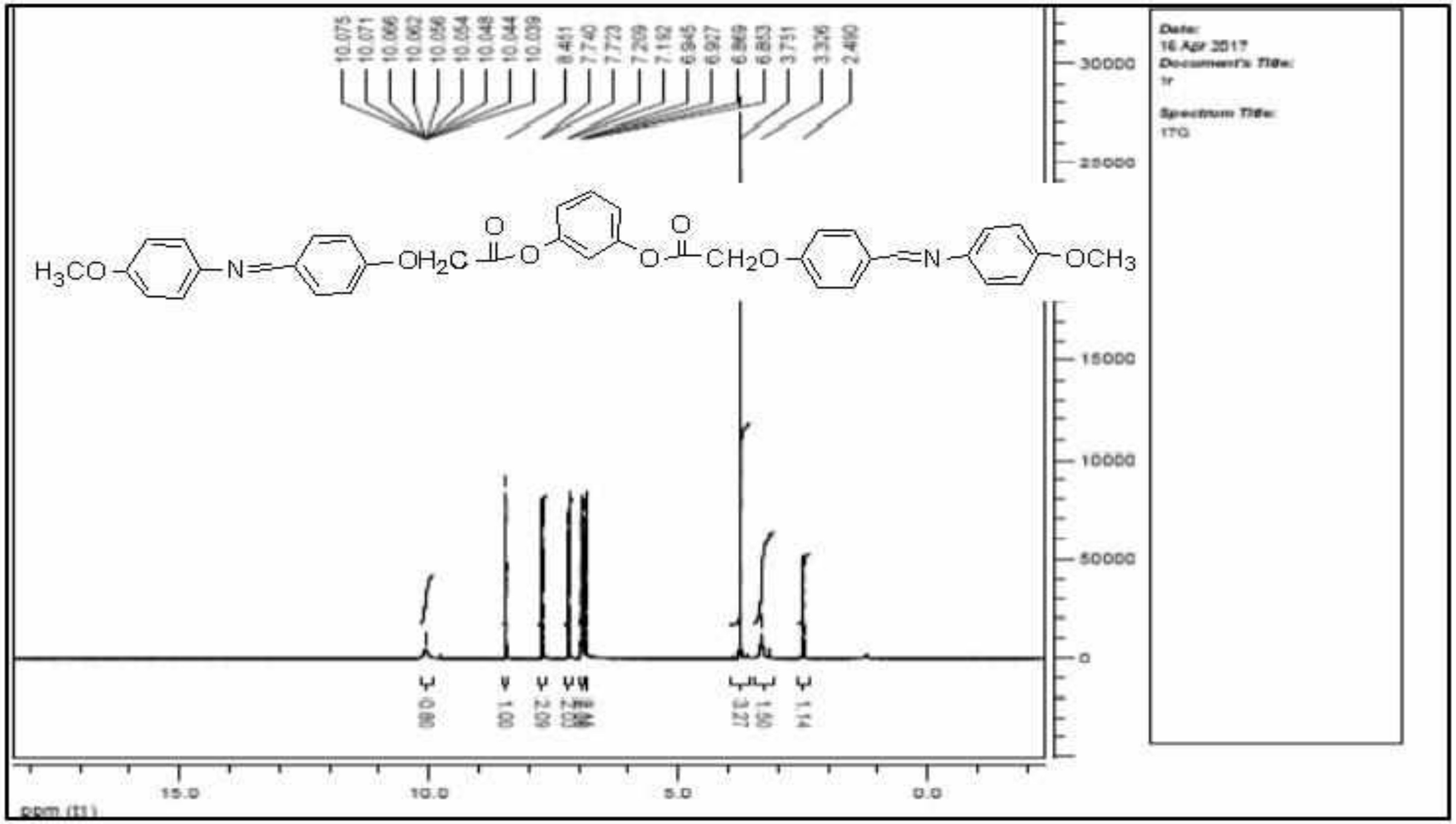
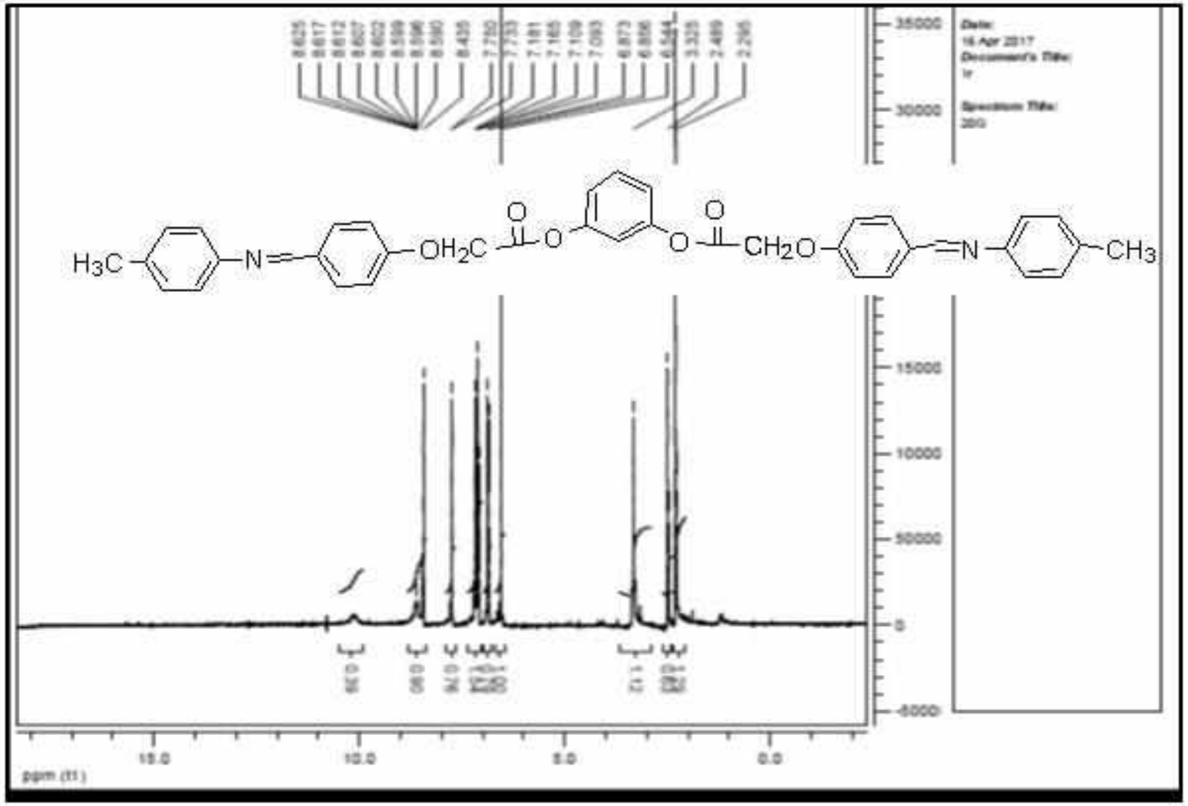


Figure (3 - 6) : FTIR spectrum for compound[X]



Figure(3-7): 1H-NMR spectrum for compound [V]



Figure(3-8): 1H-NMR spectrum for compound [IX]

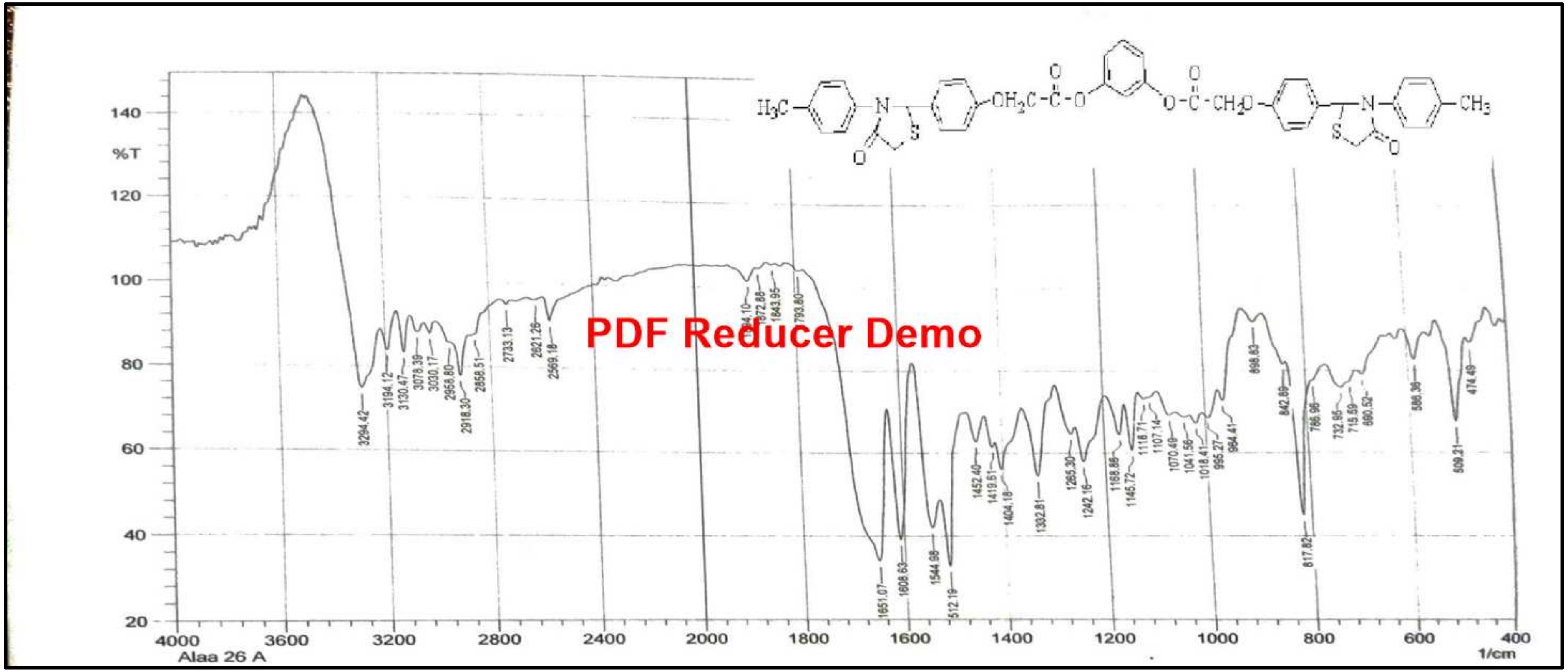
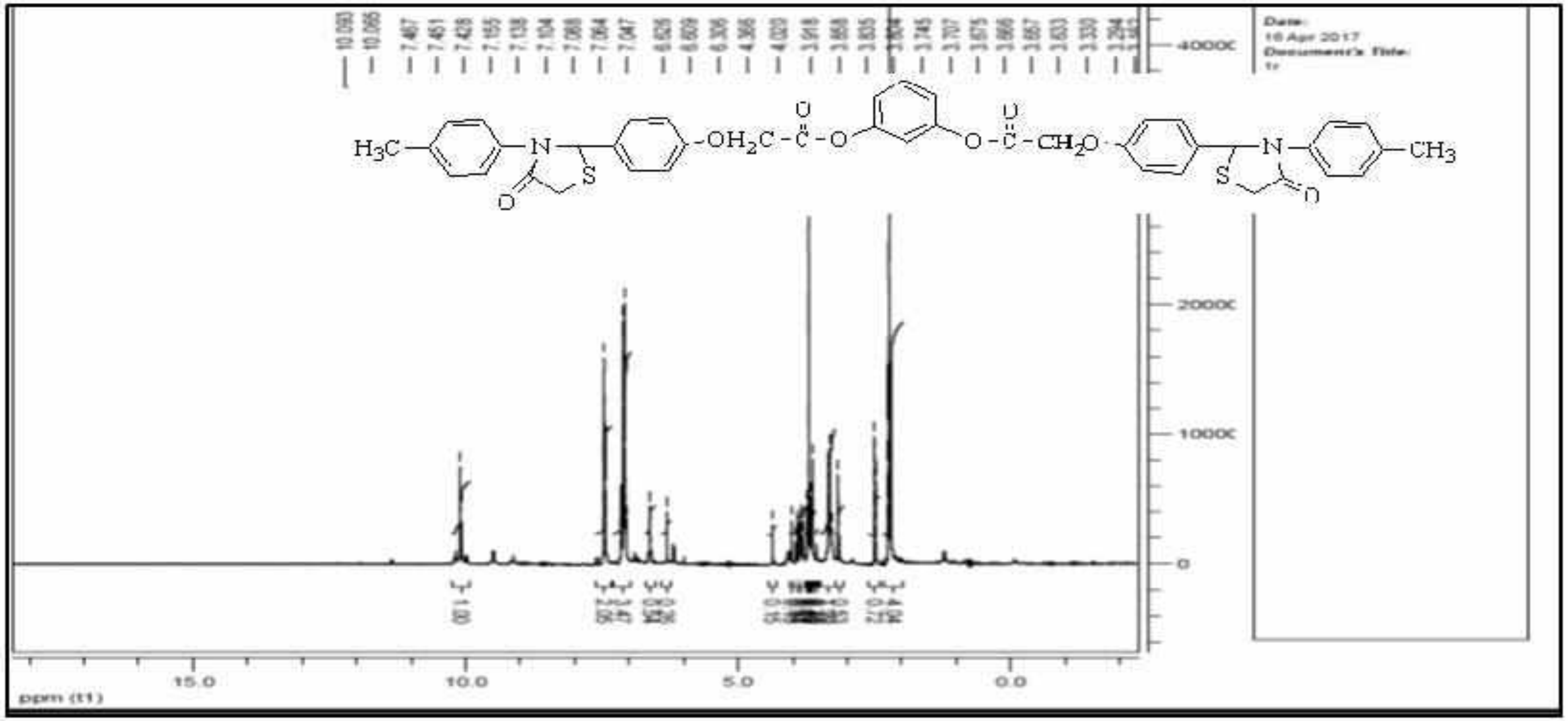
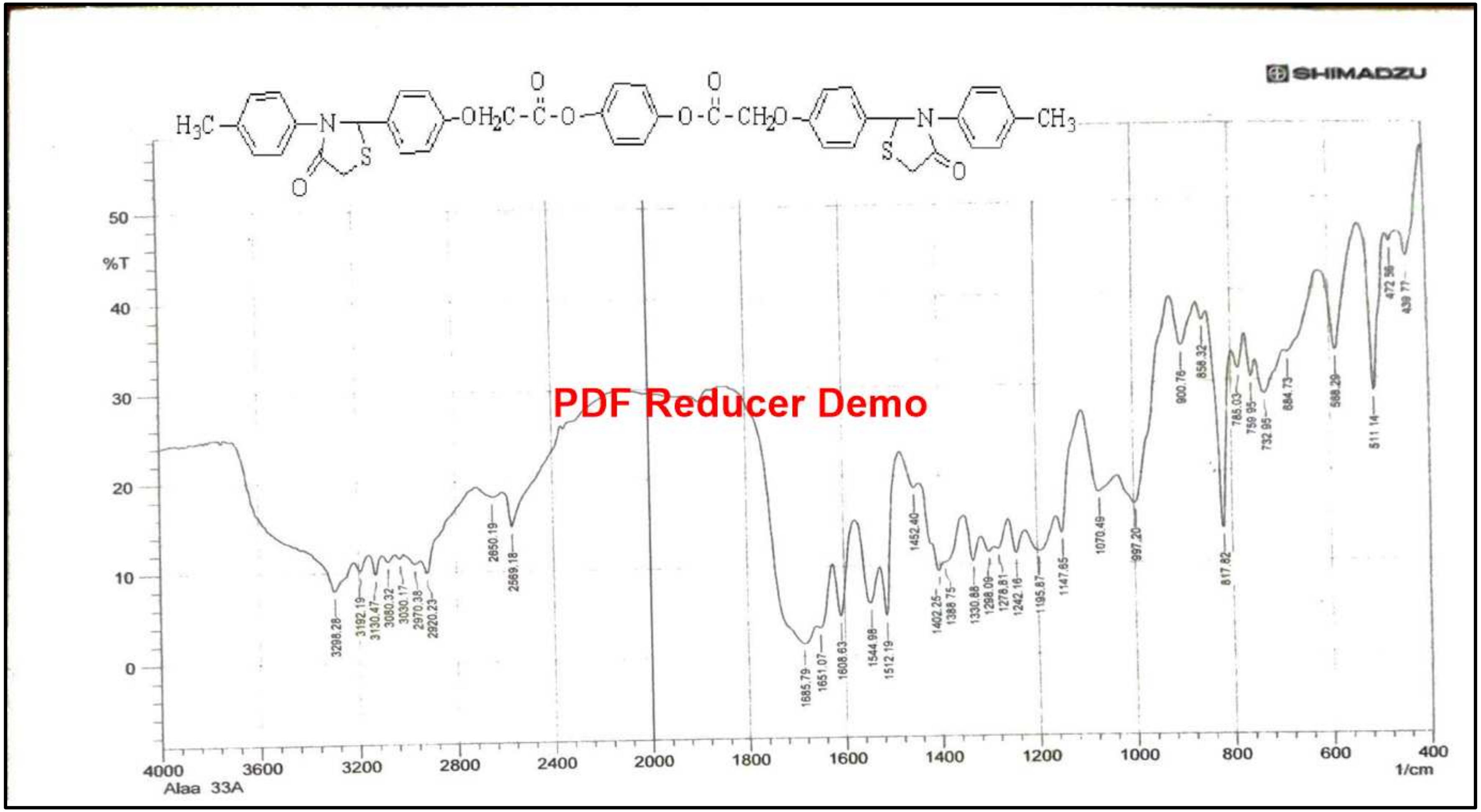


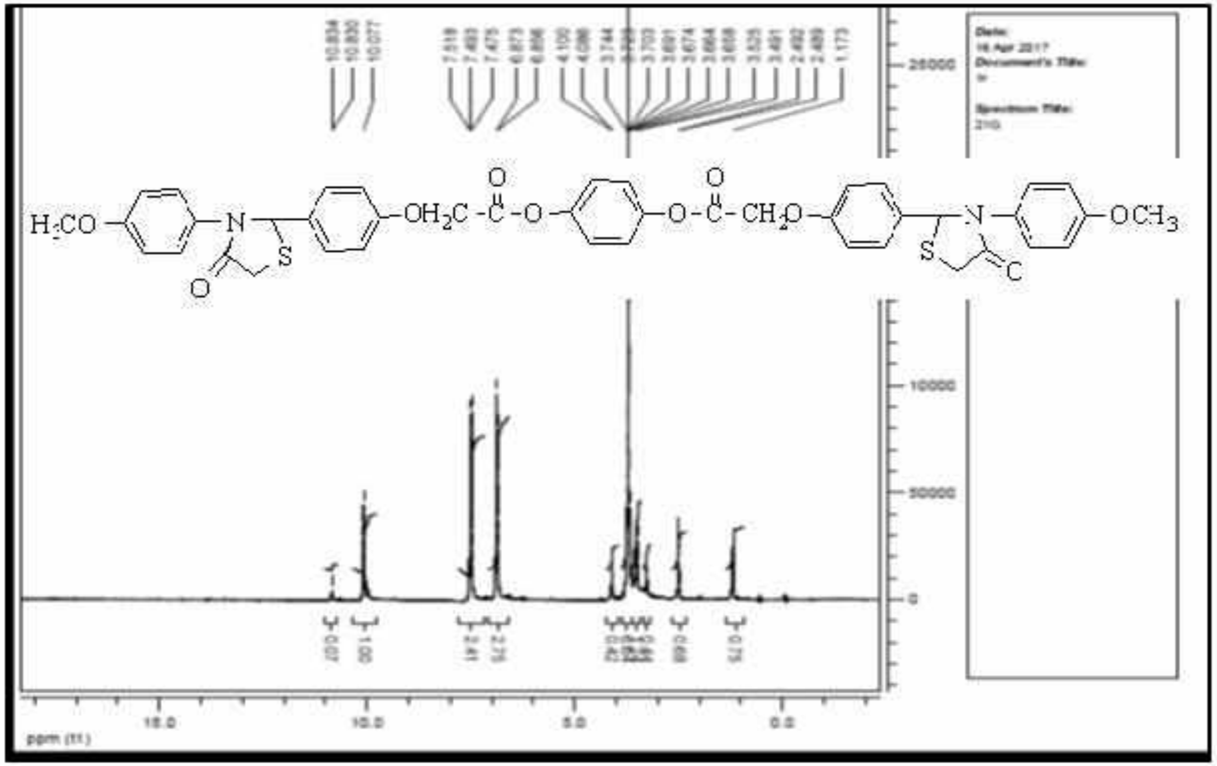
Figure (3 - 9) : FTIR spectrum for compound[XII]



Figure(3-10): 1H-NMR spectrum for compound[XII]



Figure(3-11):FTIR spectrum for compound[XV]



Figure(3-12): 1H-NMR spectrum for compound [XIV]

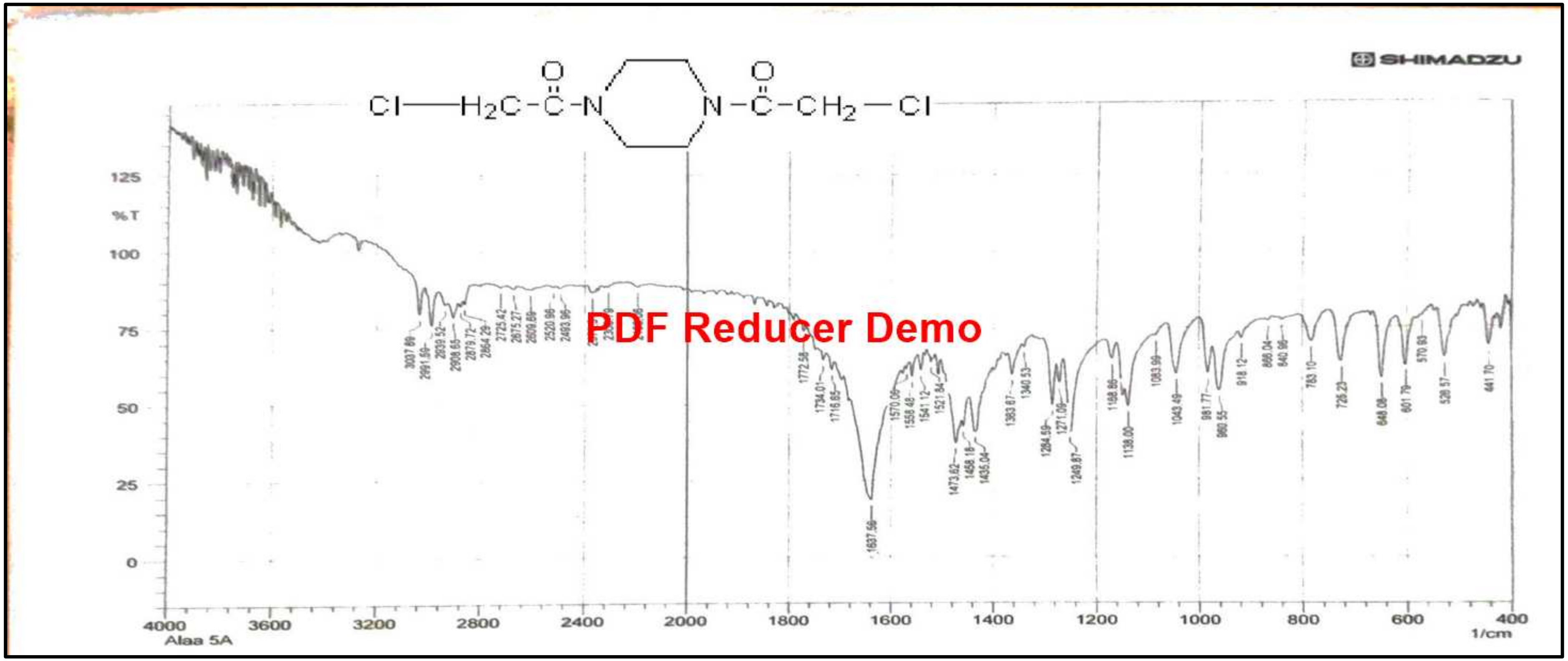


Figure (3 - 13) : FTIR spectrum for compound[XVII]

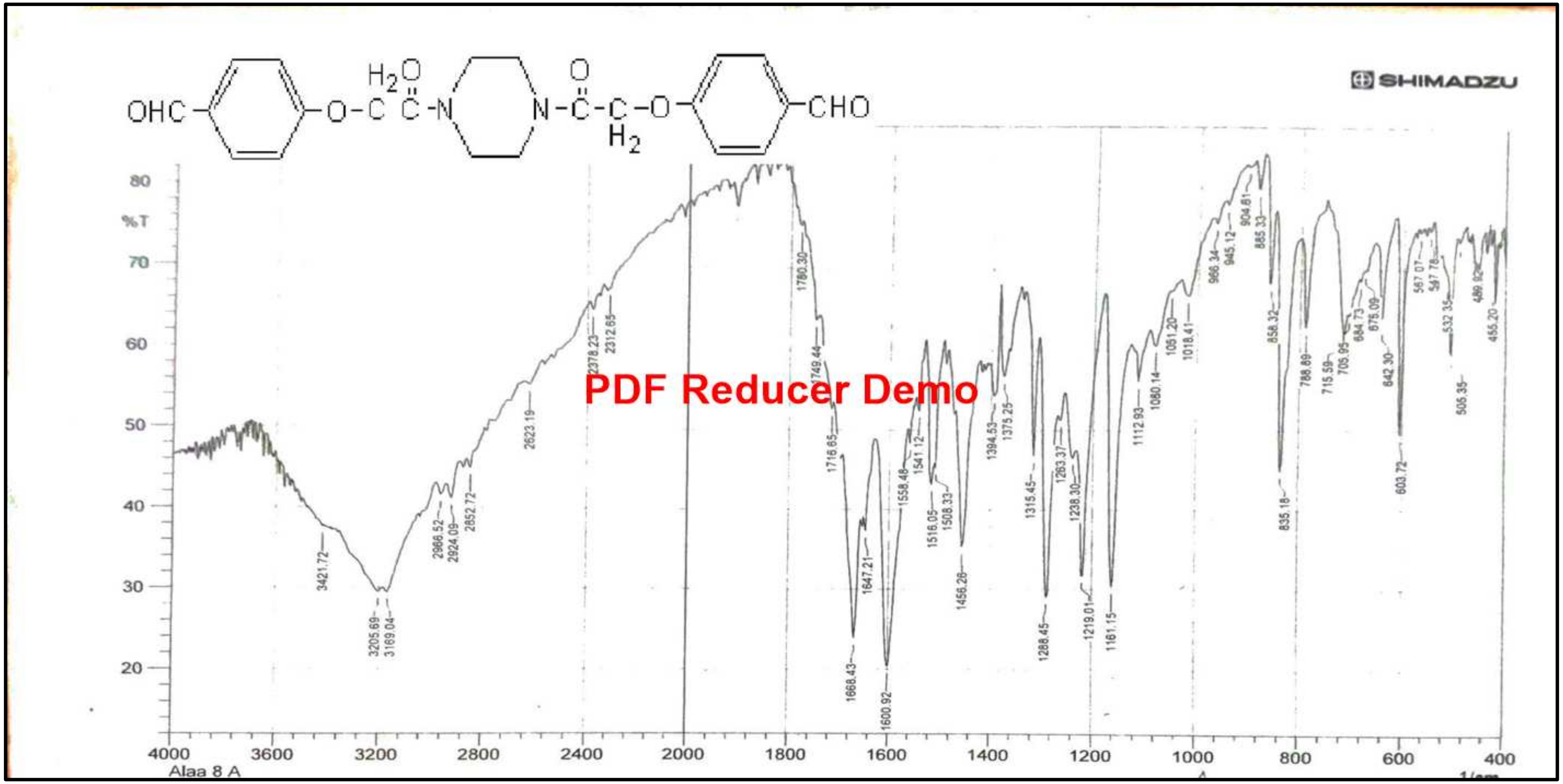
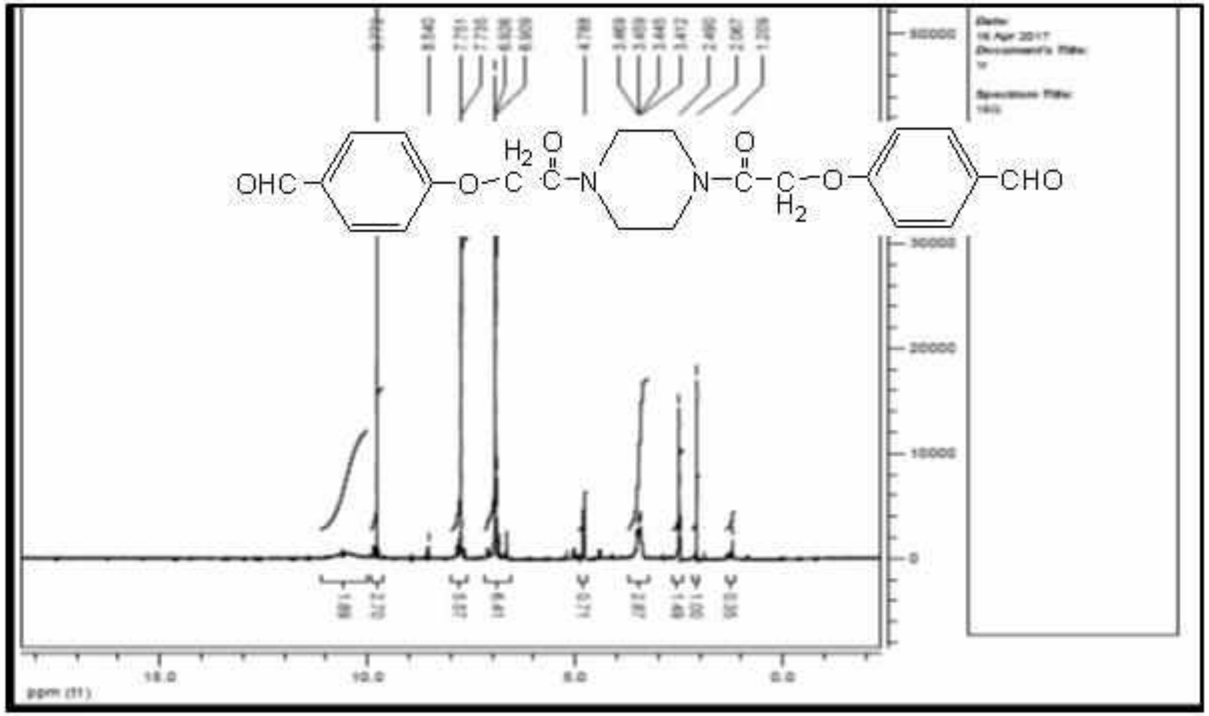


Figure (3 - 14) : FTIR spectrum for compound[XVIII]



Figure(3-15): 1H-NMR spectrum for compound [XVIII]

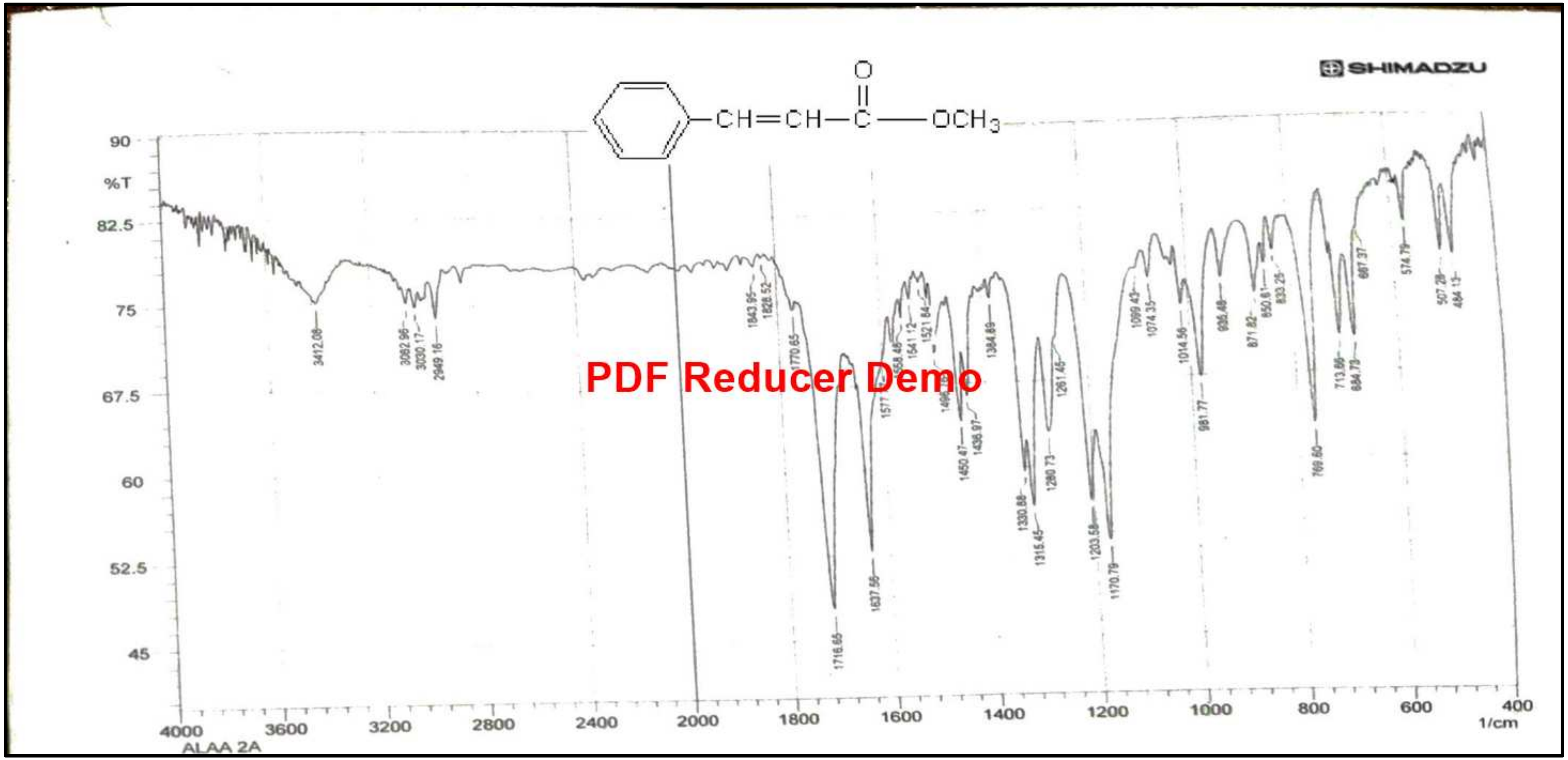


Figure (3 - 16) : FTIR spectrum for compound[XIX]

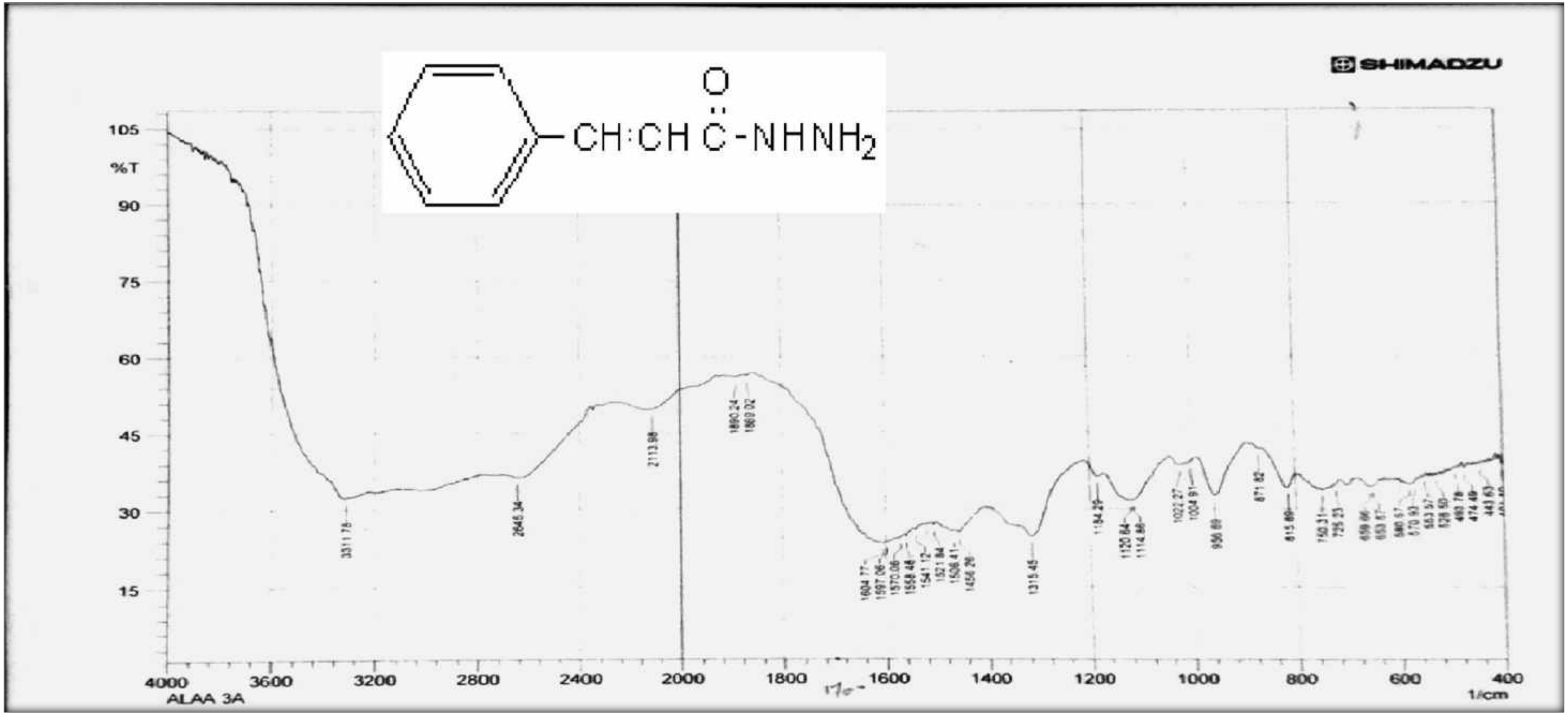


Figure (3 - 17) : FTIR spectrum for compound[XX]

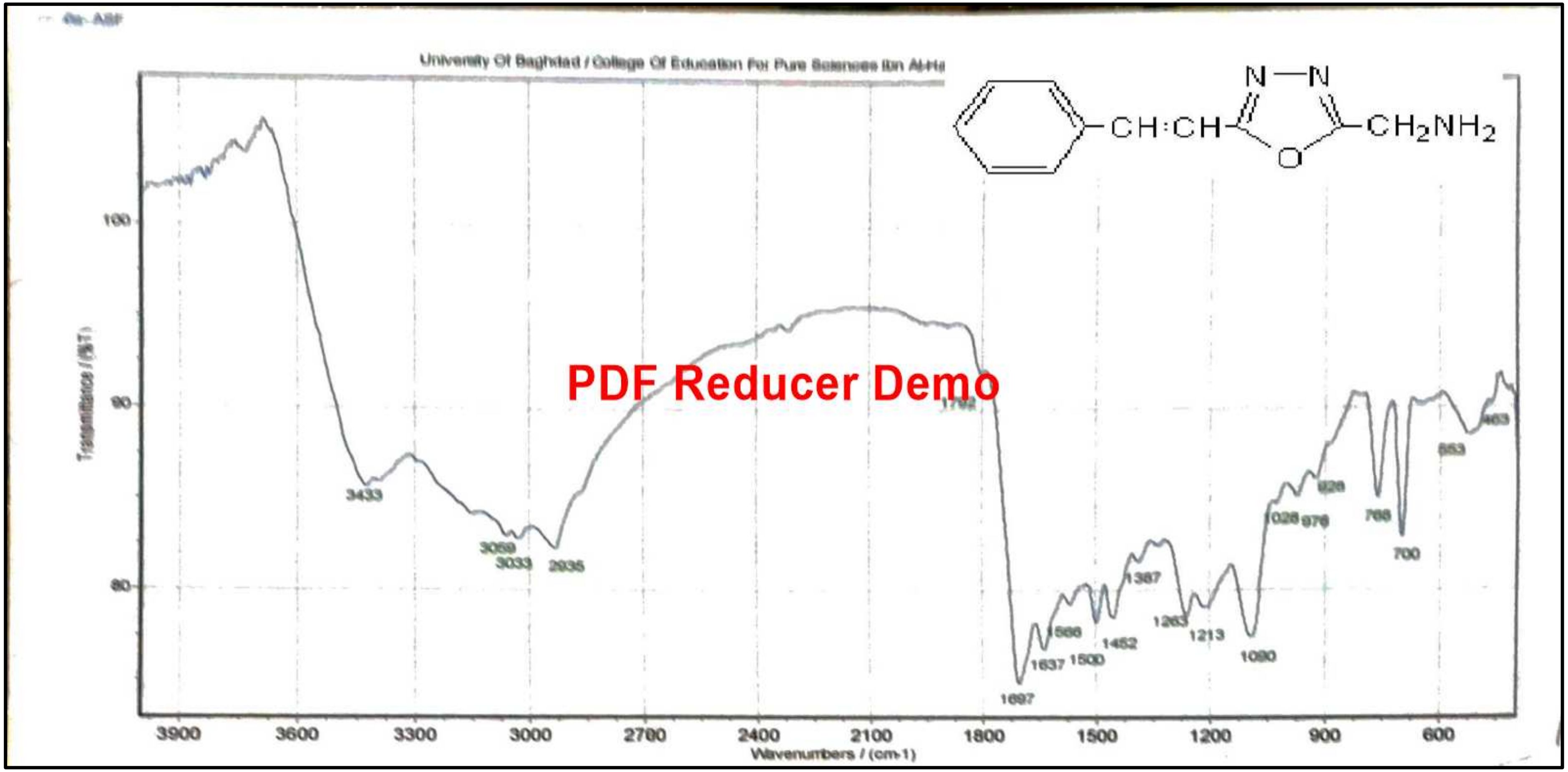


Figure (3 - 18) : FTIR spectrum for compound[XXI]

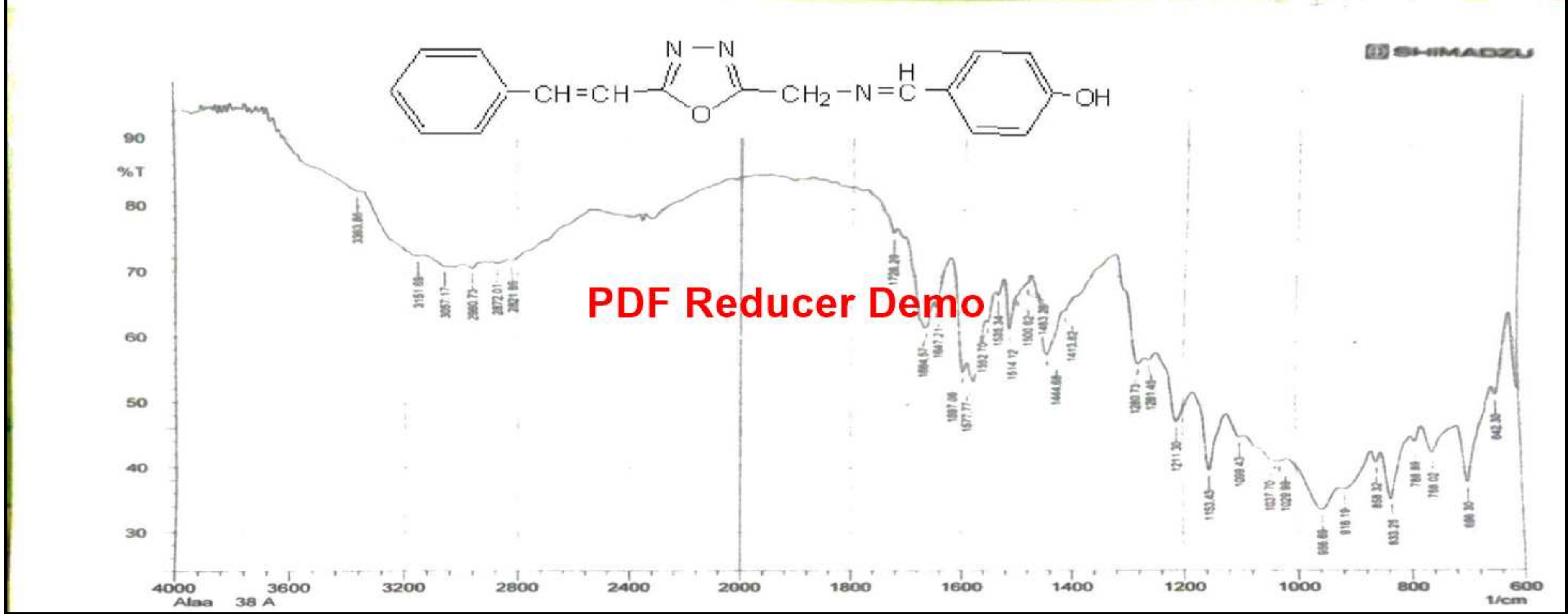


Figure (3 - 19) : FTIR spectrum for compound[XXV]

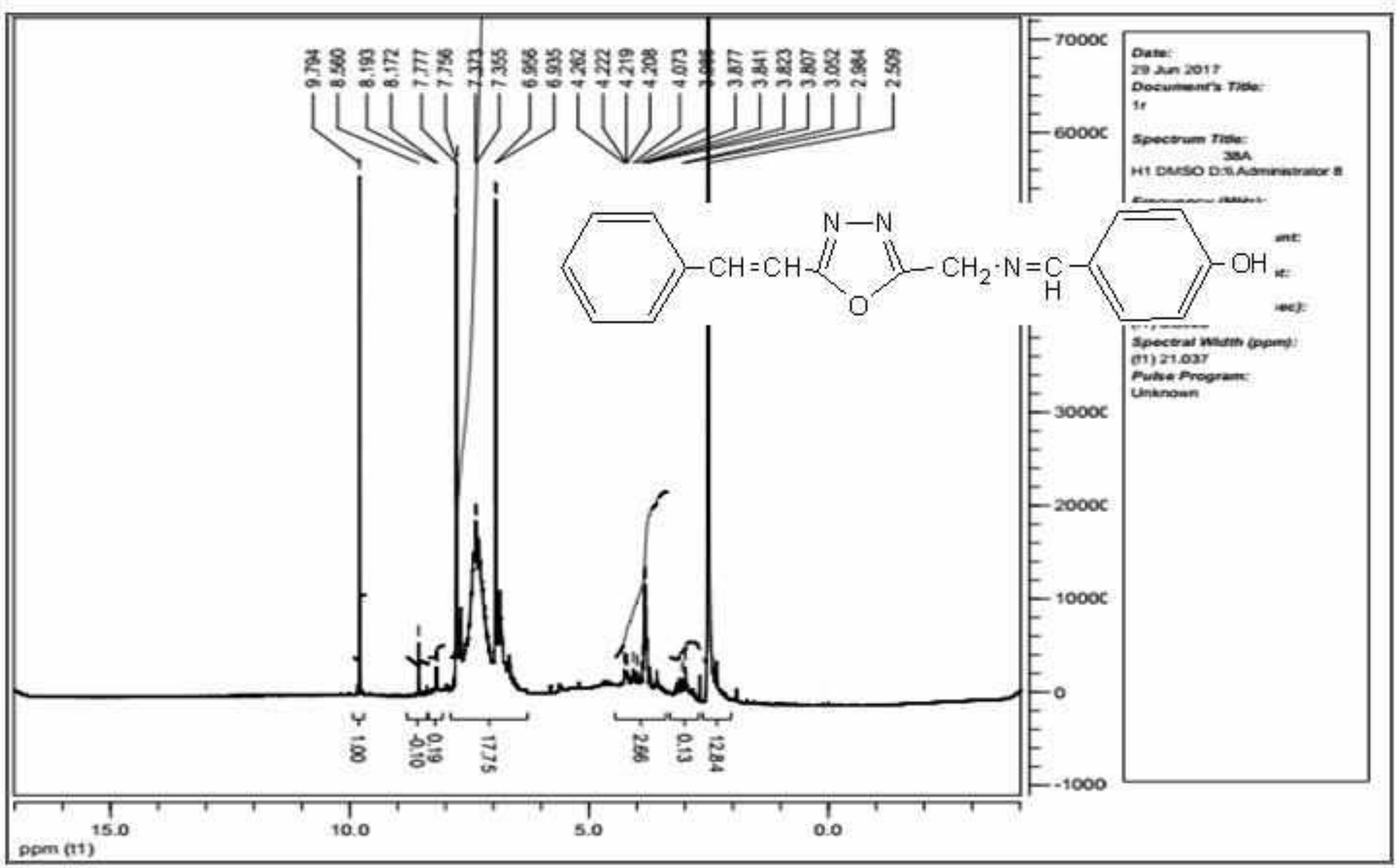


Figure (3- 20): ^{1}HNMR spectrum for compound[XXV]

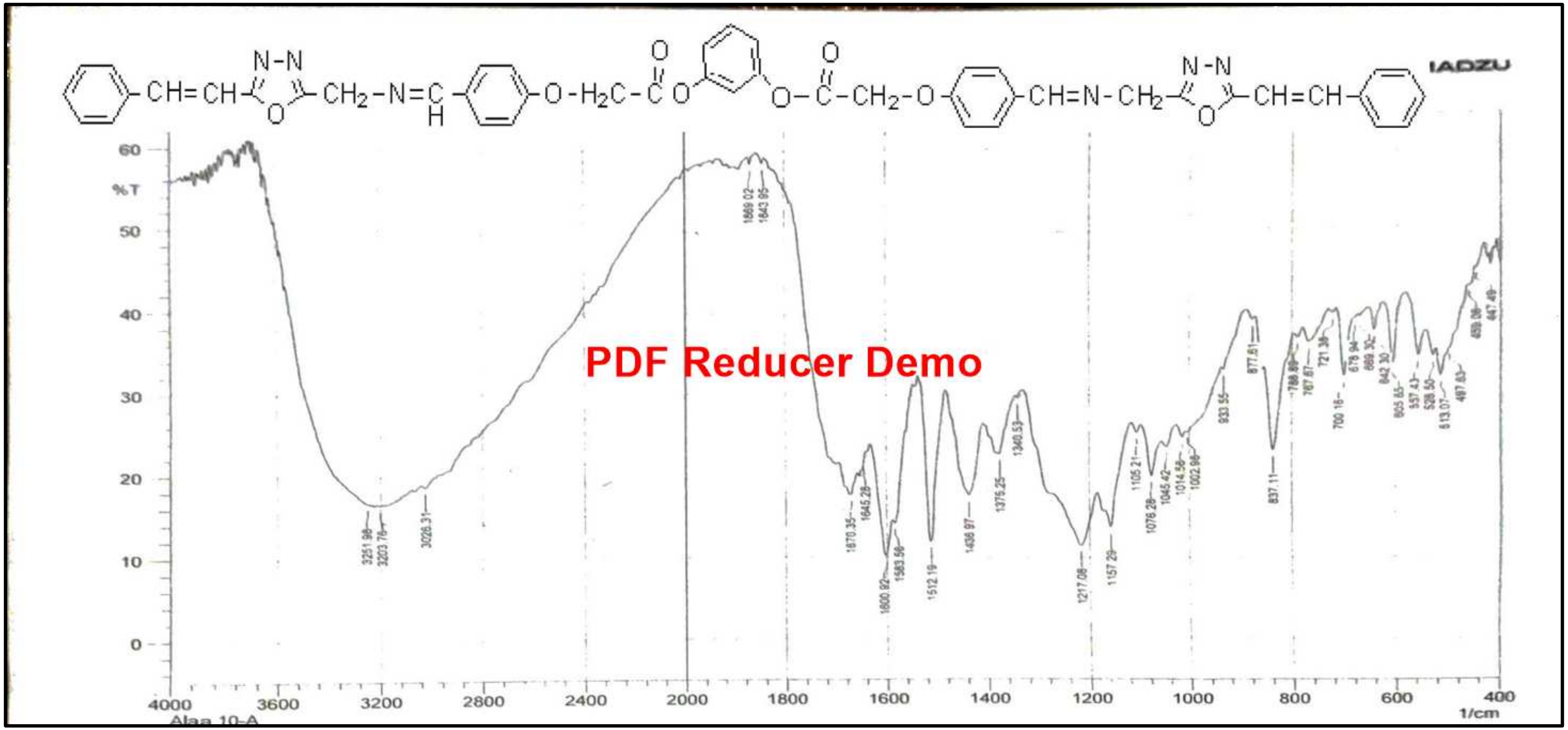


Figure (3 - 21) : FTIR spectrum for compound[XXVI]

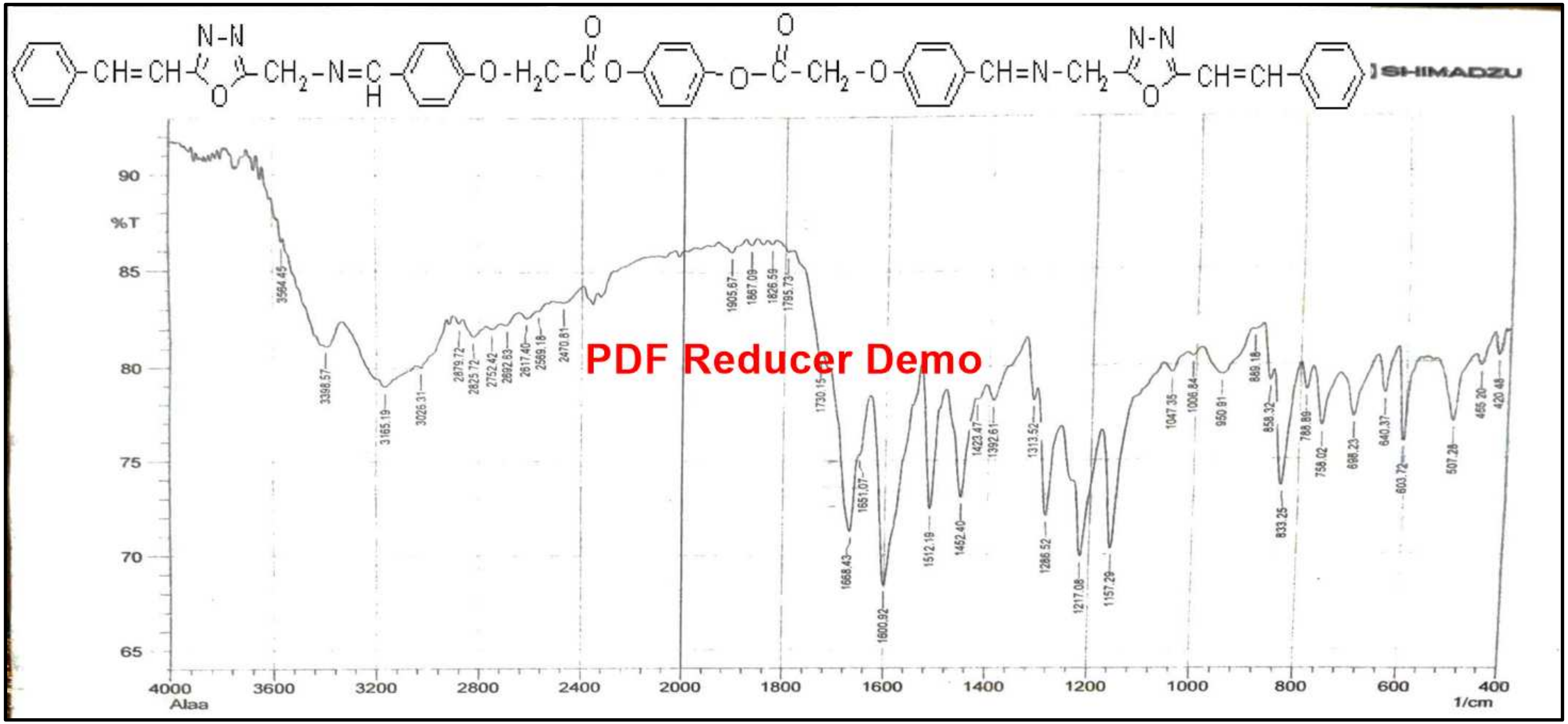
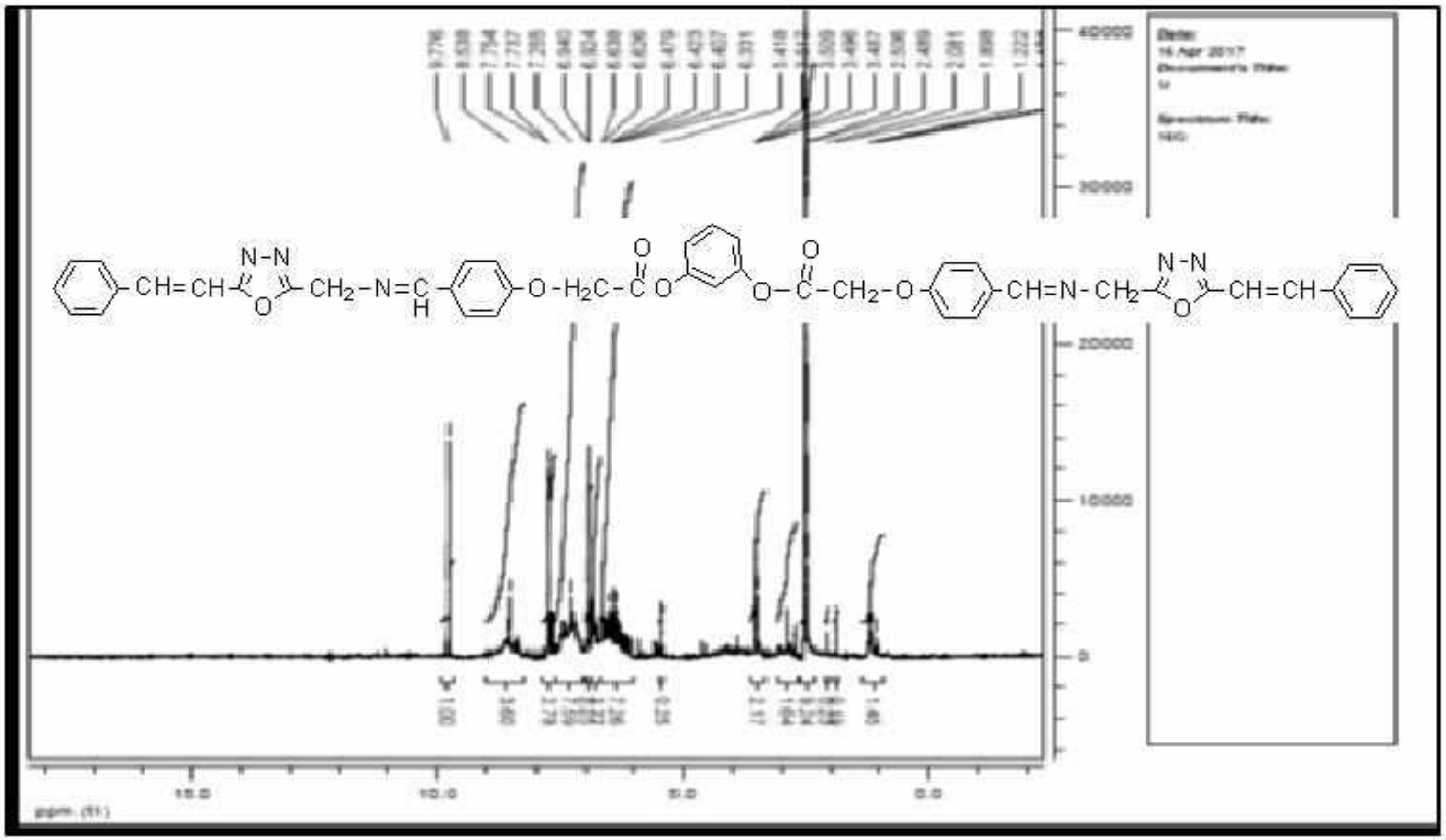


Figure (3 - 22) : FTIR spectrum for compound[XXVII]



Figure(3-23) : 1H-NMR spectrum for compound [XXVI]

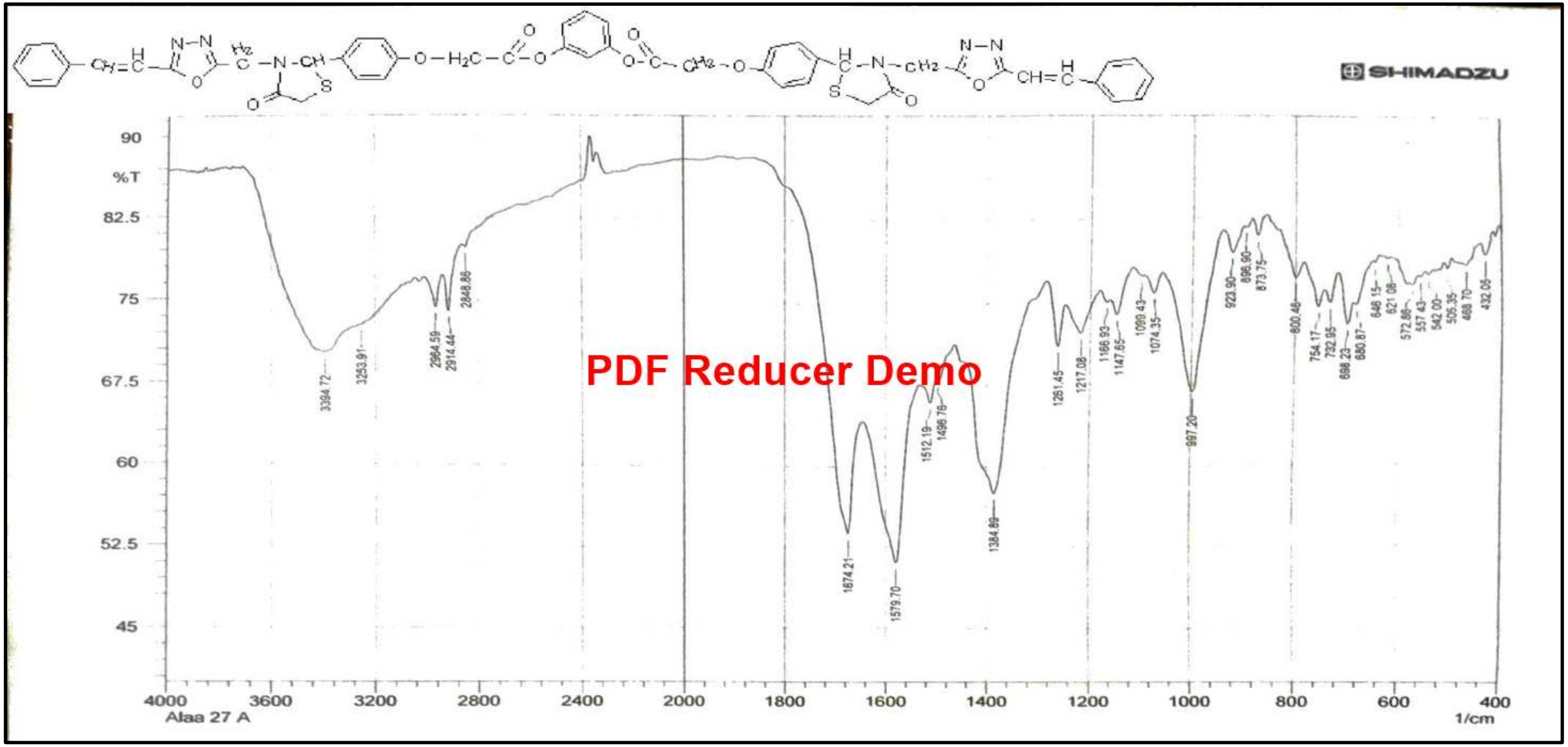


Figure (3 - 24) : FTIR spectrum for compound[XXVIII]

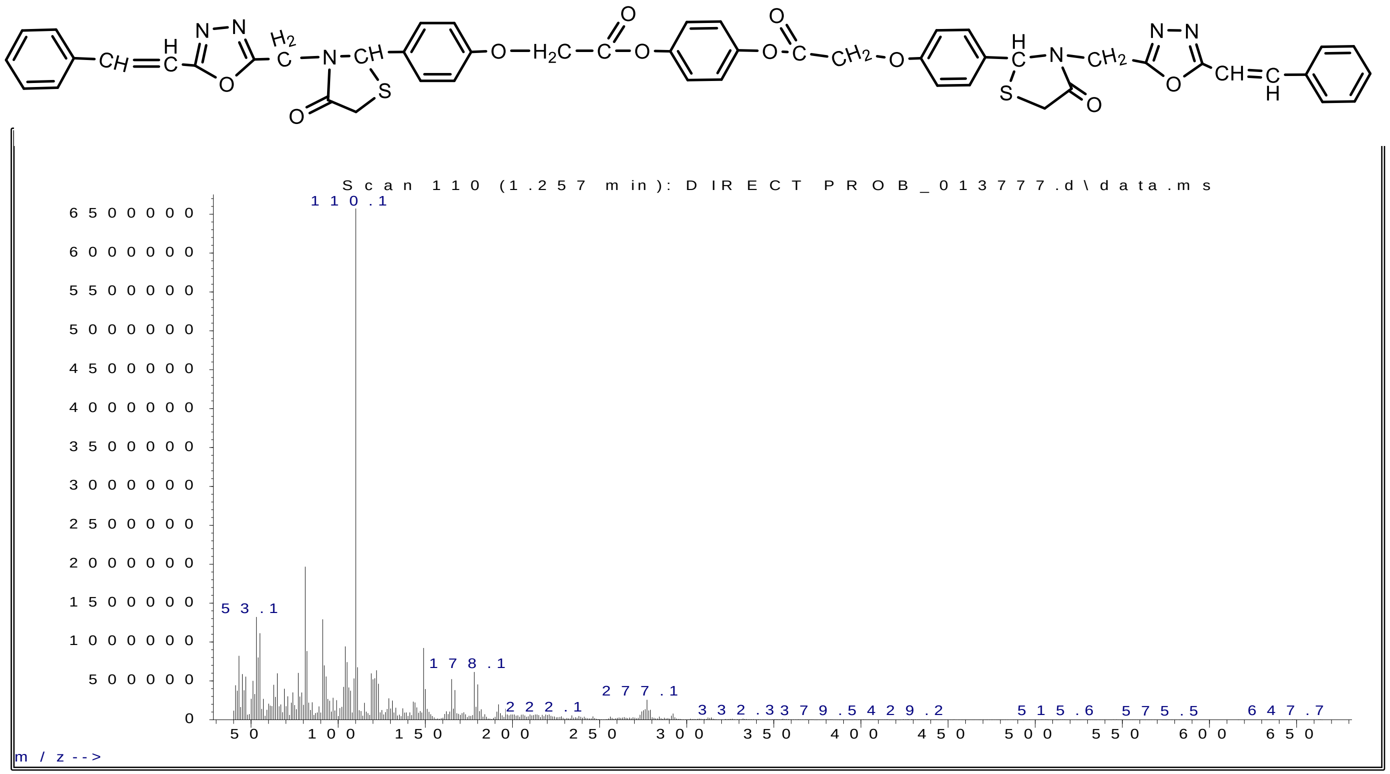


Figure (3 - 25) : Mass spectrum for compound[XXIX]

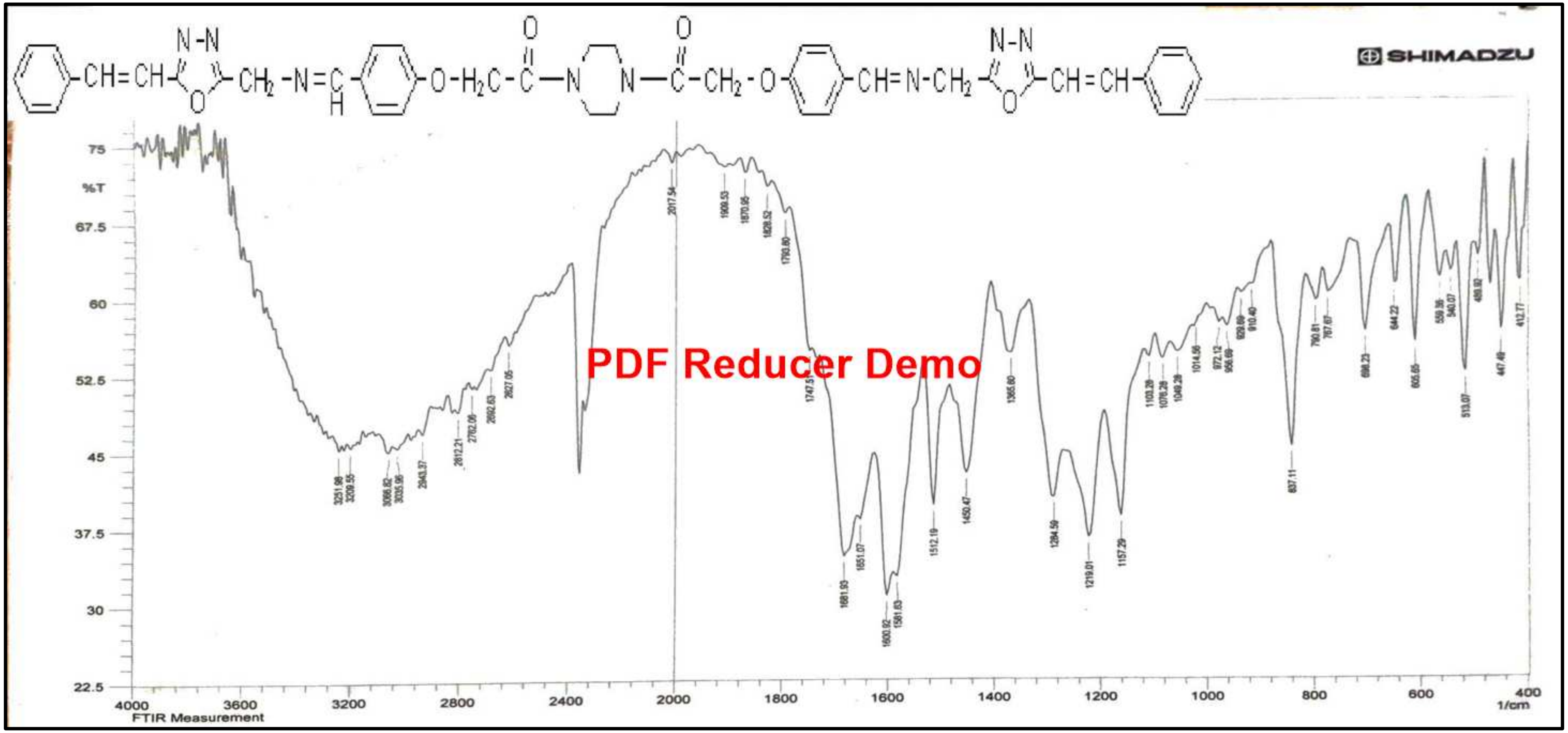
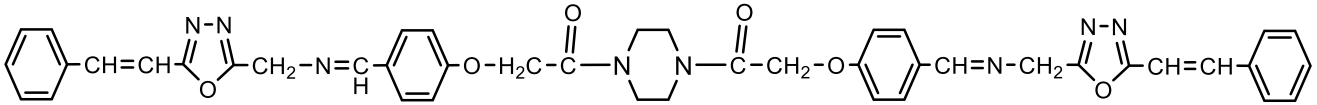
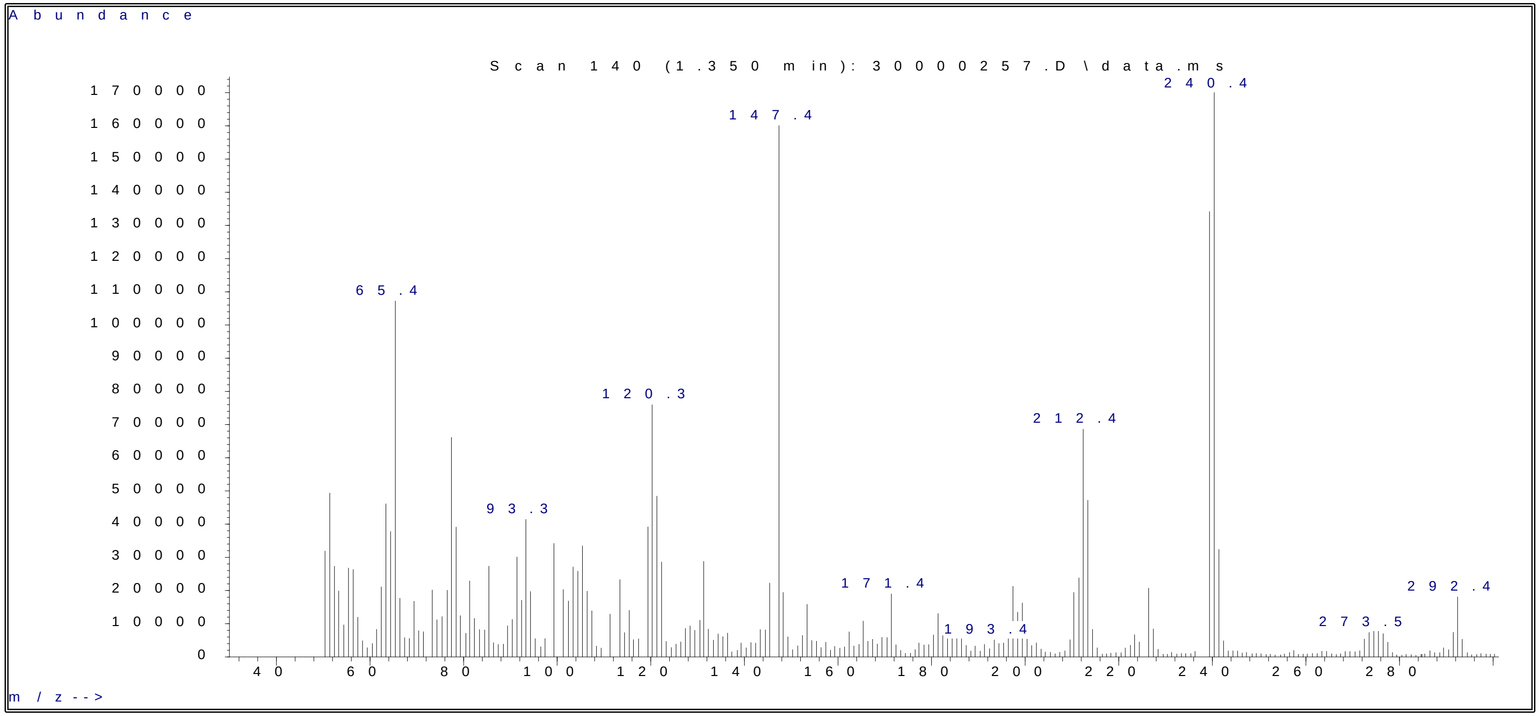
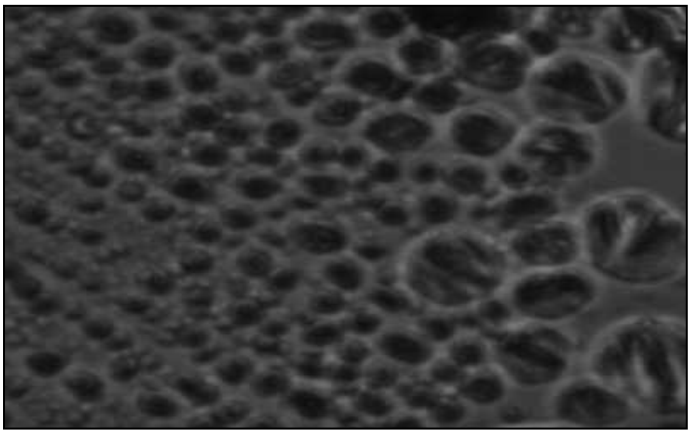


Figure (3 - 26) : FTIR spectrum for compound[XXX]

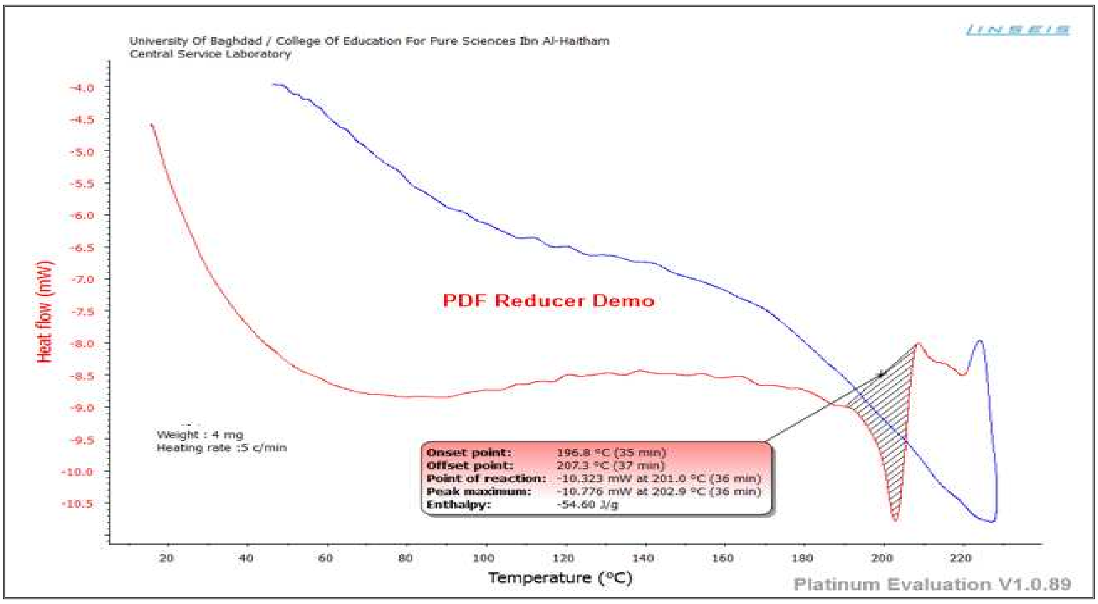




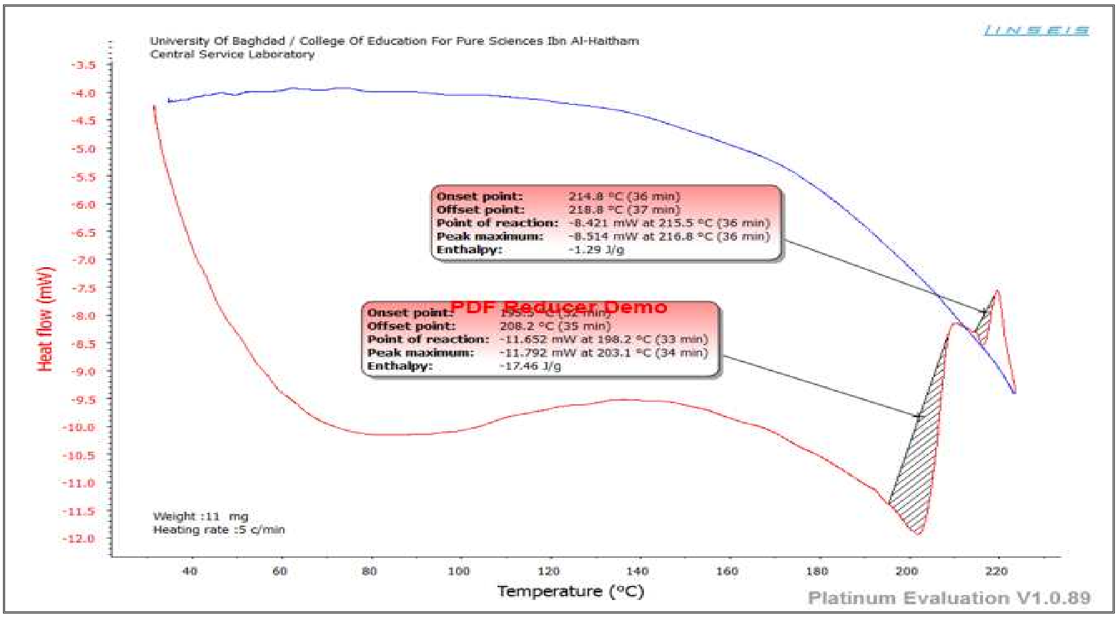
Figure(3-27):The mass spectrum of compound[XXX]



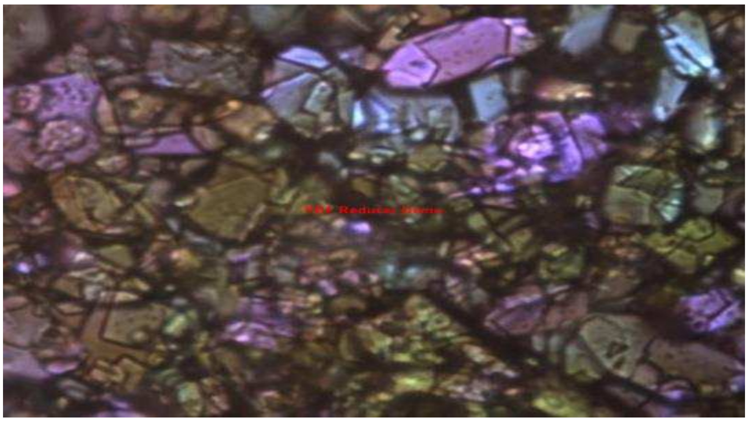
Figure(3-28):Cross polarizing optical texture of droplets nematic phase for compound [V] at 210 °C



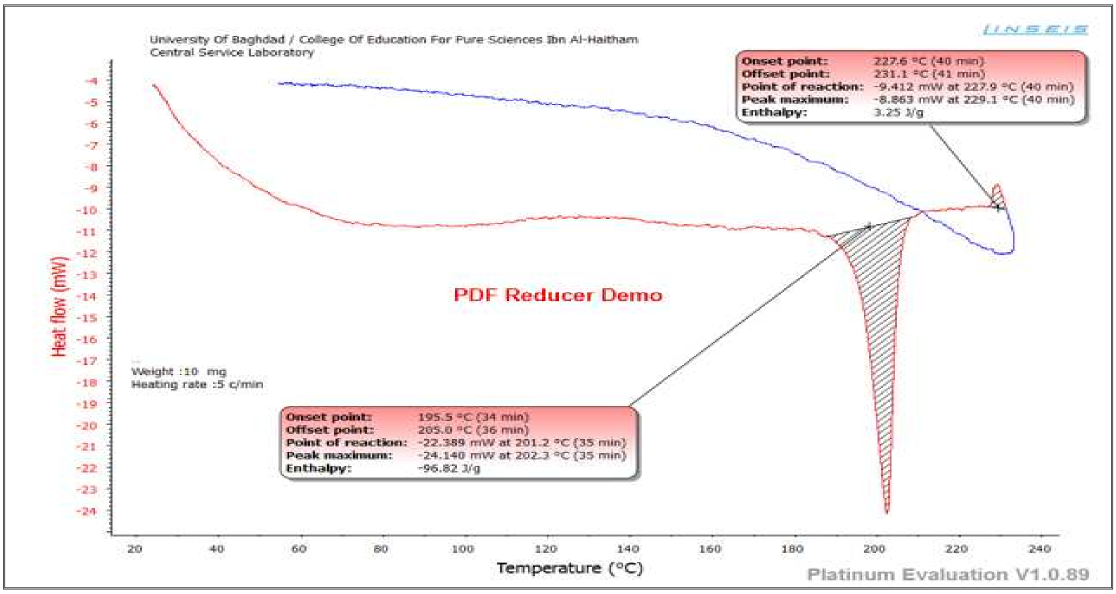
Figure(3-29) : DSC thermogram for compound [**V**]



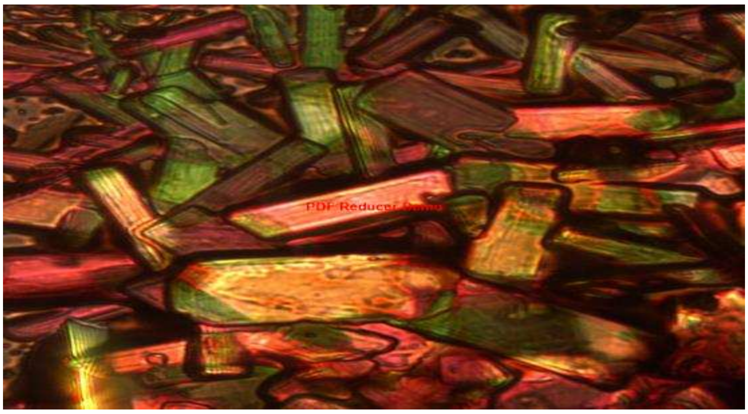
Figure(3-30) : DSC thermogram for compound [**VI**]



Figure(3-31):Cross polarizing optical textures of smecticB phase for compound [VIII] at 190°C

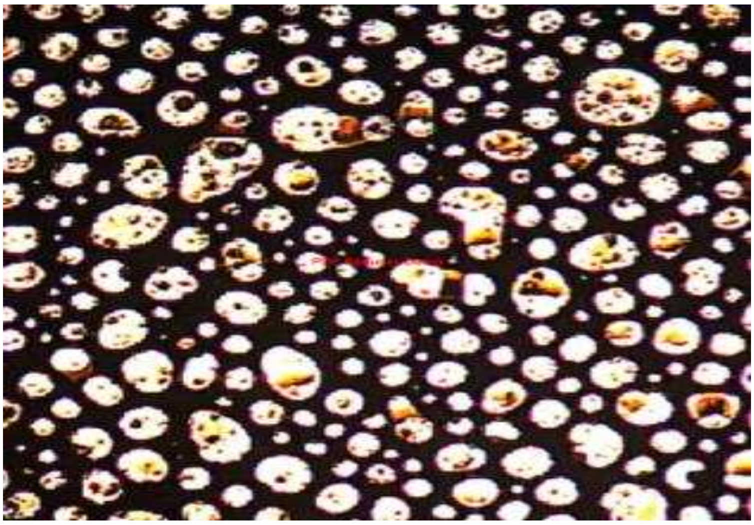


Figure(3-32) : DSC thermogram for compound [**VIII**]



Figure(3-33):Cross polarizing optical texture of smectic A phase for compound [IX] at 210^{o}C

Figure(3-36):Cross polarizing optical texture of dendritic growth of smectic B phase separating from the isotropic melt for compound [XXII] at 195^{o}C



Figure(3-37):Cross polarizing optical textures of droplets nematic phase for compound [XXII] at 225 ^{o}C

References

Refrences

1- Niori T., Sekine F., Watanabe J., Furukawa T. and Takezoe H. J. Mater. Chem., 6, 1231-1233(1996).

2- D. Demus, J. W. Goodby, G. W. Gray, H. W. Spiess and V. Vill, Physical Properties of Liquid Crystals. Wiley-VCH: New York, (1999).

3- G. Ungar and X. Zeng , Soft Matter, 1, 95-106 (2005).

4- S. J. Woltman , G. P. Crawford and G. D. Jay. , "Liquid Crystal Frontiers in Biomedical Applications ", WorldScientific Publishing Co. Pte. Ltd. (2007).

5- I. C. Khoo, Liquid Crystals 2nd ed. John Wiley & Sons: Hoboken,(2007).

6- I. C. Khoo, and S. T .Wu, Optics and Nonlinear Optics of Liquid Crystals. World Scientific: Singapore, (1993).

7- G. W. Gray,and J. W. Goodby, Smectic Liquid Crystals: Structures and Textures. Leonard Hill: London, (1984).

8- J. P. Bedel, J. C. Rouillon, J. P. Marcerou, M. Laguerre, Nguyen H. T. and M. F. Achard, Liq. Cryst . 27, 1411-1421(2000).

9- S. Kumar, Chem. Soc. Rev., 35, 83-109 (2006).

10- H. R. Brand, P.E. Cladis and H. Pleiner, Europhysics Letters ,57, 368-375 (2002).

11- L. Zou, J. Wang, V. J. Beleva, E. E. Kooijman, S. V. Primak , J. Risse, W. Weissflog , A. Jákli and E. K. Mann Langmuir, 20, 2772-2780(2004).

12- Y. Kinoshita , B. Park, H. Takezoe, T. Niori and J. Watanabe Langmuir, 14, 6256-6260(1998).

13- N. H. Karam ,Ph.D. Thesis, College of Education, Ibn-Al-Haitham for Pure Science , University of Baghdad (2013).

14- G. W. Gray ,"Molecular Structure and The Properties of Liquid

Crystals", Academic press, New York (1962).

15-M.Baron , Pure Appl. Chem., 73(5) , 845-895(2001).

16- Halle. Den , "bent-core mesogens substituent effect and phase behavior" , martin-luther-universitat,_halle-wittenberg (2004).

17- G. W. Gray, K. J. Harrison. and J. A. Nash Electronics Lett., 9, 130-131(1973).

18- H. Keiker , Fresemus ZAnal Chem. 198, 254-266 (1963).

19- G. H. Brown and JJ. Wolken, Eds. "Liquid Crystal and Biological Structures", Academic press, London, pl 86 (1979).

20- Data Sheet 11, "Liquid Crystals in Cosmetics", BDH (1989).

21- R.M.Shakir, A.Ariffin and M.A.Abdulla, Molecules,19,3436-3449,2014.

22- K. Ladva, P. Patel, P. Upadhyay and H. Parekh, Ind. J. Chem. ,35B, 1062 (1966).

23- J. A. Frump, Chem. Rev., 71, 483 (1971).

24-. C.Dobrota,; C. C.Paraschivescu, I.Dumitru,; M. Matache, I. Baciu, and L. L. Ruta, Tetrahedron Lett. 2009, 50, 1886.

25- M Al-Talib,.; H.Tashtoush, and N. Odeh, Synth. Commun. 20, 1811(1990).

26- V. K Tandon,. and R. B. Chhor, Synth. Commun. , 31, 1727 (2001).

27- H. J. Carlson and K. B. J. Jorgensen, J. Heterocyclic Chem., 31, 805 (1994).

28- M. Adib, M. R. Kesheh, S. Ansari and H. R. Bijanzadeh, Synlett, , 15751578(2009).

29- S. Guin, T. Ghosh, S. K. Rout, A. Banerjee and B. K. Patel, Org. Lett., 13, 5976-5979(2011).

30- Q. Gao, S. Liu, X. Wu, J. Zhang and A. Wu, Org. Lett., 17, 29602963(2015).

31- L. Wang, J. Cao, Q.Chen and M. He, J. Org. Chem., 80, 4743-4748(2015)

32- P. Niu, J. Kang, X. Tian, L. Song, H. Liu, J. Wu, W. Yu and J. Chang, J. Org. Chem., 80, 1018-1024(2015).

33- S. Coffey, “Rood's Chemistry of carbon compounds”, 2nd ed., Oxford, p.3 (1971).

34- N. Tokay and C. Ogretir, Arkivoc (xiv) , 88-99 (2008).

35- H. Parekh, K. Parikh and A. Parikh, J. Sci. lslamic .Rep. lran ,15(2), 143-148 (2004).

36- M.A. AL-Nemi PhD. Thesis, College of Education –Ibn AL –Haitham, University of Baghdad(2010).

37- V. vinay,M.Shikha,p.Ashish, G.Mukesh and B.Anurag,Inter. J.Res.Ayu.Pharm., 2(1),281-288(2011).

38- K. Deepthi and G. Manjunath, J. Chem., 8(1), 386-390(2011).

39- T.M. Bhagat, D.K. Swamy,S.G. Badne and S.V.Kuberkar, Ras. J .Chem., 4(1), 24-28 (2011).

40.Malipeddi,A.A.Karigar,V.R.MalipeddiandM.S.Sikarwar,Tropical.J.Pharm. Res.,11(4),611-620(2012).

41- N.H.Karam,J.H.Tomma and Ammar H.AL-dujalli Ibn-AL-Haitham J. for Pure and Appl. Sci.,Vol.26(3)2013.

42- M. A. Yehya Alkazzaz , Ph.D. Thesis, College of Education –Ibn AL – Haitham, University of Baghdad(2014).

43- A.D.Mc Naught and A.Wilkinson"Compendium of Chemical Terminology" 2nd p-776(1997), Version 2.3.3 \ 2-24-(2014).

44- ChemWiki\ The Dynamic Chemistry E-textbook. "Organic Chemistry With a Biological Emphasis by Tim Soderberg, Chapter 11: Nucleophilic carbonyl addition reactions" Section 11.6: Imine (Schiff base) formation\ 2014.

45- E. F. Pratt and M.J. Kamel., *J. Org. Chem*., **26**, 4029 (1961).

46- S. Ershad , L. A. Sagathforough , G. K. Nezhad and S. Kangari , Int. J. Electrochem. Sci. , 4 , 846-854 (2009) .

47- T. Hong and A. Schmilter, Zh. Obsheh. Khim., 83 ,194518g (1975) .

48-46- D. Shinah, A. K. Tiwari, G. Shukla, P. Mishra, H.Ghandra, and A.K.Mishra., Eur. J. Med.Chem., 43(1),160-165(2008).

49- H.M. Parekh, S.R. Mehta, and M.N.Patel., Russ.J.inorganic .Chem, 51, 67-72(2006). Nikolia T. Kuznetsov ; Russ.J.inorganic.chem. Journal no.11502(2013).

50- M. da Silva, L. da Silva, V. Modolo, B. Alves, A. de Resende, V.B. Martins and Ângelo de Fátima,. Journal of Advanced Research. Volume 2, PP 1–8 , (2011).

51- S. Jalhan , A. Jindal, A. Gupta and Hemraj. *Asian Journal of Pharmaceutical and Clinical Research* Vol. 5, Issue 3\25 ***(2012)*****.**

52- M. H. Fekri, M. Darvishpour, H. Khanmohammadi and M. Rashidipour. Journal of Chemical Health Risks; 3(4)/63-68, (2013).

53- O. Bekircan and H. Bektas , Molecules , 13 , 2126-2135 (2008) .

54- K. A. Albadrani, I. K. Al-Juboori, and O.TH. Ali, Journal pharma. Sci. of Tikrit, **(2009)** .

55- Z. Hussain, E. Yousif and A. Ahmedand A. Altaie , Organic and Medicinal Chemistry Letters, 4:1,(2014).

56- M.A. Qaban , Ph.D.Thesis, College of Science , University of AL-Mustansiriya ,(2015).

57- M. E. Azab, S. A. Rizk and A.E.G.E. Amr, Molecules, 20, 18201-18218,(2015).

58- P. J. Collings and M. Hird, "Introduction to Liquid Crystals : Chemistry and Physics" , Taylor and Francis , London (1997) .

59- D. Srividhya , S. Manjunathan , S. Thirumaran , C. Saravanan and S. Senthil ,J. Mol. Str. , 927 , 7-13 (2009) .

60- V. F. Petrov , Mol. Cryst. Liq. Cryst. , 457, 121 (2006) .

61- A. Seed , Chem. Soc. Rev. , 36, 2046-2069 (2007) .

62- B. Y. Zhang , Y. G. Jia , D. S. Yao and X. W. Dong , Liq. Cryst. , 31, 339-345(2004).

63- A. A. Kiryanov, A. J. Seed and P. Sampson , Tetrahedron Lett. , 42 , 8797-8800 (2001) .

64- C. S. Wang , I. W. Wang , K. L. Cheng and C. K. Lai , Tetrahedron, 62, 9383-9392(2006) .

65- W. L. Chia and X. M. Lin , Inter. J. Mol. Sci. , 14, 18809-18823 (2013) .

66- J. H. Tomma , Ibn-AL-Haitham J. for Pure and Appl. Sci. ,15(4b), 67-81 (2002).

67- D. Srividhya , S. Manjunathan and S. Thirumaran , E-J. Chem. , 6(3), 928-937(2009) .

68. A. AL-Rujaiby, M.Sc. Thesis, College of Education/ Ibn-Al-Haitham, University of Baghdad (1997).

69- J. Olivares, S. Stojadinovic, T. Dingemans, S. Sprunt and A. Jakli, Physical Review., E 68, 041704 (2003).

70- I. H. Rou'il, Ph.D. Thesis, College of Education , Ibn-Al-Haitham for Pure Science, University of Baghdad (2006).

71- D. R. dos Santos , A. G. S. de Oliveira , R. L. Coelho , I. M. Begnini , R. F.Magnago and L. da Silva , Arkivoc , (xvii) 157-166 (2008) .

72- M. Tariq , Sh. Hameed , I. H. Bechtold , A. J. Bortoluzzi and A. A. Merlo , J. Mater. Chem. C , 1 , 5583-5593 (2013) .

73- A. H. Al-Dujaili , N. H. Karam and J. H. Tomma , J. Inter. Acad. Res. Multidis. , 1 (11) ,184-196 , (2013).

74- C. I. Ciobanu, I. Carlescu ,G. Lisa and D. Scutaru , Croat. Chem. Acta , 87(1),7-16 (2014).

75- F.A.Abed, M.SC. Thesis, College of Education –Ibn AL –Haitham, University of Baghdad(2015).

76-N.H.Karam,A.T.Atto,andA.AL-Dujaili,Mol.Crest.Liq.Cryst.,Vol.605.pp.1-11, (2014).

77- Karam N. H .; Tomi I. H. R. and Tomma J. H.;, Iraqi Journal of Science, Vol. 57, No.3B, pp:1876-1890(2016).

78- A. R. Yuvaraj, M. Y.Mashitah, and R.Lutfor, , Molecular Crystalsand Liquid Crystals,Vol.631,pp21-30(2016).

79- Balan A. M.; Zbancioc G.; Bentea E.; Carja I.; Ungureanu M.; Tuchilusand C.and Mangalagiu I. I.,Rev. Chim . 60. 10 ,1021-1024 (2009).

80- Zhang T.; Cao X. and Wang X.; Changchun Song ,Journal of Molecular Liquids , 230, 505-510(2017).

81- J. Spekreijse, J. Le Nôtre, J. van Haveren, E. L. Scott and J.P. M. Sandersa, Green Chem., 14, Issue 10,pp2747-2751(2012).

82- S. Cao, Journal of Fluorine Chem., 117, 63-66 (2002).

83- M. Noolvi, S. Agrawal, H. patel, A. Badiger, M, Gaba and A. Zambre; Arabian Journal of Chemistry ;21(50) , p;1,(2011)

84- H. M. Abdullah , I. K. Jassim and M. N. Safi , Kerbala Journal of Pharmaceutical Science, No.4,(2012).

85- T. Zhang, X. Cao, X. Wang and C. Song, Journal of Molecular Liquids ,pp1-13(2017).

86-J. H. Tomma, Ibn Al- Haitham ,J. for pure and appl. sci., 24(2),
219-229 (2011).

87- G. Küçükgüzel, A. Kocatepe, E.De. Clercq, F. Şahin and M. Güllüce, European Journal of Medicinal Chemistry, Vol. 41, Issue 3, pp 353–359(2006).

88- T. Singh, P.K. Sharma, N. Kumar and R. Dudhe , J Pharm Negative Results;4:39-45(2013).

89- I. H. R. Tomi , A. H. J. Al-Qaisi and Z. H. J. Al-Qaisi, Ibn Al-Haitham Jour. for Pure and Appl. Sci., Vol. 23 (3) ,(2010).

90- S.Sana, K. R. Reddy, K. Chinna Rajanna, M. Venkateswarlu and M.Moazzam, International Journal of Organic Chemistry Vol. 2 No. 3, 15, (2012) .

91-T. Singh, P. K. Sharma, N.Kumar and R. Dudhe,J Pharm Negative ResultsVol. : 4 P 39-45, (2013).

92- N. H. Karam; I. H. R. Tomi and J. H. Tomma ; Iraqi Journal of Science, Vol. 57, No.3B, pp:1876-1890(2016).

93- I. Dierking ;, Textures of Liquid Crystals, Wiley-VCH, Weinheim, Germany(2003).

94- S. Singh and D.A. Dunmur ,Liquid Crystals Fundamentals, World Scientific Publishing Co. Pte. Ltd., London (2002).

الخلاصة

هذا العمل يتضمن تحضير وتشخيص ودراسة السلوك البلوري السائل لبعض المركبات الحلقية الغير متجانسة كالاتي :

تحضير سلسلتين تحتوي على حلقة ثايوزولدينون وتحضر عن طريق تحويل الريسورسينول او الهيدروكوينون الى مركبات مناظرة**[I]** و **[II]** بواسطة التصعيد العكسي مع كلورواستايلكلورايد، ومن ثم مفاعلة المركبات الناتجة مع ٤-هيدروكسي ينزالديهايد لتنتج المركبات ثنائية الالديهايد**[III]** و **[IV]** ومن مفاعلة المركبات الاخيرة تتفاعل مع امينات اروماتية مختلفة لتعطي مركبات قواعد شف [V-VII] و[VIII-X] بعد ذلك تفاعل مركبات قواعد شف مع حامض ثايوكلايكولك لتحضيرسلاسل منحنية وخطية تحتوي على حلقة ثايوزولدين-٤- ون [XI-XIII] و [XIV-XVI].

وايضا ،تحضيرمركب[XVII]من تفاعل البايبيرازين مع كلورواستايل كلورايد ومن ثم المركب الناتج يتفاعل مع ٤-هيدروكسي بنزلديهايد لينتج المركب ثنائي الالديهايد [XVIII]مركب الاستر [XIX] الذي تم تحضيره من استرة حامض السيناميك مع الميثانول ومن ثم تكثيف مركب الاستر [XIX]مع الهيدرازين المائي لينتج مركب حامض الهيدرازايد[XX] ، والذي يتفاعل بدوره مع الكلايسين في $POCl_3$ {فسفورواوكسي كلورايد} لينتج مركب (٥-ستايريل -٤,٣,١- اوكسادیازول-٢-يل)[XXI].

بالاضافة الى ذلك ، تحضير مركبات جديدة من قواعد شف [XXII-XXV]من تفاعل مركب

4،3،1 -اوكسادیازول [XXI]مع الديهايدات اروماتية مختلفة بينما يتفاعل مركب الاوكسادیازول [XXI] مع مركب ثنائي الديهايد [III] او [IV] لينتج مركبات قواعد شف جديدة [XXVI] و[XXIX]،وبعد ذلك اضافة حامض ثايوكلايكولك الى المركبات الاخيرة لتعطي مشتقات الثايوزولدين-٤- ون الجديدة [XXVIII]و[XXIX]على التوالي .

اخيرا ،تحضير قاعدة شف جديدة المركب [XXX]عن طريق مفاعلة مركب الاوكسادیازول

[XXI]مع مركب ثنائي الديهايد[XVIII] .المركبات المحضرة تم تشخيصها بواسطة طيف الاشعة تحت الحمراء وطيف الرنين النووي المغناطيسي ^{1}HNMR ،التحليل الدقيق للعناصر C, H , N وطيف الكتلة لبعضها .

تمت دراسة الخصائص البلورية السائلة بواسطة (مسعر المسح التفاضلي DSC ومجهرالضوء المستقطب) للمركبات المحضرة اظهرت كل مركبات قواعد شف [V-VII]اطواراً بلورية سائلة ،حيث اظهر المركب [V] طورا نيماتيا ، بينما المركب [VI] اظهر اطوار متعددة سمكتيا B (SmB) ونيماتيا أما المركب [VII]اظهر اطوار متعددة انعكاسية سمكتك A (SmA)ونيماتية.

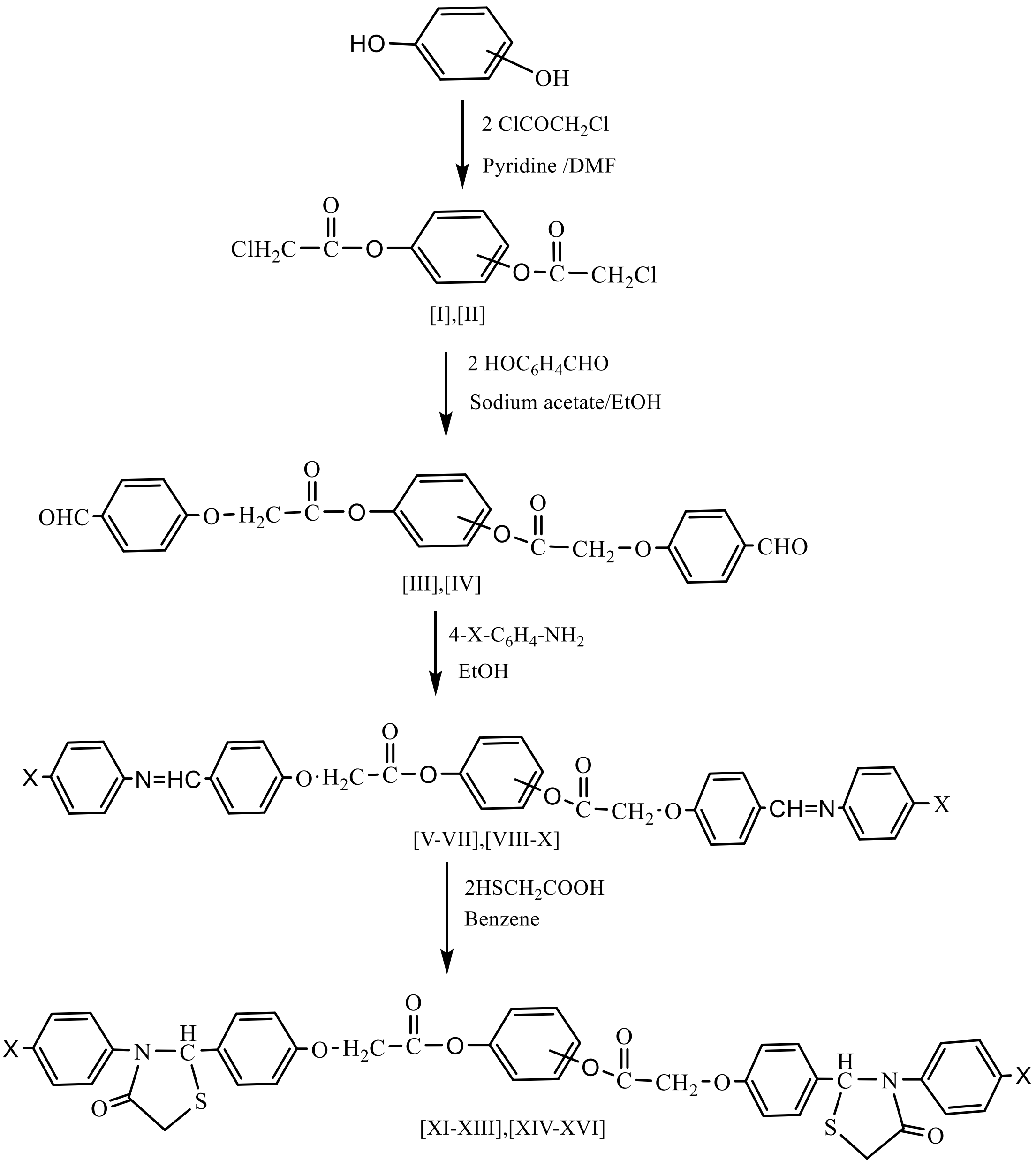
ايضا ،كل مركبات قواعد شف [VIII-X] اظهرت اطوار بلورية سائلة، لكن المركب[VIII]اظهرطورانعكاسي سمكتيا (SmB)فقط . المركب [IX] اظهر طور متعدد سمكتك B (SmB) و نيماتي ، بينما المركب [X] اظهر اطوار متعددة انعكاسية سمكتك A (SmA) ونيماتي.

كل مشتقات الثايوزولدنون[XI-XIII] و [XIV-XVI] لم تظهر اي خصائص بلورية سائلة، أما

مركبات قواعد شف [XXII-XXV] اظهرت سلوك بلوري سائل كالتالي :

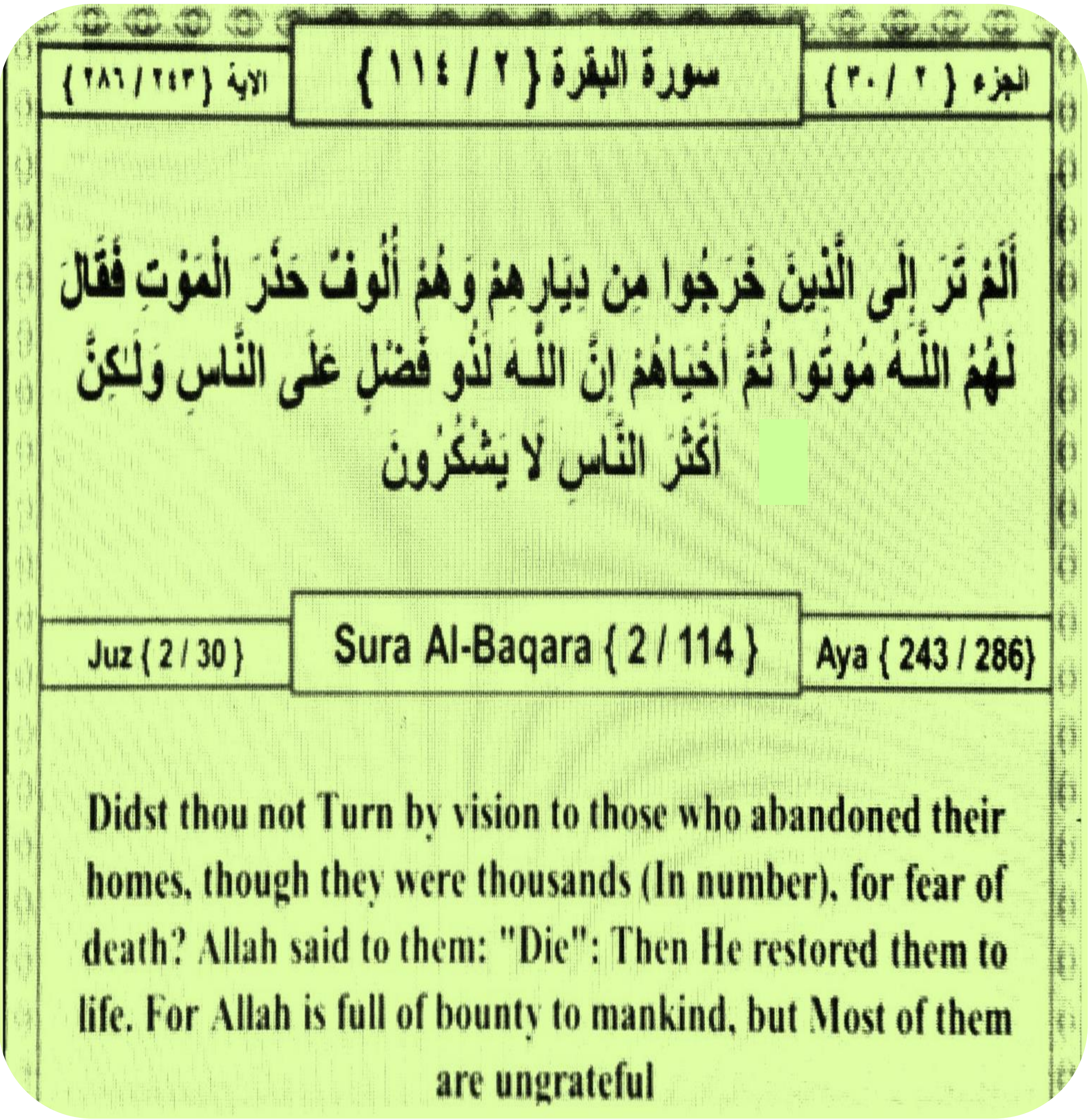
المركب [XXII] اظهر اطوار متعددة انعكاسية سمكتك B (SmB) ونيماتي ، ايضا المركب [XXV] اظهر طوارا نيماتي ، بينما المركبات[XXIV] و[XXIII] لم تظهر اي سلوك بلوري سائل المركب [XXVIII] اظهر الطور النيماتي ، بينما المركب [XXIX] لم يظهر اي خصائص بلورية سائلة ،اخيرا المركب [XXX] اظهر طورا نيماتي انعكاسي

ويمكن تلخيص هذا العمل بالمخطط I و II



X=CH_3O , CH_3 and OH

Scheme I



الجزء { ٢ / ٣٠ } سورة البقرة { ٢ / ١١٤ } الآية { ٢٤٣ / ٢٨٦ }

أَلَمْ تَرَ إِلَى الَّذِينَ خَرَجُوا مِن دِيَارِهِمْ وَهُمْ أُلُوفٌ حَذَرَ الْمَوْتِ فَقَالَ لَهُمُ اللَّهُ مُوتُوا ثُمَّ أَحْيَاهُمْ إِنَّ اللَّهَ لَذُو فَضْلٍ عَلَى النَّاسِ وَلَٰكِنَّ أَكْثَرَ النَّاسِ لَا يَشْكُرُونَ

Juz { 2 / 30 } Sura Al-Baqara { 2 / 114 } Aya { 243 / 286}

Didst thou not Turn by vision to those who abandoned their homes, though they were thousands (In number), for fear of death? Allah said to them: "Die": Then He restored them to life. For Allah is full of bounty to mankind, but Most of them are ungrateful

جمهورية العراق

وزارة التعليم العالي والبحث العلمي

جامعة بغداد

كلية التربية للعلوم الصرفة/ ابن الهيثم

قسم الكيمياء

تحضير ,تشخيص و دراسة السلوك البلوري السائل لمركبات الثايوزولدين-٤- ون و 4،3،1 – اوكسادايازول الجديدة

رسالة مقدمة إلى

مجلس كلية التربية للعلوم الصرفة-ابن الهيثم-جامعة بغداد

وهي جزء من متطلبات نيل درجة الماجستير علوم في الكيمياء

من قبل

آلاء كاظم شنشل

بكالوريوس علوم كيمياء / كلية التربية للعلوم الصرفة / ابن الهيثم / جامعة بغداد
(2002-2003) م

بأشراف

ا.م.د. نسرين حسين كرم

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