Synthesis and Characterization of Heterocyclic Compounds from 8-Hydroxyquinoline

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الخلاصة :

يتضمن البحث تحضير مركبات حلقية غير متجانسة مختلفة الحلقات عن طريق استعمال 8- هايدروكسي كوينولين كمادة أولية ومفاعلتها مع بارا- فنيلين ثنائي الامين ومشتقات البنزلديهايد بعدها يتم التأكد من صحة المركبات المحضرة بوساطة درجة الغليان وتقنية IR و^{1}HNMR .

ABSTRACT:

This research includes synthesized of heterocyclic compounds derivatives containing different rings through the use of 8- hydroxyquinoline as starting material and a reacted with p- phenylene diamine and benzldehyde derivatives, These compounds were characterized by melting point and FT.IR and ^{1}HNMR Spectroscopy.

Keywords : 8-hydroxyquinoline, Azo-compounds, Schiff base , Oxazepine , 1,3-oxazepane .

INTRODUCTION

One of the most popular and versatile organic compound 8- Hydroxyquinoline, containing two fused rings phenol with pyridine , 8- Hydroxyquinoline and its derivatives have found important variety of applications ranging from medicinal field, pharmacological, which can be used as insecticide (1), antibacterial (1-3), antifungal agents , anti- HIV agents (1,4). 8-hydroxyquinoline Ligand has been applied for analytical purposes and separation techniques (1–3) . 8- hydroxyquinoline with magnatic multi – walled carbon nanotubes was developed to remove cadmium from water, vegetable and food samples, this way considered selective, low- cost and high

capacitance for enrichment of cadmium (5) due to their chelating ability toward the metal cations (1,3,6) .

Azo dyes are compounds containing the functional group (R-N=N-R$^-$) where R and R$^-$ can be alkyl or aryl group, functional group N=N called azo group, when R$^-$ group aromatic are the azo structure are more stable than when R group are alkyl. aromatic azo group are highly coloured which used as dyes (7). In industry. the largest group of colorants compounds is azo dyes (8).

The dyes have been used in different fields such as dying textile fibers, aluminum sheet, ink printers (8), biomedical studies and high technology like lasers , liquid crystalline displass, Organic dyes been used as effective corrosion inhibitors of mild steel in different media (9), also used azo compounds in paper , leather, food and cosmetic products .Azo dyes are great importance in medicnal field ,also in biological reaction such as inhibition of DNA, RNA and protein synthesis(10), Most of azo dyes have complex structures and toxie (11), Azo dyes absorbed light in the visible region of the spectrum (400 – 700 nm) and contains at least one colour bearing group (chromophore) (12). Schiff bases are an important part of organic compounds. Schiffs bases are prepared from condensation of primary amines with carbonyl compounds. They were first reported by hugo Schiff in 1864. the functional group of these compounds is the azomethine group it is also called imine with the general formula RHC=N-R_1 , where R and R_1 are aryl, alkyl, cyclo alkyl or heterocyclic groups. Schiff bases have also been shown to exhibit a widely range of biological activities, including antimalarial , antifungal, antibacterial, antiproliferative , anti – inflammatory, antiviral, antipyretic properties (13) and Anticancer (14). Formation of Schiff basic generally takes place under acid or basic catalysis with heat. the common Schiff base are glassy solids, Some Schiff base form in soluble salts with strong acids but it’s feebly basic , Schiff base are used as intermediates for the synthesis of amino acids. or as ligands for preparation of metal complexes having a chain of different structures (15) .

EXPERIMENTAL SECTION

Materials:

Chemicals used during the current work are the 8- hydroxyquinoline (8-HQ), p-phenylene diamine, N,N-dimethylamino benzldehyde, Phathilic anhydride , maleic anhydride and succinic anhydride, NaOH, HCl, $NaNO_2$ produced by (sigma and Aldrich) company. In addition to use of ethanol, dry benzene and dioxan as a solvent .

Instrumentation

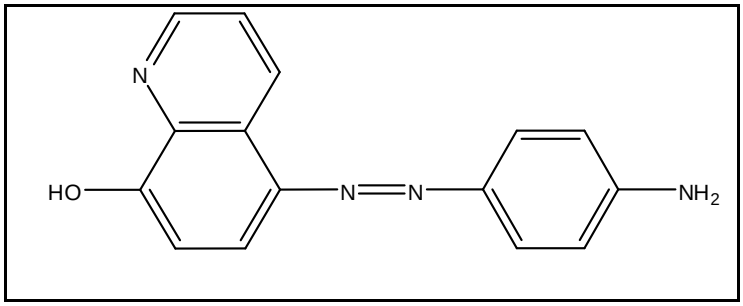
We used the following instruments

1- **M.P apparatus**
2- **TLC Chromatography**
3- **IR Spector's**
4- **^{1}HNMR Spector's**

melting point was measured by hot stage Gallen kamp. To ensure the purity of resulting compounds we used technique a thin layer chromatography (TLC), in the presence of iodine as an aspect of the spot. FT-IR spectroscopy KBr disc and ^{1}HNMR spectroscopy was used DMSO as solvent

EXPERIMANTAL

1- Preparation of azo compound (A) [16]



(A) 5-((4-(dimethylamino)phenyl)diazenyl)quinolin-8-ol

This compound was prepared in two steps.

The first step Formation diazonium salt;

Formation of diazonium salt: p- phenylene diamine (1.1gm,0.01mol) was dissolved in hydrochloric acid (2.5ml) with concentration (11N) and (20ml) of distilled water. Then cooled in ice bath (0-5) ^{0}C. Sodium nitrite (0.7gm ,0.01 mol) was dissolved in (10 ml) distilled water and cooled in ice bath (0 – 5) ^{0}C , then add slowly to p- phenylene diamine solution and mix solution together. than; the mixture was kept for 20 min, at 0-5^{0}C .

The second step Azo dye composition;

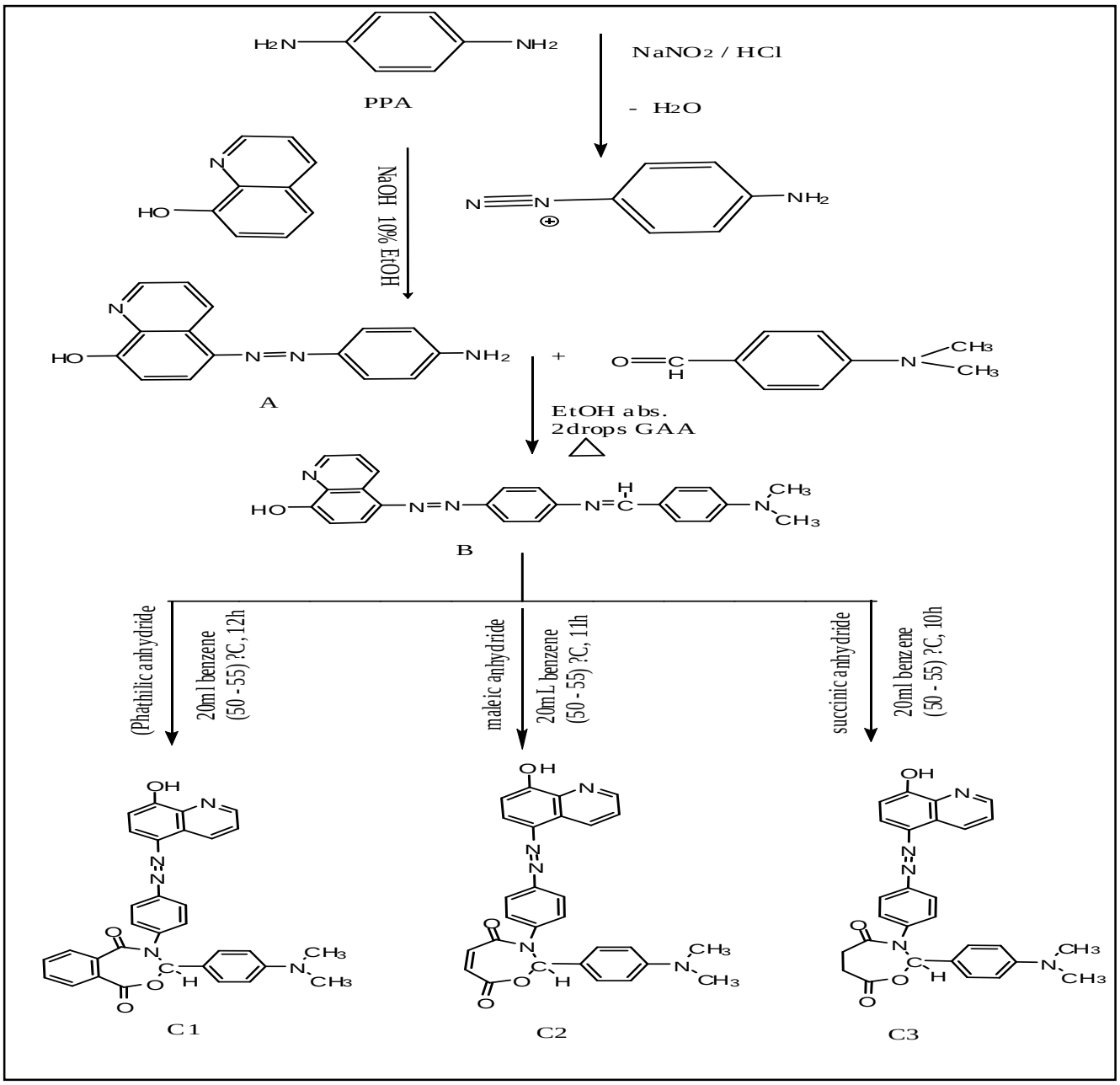
Azo dye products ; 8-hydroxyquinoline (1.45gm ,0.01mol) , was dissolved in abslute ethanol and sodium hydroxide solution (15 ml. 10%) and stirred the solution in the first step at (0 – 5) ^{0}C Then added slowly to that solution with stirring.
Leaving the reaction mixture for a period of 3 hrs. Then filtered. and collected the solid product ,and we are Re-crystallization by used abslute ethanol

2- procedure of Schiff base (B) from azo dye [17].

Azo compound (3,00gm, 0.01mol) reacts with benzldehyd derivatives (N,N-dimethylamino benzldehyd) was added to in absolute ethanol (60ml) and then a catalytic amount of GAA (two or three drops) was added at 70ºC. the reaction mixture was refluxed 8h. The products (B) were collected by filtration and recrystallized by ethanol.

3- procedure synthesis of 1,3 oxazepine and 1,3 oxazepane [18].

The Schiff base (B) (0.5gm, 0.001 mol) react with (0.15gm, 0.098gm ,0.1gm, 0.001 mol) of (Phathilic anhydride, maleic anhydride, and succinic anhydride) respectively in 20 ml dry benzene and the solution was left at temperature (50 – 55) ºC. Then reaction mixture was refluxed (12h, 11h, 10h) respectively .The products(C_1,C_2 andC_3) were collected by filtration and recrystallized in ethanol .



Scheme (1) Preparation Compounds (A-C_3)

(C_1)\3-(4-(dimethylamino)phenyl)-4-(4-((8-hydroxyquinolin-5-yl)diazenyl)phenyl)-3,4-dihydrobenzo[e][1,3]oxazepine-1,5-dione

(C_2)\2-(4-(dimethylamino)phenyl)-3-(4-((8-hydroxyquinolin-5-yl)diazenyl)phenyl)-2,3-dihydro-1,3-oxazepine-4,7-dione

(C_3)\2-(4-(dimethylamino)phenyl)-3-(4-((8-hydroxyquinolin-5-yl)diazenyl)phenyl)-1,3-oxazepane-4,7-dione

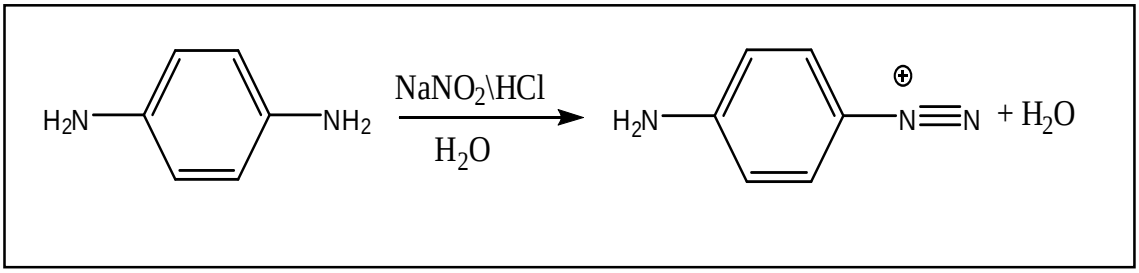
Table (1): Physical properties and other characteristics for the synthesized compound (A ,B ,C_1 ,C_2 ,C_3) :

No.	Molecular Formula	M.wt g/mol	m.p °C	Color	Rf	Solvent	Reflex Time	Yield %
A	$C_{15}H_{12}N_4O$	264	200 – 202	Black	-	EtOH	3hrs	89
B	$C_{24}H_{21}ON_5$	395	226 – 228	Brown	0.70 1Me: 4Ben	EtOH	8hrs	84
C_1	$C_{32}H_{25}O_4N_5$	543	189 – 192	Brown	0.80 2Me: 3Ben	EtOH	12hrs	79.7
C_2	$C_{28}H_{23}O_4N_5$	493	193 – 196	Brown	0.65 2Me: 3Ben	EtOH	11hrs	80
C_3	$C_{28}H_{25}O_4N_5$	495	219 – 222	Brown	0.67 2Me: 3Ben	EtOH	10hrs	76.7

RESULTS AND DISCUSSION

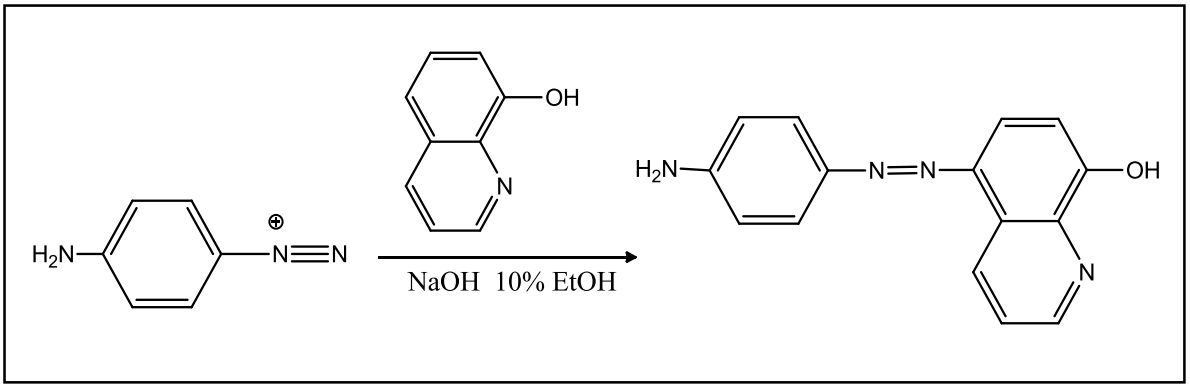
Synthesis of azo compound

P-Phenylene diamine (PPA), in acidic medium, was reacted with sodium nitrite to form the diazonium salt:



Diazotized (PPA)

After around twenty minutes; the diazonium salt which was formed are coupled with 8 – hydroxyquinoline in a basic medium (NaOH 10%) at(0-5)^{0}C to From Azo dyes .



Scheme (2) preparation of Azo dye (A)

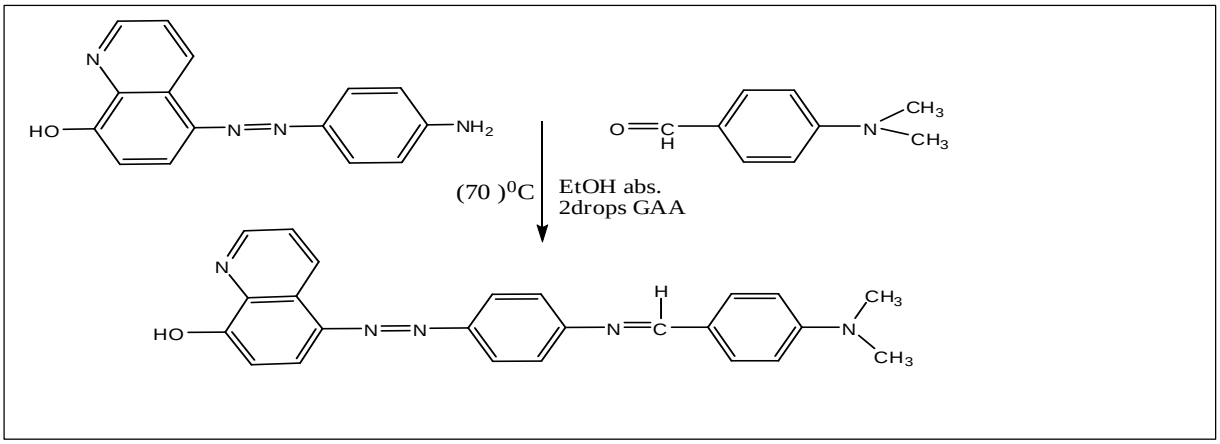
The FT-IR spectra of azo compound (A) fig (1) Show the presence of (NH_2) group at ν (3375.43 and ν3321.42)cm^{-1} (asymmetric and symmetric) respectively and CH aromatic band appear at ν (3053.32) cm^{-1} and CH aliphatic band at (ν 2924.09)cm^{-1}. and at ν (3324.98)cm^{-1} absorption (OH) phenolic group we appeared. The (N=N) azo group compound found at ν (1502,55) cm^{-1} .

The ^{1}H NMR spectrum fig(7) shows following characteristic chemical shifts for compound

(A),(DMSO) solvent at(2.5)ppm, the proton (OH) appeared at (9.2)ppm, and proton of amine aromatic group (NH_2) appeared signal at (6.0)ppm, At (6.7-8.9)ppm for aromatic ring proton .

Synthesis of Schiff base compound

The reaction between Azo compound of (A) [which contain amine group] and benzldehyde derivatives to synthesize Schiff base (B) .



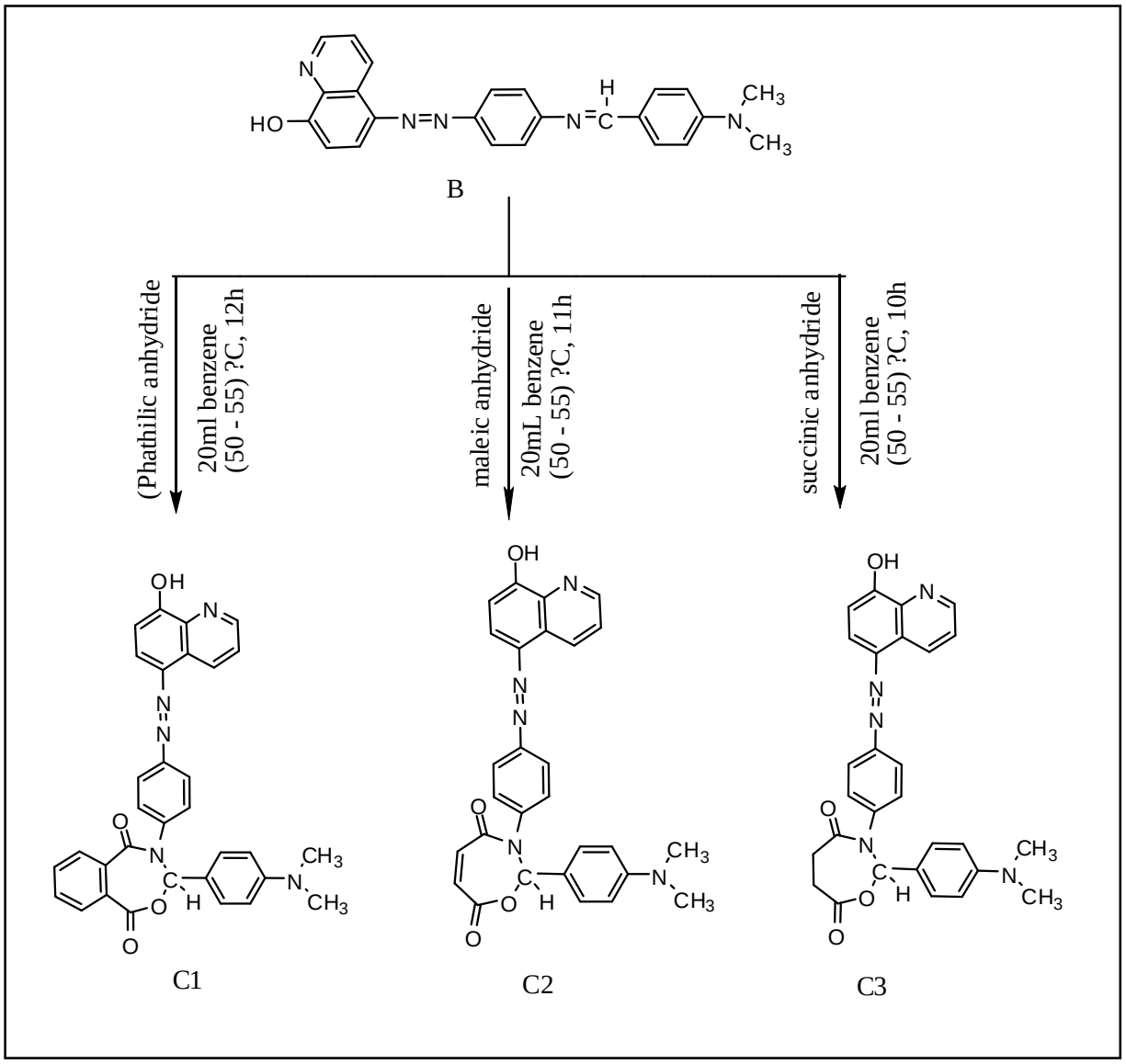
Scheme (3) Preparation of Schiff base (B)

In the FT-IR spectrum there are four major peaks; which are depending upon the substitution group appeared in the compound, and these groups are azomethane groups (-N=CH-) , (=CH-Ar) and (C-OH) group.

The fig (3) showed the appearance of the absorption bands in the region ν (1602.85) cm^{-1} due to stretching vibration for azomethane group (-HC=N-), with the disappearance of group (CHO) and the disappearance of (NH_2) at ν (3375.43 and ν 3321.42) cm^{-1} (Asymmetric and symmetric) and CH aromatic band at ν (3078.39 cm^{-1}) and CH aliphatic bands at ν (2987.74 - ν 2806.43) cm^{-1}. Besides to band at ν (3383.14)cm^{-1} absorption of (OH) phenolic.

Synthesis and characterization of compounds (1,3) Oxzazepine (C_1 and C_2) and (1,3) Oxzazepane (C_3).

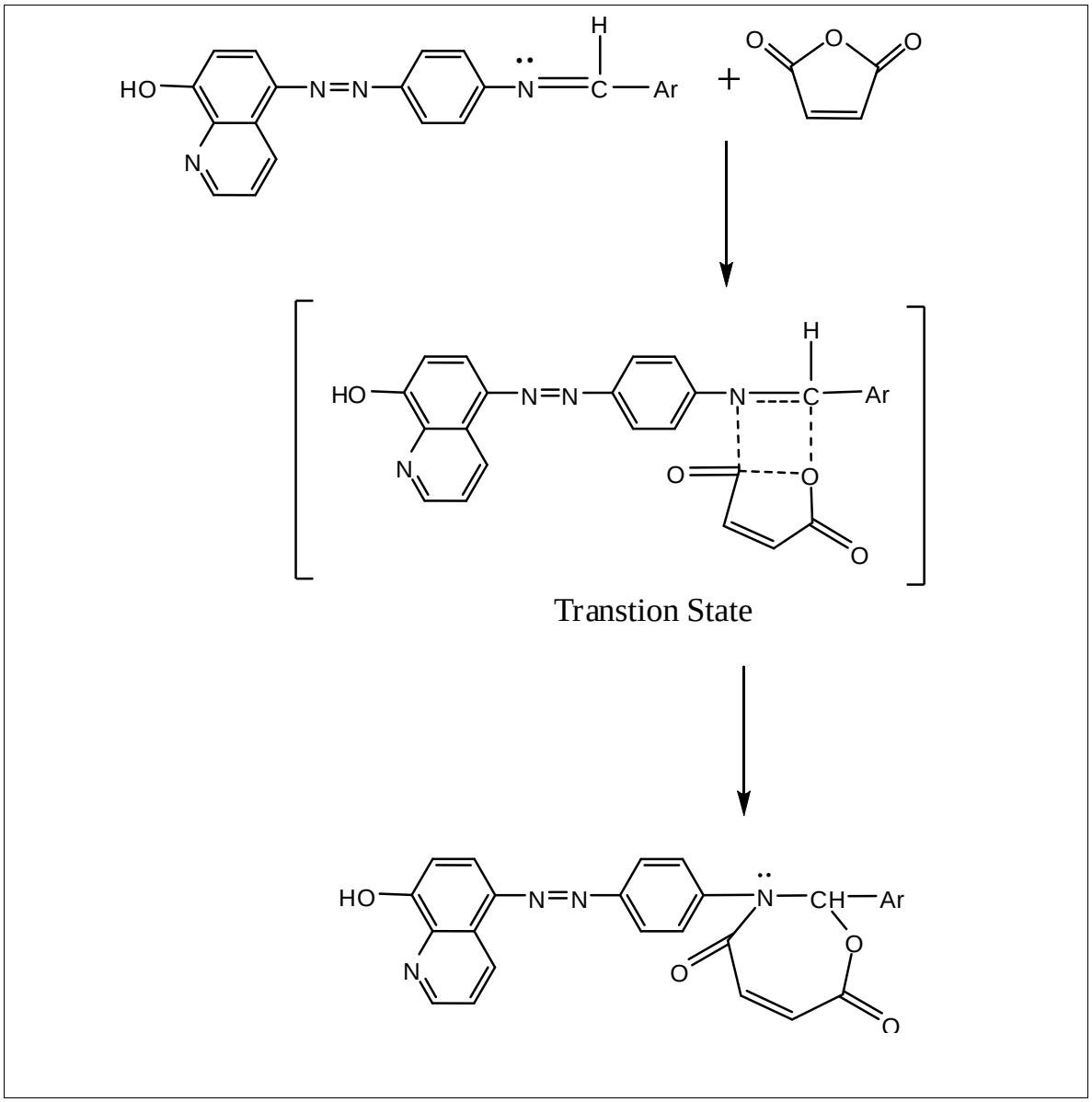
These compounds were synthesized according to the sequence in **scheme (4) .**



Scheme (4) Preparation of 1-3 oxazepine (C_1 and C_2) and (1,3) Oxzazepane (C_3).

The Schiff base (B) were reacted with (Phathilic anhydride, maleic anhydride and succinic anhydride) respectively to synthesis (C_1,C_2 and C_3) .

These compounds were characterized by their melting points, FT.IR, ^{1}HNMR and checked by TLC.



Mechanism of closed seven rings

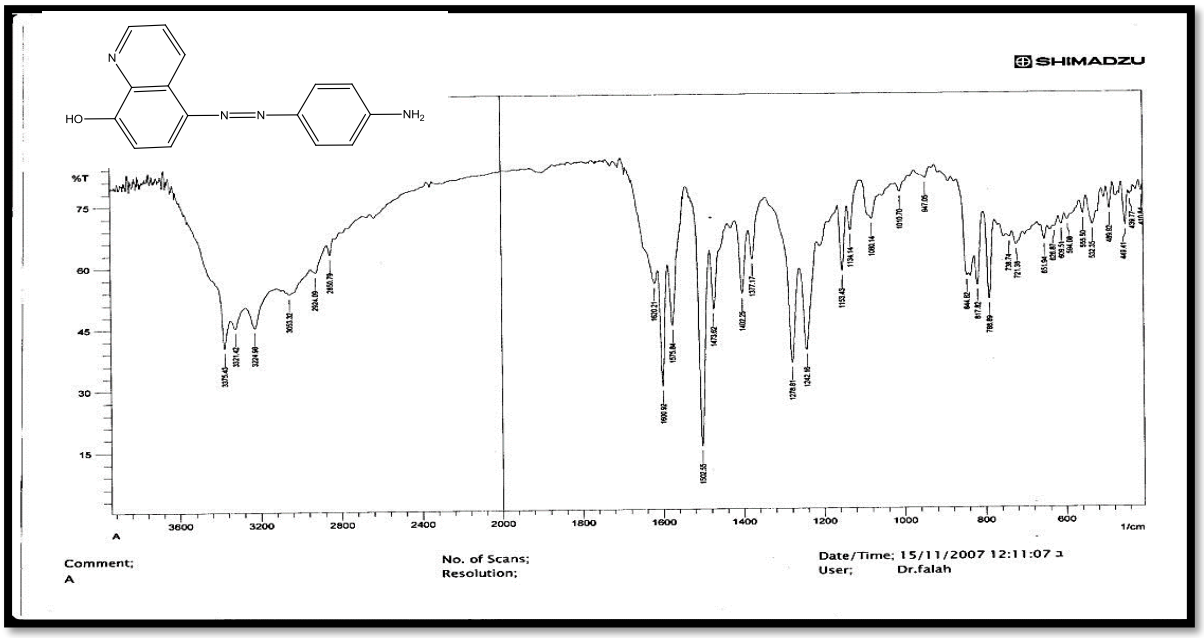
The FT.IR spectra fig (4-6) of compounds C_1,C_2 and C_3)

Show of carbonyl group band of (Lactone) at ν (1710.86 , ν 1718.58 , ν 1699.29)cm^{-1} and carbonyl group band of (Lactame) at ν (1668.43 , ν 1624.06 , ν 1660.71) cm^{-1} of compounds (C_1, C_2 and C_3) respectively and CH aromatic band at ν (3055.24 , ν 3055. 24 , ν 3051.39) and , CH aliphatic bands at ν (2800- ν 2924.09 – 2922.16)cm^{-1} respectively at ν (3377.36 – 3446.79 – 3381.21) to OH group with disappearance the stretching vibration of azomethane group (-N=C-H) at ν (1602.85)cm^{-1}.

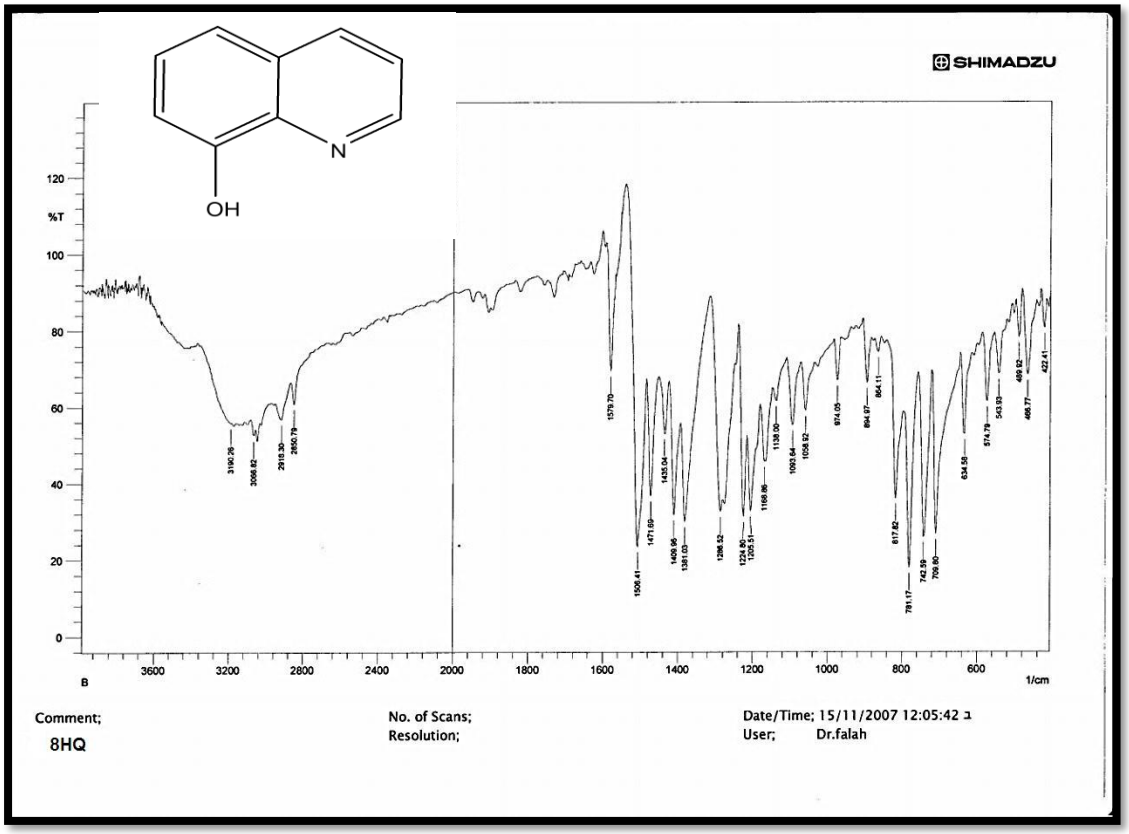
The ^{1}H NMR spectrum fig(8) shows following characteristic chemical shifts for compounds (C_1) ,(DMSO) solvent at(2.5)ppm, the proton (OH) appeared at (10.7)ppm, the proton group (-CH) cyclic closed appeared signal at (9.6)ppm, At (6.7-9.3)ppm for aromatic ring proton, appeared signal at (3.0)ppm for group (CH_3) .

The ^{1}H NMR spectrum fig(9) shows following characteristic chemical shifts for compounds (C_2) ,(DMSO) solvent at(2.4)ppm, the proton (OH) appeared at (10.6)ppm, the proton group (-CH) cyclic closed appeared signal at (9.6)ppm, At (6.6-9.2)ppm for aromatic ring proton, and proton of alkene group (CH=CH) appeared double signal at (6.3-6.5)ppm, appeared signal at (3.0)ppm for group (CH_3) .

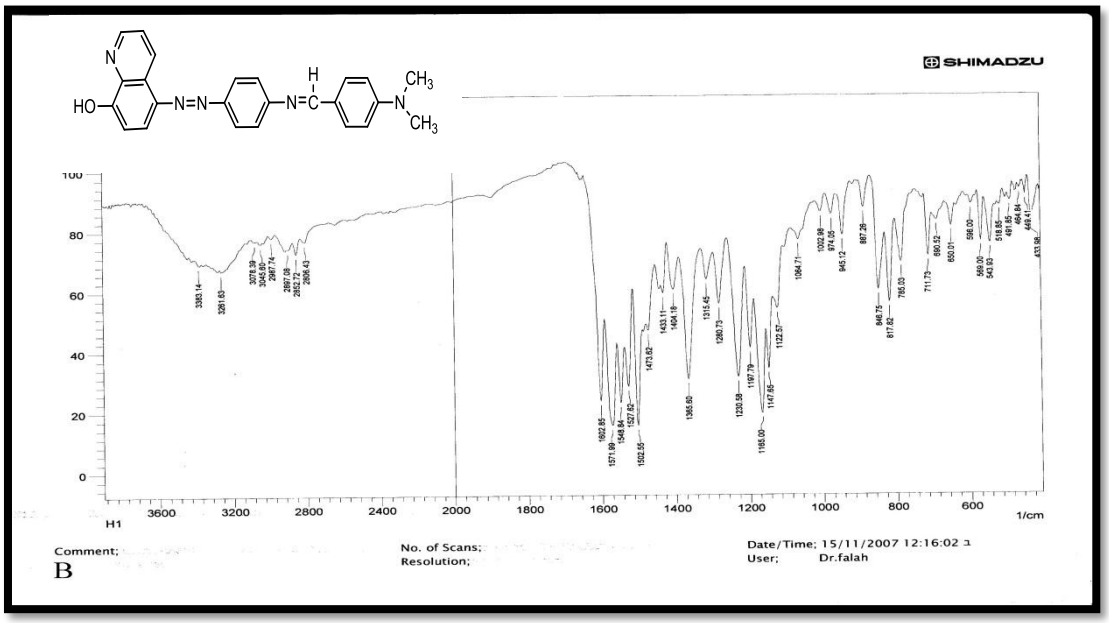
The ^{1}H NMR spectrum fig(10) shows following characteristic chemical shifts for compounds (C_3) ,(DMSO) solvent at(2.4)ppm, the proton (OH) appeared at (10.3)ppm, the proton group (-CH)) cyclic closed appeared signal at (9.6)ppm, At (6.7 -9.3)ppm for aromatic ring proton, appeared signal at (1.5)ppm and (1.2)ppm for groups lactone (O-C=O) and Lactame (N-C=O)respectively , appeared signal at (3.0)ppm for group (CH_3) .



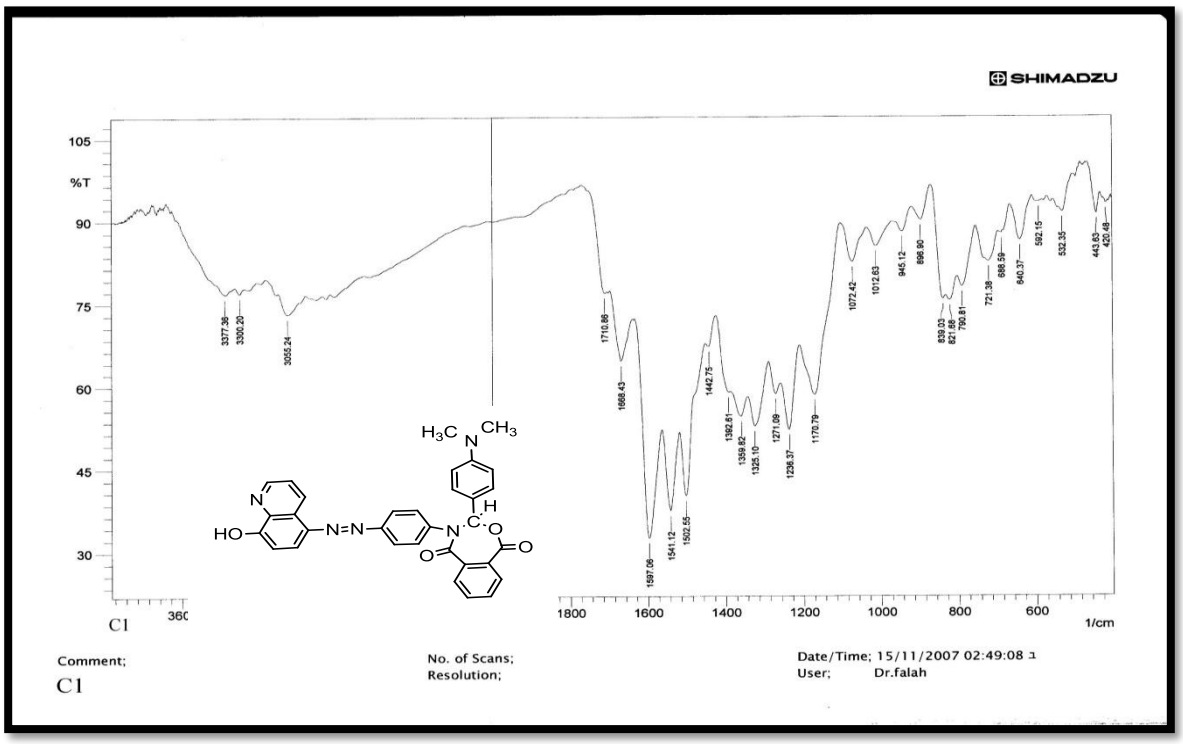
Fig(1) FT.IR spectrum of azo compound (A)



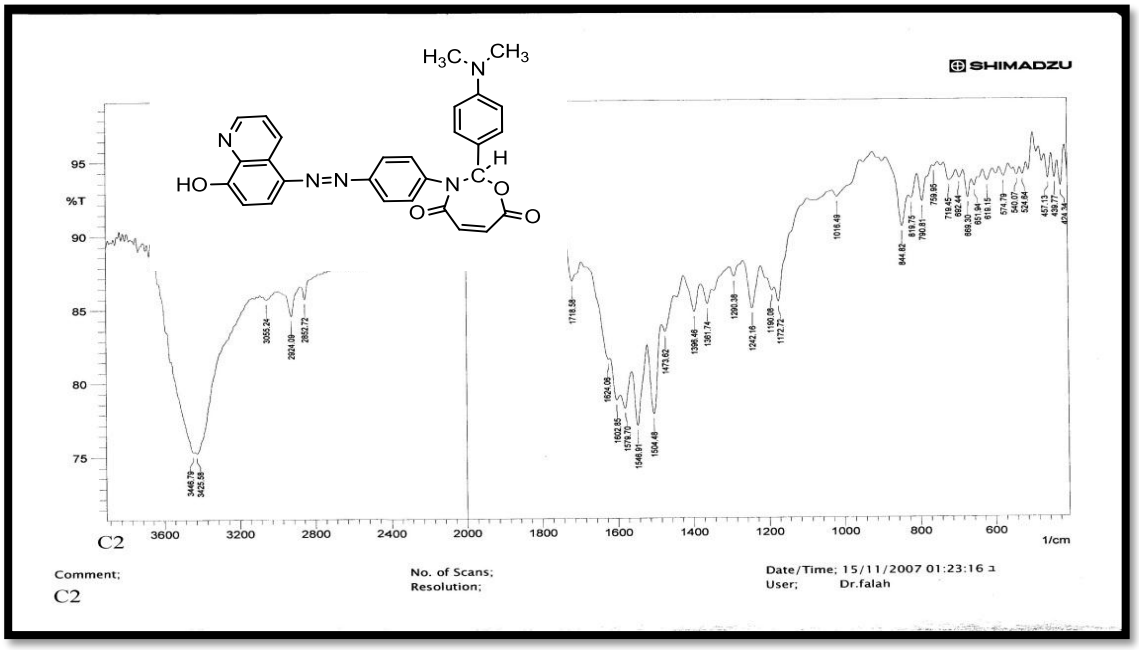
Fig(2) FT.IR spectrum of compound 8-hydroxyquinoline



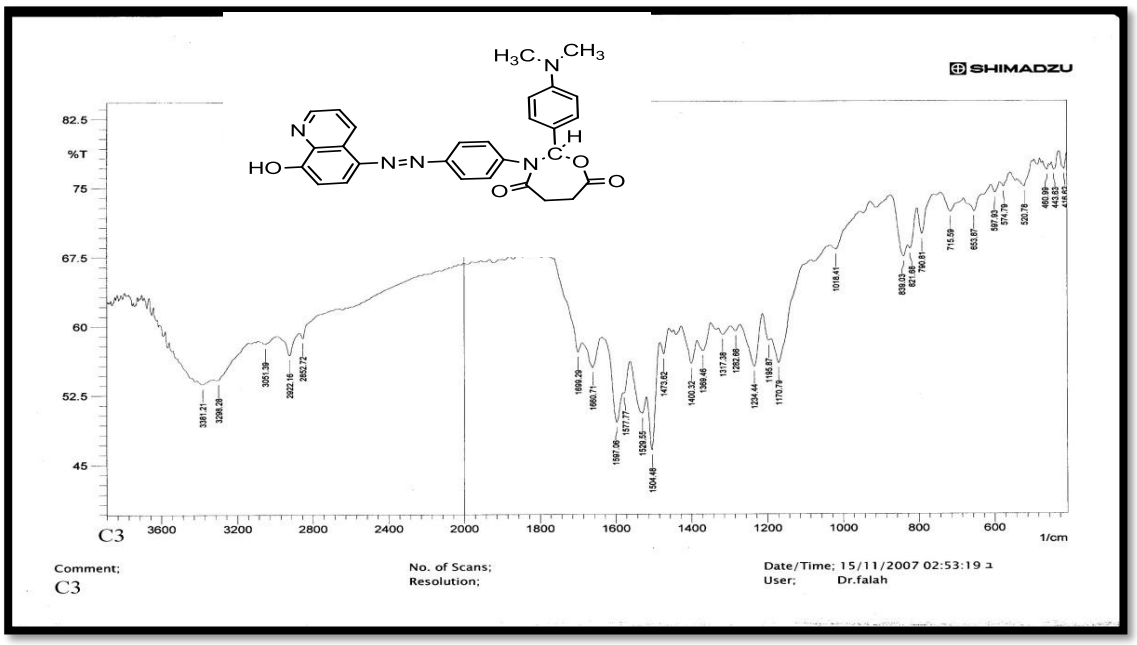
Fig(3) FT.IR spectrum of Schiff base compound (B)



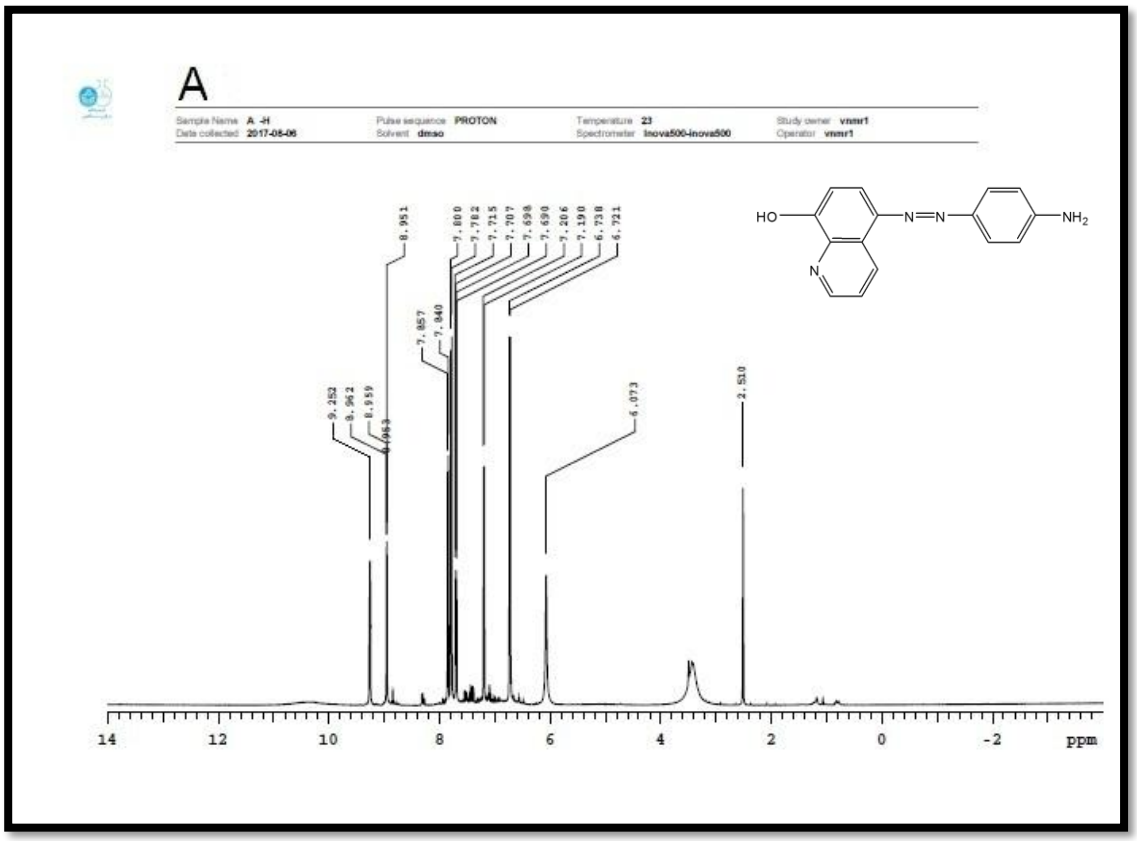
Fig(4) FT.IR spectrum of 1,3 oxazepine compound (C_1)



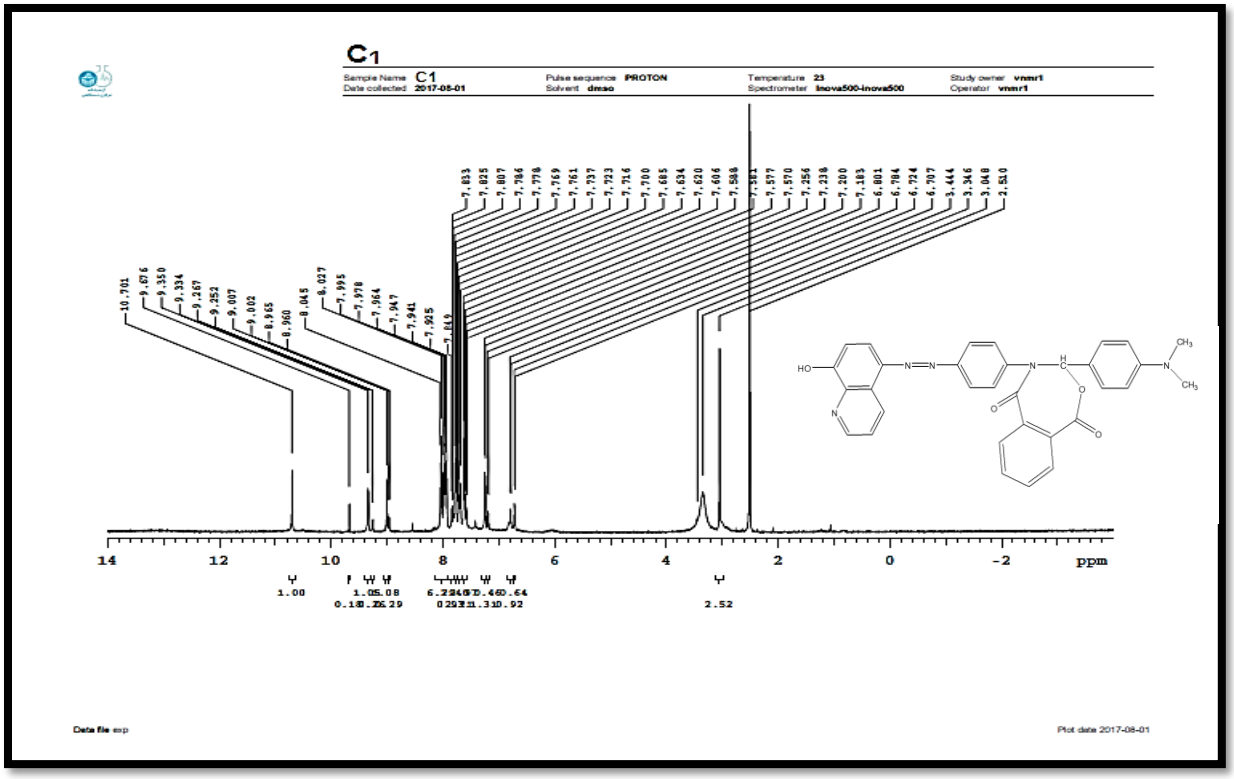
Fig(5) FT.IR spectrum of 1,3 oxazepine compound (C_2)



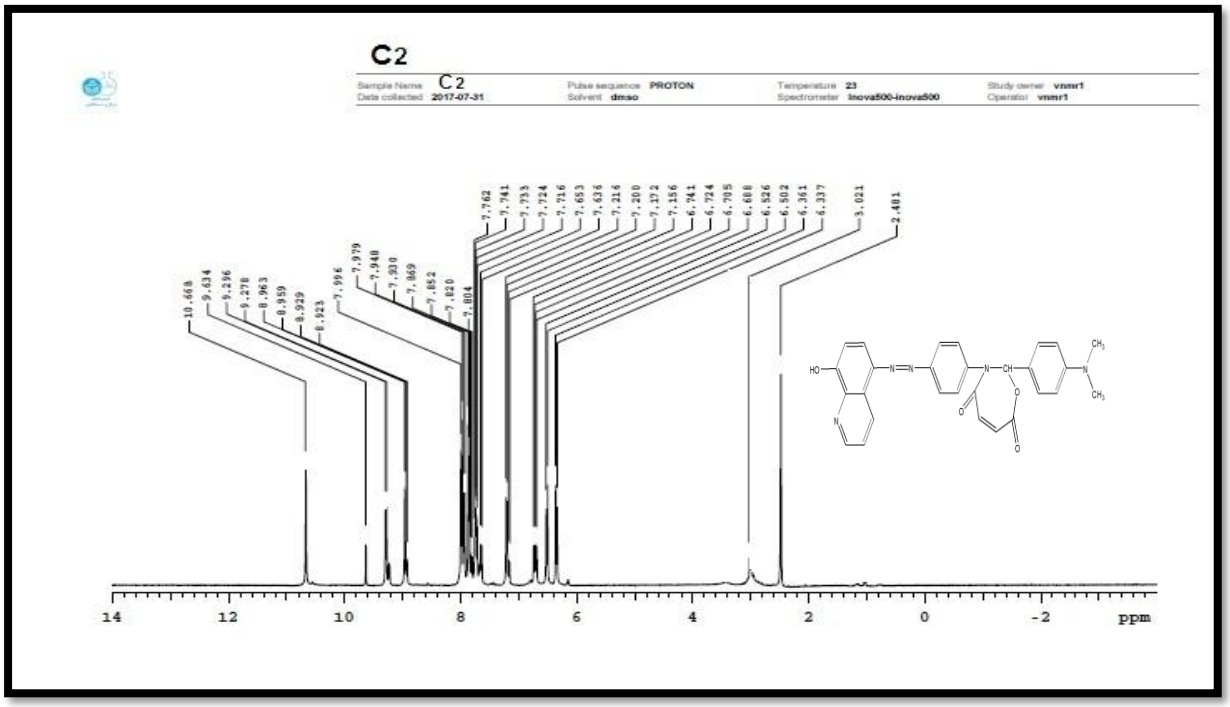
Fig(6) FT.IR spectrum of 1,3 oxazepane compound (C_3)



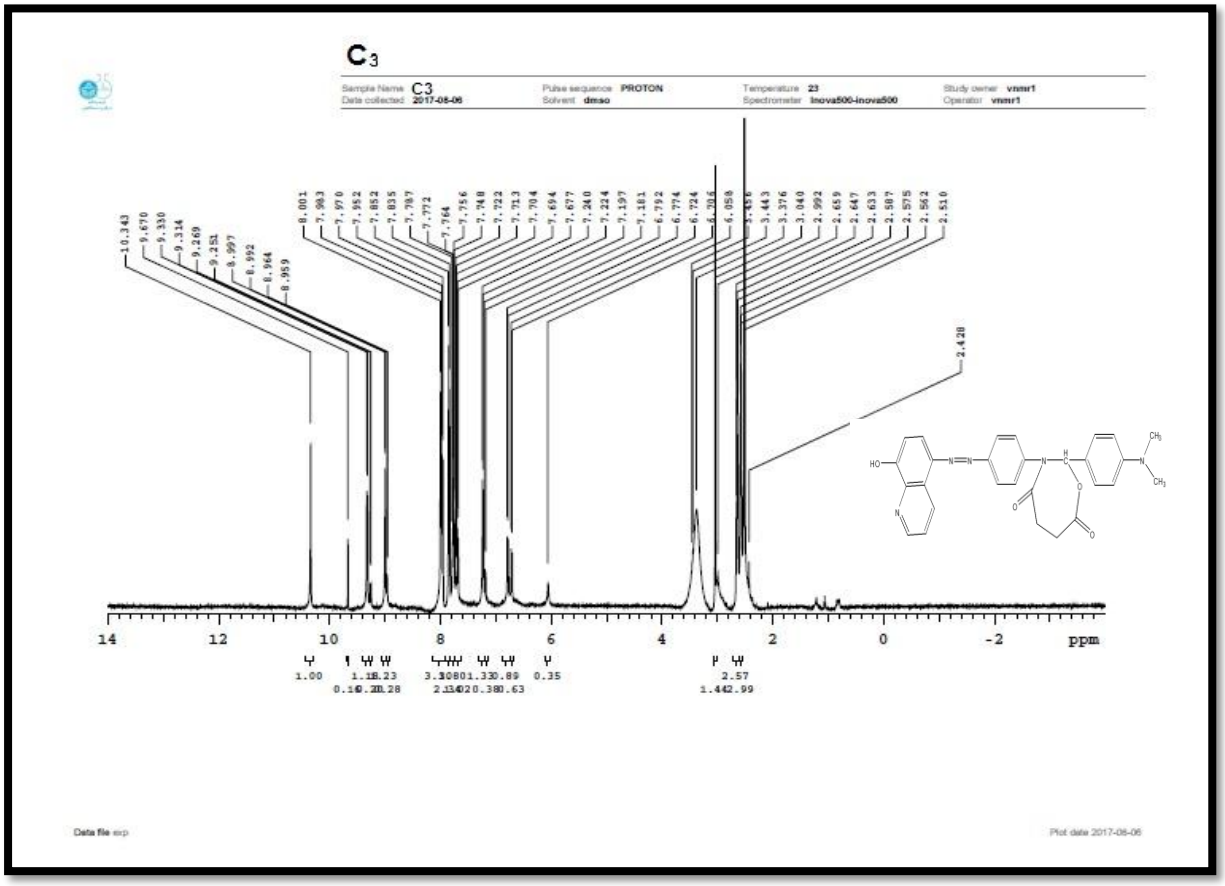
Fig(7) ^{1}HNMR spectrum of azo compound (A)



Fig(8) ^{1}HNMR spectrum of 1,3 oxazepine compound (C_1)



Fig(9) ^{1}HNMR spectrum of 1,3 oxazepine compound (C_2)



Fig(10) ^{1}HNMR spectrum of 1,3 oxazepane compound (C_3)

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