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Evaluation of Some Biochemical Parameters in Patients With Metabolic Syndrome

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Abstract

Background: Metabolic syndrome is the medical term for a cluster of metabolic abnormalities that increases in individuals risk of diabetic mellitus type 2 (T2DM) and cardiovascular diseases(CVD). ENREF 1 The components of MS are glucose intolerance, obesity, hypertension and dyslipidemia.An insulin resistance is the key phase of metabolic syndrome constitutes the major risk factor for the development of diabetes mellitus.

Objectives: The present study aimed to comprise insulin resistance values among three study groups.

Subjects: The present study included 50 metabolic syndrome patients, 50 cases who suffered at least one of the metabolic syndrome symptoms as pathological control, finally 50 individuals as healthy control.

Methods: Fasting insulin, hemoglobin A_{1C} (HbA_{1C}), fasting blood glucose and the lipid profile includedtotal cholesterol TC, triglyceride TG and high density lipoprotein cholesterol HDL- and low density lipoprotein cholesterol LDL-C concentrations were determined in present study using a different available kits.

Results:current work showed a highly significant variations among study groups, no significant differences were shown when the comparison was carried out between two genders of the same subgroups.

Keywords:*Metabolic syndrome, insulin resistance, glucose intolerance, hypertension, lipid profile.*

Introduction

The original description of the metabolic syndrome by Reaven[1] consisted of obesity, insulin resistance, hypertension, impaired glucose tolerance or diabetes, hyperinsulinemia and dyslipidemia characterized by elevated triglyceride, and low HDL concentrations[2-4]. All of the features described above are risk factors for atherosclerosis, and thus, metabolic syndrome constituted a significant risk for coronary heart disease. The features of obesity/overweight and insulin resistance also provided a significant risk for developing type 2 diabetes[5, 6]. The risks for coronary heart disease and diabetes with metabolic syndrome are greater than those for simple obesity alone[7].

Metabolic syndrome is quite common. Approximately 32% of the population in the U.S. has metabolic syndrome, and about 85% of those with type 2 diabetes have metabolic syndrome[8, 9] ENREF 8. Around 25% of adults in Europe and Latin America are estimated to have the condition, and rates are rising in developing East Asian [9].Genetics and the environment both play important roles in the development of the metabolic syndrome, genetic factors influence each individual component of the syndrome, and the syndrome itself. A family history that includes type 2 diabetes, hypertension, and early heart disease greatly increases the chance that an individual will develop the metabolic syndrome[10]. Environmental issues such as low activity level, sedentary lifestyle[11], and progressive weight gain byeating an excessively high carbohydrate diet also contribute significantly to the risk of developing the metabolic syndrome[12], additionally others factor include: Post-menopausal women and Smoking[13].

Metabolic syndrome is associated with fat accumulation in the liver (fatty liver)resulting in inflammation and the potential forcirrhosis[14]. The kidneys can also be affected, as there is an association with microalbuminuria(the leaking of protein into the urine), a subtle but clear indication of kidney damage[15].Other problems associated with metabolic syndrome include obstructive sleep apnea[16], polycystic ovary syndrome[17], increased risk of dementia with aging, and cognitive decline in the elderly[18].

Insulin resistance is a key step of metabolic syndrome, which is constitutes the main riskfactor for the development of diabetes mellitus[13, 19-21]. Thus , hyperinsulinemia, glucose intolerance , type2 diabetes , hypertriglyceridemia , and low HDL concentration could be accounted for by resistance to the action of insulin on carbohydrate and lipid metabolism[2, 5, 21].

Subjects and Design

During six months ago 50 patients (59.04 years with age range 38) with metabolic syndrome ,50 pathological control (52.06years with age range 34) and 50 healthy controls (52.39years with age range33) were enrolled in the present study. Groups of the present research were classified in to two groups according to their gender.The participated patients were collected from Diabetes Glands Deaf Center in Al-SadderMedical City in Al- Najaf Al-Ashraf governorate, Iraq.

Initial diagnosis was performed by specialist physicians who depended ondefinition of metabolic syndrome requiring the presence of five criteria elevated fasting glucose (≥ 100mg/dL), elevated blood pressure (systolic ≥130 mmHg and/ or diastolic ≥ 85 mmHg), reduced HDL-cholesterol (<40mg/dL), elevated triglycerides (≥ 150 mg/dL) and elevated body mass index (BMI)> 30[22] and through several of clinical and laboratory tests specialist for metabolic syndrome.The individuals as pathological controls suffered at least one of metabolic syndrome symptoms. Selection of healthy individual as a control group based on several criteria; included: an absence of major medical or surgical illness in the previous 5 years, no hospital admissions, no current medication, and a subjective perception of good health as determined by health questionnaire, additionally women who not pregnant or breast feeding.

More than, control group might at approximate age range with the patients group, no smoking, no alcohol drinking with similar food style to patients group. Body mass index (BMI) was calculated as theratio of weight (Kilogram) to the square of height (meters).Obesity and overweight were classified according to WHO criteria[23] [13]. A person was considered obese if the BMI value was ≥30 kg/m2, overweight if BMI ≥25 Kg/$m^2$and <30 Kg/m^2.Blood pressure was measured using an automatic BP device.

Samples Collection

Five milliliters of venous blood samples were collected from the patients and healthy individuals, after fasting period more than eight hours. Samples were allowed to clot at lab temperature, centrifuged at 5000xg for 5 minutes. Sera were collected and stored at -18°C until used.

Methods

Fasting insulin was measured using Sandwich-ELISA kit of Calbiotech[24] company,USA.

Determination of hemoglobin A_{1C} (HbA_{1C}) values by using kits of Stanbiolaboratory company, USA[25, 26]. Colorimetric method was applied for estimating fasting blood glucose using a kit of Spinract, Spain[27]. The lipid profile includedtotal cholesterol TC, triglyceride TG and high density lipoprotein cholesterol HDL- and low density lipoprotein cholesterol LDL-C concentrations were determined using a commercial available kits of Bilbao company, France.

Statistical Analysis

The statistical analysis of the result obtained in the present study was carried out using the 22th edition of the statistical package for the social science (SPSS). The result were expressed in terms of Mean ± Standard Deviation (Mean±S.D.). The analysis of variance (ANOVA) was used to compare the results of the three groups included in the study, as well the subgroups based on gender differences. Comparison between among studied parameters were done using persons correlation test. The result were statistically significant at 5% probability ($p<0.05$).

Result and Discussion

The current study included 150 individuals classified in three groups including: 50 patients suffered from metabolic syndrome (the first group). The second group included 50 pathological control persons, and the last group included the healthy individuals who were selected to participate in the current study as a control group based on the strict criteria established in the questionnaire which prepared by specialist.The current study aims for comparison the changes of insulin resistance values in patients with metabolic syndrome, pathological and healthy control taking into account differences in age, gender, and body mass index (BMI), as well as the relationship between insulin resistance values and other metabolic disorders in metabolic syndrome.

In order to investigate the most age–matched cases of metabolic syndrome in both genders,the study samples were classified based on their gender.

The present study showed the absence of the difference between females and males in healthy and pathological control groups, but there are significant variation($p=0.033$) between male and female in metabolic syndrome group was recorded, as illustrated in**table 1**.The present finding agreed with the study which mentioned to fact thatthe prevalence of the metabolic syndrome rise with age, reaching peak levels in the sixth decade for men and the seventh decade for women[28]. It suggested that the prevalence of the metabolic syndrome for Mexican American men was significantly higher at 40, 50, 60, and 80 years or older. Occurrence of overweight and obesity are key related factors in the development of visceral adiposity, insulin resistance**,** dyslipidemias, high blood pressure, and impaired glucose metabolism. In addition, aging is associated with evolution of insulin resistance, other hormonal alterations, and increases in visceral adipose tissue,[29] all of which are important in the pathogenesis of the metabolic syndrome.

Table 1: The age (year) in study groups according to their gender

Subjects (n)	Gender (n)	Age (Year) Mean ± SD	Min–Max Age (Year)	Age Range (Year)	p-value
Healthy Control 50	Female 24	52.71± 9.594	43-70	27	0.902For1vs2 0.931For 1vs3 0.115For 1vs5 0.679For 2vs4 0.000For 2vs6 0.651For 3vs4 0.086For 3vs5 0.000For 4vs6 0.033For 5vs6
	Male 26	52.3±10.116	38-73	35	
Pathological Control 50	Female 27	52.48±8.107	40-70	30	
	Male 23	51.57±10.693	36-69	33	
MS Patients 50	Female 30	56.73±7.683	44-81	37	
	Male 20	62.50±9.512	38-71	33	

1: healthy female control. 2: healthy male control, 3:female pathologicalcontrol, 4:male pathological control, 5:female metabolic syndrome, and 4:male metabolic syndrome. The mean difference is significant at 0.05 level

Almost of the participants with MS were obese (BMI ≥ 30) as compared to healthy control(BMI ≤25) with a large waist circumferencecharacteristic accumulation of the lipid layer in the abdomen (apple pattern), meaning they were classified as obese individuals.

The outcomes showed significantdifferences (p=0.000) of BMI between both genders (male and female) in the same groups of pathological control and MS, excepting control group (p= 0.960).A statistically significant variation (p<0.05) was observed when both genders in MS group were compared with their peers in the subgroups of healthy and pathological controls, excepting male in pathological control group who did not exhibit significant elevation when compared with their corsponding in healthy control.

Central obesity as a marker of body fat, which canestimated by measuring body mass index (BMI) and waist circumference (WC) that in turn might effectively predict therisk of MS[30, 31].Obesity seems to be predominant underlying risk factor not only for the development of MS but also other cardiovascularrisk factors[32].Results of many studies indicated forincreasing in body weight and BMI associatedwith the elevation of ischemic heart disease in severalpopulations [31, 33, 34], but this finding has not been reported anapproximate 2-fold increase in the 10-year risk of coronaryartery disease in subjects with a BMI of 30 Kg/m^{2}or more compared with those with BMI less than 21 Kg/m^2 after adjustment for age[35]. On the other hand, the results of the prospective cardiovascular study indicated thatBMI did not independently contribute to cardiovascularrisk in multiple logistic regression analysis[36].

Table 2: BMI (Kg/m^2)of the Study Subgroups

Subjects (n)	Gender (n)	BMI (Kg/m^2) Mean ± SD	Min–max BMI(Kg/m^2)	BMI Range (Year)	p-value
Healthy Control 50	Female 24	27.316±2.093	23.833-30.637	6.804	0.960 For1vs2 0.000For 1vs3 0.000For 1vs5 0.114For 2vs4 0.000 For 2vs6 0.000For 3vs4 0.000For 3vs5 0.000For 4vs6 0.000For 5vs6
	Male 26	27.268±2.362	21.847-30.628	8.781	
Pathological Control 50	Female 27	32.775±4.880	25.951-47.000	21.049	
	Male 23	28.771±2.766	25.000-36.198	11.198	
MS Patients 50	Female 30	38.512±3.998	31.500-45.000	13.500	
	Male 20	34.957±2.351	32.000-40.000	8.000	

1: healthy female control. 2: healthy male control, 3:female pathological control, 4:male pathological control, 5:female metabolic syndrome, and 4:male metabolic syndrome. The mean difference is significant at 0.05 level

Results of the present study showed significantly (p<0.05) different when the patients groups compared with the healthy control using ANOVA test.Thestudy created a set of individual observations, included: **(1)**A significant increase in blood sugar levels in MS patients and pathological control subjects comparing with healthy control subjects, while did not show significant differences between MS group and pathological group as shown in **table 3**. **(2)**Fasting insulin level seemed to be significantly elevation (p=0.000) in the samples of MS patients and pathological control comparison to healthy individuals, additionally there were significant variation between MS patients and pathological control, as shown in **table 3**.**(3)**The current study recognize

arise in the level of HbA1c in the samples of study patients compared to their corresponding values in the group of healthy individuals, as well asthere were significant changes between MS patients and pathological control.**(4)**The study reported a significant increasing in the levels of cholesterol and very low density lipoproteins binding cholesterol(vLDL-C) in the sera of MS patients comparison to healthy and pathological control, while no such results were noted when the levels of cholesterol and vLDL-C (p=0.234 and p=0.111; respectively) weretestedin healthy and pathological controls.**(5)Table 3** shows highly significant increase in the levelstriglycerides (TGs), high density lipoprotein binding cholesterol(HDL-C), and low density lipoproteins binding cholesterol(LDL-C) in the sera of patients with metabolic syndrome and pathological control subjects comparison to healthy individuals group**.**

Table 3: Levels (Mean±SD) of Sugar Concentration (mg/dL), Insulin Secretion (mIU/L), HbA1c%, and Lipid Profile in Sera of Study Groups

	Subjects (n)			
Parameters	Healthy Control 50 Mean ± SD Min–Max Range	PathologicalControl 50 Mean ± SD Min–Max Range	Ms Patients 50 Mean ± SD Min–Max Range	p-value
Blood Glucose mg/dL	**107.605±15.593 70.402-129.572 59.170**	**241.582±81.129 89.000-421.015 332.015**	**250.639±81.235 136.415-442.000 305.585**	0.000 For 1vs2 0.000For 1vs3 0.542 For 2vs3
Insulin (mIU/L)	**12.223±6.593 0.068-25.291 25.223**	**28.379±16.824 5.864-75.917 70.053**	**37.935±21.893 6.291-86.436 80.145**	0.000For 1vs2 0.000For 1vs3 0.011For 2vs3
HbA1c%	**4.544±0.647 3.500-5.600 2.100**	**8.742±1.671 4.525-12.000 7.475**	**9.403±1.462 5.900-12.000 6.100**	0.000For 1vs2 0.000For 1vs3 0.032For 2vs3
Cholesterol mg/dL	**184.042±38.448 79.829-266.826 186.997**	**198.392±50.607 120.000-325.157 205.157**	**225.806±42.038 154.581-340.015 185.434**	0.243For 1vs2 0.000For 1vs3 0.002For 2vs3
Triglyceride mg/dL	**143.330±40.237 74.870-215.520 140.650**	**179.919±84.007 60.969-350.541 289.572**	**283.756±90.106 118.920-598.110 479.190**	0.016For 1vs2 0.000For 1vs3 0.000For 2vs3

HDL-C mg/dL	**88.250±22.888 43.910-133.035 89.125**	**53.673±18.585 23.245-88.000 64.755**	**34.3917±7.49752 20.000-62.620 42.620**	0.000For 1vs2 0.000For 1vs3 0.000For 2vs3
LDL-C mg/dL	**71.615±33.189 25.532-126.492 100.960**	**111.065±50.810 22.912-236.526 213.614**	**135.312±44.970 62.547-248.695 186.148**	0.001For 1vs2 0.000For 1vs3 0.008For 2vs3
vLDL-C mg/dL	**28.398±7.799 16.483-43.103 26.620**	**35.395±16.498 12.193-70.108 57.915**	**56.606±18.031 23.784-119.621 95.837**	0.111For 1vs2 0.000For 1vs3 0.000For 2vs3
Systolic blood pressure (mmHg)	**114.130±24.915 110-135 124**	**133.54±19.560 100-183 83**	**153.92±23.839 180-190 172**	0.001For 1vs2 0.000For 1vs3 0.000For 2vs3
Diastolic blood pressure (mmHg)	**76.87±5.057 65-85 20**	**81.92±11.911 68-112 44**	**92.70±13.815 12-110 98**	0.119For 1vs2 0.000For 1vs3 0.000For 2vs3

1: healthy female control. 2: healthy male control, 3:female pathological control, 4:male pathological control, 5:female metabolic syndrome, and 4:male metabolic syndrome. The mean difference is significant at 0.05 level

Metabolic syndrome is characterized by a low HDL in association with an elevated triglyceride concentration. This is believed to be a result of anincreased triglyceride load in the HDL particle that is acted on by hepatic lipase, which hydrolyzes the triglyceride. The loss of the triglyceride results in a small HDL particle that is filtered by the kidney, resulting in adecrease in apolipoprotein (Apo) A and HDL concentrations. Apart from an increase in the loss of apoA, there are data demonstrating that insulin may promote apoA gene transcription[37]. Therefore, insulin resistance states may be associated with diminished apoA biosynthesis[38].

Table 4:Comparison The Levels of HOMA-IR and FIGR Among The Study Groups

	Subjects (n)			
Parameters	**Healthy Control 50 Mean ± SD Min–Max Range**	**Pathological Control 50 Mean ± SD Min–Max Range**	**Ms Patients 50 Mean ± SD Min–Max Range**	**p-value**

HOMA- IR	**3.009±1.566** **0.76-7.78** **7.02**	**16.978±12.398** **2.580-50.56** **47.98**	**23.154±17.616** **2.900-67.363** **64.463**	**0.000 For 1vs2** **0.000For 1vs3** **0.014For 2vs3**
Insulin /Glucose Ratio	**0.114±0.061** **0.033-0.26** **0.227**	**0.131±0.0792** **0.015-0.344** **0.329**	**0.158±0.106** **0.034-0.518** **0.484**	**0.298For 1vs2** **0.009For 1vs3** **0.110For 2vs3**

1: healthy control, 2:pathologicalcontrol, 3:metabolic syndrome. The mean difference is significant at 0.05 level

The insulin resistance level was represented by the HOMA-IR andfasting insulin/glucose ratio(FIGR). The HOMA-IR values in the metabolic syndrome, pathological control,and healthy control groups were 23.154±17.616, 16.978±12.398,and 3.009±1.566; respectively. Independent ANOVA test results showed that IR in the MSgroup was higher than those in pathological control and healthycontrol group, and the differences were statistically significant($p<0.05$) demonstrated in **table 4.**

Outcomes of the current parameter showed there weren't significant differences ($p>0.05$) between the two genders in the same group when HOMA IRwere tested in the six study subgroups, as demonstrated in **table 5**, on the other side; significant increases ($p=0.000$) were recorded when two genders of patients (male and female)were comparedto their matching genders in the healthy group. Additionally significant variations ($p< 0.05$) were observed when the individuals with same genders (healthy male with pathological control male, and healthy female with pathological control female) in the two groups compared together.Levels of HOMA IR of men in the MS group were not statistically different ($p=0.269$) from those in the pathological control group, while levels of HOMAIR were seemed to be statistically high ($p=0.018$)in the MS female comparison to female in pathological control group, as shown **table 5**.Insulin is the central regulator of glucose and lipid homeostasis,it decreased blood glucose concentrations by reducing hepatic gluconeogenesis and glycogenolysisand by enhancing glucose uptake into striated muscles and adipocytes, also,it enhances triglyceridesynthesis in liver and adipose tissues,additionally increases the breakdown of circulating lipoproteins by stimulating lipoprotein lipase activity in adipose tissues, and suppresses lipolysis both in adipose tissues and in muscles[39, 40].

The insulin resistance occurs when adipose, muscle, and liver cells do not response appropriately to insulin, and circulating glucose levels remain high, which leads to pathology and deregulation of feedback mechanism.Insulin resistance is a powerful predicator of T2DM and the hyper-insulinemia is a compensate marker for insulin resistance[41].Insulin resistance is recognized as a component of several Common disorders such as the metabolic syndrome, hypertension, hyperlipidemia, coronary artery disease and the polycystic ovary syndrome[42]. Metabolic syndrome establish on the basis of resistance to the metabolic actions of insulin. Thus, hyperinsulinemia, glucose intolerance, type 2 diabetes, hypertriglyceridemia, and low HDL concentrations could be accounted for by resistance to the actions of insulin on carbohydrate and lipid metabolism[43].

Table 5:HOMA-IR Levels in The Different Study Subgroups

Subjects	Gender (n)	HOMA-IR Mean ± SD	Min–Max HOMA-IR	Range HOMA-IR	p-value
Healthy Control 50	**Female 24**	**2.693±1.397**	**0.758-5.711**	**4.953**	**0.864For 1vs2** **0.001For 1vs3**
	Male 26	**3.300±1.681**	**0.896-7.780**	**6.884**	**0.000For 1vs5** **0.000For 2vs4**

Pathological Control 50	Female 27	14.853±10.662	2.580-49.404	46.824	0.000 For 2vs6 0.196For 3vs4 0.018For 3vs5 0.269For 4vs6 0.794For 5vs6
	Male 23	19.472±13.998	3.640-50.560	46.920	
MS Patients 50	Female 30	22.777±18.947	2.900-67.363	64.463	
	Male 20	23.720±15.869	5.500-60.900	55.400	

1: healthy female control. 2: healthy male control, 3:female pathological control, 4:male pathological control, 5:female metabolic syndrome, and 4:male metabolic syndrome. The mean difference is significant at 0.05 level

Fasting insulin: glucose ratio(FIGR) levels were observed to be non-significant higher ($p< 0.05$) in patient and pathological control groups than in those in healthy subjects group, as demonstrated in table 4. When the participate individuals in the present study were comparing based on their genders, ANOVA test results showed there are no significantvariation among study subgroups when the FIGR were compared whether in the same group (male with female in the same group) or between same gender subgroups, as illustrates in **table 6.**

Table 6:Levels of FIGR in the Various Study Groups

Subjects	Gender (n)	FIGR Mean ± SD	Min–Max	Range	p-value
Healthy Control 50	Female 24	0.103± 0.553	0.029-0.194	0.165	0.380For 1vs2 0.387For 1vs3 0.054For 1vs5 0.485For 2vs4 0.045For 2vs6 0.468For 3vs4 0.277For 3vs5 0.193For 4vs6 0.274For 5vs6
	Male 26	0.124±0.066	0.030-0.260	0.230	
Pathological Control 50	Female 27	0.123±0.070	0.03-0.31	0.278	
	Male 23	0.141±0.086	0.020-0.344	0.329	
MS Patients 50	Female 30	0.148±0.996	0.034-0.420	0.386	
	Male 20	0.175±0.115	0.050-0.520	0.470	

1: healthy female control. 2: healthy male control, 3:female pathological control, 4:male pathological control, 5:female metabolic syndrome, and 4:male metabolic syndrome. The mean difference is significant at 0.05 level

One of the observations recorded in present study was the significant increase of HOMA IR in patients with Metabolicsyndrome when compared to the healthy and pathological control groups, this indicates the pathogenic effect of insulin resistance, especially when all the combined strains of the syndrome are combined in one person. In addition, it was observed that HOMA IR was more accurate and acceptable than FIGR to measure the sensitivity of insulin, as the FIGR did not produce significant and acceptable results when comparing study groups, present finding agreed with the study which revealed to fact that HOMA is more appropriate for large epidemiologic studies and is more reliable than FGIR as a measure of insulin resistance among children and adolescents. The use of HOMA is simpler, cheaper, less labor-intensive, less time-consuming, and more acceptable to young people than clamp studies[44].

Conclusion

The metabolic syndrome (visceral obesity, dyslipidemia, hyperglycemia, and hypertension), has become one of the major public- health challenges worldwide[45]. The current study revealed there were significant combined between symptoms of metabolic syndrome,as well as that insulin resistance is the central component of this syndrome and have pathogenic effect on the other components such as hyperlipidemia, hypertension, hyperglycemia and obesity.

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Kinetics and mechanistic study of oxidation of alanine by cerium (IV) using Mn^{+2} as catalyst.

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Abstract

Metal ion Mn^{+2} as homogeneous catalyst has been used in the oxidation of alanine in acid medium. The reaction shows first order kinetics with respect to Ce(IV), the reactions also showedfraction order kinetics with respect to Mn^{+2} and alanine and inverse first order with respect to $[H^+]$. The reaction product (Cerium(III) Sulphate ($Ce_2(SO4)_3$) was added to the reactions and had no effect on the rate of oxidation of alanine by Ce(IV). Changing ionic strength, dielectric constant and chloride ion of the medium has no effect on the rate of oxidation. Ce^{+2} and Mn^{+2}have been suggested to be the reactive species. A reaction mechanism was suggested and rate law had been derived . Aldehyde have been identified to be the oxidation products of the reaction

Introduction:

The studies of the amino acids by various oxidants[1-5]both in acidic and alkaline media have been reported. Many reagents have been investigated towards oxidative decarboxylation of α-amino acids, which give nitrile[6-7]or a mixture of nitrile and aldehyde[8-11]as the products depending on the reaction conditions and reagents employed. Beside aldehyde and nitriles, α-keto-acids are also reported to be formed asoxidationproduct[12].The kinetic and mechanistic features of a particular oxidation reaction of amino-acids are likely to be affected by the polar and nonpolar nature of the side chain of amino acid in solution and the active species of the oxidant[13-14]. Amino acids are very attractive natural ligands for both toxic and essential metal ions. Besides acting simply as effective chelators[15-16], in many cases they are also reducing agents; e.g. for metal ions such as Ce(IV), V(V),Co(III) and Fe(III).

Gowda and co-workers have studied the oxidation of amino acids by varioushalogen oxidants viz. chloramineT[17-18], its dimer dichloramines[19]andbromamine T[20]. The oxidation product is aldehyde via hydrolysis of imine intermediate. However, Vivekanandam et al.[21]showed for the oxidation of imine by another molecule of chloramineT to nitrile.Cerium has a property, unique among the lanthanides, which explain its ability to participate in one electron transfer reactions, its ability to exist in two stable adjacent oxidation states +3 and +4[22-23]. Ce(IV) is well known oxidant in acid media having the reduction potential of the couple Ce(IV)/Ce(III) 1.70 V[24-25]. Cerium(IV) is one of the most important one equivalent oxidant in acid medium which has been used in numerous kinetic, mechanistic and analytic studies, the basic advantage of cerium(IV) over other oxidants is its reduction to a single substance cerium(III)[22]. The cerium(IV) species in perchloric acid[26-27]medium and sulphuric acid medium[28]have been established and equilibrium constants calculated. This work study the kinetics of the reaction and finding the order of the reaction and rate constants and suggesting reaction mechanism.

Experimental work

Hana digital pH meter**,** was used for the determination of pH of the reaction mixtures with the maximum uncertainity in pH of ± 0.01 unit. PyeUnicamUV spectrophotometerwas used for spectrophotometric measurements. Spectrophotometer can be used to determine kinetics and the rate constant of a chemical reaction. The rate constant of a particular reaction can be determined by measuring visible absorbance at specific time intervals. Since the rate of reaction is directly proportional to the concentration of the cerium(IV), it was necessary to find out the range of concentration of cerium(IV) in sulphuric acid in the presence of amino acid over which Beer's law

was applicable. The spectrophotometeric study of the solution containing all the reagents with Ce(IV) in sulphuric acid medium showed that the reaction can be monitored spectrophotometrically by measuring the absorbance of cerium(IV) at 390 nm where cerium(IV) has considerable absorbance and other ions have no contribution towards absorbance. At this wavelength absorbance values were obtained for different concentration of cerium(IV) solution with other reagent between the concentration range 5×10-5 to 5×10-4 mol dm-3.

Thermostat, Water bath (Macro Scientific) temperature range 30◦C -110◦C was used. All kinetic studies were done using thermostated at temperature varying from 350°C to 50°C.
Electronic Balance**,**Shimadzu electronic Balance, A × 200 was used for weighing works. The least count of balance is 0.0001 mg.

All other reagents were either of Anala R or guaranteed reagent grade and used as supplied. Doubly distilled water, second distillation being from alkaline potassium permanganate solution in all glass assembly, was employed in all the preparations and kinetic studies.

Kinetic Measurements

Appropriate quantities of the solution were placed in separate glass vessels and kept for at least 15 minutes in a thermo stated water bath at 35◦C. The calculated amounts of each reactant were then added together in a particular glass vessel followed by the requisite amount of double distilled water. The reaction mixture was then placed in a thermostatted water bath maintained at constant temperature of 35◦C (±5%) and the reaction was initiated by adding the requisite amount of oxidant solution placed separately in the same water bath. The reaction was followed by measuring the absorption of cerium(IV) at 390 nm with time in a 1 cm cell placed in the Pye All kinetic measurements were performed under pseudo first order conditions with alanine concentration in excess over cerium(IV) at a constant ionic strength of 1.50 mol dm-3. The pseudo first order rate constants (kobs) were obtained from the slope of the plots of log absorbance versus time. The observed rate constants were reproducible within the experimental error ±5%. The cerium(IV) solution was thermally stable in the visible region and undergoes photochemical decomposition only in the UV region.

Stoichiometry and Product Analysis

Different reaction mixtures with different sets of concentration of reactants, where [Ce(IV)] was in excess over [alanine] at constant ionic strength, acidity and at constant concentration of catalyst were kept for 24 hours at 308 K. After completion of the reaction, the remaining Ce(IV) was estimated in different sets of the experiment. The results indicated that two moles of Ce(IV) were consumed by one mole of alanine since,
The oxidation products were identified as Ce(III), 2-hydroxyethanal, ammonia and carbon dioxide. The reaction mixture was treated with acidified 2,4−dinitrophenyl hydrazine solution, which yielded a hydrazine.

Results and Discussion

Effect of Cerium (IV).Ceric (IV) Ammonium Sulphate [(NH4)4Ce (SO4)4.2H2O]

The concentration of Cerium (IV) was varied from $5.0 \times 10^{-5}$to 5.0×10^{-4}mol dm^{-3}at fixed concentration of [Ala] $=5\times10^{-3}$mol dm^{-3}, [H+] =1.0 mol dm^{-3}, I=1.5mol dm-3and [Mn(II)]=$5x10^{-5}$mol dm^{-3} at 35°C. The pseudo first order rate constant (kobs) are independent of the initial concentration of Cerium(IV) (Table1).

Effect of Alanine

The concentration of alanine was varied from 0.003-0.009mol dm^{-3} at fixed concentration of Cerium (IV) =5.0×10^{-4}mol dm^{-3} [H+] =1.0 mol dm^{-3}, I=1.5 mol dm^{-3},and [Mn (II)]= 5×10^{-5}mol dm^{-3}.Pseudo first order constant (kobs) increases with the increase of concentration of alanine (Table-2. and figures 1-4) The reaction order of alanine is 0.5 obtained from the linear regression of log kobs versus log [Ala], indicating fractional order with respect to alanine (figure 5).

Effect of Mn (II). Manganese Sulphate (MnSO4)

Manganese (II) concentration was varied from 2.0×10^{-5} to 2.0×4 mol dm^{-3}at constant concentration of Ce (IV)= 5.0×10^{-4}mol dm^{-3}[Ala] =5×10^{-3}moldm^{-3},(H+) =1.0 mol dm^{-3}, I =1.5mol dm^{-3} (Table 3and figure 6).

Effect of Hydrogen ion

Hydrogen ion concentration was varied from 0.2 to1.0 mol dm-3 at fixed [HSO4-] {[HSO4-]=1.0 mol dm-3 from H2SO4 and NaHSO4}, [Ala], [Mn(II)],[H+] was calculated ignoring the dissociation of [HSO4-] and assuming [H+]=[H2SO4] the rate constant decrease with increase of [H+] (Table 4, Figure 7).

Effect of [HSO4-]

The concentration of bisulphate (HSO4-) ion was varied in the range of 0.2 to1.0 mol dm-3 at fixed [H+] {[H+] =0.2 moldm-3][(Ce(IV)], [Ala], [Mn(II)], at 35^{o}C. Here [HSO4-] = [NaHSO4+H2SO4] ignoring the dissociation of [HSO4-] in strongly acidic medium. The rate shows a rate retarding effect.

Effect of ionic strength

At fixed [Ce (IV)], [Ala], [H2SO4], [Mn (II)] and temperature the ionic strength (μ) was varied 1.2-2.0 mol dm-3, employing Sodium perchlorate for adjusting ionic strength. The rate of reaction increases slightly with increasing ionic strength.

Effect of added product.(Cerium(III) Sulphate (Ce2(SO4)3)

The effect of Cerium (III) on the rate was alsostudied and was found to be independent of Cerium (III) concentration, ruling out any possibility of the rate limiting step preceded by the reversible equilibrium involving Cerium (III).

Test for free radicalsIn the reaction mixture, acrylonitrile solution was added in an inert atmosphere for 4 hour. Then dilution with methanol, a white precipitate resulted suggesting the participation of free radicals in the reaction.

Discussion

Under the kinetic conditions in presence of catalyst, excess of alanine over Cerium (IV) constant ionic strength and acidity in a thermostated water bath at 35^{o}C for 24 hour. The products were extracted from the reaction mixture with ether. An addition of 2, 4- dinitrophenylhydrazine in the reaction mixture yield brown precipitate of hydrazone derivative of aldehyde[29].

The kinetic results, 1/kobs versus1/[Ala] fits well with the MichaelisMenen model (Figure 8), suggesting that1:1 type complex of (Ala) and Mn(II) is formed in the first pre-equilibrium step. Alanine is protonized in acid media, indicating involvement of H+ is the reaction in the pre-equilibrium step. To explain the first order dependence on Ce(IV), it is assumed that the complex is oxidized by cerium(IV) is a slow step to produce Mn(II) substrate complex which collapses in a fast step to produce catalyst and free radical, which is responsible for product [30]. The condition employed in the present investigation appears to be $Ce(SO4)_2$ as the reactive species of Cerium (IV).

Scheme 1 shows the suggested mechanism and the derived rate law was suggested.
The uncatalysed cerium(IV) oxidation of alanine is very slow in sulphuric acid under the present experimental conditions. However, the reaction is appreciably faster in the presence of a minute quantity (10^{-5}mol dm-3) of manganese(II) in sulphuric acid . In the presence of perchloric acid, manganese(II) catalysis is much less efficient, possibly due to presence of active cerium(IV) species, $Ce(OH)^{3+}$ in such media. Hence, the present study was undertaken in sulphuric acid medium. The reaction is first order with respect to cerium(IV) and manganese(II) concentrations, and the order with respect to alanine was first order. The effect of hydrogen ions on the rate was studied by adding sulphuric acid and it was found that as the sulphuric acid concentration increased in the reaction mixture, the rate of reaction decreased. This is due to formation[31]of an active inhibitor $H_2Ce(SO4)_2^{2-}$. The order with H+ ion concentration was less than unity and negative. As the sulphuric acid concentration increases, the H+ concentration increases, but there is also a corresponding increase in HSO4− ion concentration. Since the rate is inversely dependent on the HSO4− concentration, the overall effect of adding sulphuric acid would be to lower the rate.

$Ce^{+4}.\ H^+ \leftrightarrow Ce^{+4} + H^+$

Mn^{+2} + alanine ↔ complex

$$\text{Complex} + Ce^{+4} \rightarrow \text{alanine}^{*}(CH_3C^{*}\text{-}COO^{-}) + Mn^{+2} + H^+ + Ce(III) \quad \text{R.D.S}$$
$$\downarrow$$
$$NH_3^+$$

$$\text{alanine}^{*}(CH_3C^{*}\text{-}COO^{-}) + Ce(IV) \rightarrow Ce(III) + RCHO + H^+ + NH_3^+$$
$$\downarrow$$
$$NH_3^+$$

Scheme 1

$$\text{Rate} = k_5\,[\text{Complex}][Ce^{+4}] \quad \rightarrow 1$$

$$-d[\text{complex}]/dt = k_3[\text{alanine}][Mn^{+2}] - k_4[\text{complex}] - k_5[\text{complex}][Ce^{+4}] = 0 \quad \rightarrow 2$$

$$[\text{complex}] = k_3[\text{alanine}][Mn^{+2}]/(k_4 + k_5[Ce^{+4}] \quad \rightarrow 3$$

$$K = [Ce^{+4}][\ H^+]/[Ce^{+4}.\ H^+] \quad \rightarrow 4$$

$$\text{Rate} = Kk_5k_3[\text{alanine}][Mn^{+2}]^+][Ce^{+4}.\ H^+]/(k_4 + k_5[Ce^{+4}])[H^+] \quad \rightarrow 5$$

Table 1: The effect of variation of Ce(IV) concentration on the rate constants [alanine]=0.005M, $[H^+]$=1M, I=1.5M, and $[Mn^{+2}]=2\times10^{-5}$M. temp.=35°C

k/min^{-1}	0.168	0.173	0.159
10^4[Ce(IV)]/M	0.5	1.0	5.0

Table 2: The effect of variation of alanine concentration on the rate constants [Ce(IV)]=0.0005M, $[H^+]$=1M, I=1.5M, and $[Mn^{+2}]=2\times10^{-5}$M. temp.=35°C

k/min^{-1}	0.148	0.168	0.194	0.267
10^3[alanine]/M	3.0	5.0	7.0	9.0

Table 3: The effect of variation of Mn^{+2} concentration on the rate constants
[Ce(IV)]=0.0005M, $[H^+]$=1M, I=1.5M, and [alanine]=0.005M. temp.=35^oC

k/min^{-1}	0.168	0.181	0.199	0.29
$10^4[Mn^{+2}]/M$	0.2	0.9	2.0	5.0

Table 4: The effect of variation of H^+ concentration on the rate constants
[Ce(IV)]=0.0005M, $[Mn^{+2}]=2x10^{-5}$ M, I=1.5M, and [alanine]=0.005M. temp.=35^oC

k/min^{-1}	0.168	0.111	0.097	0.074
$[H^+]/M$	1.0	1.3	1.5	2.0

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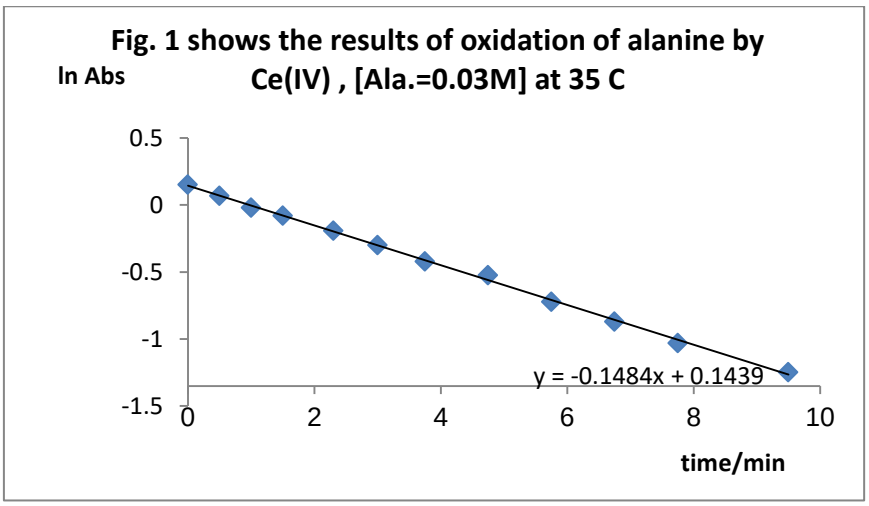


Fig. 1 shows the results of oxidation of alanine by Ce(IV) , [Ala.=0.03M] at 35 C
ln Abs
0.5
0
-0.5
-1
-1.5
0
2
4
6
8
10
y = -0.1484x + 0.1439
time/min

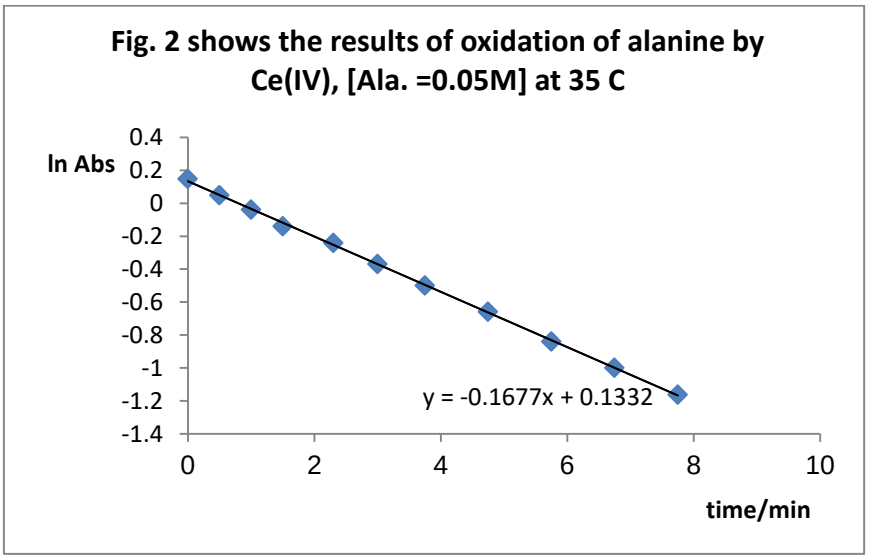


Fig. 2 shows the results of oxidation of alanine by Ce(IV), [Ala. =0.05M] at 35 C
ln Abs
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1
-1.2
-1.4
0
2
4
6
8
10
y = -0.1677x + 0.1332
time/min

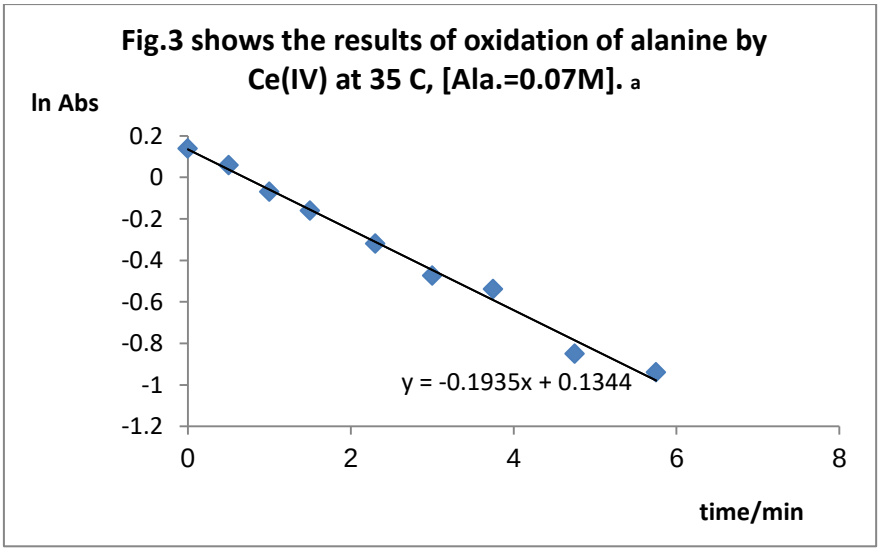


Fig.3 shows the results of oxidation of alanine by Ce(IV) at 35 C, [Ala.=0.07M]. a
ln Abs
0.2
0
-0.2
-0.4
-0.6
-0.8
-1
-1.2
0
2
4
6
8
y = -0.1935x + 0.1344
time/min

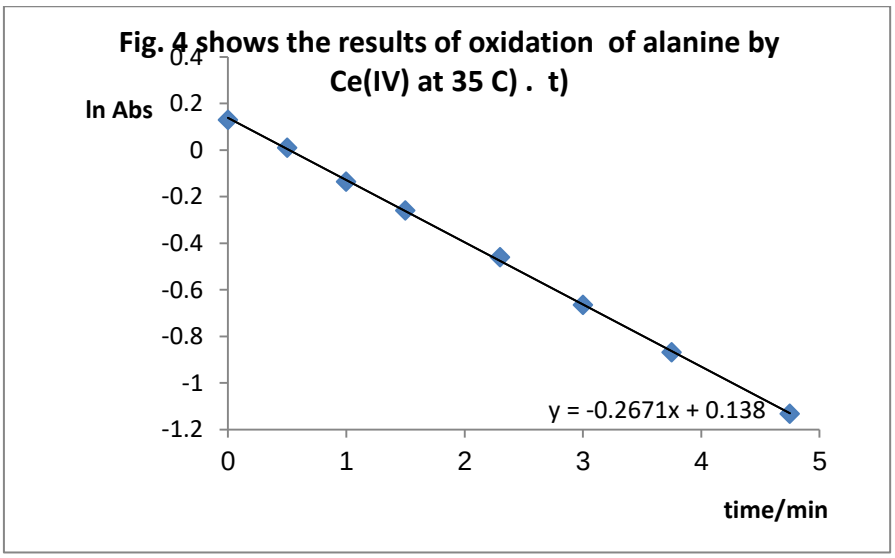


Fig. 4 shows the results of oxidation of alanine by Ce(IV) at 35 C) . t)
ln Abs
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1
-1.2
y = -0.2671x + 0.138
0
1
2
3
4
5
time/min

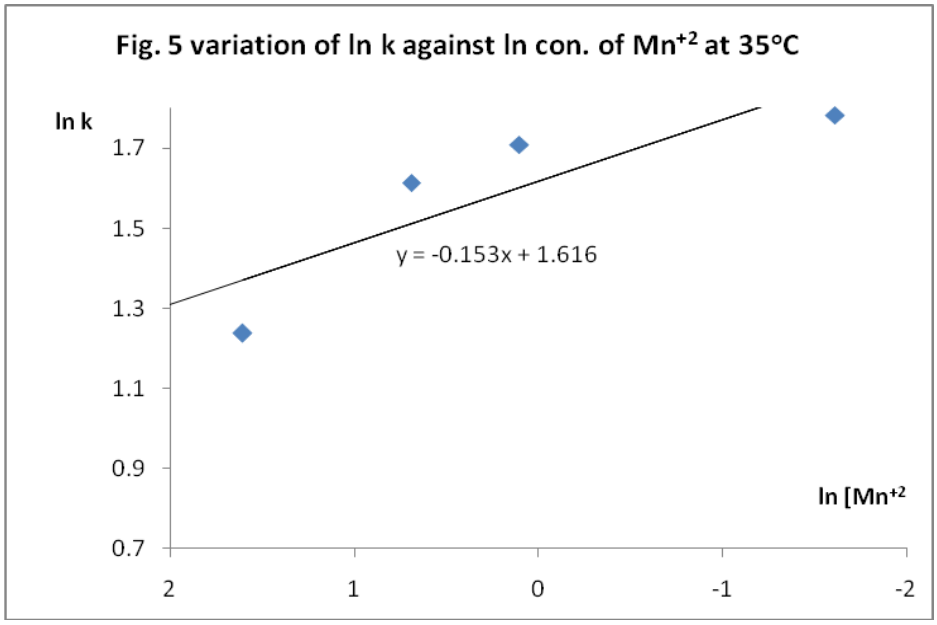


Fig. 5 variation of ln k against ln con. of Mn+2 at 35°C
ln k
1.7
1.5
1.3
1.1
0.9
0.7
y = -0.153x + 1.616
ln [Mn+2
2
1
0
-1
-2

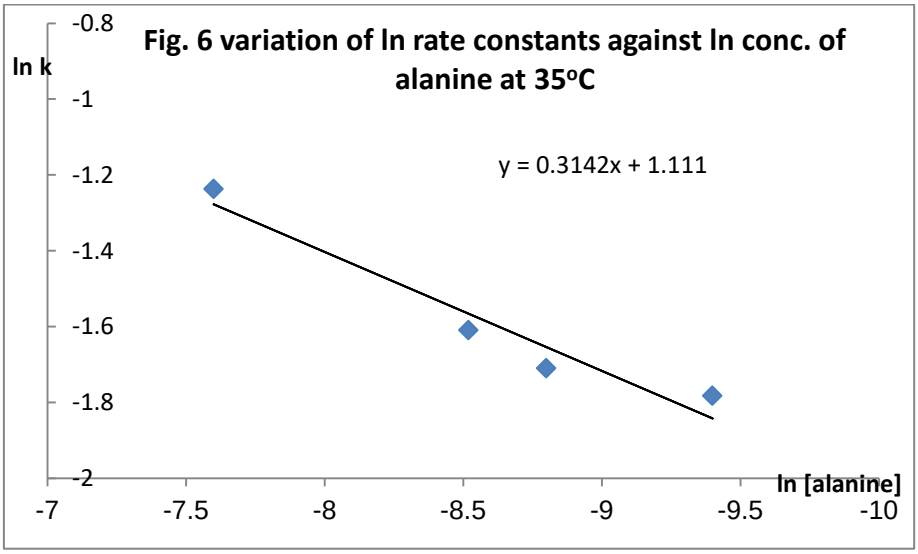
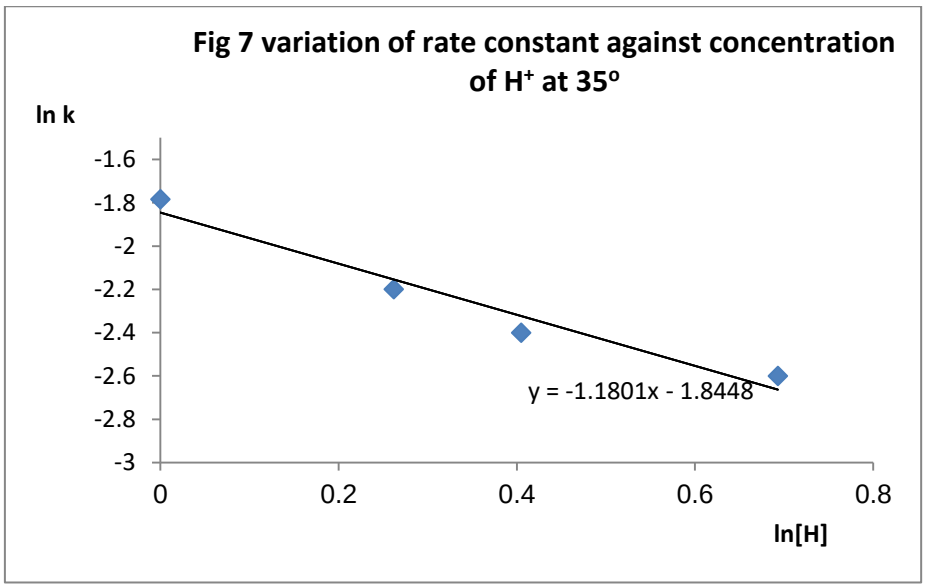
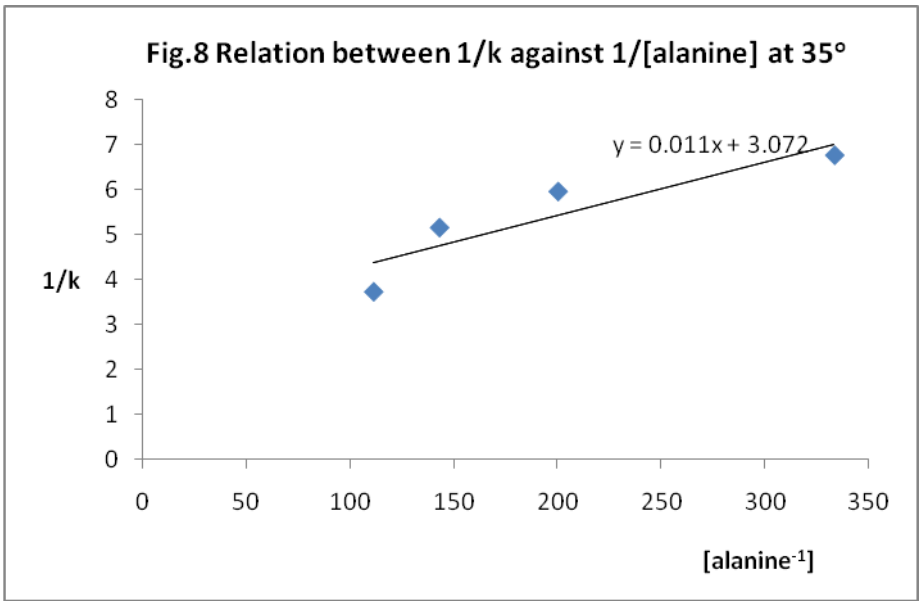


Fig. 6 variation of ln rate constants against ln conc. of alanine at 35°C
ln k
-0.8
-1
-1.2
-1.4
-1.6
-1.8
-2
y = 0.3142x + 1.111
ln [alanine]
-7
-7.5
-8
-8.5
-9
-9.5
-10





الخلاصة:-

تم استخدام ايون Mn^{+2}كعامل مساعد في عملية اكسدة الالنيين في الوسط الحامضي, اظهر التفاعل من الدرجة الاولى في Ce(IV)كما اظهر التفاعل من الدرجة الكسرية في كل من ايون المنغنيز والالنيين ومن المرتبة الاولى السالبة في ايون الهيروجين. كما تم اضافة ناتج التفاعل (Cerium(III) Sulphate $(Ce_2(SO4)_3)$ الى التفاعل ولم يلاحظ اي تاثير على سرعة التفاعل. كما درس تاثير كل من القوة الايونية وثابت عزل الوسط وايون الكلوريد على وسط التفاعل ولم يلاحظ اي تاثير على سرعة التفاعل . تم اقتراح ميكانيكية للتفاعل وتم اشتقاق قانون سرعة للتفاعل و كما تم تشخيص ناتج التفاعل وكان مركب الدهايدي

Preparation , Spectral Characterization and anti Corrosion Property of new azo- azomethine ligand and its Chelate complexes for Carbon Steel in Acid Solution

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Abstract :

Anew azo–Schiff base ligand(4-((E)-(3-iodophenyl)diazenyl)-2-((3-(trifluromethyl) phenyl imino)methyl) phenol (IFPMP) was prepaered by condensation of ((E)2-hydroxy-5-((3-iodophenyl) diazenyl) benzaldehyde with 3- (trifluromethyl)aniline .This azo-azomethine ligand was reacted with some transition metal ions such as Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) forming seven chelate complexes . The structural features have been arrived from their C.H.N elemental analysis ,FT-IR , UV-Vis , ^{1}HNMR , Mass spectra, magnetic moment measurement and molar conductance. The data show that complexes have the composition of $[M(L)_2(H_2O)_2]$ for all chelate complexes except of Cr(III) and Fe(III) which were found that the composition as $[M(L)_2Cl(H_2O)]$ .Based on this data we propose octahedral geometry for all metal complexes. The influence of the prepared new ligand and its chelate complex on the corrosion inhibition of carbon steel in (0.5M) HCl solution was studied by weight loss. Results show that maximum inhibition efficiency of 47.8% is afforded by the studied concentration of the ligand (4ppm) at 298K , while the maximum inhibition efficiency of its ligand complex is 29.5% by (20ppm) at 298K from weight loss method measurements.

Key words: Corrosion protection, Azo-Schiff base ligand, Metal chelate complexes,Acid corrosion , Carbon steel

1.Introduction :

Azo dyes are an interesting class of organic compounds that have found wide application, such as food colorant, pharmaceutical precursor , paints and polymers[1,2].About 50% of the dyes produced in the world are derived from azo compounds. The main characteristic of there dyes is the presence of the azo group (−N=N−), which allows larger extension of π-electronic conjugation and, therefore, intense absorption of light in the visible region of the electromagnetic spectrum. Schiff base ligands are able to coordinate with many different metals and large number of there complexes have been used in catalytic reactions [3] and as models for biological systems[4]. The protection of C-steel in aqueous solutions is universal request, economic, environmental, and aesthetical important[5]. The organic assembled was commonly utilized as corrosion inhibitors as it contains heteroatom such as O, N, P, S, and heavy metals. But the organic compounds are hazards and unfriendly environment inhibitors [6-8].

2. Experimental

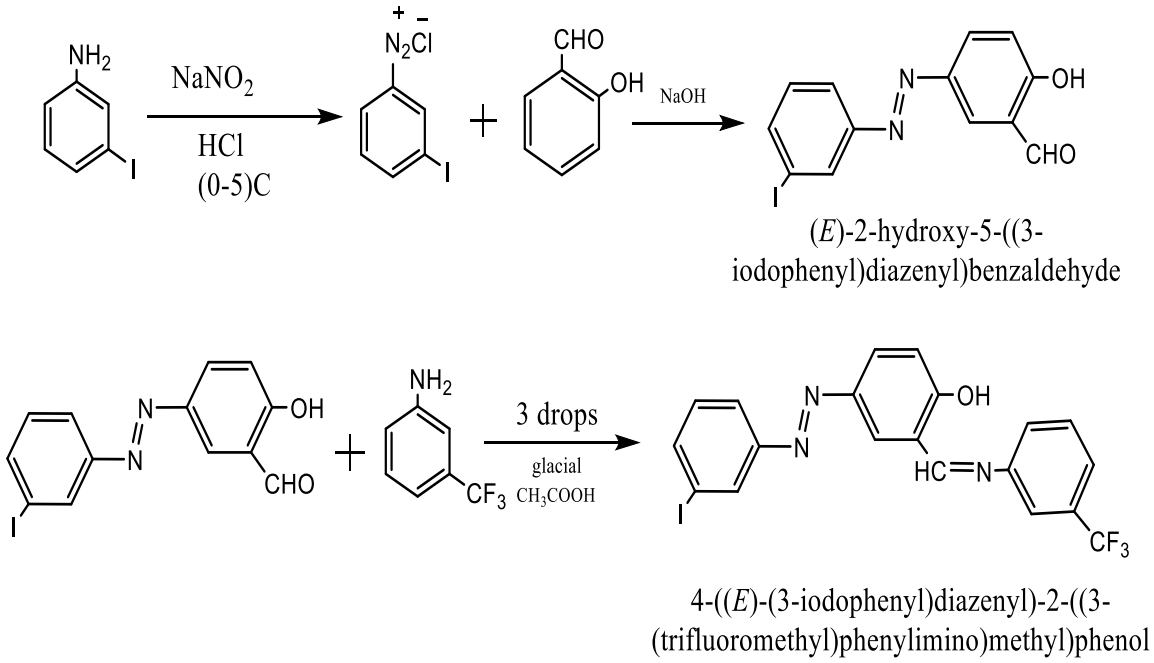
2.1. Materials and measurements

All chemicals are of highest purity and used as supplied by the manufactures . Melting points was determined by open capillary tube method and are uncorrected by using a Stuart melting point SMP10. Elemental analyses (C.H.N) were carried out using Euro vector, EA 2000 A elemental analyzer. The metal contents of chelate complexes were measured using atomic absorption technique by Shimadzu AA-6300. Mass spectrum of organic ligand was obtained using Gc-Mass Qp 2010 (Shimadzu Instruments), but mass spectrum of Ni(II) complex was obtained by using, Agilent technologies (5975 C) Mass spectrophoto-meter at (70eV). The ^{1}HNMR spectrum of azo ligand was recorded on Bruker 500 MHz spectrophotometer in DMSO-d6 using (TMS) as internal reference. IR spectra were recorded on a Shimadzu 8000S FT-IR spectrophotometer in the (4000-400) cm^{-1} range using KBr discs. Electronic spectra were obtained on a Shimadzu 1700 UV spectrometer using ethanol as solvent in the (1100-200) nm range. Magnetic susceptibilities were determined by faraday method at room temperature using Sherwood scientific Balance apparatus, and diamagnetic corrections for the ligand were calculated using Pascal's constant[17].Molar conductance of the metal chelate complexes were determined in DMSO using conductivity meter Alpha-800 at 25°C

2.2. Synthesis of azo-Schiff dye(IFPMP)

Organic ligand was prepared according to the following general procedure (Scheme 1). 3- iodo aniline (2.19g, 10 mmol) was dissolved in 30 mL of water and 3.0 mL of concentrated hydrochloric acid. This solution was diazotized below 5°C with 10 ml of aqueous (0.7g, 0.01 mol) sodium nitrite which added dropewise and the reaction mixture is tested from time to time with starch-iodide paper until nitrous acid persists in the solution during a 10 min interval. The resulting diazonium chloride, solution was mixed with salcyaldehyde (1.22g, 10 mmol) dissolved in 150 mL alkaline ethanol cooled below 5°C. After leaving in the refrigerator for 10hrs, the mixture was acidified with (0.1 $molL^{-1}$) hydrochloric acid until (pH ~ 7). The precipitate was filtered off, air dried and twice recrystallized from hot ethanol, then dried in the oven at 50°C for several hrs.

The pure solid azo compound (E)- 2-hydroxy-5-((3-iodophenyl)diazenyl)benzaldehyde (3.52g,0.01mol)dissolved in 50 mL absolute ethanol was mixed with 30 mL solution of (1.61g,0.01mol) from 3-(trifluromethyl)aniline .The mixture was reflexed 10 hrs after added few drops of glacial acetic acid .Solid precipitate was filtered, air dried and was recrystallized from hot ethanol and dried in electronic oven at 50℃ for 1hr.



Scheme .1. preparation of azo Schiff base ligand (IFPMP)

2.3. Synthesis of complexes

The chelate complexes have been obtained by adding (0.495 g, 0.001mol) of ligand dissolved in ethanol 30 mL to 20mL of ethanolic solution of ($CrCl_3.H_2O$, $MnCl_2.4H_2O$, $FeCl_3$, $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CuCl_2.2H_2O$ and $ZnCl_2$ metal salts (1:2) (metal:ligand) mole ratio. The reaction mixture was refluxed for one hour, then concentrated until the solid compounds precipitated. They were filtered off, washed with ethanol 5 mL to remove the remaining un reacted substances, and dried in the electric oven at 100 ℃ for 6hrs.

2.4. Corrosion

The corrosion rate of steel sample in 0.5 M HCl was determined by weight loss technique, the mild steel was of composition given as :C= 0.17, Si= 0.3, Mn= 1.4, S=0.045, P= 0.045, N=0.009 ,Fe to 100 (by weight). Before the measurement the samples were mechanicaly polished with a series of emery papers with different grades(600,800,1000) to obtain a smooth surface, then washing with distilled water and dried .Weight loss measurements were carried out by weighing the mild steel specimens before and after immersion in 500 mL acid solution for different time intervals in the presence and absence of various concentrations of ligand (IFPMP) and Cu(II) complex. Experiments were also performed at room temperature in HCl solutions.

The rate corrosion (C.R), the inhibition efficiency (IE%) and the surface coverage(θ) , that represents the weight of metal surface covered by inhibitor molecules ,was calculated using the following equations[9]:

$\Delta W = W_o - W_{corr.}$ …… (1)

$CR(mpy) = (K \Delta W) / (D A T)$ …….. (2)

$(IE\%) = (W_o - W_{corr.} / W_o) \times 100$ ……. (3)

$\Theta = W_o - W_{corr.} / W_o$ …….. (4)

2.5. Inhibitors

All the chemical used are analytical grade. Distilled water was used in all preparation. Organic ligand (IFPMP) and its complex of Cu(II) as corrosion inhibitors in 0.5M HCl medium was prepared in ethanol. All tested solutions containing 15mL present of ethanol to maintain complete soluble.

3. Results and Discussion

3.1. Characterization of ligand and its complexes

The azo-azomethine ligand (IFPMP) was deep red crystal, but the prepared complexes of this ligand vary in color from red to brown. The solid complexes are stable at room temperature and soluble in acetone, DMF and DMSO, but insoluble in water. The elemental analyses and metal contents data were surmised in Table.1, for the ligand and complexes are in a good agreement with the suggested formula.

The elemental analyses of the metal complexes indicate that the (M : L) ratios were (1:2) and the chemical formula was $[M(IFPMP)_2(H_2O)_2]$,when[M=Mn(II), Co(II), Ni(II) and Zn(II)] or $[M(IFPMP)_2 (H_2O)Cl]$ when [M=Cr(III) and Fe(III)],chelate complexes, while Cu(II) complex unique $[CuL_2].2H_2O$. All prepared compounds were quiet air stable, insoluble in distilled water but soluble in common organic solvents such as methanol, ethanol, acetone, chloroform, and pyridine giving stable solutions at room temperature.

Table .1: Some physical and analytical data of azo Schiff ligand and its complexes

No.	*Formula*	*M:L*	*Color*	*M.P°C*	*Yield%*	*C % (cal.)*	*H % (cal.)*	*N % (cal.)*	*M % (cal.)*
1	$C_{20}H_{13}N_3OF_3I$	----	Deep red	127-129	69	48.37 (48.48)	2.56 (2.62)	8.50 (8.48)	-------
2	$[Cr(C_{20}H_{12}N_3OF_3I)_2 Cl(H_2O)]$	1:2	Brown	220-223	77	43.55 (43.89)	2.12 (2.21)	7.63 (7.75)	5.33 (5.41)
3	$[Mn(C_{20}H_{12}N_3OF_3I)_2(H_2O)_2]$	1:2	Brown	114-116	79	44.37 (44.48)	2.14 (2.22)	7.59 (7.78)	4.99 (5.08)

4	**$[Fe(C_{20}H_{12}N_3OF_3I)_2\ Cl(H_2O)]$**	**1:2**	**Deep brow**	**153-155**	**80**	**43.55 (43.74)**	**2.10 (2.18)**	**7.40 (7.65)**	**4.98 (5.08)**
5	**$[Co(C_{20}H_{12}N_3OF_3I)_2(H_2O)_2]$**	**1:2**	**Brown**	**130-132**	**71**	**44.21 (44.34)**	**2.09 (2.21)**	**7.57 (7.76)**	**5.21 (5.40)**
6	**$[Ni(C_{20}H_{12}N_3OF_3I)_2(H_2O)_2]$**	**1:2**	**red**	**132-35**	**64**	**44.17 (44.32)**	**2.09 (2.21)**	**7.52 (7.75)**	**5.24 (5.4)**
7	**$[Cu(C_{20}H_{12}N_3OF_3I)_2].2H_2O$**	**1:2**	**Red brow**	**247-248**	**82**	**43.99 (44.13)**	**2.11 (2.20)**	**7.59 (7.72)**	**5.59 (5.83)**
8	**$[Zn(C_{20}H_{12}N_3OF_3I)_2(H_2O)_2]$**	**1:2**	**Light red**	**113-115**	**73**	**43.93 (44.06)**	**2.12 (2.20)**	**7.56 (7.71)**	**5.88 (6.00)**

3.2. Mass spectrum of azo -Schiff ligand (IFPMP)

Mass spectrometer data support the proposed structure. The ligand was analyzed as the direct inlet probe. The peak M^+ at (m/z=495) that is corresponding to a molecular formula of $[C_{20}H_{12}N_3OF_3I]$, the calculated formula weight is (495). This is the ligand formula. The fragments at (m/z=476 and 450) corresponding to $(C_{20}H_{13}N_3OF_2I$ and $(C_{19}H_{13}N_2OF_2I)^+$respectively. This two fragments due to losing of florid and azomethine group respectively. Another fragments at (m/z = 390,264,203,76and 65), which due to $(C_{18}H_{12}OFI)^+$,$(C_{18}H_{13}OF)^+$, $(C_{16}H_{12})^+$, $(C_6H_4)^+$ and $(C_5H_5)^+$ respectively .Figure.1 and scheme .2, showed the mass spectrum and fragmentation pattern of azo-Schiff base ligand.

Mass Spectrum of Ni(II) complex

The mass Fragment and fragmentation pattern of the metal chelate complex are shown in figure .2 and scheme.3. The spectrum would not have originated a molecular ion peak M^+ at (m/z 1082) that is equivalent to molecular weight of $[Ni(IFPMP)_2(H_2O)_2]$. The molecular ion loss of ligand molecule gate ion peak at (m/z= 552) due to the fragment $[Ni(IFPMP)(H_2O)_2]^+$. Another ion peaks at (m/z= 497-2H, 478, 450, 256, 167 and 93) were appeared in this spectrum which due to the fragments $(C_{20}H_{13}N_3OF_3I)^+$,$(C_{20}H_{12}N_3F_3I)^+$,$(C_{20}H_{13}NF_3I)^+$,$(C_{20}H_{15}N)^+$,$(C_{13}H_{11})^+$ and $(C_7H_8)^+$ respectively.

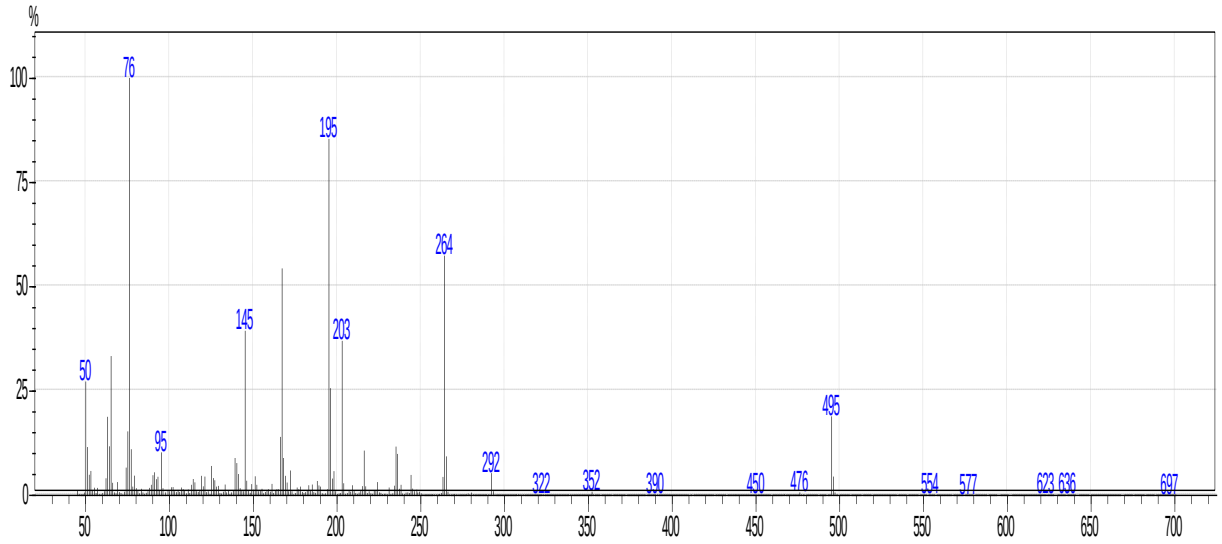


Fig.1 **Mass spectrum of (IFPMP) ligand**

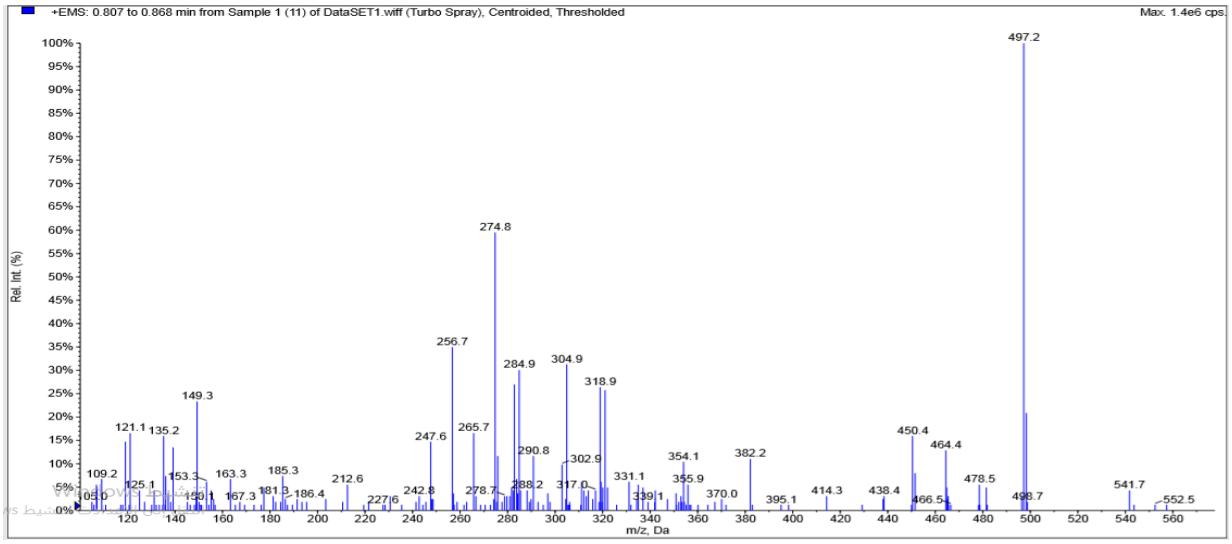
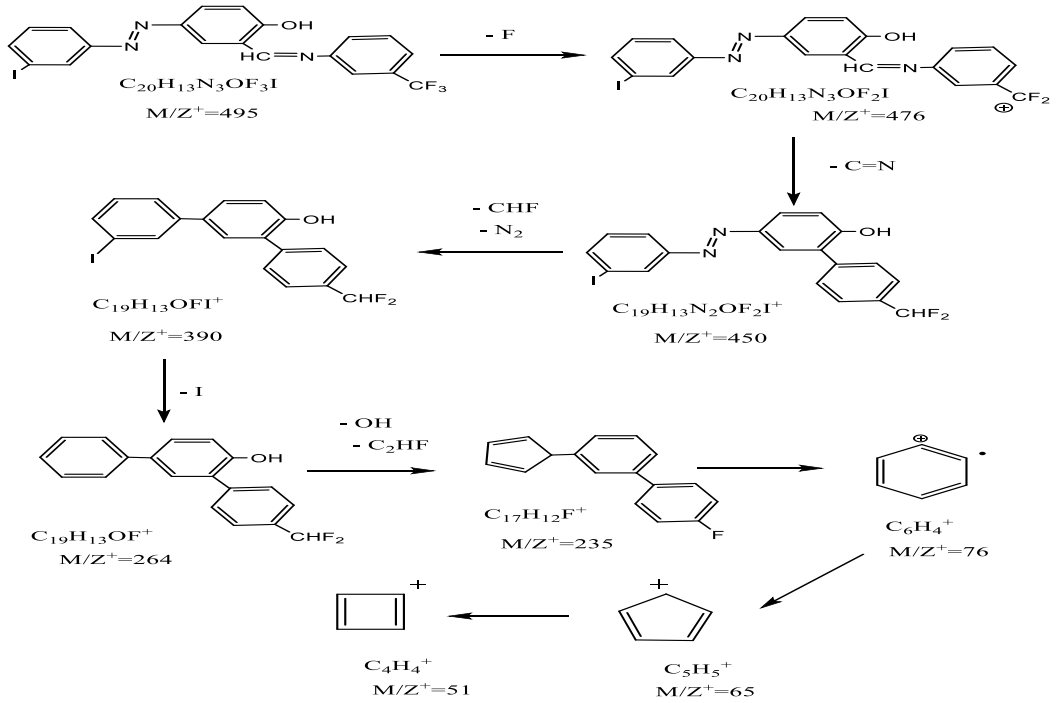
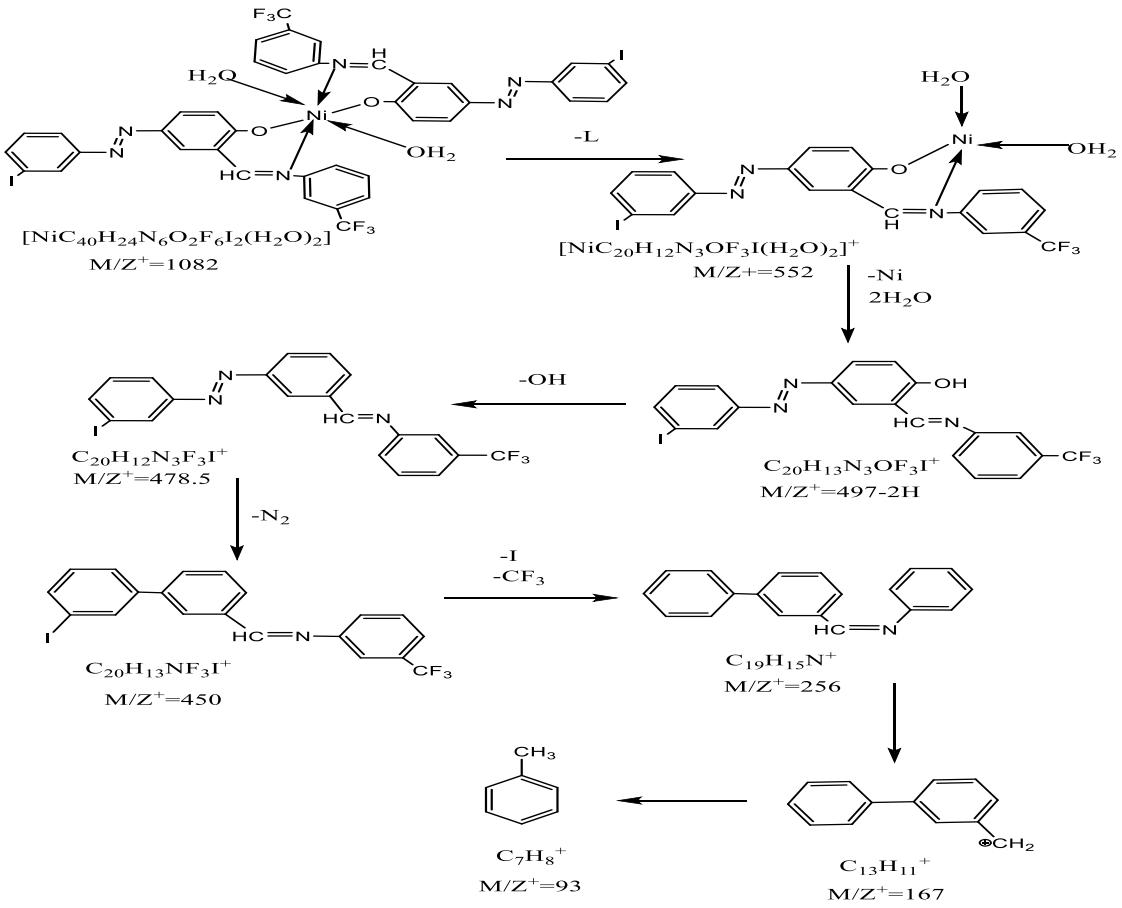


Fig .2: Mass spectrum of Zn(II) complex



Scheme (2):The Proposed Fragmentation Pattern of (IFPMP)



Scheme (3): The Proposed Fragmentation Pattern of $[Ni(IFPMP)_2(H_2O)_2]$

3.3. ^{1}HNMR spectra

^{1}HNMR spectrum of organic ligand Fig.3 showed clear signals involved singlet at =2.5ppm belong to (DMSO) solvent proton. The multiplet signals at (6.9-7.9) ppm which were assigned to aromatic protons[10] . Another Singlet signal at= (9.1 and 10.3 ppm) due to proton of azomethine (CH=N) and hydroxyl (O-H) groups respectively[11,12]. This peak noted in spectrum of the complex, disappear the signal at 10.3 ppm indicates to contribute hydroxyl group in complexity. Another group there is no appreciable change signals in this complex. as shown in Fig.3.

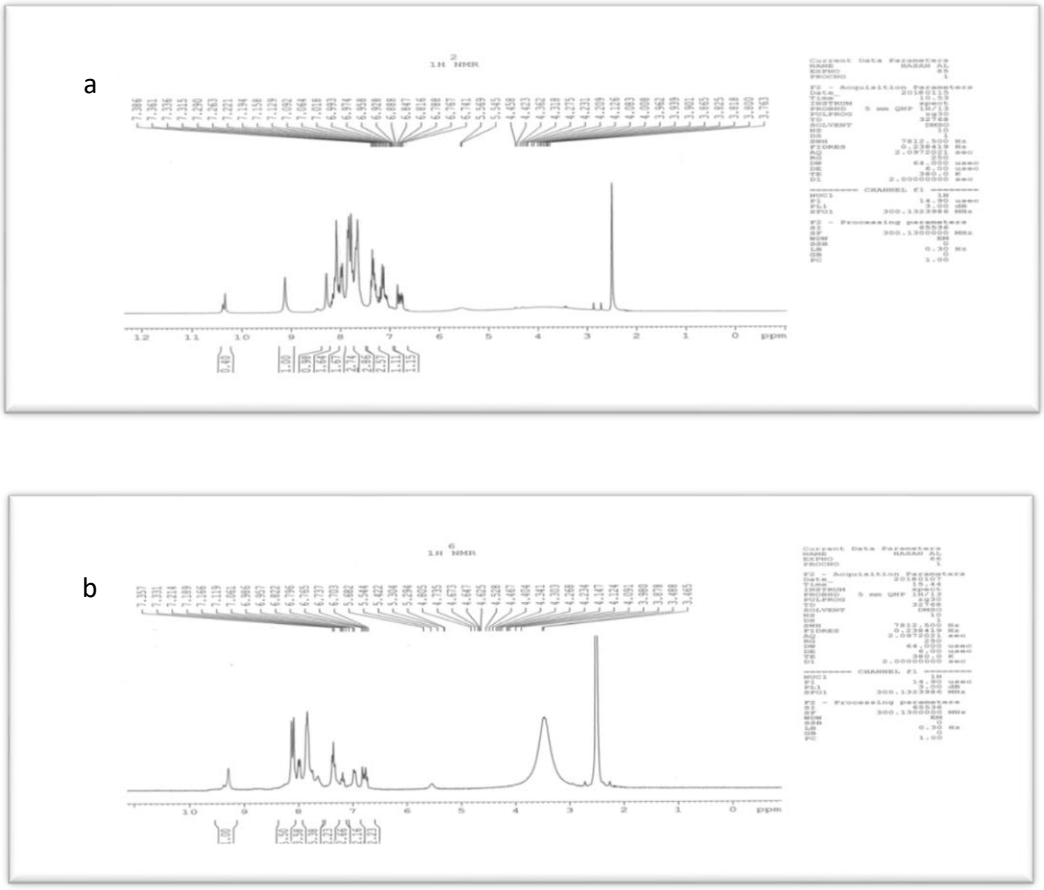


Fig .3: ^{1}H-NMR spectrum of : (a) the azo- schiff base ligand & (b) Zn (II)complex

3.4. IR spectra

The IR spectra of (IFPMP) ligand and its metal complexes were recorded between 4000-400 cm^{-1} and the obtained data were summarized in Table.2 with some assignments of the important characteristic bands.

The spectrum of free ligand show broad and medium band in the region 3446 cm^{-1} assignable to (OH) group. Abroad band is observed in all the complexes in the range 3398-3425 cm^{-1} due to υ(OH) of the coordinated water molecule[13] , this is supported by the appearance of an additional

band in the rang 829-898 cm^{-1} for (O-H) vibration deformation. These bands were not observed in the spectrum of the azo-shiff ligand. The band observed at 1618 cm^{-1} is characteristic of the azomethine group in free ligand[14]. In the complexes spectra, this band is shifted to lower frequency 1600-1612 cm^{-1}, indicating the coordination of nitrogen atom of azomethine group[15]. The presence of bands at 503-530 cm^{-1} in the IR spectra of complexes are due to M-O stretching vibrations[16]. In the spectra of these complexes, the new bands which appear in the 420-460 cm^{-1} region are assigned to the υ(M-N)[17]. While a band at 1487 cm^{-1} which observed in the spectrum of the free ligand due to υ(N=N) stretching vibration negligible change is observed for this band in the spectra of chelate complexes this indicate that no coordination from this group[18]. Representative example for there is given in Fig .4.

Table.2: Some IR frequencies in (cm^{-1}) of the ligand and its chelate complexes

Ligand/complexes	***υ(OH) water***	***υ(C=N)***	***υ(N=N)***	***υ(H_2O)***	***υ(M-O)***	***υ(M-N)***
$C_{20}H_{13}N_3OF_3I$	**3446**	**1618**	**1487**	**---**	**---**	**---**
[Cr($C_{20}H_{12}N_3OF_3I)_2$ Cl(H_2O)]	**3410**	**1612**	**1450**	**898**	**524**	**420**
[Mn($C_{20}H_{12}N_3OF_3I)_2(H_2O)_2$]	**3425**	**1600**	**1452**	**835**	**526**	**441**
[Fe($C_{20}H_{12}N_3OF_3I)_2$ Cl(H_2O)]	**3398**	**1604**	**1485**	**885**	**524**	**439**
[Co($C_{20}H_{12}N_3OF_3I)_2(H_2O)_2$]	**3421**	**1612**	**1462**	**829**	**509**	**440**
[Ni($C_{20}H_{12}N_3OF_3I)_2(H_2O)_2$]	**3412**	**1612**	**1463**	**835**	**503**	**437**
[Cu($C_{20}H_{12}N_3OF_3I)_2$].2H_2O	**3419**	**1604**	**1462**	**---**	**530**	**433**
[Zn($C_{20}H_{12}N_3OF_3I)_2(H_2O)_2$]	**3415**	**1608**	**1450**	**831**	**507**	**460**

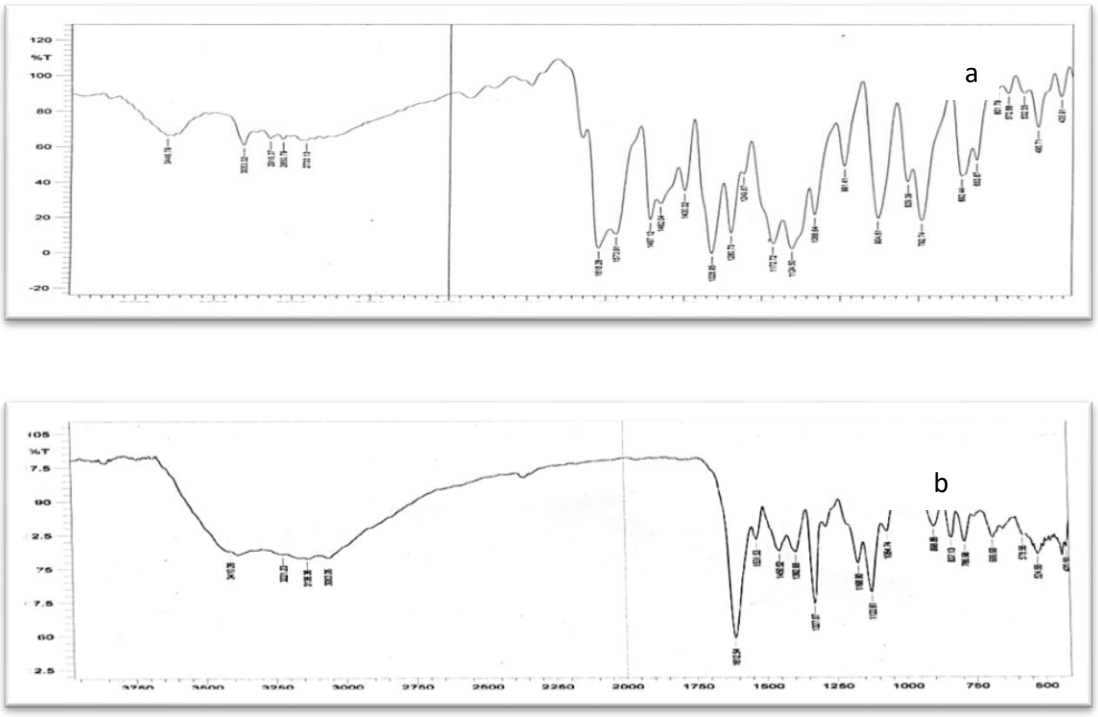


Fig .4:IR spectra of :(a) the azo- schiff base ligand & (b) Cr(III) complex

3.5. Magnetic Preparation and Electronic Spectra

The spectral data and the magnetic moment of prepared complexes are listed in Table.3. Fig.5. shows the spectra of ligand and its $[Co(L)_2(H_2O)_2]$ complex.

The electronic absorption spectrum of the ligand shows two bands at (273nm) 36630 cm^{-1} and (350nm) 28571 cm^{-1} which assigned to π-$\pi^*$and n-π^* respectively.

1- Chromium (II) complex

The Uv-vis spectrum of Cr(III) complex display three peaks at (984nm) 10162 cm^{-1} , (636nm) 15723 cm^{-1} and (376 nm) 26595 cm^{-1} which attributed to $^4A_2g \rightarrow {}^4T_2g_{(F)}$, $^4A_2g \rightarrow {}^4T_1g_{(F)}$ and $^4A_2g \rightarrow {}^4T_1g_{(P)}$ electronic transition respectively[19]. The magnetic moment value of these complex was found to be (3.8 BM) suggested the octahedral geometry for this complex[20].

2-Manganese(II) complex

The spectrum of this complex showed three peaks at (409nm) 24449 cm^{-1} , (396nm) 25252 cm^{-1} and (380nm) 26315cm^{-1} which assigned to charge transfer transition [21,22]. The magnetic moment value of solid complex (5.4 B.M) which is well within the range of high spin octahedral complex (t_2g^3 eg^2)[23].

3-Iron(III) complex

The spectrum of this complex showed three peaks at (993nm) 10070 cm^{-1}, (404nm) 24752

$cm^{-1}$and(347nm) 28818cm^{-1} there peaks assignable to $^6A_1g_{(S)} \rightarrow {}^4T_1g_{(G)}$, $^6A_1g_{(S)} \rightarrow {}^4T_2g_{(G)}$ and $^6A_1g_{(S)} \rightarrow {}^4Eg, {}^4A_1g_{(G)}$ transitions respectively [24]. The Fe(III) complex showed magnetic value at μeff (5.42B.M) which is consistent with a high spin octahedral geometry[25].

4- Cobalt (II) Complex

The magnetic moment value of the Co(II) (d^7) complex is (4.76B.M). The electronic spectrum of this complex show bands at (886nm) 11286 cm^{-1}, (657nm) 15220 cm^{-1} and (377nm) 26525cm^{-1} which can be assigned to $^4T_1g \rightarrow {}^4T_2g(F)$, $^4T_1g \rightarrow {}^4A_2g(F)$,and $^4T_1g \rightarrow {}^4T_1g(P)$, respectively. The spectrum resemble those reported for octahedral complexes[26].

5- Nickel (II) Complex

The magnetic moment for the complex of Ni(II) (d^8) was found to be (3.85 B.M), which is with the range of octahedral Ni(II) complexes[27]. The electronic spectrum of this complex show bands at (771nm) 12970 cm^{-1}, (405nm) 24691 $cm^{-1}$and (295nm) 33898 cm^{-1} which can be assigned to $^3A_2g \rightarrow {}^3T_1g(F)$, $^3A_2g \rightarrow {}^3T_1g(F)$ and charge transfer, respectively[28].

6- Copper (II) Complex

The magnetic moment value of the Cu(II) complex is (1.84B.M), which may suggest an tetrahedral structure[29]. It's electronic spectrum show bands at (901nm) 11098 cm^{-1} which may assigned to$^2T_2 \rightarrow {}^2E$ transition an approximately tetrahedral environment.

7- Zinc(II) complex

This metal complex is diamagnetic consistent with the ($3d^{10}$) configuration and the electronic spectrum of this complex exhibit high intense charge transfer transition to (INCT)[30].

Table.3 : Electronic spectra, conductivity and magnetic moment of complexes

Compound	Assigument	Absorption band(nm)	Wave number cm^{-1}	Λ_M ($S.cm^2.mol^{-1}$) In (DMSO)	μ eff. B.M
HL_2	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	350nm 273nm	28571 36630	--------	
$[CrL_2Cl(H_2O)]$	$^4A_2g \rightarrow {}^4T_2g_{(F)}$ $^4A_2g \rightarrow {}^4T_1g_{(F)}$ $^4A_2g \rightarrow {}^4T_1g_{(P)}$	984nm 636nm 376nm	10162 15723 26595	12.65	3.8
$[MnL_2(H_2O)_2]$	$^6A_1g \rightarrow {}^4Eg$ C. T C. T	409nm 396nm 380nm	24449 25252 26315	11.98	5.4
$[FeL_2Cl(H_2O)]$	$^6A_1g \rightarrow {}^4T_1g(G)$ $^6A_1g \rightarrow {}^4T_2g(G)$	993nm 404nm	10070 24752	10.70	5.42

	$^6A_1g(S)\rightarrow{}^4Eg,{}^4A_1g(G)$	347nm	28818		
$[CoL_2(H_2O)_2]$	$^4T_1g\rightarrow{}^4T_2g(F)$ $^4T_1g\rightarrow{}^4A_2g(F)$ $^4T_1g\rightarrow{}^4T_1g(P)$	886nm 657nm 377nm	11286 15220 26525	11.77	4.76
$[NiL_2(H_2O)_2]$	$^3A_2g\rightarrow{}^3T_2g(F)$ $^3A_2g\rightarrow{}^3T_1g(F)$ $^3A_2g\rightarrow{}^3T_1g(P)$	771nm 405nm 295nm	12970 24691 33898	12.56	3.85
$[CuL_2].2H_2O$	$^2T_2\rightarrow{}^2E$ C.T C.T	901nm	11098	10.84	1.84
$[ZnL_2(H_2O)_2]$	C.T	375nm	26666	13.34	Dia

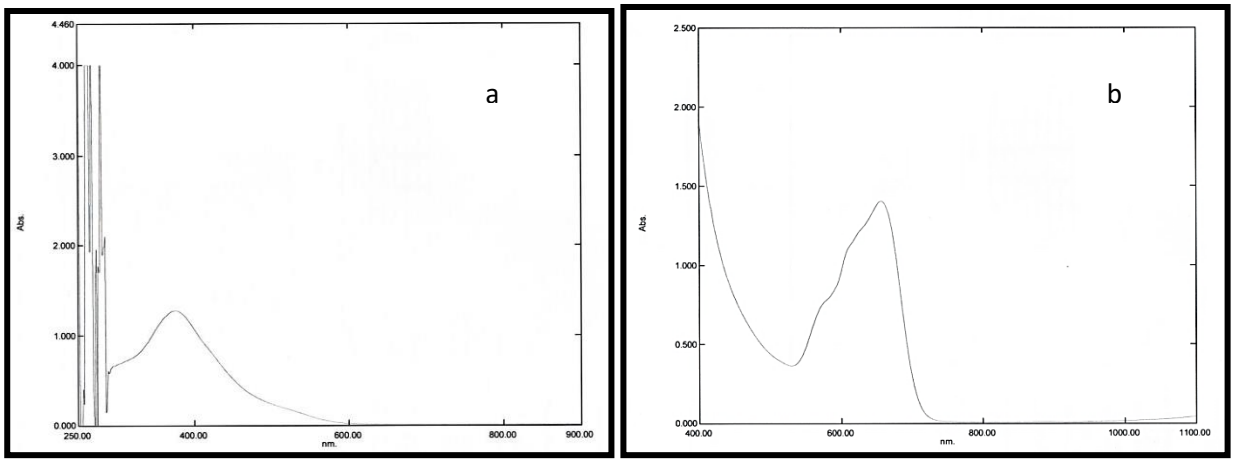
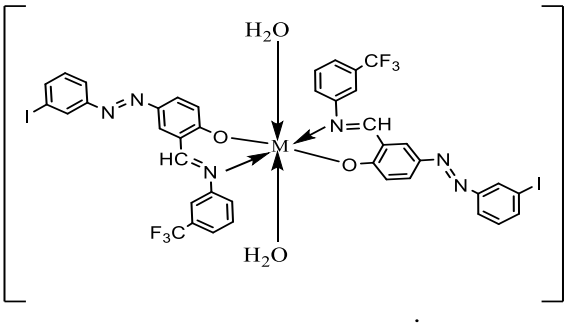
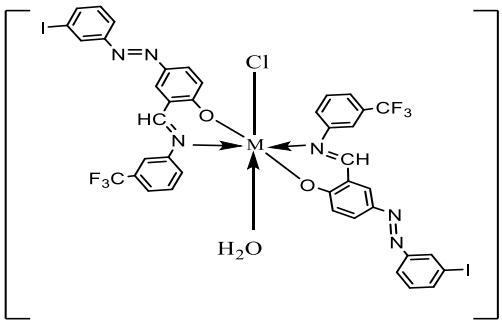


Fig.5: Uv-Vis of (a) (IFPMP) ligand & (b) $[Co(L)_2(H_2O)_2]$ complex

3.6. Conductivity measurement

The values obtained from the measurements of molar conductance of each metal complexes included in Table(3). Molar conductance measurements (10.70 -13.34 S. cm^2. Mol^{-1}) in DMSO (10^{-3} M) at room temperature exhibit non electrolytic behavior of the complexes. According to these results the following structural formula of these complexes may be proposed in figure.6 .





M= Mn(II), Co(II) ,Ni(II) and Zn(II) **M= Cr(III) and Fe(III)**

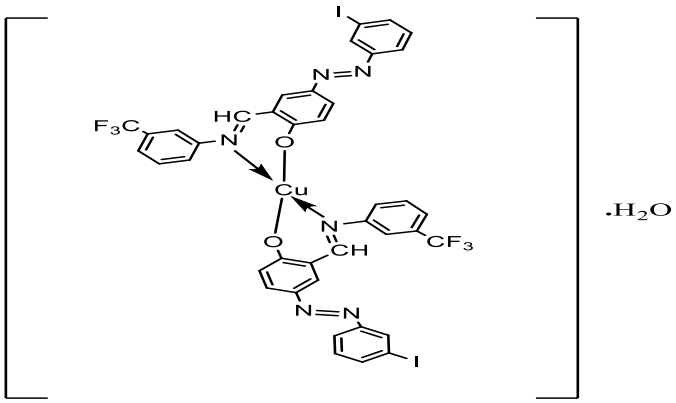
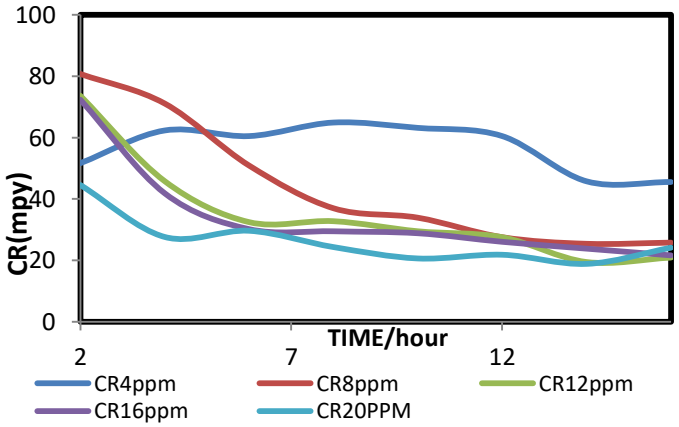
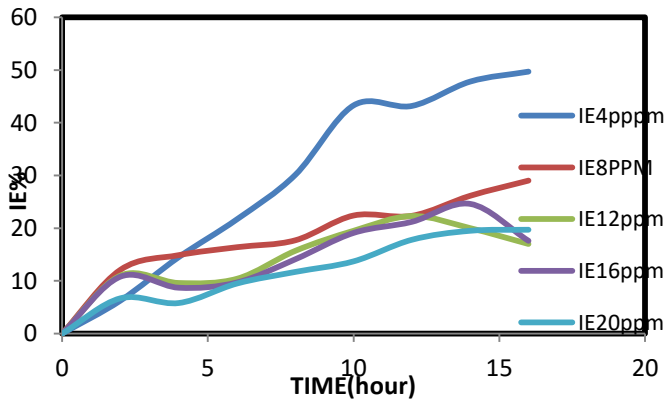


Fig.6: The proposed structural formula of the metal chelate complexes.

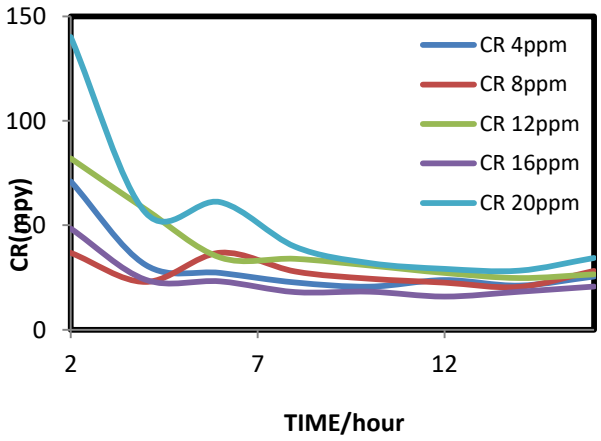
3.7. Weight loss measurements

Weight loss of mild steel electrode was determined at various time intervals in absence and present of different concentrations of azo dye and Cu(II) complex at 298K .Table 4 gives the corrosion rate and inhibition efficiency for carbon steel in 0.5M HCl. This shows that the corrosion rate decreases and inhibitor efficiencies decrease with increasing concentration of ligand and increase with increasing concentration of its complex at given temperature.

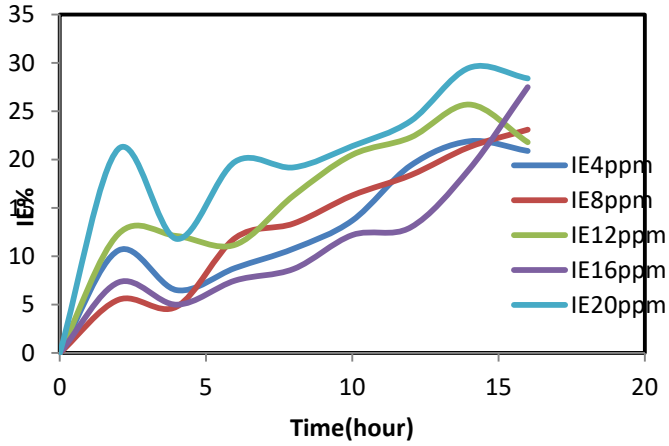




Relation between C.R and time in 0.5M HCl of ligand **Relation between I.E% and time in 0.5M HCl of ligand**



Relation between C.R and time in 0.5M HCl Cu(II) Cu(II)complex



Relation between I.E% and time in 0.5M HCl of of complex

Table :4 The value of (CR)and (%IE) in (0.5M) of HCl at 298K of ligand and its complex

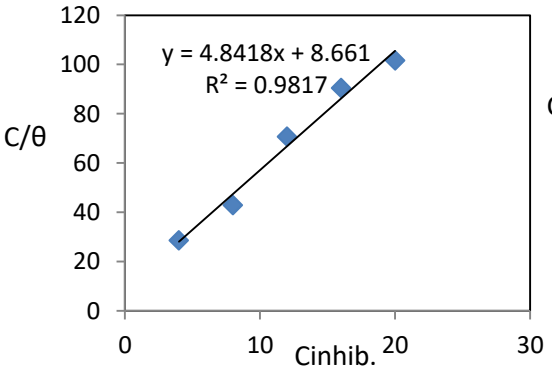
Immersion time																
Conc.of ihib. ppm	**2h**		**4h**		**6h**		**8h**		**10h**		**12h**		**14h**		**16h**	
	CR mpy	%IE	CR mpy	%IE	CR mpy	%IE	CR mpy	%IE	CR mpy	%IE	CR mpy	%IE	CR mpy	%IE	CR mpy	%IE
Blank HL_2	103	-	68.98	-	49.32	-	39.89	-	32.75	-	28.87	-	34.60	-	31.07	-
4	51.66	6.26	62.32	14.5	60.49	21.69	64.9	30.11	63.16	43.2	60.49	43.18	45.76	47.8	45.53	14.0
8	80.73	12.1	71.09	14.8	50.9	16.39	36.99	17.7	33.91	22.4	27.56	22.34	25.42	26.14	25.8	29.02
12	73.62	11	45.81	9.6	32.47	10.4	32.78	15.7	29.49	19.5	27.56	22.3	19.48	20	20.93	17
16	72.336	10.8	41.86	8.7	30.19	9.7	29.49	14.1	28.85	19.1	26.06	21.2	23.84	24.6	21.65	17.7
20	44.56	6.7	27.64	5.8	29.66	9.5	24.35	11.7	20.64	13.7	21.85	17.8	18.88	19.5	24.15	19.7
HL_2+Cu																
4	71.04	10.6	31.07	6.5	27.20	8.8	22.64	10.8	20.64	13.7	23.78	19.4	21.14	21.9	25.47	20.9
8	36.81	5.5	22.90	4.8	36.86	11.9	27.91	13.4	24.43	16.3	22.55	18.4	20.53	21.3	28.17	23.1
12	82.02	12.3	57.66	12.1	34.58	11.2	33.96	16.3	30.75	20.5	27.20	22.3	24.75	25.7	26.52	21.8
16	48.43		23.96	5	23.17	7.5	18.03	8.7	18.22	12.2	15.88	13	18.20	19	20.67	27.5
20	140.15	7.3	56.08	18	61.08	19.8	39.76	19.2	31.91	21.4	29.14	24	28.28	29.5	34.36	28.4
		21.1														

3.8. Adsorption Isotherm

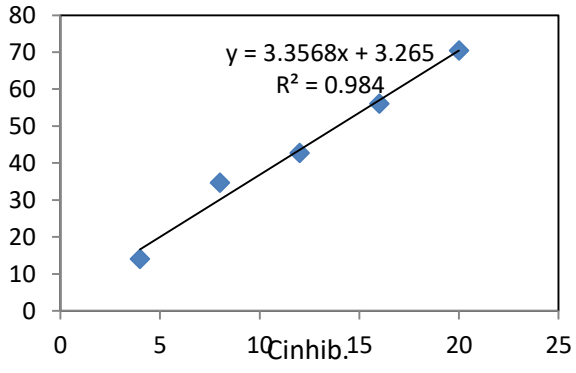
In order to confirm the adsorption of the investigated inhibitor on metal surface, the adsorption isothermwas studied. The adsorption isotherm can provide basic information on the interaction of inhibitor with metal surface. The use of Langmuir equation for adsorption was found to be suitable for adsorption of ligands (HL_2) and its complex of Cu(II) in medium of hydrochloric acid (0.5M) .

Table 5: The value of Cinhi./θ and Kads. of ligand and its complex in (0.5M) HCl at 298K

Immersion time **(16h)**				
Conc. Of inhib.ppm	**θ**	**$C_{inhib.}$/ θ**	**$K_{ads.}$**	**$-\Delta G_{ads.}$ KJ mol^{-1} K^{-1}**
HL_2				
	0.140	**28.50**		
4	**0.290**	**42.79**	**0.2065**	**6.041**
8	**0.170**	**70.59**		
12	**0.177**	**90.40**		
16	**0.197**	**101.53**		
20				
16h				
HL_2+Cu				
	0.209	**13.97**		
4	**0.231**	**34.63**	**0.2980**	**6.949**
8	**0.218**	**42.71**		
12	**0.275**	**56.0**		
16	**0.284**	**70.42**		
20				



Adsorption Isotherm of ligand at 16 h



Adsorption Isotherm of Cu(II)complex at 16 h

3.9. Study of SEM

The SEM obtained of carbon steel samples after immersion in 0.5M HCl in absence and presence of 20ppm inhibitor for 16 hours. It is clear that carbon steel surface in the absence of the inhibitor are strongly damaged. While the morphology of carbon steel surface in presence of inhibitor is quite different from the previous one, the specimen surface was smoother.

A **B**

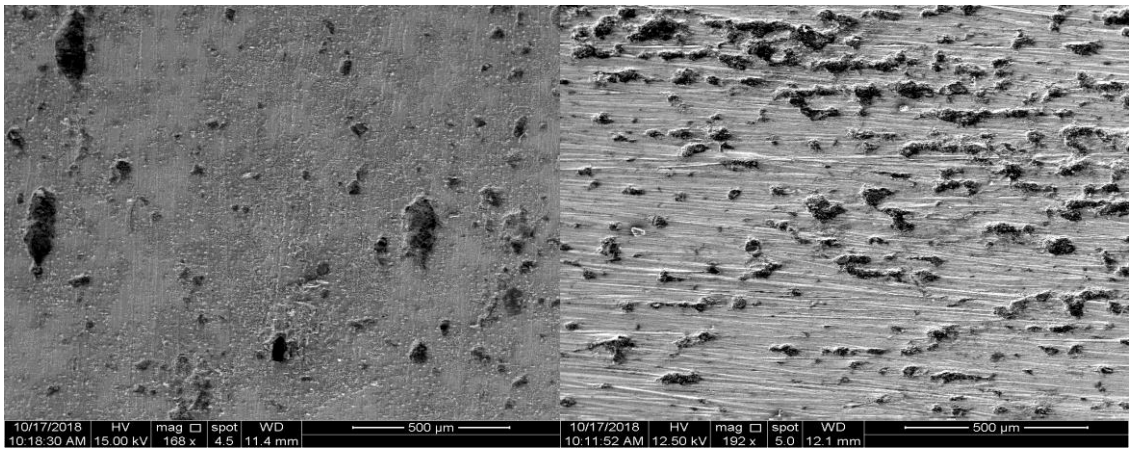


Fig.7: SEM micrographs for C-steel in (0.5M) HCl (A) and presence of inhibitor HL_2 (B).

A **B**

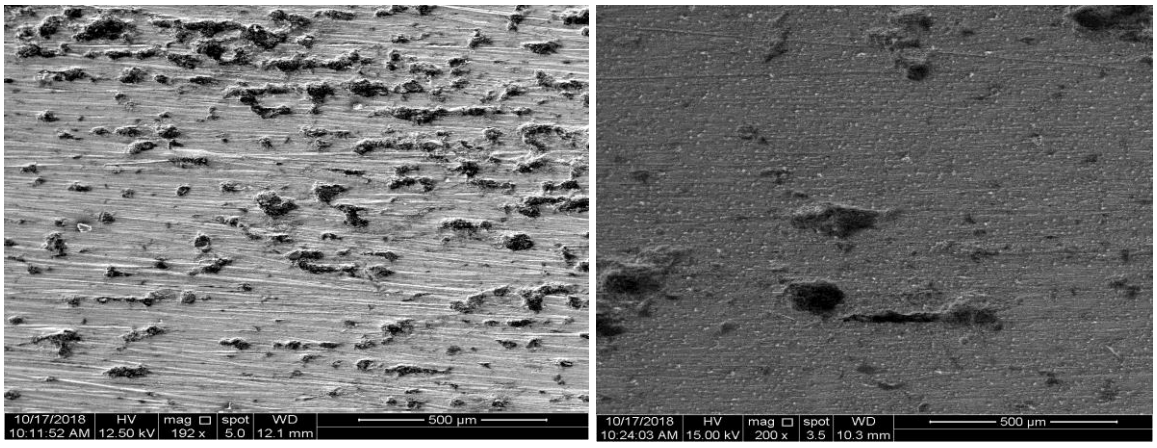


Fig.8:SEM micrographs for C-steel in (0.5M) HCl (A)and presence of inhibitor Cu(II) complex(B).

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Synthesis and Characterization of some Heterocyclic Compounds from Indole Derivatives

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ABSTRACT:

This research involves preparation of heterocyclic compounds from indole -2- carboxylic acid. The first step synthesized of ester compound from indole -2- carboxylic acid and prepared hydrazinamide from ester.Then prepared Schiff bases from hydrazinamide derivatives with benzaldehyde derivatives. The last step preparedoxazepine and oxazepane derivatives from Schiff bases with(malice, phthalic and succinic)inhydride .These compounds were characterized by melting point ,FT.IR,^{1}HNMRand^{13}C-NMRKey words: indole -2- carboxylic acid,Schiff bases,Oxazepine , 1,3-oxazepane, biological activity.

الخلاصة:

يتضمن البحث تحضير مركبات حلقية غير متجانسة عن طريق استعمال 2- كاربوكسياندول كمادة أولية ,تتضمن الخطوة الاولى تحضير الأستر من 2- كاربوكسياندول وتحضير الهايدرازايناميد من الاستر ومن ثم تحضير قواعد شف من الهايدرازايناميدبأستعمال مشتقات البنزالديهايد.الخطوة الأخيرة تتضمن تحضير مشتقات الاوكسازبينوالاوكسازبان معانهدريد (المالك ,الفثالكوالسكسنك) بعدها يتم التأكد من صحة المركبات المحضرة بوساطة درجة الانصهار وتقنية FT.IR, ^{1}HNMR , ^{13}C-NMR .

INTRODUCTION

Indoles and substituted indoles are the basic skeleton ofseveral biologically active organic scaffolds such as Turbomycin, BVibrindoles,Arsindoles, Arundine, Ajamalicine.(1)All indole compounds have a bicyclic structure,consisting of a sixmembered benzene ring fused toa five-membered nitrogen-containing pyrrole ring.(2)Indole derivatives are one of the most promising heterocyclicMoieties(3), which have active sites in treating various diseases.(4)its pharmacological significance providestremendous opportunities to discover novel drugswith different modes of action.(5)Indole-2-carboxylic acid is a versatile intermediate in the preparation of many pharmaceuticallyactive agents(6) showed significant structural and biological diversity through several methods of these compounds. The conventional method is the Hemetsberger-Knittel indole synthesis(7) Here the five atom involved in the synthesis of oxazepinedionederivative component is the anhydride nucleus of phthalic anhydrideand the two atom comgroup is C=N of schiff base or imine(8)its symbol (R-N=CH-R1) (9).They are the result of mixing the aromatic primary amines with the carbonyl compounds (aldehydes or ketones)(10)Azomethine (C=N). These are known as "Schiff's bases", named after the German scientist (Hugo Schiff)(11) , and which are famous for their biological importance and for its uses as anti-dioxides, anti-viruses (antibacterial, antiproliferative , anti – inflammatory, antiviral, antipyretic properties (12), and for the curing of tumors as well(13).The stability of the resulting Schiff bases depends on the type of amine and the used carbonyl compounds(14). It depends on the ringing state (15)

EXPERIMENTAL SECTION

Materials

Chemicals used during the current work are indole -2- carboxylic acid ,H2SO4, Phathilic anhydride , maleic anhydride and succinic anhydride,produced by (sigma and Aldrich) company, In addition to use of ethanol, dry benzene and methanol as a solvent .

.Instrumentation

Recorded melting point by hot stage Gallen Kamp. To ensure the purity of the resulting compounds used techniqueThin layer chromatography (TLC)was carried out, the presence of iodine an aspect of the spot. F.T.I.Ras spectroscopy was used KBr disc,^{1}HNMR and^{13}C-NMR Bruker-UItra Shield-300MHz spectra was used DMSO-d6 as solvents.

EXPERIMANTAL

Synthesis of ester derivative compound (**M $_1$:** Ethyl 1H-indole-2-carboxylate)

The compound (M1) was prepared by reactionindole-2-carboxylic acid taking(2g,0.01mol) of compound is dissolved in (50ml) of ethanol absolute. Then added 6 drops of H_2SO_4concentrate. Esterification for (6hrs), follow up the reaction by (TLC). After cooling the mixture was neutralized. The titled product was achieved by evaporating the solution under reduced pressure.

Synthesis of hydrazineamide derivative (M2: 1H-indole-2-carbohydrazide**).**

Compound (M1) (2g,0.01mol) was dissolved in refluxed ethanol (50ml), hydrazine hydrate (1ml) was slowly added to the mixture. The solution was refluxed for (13hrs) the solvent was removed by evaporating, the residue was cooled .The product was recrystallized from absolute ethanol to give titled compound.

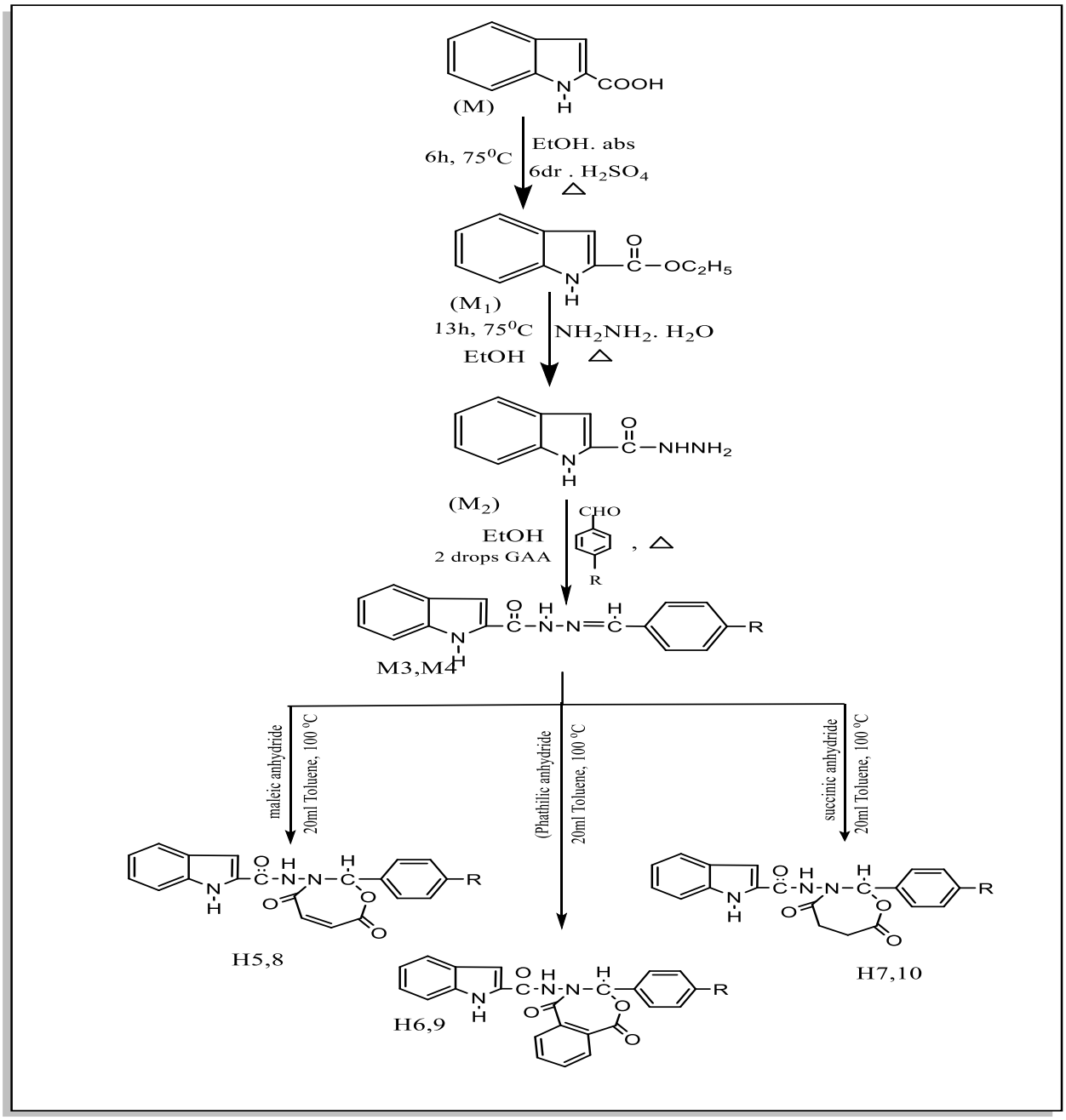
Synthesis of Schiff bases (M3:N'-(4-chlorobenzylidene)-1H-indole-2-carbohydrazide**,**

M4:N'-(4-Florobenzylidene)-1H-indole-2-carbohydrazide**).**

Amixtuer of (0.4g and 0.7g) of aromatic benzaldehyde derivatives and compound (M2) was refluxed for (7-10)hrs in (20ml) of absolute ethanol,The reaction mixture was cooled and kept for (24hrs), The crystals found were filtered,dried and recrystallized from absolute ethanol to give derivatives (M3,M4).

procedure synthesis of 1,3 oxazepine and 1,3 oxazepane[18] (H5-H10)

Amixtuer of Schiff bases (M3,M4) (0.3g,0.001mol) dissolved inToluene(20ml) and (malice, phthalic and succinic)anhydride (0.11g, 0.001mol) and refluxed for (8-10)hrs. The reaction was then cooled and the resulting final(H5-H10), recrystallized from absolute ethanol and ether. Scheme(1).



R= F ,Cl

Scheme(1):synthesis of 1,3 oxazepine and 1,3 oxazepane

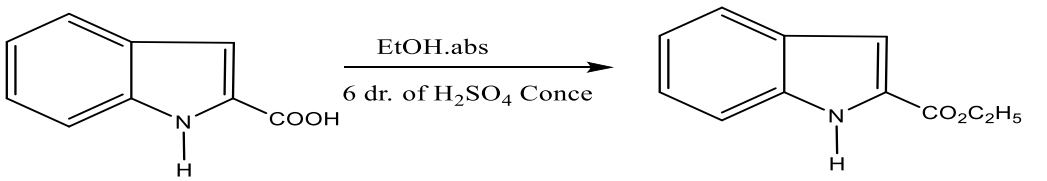
Table (1): Physical properties and other characteristics for the synthesizedcompounds (M1-M4,H5-H10)

NO.	Molecular Formula	M.wt g/mol	m.p °C	Color	Rf	Solvent	Reflex Time
M	C9H7NO2	161.16	209 -211	White	0.57	EtOH	-----
M1	$C_{11}H_{11}NO2$	189	191 – 193	Light Yellow	0.55	EtOH	6hrs
M2	C_9H_9N3O	175	158 – 161	Brown	0.75	EtOH	13hrs
M_3	$C_{16}H_{12}\ N_3OCl$	297.5	211 – 213	DarkYellow	0.52	EtOH	7hrs
M_4	$C_{16}H_{12}\ N_3OF$	281	177 – 179	Brown	0.48	EtOH	7hrs
H5	$C_{20}H_{14}\ FN_3O4$	379	245 – 248	Yellow	0.42	Toluene	7hrs
H6	$C_{24}H_{16}\ FN_3O4$	429	203 – 206	Brown	0.46	Toluene	8hrs
H7	$C_{20}H_{16}\ FN_3O4$	381	199 – 201	Yellow	0.57	Toluene	7hrs
H8	$C_{20}H_{14}\ ClN_3O_4$	395.80	171 – 174	Yellow	0.48	Toluene	7hrs
H9	$C_{24}H_{16}\ ClN_3O_4$	445.86	179 – 181	Yellow	0.45	Toluene	8hrs
H10	$C_{20}H_{16}\ ClN_3O_4$	397	186 – 189	Light Yellow	0.40	Toluene	9hrs

RESULTS AND DISCUSSION

Synthesis derivatives (M1: Ethyl 1H-indole-2-carboxylate**)**

The reaction between Indole-2-carboxylic acid (M) and absolute ethanol in the presence concentration H_2SO_4 to synthesis ester derivative(M1)



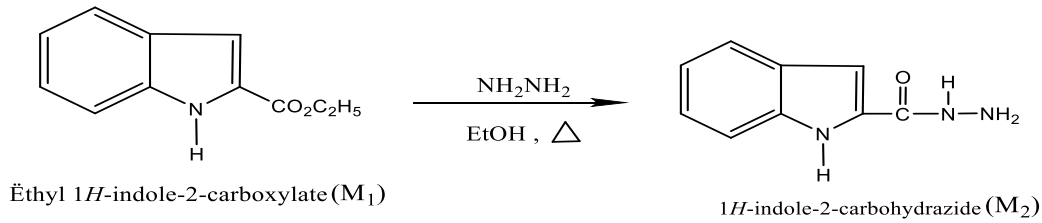
1*H*-indole-2-carboxylic acid Ethyl 1*H*-indole-2-carboxylate (M_1)

The FT-IR spectrum of Indole-2-carboxylic acid dye (M) fig(1), show stretching vibration bond of (OH) group of carboxylic acid is broad at (2500-3400cm^{-1}), the ($CH_{aromatic}$) group at (3051cm^{-1}), the stretching vibration band of (N-H)occur at 3421cm-1 .

The FT-IR spectrum of ester derivative (M1), fig(2) show the stretching vibration band of (NH) group occur at (3356cm^{-1}), the carbonyl group of ester at (ν 1708 cm^{-1}),($CH_{aromatic}$) ν3055, ν2999($CH_{aliphatic}$), $(C=C)_{aromatic}$ ν1523 and disappearance the stretching vibration of(OH) of carboxylic acid at (2500-3400cm^{-1}) .

Synthesis of hydrazineamide derivative (M2:1H-indole-2-carbohydrazide**)**

The reaction between ester derivative (M1) with hydrazine hydrate in the presence absolute ethanol as solvent at 70^0C .to prepare the hydrazine derivative (M2).



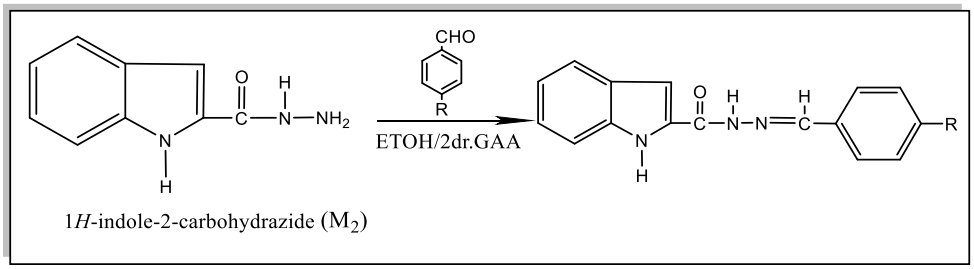
Ëthyl 1*H*-indole-2-carboxylate (M_1) — 1*H*-indole-2-carbohydrazide (M_2)

The FT-IR spectrum of hydrazide derivative (M2), fig(3) show the stretching vibration band of (NH_2) group at (3454&3425)cm^{-1}, the stretching vibration band of (NH) group at (3332cm^{-1}) the carbonyl group of amide at(1691cm^{-1}) .

Synthesis Schiff bases (M3:N'-(4-chlorobenzylidene)-1H-indole-2-carbohydrazide,

M4:N'-(4-Florobenzylidene)-1H-indole-2-carbohydrazide)

The reaction between hydrazineamide derivative (M2) and benzaldehyde derivatives(4-chlorobenzaldehydeand4-floro benzaldehyde)respectivly in the presence(GAA 2 drops)as catalyst reagent to synthesisschiff bases(M3,M4).



1*H*-indole-2-carbohydrazide (M_2)

R= F ,Cl

M_3 :N'-(4-chlorobenzylidene)-1H-indole-2-carbohydrazide

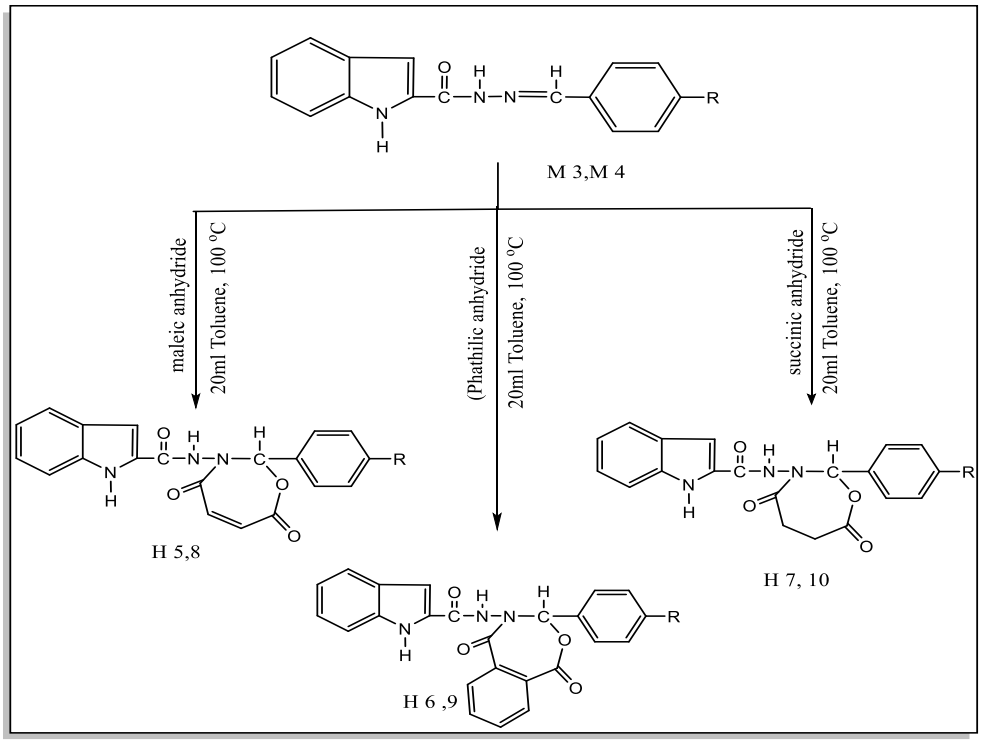
FT-IR(KBr) cm^{-1} ,ν3448(NHindole),ν3047($CH_{aromatic}$) , ν2995-2850($CH_{aliphatic}$), ν1624(C=ONH), ν1589($C=N_{imine}$),ν1566$(C=C)_{aromatic}$, ,(C-Cl)at(721.38)cm-1.

M_4 :N'-(4-Florobenzylidene)-1H-indole-2-carbohydrazide

FT-IR(KBr) cm^{-1} ,ν3419(NHindole),ν3059 ($CH_{aromatic}$) , ν2709 ($CH_{aliphatic}$), ν1631(C=ONH), ν1600($C=N_{imine}$),ν1508$(C=C)_{aromatic}$

Synthesis derivatives (H5-H10).

These compounds were synthesized according to the sequence in scheme(2)



scheme(2)Synthesis derivatives (H5-H10)

The Schiff bases (M3,M4) were reacted with (Phathilic anhydride, maleic anhydride and succinic anhydride) respectively to synthesis (H5-H10) .

These compounds were characterized by their melting points, FT.IR, ^{1}HNMR , ^{13}C-NMR and checked by TLC.

H_5:N-(2-(4-fluorophenyl)-4,7-dioxo-4,7-dihydro-1,3-oxazepin-3(2H)-yl)-1H-indole-2-carboxamide

FT-IR(KBr)cm^{-1}Fig(4) ν3406(NHindole),ν3070($CH_{aromatic}$),2978 ($CH_{aliphatic}$),ν 1724(C=O)lactone ,1674(C=O)lactam.

^{1}H-NMR(DMSO), fig(11) 6.9-7.4(m,aromatic ring), 8.976(d,1H,N-CH), 9.310 (s,1H,NH_{amide}), 10.926 (s,1H,NH_{indol}) , ^{13}C-NMR(DMSO) ,fig(12)δ 107-124ppm C for C=C ring ,, δ130ppm C for N-CH_{ring}, δ177.788,169.308 ppm C for lactone and lactam respectively.

H_6:N-(3-(4-fluorophenyl)-1,5-dioxo-1,5-dihydrobenzo[e][1,3]oxazepin-4(3H)-yl)-1H-indole-2-carboxamide

FT-IR(KBr) cm^{-1}fig(6)ν3396(NHindole)ν3020($CH_{aromatic}$),2899($CH_{aliphatic}$),ν1697(C=O)lactone ,1664(C=O)lactam, ^{1}H-NMR(DMSO),fig(13)6.8-7.8(m,aromatic ring), 8.750(d,1H,N-CH), 9.740 (s,1H,NH_{amide}), 10.300 (s,1H,NH_{indol}) , ^{13}C-NMR(DMSO) ,fig(14) δ 125-133ppm C for C=C ring ,, δ155ppm C for N-CH_{amide}, δ 169.091 ,160.510 ppm C for lactone and lactam respectively.

. **H_7**:N-(2-(4-fluorophenyl)-4,7-dioxo-1,3-oxazepan-3-yl)-1H-indole-2-carboxamide

FT-IR(KBr) cmfig(7)v3211 (NHindole)v3051 ($CH_{aromatic}$),2943 ($CH_{aliphatic}$),v 1693(C=O)lactone ,1623(C=O)lactam, ^{1}H-NMR(DMSO),fig(15)6.8-7.9(m,aromatic ring), 8.880(d,1H,N-CH), 9.870 (s,1H,NH_{amide}), 10.335(s,1H,NH_{indol}) , ^{13}C-NMR(DMSO) fig(16), δ 107-135ppm C for C=C ring , δ153ppm C for N-CH_{ring}, δ 173.971 ,170.354 ppm C for lactone and lactam respectively..

H_8:N-(2-(4-chlorophenyl)-4,7-dioxo-4,7-dihydro-1,3-oxazepin-3(2H)-yl)-1H-indole-2-carboxamide

FT-IR(KBr)cm^{-}
^{1}fig(8)v3354(NHindole),v3049(CHaromatic),2995(CHaliphatic),v1705(C=O)lactone ,1624(C=O)lactam, 1H-NMR(DMSO),fig(17)6.2-7.2(m,aromatic ring), 8.663(d,1H,N-CH), 9.773(s,1H,NHamide), 10.103 (s,1H,NHindol) , , ^{13}C-NMR(DMSO) ,fig(18) δ 128-134ppm C for C=C ring ,δ160ppm C for N-CHring, δ 176.112,168.140 ppm C for lactone and lactam respectively.

H_9:N-(3-(4-chlorophenyl)-1,5-dioxo-1,5-dihydrobenzo[e][1,3]oxazepin-4(3H)-yl)-1H-indole-2-carboxamide

FT-IR(KBr) cmfig(9)v3446 (NHindole)v3028 ($CH_{aromatic}$),2997 ($CH_{aliphatic}$),v 1697(C=O)lactone ,1625(C=O)lactam, ^{1}H-NMR(DMSO),fig(19)7.0-8.0(m,aromatic ring), 8.708 (d,1H,N-CH), 9.868 (s,1H,NH_{amide}), 10.317 (s,1H,NH_{indol}) , ,^{13}C-NMR(DMSO) ,fig(20) δ 128-1301ppm C for C=C ring ,, δ133ppm C for N-CH_{ring}, δ 178.199 ,169.109 ppm C for lactone and lactam respectively.

H_{10}:N-(2-(4-chlorophenyl)-4,7-dioxo-1,3-oxazepan-3-yl)-1H-indole-2-carboxamide

FT-IR(KBr)cm^{-1}fig(10)v3442(NHindole),v3051($CH_{aromatic}$),2995 ($CH_{aliphatic}$),v 1703(C=O)lactone ,1645(C=O)lactam, ^{1}H-NMR(DMSO),fig(21)7.0-7.8(m,aromatic ring), 8.697(d,1H,N-CH), 9.764 (s,1H,NH_{amide}), 10.006 (s,1H,NH_{indol}) , , ^{13}C-NMR(DMSO) ,fig(22) δ 105-132ppm C for C=C ring ,, δ164ppm C for N-CH_{ring}, δ 183.258 ,172.472 ppm C for lactone and lactam respectively. .

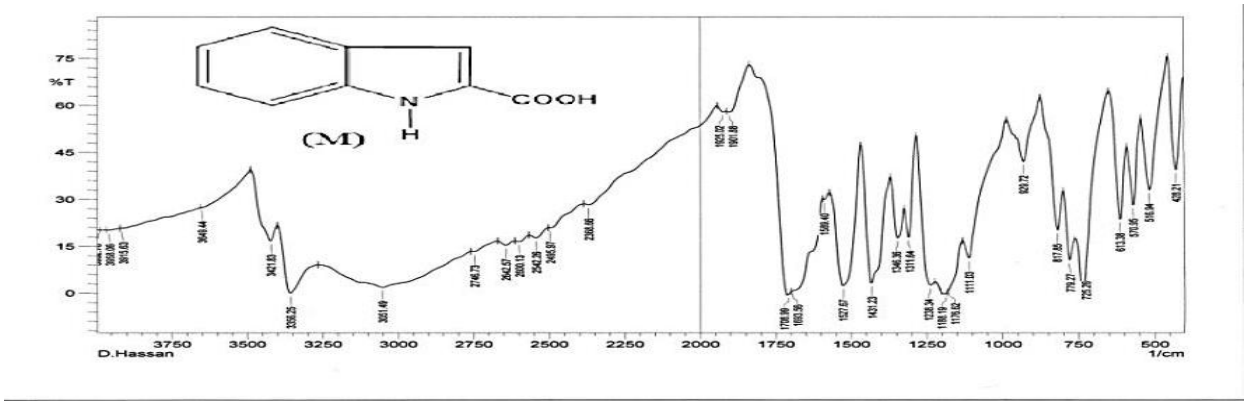


Figure 1: FT.IR spectrum of Indole-2-carboxylic acid compound (M)

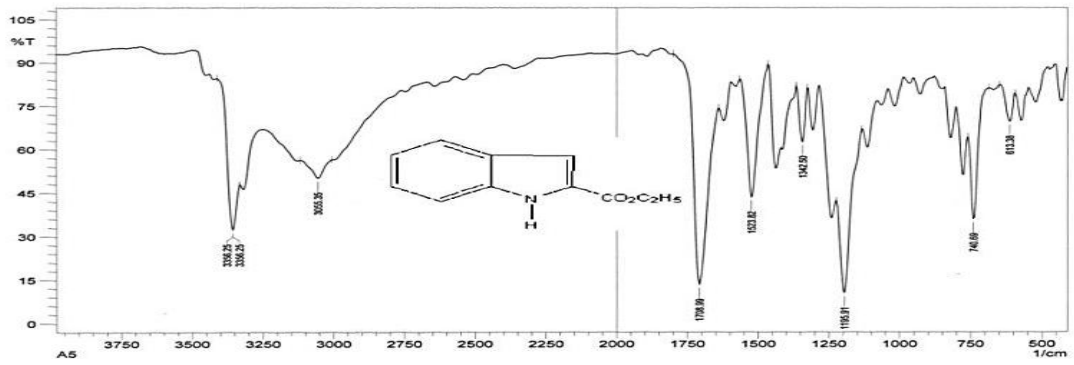


Figure 2: FT.IR spectrum of ester compound (M1)

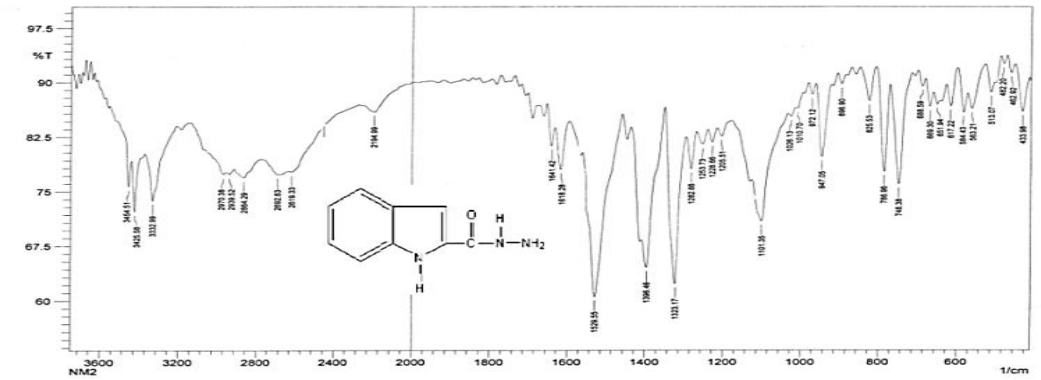


Figure 3: FT.IR spectrum of hydrazide compound (M2)

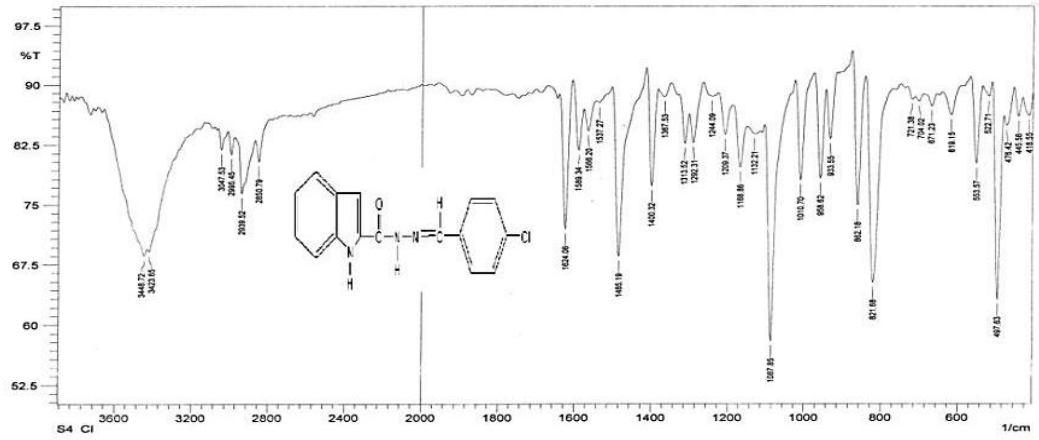


Figure 4: FT.IR spectrum of Schiff base compound (M3)

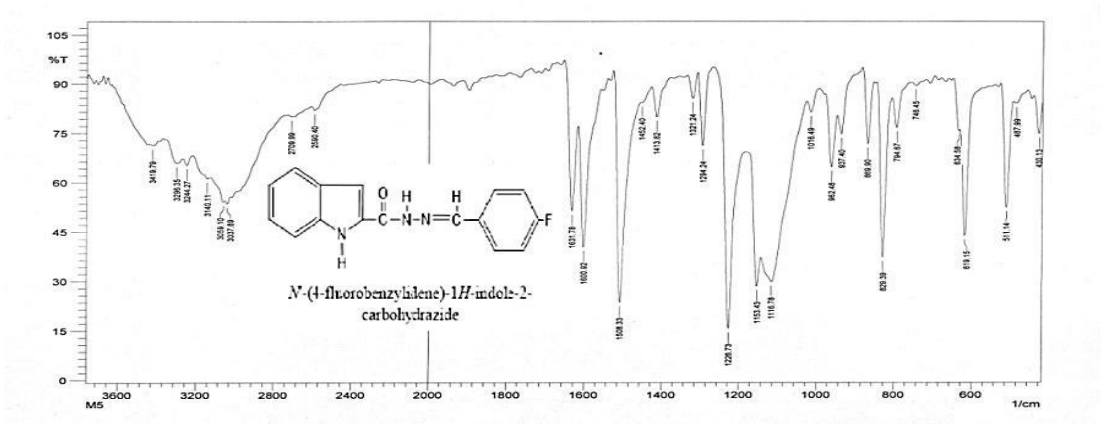
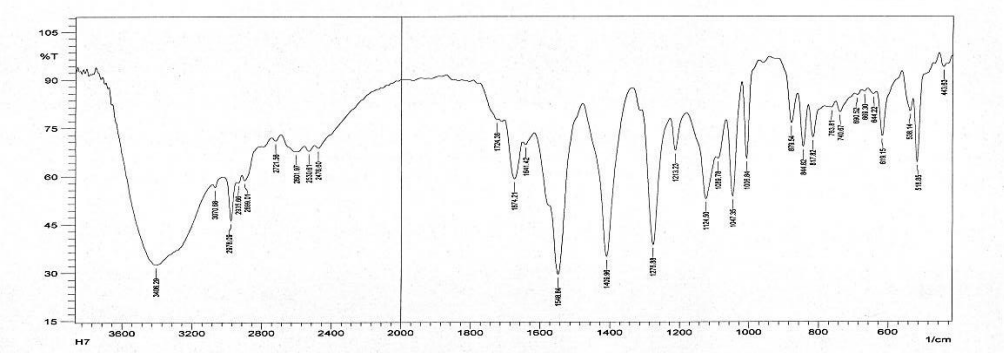
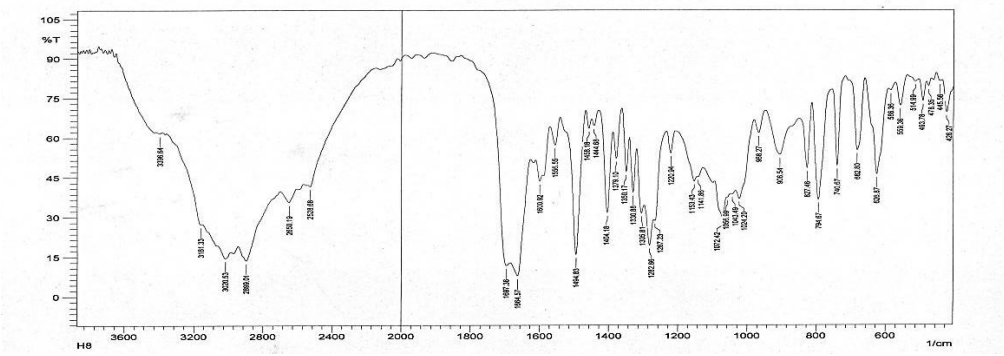


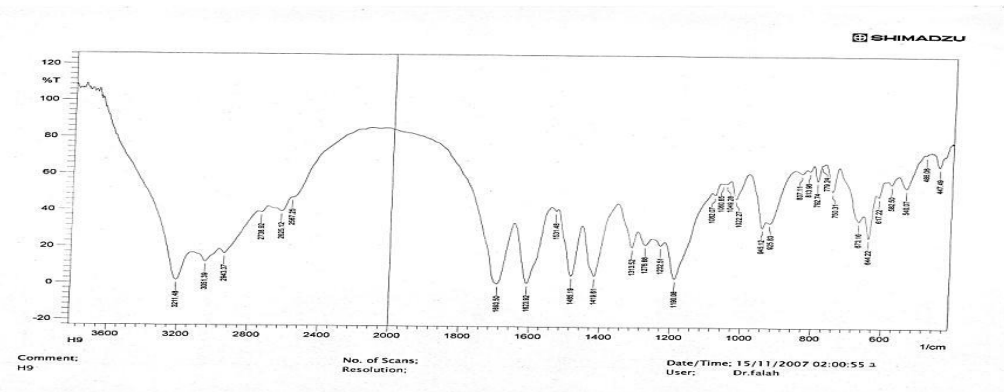
Figure 4: FT.IR spectrum of Schiff base compound (M4)



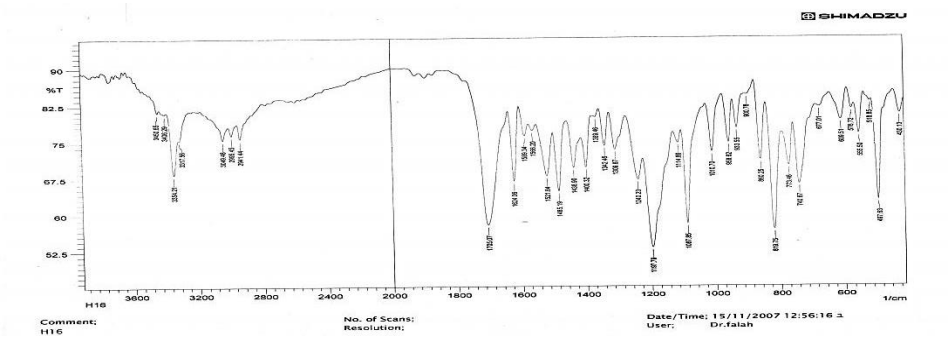
FT.IR spectrum of the compound (H5**)**:5 Figure



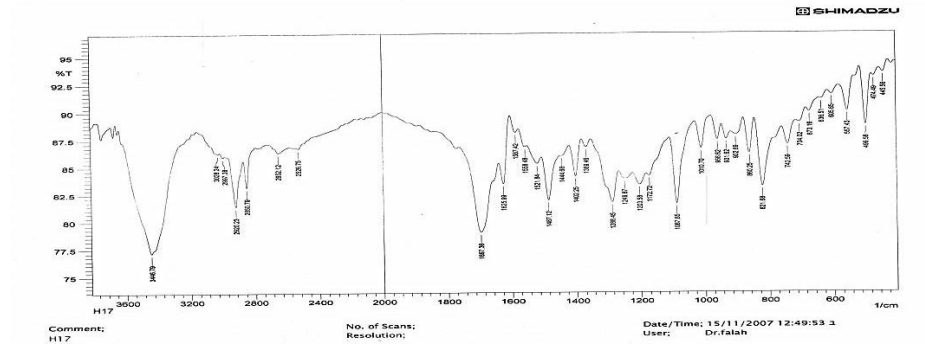
FT.IR spectrum of the compound (H6): Figure6



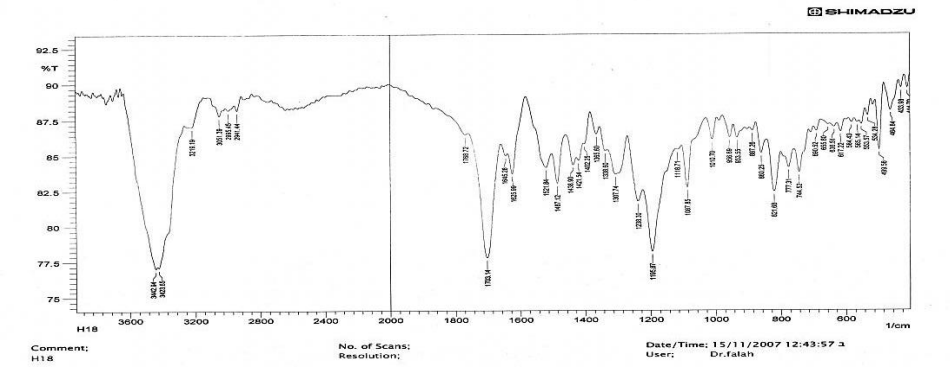
FT.IR spectrum of the compound (H7): Figure 7



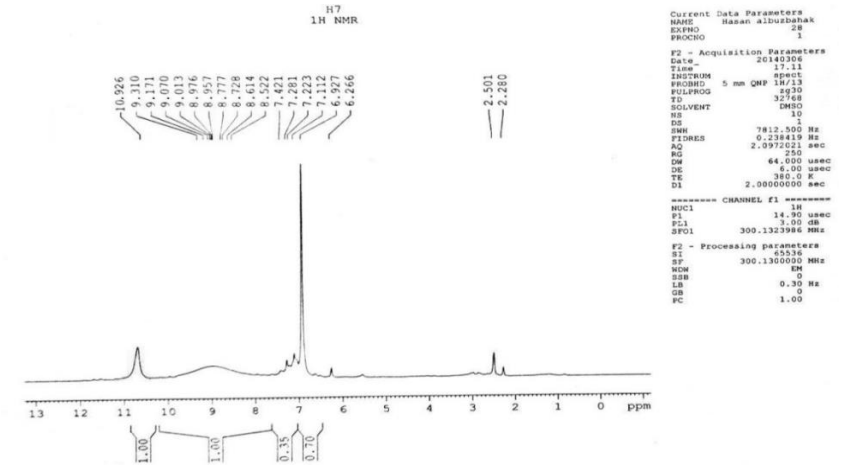
FT.IR spectrum of the compound (H8) :Figure8



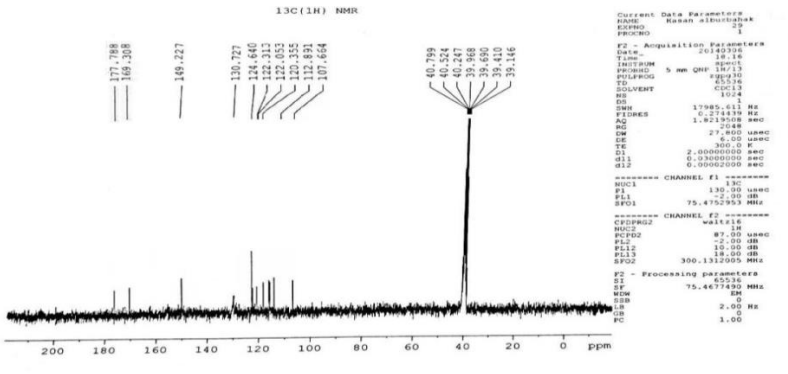
FT.IR spectrum of the compound (H9): Figure9



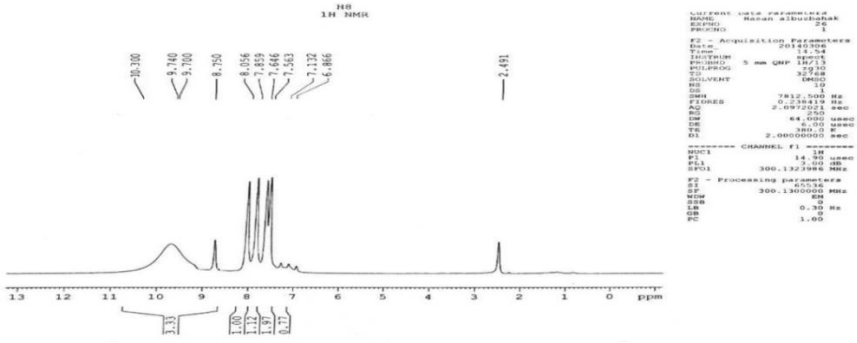
FT.IR spectrum of the compound (H10) :Figure10



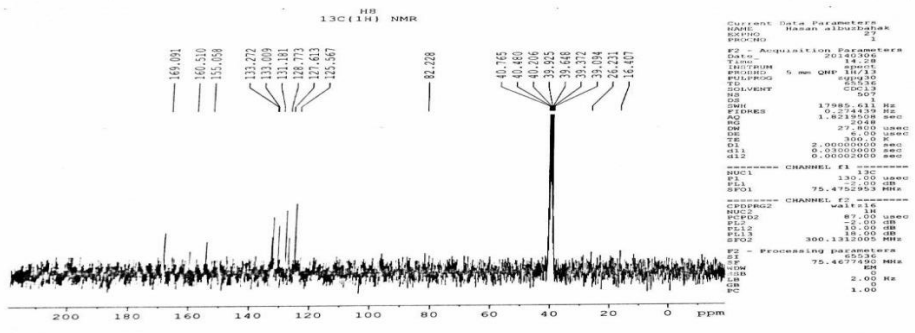
Fig(11): [1]HNMR spectrum of the compound H5



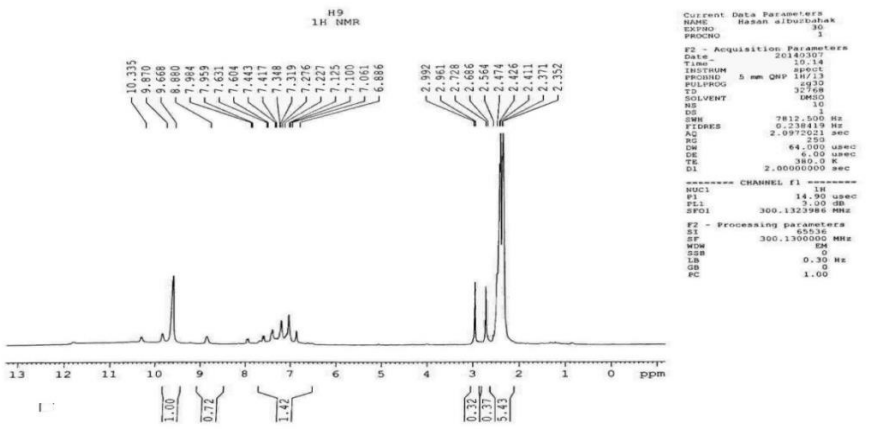
Fig(12) :[13]CNMR spectrum of the compound (H5)



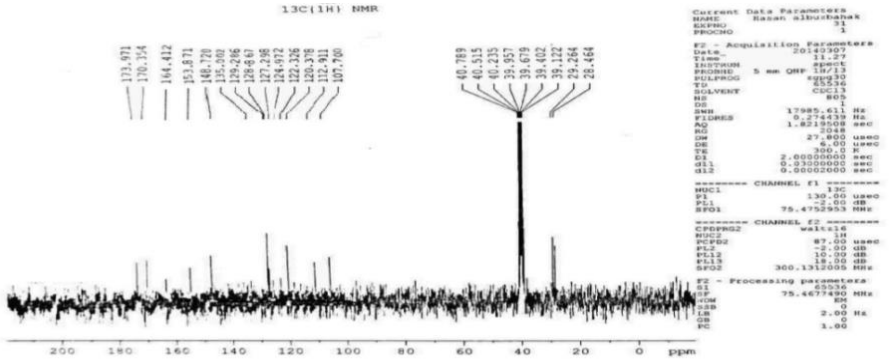
Fig(13):[1]HNMR spectrum of the compound(H6)



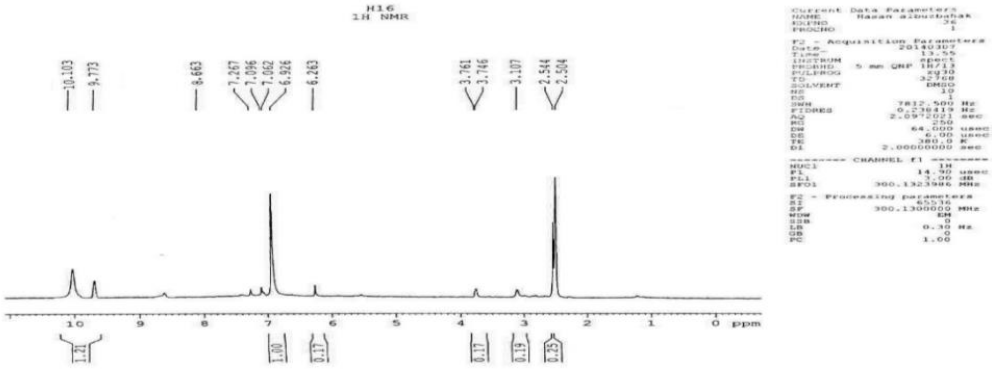
Fig(14) : [13]CNMR spectrum of the compound (H6)



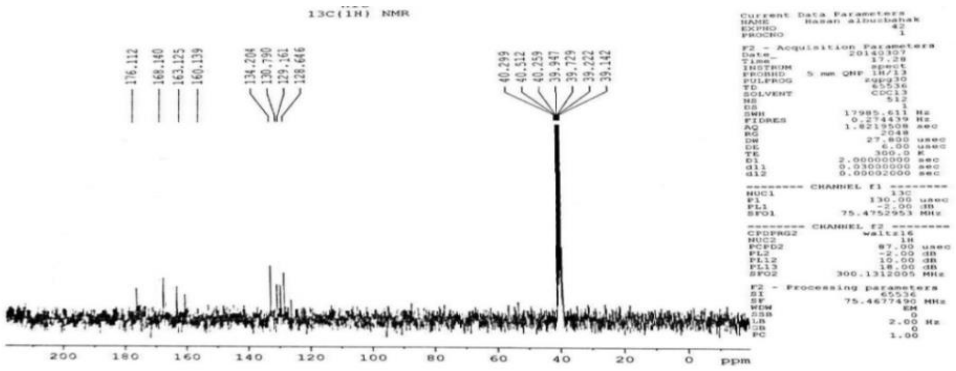
Fig(15):[1]HNMR spectrum of the compound(H7)



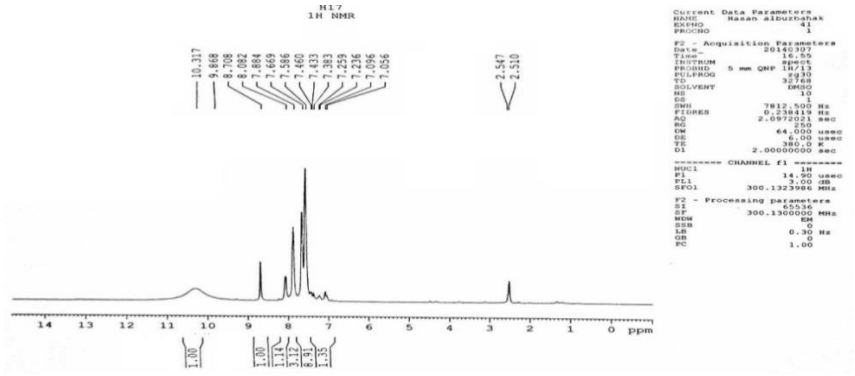
Fig(16) : ^{13}CNMR spectrum of the compound (H7**)**



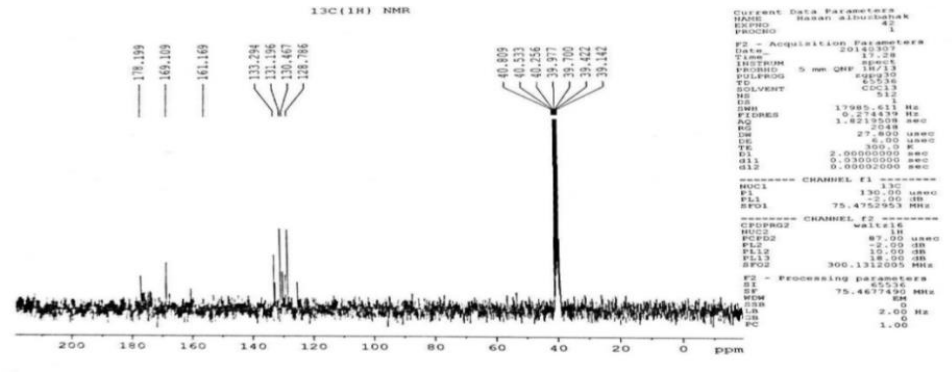
Fig(17):^{1}HNMR spectrum of the compound H8



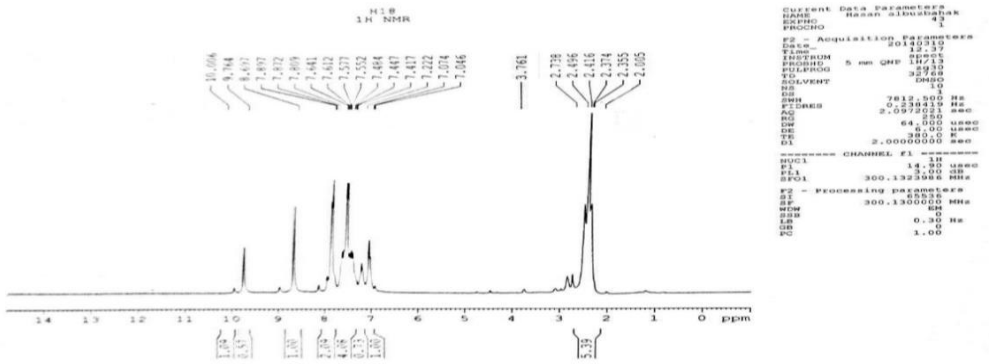
Fig(18) : ^{13}CNMR spectrum of the compound (H8)



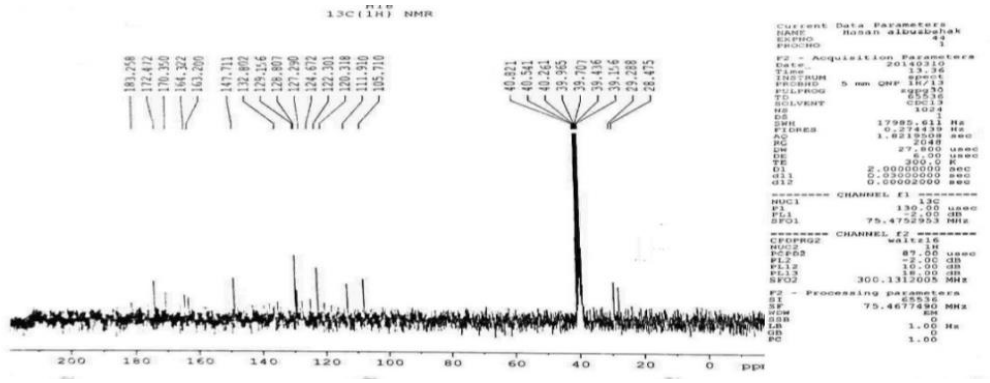
Fig(19) ^{1}HNMR spectrum of the compound(H9)



Fig(20) : ^{13}CNMR spectrum of the compound (H9)



Fig(21):^{1}HNMR spectrum of the compound(H10)



Fig(22) : ^{13}CNMR spectrum of the compound (H10)

Study of the biological activity of the compounds by paper technique disks.

Antibacterial activity has been conducted according to Kirby bauer[16] method, by using filter paper type (Whiteman NO.1) to prepared (200) pills, after that ,the pills put in the test tube with average of (5) pills for every tube then added (1 mml) from syntheses solution .

Preparing the nutrient agar:

The nutrient agar was prepared by 37 gm from agar and dissolved in one liter of distilled water and heating the mixture, the resulting agar was sterilized by the autoclave at $121C^0$ for 15 minutes .the surface of the agar was left for dryness and then used in the following work.

Preparing the bacterial inoculums

Four type of isolated and diagnosed bacterial inoculum .these bacteria were cultivated and incubated overnight at $37C^0$,then isolated by the gram stain and separated to gram positive and gram negative bacteria, in clued

1-staphylococcus :gram positive
2- Enterococcus faecalis : gram positive
3- Proteus mirabilis:gram negative
4 -klebsiella pneumonia :gram negative

Antimicrobial Activity

An antibacterial activity has been managed according to Kirby Bauer method ,the prepared compounds were projected for their antibacterial activity against gram negative bacteria(*klebsiella pneumonia, Proteus mirabilis)* , gram positive (*staphylococcus, Enterococcus faecalis,)* ,the result are given in table (2) ,The compound H_5 was given high inhibition against Proteus mirabilis*: gram negative*, staphylococcus.

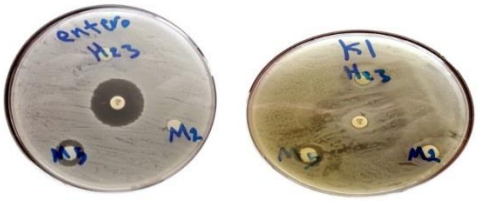
Table (2):

Type of bacteria / Comp.NO.	inhibition zone(mm) $1x1o^{-5}M$,$1x10^{-4}M$,$1x10^{-3}M$			
	klebsiella pneumonia	***Staphylococcus***	***Enterococcus faecalis***	***Proteus mirabilis***
M_1	**-**	**-**	**-**	**-**
M_2	**-**	**-**	**-**	**-**
M_3	**-**	**-**	**-**	**,-,5-**
M_4	**-, -, 5**	**-, -, 8**	**,-,5-**	**,-,4-**
H_5	**-,-,4**	**-,-,8**	**-**	**5,12,18**
H_6	**-**	**,-,5-**	**-**	**,-,5-**
H_7	**-**	**-,-,5**	**-**	**-,-,6**
H_8	**-**	**,-,6-**	**-**	**-**
H_9	**-**	**-**	**-**	**-**
H_{10}	**-**	**,-,9-**	**-,-,5**	**-**

*Staphylococcus*Proteus mirabilis

H7:N-(2-(4-fluorophenyl)-4,7-dioxo-4,7-dihydro-1,3-oxazepin-3(2H)-yl)-1H-indole-2-carboxamide

H12:N-(2-(4-chlorophenyl)-4,7-dioxo-4,7-dihydro-1,3-oxazepin-3(2H)-yl)-1H-indole-2-carboxamide



Enterococcus faecalis-klebsiell a pneumonia

M5: N'-(4-Florobenzylidene)-1H-indole-2-carbohydrazide

CONCLUSION

In the present study preparation of Some Heterocyclic compounds From Indole Derivative, which arecharacterized by the spectral measurements (IR ,^{1}H NMR ,^{13}C NMR). We conclude that it is possible to be Indole derivative antibiotics effectiveness of the compounds is vital in the futurecompared with drugs that contain derivatives.

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Synthesis And Characterization Of New Azetidinone Ring Derivative From Sulphadiazine Drug

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الخلاصة:تضمنت الدراسة تحضير مشتق حلقة الازيتيدينون الجديد من مركب الازو المحضر سابقا (N1) -4))--3-Amino-4] [methoxy-2-nitrophenyl)diazenyl)-N-(Pyrimidine-2-yl)benzen-esulfonamide, بواسطة تفاعله مع بارا-أمينو اسيتوفينون ليعطي قاعدة شف(I).من مجموعة الايمين ومجموعة الامين الاروماتية الحرة في قاعدة شف (I).حضر المشتق الحاوي على حلقات سباعية ورباعية غير متجانسة بعدة خطوات.أغلب هذه المشتقات أثبتت من خلال أطياف الأشعة تحت الحمراء وأطياف رنين البرتون والكاربون المغناطيسي.

الكلمات المفتاحية: تفاعل ستدنكر, ازيتيدينون,سلفاديازين,اوكسازبين.

Abstract

The study Included synthesis of some new azetidinone ring Derivatives from prepared Azo Compound [4-Amino-3--((4-methoxy-2-nitrophenyl)diazenyl)-N-(Pyrimidine-2-yl)benzen-esulfonamide](N1) by the reaction of it with p-amino acetophenone " to give the Schiff base (I). From the imine group and free aromatic amine group in the Schiff base (I), a derivative containing seven and four rings was prepared in several steps.Most of these derivatives were confirmed by "FT-IR,^{1}HNMR and ^{13}CNMR" spectra.

Keywords: Staudinger reaction, Azetidinone, Sulphadiazine,Oxazepine.

Introduction:

[2+2] cycloaddition or The Staudinger reaction is a reaction between imine and ketene which Represent as one of the most essential and flexible strategies for the synthesis of structurally varied derivatives of 2-azetidinone[1]. by using acid chlorides in the presence of (Et_3N) triethylamine or a-diazoketones as precursors for ketene, The Staudinger reaction gets thermally or photochemically[2]. Azetidinone is a four-membered cyclic has been known as a beneficial building block for the preparation of numerous of organic compounds by take advantage of the strain energy that linked with it[3] .Sulfadiazine is a sulfonamide antibiotic and it is recognized as one of " the World Health Organization's List of Essential Medicines".It removes bacteria that causes infections by stopping the production of folic acid into the bacterial cell, and is usually used to treat" urinary tract infections" (UTIs) and burns[4,5].1,3-Oxazepine is unsaturated cyclic compound of seven atoms, containing an oxygen replacing carbon No.1and a nitrogen replacing carbon No.3. Prepared by the peri- cyclic cycloaddition of schiff bases with phthalic, nitro phthalic , succinic and maleic anhydrides [6,7]." 2-Azetidinone" also known "β-lactam" are four-membered cyclic amide derived from 3-amino-propanoic acid[8,9].The parent heterocyclic ring of azetidinone is azetidine that is a four member heterocyclic ring system with (N) as hetero atom . 2-Azetidinone includes a carbonyl group on the second position which is one of the most common heterocyclic rings found in many antibiotics[10].Although the ring of azetidinone was known since (1907) but the realization of their chemistry began from (1947) only.These are presently used for chemotherapy of bacterial infections[11-13].

MATERIALS AND METHODS

The melting points were recorded and expressed in degree (0 ^{o}C) by using the electro thermal 9300 melting point LTD, UK. Thin layer chromotography T.L.C was performed on aluminum and glass plates coated with 0.25mm layer of silica-gel (Fluka). Some of the derivatives were detected by iodine vapor. FT-IR spectra, Fourier transform infrared (SHIMADZU, 8400) spectroph-otometer,

Japan the prang 4000-600cm-1. The samples were run in KBr disc. ^{13}C , ^{1}H-NMR spectra in (ppm) unit were operating in DMSO -*d6* as solvent using (Bruker- Ultra Shield 300 MHz Switzerland).

Synthesis of Basic compound(Azo) (N1) **[4-Amino-3--((4-methoxy-2-nitrophenyl) diazenyl)-N-(Pyrimidine-2-yl)benzenesulfonamide]**according to the previously paper[3].

Synthesis comp. (I)[4-((Z)-1-(4-aminophenyl)ethylideneamino)-3-((E)-(4-methoxy-2-nitrophenyl)diazenyl)-N-(pyrimidin-2-yl)benzenesulfonamide][14].

Azo Compound (N1) (0.43gm ,0.001 mol) was dissolved in hot concentration glacial acetic acid about (50 ml) then added to (0.164gm ,0.001 mol) of p-amino aceto phenonewas dissolved in (5 ml) of glacial acetic acid. The reaction mixture was refluxed at (100 ^{0}C) with stirring for (50) hour. The progress of the reaction was followed by T.L.C .After the completion the mixture was poured onto ice crushed. The yielded solid was filtered off and wash with (2%)Sodium bicarbonate solution and distilled water then recrystallized from abs. Ethanol. Yield,Dark red, (67%), m.p. (80-84) ^{0}C and (R_f = 0.52) (Met: Tol)(2:3).

FT-I.R spectrum (Cm^{-1})(NH_2)str. (3489-3442), (N-H) str. sulfone (3373), (C=N) str.imine (1641), (C=N) str. Pyrimidine(1678), (C-H) str . Pyrimidine(3172), (C-H) str aliphatic (2918-2850),(C=C) str. aromatic (1595-1573), (C-NO_2)(1516-1338),(N=N)(1419), SO_2(1253), (C-O) (1220).

^{1}HNMR spectrum, (δ ppm), (DMSO-*d6* MHz), **(** s,3H, CH_3,)(3.36), ,(s,3H,OCH_3)(3.713), (2H,NH_2 ,Aromatic) (s, 6.004), (Ar-H) (m 6.035-- 7.355), (Ar-H) Pyrimidine(m ,7.693-7.916) , (NH, sulfon)(s ,10.3).

^{13}C-NMR-spectrum, (δ ppm) ,(DMSO *d6*,MHz)(C)(CH_3) (24.607), (C)(OCH_3)(55.945), (C)phenyl rings (121.229, 127.576,129.544,129.895), (C)imine(142.375),(C) pyrimidine ring(105.346, 149.637).

Synthesis Comp. (II)[4-((Z)-2-(4-aminophenyl)-2-methyl-4,7-dioxo-1,3-oxazepin-3(2H,4H,7H)-yl)-3-((E)-(4-methoxy-2-nitrophenyl)diazenyl)-N-(pyrimidin-2-yl)benzenesulfonamide][15].

A mixture contain equivalent moles from Schiff base(I)(0.55g,0.001 mol) and Maleic anhydride(0.098g ,0.001mol) in dry benzene about(50mL) , was refluxed at 78 ºC for 24 hrs. the reaction was followed by T.L.C. then the mixture was allowed to cool down to room temperature . The resulting solid re-crystallized from Abs. Ethanol. The product is Brown, 68 %, m.p. (52-54)ºC (R_f = 0.53) (Met : Tol) (1: 4).

F.T.I.R spectrum(cm^{-1}) (NH_2)str. (3373-3288), (N-H) str. sulfone (3489), (C=O) lacton and (C=O) lactam str. at (1720, 1680) ,(C=N) str. Pyrimidine(1629), (C-H) str . Pyrimidine(3170), (C=C) oxazepine ring(1595),(HC=C, oxazepine ring)(3113),(C-H) str aliphatic (2916-2848),(C=C) str. aromatic (1577,1475), (C-NO_2)(1516-1338), (N=N)(1421), SO_2(1251), (C-O) (1215).

1HNMR spectrum, (δ ppm), (DMSO-*d6* MHz) (3H,OCH_3)(s 3.8),(3H,CH_3,)(s 2.086), (s 2H,NH_2 ,Aromatic) (4. 716), (d,2H,CH=CH , Oxazepine ring) (6.130-6.330), (Ar-H) (m 6.475-- 7.999), (Ar-H) Pyrimidine(m ,8.271-8.996) , (NH, sulfon)(s ,11.191).

C^{13}-NMR-spectrum, (δ ppm) ,(DMSO *d6*,MHz)(C)(CH_3) (29.491),(C)(OCH_3)(55.963-56.532),(C)(N-C-O)$_{oxazepin}$ (60.920),(C)phenyl rings (105.328,121.263, 123.717, 127.636,127.995, 129.532, 130.982,131.711, 142.330,142.423, 144.142) (C)(CH=CHcyclic)(120.673,130.125),(C) pyrimidine ring (109.623,149.650), (C)(C=O lactam)(156.990), (C)(C=O lacton)(167.284).

Synthesis comp.(III)4-((5Z)-2-(4-(4-(dimethylamino)benzylideneamino)phenyl)-2-methyl-4,7-dioxo-1,3-oxazepin-3(2H,4H,7H)-yl)-3-((E)-(4-methoxy-2-nitrophenyl)diazenyl)-N-(pyrimidin-2-yl)benzenesulfonamide [16]: This Schiff base was prepared from the reaction of comp. (II) (0.644gm ,0.001 mole), with(0.15gm, 0.001mole)of (p-N,N-dimethyl benz aldehyde) in (25ml) absolute ethanol and (2) drops of glacial acetic acid. This mixture was refluxed for (30)hrs at (80 ºC). The progress of the reaction was followed by TLC. After the completion The mixture was cooled down to room temperature then the solid rercystallized from absolute ethanol . T.L.C. (Met:Tol) (1: 4) R_f = 0.64 , Sienna ,50 % , m.p.(200 ºC decomp.).

F.T.I.R spectrum(cm^{-1})(N-H) str. sulfone (3427),(C-H) aliphatic str.(2927-2854), (O-C=O) lacton str. (1726), (N-C=O) lactam str. (1691),(C=N)imine group interference with (C=C) oxazepine ring (1577), (C=N) Pyrimidine str. (1660), (C=C) str. aromatic (1533,1498), (C-NO_2)(1514-1381), (N=N)(1427), SO_2(1240), (C-O).

1HNMR spectrum(δ ppm), (DMSO-*d6* MHz),(s 6H, N-$(CH_3)_2$) (3.022), (s 3H,CH_3,)(1.864), (3 H,OCH_3)(s 3.854), (d,2H,CH=CH , Alkene) (6.642-6.804), (Ar-H) (m 6.913-7.926), (Ar-H) Pyrimidine(m ,8. 089-8.505) , (1H, CH=N) (s 8.614), (NH, sulfon)(s ,11.039).

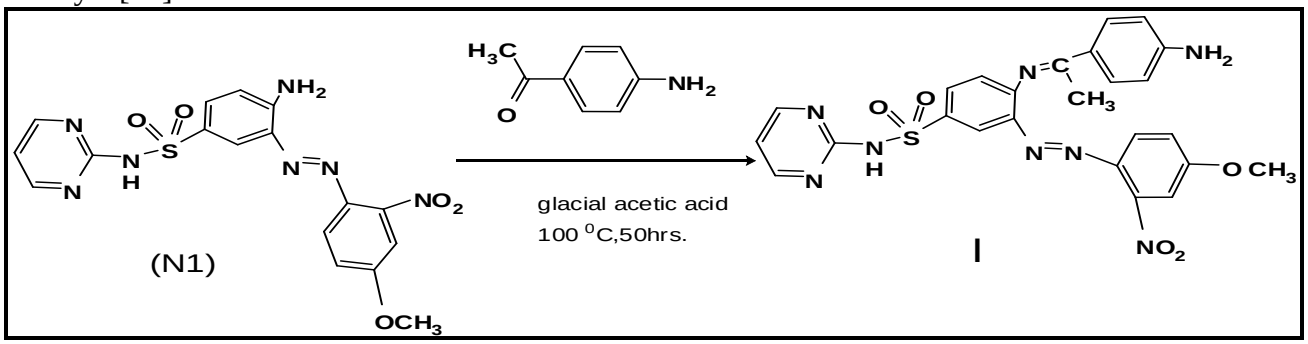
C^{13}-NMR-spectrum, (δ ppm) ,(DMSO *d6*,MHz),(C) (CH_3)(24.647),(C)(N$(CH_3)_2$)(26.865),(C)(OCH_3)(55.978).(C)(C=O lactam and lacton) (169.410),(C)(C=C cyclic)(121.273, 129.924) ,(C) imine group (142.426),(C)(N-C-O)$_{oxazepin}$(105.366), (C) pyrimidine ring(149.667,118.624),(C)phenyl rings(127.622,129.566, ,131.988,144.128).

Synthesis comp.(IIII)[4-((Z)-2-(4-(3-chloro-2-(4-(dimethylamino)phenyl)-4-oxoazetidin-1-yl)phenyl)-2-methyl-4,7-dioxo-1,3-oxazepin-3(2H,4H,7H)-yl)-3-((E)-(4-methoxy-2-nitrophenyl)diazenyl)-N-(pyrimidin-2-yl)benzenesulfonamide][17].

To a mixture of Schiff bases(III) (0.775gm,0.001 mol) in dioxane (30ml)and Et_3N (0.35 ml, 0.0025 mol), chloro acetyl chloride (0.2 ml, 0.0025 mol) was added drop-wise at(5-10 ^oC). The reaction mixture was stirred for (48 hrs) at room temperature ,then poured into crushed ice to dissolveThe salt(Et_3N^+ HCl) tri ethyl amine hydrochloride. The mixture was extracted by using chloroform($CHCl_3$) ,then the solvent was evaporated and the yield was re-crystallized from absolute ethanol. the reaction was monitored by (T.L.C).

RESULTS AND DISCUTION

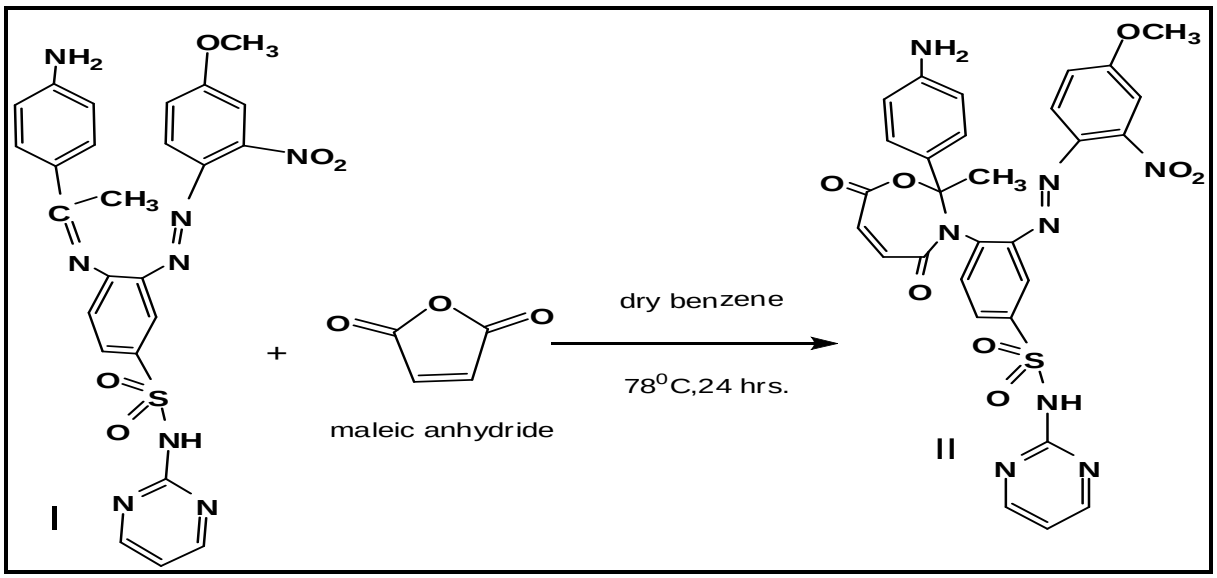
In this study, the derivatives prepared from Azo comp. were identified by comparing their spectra. The derivative(I) was prepared from Azo comp. (N1) with "p-amino acetophenone " via the condensation reaction by using glacial acetic acid as solvent. Here the reaction time about (50 hrs.)is longer than in the case of aldehyde In other words, in the condensation reaction the ketone react more slowly than the aldehyde, due to that the reaction centre of ketone are sterically more hindered than that of aldehyde, also the carbon of ketone less "electrophilic" compared to an aldehyde[18].



Scheme 1: preparation of Schiff Base (I)

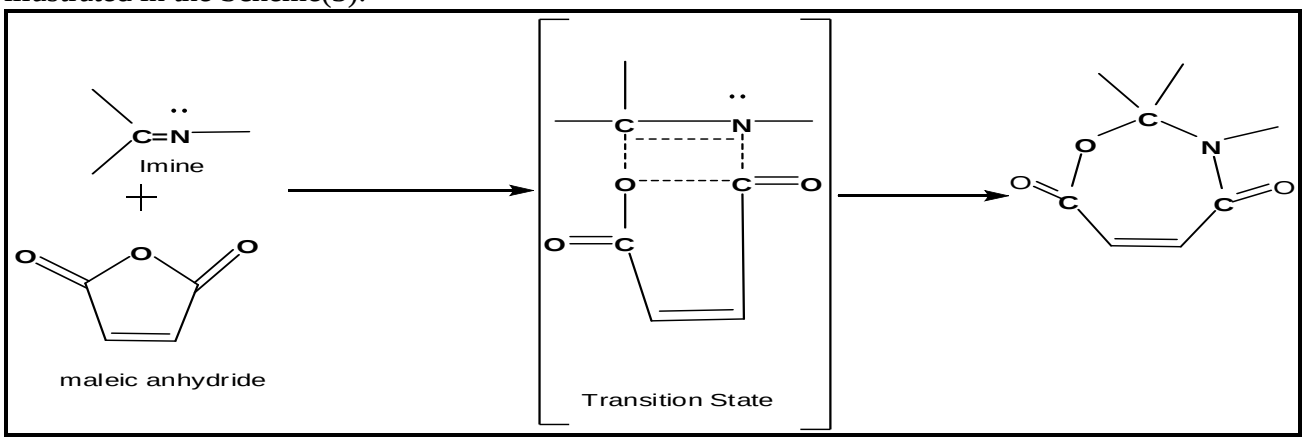
By FT-IR spectrum appearance the absorption band of imine group (C=N) at (1641) cm^{-1}, (C=N) str. Pyrimidine at(1678) cm^{-1} and appearance the low intensity absorption bands than in comp. (N1) attributed to aromatic amine and (NH)sulfon amide at (3489-3442) & (3373) cm^{-1} respectively. Moreoverappearancethe stretching absorption of(C-H) aliphatic at(2918-2850) cm^{-1}. ^{1}H-NMR spectrum(ppm)(DMSO-*d6*) gives (s,2H, NH_2) at (6.004) , (s,3H, CH_3) which linked with imine group at (2.498), (s,3H,OCH_3) at (3.713) and(s,1H,NH) sulfon amide at(10.3). ^{13}C-NMR spectrum(ppm)(DMSO-*d6*) for the Schiff base (I) gives (C) of Methyl group at (24.607), (C) of the Methoxy group at (55.945) and (C)imine group at (142.375).

The derivative(II) was prepared via [2+5] cyclo addition reaction between Schiff base (I) and maleic anhydride in dry benzene as solvent with reflux at 78^{0}C for (24)hrs.



Scheme 2: preparation of Comp. (II)

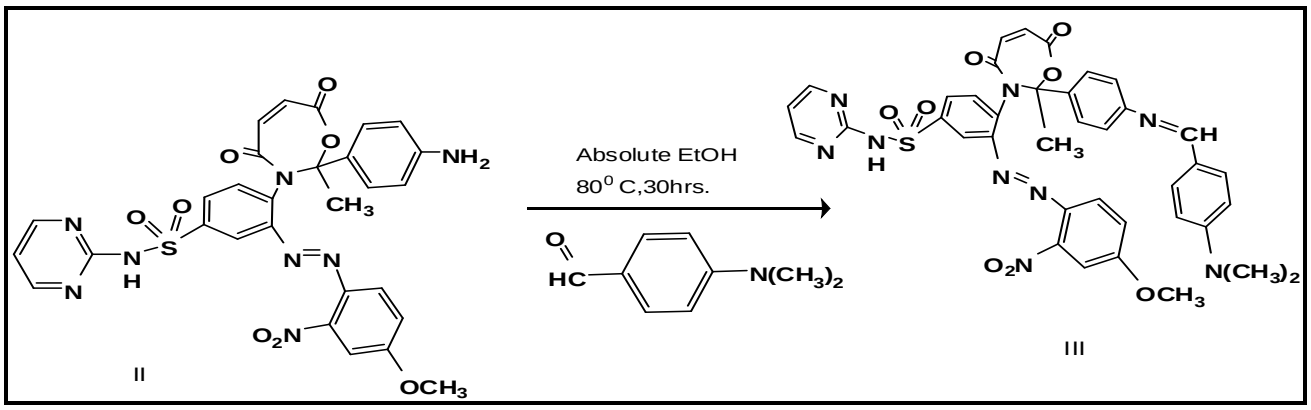
The proposed mechanism[19] for the addition of Maleic anhydride to the imine group(C=N) is illustrated in the Scheme(3).



Scheme(3):Mechanism formation of oxazepine ring

The derivative identified by FT-IR,^{1}H-NMR and ^{13}C-NMR techniques. in FT-IR spectrum observed appearance the stretching vibration of lacton and lactam for Oxazepine ring at (1720,1680) cm^{-1}respectivly and the two stretching bands of aromatic amine at lower wave number in(3373-3288) cm^{-1} while the band of (NH)sulfon amide appeared at higher wave number in(3489) cm^{-1}.(C=C) olefinic of oxazepine ring at (1595) cm^{-1}. ^{1}H-NMRspectrum (ppm)(DMSO-*d6*) shows the signals at(2.066),(3.8)and(4. 716) due to (s,3H,CH_3) linked with oxazepine ring ,(s,3H,OCH_3) and (s,2H,NH_2) respectively. The olefinic protons of oxazepine ring showed at (6.130-6.330)and (s,1H,NH-sulfonamide) at(11.191). ^{13}C-NMR spectrum (ppm)(DMSO-*d6*) gives signals at(29.491,55.963-56.532, 60.920) due to (C) atoms of (CH_3) Associated with oxazepine ring ,(OCH_3) and (N-C-O) oxazepine ring respectively. (C) of carbonyl lacton and lactam Oxazepine ring at(167.284,156.990). The signal of carbonyl lacton isHigher value because of link it with (O) atom for Oxazepine ring.(C=C cyclic)(130.125 for (C) close to lacton , 120.673 for (C) close to lactam)[20,21].

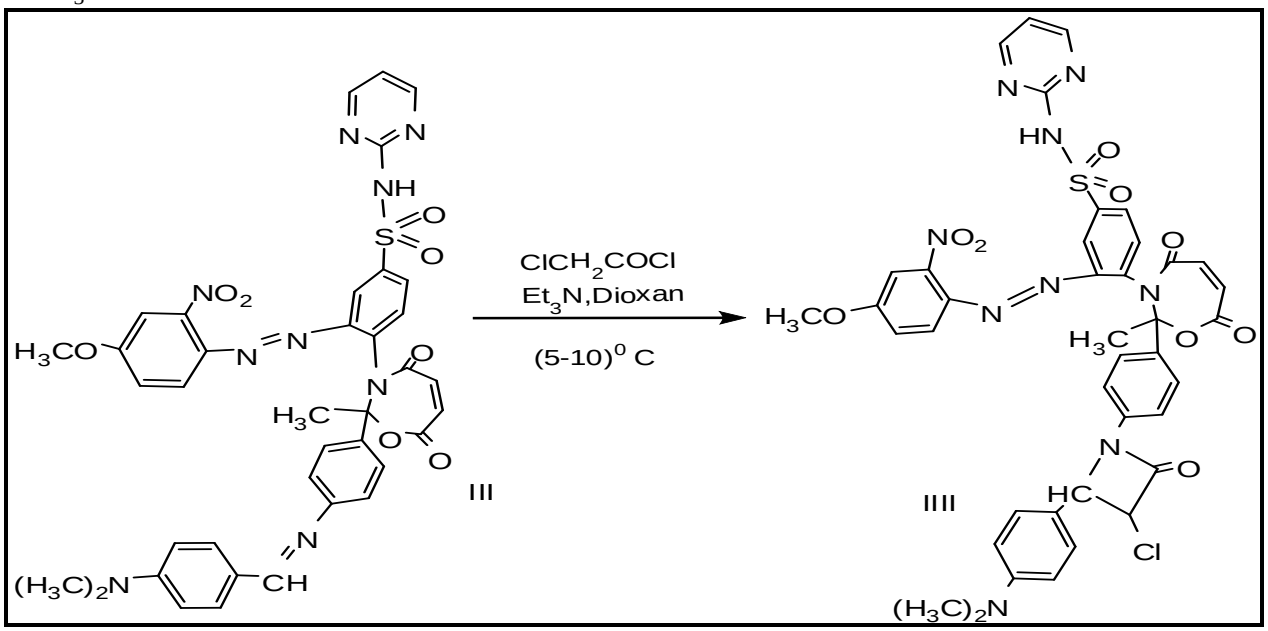
The Schiff base(III) was prepared through condensation reaction between the derivative (II)and (p-N,N-Di methyl benzaldehyde) in absolute ethanol with drops of glacial acetic acid.



Scheme 4: preparation of Comp. (III)

The derivative identified by FT-IR spectrum through disappearance the two vibration bands of amine group and appearance the vibration band for imine group interference with band of (C=C $_{Oxazepine}$) olefinic at(1577) cm^{-1}because of many functional groups in same position from spectrum , expecting that it appeared under other bands which in same position such as (C=N) pyrimidine or (C=C $_{Oxazepine}$) due to crowding of functional groups in this area. in addition to appearance sholder band due to the lacton oxazepine ring at (1726) cm^{-1}while the lactam appeared at(1691) cm^{-1}.the band at(1660) cm^{-1} belong to (C=N)pyrimidine also the band of (NH)sulfon amide was appeared at (3427) cm^{-1}. ^{1}H-NMR spectrum(ppm)(DMSO-*d6*) shows (s,6H,N-$(CH_3)_2$) at(3.022), (s, 3H, CH_3,) linked with Oxazepine ring at(1.864), (s,3 H ,OCH_3) at(3.854) , (CH=CH olifinic cyclic) at(6.642-6.804) and (s,1H ,NH- sulfonamide) at(11.039).[13] C-NMR spectrum(ppm)(DMSO-*d6*) gives (C)atoms for (CH_3),($N(CH_3)_2$) and (OCH_3)at(24.647, 26.865and 55.978) respectively, (C) carbonyl lacton and lactam at (169.410), (C=C cyclic)at (121.273, 129.924) and (C) (C=N) group at(142.426).

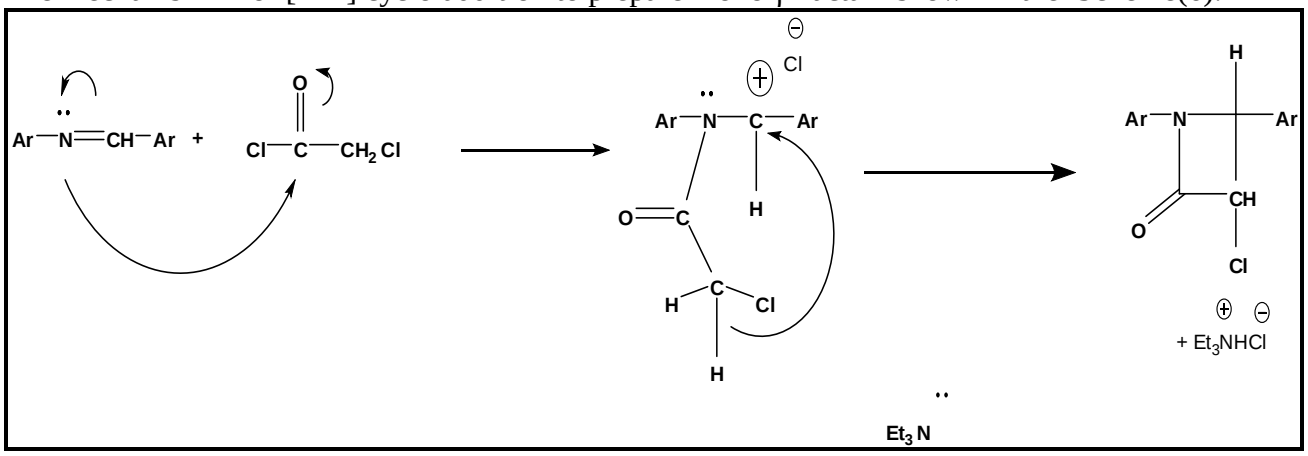
The derivative (IIII)was prepared by[2+2] cycloaddition reaction from (III),chloro acetyl chloride and Et_3N in dioxane.



Scheme 5: preparation of Comp. (IIII)

The chemical structure of (IIII) was confirmed through FT-IR spectrum by appearance the stretching vibration of carbonyl lactam (four membered ring) and carbonyl lacton of oxazepine ring at high wave number (1757) cm^{-1},while the carbonyl lactam in oxazepine ring appeared at (1691) cm^{-1}, the band at(1670) cm^{-1} belong to (C=N)pyrimidine. the band of (C=C $_{Oxazepine}$) olefinic at(1620) cm^{-1}also the band of (NH)sulfon amide was appeared at (3408) cm^{-1}.^{1}H-NMR spectrum(ppm)(DMSO-*d6*) figure(3-50) gives (s,6H,N-$(CH_3)_2$) at(3.523) , (s, 3H,CH_3) at(1.255),

(s,3H,OCH_3) at(3.865), (d,1H ,N-CH-) at (4.340) ,small (d,1H ,O=C-CH-Cl)at about(4.8), (HC=CH cyclic)olifinic small signals at about(6.8) and (s,1H ,NH- sulfonamide)at (10.494).
The mechanism[14] of [2+2] cyclo addition to prepare mono-β-lactam shown in the Scheme(6).



Scheme 6: mechanism of [2+2] cyclo addition

Table(1) some physical properties of prepared derivatives

Comp.	m.p.°C	Yield%	Color	M .Wt	M.F	*R f* of T.L.C.
I	80-84	67	Dark red	546	$C_{25}H_{22}N_8O_5S$	0.52 (*Met: **Tol)2:3
II	52-54	68	Brown	644	$C_{29}H_{24}N_8O_8S$	0.53 (Met: Tol)1:4
III	200 decomp.	50	Sienna	775	$C_{38}H_{33}N_9O_8S$	0.64 (Met: Tol)1:4
IIII	280 decomp	49	Brown	851.5	$C_{40}H_{34}ClN_9O_9S$	0.54 (Met: Tol)1:4

* Methanol , **Toluene

Table(2) FT-IR bands of prepared derivatives

Comp.	FT-IR(cm^{-1})
I	(NH_2)str. (3489-3442), (N-H) str. sulfone (3373), (C=N) str.imine (1641), (C=N) str. Pyrimidine(1678), (C-H) str . Pyrimidine(3172), (C-H) str aliphatic (2918-2850),(C=C) str. aromatic (1595-1573), (C-NO_2)(1516-1338),(N=N)(1419), SO2(1253), (C-O) (1220)
II	(NH_2)str. (3373-3288), (N-H) str. sulfone (3489), (C=O) lacton and (C=O) lactam str. at (1720, 1680) ,(C=N) str. Pyrimidine(1629), (C-H) str . Pyrimidine(3170), (C=C) oxazepine ring(1595),(HC=C, oxazepine ring)(3113),(C-H) str aliphatic (2916-2848),(C=C) str. aromatic (1577,1475), (C-NO_2)(1516-1338), (N=N)(1421), SO_2(1251), (C-O) (1215).
III	(N-H) str. sulfone (3427),(C-H) aliphatic str.(2927-2854), (O-C=O) lacton str. (1726), (N-C=O) lactam str. (1691),(C=N)imine group interference with (C=C) oxazepine ring (1577), (C=N) Pyrimidine str. (1660), (C=C) str. aromatic (1533,1498), (C-NO_2)(1514-1381), (N=N)(1427), SO_2(1240), (C-O) (1180).
IIII	(N-H) str. sulfone (3408),(C-H) aliphatic str.(2972-2926), (C=O) str. (1757) including (β-lactam ring and lacton oxazepine), lactam oxazepine ring (1691),(C=C)str. oxazepinering(1620),(C=N)str.pyrimine ring(1670),(C=C) str. aromatic(1593),(C-NO_2)(1519-1354), (N=N)(1458-1444), (C-Cl)(881).

Table(3) ^{1}H-NMR Signals of prepared derivatives

Comp.	^{1}H-NMR(ppm)
I	(s,3H, CH_3,)(3.36), ,(s,3H,OCH_3)(3.713), (2H,NH_2 ,Aromatic) (s, 6.004), (Ar-H) (m 6.035-- 7.355), (Ar-H) Pyrimidine(m ,7.693-7.916) , (NH, sulfon)(s ,10.3)
II	(3H,OCH_3)(s 3.8),(3H,CH_3,)(s 2.086), (s 2H,NH_2 ,Aromatic) (4. 716), (d,2H,CH=CH , Oxazepine ring) (6.130-6.330), (Ar-H) (m 6.475-- 7.999), (Ar-H) Pyrimidine(m ,8.271-8.996) , (NH, sulfon)(s ,11.191).
III	(s 6H, N-(CH_3)$_2$) (3.022), (s 3H,CH_3,)(1.864), (3 H,OCH_3)(s 3.854), (d,2H,CH=CH , Alkene) (6.642-6.804), (Ar-H) (m 6.913-7.926), (Ar-H) Pyrimidine(m ,8. 089-8.505) , (1H, CH=N) (s 8.614), (NH, sulfon)(s ,11.039)
IIII	(6H, N-(CH_3)$_2$) (s 3.523), (3H,CH_3)(s 1.255), (3 H,OCH_3)(s3.865),(1H,N-CH-$_{lactam}$)(d4.340),(1H,O=C-CH-Cl_{lactam})(d,4.8), small signals about(6.8)(HC=CH cyclic)olifinic.(1H)(NH sulfon)(s,10.494),(Ar-H) (m 7.339-7.948), (NH, sulfon)(s ,11.039)

Table(4) ^{13}C-NMR Signals of prepared derivatives

Comp.	C-NMR(ppm)[13]
I	(C)(CH_3) (24.607), (C)(OCH_3)(55.945), (C)phenyl rings (121.229, 127.576,129.544,129.895), (C)imine(142.375),(C) pyrimidine ring(105.346, 149.637).
II	(C)(CH_3) (29.491),(C)(OCH_3)(55.963-56.532),(C)(N-C-O)$_{oxazepin}$ (60.920),(C)phenyl rings (105.328,121.263, 123.717, 127.636,127.995, 129.532, 130.982,131.711, 142.330,142.423, 144.142) (C)(CH=CHcyclic)(120.673,130.125),(C) pyrimidine ring(109.623,149.650), (C)(C=O lactam)(156.990), (C)(C=O lacton)(167.284).
III	(C) (CH_3)(24.647),(C)($N(CH_3)_2$)(26.865),(C)(OCH_3)(55.978).(C)(C=O lactam and lacton) (169.410),(C)(C=C cyclic)(121.273, 129.924) ,(C) imine group (142.426),(C)(N-C-O)$_{oxazepin}$(105.366), (C) pyrimidine ring(149.667,118.624),(C)phenyl rings(127.622,129.566, ,131.988,144.128).

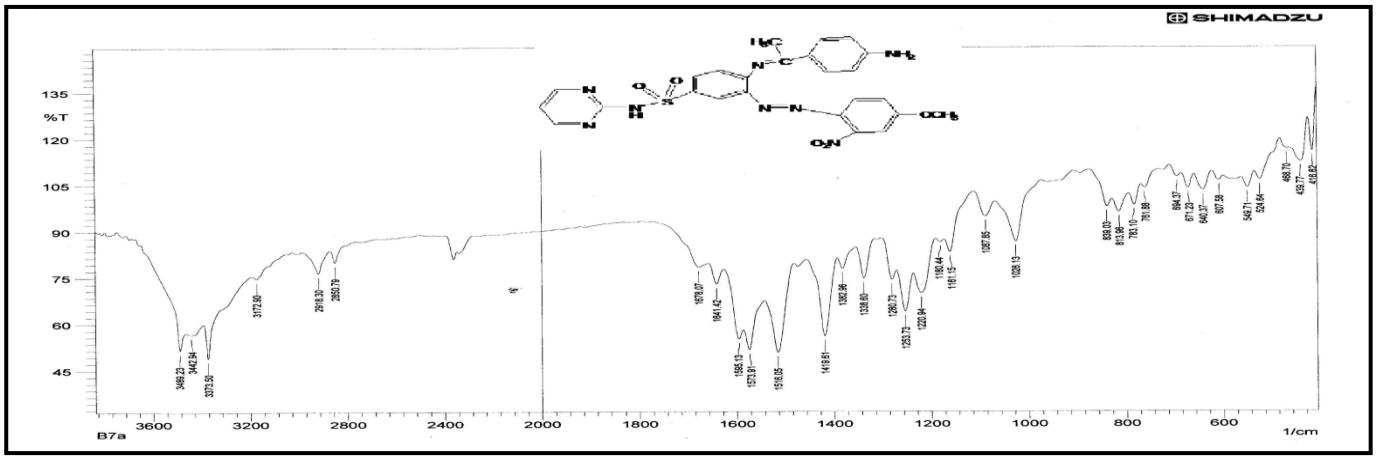


Figure (1) FT-IR spectrum of Schiff base(I)

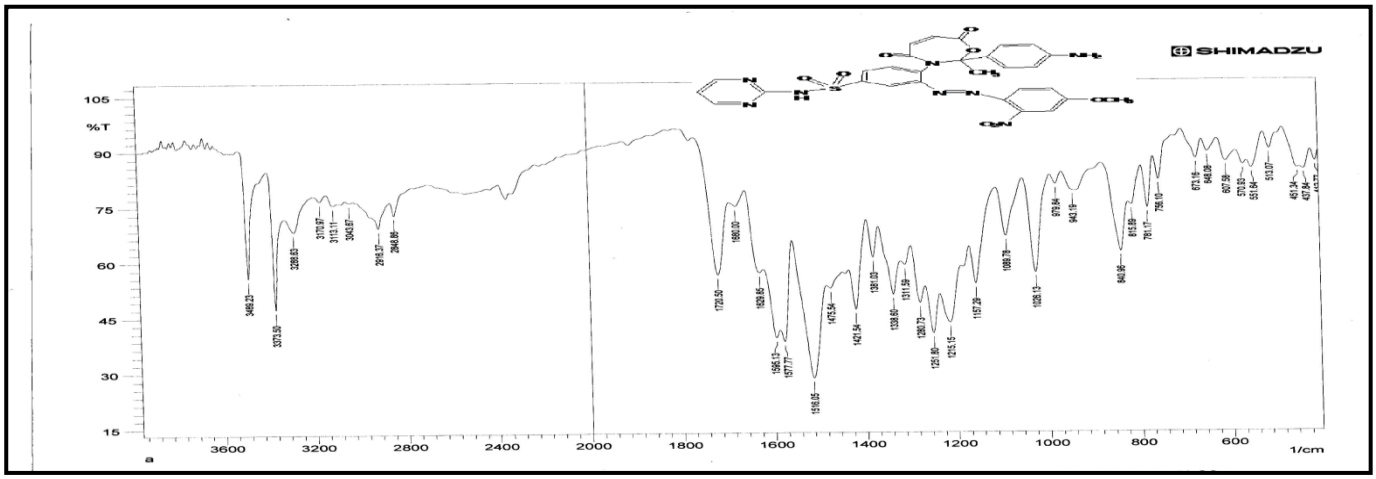


Figure (2) FT-IR spectrum of Oxazepine ring derivative(II)

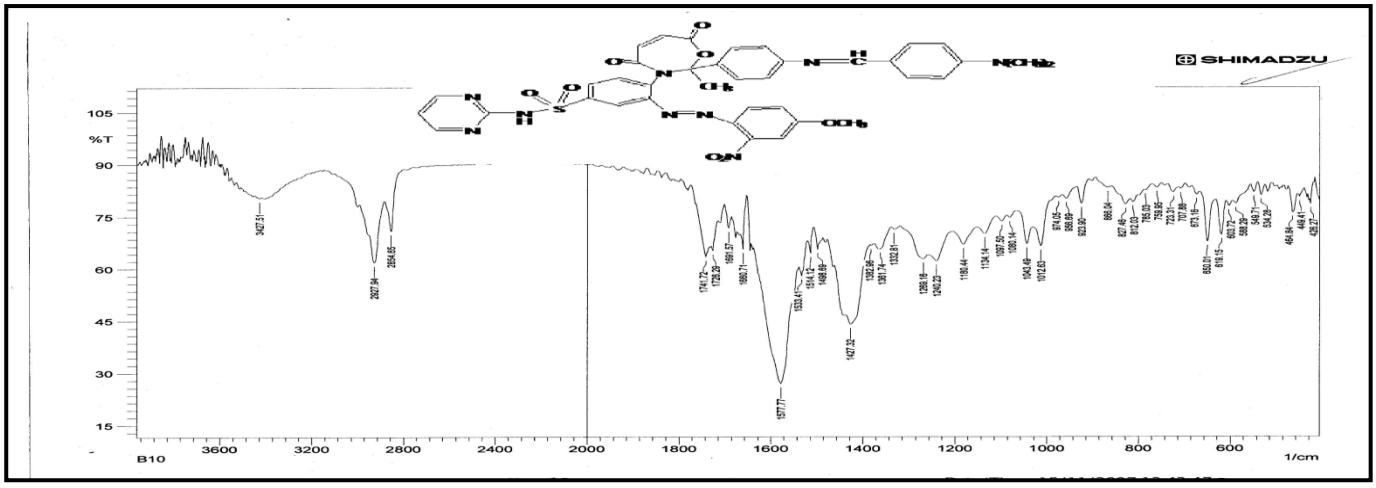


Figure (3) FT-IR spectrum of Schiff base(III)

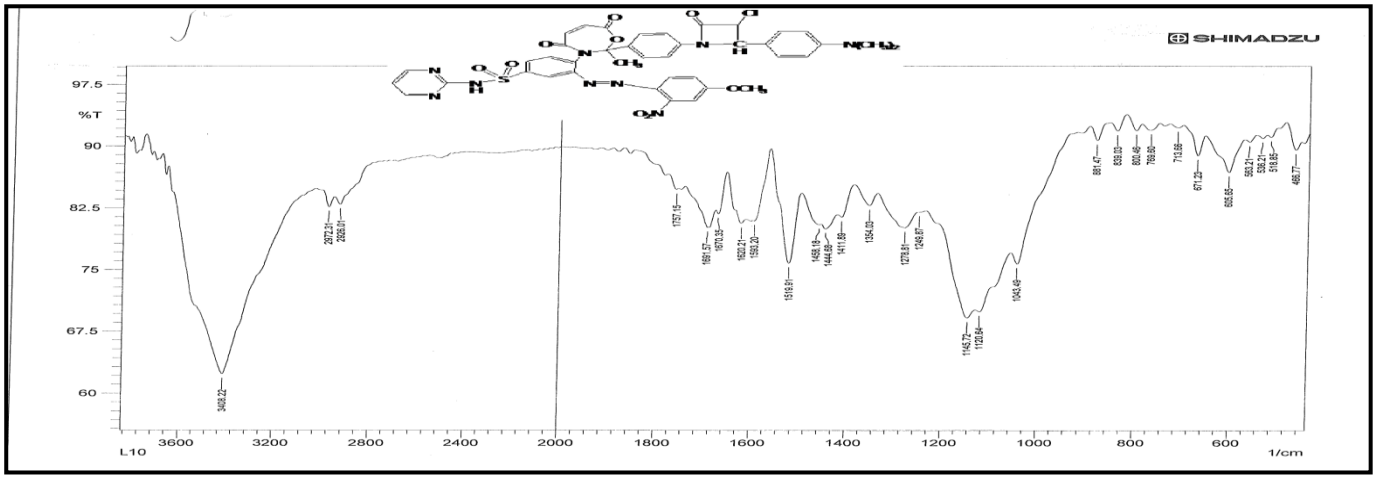


Figure (4) FT-IR spectrum of Lactam ring derivative(IIII)

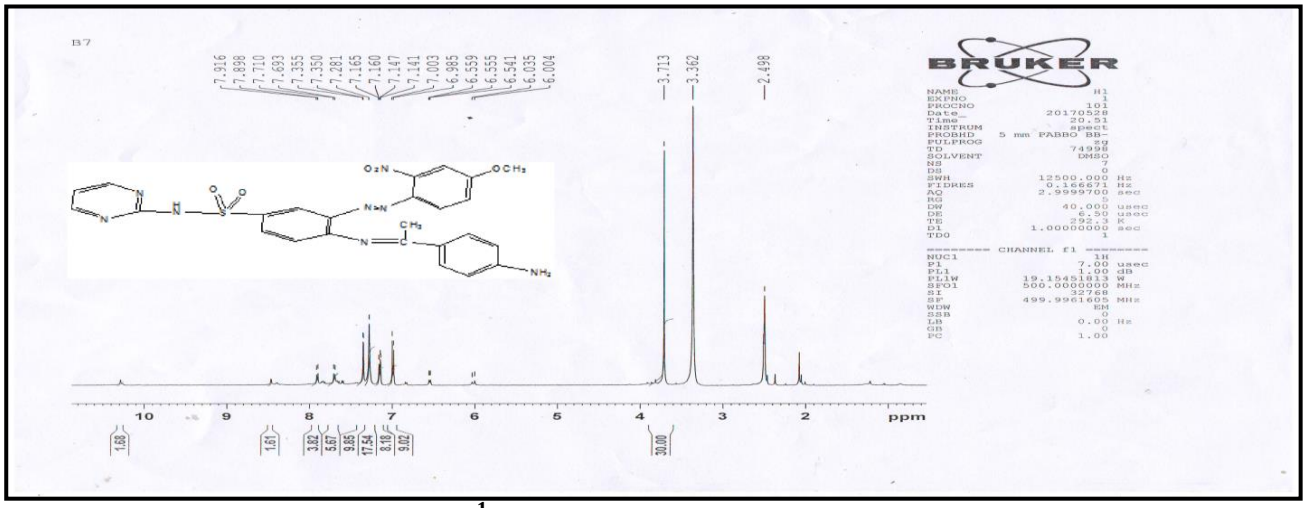


Figure (5) ^{1}H-NMR spectrum of Schiff base(I)

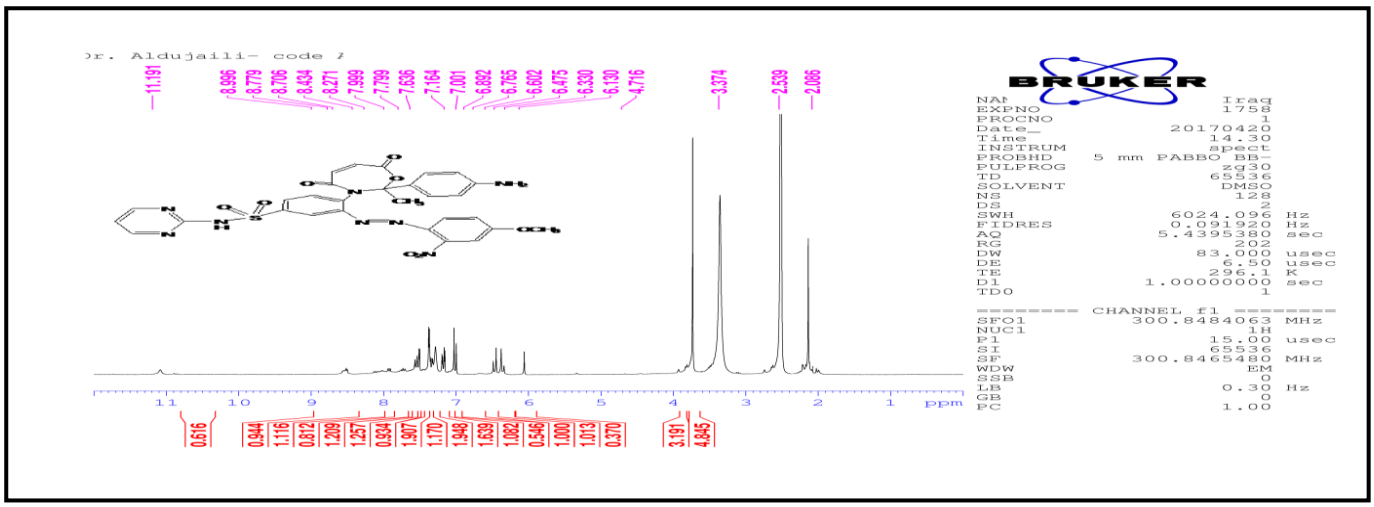


Figure (6) ^{1}H-NMR spectrum of Oxazepine ring derivative(II)

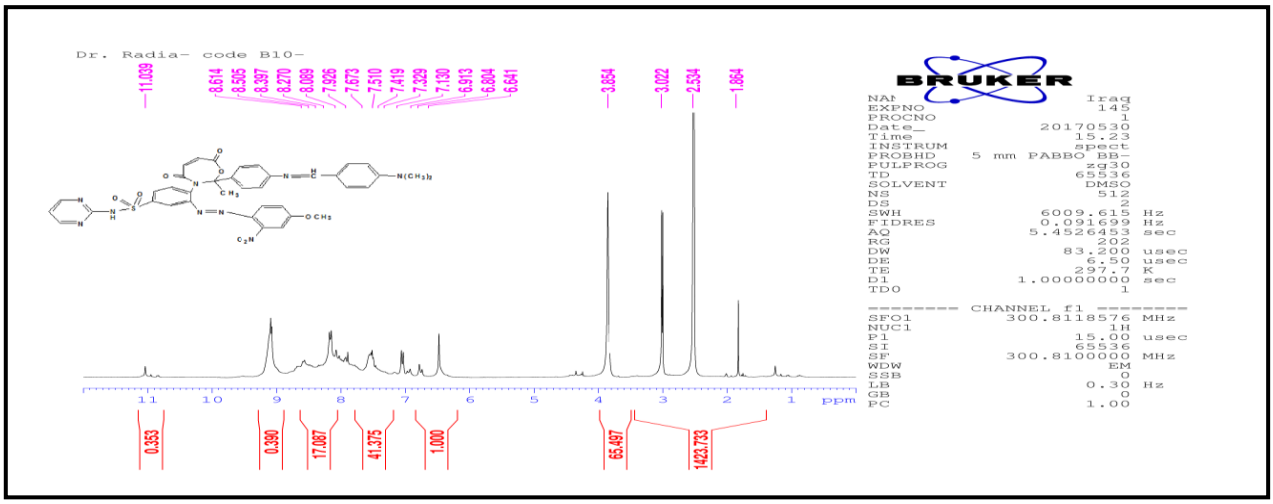


Figure (6) ^{1}H-NMR spectrum ofSchiff base(III)

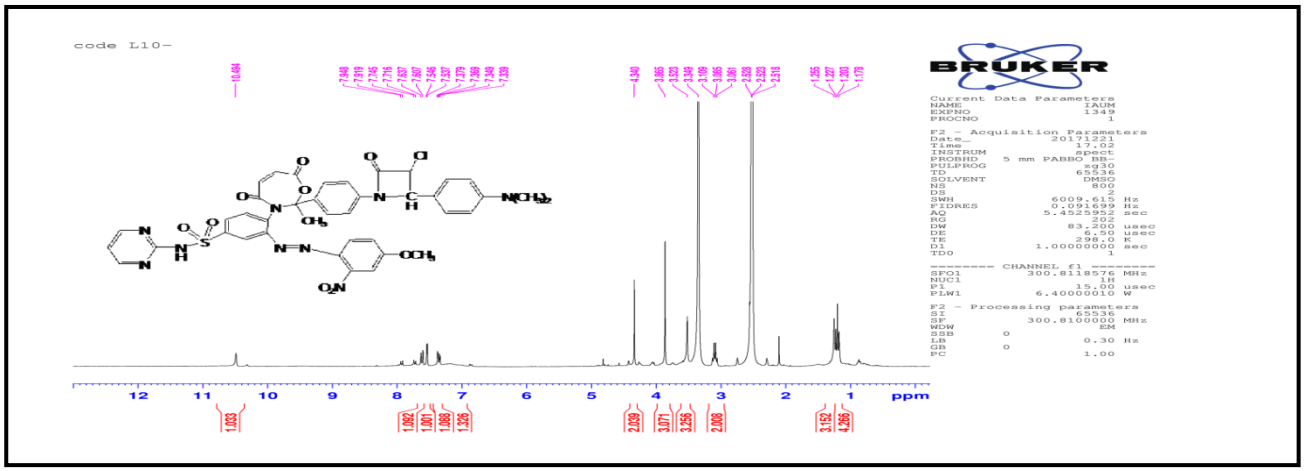


Figure (7)^{1}H-NMR spectrum ofLactam ring derivative(IIII)

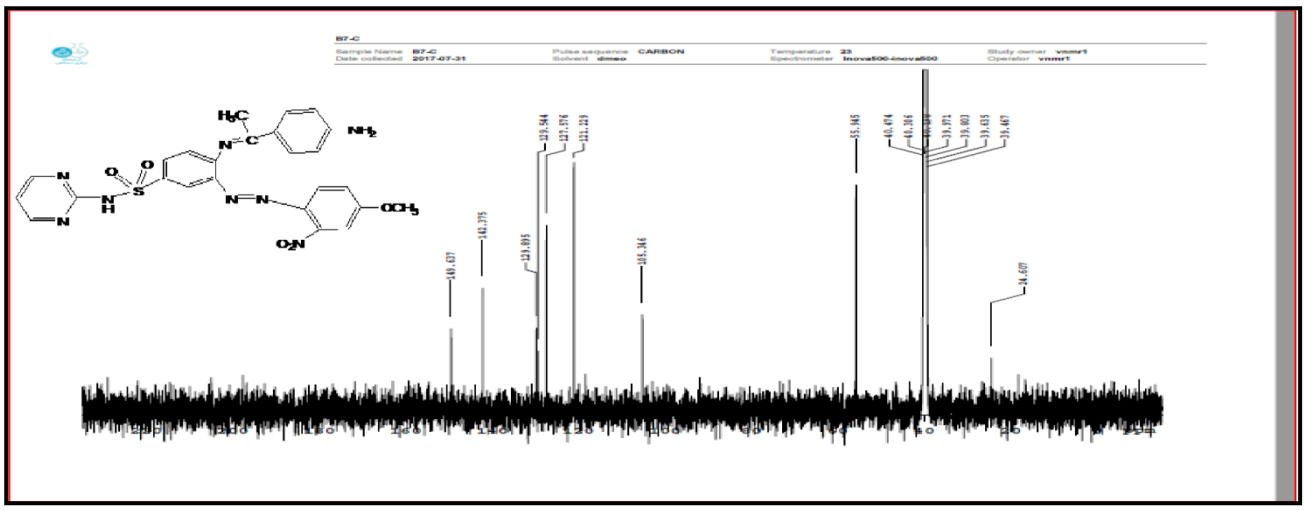


Figure (8) ^{13}C-NMR spectrum of Schiff base(I)

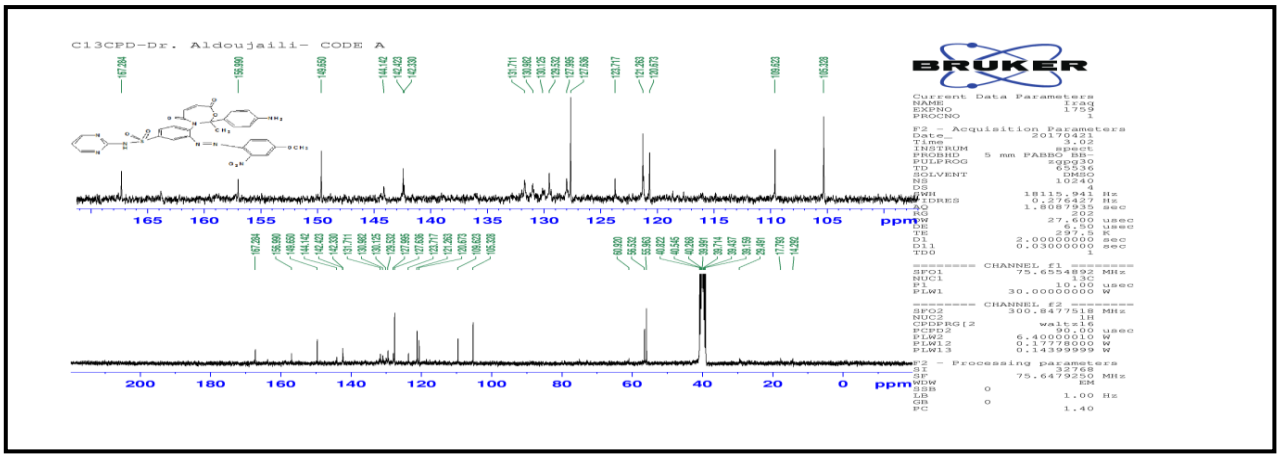


Figure (9) ^{13}C-NMR spectrum of Oxazepine ring derivative(II)

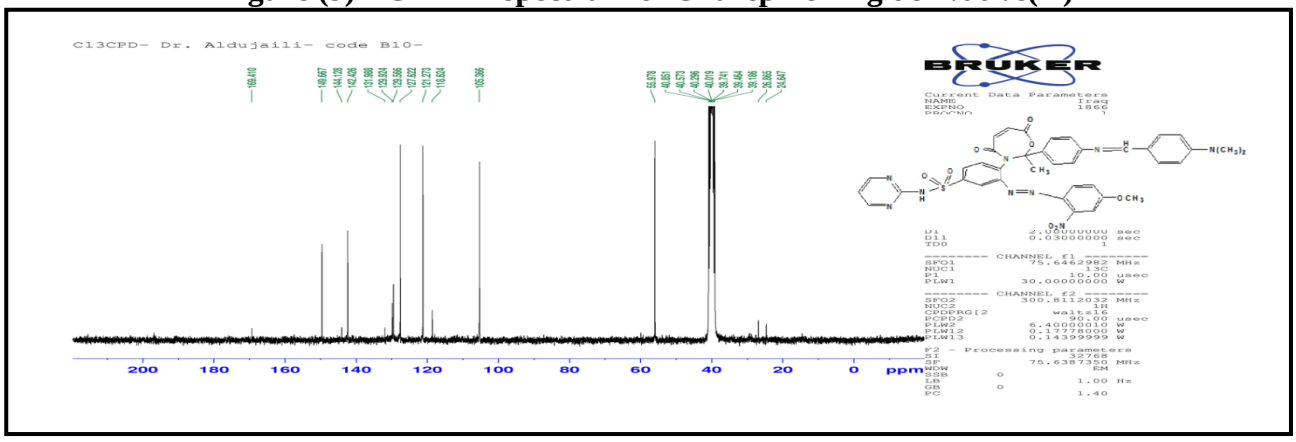


Figure (10) ^{13}C-NMR spectrum ofSchiff base(III)

CONCLUSION

In this study we are reported synthesis of many β-Lactam derivatives via Staudinger Reaction[2+2]cyclo addition. The work included preparation of Azo-Schiff base compounds from sulphadiazine as the first step then cyclization process for these compounds by using chloro acetyl chloride in the basic medium and low temp. (0-10) °C These derivatives were found to be stable at room temperature .These derivatives confirmed from spectral data analysis; FT-IR ,H^1NMR andC^{13}NMR.

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Synthesis, Characterization and Study of Antibacterial and Electrical Conductivity of New Schiff Bases from Thiophene -3-Carboxyaldehyde and Two Different Para Substituted Aniline

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Abstract

Schiff base derived from (3-thiophene carboxyaldehyde with p-amino aniline, and 4-N, N-diethyl aniline) has been prepared and characterized by Infrared and, and C.H.N. elemental analysis. Results of the in vitro antibacterial activity showed that the N-[(thiophene-3-yl) methylidene]-4 (N, N diethylamino) benzene (compound A) was found to be more active than N-[(thiophene-3-yl) methylidene] -4-nitrobenzene (compound B) against most pathogenic bacterial strain for both of Gram-positive bacteria, *Staphylococcus aureus* and Gram-negative bacteria, such as *E. coli* under study. Some of these compounds showed potential antimicrobial activities. In addition, the electrical conductivity of new Schiff bases was characterized; new Schiff bases were showed high electrical conductivity and that increase of ability to prepare anew-organic diodes.

Keywords: Schiff base, antibacterial, electrical conductivity, pathogenic bacteria.

1. Introduction

Compounds of Schiff base produced from aromatic amines with aldehydes by condensation have a enormous range of applications [1-4] in many biological field [5-9], inorganic ligands applications [10-11] and analytical chemistry as chelating compounds for [121]. In the latest years, Schiff bases from thiophene compounds have been getting larger profits in conjugated organic materials due to their attractive electronic properties [13,14]Many studies on small molecules have been focused on thiophene [15], which has been used as an effective p-type semiconductor for organic field-effect transistors. Schiff bases remained an important area of research due to their simple synthesis, and wide applications. In this, work the synthesis and characterization of the new Schiff bases obtained by reaction of 3-thiophene carboxyaldehyde with 4-nitroaniline and 4-N, N-dimethyl aniline. Because of the development of resistance to the major classes of antibacterial materials are renowned as a serious health worry, the study for new antibacterial materials with different action modes has constantly continue essential. Due to the development of resistance of some types of bacteria to chemical treatments, this is the reason for the constant search for the creation and preparation of new compounds with appropriate behavior and action and is compatible with the development of resistance to these types of bacteria [16].

2. Materials and Instruments

Thiophene-3-carboxaldehyde, 4-N, N-diethyl aniline, and 4-nitroaniline were purchased from Merck and Used without treatment. Other reagents and solvents were of analytical grade and purchased commercially.

FTIR spectra (potassium carbonate discs) were recorded on a JASCO FT/IR 4200 instrument, with a wave number range of 400-4000 cm^{-1}. The electronic spectra were measured in the range of 200 -

1100 nm for 10^{-3} by using DMSO solvent by using UV-Visible spectrophotometer type Shimadzu UV-160A using quartz cell of (1.0 cm) length, Available at Polymer Research Center, Basrah University, Iraq. In addition, the micro elemental analyses were obtained on Exeter Metal Analytical CE 440. Available at Chemistry Department /College of Science/ University of Basrah, Iraq.

2.1. Synthesis of N-[(thiophene-3-yl) methylidene]-4 (N, N diethyl amino) benzene (A).

An ethanolic solution of 3- thiophenecarboxaldehyde (1 mmol, 25 mL) was added to an ethanolic solution of 4-N, N-diethyl aniline (1 mmol, 25 mL) with added 2 drops of glacial acetic acid and the reaction was continued for 4 hours with refluxed on a hotplate at 75 ^{o} C with stirrer. After cooling, the solution, the product was precipitate, separated, filtered, recrystallization with ethanol, and dried over anhydrous $CaCl_2$ under vacuum. The obtained product was showed in Figure (1).

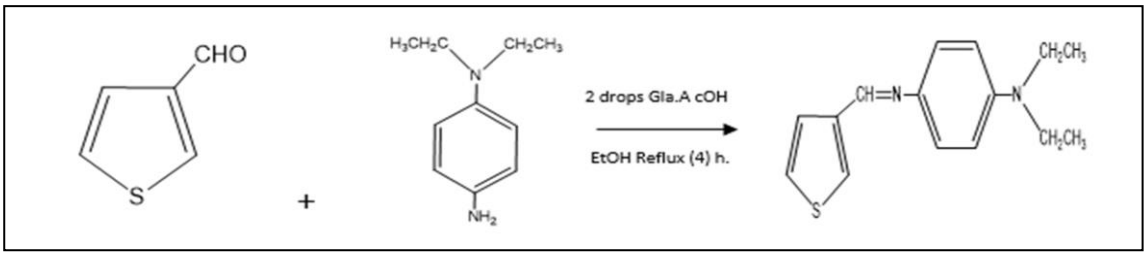

Fig (1): Synthesis of N-[(thiophen-3-yl) methylidene]-4 (N, N diethyl amino) benzene (A).

2.2. Synthesis of N-[(thiophen-3-yl) methylidene]-4-nitrobenzene (B)

An ethanolic solution of 3- thiophenecarboxaldehyde (1 mmol, 25 mL) with added 2 drops of glacial acetic acid was added to an ethanolic solution of 4-nitroaniline (1 mmol, 25 mL) and the reaction was continued refluxed for 4 hours with refluxed on a hotplate at 75 ^{o}C with stirrer. After cooling, the solution, the precipitate was separated, filtered, recrystallization with ethanol, and dried over anhydrous $CaCl_2$ under vacuum. Figure (2) showed the chemical reaction of the preparation.

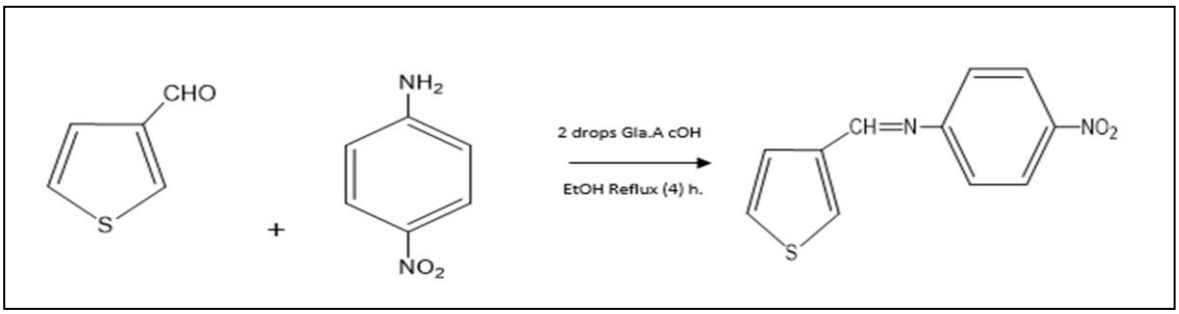

Fig. (2) Synthesis of N-[(thiophen-3-yl) methylidene]-4-nitrobenzene (B).

2.3. Biological activity

To determination of the Antibacterial Activity against anew Schiff bases, six clinical bacterial strains were studied: *Staphylococcus aureus*, *Salmonella typhi*, *Escherichia coli* and *Vibrio parahaemolyticus*.

A bacterial suspension of each isolate was prepared and equalized to 0.5 Mc Far land standard then the solution was spread on the entire surface of Muller Hinton agar by sterilized cotton bud [17], after drying 9 mm, diameter pore was made in the center of each plate by using cork borer with duplicate and control plates. All inoculated Petri dishes incubated at $37°_C$ overnight. Inhibition zone was measured as the diameter of the clearing zone in millimeters [18].

3. Results and Discussions

3.1. Spot Test (Ligands Complex) agents

Spot test technique used to study the ability of prepared ligands to form chelating complexes with various metal, spot-test technique was used by preparation of (1N) of ligands solution in absolute ethanol and (1N) of each metal salt in absolute ethanol, then two drops of ligands solution was added to 2 drops of metal salt solution (1:1) and the changes were noticed and recorded. In addition, Table (1) was showed the results of this technique. We note the ability to formation complex of the metal ions of elements with Schiff bases from the reaction of aniline substituted with donor group of $-N(Et)_2$ especially with Fe^{+3}, Mn^{+2}, Co^{+2}, In^{+3}, and Cu^{+2}.

Schiff base which substituted with electron with drawing group (NO_2) did not complexes with iron ions because of the nitro group is drawing the electronic density and then decrease the electrical negativity of nitrogen of azomethine group by interaction of the double electron of π- system of the ring, that make the group of azomethine weak donor group which make the ability to make complex with metal ion by nitrogen atom and sulfur atom in the Schiff base ligands, but, we think that the Schiff base complex with Pt^{+4} chelate by sulfur atom only of the thiophene-3-carboxaldehyde.

Table (1) show the Ligand complexes

compound	Cd^{+2}	Pt^{+4}	Co^{+2}	In^{+3}	Fe^{+3}	Ga^{+3}	Nd^{+3}	Bi^{+3}	Cr^{+3}
A	-	-	-	+	+	+	-	-	-
B	-	+	-	-	-	-	-	-	-

Compound	CS^{+1}	Ni^{+2}	Mn^{+2}	Pb^{+2}	Cu^{+2}	Sr^{+2}	Ba^{+2}	Mg^{+2}
A	-	-	+	-	+	-	-	-
B	-	-	-	-	-	-	-	-

3.2. C.H.N. Elemental analysis

The micro elemental analyses were obtained on Exeter Metal Analytical CE
440. available at the Chemistry department /college of science/ University of Basrah, Basrah-Iraq. The elemental analysis data for the prepared Schiff bases are shown in Table (2). The results imply that the experiment % of metals are in a good agreement with the Calculated %, this reflects the expected compositions of the prepared Schiff bases. The melting point is shown in the table (3). Sharp melting point values show the purity of the prepared Schiff bases.

Table (2) C.H.N. Elemental analysis

compounds	theoretical			practical		
	C%	H%	N%	C%	H%	N%
A	**69.77**	**6.977**	**10.853**	**69.978**	**7.254**	**10.698**
B	**56.897**	**3.448**	**12.069**	**56.198**	**3.554**	**11.997**

3.3. FTIR Spectrum

(FTIR) analysis with of each Schiff base was done to affirm the creation of Schiff bases. The FTIR data of the spectra of Schiff bases (A and B) showed a sharp band at 1604-1633 cm^{-1}assigned to the azomethine group (-C=N),their bands are showed in Table (4), and disappearances of the carbonyl group and amine group, thus clearly gave evidence of condensation between aldehydes and amines. Figures (3 and 4) showed spectrum of (A) and (B). Many other researchers who have synthesis Schiff bases using varieties starting material made similar kinds of observation.

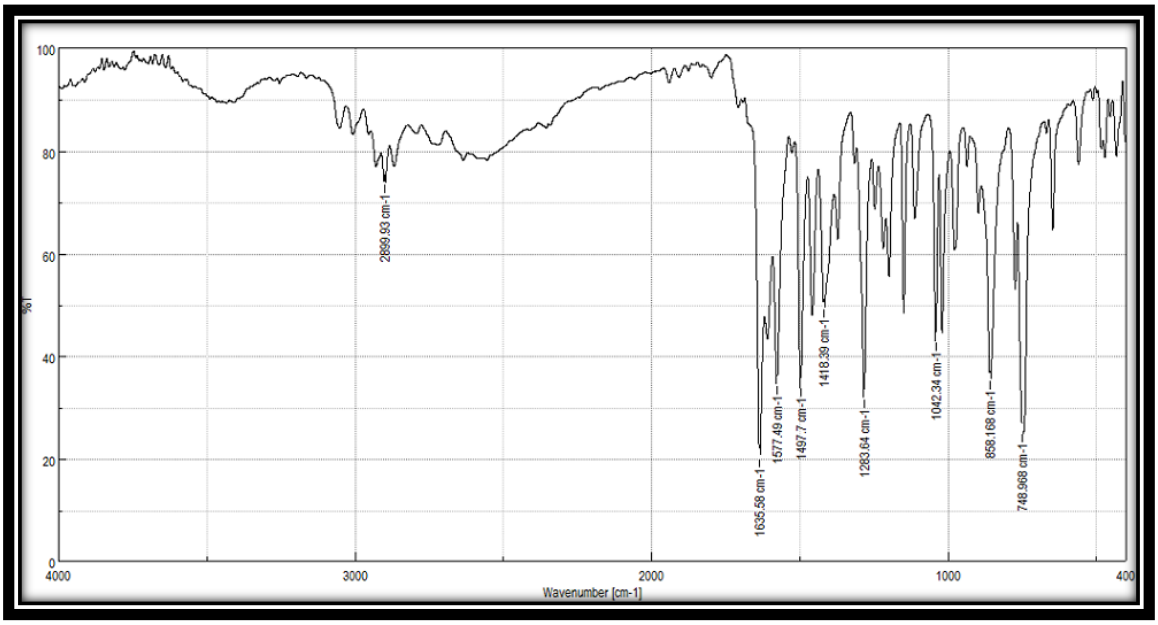

Figure (3) FTIR Spectrum of compound A

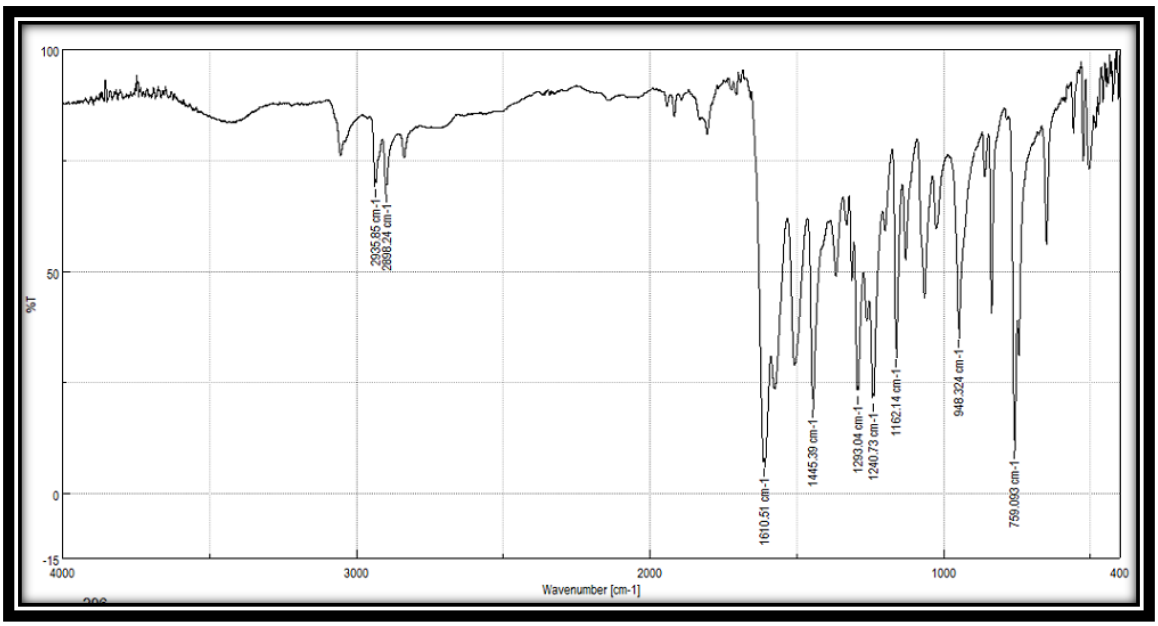

Figure (4) FTIR Spectrum of compound B.

Table (3) Some Physical Properties.

Compounds	Melting point	Physical state
(A)	116-118c^{o}	Solid gold crystal
(B)	90-91c^{o}	Solid Yellow crystal

3.4. Ultra violet –Visible Spectroscopic study

The (Uv-Vis) spectrum for the compound (A) exhibits high absorption peak at (209 nm) (ε_{max}=1720molar^{-1} .cm^{-1}), high absorption peak at (258nm)(ε_{max}=1700 molar^{-1}.cm^{-1}) and intense absorption peak at (378nm) (ε_{max}= 1600 1molar-^{1}. cm^{-1}), which were assigned to ($\pi\rightarrow\pi^*$), ($\pi\rightarrow\pi^*$) and ($n\rightarrow\pi^*$) transition respectively, Table (4) showed the value of UV-Visible spectroscopic of (A) and (B).

Table (4) Absorption bands of Schiff bases in Uv, Visible in an alcoholic solvent and IR vibration bands of imines group.

Compound	(-C=N) Vibration in IR	λ_{max}/nm molar^{-1}.cm^{-1}
A	**1635cm^{-1}**	**209(1720), 258(1700), 378(1600)**
B	**1610 cm^{-1}**	**207(1750), 228(1650), 377(2415)**

3.5. Antibacterial activity

In the present study, two compound (A) and (B) were tested against *Salmonella typhi*, *Vibrio parahaemolyticus*, *Escherichia coli* and Gram-positive *Staphylococcus aureus.* The results indicate that the first compound **(A)** showed a significant and strong effect against most of the pathogenic bacteria under the study while the second compound (B) show less antibacterial activity in comparison with the first compound. This can be seen in Table (5), which shows the diameters of the inhibitory zones and the photographs of inhibition of bacteria was shown in Figure (5).

The reason for these results can be attributed to the electron density on the amine group by the payment of the ethyl aggregates, which are electron aggregates. This electronic density activates the biologic activity of the compound against the bacteria.

Table (5). Showed the effect of (two Schiff bases A and B) against 4 pathogenic bacterial isolates. The results determined by measuring the inhibition zone diameter millimeter (mm):

Bacteria	Diameters of inhibition zones mm	
	A	**B**
Staphylococcus aureus	**14**	**8**
Vibrio parahaemolyticus	**12.5**	**R**
Salmonella typhi	**20**	**7.5**
Escherichia coli	**16**	**6**

- Where R means resistance.

For compound **(A**), it was observed that the zone of inhibition for *Salmonella typhi* was large than the other bacteria, this indicates the efficacy of the compound to penetrate the bacterial cell wall, such changes may produce to raise in membrane permeability and seepage of intracellular constituents and cause severe damage, in the end causing in cell death. These results were in a good agreement with previously investigation onto antibacterial properties it has been recorded that some chemical compound could cause structural changes when they interact with the outer membrane of bacteria [19]. These results in agree with many researchers who have specified with differences in bacterial susceptibility may be due to structural and compositional differences in the cell membrane of Gram-positive and Gram-negative bacteria [20-22].

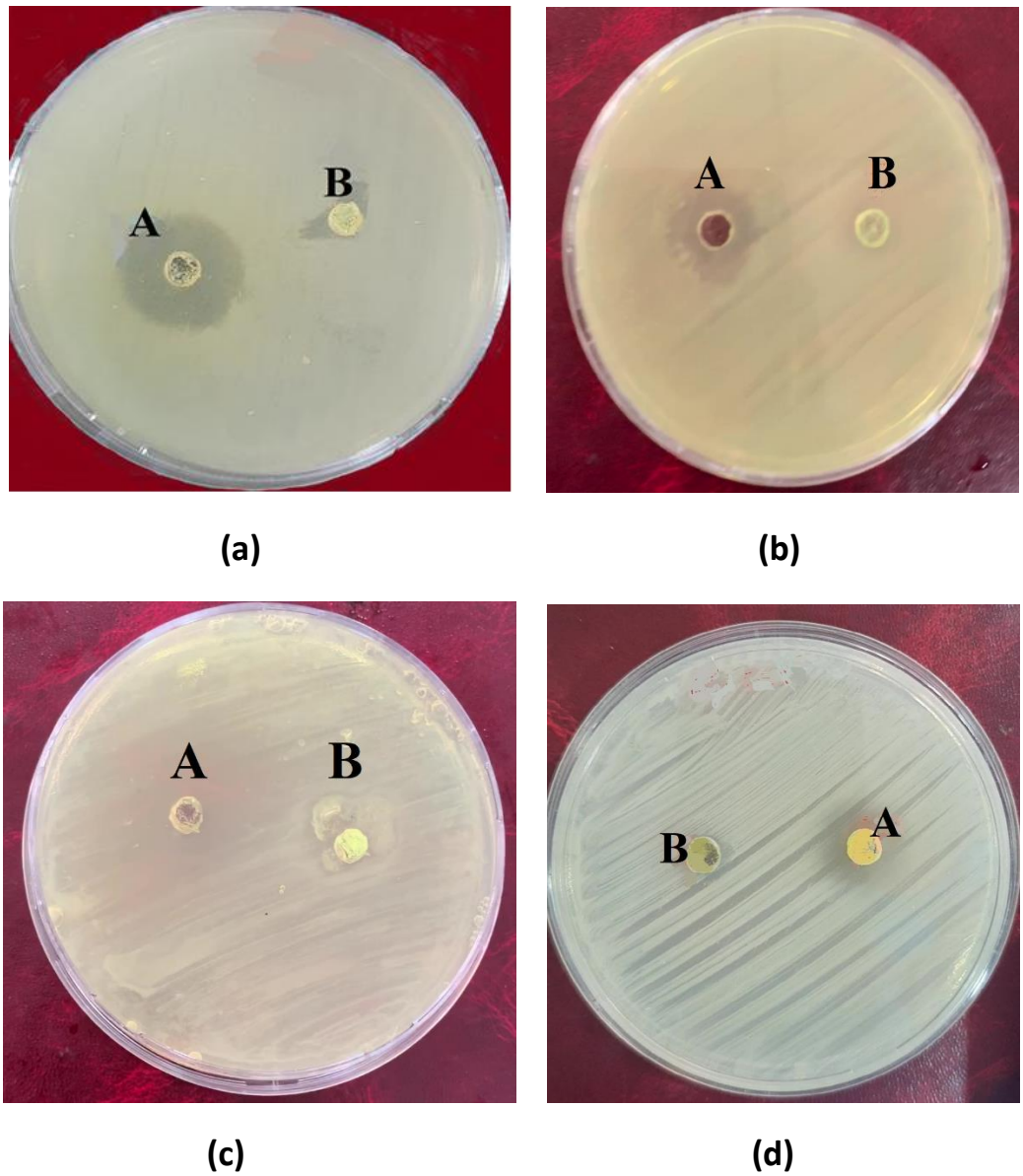

Figure 5: The effect of (A&B) against bacterial growth. (a) Inhibition zones (mm) of *Escherichia coli*. (b) Inhibition zones (mm) of *Staphylococcus aureus*. (c) Inhibition zones (mm) of *Salmonella typhi.* (d) inhibition zones (mm) of *Vibrio parahaemolyticus.*

3.6. Electrical properties

After the process of cleaning the slides with acetone and the distilled water, the slides were attached to plastic parts by a wire of 0.015mm diameter, and then the electrodes were heated by high purity aluminium. After the evaporation process, the wire was raised. Regular casting for electrical properties study did this process of casting the materials used. For the purposes of measurement, we select two electrodes, each with a membrane on the glass slide and connected to the circuit.

The prepared models were measured within voltages (1-10 volt) and at room temperature. If the current values are observed starting from 6×10^{-8} and settling at 3×10^{-7} for compound (A) and the current values of compound (B) starting from 4×10^{-8} and settling at $5\times10^{-7}$and that showed in Figure (6) and Figure (7). The voltage is increased by increasing the voltages at 4.5V. We observe a surprising increase in current. At 6.5V, the current stabilizes. This behaviour is due to the connection of Schottky [23, 24]. If it is possible to conclude that, these compounds are diodes (possible as one of the layers of a solar cell)

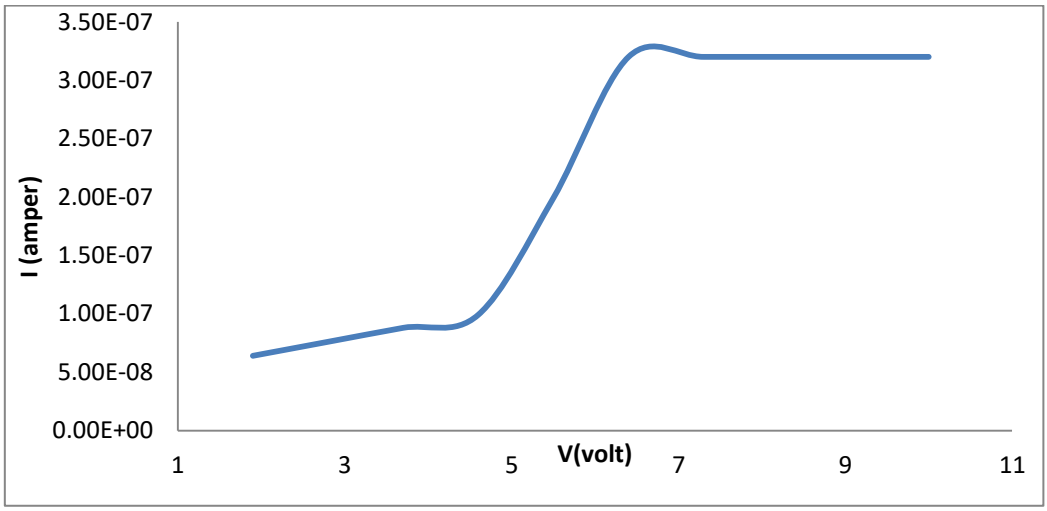

Figure (6) Represents the relationship between the voltages and the current of compound A.

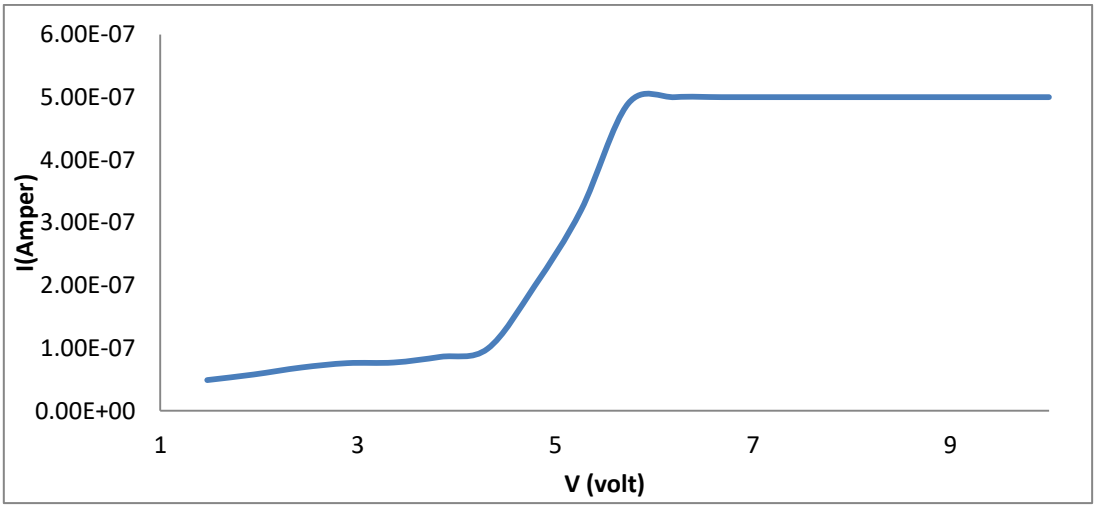

Figure (7) Represents the relationship between the voltages and the current of compound B.

4. Conclusion

Schiff bases of N-[(thiophene-3-yl) methylidene]-4 (N, N diethyl amino) benzene and N-[(thiophene-3-yl) methylidene]-4-nitrobenzene (B).were synthesized and characterized by analytical and spectral techniques, from the study of the ability of compounds (A) and (B) to form complexes, it was observed that compound (B) has a high selectivity towards platinum without any other ions, this behavior is of great importance in the fields of analytical chemistry and element capture. (A) and (B) exhibited significant activity against all the tested bacterial isolates and compound **(**A**)** showed a significant and strong effect against most of the pathogenic bacteria under the study while the second compound (B) show less antibacterial activity in comparison with the first compound, the ethyl aggregates, which are electron aggregates. This electronic density activates the biologic activity of the compound against the bacteria. The new Schiff bases have a good electrical conductivity that the current values are observed starting from 6×10^{-8} and settling at 3×10^{-7} for compound A and the current values of compound B starting from 4×10^{-8} and settling at 5×10^{-7}. The behaviour of the tow new Schiff bases was due to the connection of Schottky that, make the possibility of considering that, these compounds are diodes (possible as one of the layers of a solar cell).

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Synthesis and Spectrochemical Studies for Some Transition Divalent Metal Complexes with New Azo Ligand Derived from Pyrimidine ring

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Abstract:-

The New Heterocyclic ligand 4-[(2,4,6-trioxohexahydropyrimidin-5-yl)diazenyl]benzoic acid (L) was prepared to give the final Didentate Heterocyclic compound with different donor atom system. The Prepared ligand was characterized using FTIR, ^{1}H-NMR, C.H.N. Elemental analysis and UV.-Vis. techniques.

Some chelating metal complexes were Prepared with Co (II), Ni(II) and Cu(II) ions and characterized by FTIR, UV.-Vis. ,Molar conductance, C.H.N. Elemental analysis and magnetic susceptibility. The Purity of azo dye ligand and prepare complexes were tested by Thin – Layer Chromatography (TLC) Technique . The complexes were found to have the general formula $[M(L)_2Cl_2]$ where M= Co (II), Ni(II) and Cu(II) . The FTIR results demonstrated that the coordination site were the azo Nitrogen atom and Oxygen atom of Carbonyl group of the azo ligand . The electronic spectral and magnetic measurement data indicated that the complexes exhibited octahedral geometry were suggested for there complexes, (M:L) ratio was (1:2) for all prepared complexes while the conductivity measurements shows non – electrical properties.

Keywords: New Heterocyclic azo ligand , Transition metal complexes , Pyrimidine ring.

Introduction

Heterocyclic azo compounds are a class of molecules that contain hetero atom in ortho position of azo group (-N=N-) (1) .The chemistry of Heterocyclic azo compounds had the subject of much investigation not only for their medicinal values and physiological significance but also for the fact that all Heterocyclic azo compounds with at least one hetero-atom (acting as bonding site) in their structures, can assist as potential azo ligands for complex formation mainly with transition metal ions(2). At present, the numbers of Heterocyclic azo compounds are used in analytical chemistry substantially(3). The application of these azo dyes in spectrophotometry is based on the color resulting from reaction with most of transition metals in order to form stable chelates (4). The simplest six-membered N-heterocyclic, Pyridine, has been attending for many years as a ligand with metal ions and the chemistry of coordination of the derivatives of pyridine is currently well-documented(5). The investigation of coordination behavior of azo compounds with heterocyclic having more than one hetero atom such as imidazole, pyrimidine and pyrazine (6). By complex formation with transition and non-transition metal ions in

order to form chelate complexes containing heterocyclic azo compounds, the electrons on the hetero-atom actively participate in the formation of stable metal-ligand bonds(7).

The wide spectrua of Pyrimidine derivatives and their several chemical properties had led to their progressively extended use as originators for the preparation of many biologically active compounds.(8), and possess a wide spectrum of pharmaceutical properties and had study for activity against fungal,(9-11) and bacterial(12,13) infections .Therefore the antimicrobial activity determination of these type of azo ligands were already been performed by the diameter of zone of inhibition method as well antimicrobial activity(14).

Experimental

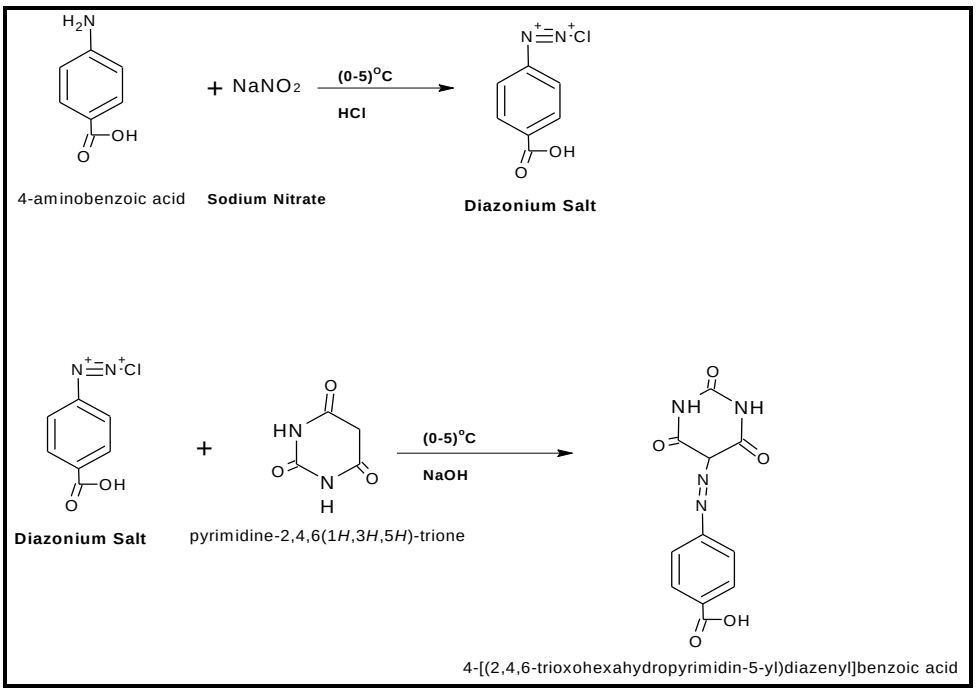
Materials and physical measurements

All chemicals used were of highest purity (BDH or Fluka) and used with out further purification.

Elemental analysis was carried out by means of micro analytical unit of (Euro2012, EA300A,Italy) C.H.N element analyzer .Absorption spectra were recorded using Shimadzu UV-Vis 1700 spectrophotometer, for solution of the complexes in aqueous ethanol at room temperature. Using 1cm quartz cell. IR spectra were recorded with FT-IR-8000 Shimadzu, in the range of (4000-400) cm^{-1} using KBr disc. Auto .Electrical conductivity measured by Digital conductivity Series Ino.Lab720 with solute concentration of 10^{-3}M in DMSO at room temperature.. ,the metal percentages were determined using atomic absorption technique by Shimadzu - AA-6300/Flame.

Synthesis of Heterocyclic azo ligand (4-[(2,4,6-trioxohexahydropyrimidin-5-yl)diazenyl] benzoic acid)

The ligand prepared by dissolving (1.37 g, 0.01 mol) of 4-aminobenzoic acid in 30 ml of distilled water and 5ml of concentrated hydrochloric acid, then the filtrated solution was cooled below 5 °C. To this mixture a solution of (0.75g, 0.01 mol) of sodium nitrate in 20 ml of distilled water was added drop wise at 0-5 °C. This diazonium solution was added drop wise to a 500 ml beaker containing (1.280 g, 0.01 mol) of pyrimidine-2,4,6(1H,3H,5H)-trione dissolved in 150 ml of alkaline ethanol. The mixture was allowed to stand over night and acidified with dilute hydrochloric acid to pH = 7.0. The crude dye was collected by filtration and recystallized twice from ethanol and then dried in the oven at 60 °C for two hrs (5). the melting point of the ligand was (210°C) and The structural formula of our ligand is shown in Scheme 1 .



Scheme 1: Preparation of the ligand(L)

Synthesis of complexes

The chelate complexes have been synthesized by dissolved (0.552 gm, 0.002 mol) of ligand (L) in 10 ml ethanol and then (0.001 mol) of metal chloride, M= Co(II), Ni(II), or Cu(II) dissolved and added drop wise with vigorous stirring to the ligand solution. The reaction mixture was left over night then the complexes were filtered off washed with distilled water, then with ethanol and dried in desiccators over anhydrous $CaCl_2$. Table.1 collects the some physical properties and analytical data for those complexes.

Table(1):- Some Physical properties and analytical data of the ligand (L) and its complexes.

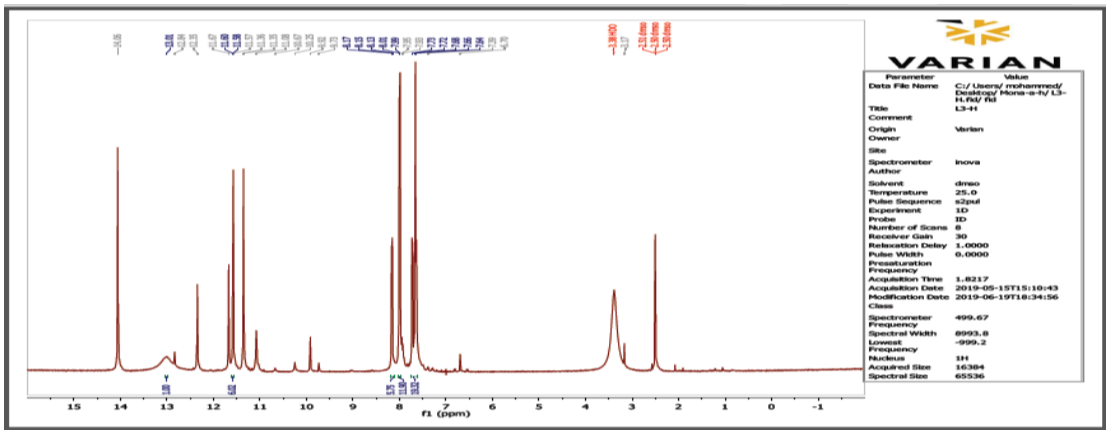
No.	Compound	Color	m.p C°	Found (Calc.)%			
				C	H	N	M
1	$C_{11}H_8N_4O_5$	Light Yellow	210	47.283 (47.826)	2.179 (2.89)	19.780 (20.028)	—
2	$[Co(C_{11}H_8N_4O_5)_2Cl_2]$	Reddish Brawn	290	38.299 (38.695)	1.965 (2.345)	15.891 (16.416)	8.188 (8.638)
3	$[Ni(C_{11}H_8N_4O_5)_2Cl_2]$	Reddish Brawn	300<	38.301 (38.709)	1.767 (2.346)	16.054 (16.422)	8.311 (8.605)
4	$[Cu(C_{11}H_8N_4O_5)_2Cl_2]$	Yellow	285	37.900 (38.435)	1.679 (2.329	15.878 (16.306)	8.949 (9.251)

Results and discussion

The metal complexes are insoluble in water and soluble in methanol ,ethanol, DMF, DMSO, acetone and $CHCl_3$.

^{1}H-NMR Spectrum of the Ligand (L)

The H^1-NMR Spectrum of the ligand was recorded in DMSO-d6 . The H^1-NMR spectrum of the ligand shows the following signals :δ 6.70-7.66 (m,4$H_{\text{benzene ring}}$) , δ3.12(m,1$H_{\text{pyrimidine ring}}$),12.84 (s,1H,O=C-OH $_{\text{Carboxylic acid}}$), δ 11.08-11.35(d,2H,$NH_{\text{barbituric acid}}$). As showed in(Fig1)(15,16).



(Fig.1):- 1H-NMR Spectrum for Ligand

Electronic spectra and Magnetic susceptibilities

The Electronic spectra of the ligand (L) (Fig.2) and its metal complexes were studied and the spectral data were listed in table (2) . The UV-Vis spectra of the Heterocyclic azo ligand was characterized mainly by three absorption peaks at (203 and 236) nm assigned to(π ⟶ π *) and at (310)nm assigned to (n ⟶ π*) these electronic transition were shifted towards higher or lower frequency in the electronic spectra of the prepared complexes , confirming the coordination of the ligand with metal ions .

The electronic spectrum of Co (II) complex in (Fig.3) showed three absorption peaks , at (15243 , 17301 and 25947)cm^{-1} , There are assigned to (^{4}**T$_1$g(F)** ⟶ ^{4}**T$_1$g(F)(V1)** , ^{4}**T$_1$g(F)** ⟶^{4}**T$_1$g(P)(V3)** and Charge Transfer (C.T.) respectively. This suggests that the complex octahedral (17). The magnetic moment of Co (II)complex(4.37 B.M) suggest a high – spin octahedral configuration .The high values of (Meff) may be due to orbital contribution.

The electronic spectrum of Ni (II) complex in (Fig.4) showed one absorption peak at ((25316 cm^{-1}) assigned to ligand to metal charge transfer (LMCT)

Transition(18),Suggesting an octahedral geometry around Ni(II) complex. The magnetic moment value of Ni(II) complex(3.32 B.M) suggesting an octahedral environment.

The electronic spectrum of Cu (II) complex in (Fig.5) showed one absorption peak at (25974 cm^{-1}) assigned to charge transfer spectrum. This peak was a good agreement of Octahedral geometry, The magnetic moment value (1.70B.M) suggesting an octahedral environment. (19).

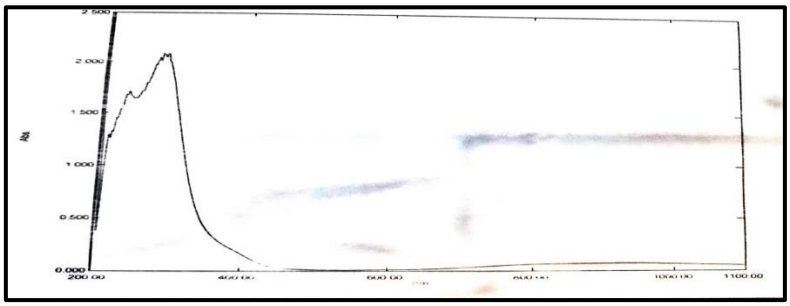
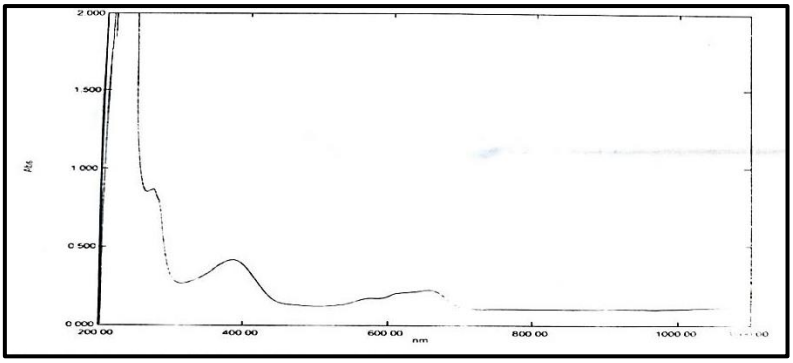
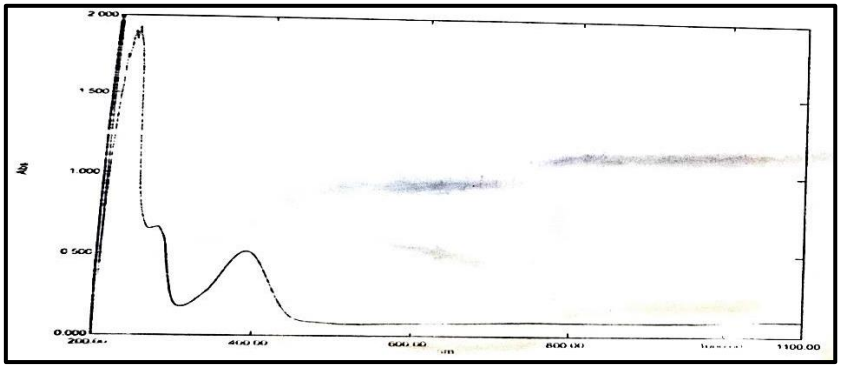


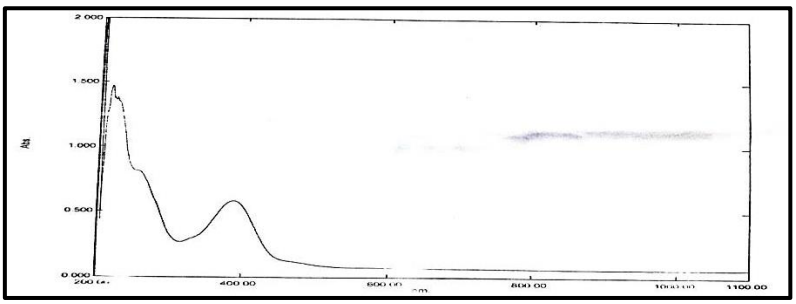
Fig. (2):- Absorbance spectrum of ligand (L_1)



Figure(3):- Absorbance spectra of Co(II) complex



Figure(4):- Absorbance spectra of Ni**(II) complex**



Figure(5):- Absorbance spectra of Cu(II) complex .

Table (2):-The electronic spectra of the ligand and its chelate complexes.

Compounds	$\lambda_{Max.}$ nm(cm^{-1})	Transition	Magnetic susceptibilities
$C_{11}H_8N_4O_5$	203nm (49261 cm^{-1}) 236nm (42.372 cm^{-1}) 310nm (32258 cm^{-1})	$\pi \longrightarrow \pi^*$ $\pi \longrightarrow \pi^*$ $n \longrightarrow \pi^*$	
$[Co(C_{11}H_8N_4O_5)_2Cl_2]$	385 nm (25974 cm^{-1}) 578nm (17301 cm^{-1}) 656nm (15243 cm^{-1})	C.T $^4T_1g(F) \longrightarrow {}^4T_1g(P)$ $^4T_1g(F) \longrightarrow {}^4T_2g(F)$	4.37
$[Ni(C_{11}H_8N_4O_5)_2Cl_2]$	395nm (25316 cm^{-1})	C.T	3.32
$[Cu(C_{11}H_8N_4O_5)_2Cl_2]$	385nm (25974 cm^{-1})	C.T	1.70

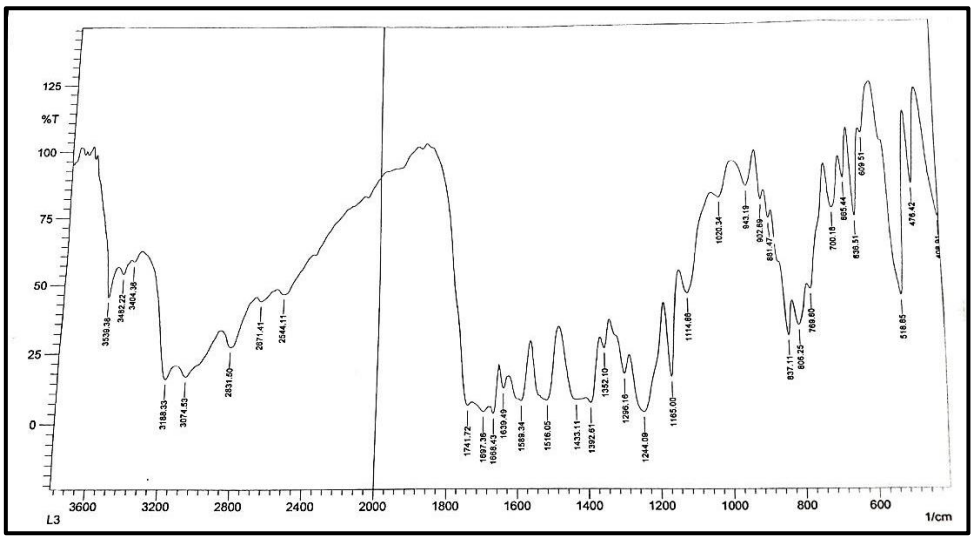
Infrared spectra

The infrared spectra of the free ligand (L) and its complexes with Co (II),Ni (II) and Cu(II) are given in Table.3. These spectra are complicated owing to the extensive overlap of number of bands arising from υ(C═O), υ(N═N) and other bands due to the pyrimidine ring which appeared in the region below 1700 cm^{-1}. The comparison between the IR spectral data of the free ligand with that of its complexes are illustrated as follow:-

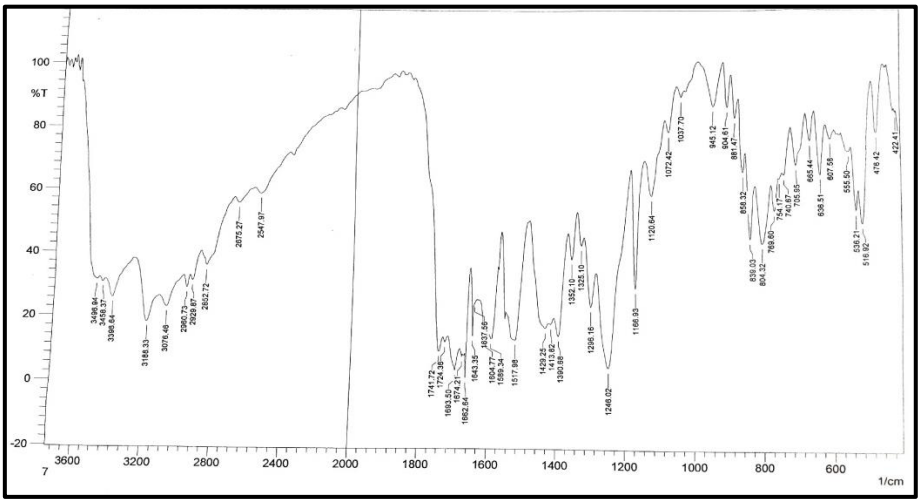
The Band in IR spectrum of free ligand at (1741 and 1697) cm^{-1}, assignable to stretching vibration υ (C=O) groups of pyrimidine ring respectively these bands are in stable positions in the ligand and its complexes (5,20). The band at (1668) cm^{-1} in IR spectrum of free ligand can be attributed to the stretching vibration of Carbonyl group υ (C=O)in pyrimidine ring, which was shifted to higher or lower frequency in the IR spectra of the complexes. These shifting indicated the coordination of the ligand with metal ion via oxygen atom (21) The appearance of a new non-ligand band around (432- 420) cm^{-1} in IR spectra of complexes with L_1 due to υ (M-O) substantiates (13) This is further substantiated by the presence of a new band around (557-516) cm^{-1} respectively assignable to υ(M-N)(15). It is concluded that the ligand behaves as a didentate ligand coordinated to the metal ions via oxygen atom of carbonyl group of pyrimidine ring and nitrogen atoms of azo group (N=N) as showed in Figuer (5,6,7 and 8).

Table (3):- Characteristic IR absorption bands of the ligands L_1 and its complexes in cm^{-1} units.

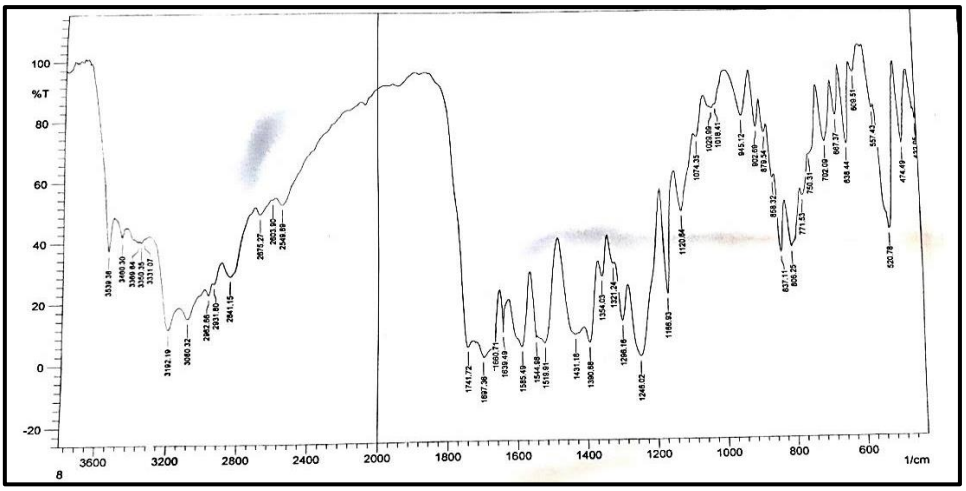
Compound	(O-H) carboxylic	υ(N-H-)	(C-H) aroma.	N=N	υ(HO-C=O) carboxylic and υ(C=O) Pyrimidine Ring	υ(C=O)	υ(M–N)	υ(M–O)
$C_{11}H_8N_4O_5$	2544-3539	3188	3074	1516	1741& 1697	1668 .	. ---	---
$[Co(C_{11}H_8N_4O_5)_2Cl_2]$	2547-3496	3188	3076	1517	1741& 1697	1674	536	422
$[Ni(C_{11}H_8N_4O_5)_2Cl_2]$	2549-3539	3192	3080	1519	1741& 1697	1660 .	557	432
$[Cu(C_{11}H_8N_4O_5)_2Cl_2]$	2553-3489	3186	3078	1521	1739& 1693	1641.	516 .	420



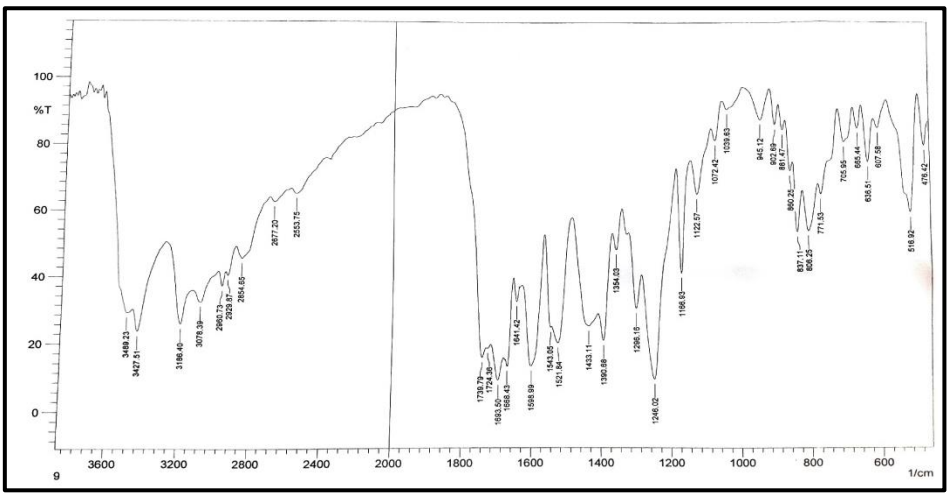
Figure(5):- IR spectrum of the ligand (L)



Figure(6):- IR spectrum of ion complex of Co(II) with the ligand (L)



Figure(7):- IR spectrum of ion complex of Ni(II) with the ligand (L)



Figure(8):- IR spectrum of ion complex of Cu(II) with the ligand (L)

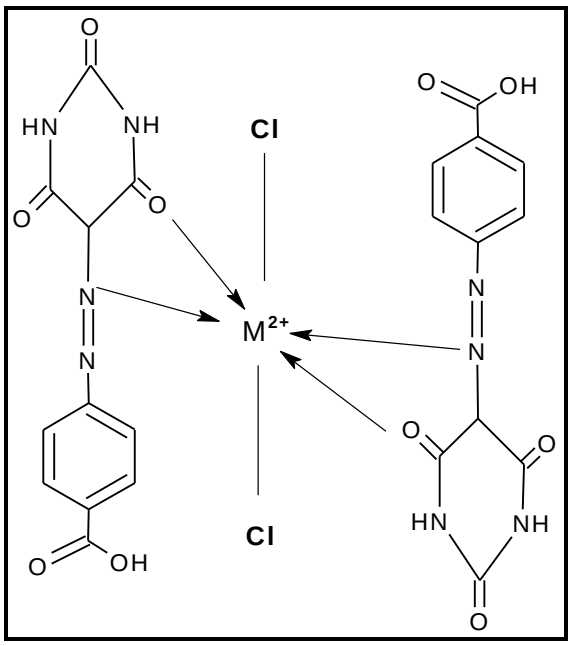
Conductivity measurements

All complexes showed the conductivity measurement values ranging between (9.67 – 11.74) $S.cm^2.\ mol^{-1}$in DMSO at room temperature, these values indicating Nonionic structure of these complexes (22).The conductivity values are listed in table 4.

Table(4):- Conductivity measurements of complexes

Complex	Conductivity $S.cm^2.mol^{-1}$
[Co ($C_{11}H_7N_4O_5)_2Cl_2$]	9.67
[Ni ($C_{11}H_7N_4O_5)_2Cl_2$]	10.32
[Cu ($C_{11}H_7N_4O_5)_2Cl_2$]	11.74

According to the results the coordination number of all metal ions is found to be six with bonding through the Nitrogen atom of azo group and the Oxygen atom of carbonyl group of heterocyclic pyrimidine ring. The structural formula of prepared complexes is most probably octahedral geometry shown in fig.9.



M= Co (II), Ni(II) and Cu (II)

Figure(9):- The proposed structural formula of Co (II), Ni(II) and Cu (II) with the ligand (L)

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Synthesis and Characterization of Some Imidazolidien , tetrazole derivatives

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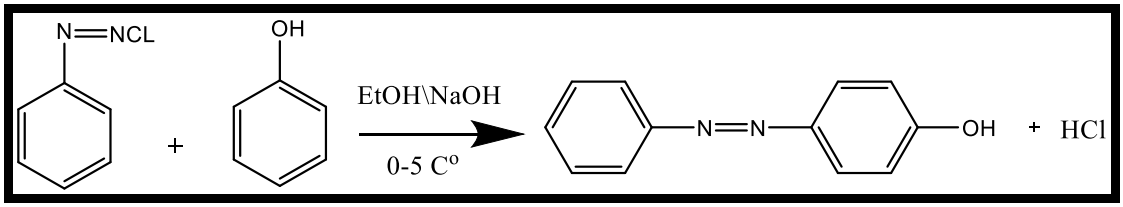
Abstract:
The present work included synthesis of novel (azo-shiff) via compounds in high yield, which react with (4-amino phenol , 3-nitro anilin and 4- methyl anilin) condensation reaction to produce various heterocycles (Five membered) ring like (Imidazolidine and tetrazole).The strcture of the newly synthesized compounds were monitored by (TLC) and identified by many techniques (FTIR , ^{1}HNMR and C^{13}NMR) and melting points.

Key words : Azo compounds , Schiff bases , Imidazolidien , tetrazole.

Introduction

Azo compounds are Organo-nitrogen derivative with the characteristic **–N=N-**[1] functionaliy and general formula **R'-N=N-R**[2]. where **R',R** group alphatic or aromatic, azo group is considerd biological active group , the most important method for preparing azo compounds is the coupling reaction between diazonium salts and phenols ,The diazonium salts attack as an electrophile reaction with the benzene ring of the coupling agent[3] .



Shiff bases or anils group are prepared of condensation reaction aromatic alhdehydes or ketone with primary amines The first report of the synthesis was obtained by Hugo Schiff 1864 [4] .Azo-Shiff bases are prepared by the reaction of azoketone with primary amine [5] .Various azo-shiff bases derivatives were prepared and some of them showed biological activity such as antivial [6] , antifungal [7], anticancer[8] , antibacterial and anticonvulsant[9] . Imidazolidine consist of adding (4) hydrogen atoms to the imidazole ring[10] , and the importance of the imidazolidien ring is due to its important roles as building blocks for the formation of biological active compounds [11] . The imidazolidien derivatives have interesting biotic activities such as antidepressants [12] , antifungal [13],antiviral [14] , antibiotic and digestive antibotiocs [15]. Extensive clinical practice[16]. Tetrazole ring was classified as (2+3) cycloddition [17] ,in which two atoms of the first component (anils) react with three atoms of the second component (azide group) [18].Tetrazole derivatives showed up fungicidal and antiviral activities [19].

Preparation Methods

(1) Synthesis 1-(3-((2-hydroxynaphthalen-1-yl)diazenyl)acetophenone (A)

3-aminoacetophenone (0.03 mol , 4.05 gm) was dissolved in (3ml)of concentrated hydrochloric acid and (20 ml) of distilled water . The solution was cold at (0 c^{o}) in ice-water bath. The sodium nitrite (0.03 mol ,2.07 gm)was dissolved in (10 ml) of distilled water and added drop wise to the

solution with stirring .2- naphthol (0.03 mol ,4.32 gm) was dissolved in (20 ml) of ethanol and (10 ml) of sodium hydroxide 10% and cooled to ($0C^o$), added to the diazonium solution in drope wise and stirring at ($0C^o$)for (2h) for obtaining the coupling agent .The result of the orange gold compound was prcipited , filtered and washed with water **.**

(2)Synthesis of azo Schiff bases derivatives :

1-((3-(1-((4-hydroxyphenyl)imino)ethyl)phenyl)diazenyl)naphthalen-2-ol (S_1) **and** 1-((3-(1-((3-nitrophenyl)imino)ethyl)phenyl)diazenyl)naphthalen-2-ol (S_2) **and** 1-((3-(1-(p-tolylimino)ethyl)phenyl)diazenyl)naphthalen-2-ol (S_3)

Ethanolic mixture (30 ml) containing 1 drop of concentrated hydrochloric acid to azo acetophenone derivative (A) of (0.003 mol , 1.0 gm)then adding (0.37gm,0.47gm ,0.36 gm) of a primary aromatic amines (4-amino phenol ,3-nitro aniline and 4- methyl aniline) .The reaction mixture was refluxed with stirring for (10-35) hours at (78) C^o , the reaction was complete and monitored by using TLC (Methanol : dry benzene 1:4)recrystallized from ethanol.

(3)Synthesis of 2-(3-((2-hydroxynaphthalen-1-yl)diazenyl)phenyl)-3-(4

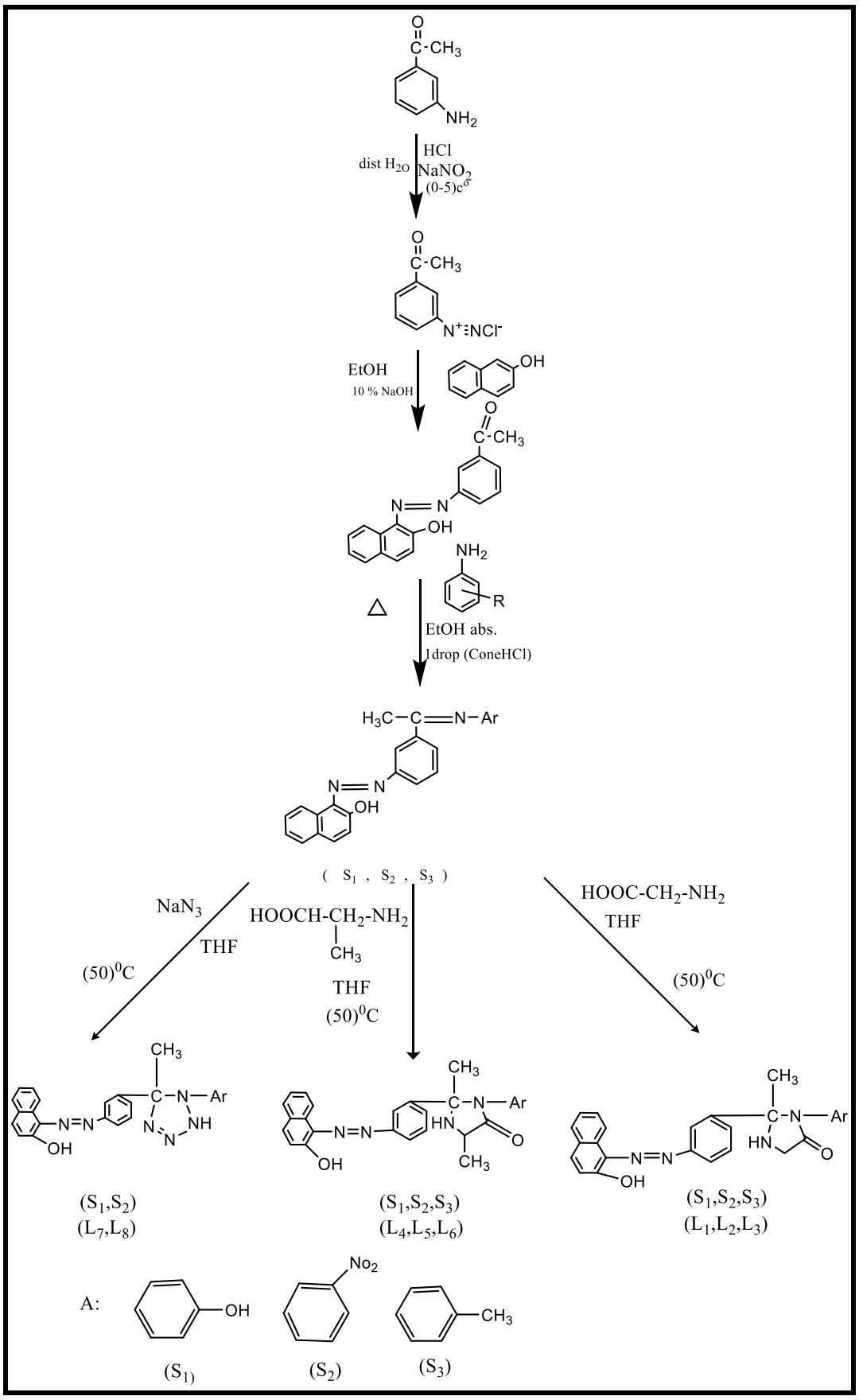
hydroxyphenyl)-2-methylimidazolidin-4-one (L_1) **and** 2-(3-((2-hydroxynaphthalen-1-yl)diazenyl)phenyl)-2-methyl-3-(3-nitrophenyl)imidazolidin-4-one (L_2) **and** 2-(3-((2-hydroxynaphthalen-1-yl)diazenyl)phenyl)-2-methyl-3-(p-tolyl)imidazolidin-4-one (L_3) A mixture of azo-schiff bases derivatives (S_1-S_3) (0.3 gm ,0.2 gm ,0.2 gm) with (0.1 gm , 0.036 gm , 0.05 gm) amino acid glycine respectively in (30 ml) of Tetrahydrofuran (THF) was refluxed for (23 , 10 ,13) hours for compounds (L_1-L_3) .

(4)Synthesisof2-(3-((2-hydroxynaphthalen-1-yl)diazenyl)phenyl)-3-(4-hydroxyphenyl)-2,5-dimethylimidazolidin-4-one (L_4) **and** 2-(3-((2-hydroxynaphthalen-1-yl)diazenyl)phenyl)-2,5-dimethyl-3-(3-nitrophenyl)imidazolidin-4-one (L_5) **and** 2-(3-((2-hydroxynaphthalen-1-yl)diazenyl)phenyl)-2,5-dimethyl-3-(p-tolyl)imidazolidin-4-one (L_6): A mixture of azo-schiff bases derivatives (S_1-S_3) (0.3 gm ,0.2 gm ,0.2 gm) with (0.1 gm , 0.043 gm , 0.05 gm) amino acid alanine respectively in (30 ml) of Tetrahydrofuran (THF) was refluxed for (23 , 8 ,13) hours for compounds (L_4-L_6) .

(5) Synthesis of 1-((3-(1-(4-hydroxyphenyl)-5-methyl-2,5-dihydro-1H-tetrazol-5-yl)phenyl)diazenyl)naphthalen-2-ol (L_7) **and**1-((3-(5-methyl-1-(3-nitrophenyl)-2,5-dihydro-1H-tetrazol-5-yl)phenyl)diazenyl)naphthalen-2-ol (L_8) : A mixture of azo-schiff bases derivatives (S_1-S_2) (0.3 gm ,0.1 gm) with (0.07 gm , 0.015 gm) sodium azied respectively in (30 ml) of Tetrahydrofuran (THF) was refluxed for (23 , 7) hours for compounds (L_7-L_8)

Table-1-show the physical properties of the prepared compounds:

No.	M.F	M.wt	m.p ^{0}C	Color	R_f	Time	Solvent	Yield %
A	$C_{18}H_{14}N_2O_2$	290.32	156-158	Golden Orange	…	3 hrs	EtOH +H_2O	91
S_1	$C_{24}H_{19}N_3O_2$	381.44	162-164	Green	0.9	35hrs	EtOH abs.	87
S_2	$C_{24}H_{18}N_4O_3$	409.43	160-162	Dark red	0.9	20 hrs	EtOH abs.	81
S_3	$C_{25}H_{21}N_3O_1$	379.46	174-176	Light red	0.7	10hrs	EtOH abs.	87
L_1	$C_{26}H_{22}N_4O_3$	438.49	132-134	Light Yellow	0.9	23hrs	THF	87
L_2	$C_{26}H_{21}N_5O_4$	467.49	100-102	Light brown	0.9	10 hrs	THF	88
L_3	$C_{27}H_{24}N_4O_2$	436.52	126-128	Dark red	0.9	13 hrs	THF	85
L_4	$C_{27}H_{24}N_4O_3$	452.51	136-138	Dark Yellow	0.8	23hrs	THF	84
L_5	$C_{27}H_{23}N_5O_4$	481.51	122-124	Aredish orang	0.8	8hrs	THF	90
L_6	$C_{28}H_{26}N_4O_2$	450.54	125-127	Light red	0.9	13hrs	THF	86
L_7	$C_{24}H_{20}N_6O_2$	424.46	130-132	Brown	0.9	23hrs	THF	90
L_8	$C_{24}H_{19}N_7O_3$	453.46	144-142	Light Pink	0.9	7hrs	THF	91



Scheme (1): The structares of all synthesis compounds

Spectral Characterization

Our derivative was identified with variety spectral methods like (FTIR , H.NMR , C^{13}.NMR) spetra:

(A) **FT-IR:** 1498 (N=N), 3421.72(OH) , 3062.96-3014.74(C-H , aromatic) , 1618.28 (C=C) , 1224.16-1203.58 (C-O) , 1147.65 (C-N) .**^{1}HNMR :** Singlet 2.101 ppm(CH_3),singlet 2.5 ppm (DMSO), multipleting singal at 6.996-7.377 ppm (phenol ring), singlet 11.01ppm(OH).**C^{13}NMR:** A\Singlet 26.36 ppm(CH_3),197.52ppm(C=O), multipleting singal at 111.1-149.148 ppm (phenol ring), singlet 155. 1ppm(OH).

(S_1) **FT-IR:** 1683.86 (C=N) , 1502.55 (N=N) , 3061.03 -3030.17 (-CH,aromatic), 3414.00-3406.29(OH) , 1618.28 (C=C) , 1355.96(CH_3) .**^{1}HNMR :** Singlet 2.077ppm(CH_3), 2.512 ppm(DMSO) , multipleting singal at 6.998-7.643 ppm (phenal ring), 10.743-11-381 ppm (OH). **C^{13}NMR:** Singlet273ppm(CH_3), 159PPM (C=N) ,153-154 ppm (OH).

(S_2) **FT-IR:** 1683.86 (C=N) , 1500.62 (N=N) , 3066.82 -32972.31 (-CH,aromatic) , 3458.37-3437.15 (OH) , 1620.21 (C=C) , 1357.89 (CH_3) .**^{1}HNMR :** Singlet 2.064ppm(CH_3) , singlet 2.51ppm (DMSO) ,multipleting singal at 7.038-7.980 ppm (phenal ring) ,11.814 ppm (OH) . **C^{13}NMR:** Singlet 26.411(CH_3) , 159.054PPM(C=N) ,154 ppm (OH) .

(S_3) **FT-IR:** 1689.64 (C=N) , 1581.63 (N=N) , 3099.61 -3062.96 (-CH,aromatic) , 3439.08-3360.00(OH) , 1641.42 (C=C) , 1355.96 (CH_3) . **^{1}HNMR :** Singlet 1.718-2.088ppm (CH_3) , singlet 2.518ppm (DMSO) , multipleting singal at 7.401-8.498 ppm (phenal ring) , single 11.518ppm (OH) . **C^{13}NMR :** Singlet 21.605-25605 (CH_3) , 159.432PPMsi , ngle153.442PPM (OH) .

(L_1)FT-IR:1678.07 (N-C=O),1616.35(C=C)aromatic,1504.48(N=N),1359.82 (CH_3),3080.32 (NH),3394.72 (OH).HNMR: Single(2.510)ppm(CH_3),Single (2.521)ppm(DMSO-d^6), single (6.996)ppm(CH_2),multipeting single (7.377-7.027)ppm(phenal ring),Single (9.3520)ppm(NH),single (10.352)ppm (OH Phenol),(11.251)ppm(OH naphthol).C^{13}NMR: Signal (176.358)ppm (C=O), signal (161.253) ppm (C-N),), signal (155.684)ppm (OH naphthol) , signal (154.253) ppm (OH phenol), multipeting signl(105.199-142.462) ppm (C aromatic),Signal (55.798)ppm(C-CH_3) , Signle (39.116-40.779)ppm(DMSO-d^6 , signle (23.253) ppm (CH_3).

(L_2)FT-IR:1672.93 (N-C=O),1618.28(C=C)aromatic,1500.62(N=N),1355.96 (CH_3),3064.89 (NH),3448.72 (OH). **^{1}HNMR**: Single(1.685)ppm(CH_3),Single (2.528)ppm(DMSO-d^6), single (6.787)ppm(CH_2),multipeting single (6.976-8.155)ppm(phenal ring),Single (9.585)ppm(NH),(11.529) ppm(OH naphthol) .C^{13}NMR: Signal (176.971)ppm (C=O), signal (161.453) ppm (C-N),), signal (155.701)ppm (OH naphthol), multipeting signl(121.145-131.253) ppm (C aromatic),Signal (64.666)ppm(C- CH_3) , Signle (39.480-40.866)ppm(DMSO-d^6 , signle (25.408) ppm (CH_3).

(L_3)FT-IR:1681.93 (N-C=O),1618.28(C=C)aromatic,1498.69(N=N),1357.89 (CH_3),061.03(NH),3446.79 (OH). **^{1}HNMR**: Single(1.374)ppm(CH_3), Signal (1.874)ppm (CH_3),Single (2.606)ppm(DMSO-d^6), single (6.402) ppm (CH_2), multipeting single (7.419-8.144)ppm(phenal ring),Single (9.3520) ppm(NH) ,(11.251)ppm(OH naphthol).C^{13}NMR: Signal (175.349)ppm (C=O), signal (162.284) ppm (C-N),), signal (155.684) ppm (OH naphthol), multipeting signl(112.561-130.038) ppm (C aromatic),Signal (58.225)ppm(C-CH_3) , Signle (39.116-40.779)ppm(DMSO-d^6 , signle (24.253) ppm (CH_3).
(L_4)**FT-IR**:1680.00 (N-C=O),1612.49(C=C)aromatic,1504.48(N=N),1357.89 (CH_3),3061.03

(NH),3169.04 (OH).**^{1}HNMR** : Single(1.721)ppm(CH_3),Single (2.516)ppm(DMSO-d^6),double Signal (3.474-3.452)ppm (C-CH_3), single (6.589) ppm(C-N),multipeting single (7.628-7.973) ppm(phenal ring) ,Single (9.818) ppm (NH) ,single (10.718) ppm (OH Phenol),(11.797) ppm (OH naphthol) .C^{13}NMR: Signal (177.411)ppm (C=O), signal (162.411) ppm (C-N),), signal (155.967) ppm (OH naphthol),Signal (154.967)ppm (OH phenol0 , multipeting signl(116.632-131.524) ppm (C aromatic),Signal (61.632)ppm(C-CH_3) , Signle (39.203-40.866) ppm (DMSO-d^6) , signle (18.411) ppm (CH_3).

(L_5)FT-IR:1678.07 (N-C=O) ,1622.13 (C=C) aromatic ,150419.91 (N=N) , 1348.24 (CH_3), 3332.99 (NH) ,3431.36 (OH) .^{1}HNMR : Single(1.719) ppm (CH_3),Single (2.522) ppm(DMSO-d^6), double single (3.393-3.385) ppm (C-CH_3) , Signal (6.526)ppm (CH_2) , multipeting single (7.458-8.292) ppm (phenal ring), Single (9.672) ppm(NH), (11.555) ppm (OHnaphthol) .C^{13}NMR: Signal (175.422)ppm (C=O), signal (162.745) ppm (C-N),), signal (155.701) ppm (OH naphthol), multipeting signl(117.632-131.426) ppm (C aromatic),Signal (59.431)ppm(C-CH_3) , Signle (39.203-40.866) ppm (DMSO-d^6) , signle (24.408) ppm (CH_3).

(L_6)FT-IR:1680.00 (N-C=O),1616. 35 (C=C) aromatic ,1500.62 (N=N) , 1357.89 (CH_3),3059.10 (NH),3428.72 (OH).^{1}HNMR : Single(1.587) ppm (CH_3),Signal (1.814)ppm (CH_3),Single (2.523) ppm(DMSO-d^6),dopel single (3.398-3.385)ppm(C-CH_3)),Signal (6.746)ppm (CH_2),multipeting single (7.494-7.811)ppm(phenal ring),Single (9.427)ppm (NH),single (11.627)ppm(OH naphthol).C^{13}NMR: Signal (178.465)ppm (C=O), signal (162.411) ppm (C-N),), signal (155.967) ppm (OH naphthol), multipeting signl(116.632-131.426) ppm (C aromatic),Signal (64.632)ppm(C-CH_3) , Signle (39.203-40.866) ppm (DMSO-d^6) , signle (18.589) ppm (CH_3) aromatic ring , signal (22.312)ppm (CH_3)cyclic ring , signal (24.408)ppm (CH_3)ketone.

(L_7)FT-IR:16780.00 (N-C) ,1610.56 (C=C) aromatic ,1504.48 (N=N) , 1357.89 (CH_3),3261.63 (NH),3396.64 (OH). ^{1}HNMR: Single (2.051) ppm (CH_3) ,Single (2.510)ppm(DMSO-d^6), multipeting single (7.042-7.947) ppm (phenal ring),Single (9.612)ppm(NH),single (10.685)ppm (OH Phenol),(11.627)ppm(OH naphthol).C^{13}NMR: Sign (160.922) ppm (C-N),), signal (155.673)ppm (OH naphthol) , signal (153.248) ppm (OH phenol), multipeting signl(116.644-132.007) ppm (C aromatic), Signle (39.207-40.871)ppm(DMSO-d^6 , signle (27.410) ppm (CH_3).

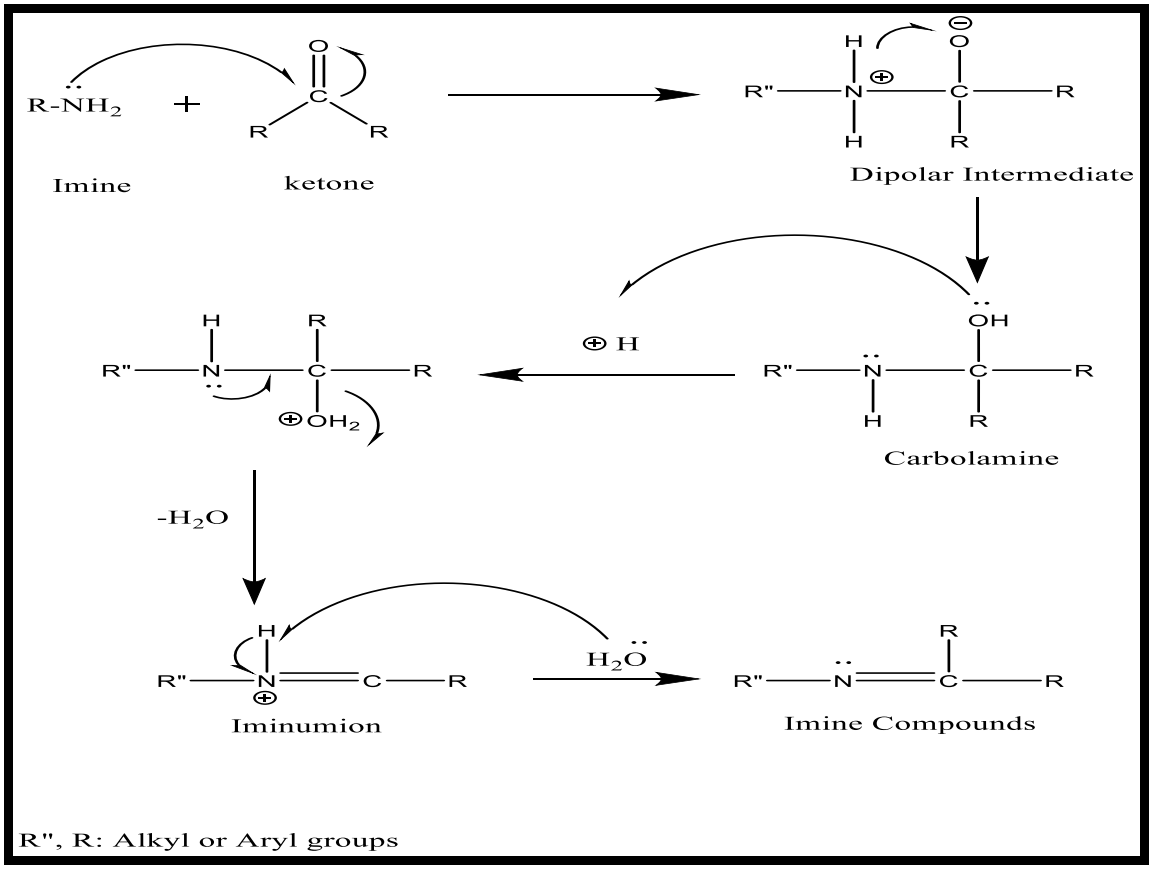
(L_8)FT-IR:1666.86 (N-C),1618.28(C=C)aromatic,1500.62(N=N),1398.39 (CH_3),3390.03 (NH),3458.37 (OH).HNMR: Single(1.969)ppm(CH_3),Single (2.528)ppm(DMSO-d^6), multipeting single (7.187-8.153)ppm (phenal ring) ,Single (9.685)ppm(NH), (11.069)ppm(OH naphthol).C^{13}NMR: signal (161.973) ppm (C-N),), signal (155.673)ppm (OH naphthol) , multipeting signl(116.644-130.662) ppm (C aromatic), Signle (39.207-40.871)ppm(DMSO-d^6 , signle (26.485) ppm (CH_3).

Result and Discussion:

Imine was prepared by thermal condensation reaction of 1-(3-((2-hydroxynaphthalen-1-yl)diazenyl)acetophenone with 4-aminophenol , 3-nitro aniline , 4- Methal aniline . In absolute ethanol under reflux condition and used as starting materials for the synthesis Imidazolidine , tetrazole derivatives .Characterization by confirming their structure by some physical properties and

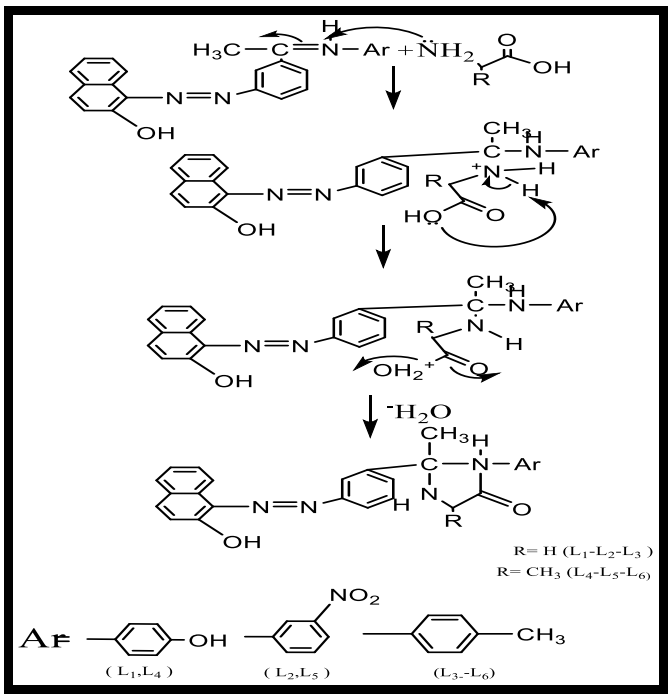
FTIR spectra .The FTIR spectra of compounds (S_1,S_2,S_3) showed that the disappearance of the stretching frequency absorption bands of (-NH_2) and (C=O) group for amine and ketone respectively and the appearance of characteristic absorption bands at (3421.72) Cm^{-1} due to **OH** , due to (1683.86,1683.86 ,1689.64) Cm^{-1} respectively **C=N** imine group , due to (1618.28.1620.21,1600.92) Cm^{-1} respectively **C=C** aromatic , due to (1502.55,1500.62,1581.63) Cm^{-1} **N=N** .

The formation of Imine compounds is general mechanism is suggested to take place by nuclophilic addition of the amine group to the carbonyl group associated ,following by extract of water to give the product as shown in scheme(2).



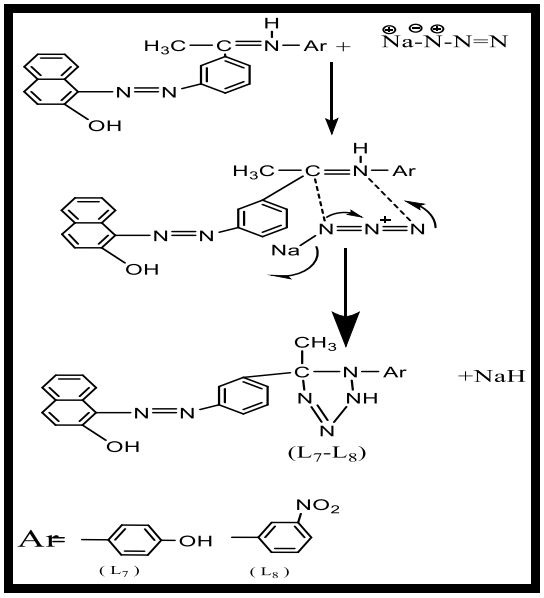
Scheme 2: proposed mechanisam for the formation of Imine compounds

The amino acid (glycine , alanine) are then added to Imine group C=N to take place by nuclophilic attack from the electron double of the nitrogen atom and extract of water to give the product as shown in scheme (3).



Scheme 3: proposed mechanisam for the formation of five- membered ring (Imidazolidien)

Then synthesis tetrazole compounds by reaction of Imine group with Sodium azied in THF is suggested of mechanism for the reaction (1,3-dipolar cyclo addition) one of the types of cyclic addition the product as shown in scheme (4).



Scheme 4: proposed mechanisam for the formation of five- membered ring (tetrazole.)

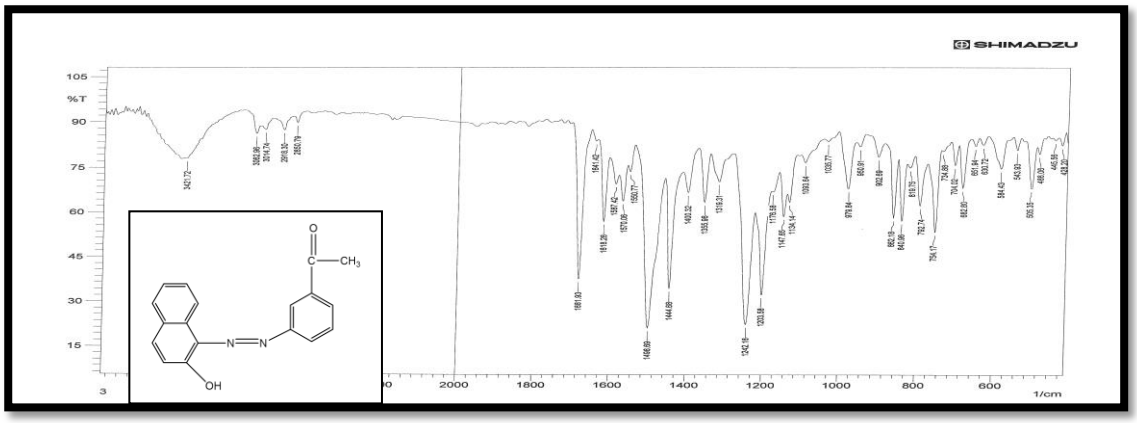


Figure1: FTIR Spectra of Azo compound(A)

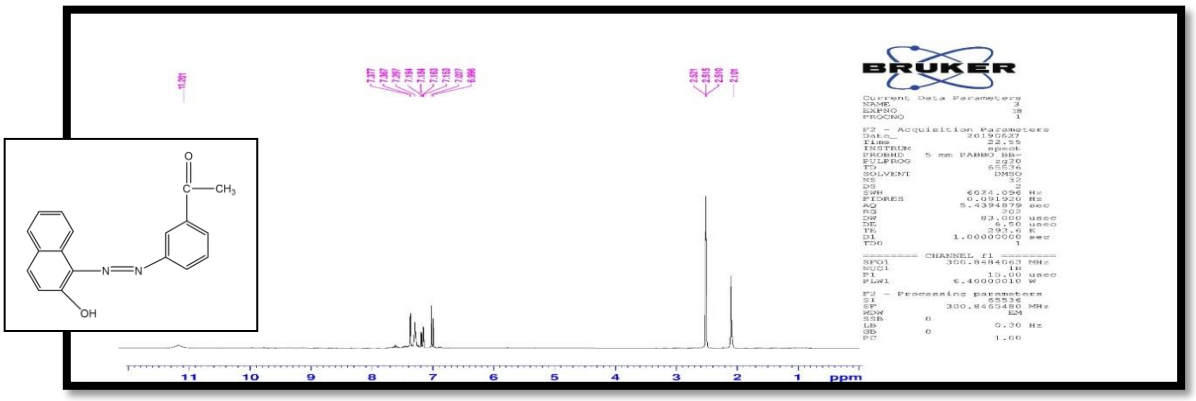


Figure2: ^{1}HNMR Spectra of Azo compound (A)

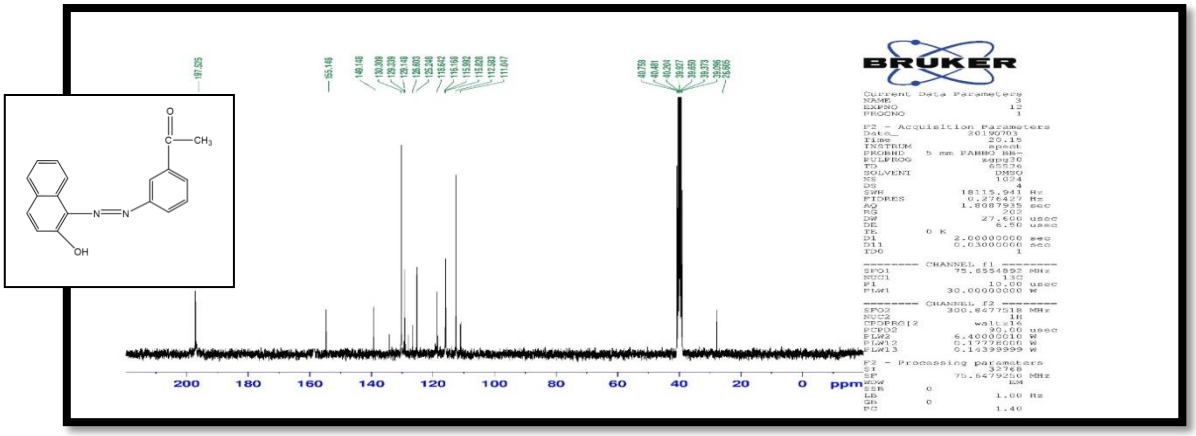


Figure3: ^{13}CNMR Spectra of Azo compound(A)

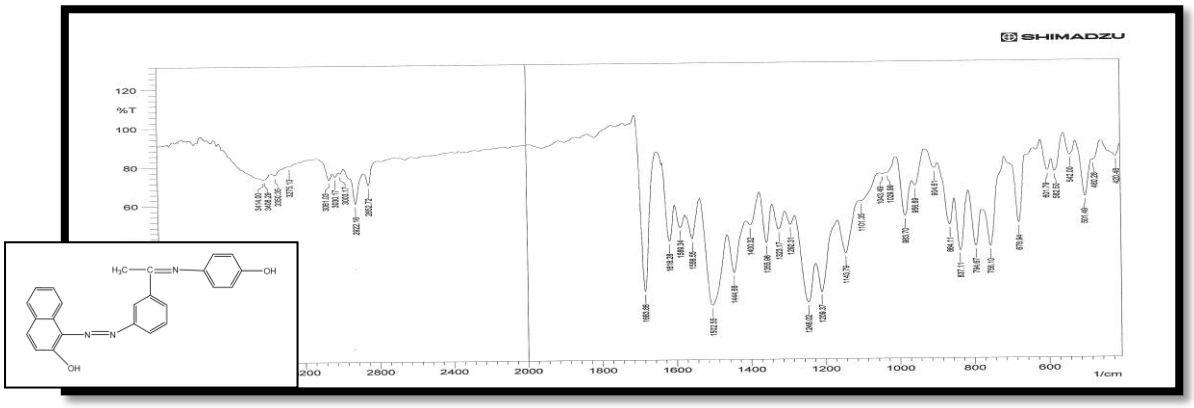


Figure4: FTIR Spectra of compound (S_1)

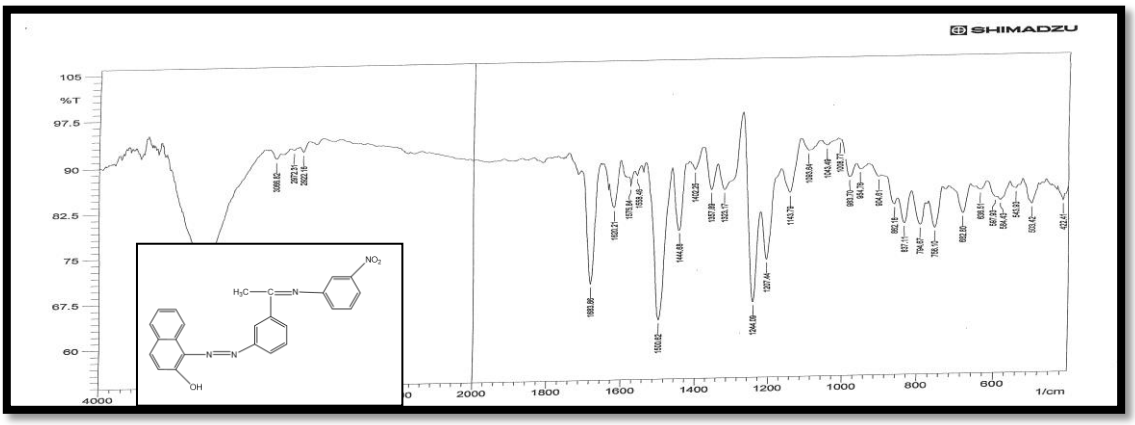


Figure5: FTIR Spectra of compound (S_2)

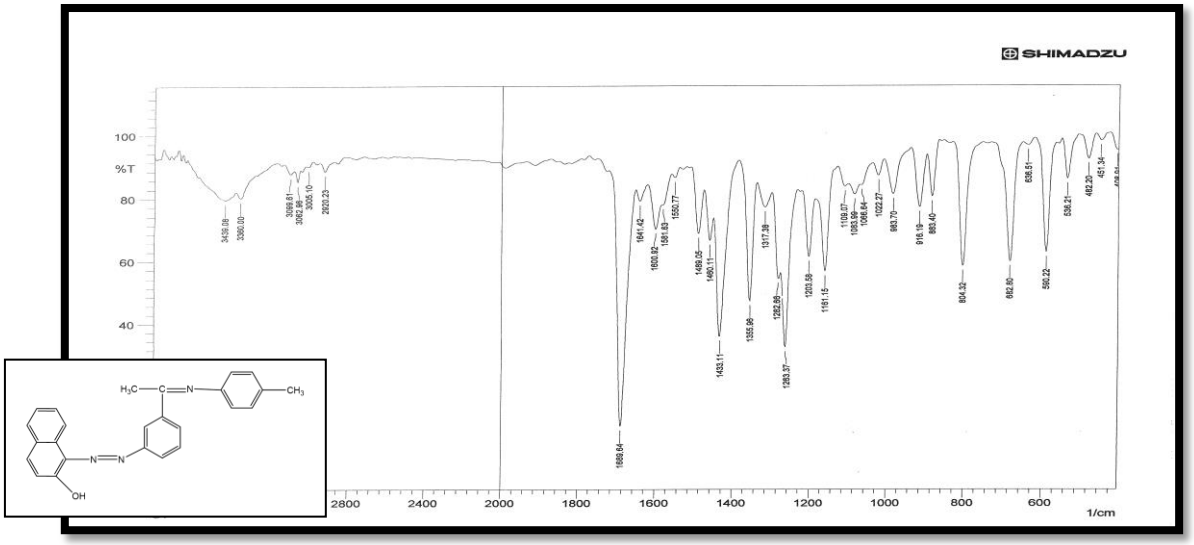


Figure6: FTIR Spectra of compound (S_3)

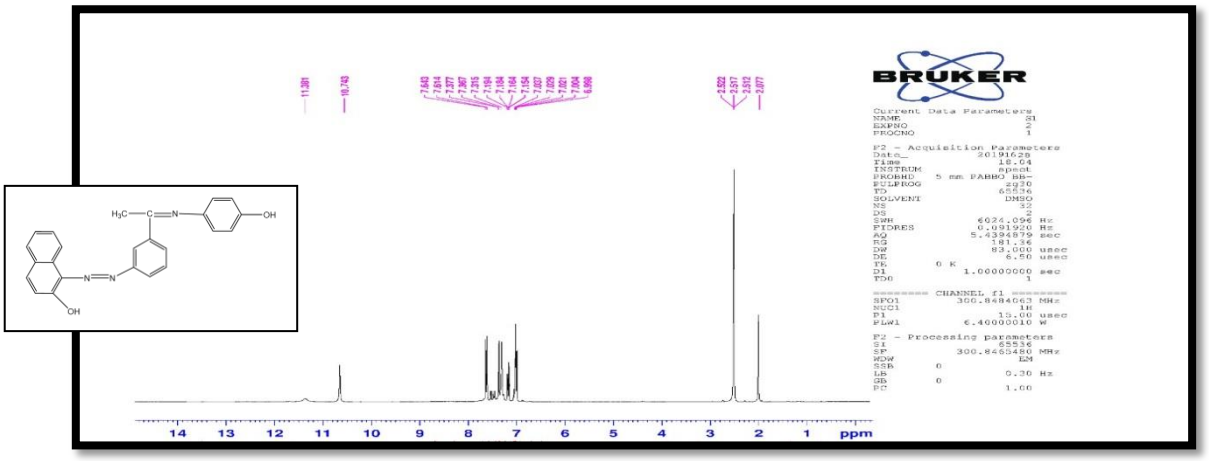


Figure7: ^{1}HNMR Spectra of compound (S_1)

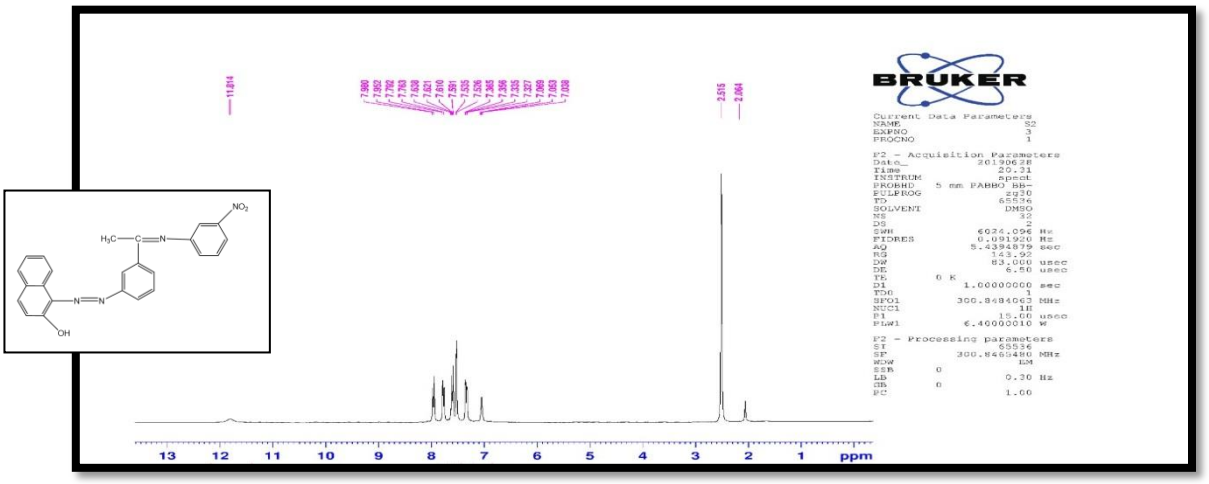


Figure8: ^{1}HNMR Spectra of compound (S_2)

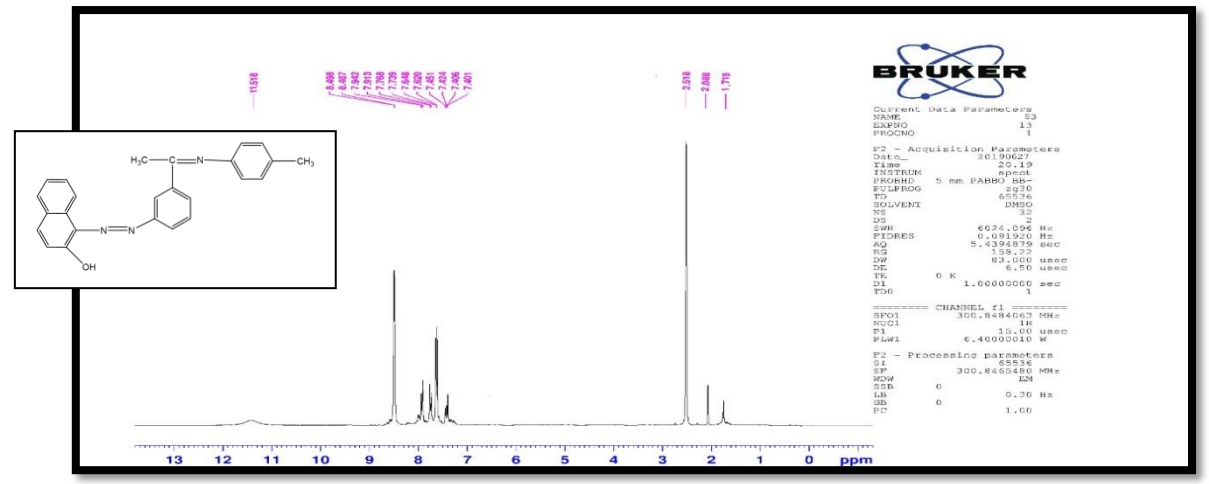


Figure9: ^{1}HNMR Spectra of compound (S_3)

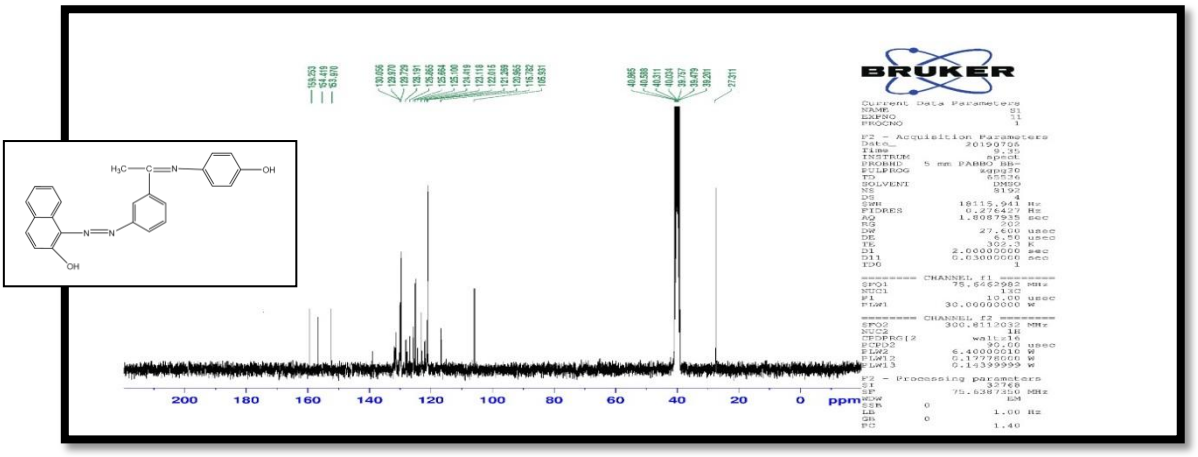


Figure10: ^{13}CNMR Spectra of compound (S_1)

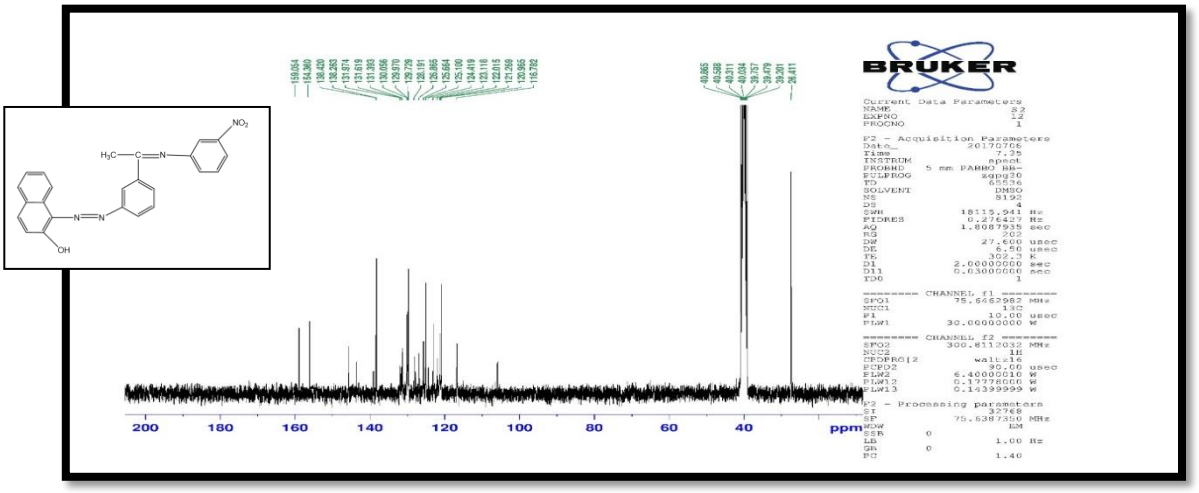


Figure11: ^{13}CNMR Spectra of compound (S_2)

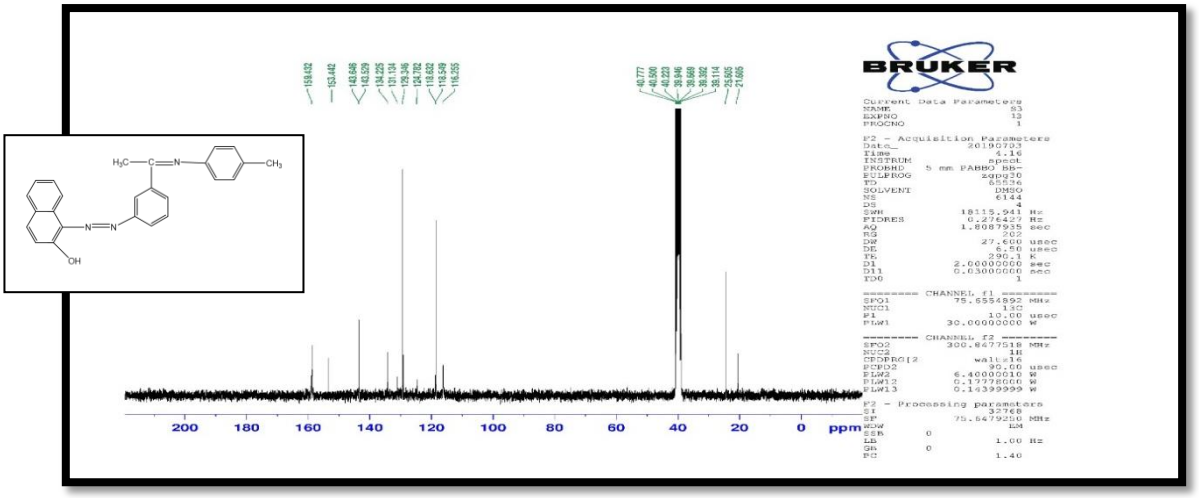


Figure12: ^{13}CNMR Spectra of compound (S_3)

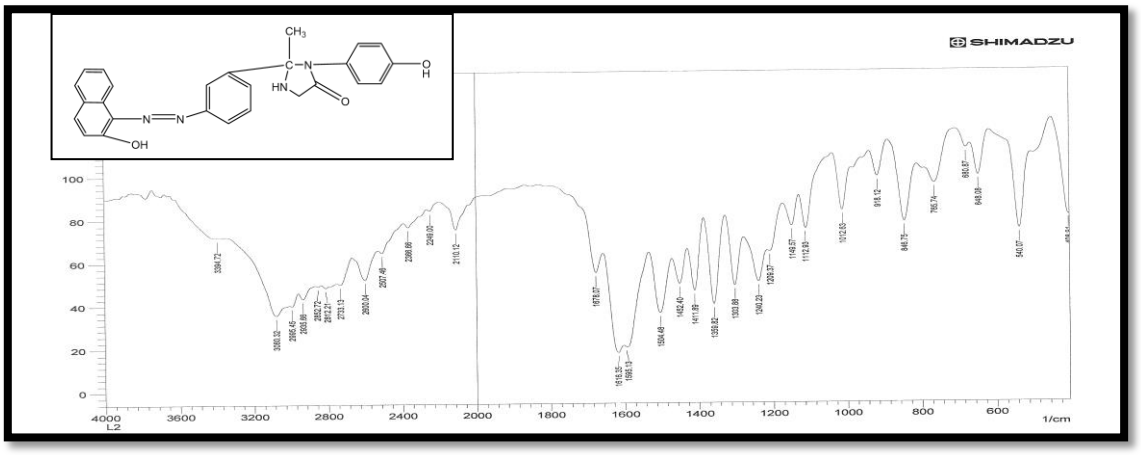


Figure13: FTIR Spectra of compound (L_1)

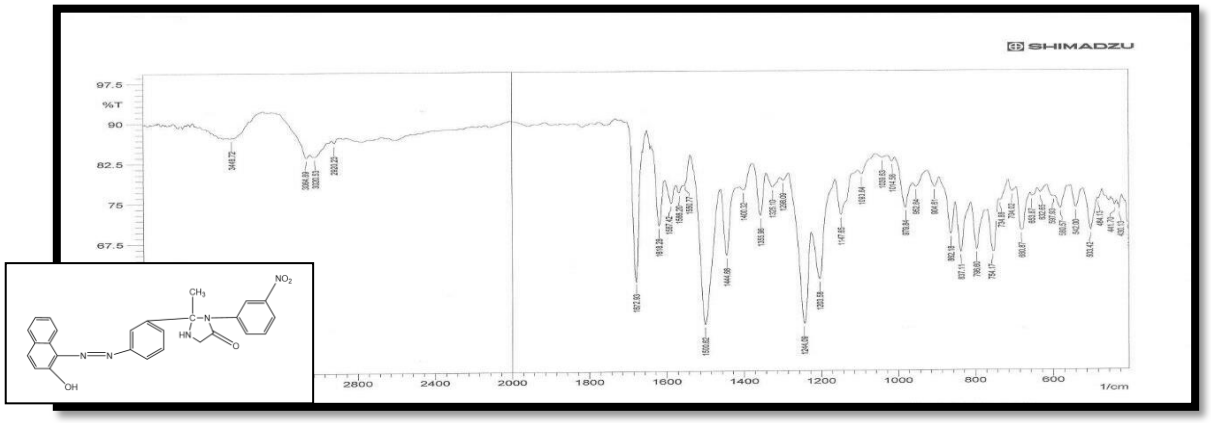


Figure14: FTIR Spectra of compound (L_2)

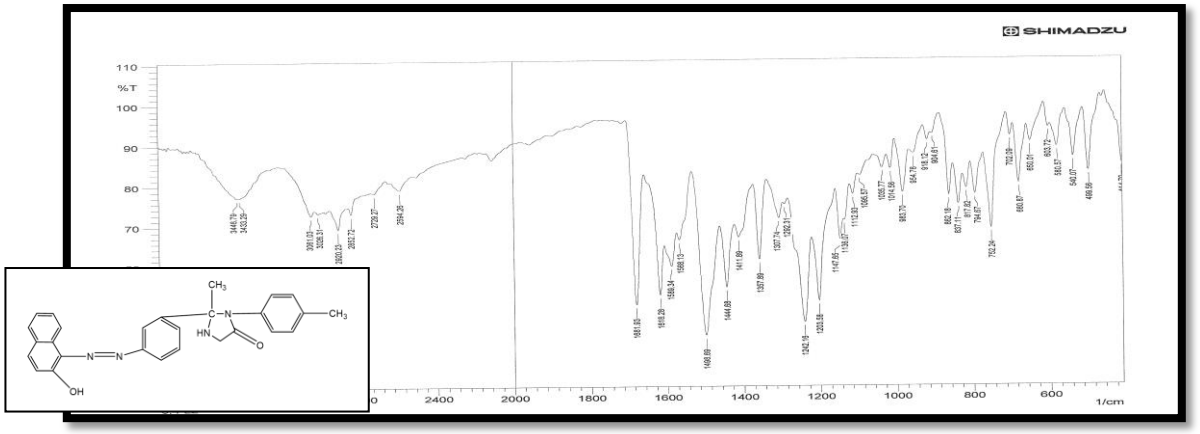


Figure15: FTIR Spectra of compound (L_3)

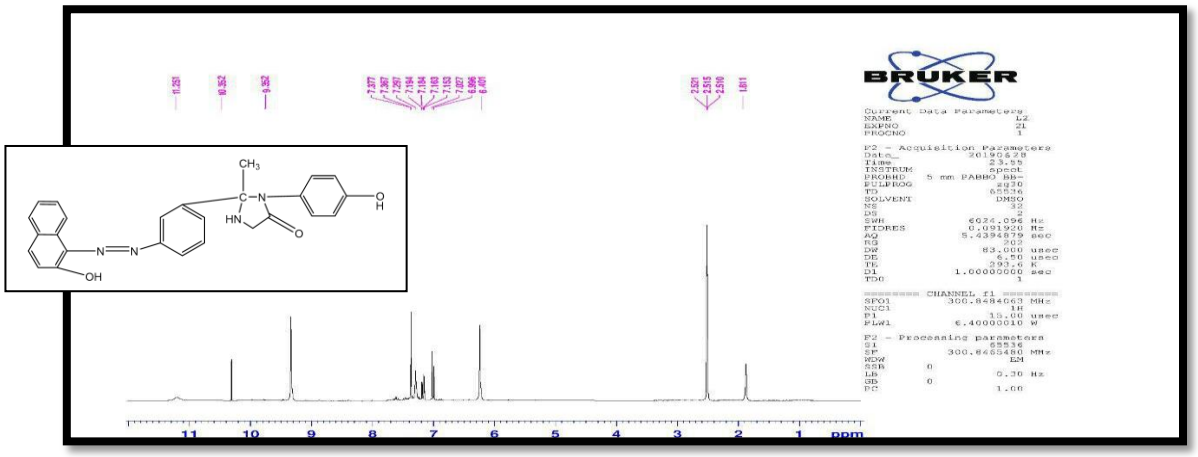


Figure16: ^{1}HNMR Spectra of compound (L_1)

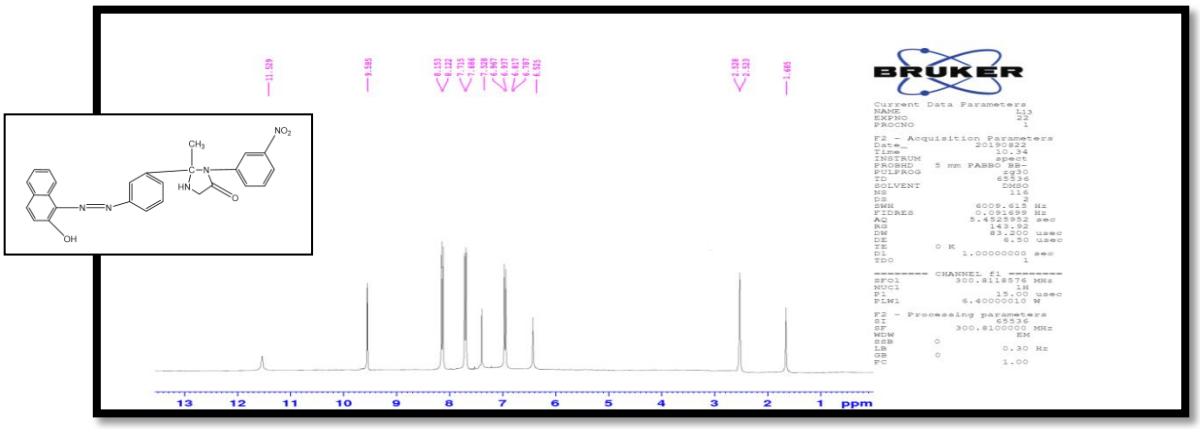


Figure17: ^{1}HNMR Spectra of compound (L_2)

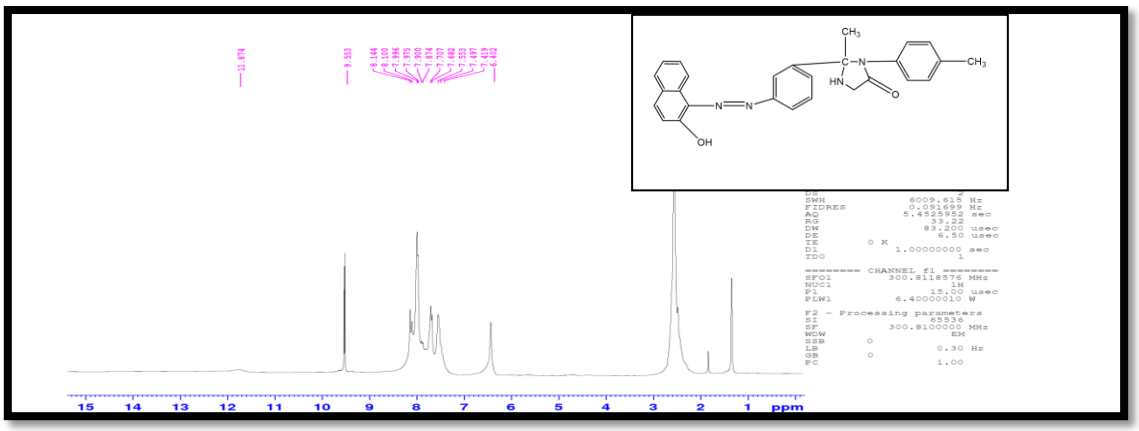


Figure18: ^{1}HNMR Spectra of compound (L_3)

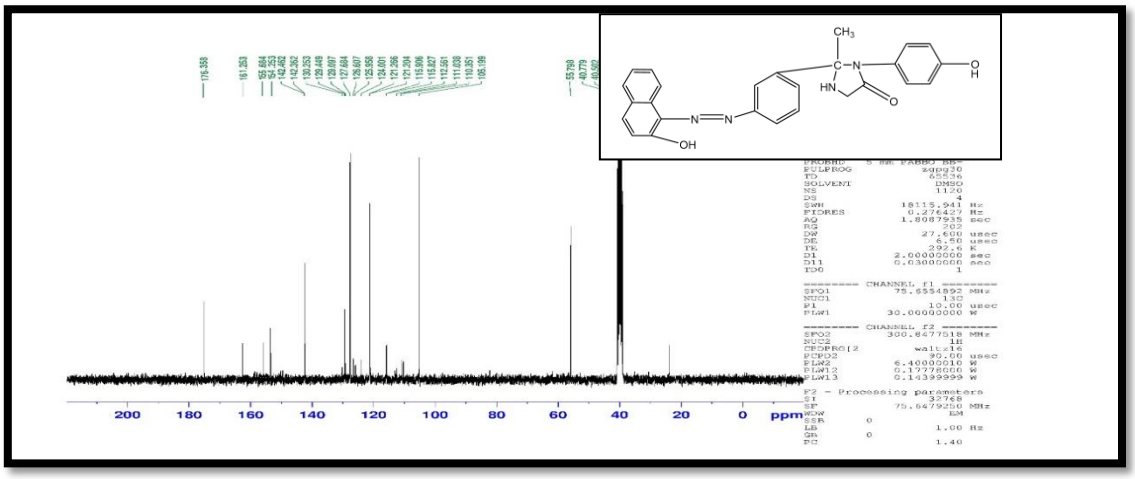


Figure19: ^{13}CNMR Spectra of compound (L_3)

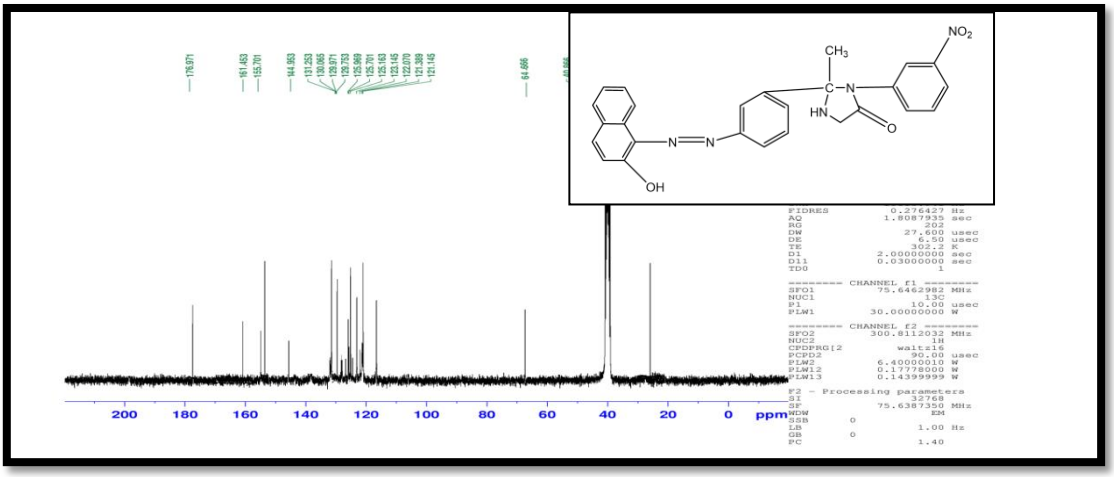


Figure20: ^{13}CNMR Spectra of compound (L_3)

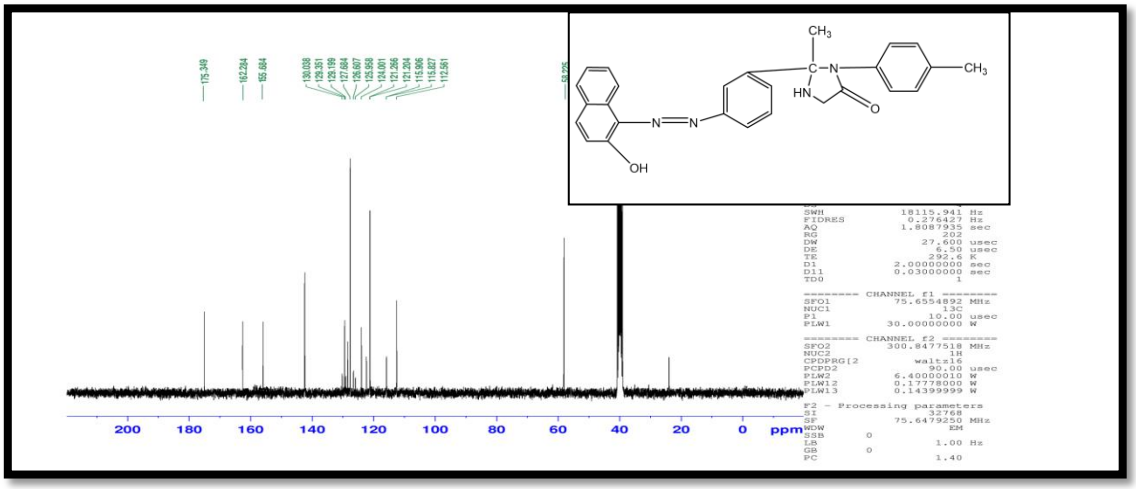


Figure21: ^{13}CNMR Spectra of compound (L_3)

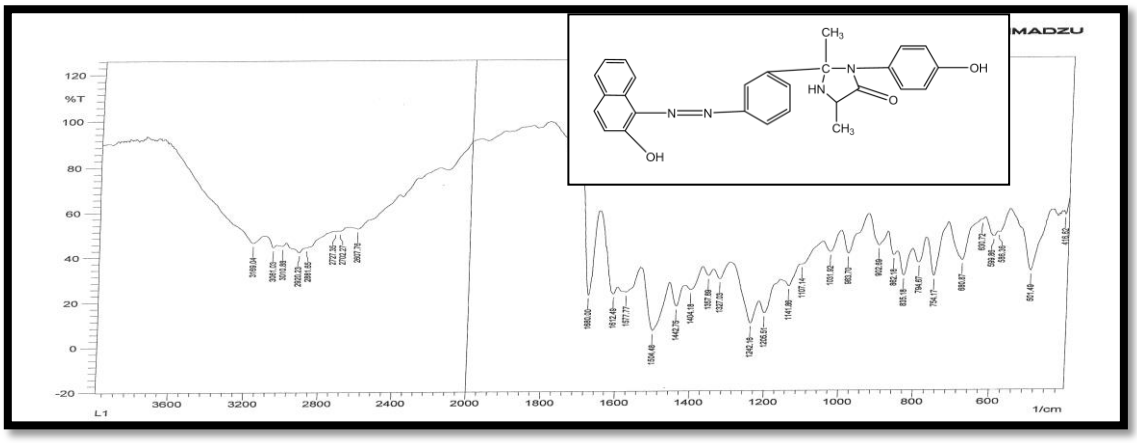


Figure22: FTIR Spectra of compound (L_4)

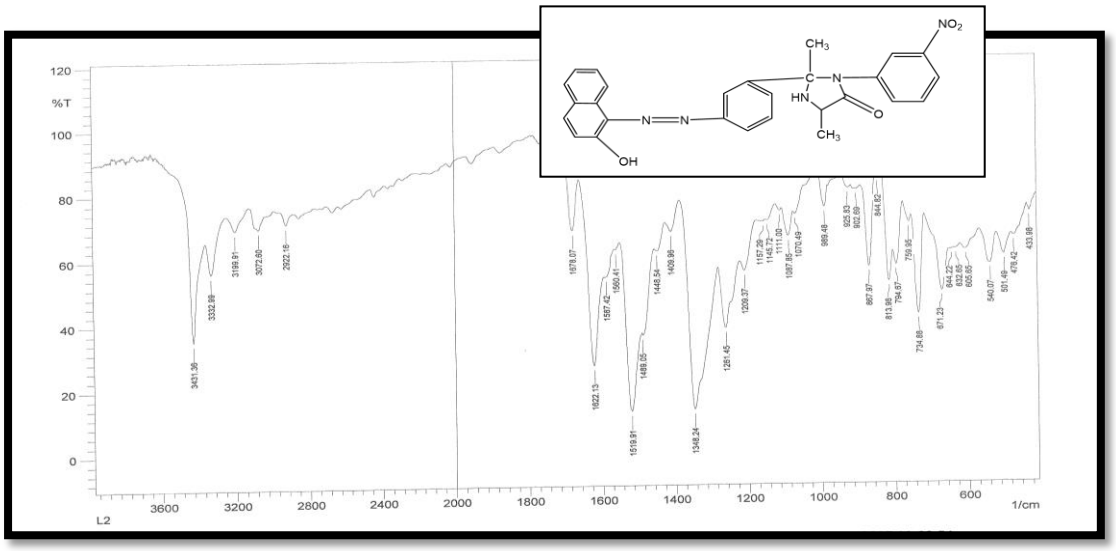


Figure23: FTIR Spectra of compound (L_5)

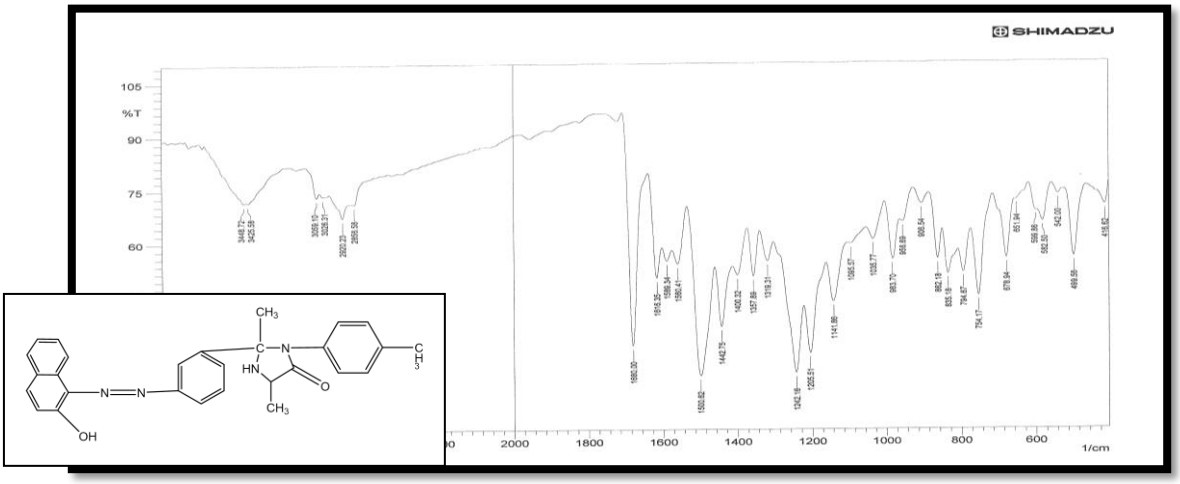


Figure24: FTIR Spectra of compound (L_6)

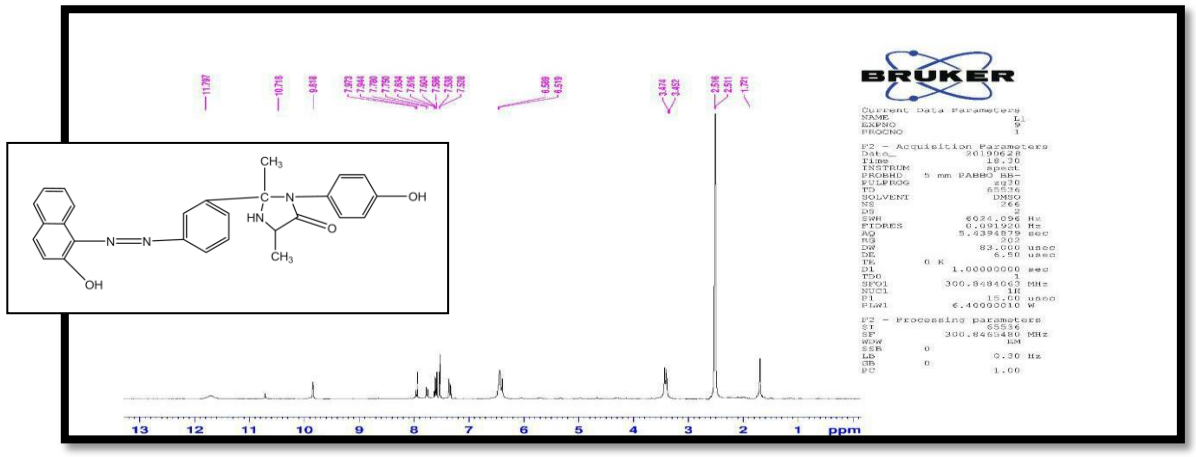


Figure25: ^{1}HNMR Spectra of compound (L_4)

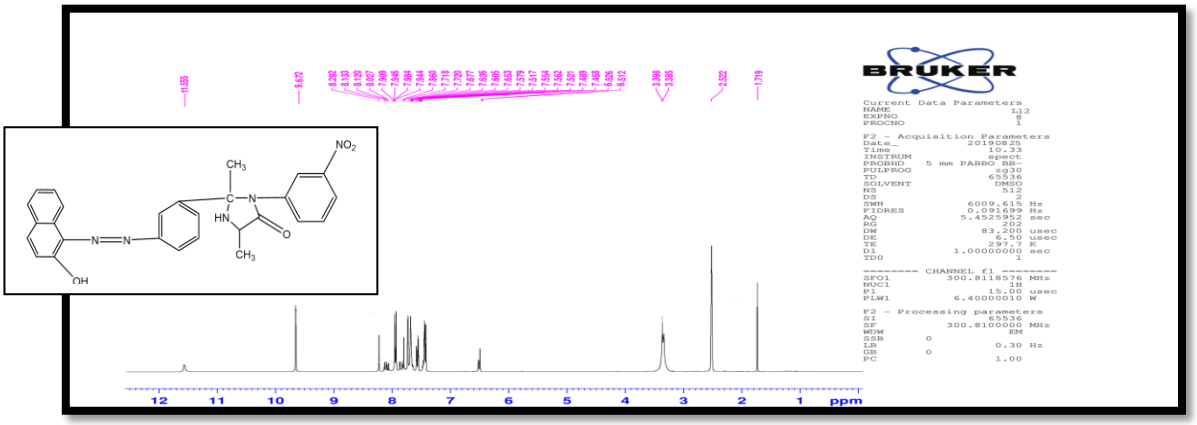


Figure26: ^{1}HNMR Spectra of compound (L_5)

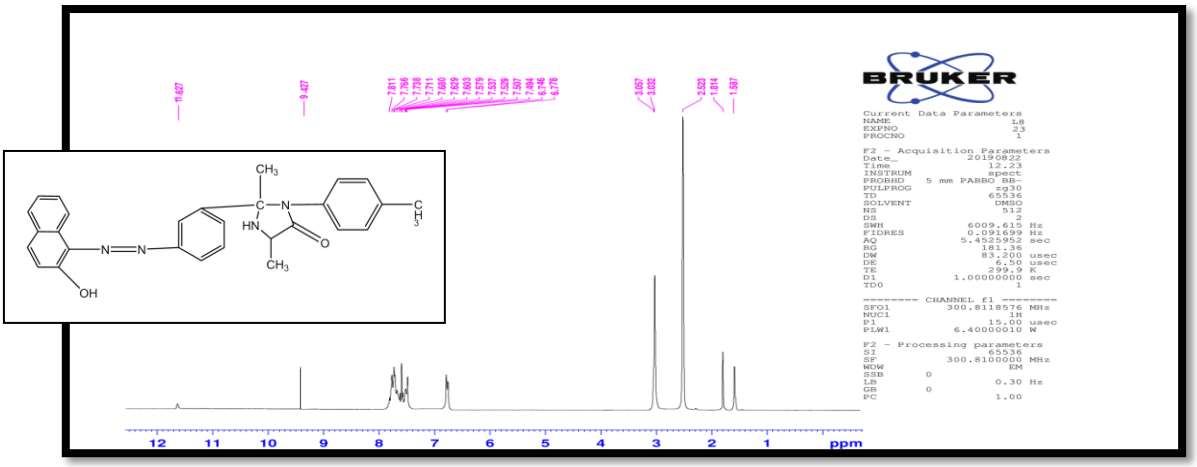


Figure27: ^{1}HNMR Spectra of compound (L_6)

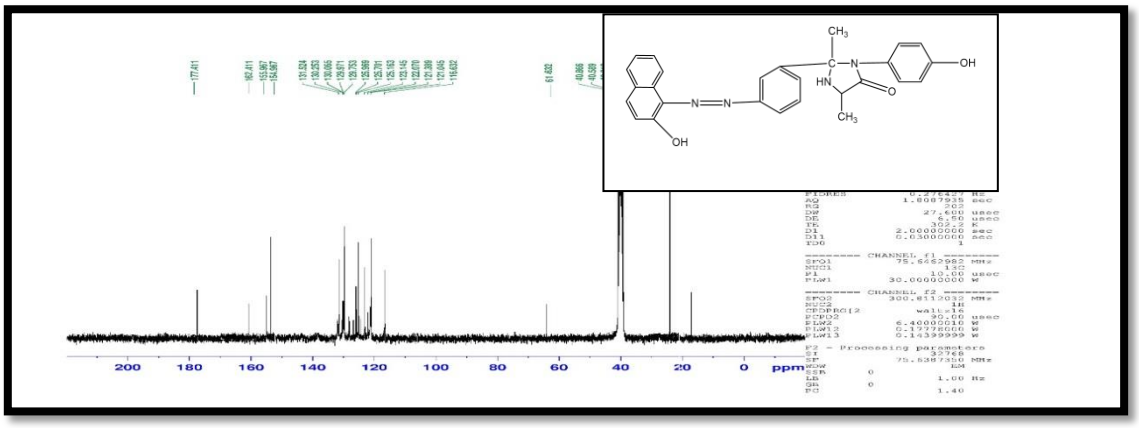


Figure28: ^{13}CNMR Spectra of compound (L_4)

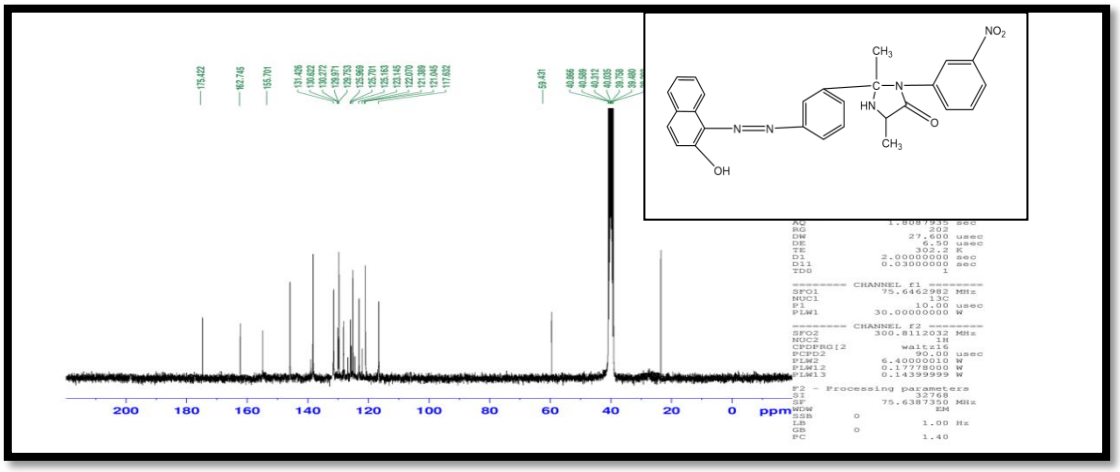


Figure29: ^{13}CNMR Spectra of compound (L_5)

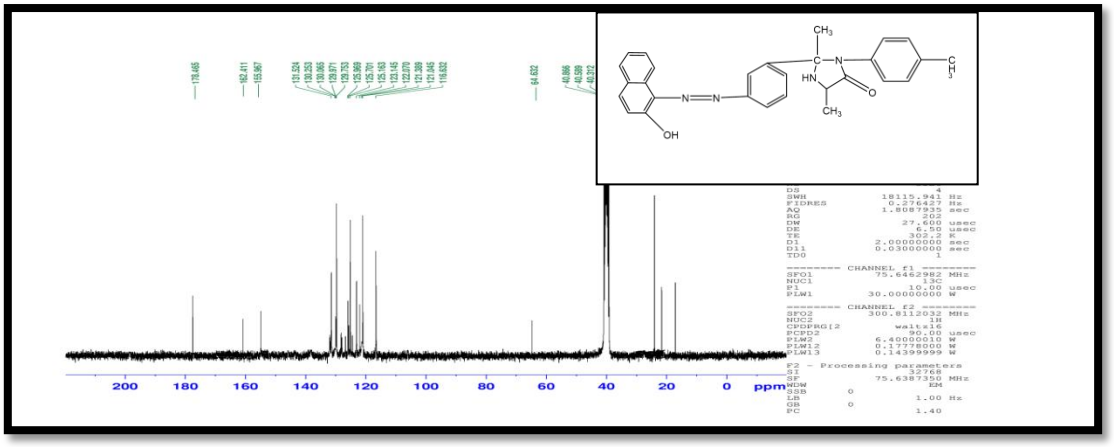


Figure30: ^{13}CNMR Spectra of compound (L_6)

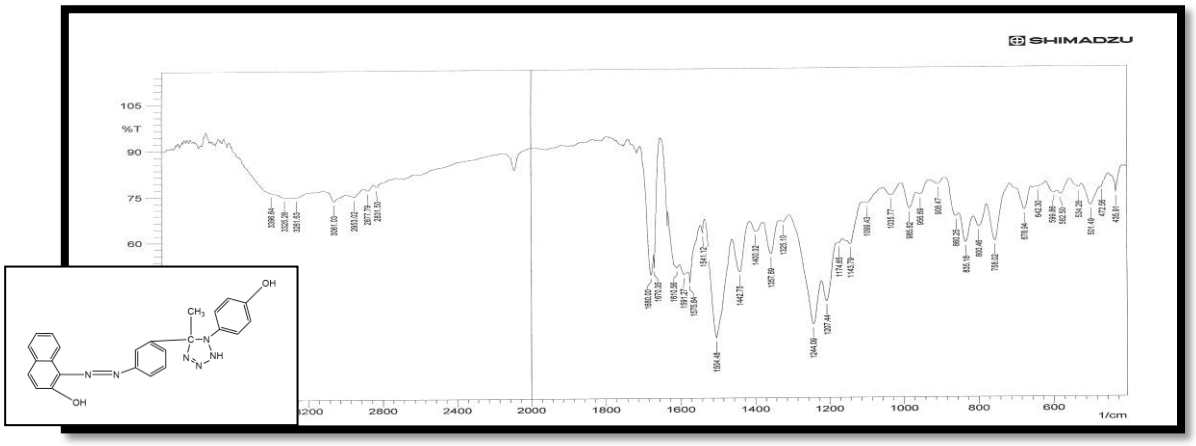


Figure31: FTIR Spectra of compound (L_7)

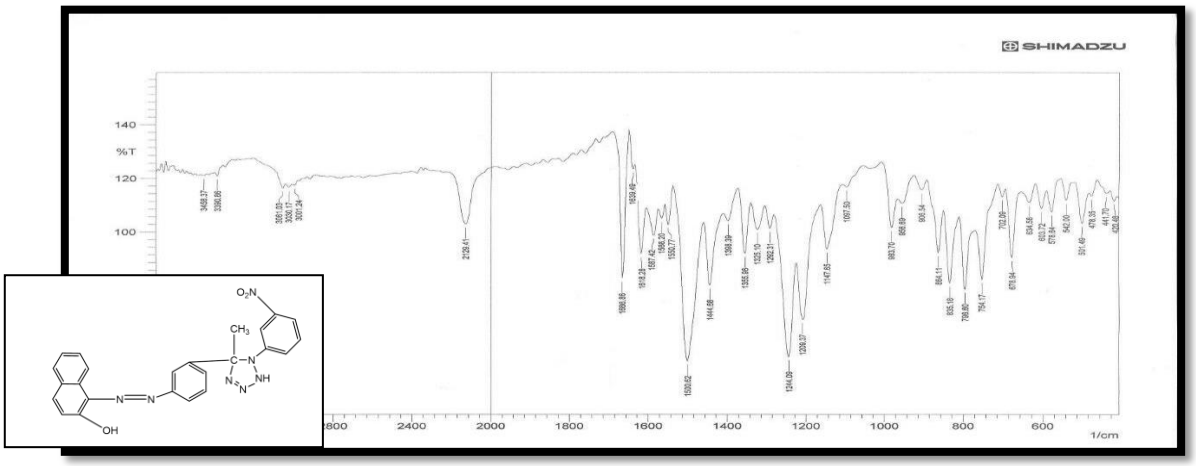


Figure32: FTIR Spectra of compound (L_8)

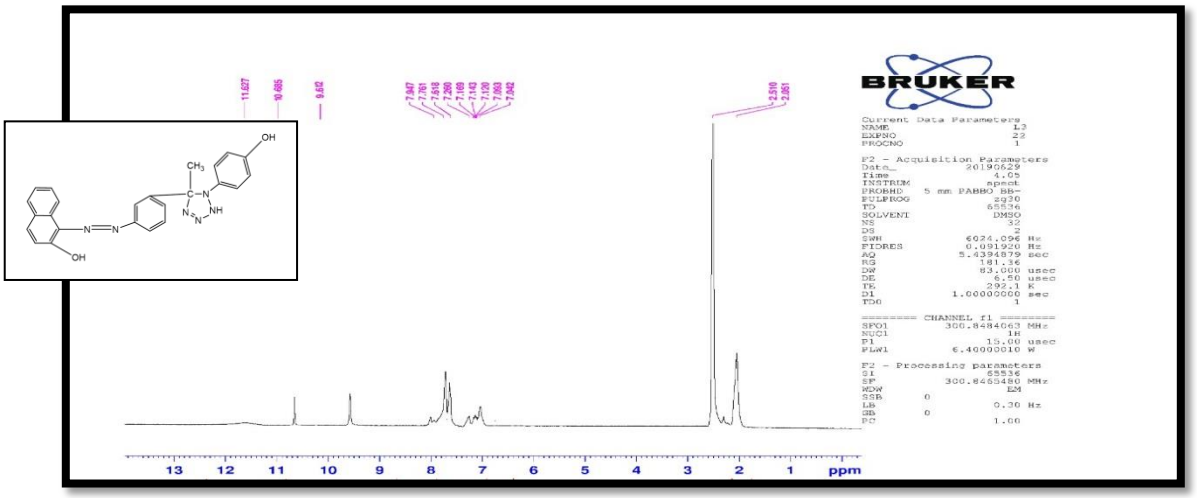


Figure33: ^{1}HNMR Spectra of compound (L_8)

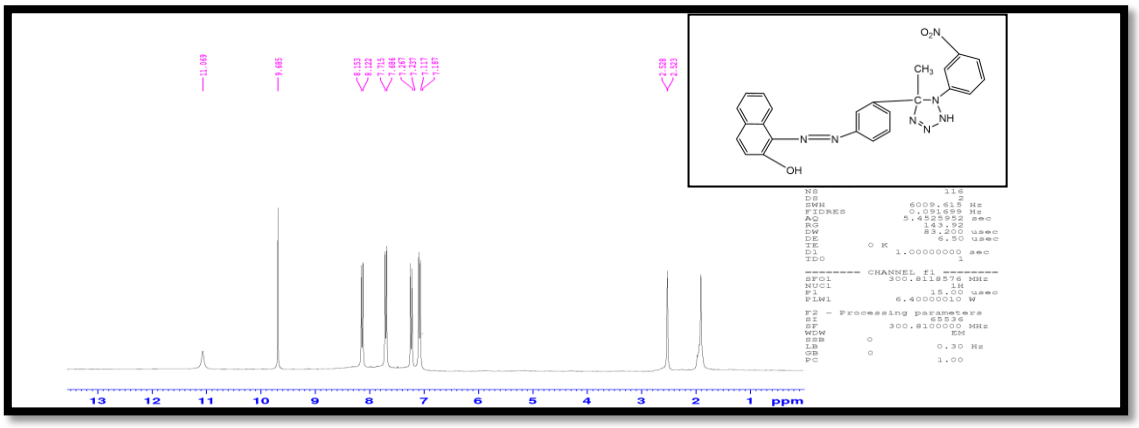


Figure34: ^{1}HNMR Spectra of compound (L_8)

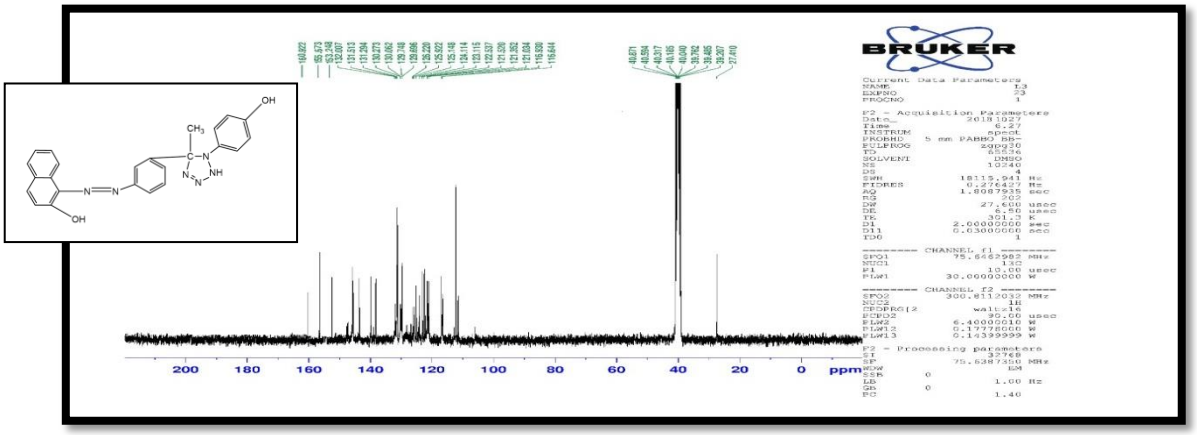


Figure35: ^{13}CNMR Spectra of compound (L_7)

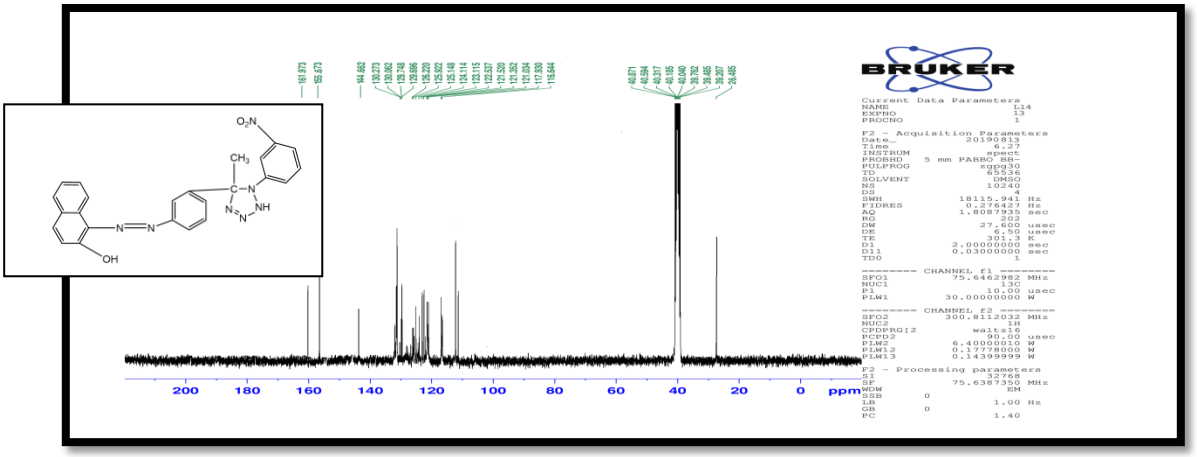


Figure36: ^{13}CNMR Spectra of compound (L_8)

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