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Synthesis and characterization of Some New Tetrazole and 1,3-Oxazepine Derivatives

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Abstract

In this work new Schiff bases [3-4], tetrazole [7] and [10] and 1,3-oxazepine [5-6] and [8-9] derivatives were prepared starting from azoaldehyde derivative 5,5'-(3,3'-dimethylbiphenyl-4,4'-diyl)bis(diazene-2,1-diyl)bis(2-hydroxybenzaldehyde) [2] and the primary amines 5-Amino-1,3,4-thiadiazole-2-thiol and 2-Amino benzothiazole.

Azo aldehyde derivative [2] was prepared *via* coupling reaction between ***o***-Hydroxy benzaldehyde and diazonium salt which was formed *via* reaction of toluidine [1] with concentrated hydrochloric acid and sodium nitrite .The new Schiff bases [3] and [4] were prepared by reaction of azo aldehyde derivative [2] with each primary amines, 5-Amino-1,3,4-thiadiazole-2-thiol and 2-Amino benzothiazole,respectively , in presence of glacial acetic acid as catalyst .The new 1,3-oxazepine derivatives [5] , [6] and [8], [9] were obtained from treatment of each prepared Schiff bases derivatives [3] and [4] with each maleic anhydride and 3-nitro phthalic anhydride , respectively ,in dry benzene .Treatment of each Schiff bases [3] and [4] with sodium azide in dry dioxan resulted the formation of new tetrazole derivatives [7] and [10] ,respectively .These new synthesized derivatives might have some biological activity.

All new derivatives were characterized by (C.H.N.) elementary analysis and FT-IR spectra.

الخلاصة:

تم في هذا البحث تحضير مشتقات قواعد شيف [3-4] وتترازول [7] ، [10] و 1،3- اوكسازيبين [5-6] ، [8-9] جديدة من مشتق الازوالديهايد 5,5'-(3,3'- داي مثل بايفنل -4,4'-دابيل بس(دايازين-1،2-دابيل)) بس (2-هيدروكسي بنزالديهايد [2] والامينات الاولية 5- امينو- 1،3،4-ثاياديازول-2-ثايول و 2-امينو بنزو ثيازول .

حضر مشتق الازوالديهايد [2] من خلال تفاعل الازدواج بين *O* - هيدروكسي بنزالديهايد وملح الدايازونيوم المتكون من تفاعل التولدين [1] مع حامض الهيدروكلوريك المركزو نتريت الصوديوم. حضرت قواعد شيف الجديدة [3] و[4] عن طريق تفاعل مشتق الازو الديهايد [2] مع كل من الامينات الاولية ، 5- امينو- 1،3،4-ثاياديازول-2-ثايول و 2- امينو بنزو ثيازول ، على التوالي ، في الايثانول المطلق بوجود حامض الخليك الثلجي كعامل مساعد . تم الحصول على مشتقات 1،3 – اوكسازيبين الجديدة [5]، [6] و [8] ، [9] من معاملة كل من مشتقات قواعد شيف المحضرة [3] و [4] مع كل من انهدريد الماليك و3- نترو انهدريد الفثاليك ، علي التوالي في البنزين الجاف . ان معاملة كل من مشتقات قواعد شف المحضرة [3] و [4] مع ازيد الصوديوم في الدايوكسان الجاف اعطت مشتقات تترازول جديدة [7] و [10] على التوالي. ان هذة المشتقات الجديدة قد تمتلك فعالية حيوية .

كافة المركبات الجديدة تم تشخيصها بوساطة التحليل الكمي الدقيق للعناصر (C.H.N.) واطياف الاشعة تحت الحمراء.

Introduction

Azo group is considered biological active group[1,2].The most important method for preparing azo compounds is the coupling reaction between diazonium salts and phenols [3] .

Schiff bases or imines are prepared via acid-catalysed condensation reaction of aromatic aldehydes or ketones with primary amines [4,5].Azo Schiff bases are prepared by reaction of azoaldehydes with primary amines [6] . Mechanism of Schiff base formation was well known [4,5].Various azo Schiff bases derivatives were prepared and some of them showed biological activity such as anticancer [7] antiviral [8],antifungal [9] , antibacterial [10] and anticonvulsant [11] .Thiadiazoles have a variety of potential biological activities [12,13] , therefore a large number of

thiadiazole derivatives have been prepared [14,15] .Many synthesis of 1,3,4-thiadiazoles proceed from thiosemicarbazide or substituted thiosemicarbazide [16,17] .). For a long time, the synthesis of 1,3- and 1,4-oxazepine rings was based on two limited classical types of reactions, the first reaction is called Valence-bond isomerization which is carried out via irradiation of polyarylpyridine N-oxides. This irradiation results in ring expansion to 1,3-oxazepine in high yield and some deoxygenation to the parent amines[18] . The second reaction is called Enamines condensation which is carried out by reaction of Erythro 1,2-diphenyl-2-phenylaminoethanol with dimethylacetylene dicarboxylate in methanol at room temperature to give a mixture of the Michael adduct and tetrahydro-1,4-oxazepin-7-one[19]. Recently, a pericyclic reactions are used to synthesis of 1,3-oxazepine ring[20-23]. This type of reactions is not limited and gives various 1,3-oxazepine ring derivatives. The type of cycloaddition reaction that used to synthesis of 1,3-oxazepine ring was classified as (2+5) → 7 cycloaddition reaction in which two atoms of imine group as two-membered component was added to five-membered component such as maleic or phthalic anhydrides to give a seven-membered heterocycle[20-23].Some oxazepine derivatives showed biological activities against various types of bacteria [24] and some of them act as inhibitors of some enzymes action [25].

Also , the 1,3-dipolar cycloaddition reaction,which was used to synthesis of tetrazole ring was classified as (2+3) cycloaddition , in which two atoms of the first component (imine or nitrile groups as a 1,3-dipolarphiles) react with three atoms of the second component (azide group as a 1,3-dipolar molecule) [26,27].Tetrazole derivatives showed fungicidal and antiviral activities [28].

The aim of this research is synthesis of some new oxazepine and tetrazole derivatives containing the biologically active azo group and thiadiazole ring all together,as attempt for increasing the biological activity and its variety.

Experimental:

General

1) TLC were performed on pre-coated sheets with 0.25 mm layer of Silica Gel GF254 of the Merck company, the detection was followed by coloring with iodine or H_2SO_4 in ethanol (60%) followed by
2) Melting points (M.P.) were determined by Stuart melting point apparatus.
3) Elemental analysis measured on E.A.300, Euro- Vector, Italy, 2003-AL-albayt University (Jordan).
4) FT-IR spectra were recorded on FT-IR 8400_S, Schimadzu-Spectrophotometer and using KBr discs- Kerbala university.

Preparation Methods:

Synthesis of 5,5'-(3,3'-dimethylbiphenyl-4,4'-diyl)bis(diazene-2,1-diyl)bis(2-hydroxybenzaldehyde)[2][3]

Toluidine [1] (2.12g, 0.01 mol) was dissolved concentrated hydrochloric acid (16mL) and distilled water (16 mL) contained in a small beaker. The mixture was cold at 0°C in an ice bath,then a solution of sodium nitrite (1.656g, 0.024 mol) dissolved in distilled water (20 mL) was added dropwise to the mixture with stirring. The temperature of the ice bath was controlled between 0-5°C.A solution of 2- hydroxybenzaldehyde (2.44g, 0.02 mol) dissolved in (20 mL) of (10%) sodium hydroxyide solution in (150 mL) beaker was prepared and cold to 5°C by immersion in an ice bath. 2-Hydroxybezaldehyde solution was then stirred vigorously,then the diazonium salt solution was added very slowly to the 2- hydroxybezaldehyde solution, a red colour developed and red crystals soon separated. When all the diazonuim salt solution was added, the mixture was allwoed to stand in an ice bath for 30 min. with occasional stirring. The solution was filtered, washed well with distilled water, recrystallized from ethanol and dried upon filter paper, yield 57%, M.P. 95-97 °C .

Synthesis of 4,4'-(3,3'-dimethylbiphenyl-4,4'-diyl)bis(diazene-2,1-diyl)bis(2-((E)-(5-mercapto-1,3,4-thiadiazol-2-ylimino)methyl)phenol) [3]

Azo aldehyde derivative [2](0.478g, 0.001 mol) was dissolved in absolute ethanol (15 mL) containing a drop of glacial acetic acid ,then 5-Amino-1,3,4-thiadiazol-2-thiol (0.266 g ,0.002 mol) was dissolved in absolute ethanol (15 mL) and added dropwise . The reaction mixture was refluxed with stirring on a water bath at 70 ^{o}C for 2hrs.T.L.C. (ethanol:pet.ether)(1:1) ,R_f = 0.7.Then the mixture was allowed to cool down to room temperature , the coloured precipitate was filtered and recrystallized from ethanol ,yield 79% , M.P.138-140 ºC.

Synthesis of 4,4'-(3,3'-dimethylbiphenyl-4,4'-diyl)bis(diazene-2,1-diyl)bis(2-((E)-(benzo[d]thiazol-2-ylimino)methyl)phenol) [4]

Azo aldehyde derivative [2](0.478g , 0.001 mol) was dissolved in absolute ethanol (15 mL)containing a drop of glacial acetic acid ,then 2-Amino benzothiazole (0.3g ,0.002 mol) was dissolved in absolute ethanol (15 mL) and added dropwise . The reaction mixture was refluxed with stirring on a water bath at 70 ^{o}C for 2hrs.T.L.C. (ethanol:pet.ether) (1:1) R_f = 0.66.Then the mixture was allowed to cool down to room temperature , the coloured precipitate was filtered and recrystallized from ethanol ,yield 81% , M.P.118-120 ºC.

Synthesis of (5Z,5'Z)-2,2'-(5,5'-(3,3'-dimethylbiphenyl-4,4'-diyl)bis(diazene-2,1-diyl)bis(2-hydroxy-5,1-phenylene))bis(3-(5-mercapto-1,3,4-thiadiazol-2-yl)-2,3-dihydro-1,3-oxazepine-4,7-dione) [5]

A mixture of imine derivative [3](0.708g, 0.001 mol) and maleic anhydride (0.196 g ,0.002mol) in dry benzene(20 m**L)** , was refluxed on a water bath at 75ºC for 4hrs. T.L.C. (benzene:methanol) (3:1) R_f = 0.8. , then the mixture was allowed to cool down to room temperature . The resulting solid crystals were filtered and recrystallized from dioxan, yield 67% , M.P. 170-172 ºC.

Synthesis of 3,3'-(5,5'-(3,3'-dimethylbiphenyl-4,4'-diyl)bis(diazene-2,1-diyl)bis(2-hydroxy-5,1-phenylene))bis(4-(5-mercapto-1,3,4-thiadiazol-2-yl)-6-nitro-3,4-dihydrobenzo[e][1,3]oxazepine-1,5-dione) [6]

A mixture of imine derivative [3](0.708 g, 0.001 mol) and 3-Nitro phthalic anhydride (0.386g ,0.002mol) in dry benzene(20 m**L)** , was refluxed on a water bath at 75ºC for 4hrs. T.L.C. (benzene:methanol) (3:1) R_f = 0.77. , then the mixture was allowed to cool down to room temperature . The resulting solid crystals were filtered and recrystallized from dioxan, yield 65% , M.P.199-200 ºC.

Synthesis of 4,4'-(3,3'-dimethylbiphenyl-4,4'-diyl)bis(diazene-2,1-diyl)bis(2-(1-(5-mercapto-1,3,4-thiadiazol-2-yl)-1H-tetrazol-5-yl)phenol) [7]

A mixture of imine derivative [3] (0.708g, 0.001 mol) and sodium azide (0.13 g , 0.002mol) in dry dioxan(20 m**L)** was refluxed on a water bath at 75ºC for 5hrs, T.L.C. (benzene:methanol) (1:1) R_f = 0.6.The reaction mixture was allowed to cool to room temperature , filtered and recrystallized from ethanol , yield 64 % , M.P. 161-163 ºC.

Synthesis of (5Z,5'Z)-2,2'-(5,5'-(3,3'-dimethylbiphenyl-4,4'-diyl)bis(diazene-2,1-diyl)bis(2-hydroxy-5,1-phenylene))bis(3-(benzo[d]thiazol-2-yl)-2,3-dihydro-1,3-oxazepine-4,7-dione) [8]

A mixture of imine derivative [4](0.742g, 0.001 mol) and maleic anhydride (0.196g, 0.002mol) in dry benzene(20 m**L)** , was refluxed on a water bath at 75ºC for 4hrs. T.L.C. (benzene:methanol) (3:1) R_f = 0.66. , then the mixture was allowed to cool down to room temperature . The resulting solid crystals were filtered and recrystallized from dioxan, yield 70 % ,M.P. 155-157 ºC.

Synthesis of 3,3'-(5,5'-(3,3'-dimethylbiphenyl-4,4'-diyl)bis(diazene-2,1-diyl)bis(2-hydroxy-5,1-phenylene))bis(4-(benzo[d]thiazol-2-yl)-6-nitro-3,4-dihydrobenzo[e][1,3]oxazepine-1,5-dione) [9]

A mixture of imine derivative [4](0.742g g,0.001 mol) and 3-Nitro phthalic anhydride (0.386g ,0.002mol) in dry benzene(20 m**L)** , was refluxed on a water bath at 75ºC for 4hrs. T.L.C. (benzene:methanol) (3:1) R_f = 0.61. , then the mixture was allowed to cool down to room temperature . The resulting solid crystals were filtered and recrystallized from dioxan, yield 72 % , M.P. 162-164 ºC.

Synthesis of 2-(1-(benzo[d]thiazol-2-yl)-1H-tetrazol-5-yl)-4-((4'-((4-hydroxy-3-(1-(5-mercapto-1,3,4-thiadiazol-2-yl)-1H-tetrazol-5-yl)phenyl)diazenyl)-3,3'-dimethylbiphenyl-4-yl)diazenyl)phenol [10]

A mixture of imine derivative [4] (0.742g , 0.001 mol) and sodium azide (0.13g ,0.002 mol) in (20 m**L)** of dry dioxan , was refluxed on a water bath at 75ºC for 5hrs, T.L.C. (benzene:methanol)(1:1) R_f = 0.59. The reaction mixture was allowed to cool down to room temperature , filtered and recrystallized from ethanol , yield 66 % , M.P. 145-147ºC.

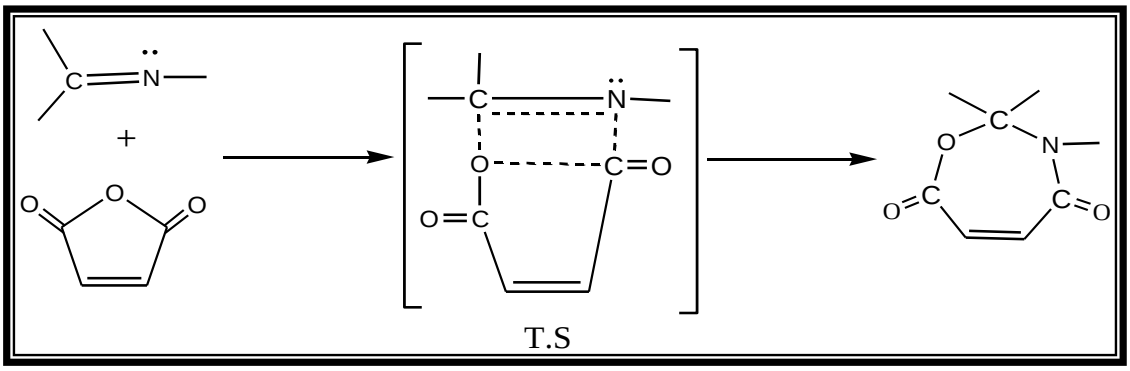
Table (1): Melting points, percent yields and (C.H.N.)analysis of the prepared compounds (2-10)

Comp. No.	M.P ºC	Yield %	M.F	M.Wt g/mole	C.H.N analysis					
					Calculated%			Found%		
					C	H	N	C	H	N
[2]	95-97	57	$C_{28}H_{22}N_4O_4$	478	70.29	4.60	11.71	70.03	4.81	11.92
[3]	138-140	79	$C_{32}H_{24}N_{10}O_2S_4$	708	54.23	3.38	19.77	53.95	3.11	19.99
[4]	118-120	81	$C_{42}H_{30}N_8O_2S_2$	742	67.92	4.04	15.09	68.13	3.82	14.93
[5]	170-172	67	$C_{40}H_{28}N_{10}O_8S_4$	904	53.09	3.09	15.48	53.30	2.94	15.66
[6]	199-200	65	$C_{48}H_{30}N_{12}O_{12}S_4$	1094	52.65	2.74	15.35	52.89	3.02	15.59
[7]	161-163	64	$C_{32}H_{22}N_{16}O_2S_4$	790	48.60	2.78	28.35	48.39	3.05	28.22
[8]	155-157	70	$C_{50}H_{34}N_8O_8S_2$	938	63.96	3.62	11.94	46.10	3.44	12.13
[9]	162-164	72	$C_{58}H_{36}N_{10}O_{12}S_2$	1128	61.70	3.19	12.41	61.88	3.42	12.70
[10]	145-147	66	$C_{42}H_{28}N_{14}O_2S_2$	824	61.16	3.39	23.78	60.85	3.67	24.01

Results and Discussion

Toluidine [1]was converted to the corresponding diazonium salt , *via* reaction with concentrated hydrochloric acid and sodium nitrite at (0 ºC) , which was directly introduced in a coupling reaction with 2-hydroxy benzaldehyde dissolved in sodium hydroxide solution at (0-5) ºC to give azo aldehyde derivative [2] [(3)] ,then the two carbonyl groups in azo aldehyde derivative [2] were introduced in acid -catalysed condensation reaction with amino groups for each 5-Amino-1,3,4-thiadiazol-2-thiol and 2-Amino benzothiazole ,respectively in absolute ethanol to give new azo Schiff bases derivatives [3] and [4] , respectively [(6,23,27)] .

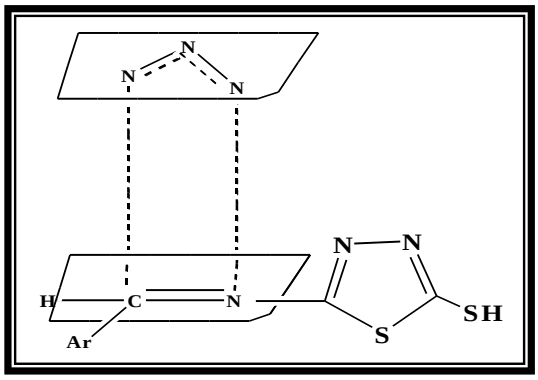
A pericyclic reactions, between imine groups of Schiff bases derivatives [3] and [4], as two-membered components, and cyclic anhydrides (maleic anhydride and 3-nitro phthalic anhydride) as five-membered components in dry benzene, were carried out to synthesis of 1,3-oxazepine derivatives [5] , [6] and [8], [9] [(20-23)]. A pericyclic reaction is a concerted process based on principle of conservation of molecular orbital symmetry between the reaction components during the reaction proceeding which is leading to a cyclic transition state corresponds with arrangement of participating orbitals[(20,22)]. Concerted reaction means that breaking and formation of bonds occur simultaneously via a single transition state and there is no intermediate in the process. Mechanism of the pericyclic reaction for the synthesis 1,3-oxazepine ring shown in scheme (1)[(20,22)]:



Scheme (1): Approximate transition state geometry for maleic anhydride addition to imine group

Tetrazole derivatives [7] and [10] were prepared by reaction of Schiff bases derivatives [3] and [4] with sodium azide in dioxan,respectively .The mechanism of this reaction was systematically investigated as [2+3] cycloaddition which christened as 1,3-dipolar cycloaddition.It is involved the addition of unsaturated systems ,dipolarphiles ,to 1,3-dipoles,a molecule possessing resonance contributors in which the positive and negative charges are located in 1,3-positions relative to each other.The addition results in a five-membered ring .Azides are a prominent class of 1,3-dipoles and azides 1,3-dipolar cycloadditions are of great synthetic value and have been studies mechanistically in great detail[(5,29)].

The common features of this type of reactions is best accommodated by transition state geometry in which the dipolarphile and its ligands lies in one plane ,and the azide lies in a parallel plane above or below,so that the orbitals perpendicular to the planes interact to form bonds,as it was shown in scheme(2) [(5,29)]:



Scheme (2): Approximate transition state geometry for azide addition to imine

The structures of all synthesised compounds[2-10] were shown in scheme (3) .The new synthesised compounds were characterized by their melting points ,(C.H.N.) Elementary analysis which showed nearness between the found and calculated values for all compounds as it was shown in Table (1) and FT-IR spectra as it was shown in Table (2).

FT-IR spectrum of azoaldehyde derivative [2] showed the following characteristic absorption bands: the sharp strong absorption bands at 1630 cm^{-1} attributed to υ(C=O) . The sharp absorption bands at 3477 cm^{-1} , 3423 cm^{-1} and 3280 cm^{-1}due to the υ(OH) which were shifted to lower frequencies due to intramolecular hydrogen bonding with ***ortho*** aldehyde carbonyl group[30] .The two weak absorption bands at 3110 cm^{-1} and 3060 cm^{-1} attributed to the υ(C-H) aromatic.The three weak absorption bands at 2940 cm^{-1} ,2900 cm^{-1} 2856 cm^{-1} attributed to the υ (C-H) aliphatic of methyl groups. The two weak absorption bands 2720 cm^{-1} and 2654 cm^{-1} attributed to the υ (C-H) aliphatic of aldehyde groups (-CHO) .The sharp strong absorption band at 1658 cm^{-1} due to the υ(C=O) of aldehyde groups which was shifted to lower frequency due to intramolecular hydrogen bonding with ***ortho*** hydrxy group[30] .The two medium and strong absorption bands at 1589$cm^{-1}$and 1475 cm^{-1} attributed to the υ (C----C) aromatic of benzene ring. The medium absorption band at 1373 cm^{-1} attributed to the δ (O-H) [30] in plane. The absorption band for azo group did not appear due to the high symmetry of the molecule. The weak absorption bands at 1150 cm^{-1} and 1043 cm^{-1}attributed to the δ(C-H) aromatic in plane [30].The two strong absorption bands at 1276 cm^{-1} and 1199 cm^{-1} attributed to the υ(C-O) of phenol. The three strong absorption bands at 887 cm^{-1} , 829 $cm^{-1}$and 759 cm^{-1} attributed to the δ(C-H) aromatic out of plane.The weak absorption band at 694cm^{-1} due to δ(O-H) out of plane.

FT-IR spectrum of Schiff base derivative [3] showed disappearance of the strong absorption band at 1658 cm^{-1} attributed to the υ (C=O) of aldehyde group and appearance of medium, absorption band at 1664 cm^{-1} due to the υ(C=N) exocyclic of thiadiazole ring.Also ,disappearance of the absorption bands at 3392 cm^{-1} and 3279 cm^{-1} attributed to υ(-NH_2)[31,32]. FT-IR spectrum of compound [3] also showed appearance of another important characteristic absorption bands as follow : the strong absorption band at 1600 cm^{-1} attributed to the υ(C=N) endocyclic of thiadiazole ring . The weak and strong absorption bands at 1520cm^{-1} and 1471cm^{-1}attributed to the υ (C----C) aromatic of benzene ring.The sharp absorption bands at 3624 cm^{-1} and 3550 cm^{-1} due to the υ(free O-H) .The five absorption band at (3480-3240 cm^{-1}) due to the υ(bonding O-H) . The mediuim absorption band at 3198 cm^{-1} attributed to the υ(N-H) in the thione form[31,32].The weak absorption bands at 3150 cm^{-1},3099 cm^{-1} and 3060 cm^{-1} attributed to the υ(C-H) aromatic of benzene ring. The weak absorption bands at 2980 cm^{-1} ,2920 cm^{-1} and 2860 cm^{-1} attributed to the υ(C-H) aliphatic of methyl groups. The weak bands at 2800 cm^{-1} and 2665 cm^{-1} attributed to the υ(C-H) of

imine group. The weak band at 2557 cm^{-1} due to the υ(S-H) in thiol form.

The medium band at 1363 cm^{-1} attributed to the δ (O-H) in plane [30].The strong absorption bands at 1143 cm^{-1} and 1058 cm^{-1} attributed to the δ (C-H) aromatic in plane.The strong absorption bands at 1271 cm^{-1} and 1197 cm^{-1} attributed to the υ (C-O) of phenol. The three absorption bands at 905 cm^{-1}, 820 cm^{-1} and 760 cm^{-1} attributed to the δ(C-H) aromatic of benzene ring out of plane. The weak absorption band at 690 cm^{-1} due to the δ(O-H) out of plane. FT-IR spectrum of Schiff base derivative [4] showed disappearance of the strong absorption band at 1658 cm^{-1} attributed to the υ (C=O) of aldehyde group and appearance of medium absorption band at 1693 cm^{-1} attributed to the υ(C=N) groups exocyclic of benzothiazole ring. FT-IR spectrum of compound [4] also showed appearance of another important characteristic absorption bands as follow : the srong absorption band at 1606 cm^{-1} due to the υ(C=N) inside benzothiazole ring.The weak and strong absorption bands at 1530cm^{-1} and 1479cm^{-1} due to the υ (C=C) aromatic of benzene ring.The sharp absorption bands at 3650 cm^{-1} and 3600cm^{-1} attributed to υ(free O-H). The sharp absorption bands at (3470-3200 cm^{-1}) due to the υ(bonding O-H).The weak absorption band at 3148 cm^{-1} attributed to the υ(C-H) aromatic of benzene ring.The two weak absorption bands at 2920 cm^{-1} and 2830cm^{-1} due to the υ (C-H) aliphatic of methyl groups.The two weak bands at 2790 cm^{-1} and 2720 cm^{-1} due to the υ (C-H) of imine group. The weak absorption band at 1430 cm^{-1} attributed to the υ (N=N). The weak absorption band at 1370 cm^{-1} attributed to the δ (H-O) in plane. The two medium absorption bands at 1278 $cm^{-1}$and 1190 cm^{-1} attributed to the υ(C-O) of phenol. The absorption bands at 1138 cm^{-1}, 1065 cm^{-1}, 1045 cm^{-1} and 990 cm^{-1} attributed to the δ (C-H) aromatic of benzene ring in plane.The absorption bands at 890 cm^{-1} ,829cm^{-1} and 754cm^{-1} attributed to the δ(C-H) aromatic out of plane . The weak absorption band at 670 cm^{-1} attributed to the δ (O-H) out of plane. FT-IR spectrum of oxazepine derivative [5] showed disappearance of the strong band at 1664cm^{-1} attributed to the υ (exoC=N) and appearance of strong absorption band at 1795 cm^{-1} attributed to the υ (C=O) for lactone and lactam in oxazepine ring,(interacted). The strong absorption band at 1604 cm^{-1} attributed to the υ(C=N) inside thiadiazole ring .The two weak and strong absorption bands at 1520cm^{-1} and 1477cm^{-1} attributed to the υ (C=C) aromatic of benzene ring. The weak absorption band at 1369 cm^{-1} due to the δ (O-H) in plane. The two strong and weak absorption bands at 1282 cm^{-1} and1210 cm^{-1} attributed to the υ (C-O) in phenol. The medium absorption band at 1103 cm^{-1} attributed to the υ(C-O) for lactone in Oxazepine ring. The absorption band at 990 cm^{-1} attributed to the δ(C-H) aromatic in plane. The three absorption bands at 906 cm^{-1}, 840 cm^{-1} and 770 cm^{-1}due to the δ(C-H) aromatic of benzene ring out of plane. The medium absorption band at 707 cm^{-1} attributed to the δ (O-H) out of plane. FT-IR spectrum of compound [5] also showed appearance of the following absorption bands: The two medium and weak absorption bands at 3051cm^{-1} and 2987cm^{-1} attributed to the υ (C-H) aromatic of benzene ring. The two weak absorption bands at 2922 cm^{-1} and 2850cm^{-1} due to the υ (C-H) aliphatic of methyl groups . The two sharp absorption bands at 3630 cm^{-1} and 3572cm^{-1} due to the υ(free O-H) groups.The two sharp bands at 3416 cm^{-1} and 3336cm^{-1} attributed to the υ(bonding O-H) .The weak band at 3200 cm^{-1} attributed to the υ(N-H) in thione tautomer.The weak band at 2602 cm^{-1} due to the υ(S-H) in thiol tautomer.

FT-IR spectrum of oxazepine derivative [6] showed disappearance of the strong band at 1664cm^{-1} attributed to the υ (exoC=N) and appearance of strong band at 1730 cm^{-1} attributed to the υ (C=O) for lactone and lactam groups in oxazepine ring(interacted).The spectrum also showed appearance of two strong bands at 1540 cm^{-1} and 1320 cm^{-1} attributed to the asymmetric and symmetric stretching vibrations of (NO2)groups, respectively.

.The strong absorption band at 1606 cm^{-1} attributed to the υ(C=N) inside thiadiazole ring. The strong absorption band at 1481 cm^{-1} attributed to the υ (C=C) aromatic of benzene ring.The medium absorption band at 1373cm^{-1} attributed to the δ (O-H) in plane. The two absorption bands at 1280 cm^{-1} and 1220 cm^{-1} attributed to the υ(C-O) of phenol. The medium absorption band at 1099 cm^{-1} attributed to the υ(C-O) inside oxazepine ring. The absorption bands at 1145 cm^{-1} and at 1000 cm^{-1}due to the δ(C-H) aromatic of benzene ring in plane. The bands at

910 cm^{-1}, 840 cm^{-1} and 760 cm^{-1}attributed to the δ(C-H) aromatic of benzene ring out of plane. The weak absorption band at 700 cm^{-1} attributed to the δ (O-H) out of plane.FT-IR spectrum of compound [6] also showed appearance of the following absorption bands: The absorption bands at 2950cm^{-1} , 2922cm^{-1} and 2862cm^{-1}due to the υ (C-H) aliphatic of methyl groups. The three weak bands at 2800cm^{-1} ,2740cm^{-1} and 2660cm^{-1} due to the υ (C-H) in oxazeine ring. The weak band at 2590cm^{-1} due to the υ (S-H).The three weak absorption bands at3110cm^{-1} ,3070cm^{-1} and 3020cm^{-1} attributed to the υ (C-H) aromatic of benzene ring.The weak band at 3170cm^{-1}attributed to the υ (N-H) in thione tautomer[31,32]. The sharp absorption bands at 3640 cm^{-1},3620 cm^{-1} and 3556cm^{-1} attributed to the υ(free O-H). The sharp bands at 2464 cm^{-1} , 3410 cm^{-1} ,3383 cm^{-1} and 3252 cm^{-1} attributed to the υ(bonding O-H).

FT-IR spectrum of tetrazole derivative [7] showed disappearance of the strong absorption band at 1664 cm^{-1}due to the υ(C=N) exocyclic and appearance of strong absorption band at 1690cm^{-1} due to the υ(C=N) inside tetrazole ring [5,33].Beside this FT-IR spectrum of tetrazole derivative [7] was devoid of a strong band at 2160-2120 cm^{-1} attributed to the stretching vibration of azide group ($-N_3$) .FT-IR spectrum of compound [7] showed appearance of the following absorption bands: The strong absorption band at 1604 cm^{-1} attributed to the υ(C=N) inside thiadiazole ring. The weak and medium absorption bands at 1529 cm^{-1} and 1479 cm^{-1} attributed to the υ (C=C) aromatic of benzene ring. The medium absorption band at 1369 cm^{-1} attributed to the δ (O-H) in plane. The strong absorption bands at 1282 cm^{-1} and 1199 cm^{-1} attributed to the υ(C-O) of phenol. The bands at 1145 cm^{-1} , 1105 cm^{-1} and at 1060 cm^{-1}due to the δ(C-H) aromatic of in plane.

The strong absorption bands at 970 cm^{-1} ,910 cm^{-1} , 829 cm^{-1} and 770 cm^{-1} due to the δ(C-H) aromatic out of plane. The medium absorption band at 694cm^{-1} attributed to the δ (O-H) out of plane. The weak absorption band at 2610 cm^{-1}attributed to the υ(S-H). The weak absorption bands at 2928 cm^{-1} , 2860 $cm^{-1}$and 2798 cm^{-1}attributed to the υ (C-H) aliphatic of methyl groups.The weak absorption band at 3120cm^{-1} and 3022 cm^{-1}attributed to the υ (C-H) aromatic of benzene ring.The sharp medium absorption band at 3176 cm^{-1} due to the υ (N-H) in thione tautomer. The three sharp strong absorption bands at 3640cm^{-1}, 3590cm^{-1} and 3525 cm^{-1} attributed to the υ (free O-H). The five sharp weak bands at 3460 cm^{-1} , 3419 cm^{-1} ,3342 cm^{-1} ,3300 cm^{-1} and 3240 cm^{-1} attributed to the υ(bonding O-H).

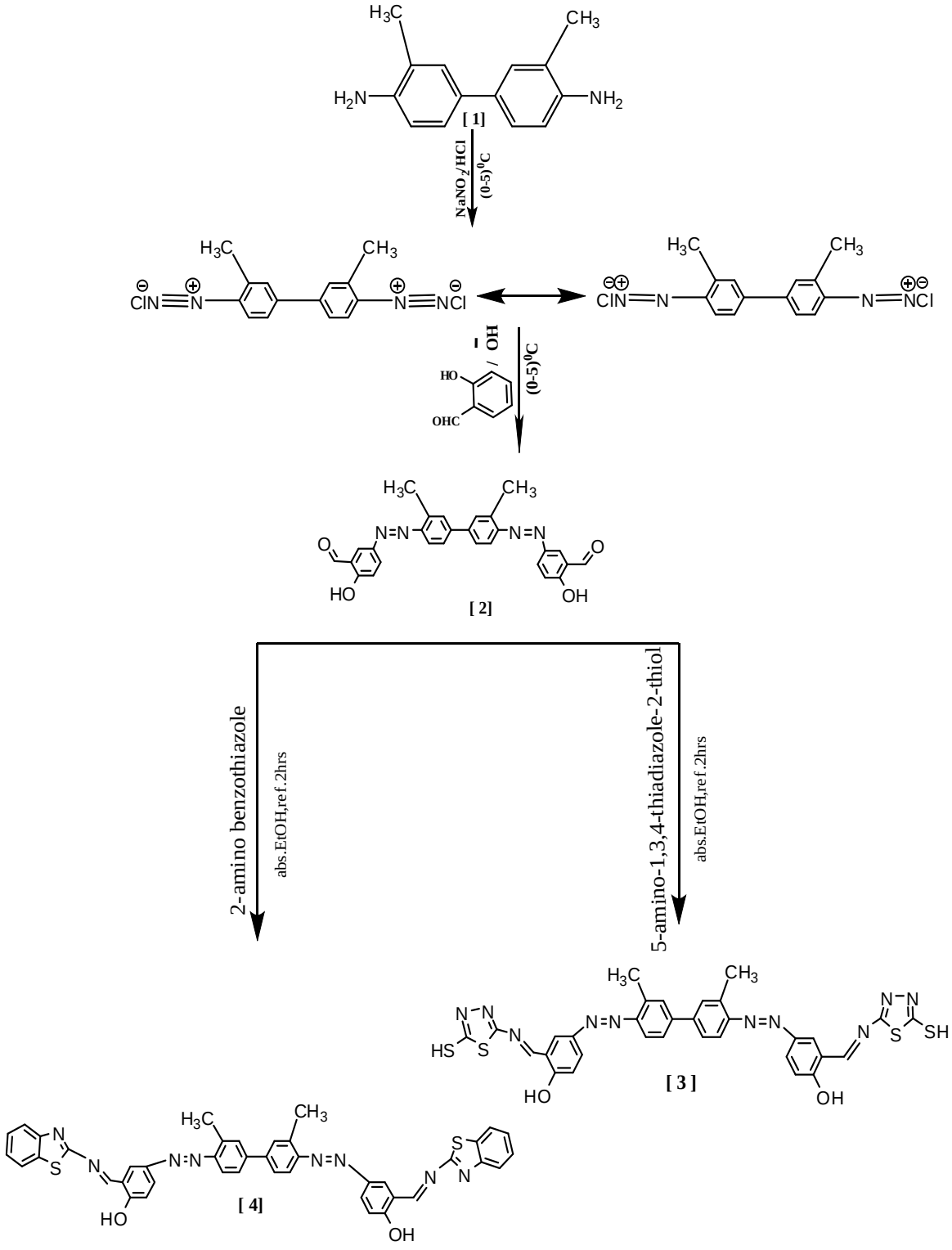
FT-IR spectrum of oxazepine derivative [8] showed disappearance of the strong band at 1693cm^{-1} attributed to the υ (exoC=N) and appearance of two medium and strong absorption bands at 1790 $cm^{-1}$and 1662 cm^{-1} attributed to the υ (C=O) of lactone and lactam groups in oxazepine ring, respectively .The strong absorption band at 1595cm^{-1} due to the υ(C=N) inside benzothiazole ring. The strong absorption band at 1479 cm^{-1} due to the υ (C=C) aromatic of benzene ring.The medium absorption band at 1371cm^{-1} attributed to the δ (O-H) in plane. The strong absorption bands at 1280cm^{-1} and 1205 cm^{-1} attributed to the υ (C-O) of phenol. The strong absorption band at 1105 cm^{-1} attributed to the υ(C-O) of lactone in oxazepine ring. The weak absorption bands at 1041 cm^{-1} and 985 cm^{-1} cm^{-1} due to the δ (C-H) aromatic in plane of benzene ring. The three absorption bands at 893cm^{-1} , 835 cm^{-1} and 754cm^{-1} attributed to the δ (C-H) aromatic out of plane. The weak absorption band at 698cm^{-1} due to the δ (O-H) out of plane..The two sharp absorption bands at 3640$cm^{-1}$and 3605 cm^{-1} attributed to the υ (free O-H) . The five weak bands at (3500 cm^{-1} , 3220 cm^{-1}) due to the υ(bonding O-H).

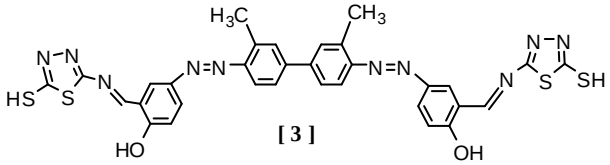
The weak absorption bands at 3130cm^{-1}, 3061cm^{-1} and 3000cm^{-1} due to the υ (C-H) aromatic of benzene ring. The weak absorption bands at 2970cm^{-1} , 2910cm^{-1} and 2850cm^{-1} attributed to the υ (C-H) aliphatic of methyl groups.The two weak bands at 2790 $cm^{-1}$and 2720 cm^{-1} attributed to the υ (C-H) in oxazeine ring.

FT-IR spectrum of oxazepine derivative [9] showed disappearance of the strong band at 1693cm^{-1} attributed to the υ (exoC=N) and appearance of two strong absorption bands at 1728 $cm^{-1}$and 1660 cm^{-1} attributed to the υ (C=O) of lactone and lactam inside oxazepine ring, respectively .The strong absorption band at 1604cm^{-1} attributed to the υ(C=N) inside benzothiazole ring. The

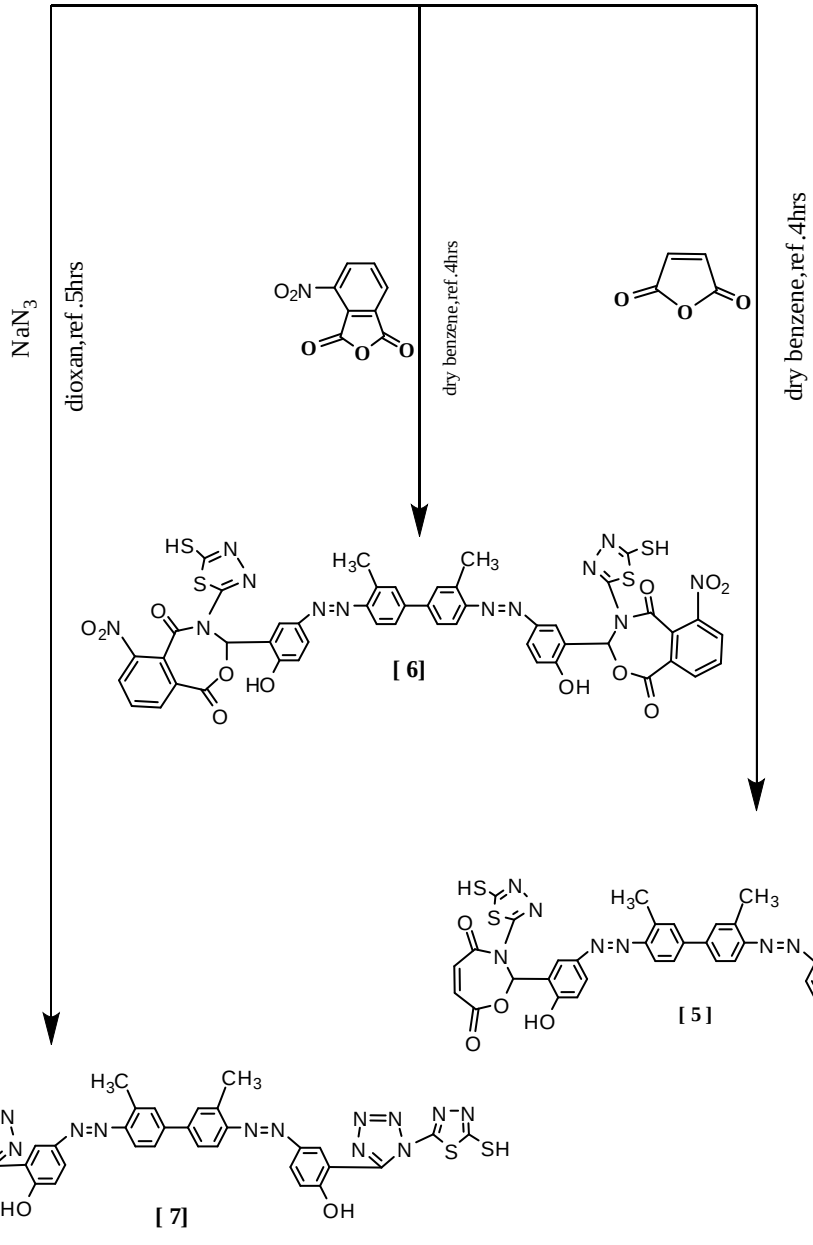
strong absorption band at 1485 cm^{-1} due to the υ(C⁻⁻⁻⁻C) aromatic of benzene ring. The medium absorption band at 1354 cm^{-1} due to the δ (O-H) in plane. The two characteristic medium absorption bands at 1520 cm^{-1} and 1290 cm^{-1} attributed to the asymmetric and symmetric stretching vibrations of (NO2) groups.The medium absorption bands at 1275cm^{-1} and 1224 cm^{-1} attributed to the υ(C-O) of phenol. The strong absorption band at 1138 cm^{-1} due to the υ(C-O) for lactone in Oxazepine ring. The two weak absorption bands at 1030 cm^{-1} and 1000 cm^{-1} attributed to the δ (C-H) aromatic in plane. The absorption bands at 902cm^{-1} , 808 cm^{-1} and 755cm^{-1} attributed to the υ (C-H) aromatic out of plane.The absorption band at 670 cm^{-1} due to the δ (O-H) out of plane. The sharp absorption bands at 3641cm^{-1} and 3576cm^{-1} attributed to the υ (free O-H).The four sharp bands at 3510 cm^{-1} , 3414 cm^{-1} ,3270 cm^{-1} and 3213 cm^{-1} attributed to the υ(bonding O-H).

The weak absorption bands at 3175cm^{-1} , 3130cm^{-1} , 3070 $cm^{-1}$and 3036cm^{-1} attributed to the υ (C-H) aromatic. The weak absorption bands at 2960cm^{-1} , 2920$cm^{-1}$and 2862cm^{-1} attributed to the υ (C-H) aliphatic of methyl groups .The weak band at 2733cm^{-1} attributed to the υ (C-H) in Oxazepine ring.FT-IR spectrum of terazole derivative [10] showed disappearance of the strong absorption band at 1693 cm^{-1} due to the υ (exo C=N) and appearance of strong absorption band at 1707 cm^{-1} due to the υ (C=N) inside tetrazole ring [5,33].Beside this FT-IR spectrum of tetrazole derivative [10] was devoid of a strong band at 2160-2120 cm^{-1} due to the υ(-N_3). The strong absorption band at 1602cm^{-1} attributed to the υ(C=N) inside benzothiazole ring. The weak and medium absorption bands at 1510 cm^{-1} and 1477 cm^{-1} attributed to the υ (C⁻⁻⁻⁻C) aromatic .The weak absorption band at 1431 cm^{-1} attributed to the υ (N=N). The weak band at 1385cm^{-1} due to the δ (O-H) in plane.The medium absorption bands at 1282 cm^{-1}, 1195 cm^{-1} attributed to the υ(C-O) of phenol. The medium absorption bands at 1141 cm^{-1} and 1101 cm^{-1} attributed to the δ (C-H) aromatic in plane. The strong and weak absorption bands at 835cm^{-1} and 754cm^{-1} attributed to the υ (C-H) aromatic out of plane.The weak absorption band at 675 cm^{-1} attributd to the δ (O-H) out of plane. The sharp absorption bands at 3660cm^{-1}, 3640cm^{-1} and 3585 cm^{-1} attributed to the υ (free O-H). The eight sharp absorption bands at (3535 cm^{-1} - 3227 cm^{-1}) attributed to the υ(bonding O-H). The four weak absorption bands at 3173cm^{-1}, 3140cm^{-1} , 3091cm^{-1} and 3030 cm^{-1} attributed to the υ (C-H) aromatic of benzene ring.The weak absorption bands at 2960 cm^{-1} , 2920 $cm^{-1}$and 2850 cm^{-1}attributed to the υ (C-H) aliphatic of methyl groups.


[1]
NaNO2/HCl
(0-5)0C
I OH
(0-5)0C
[2]
2-amino benzothiazole
abs.EtOH,ref.2hrs
5-amino-1,3,4-thiadiazole-2-thiol
abs.EtOH,ref.2hrs
[3]
[4]



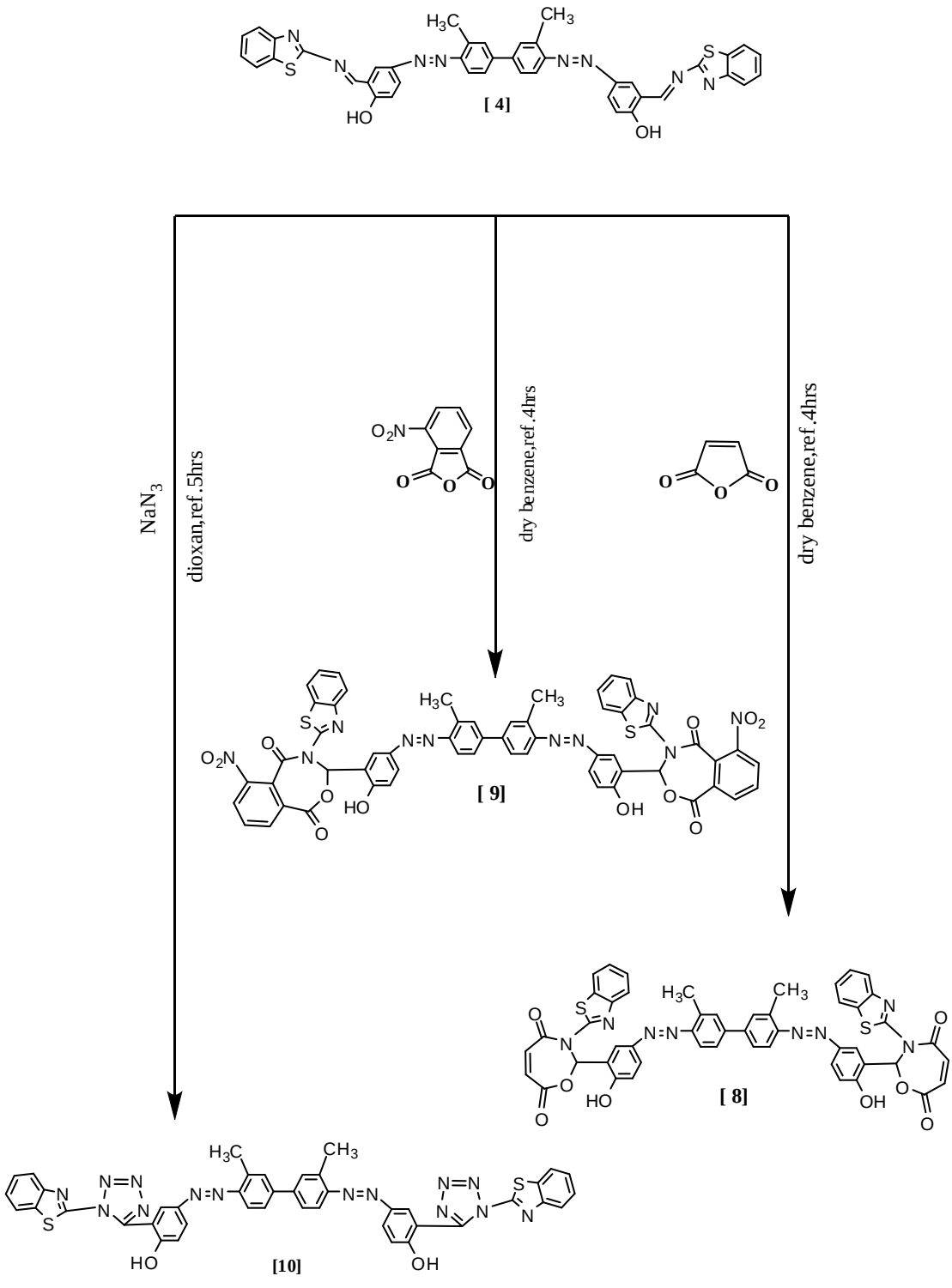
[3]


NaN3
dioxan,ref .5hrs
dry benzene,ref.4hrs
dry benzene,ref .4hrs

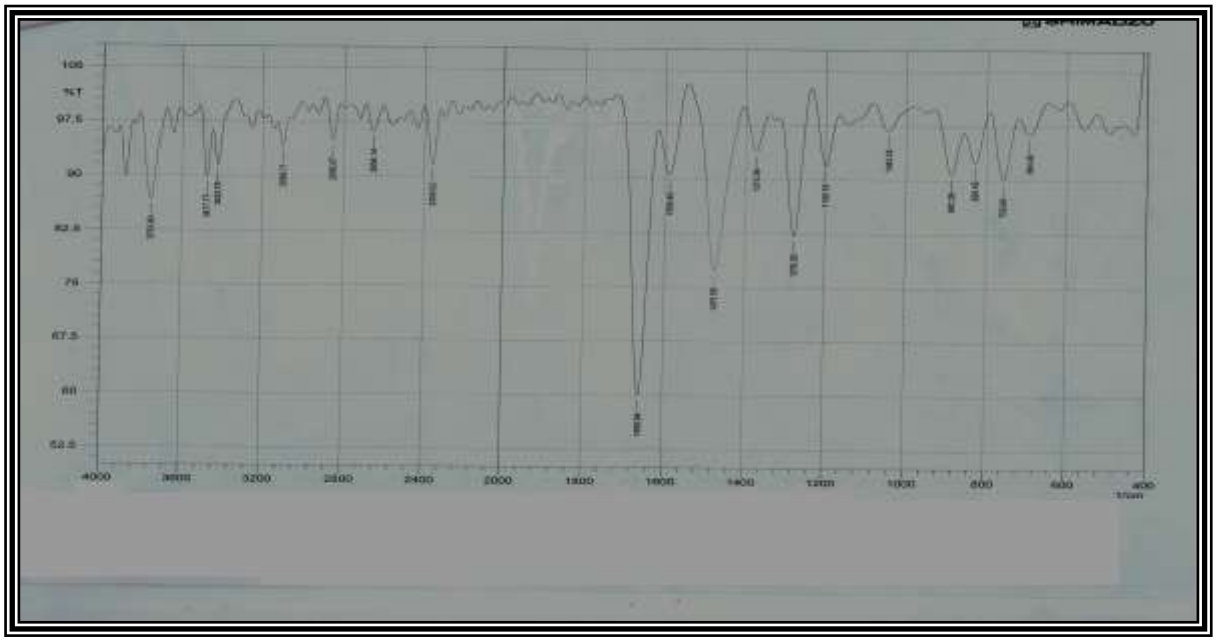
[6]

[5]

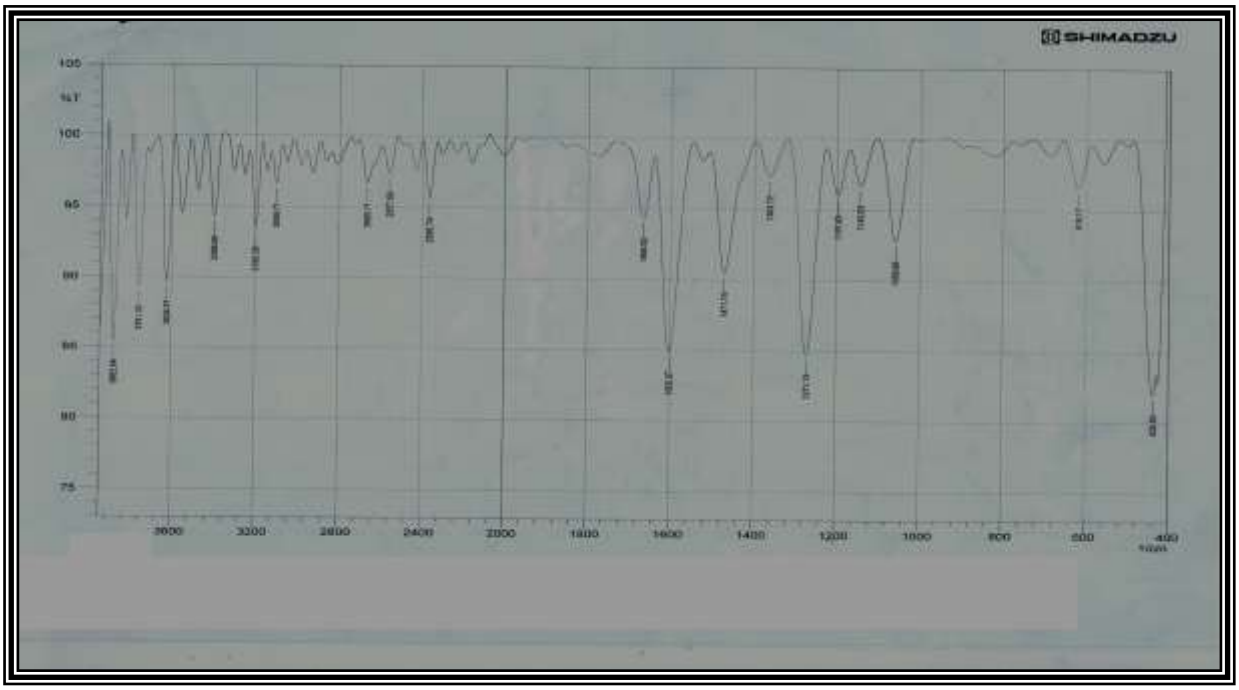
[7]



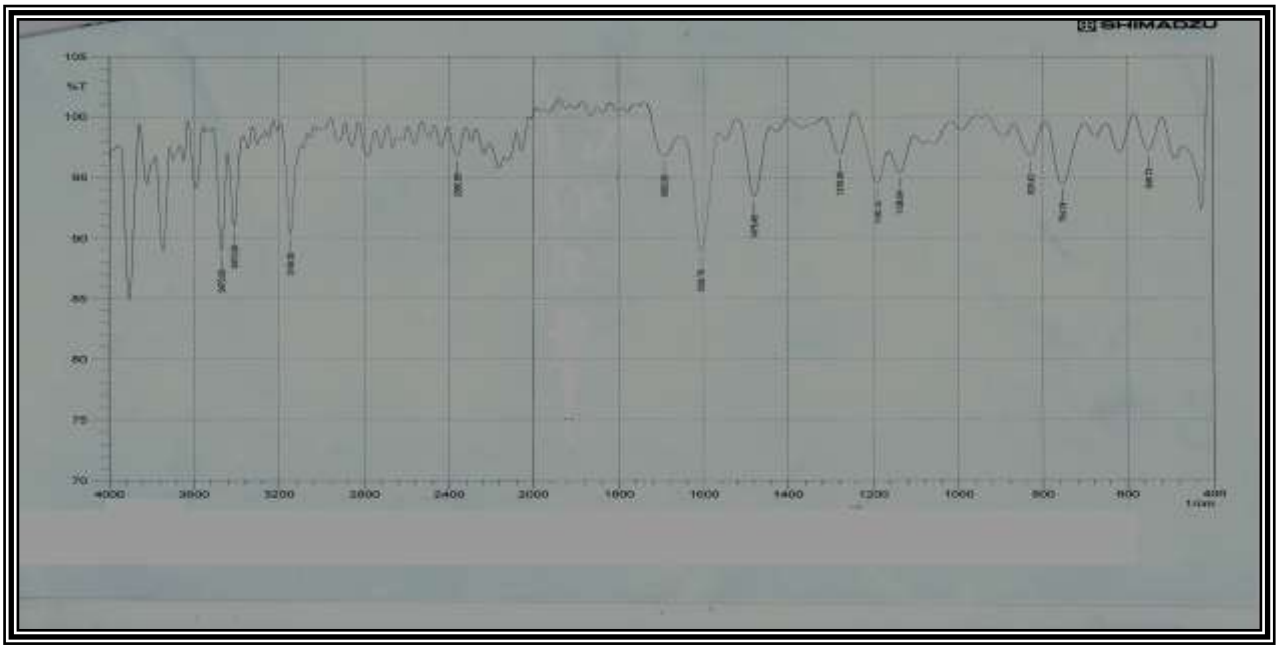
Scheme(3):Reactionspathway



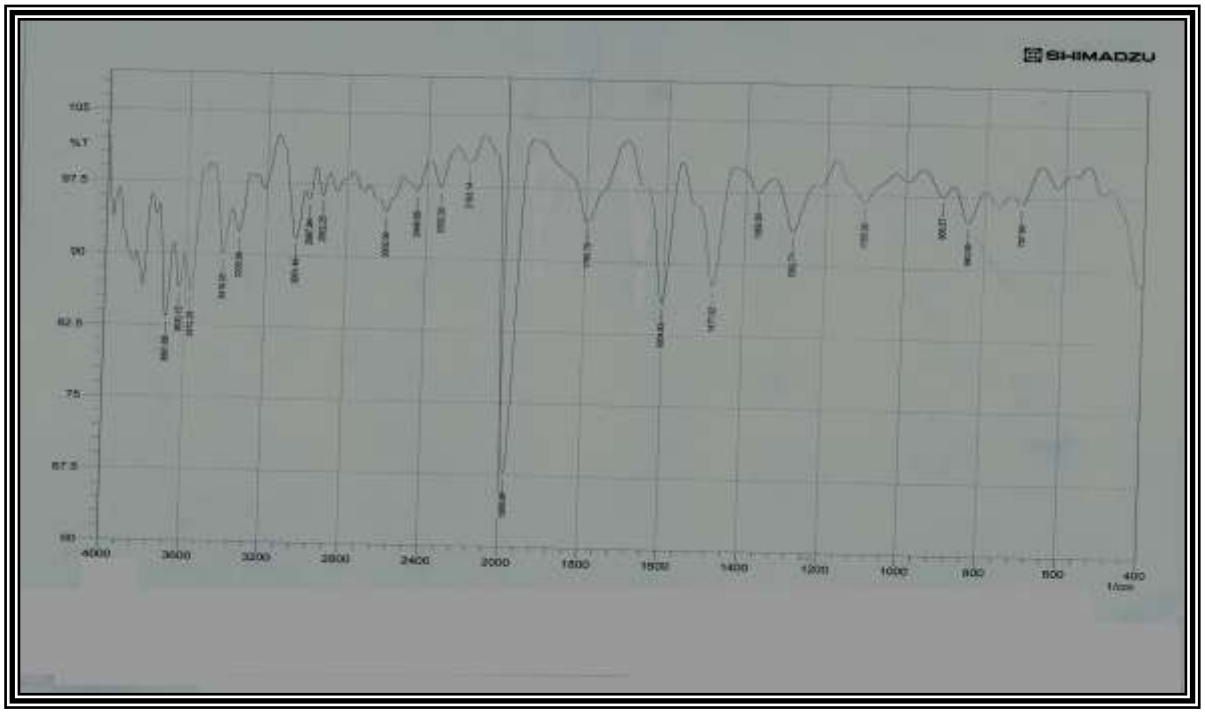
FT-IR spectrum of compound [2]



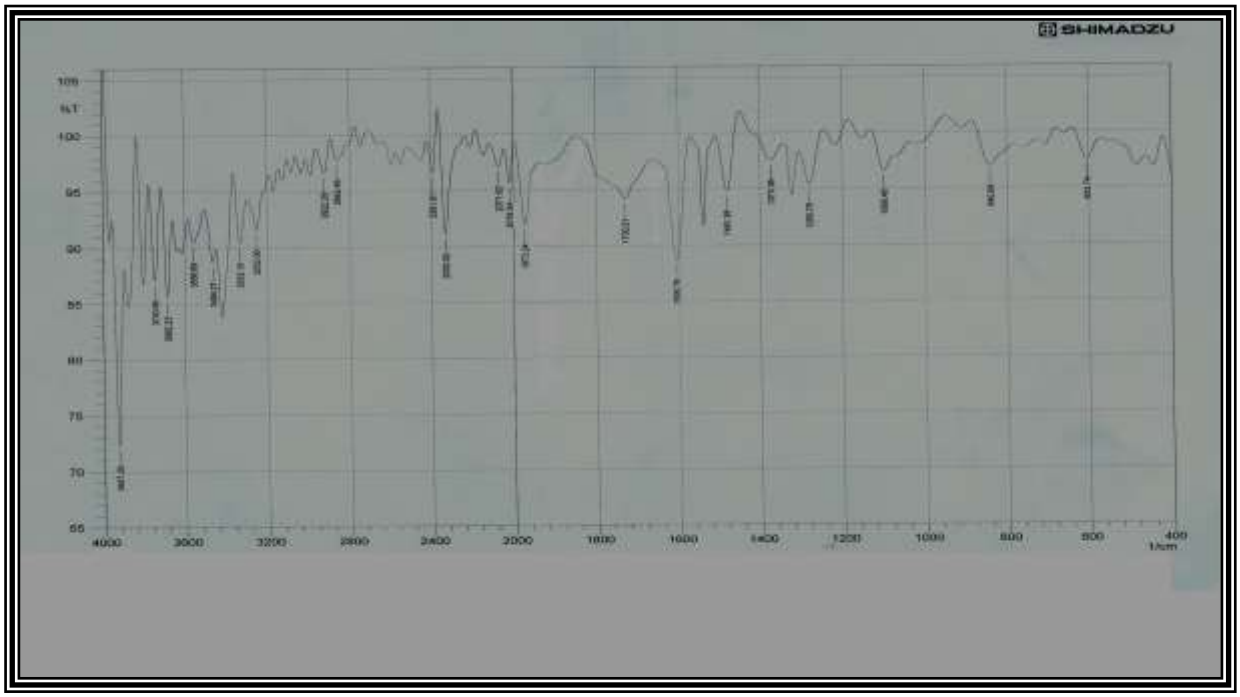
FT-IR spectrum of compound [3]



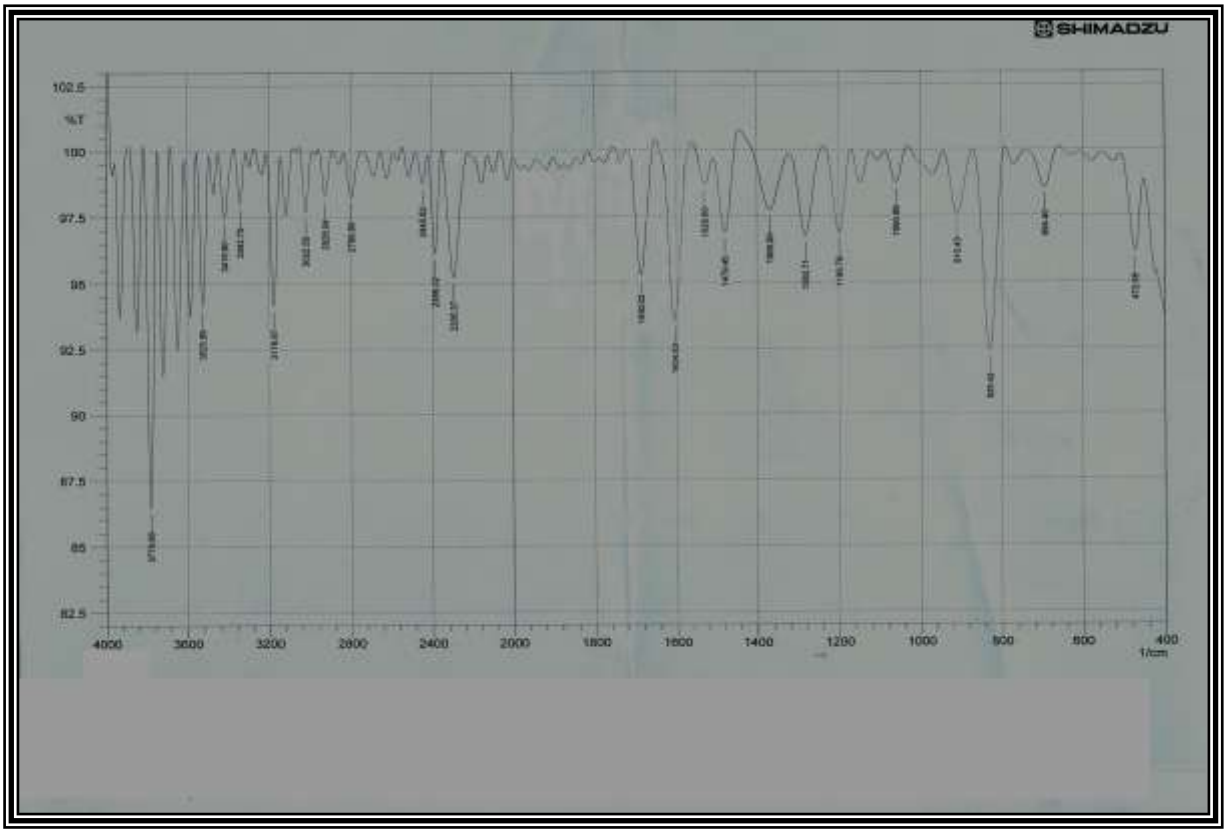
FT-IR spectrum of compound [4]



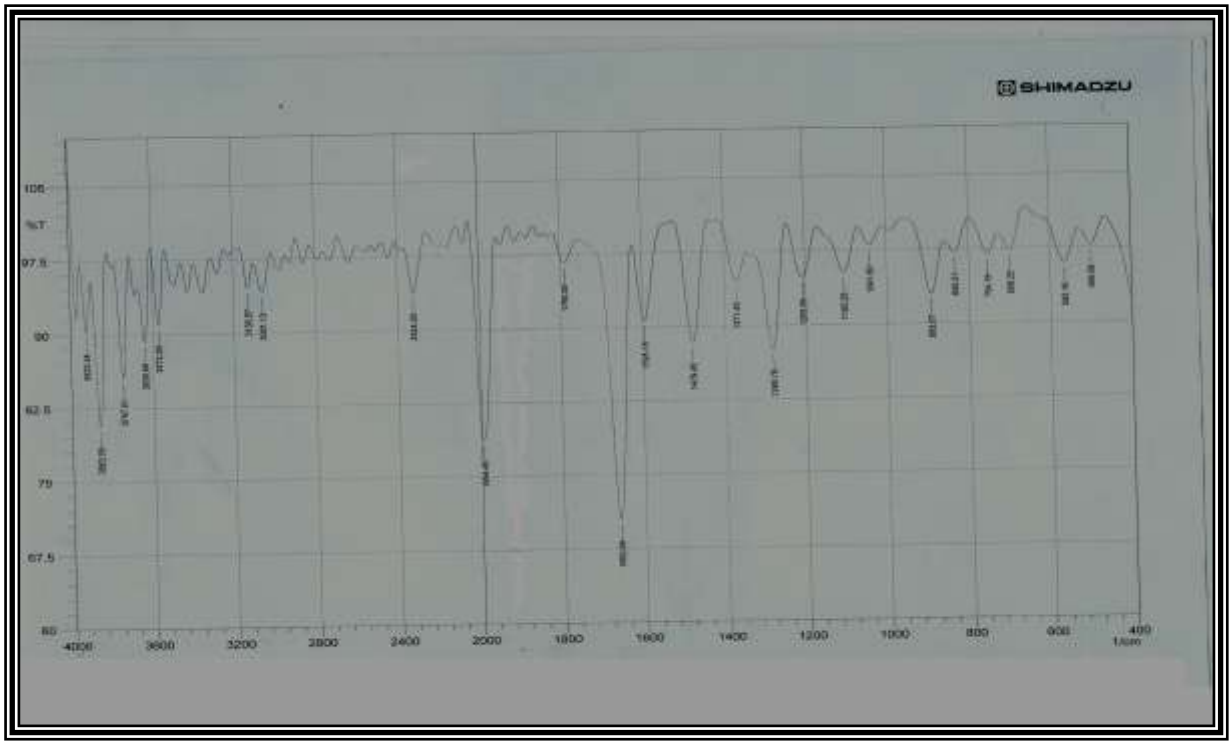
FT-IR spectrum of compound [5]



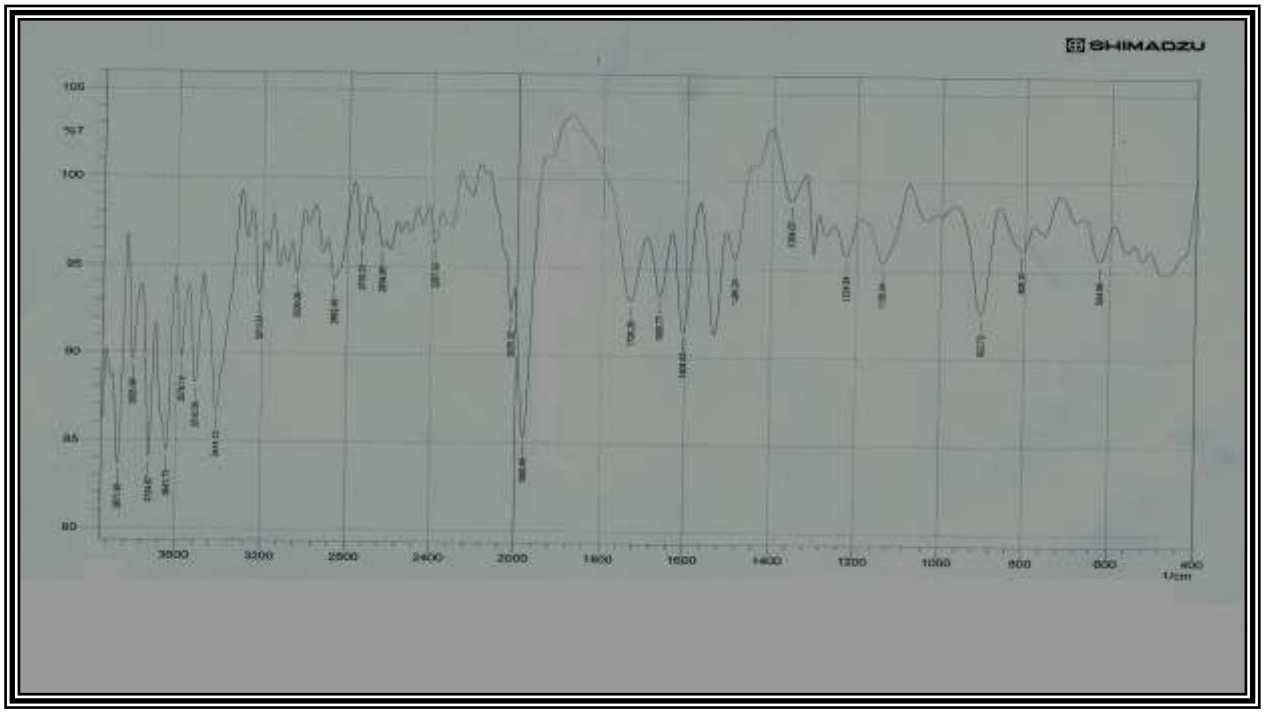
FT-IR spectrum of compound [6]



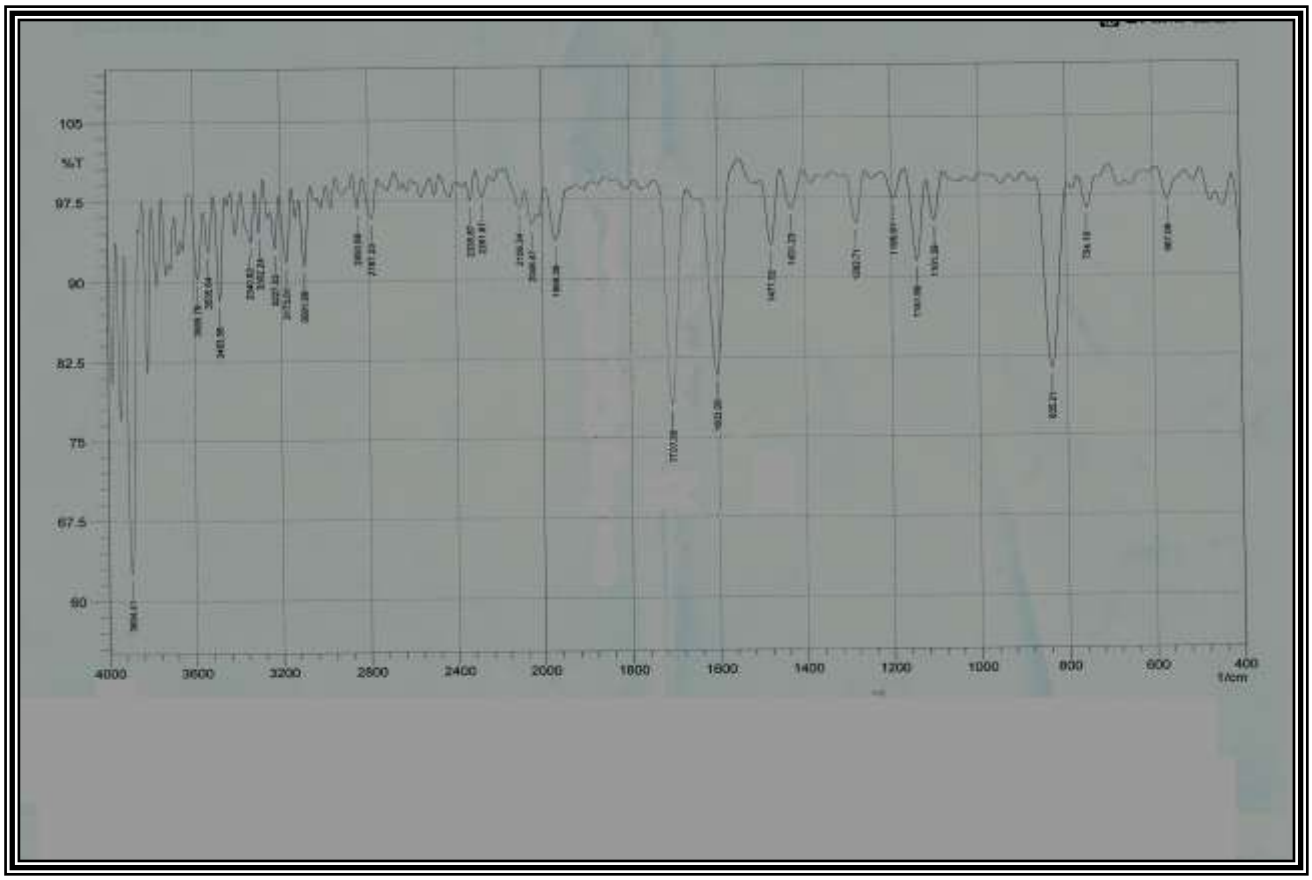
FT-IR spectrum of compound [7]



FT-IR spectrum of compound [8]



FT-IR spectrum of compound [9]



FT-IR spectrum of compound [10]

Comp. no.	υ(-OH)	υ($-NH_2$)	υ(N-H)	υ(C-H) arom.	υ (C-H) aliph.	υ(S-H)	υ(C=O)	υ(C=N)	υ (C=C) arom.	δ (O-H) in plane	υ(NO_2)	υ(C-O)	δ (C-H) in plane	υ(C-H) arom. o.o.p.	δ (O-H) o.o.p
[2]	3630 (sp) free(OH) 3477-3280- (sp)bonding (OH)	-	-	3110(w) 3060(w)	2940(w) 2900(w) 2856(w)	-	1658(s)	-	1589(m) 1475(s)	1373(m)	-	1276(s) 1199(s) phenol	1150(w) 1043(w)	887(s) 829(s) 759(s)	694(w)
[3]	3624 (sp),3550(sp)free(OH) 3480-3240- (sp)bonding (OH)	-	3198(m)	3150(w) 3099(w) 3060(w)	2980(w) 2920(w) 2860(w)	2557(w)	-	1664(s) exo 1600(s) endo	1520(w) 1471(s)	1363(m)	-	1271(s) 1197(s) phenol	1143(s) 1058(s)	905(w) 820(w) 760(w)	700(w)
[4]	3650(sp),3600(sp)free(OH) 3470-3200- (sp)bonding (OH)	-	-	3148(w)	2920(w) 2830(w)	--	-	1693(m) exo 1606(s) endo	1530(w) 1479(s)	1370(w)	-	1278(m) 1190(m) phenol	1138(m) 1065(w) 1045(w) 990(w)	890(w) 829(m) 754(s)	670(w)
[5]	3630(sp),3572(sp)free(OH) 3416,3336- (sp)bonding (OH)	-	3200(w)	3051(m) 2987(w)	2922(w) 2850(w)	2602(w)	1795(s)	- 1604(s)endo	1520(w) 1477(s)	1369(w)	-	1282(s) 1210(w) Phenol 1103(m) lactone	990(w)	906(w) 840(m) 770(w)	707(m)
[6]	3640(sp),3620(sp),3556 (sp)free(OH) 3464-3252- (sp)bonding (OH)	-	3170(w)	3100(w) 3070(w) 3020(w)	2950(w) 2922(w) 2862(w)	2590(w)	1730(s)	- 1606(s)endo	1481(s)	1373(m)	1540(s) 1320(s)	1280(s) 1220(m) Phenol 1099(s) lactone	1145(w) 1000(w)	910(w) 940(w) 760(w)	700(w)

[7]	3640(sp),3590(sp),3525 (sp)free(OH) 3460-3240- (sp)bonding (OH)	-	3176(m)	3120(w) 3022(w)	2925(w) 2860(w) 2798(w)	2610(w)	-	- 1604(s) endo thiadiazole 1690(s) endo tetrazole	1529(w) 1479(m)	1369(m)	-	1282(s) 1199(s) Phenol	1145(m) 1105(w) 1060(m)	970(w) 910(m) 829(s) 770(w)	694(m)
[8]	3640(sp),3605(sp)free(OH) 3470-3220- (sp)bonding (OH)	-	-	3130(w) 3061(w) 3000(w)	2970(w) 2910(w) 2850(w)	-	1790(m) lactone 1662(s) lactam	- 1595(s) endo	1479(s)	1371(m)	-	1280(s) 1205(s) Phenol 1105(s) lactone	1041(w) 985(w)	893(s) 835(w) 754(w)	698(w)
[9]	3641(sp),3576(sp)free(OH) 3510-3213- (sp)bonding (OH)	-	-	3175(w) 3130(w) 3079(w)	2960(w) 2920(w) 2862(w)	-	1728(s) lactone 1660(s) lactam	- 1604(s) endo	1485(s)	1354(m)	1520(s) 1290(s)	1275(m) 1224(m) Phenol 1138(s) lactone	1030(w) 1000(w)	902(s) 808(m) 755(w)	670(w)
[10]	3660(sp),3640(sp),3585(sp) free(OH) 3535-3227- (sp)bonding (OH)	-	-	3173(w) 3140(w) 3091(w) 3030(w)	2960(w) 2920(w) 2850(w)	-	-	- 1602(s) endo benzothiazol 1707(s) endo tetrazole	1510(w) 1477(m)	1385(w)	-	1282(m) 1195(m) Phenol	1141(m) 1101(m)	835(s) 754(w)	675(w)

Table (2): FT-IR Data of the prepared Compounds [2-10] in cm^{-1}

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