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Research Article

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Synthesis and Characterization of Some Heterocyclic Compounds from Salicylic Acid

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ABSTRACT

The present paper involve prepared of heterocyclic compounds from salicylic acid. The first step synthesized of azo compound from p-phenylinediamine with salicylic acid.Then prepared Schiff bases from azo derivatives with benzaldehyde derivatives. The last step prepared Tetrazole derivatives from Schiff bases with sodium azide. These compounds were characterized by melting point. FTIR spectra and some derivatives by ^{1}HNMR spectra,finally,the biological activity of the compounds were have been measured.

Keywords: Salicylic acid; Schiff bases; Tetrazole; Azo compound

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INTRODUCTION

Salicylic acid is an organic aromatic carboxylic acid [1]. It is called Arthohyrocedbenzoic acid. It is found in willow. That's why it is usually called willow acid. Its melting degree is 159-157C^{0}, and its pH =2.4 [2] .The salicylic acid represents the main source of many heterocyclic compounds which have many medications significance; for instance, anti-colon bacteria and anti-allergy [3]. On the other hand, the azo compounds which have been prepared by mixingthesalicylic acid with certain chemical compounds, are characterized by having active groups (N=N) [4-5]. They are also called Nitrogen dyes. In fact they are divided into two groups: Aromatic and Aliphatic. The Aromatic group is more popular [6-7]. Schiff bases are organic compounds; its symbol (R-N=CH-R_1).They are the result of mixing the aromatic primary amines with the carbonyl compounds (aldehydes or ketones) [8-10]. R,R_1 are Aromatic,Allipathic, cyclic Allipathic or non heterocyclic compounds [11].Sometimes, Schiffbases are called izomethine (C=N) [12]. the schiff bases (SB) were first prepared by H.schiff in 1864 [13].finally, tetrazol can be defined as quintuple non-heterocyclic compounds which contain one carbon atomic, four nitrogen atomic and one hydrogen atomic [14].tetrazol compounds have (CN_4H). They have billogical significance [15].

EXPERIMENTAL SECTION

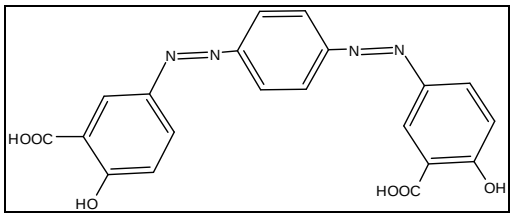
Materials

Chemicals used duning the persent work are manufactured from merck and BDH company.

Instrumentation

Unrecorded melting point by hat stage Gallen kamp. To ensure the pueity of the resulting derivatives used technique thin layer chromatography (TLC).FTIR spectroscopy was used KBr disc. ^{1}HNMR spectra was used $CDCl_3$ and DMSO-d_6 as solvents.

Synthesis of azo compound [H][16]



(H)

This compound was prepared in two steps.

The first step: p-phenylinediamine was dissolved in (HCl) (3ml) and (10ml) distilled water, then cooled in ice bath (0-5 C^0), Sodium nitrite (0.7g, 0.01mo) was dissolved in (10ml) distilled water and cooled in ice bath (0-5C^0),then slowly mix solution together.

The second step: The salicylic acid (1.38g,0.01mol) was dissolved in NaOH solution (15ml,10%) stirred the solution in the first step then added slowly to the solution with stirring.leaving the eraction solutionfor a period 4hrs. Then filtered and collected the solid product.

Synthesis ester derivative [H_1]

Taking (1g,0.002mol) of azo compound is dissolved in (30ml) of ethanol absolute.Then added 6 drops of H_2SO_4 concentrat. Esterfication for (9hrs), follow up the reaction by (TLC). After cooling the mixture was neutralized.The titled product.was achieved by evaporting the solution under reduced presure.

The physical properties in table (1)

Synthesis of hydrazide derivative (H_2)

Compound (H_1) (1g,0.002mol) was dissolved in refluxed ethanol (30ml), hydrazine hydrate (0.5g, 0.01mol) was slowly added to the mixture. The solution was refluxed for (10hrs) the solvent was removed by evaporting, the residue was cooled in an ice bath forming aprecipitate.The product was recrystallized from absolute ethanol togive titled compound.

Synthesis of Schiff bases (H_3-H_7)

Amixtuer of (0.02mol) of aromatic benzaldehyde derivatives and compound (H_2) was refluxed for (3-8)hrs in (30ml) of absloute ethanol.The reaction mixture was cooled and kept for (24hrs). Thecrystals found were filtered,dried and recrystallized from absolute ethanol to give derivatives (H_3-H_7).

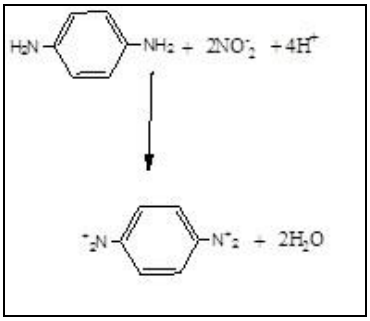
Synthesis of Tetrazole derivatives (H_8-H_{12})

Amixtuer of Schiff bases (H_3-H_7)(0.3g,0.004mol) dissolved in THF (15ml) and sodium azide (0.3g.0.004mol) was dissolved in THF (15ml) and refluxed for (8-10)hrs.The reaction was then cooled and the resulting final(H_8-H_{12}), recrystallized from ethanol.

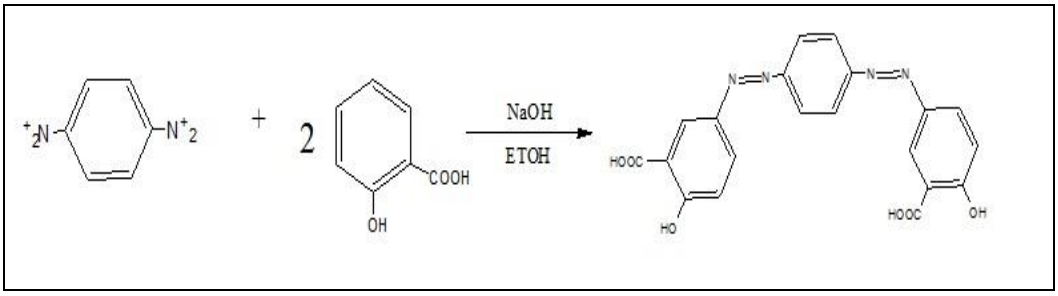
RESULTS AND DISCUSSION

Synthesis of azo dye

p-phenyline diamine, in acidic medium,is react with sodium nitrite to form the diazonium salt.



After (15) minutes; diazonium salt formation is coupled with salicylic acid in a basic medium at (0-5C^0) to form azodye.

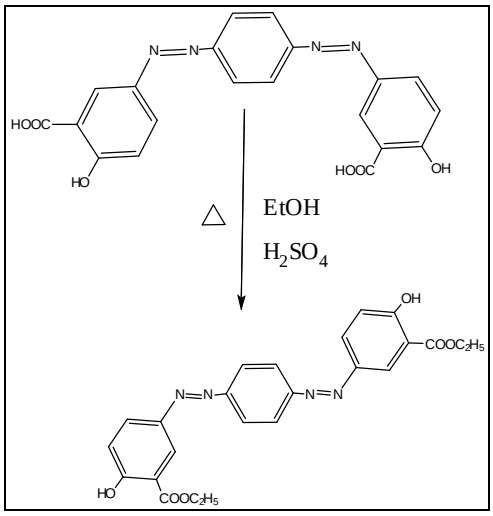


Scheme (1) preparation of Azo dye

The FT-IR spectrum of azo compound(H) fig(1), show stretching vibration bond of (COOH) carboxylic acid group at (2500-3500cm^{-1}), the OH group at (3377cm^{-1}), the stretching vibration band of (N=N)occur at 1508cm^{-1}, with disappearance the stretching vibration of (NH_2) group at (3377,3442)cm^{-1} (symmetric & asymmetric). The ^{1}HNMR spectrum,. Show sginal at 2.5ppm return to solvent DMSO-d_6 , CH aromatic occur at (6.9-7.8 ppm), the OH group of carboxylic at (11.6 ppm) and the OH group of phenolic occur at (10.5 ppm).

Synthesis derivatives (H_1-H_2)

The reaction between azo compound (H) and absolute ethanol in the presence concentration H_2SO_4 to synthesis ester derivative.



Scheme (2) preparation of ester derivative

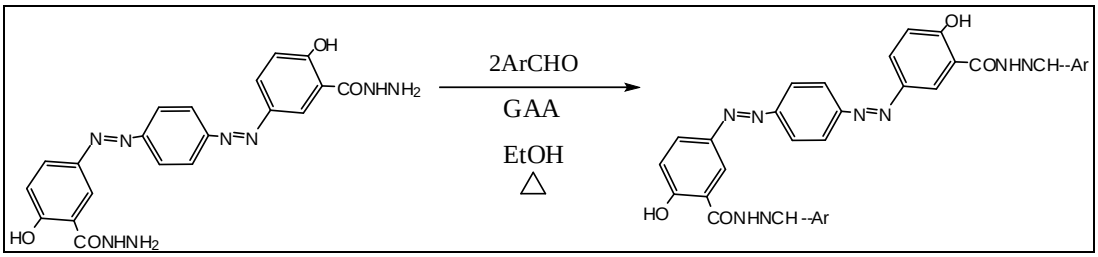
The FT-IR spectrum of ester derivative (H_1), fig(2) show the stretching vibration band of (OH) group occur at (3312cm^{-1}), the carbonyl group of ester at (1676cm^{-1}) and (N=N) group occur at (1490cm^{-1}).

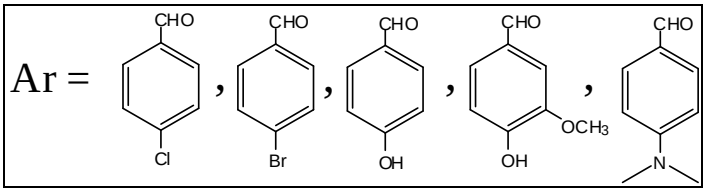
The FT-IR spectrum of hydrazide derivative (H_2), fig(3) show the stretching vibration band of (NH_2) group at (3379&3217)cm^{-1}, the stretching vibration band of (NH) group at (3379cm^{-1}) and (N=N) group occur at (1514cm^{-1}).

The ^{1}HNMR spectrum, fig(4) occur signalt at (10.2 ppm) towrd to OH group, signal at (8.3ppm) and to NH group of amide, the protons of NH_2 group occur at (6.5ppm), the proton of aromatic ring occurat (6.6-7.3ppm).

Synthesis Schiff bases (H_3-H_7)

The reaction between hydrazzide derivative (H_2) and benzaldehyde derivatives(4-chlorobenzaldehyde,4-bromobenzaldehyde, 4-hydroxybenzaldehyde, 4-hydroxy-3-methoxybenzaldehyde and
4-(dimethylamino)benzaldehyde) respectivly in the presence (GAA) as catalyst reagent to synthesis schiff bases (H_3-H_7)



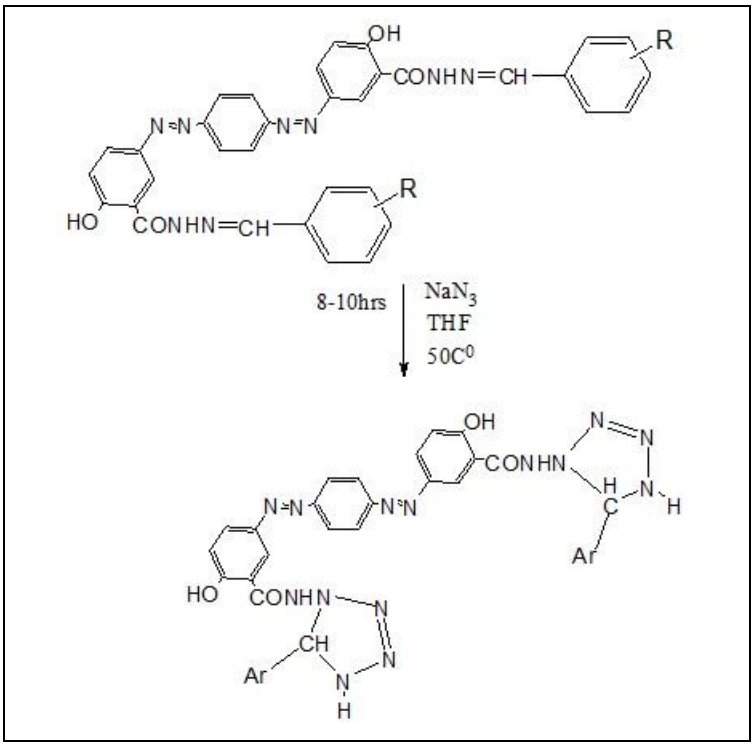


The FT-IR spectrum of Schiff bases (H_3-H_7), figs (5) . Show the stretching vibration band of (CH=N) occur at (1622__ 1598) cm^{-1} , the bands at (1666__ 1640) cm^{-1} due to cabronyl amide. The ^{1}HNMR spectra of compound (H_5), figure (6) occur signal at (10.6 ppm) due to proton of (OH) salicylic acid, signal at (9.8)ppm due to proton of (OH), phenolic, the proton of NH group occur at 9.1 ppm. And the proton of schiff base occur at 8.5 ppm.The proton of aromatic ring occur at (7.7_ 6.8)ppm.

The ^{1}HNMR spectra of compound (H_6), occur signal at (10.6 ppm) due to proton of OH group salicylic, the signal at 9.7 ppm due to proton of OH group of phenolic, the proton of NH group occur at 9.0ppm, but the proton of schiff base group occur at 8.5 ppm, the proton aromatic ring occur at (7.4_ 6.8) ppm, the proton of methoxy occur at (3.8)ppm.

Synthesis Tetrazole derivatives (H_8-H_{12}) .

The reaction between schiff base and sodium azide in the THF as solvant at($50C^0$) to synthesis tetrazole derivative.



The FT-IR spectra of tetrazole derivatives (H_8-H_{12}), figure (7) show stretching vibration band at (3228- 3387) cm^{-1} due to (NH) group of amide and NH group of tetrazole cyclic. The (C-N) group of tetrazole occur at (1139-1145) cm^{-1}.

Table1: Physical properties and characteristics for the synthesis compounds (H-H_{12})

Solvent	R_f	*Color*	*Yield%*	*M.P*	*M.Wt g/mol*	*Molecular formula*	*NO*
Ethanol	0.55	brown	88%	207	406	$C_{20}H_{14}N_4O_6$	**H**
Ethanol	0.43	Dark brown	72%	222	462	$C_{24}H_{22}N_4O_6$	**H_1**
Ethanol	0.33	pale brown	75%	216	434	C20H18N8O4	**H2**
Ethanol	0.48	brown	90%	219	679	$C_{34}H_{24}N_8O_4Cl_2$	**H_3**
Ethanol	0.4	brown	91%	227	770	$C_{34}H_{24}N_8O_4Br_2$	**H_4**
Ethanol	0.43	Pale brown	80%	261	642	C34H26N8O6	**H5**
Ethanol	0.32	Pale brown	74%	262	702	C36H30N8O8	**H6**
Ethanol	0.38	Red	85%	240	696	$C_{38}H_{36}N_{10}O_4$	**H_7**
THF	0.47	brown	78%	255	765	$C_{34}H_{26}N_{14}O_4Cl_2$	**H_8**
THF	0.41	brown	88%	263	856	$C_{34}H_{26}N_{14}O_4Br_2$	**H_9**
THF	0.4	Pale brown	85%	305	726	$C_{34}H_{26}N_{14}O_6$	**H_{10}**
THF	0.35	Pale brown	80%	307	788	$C_{36}H_{32}N_{14}O_8$	**H_{11}**
THF	0.38	Pale brown	81%	283	782	$C_{38}H_{38}N_{16}O_4$	**H_{12}**

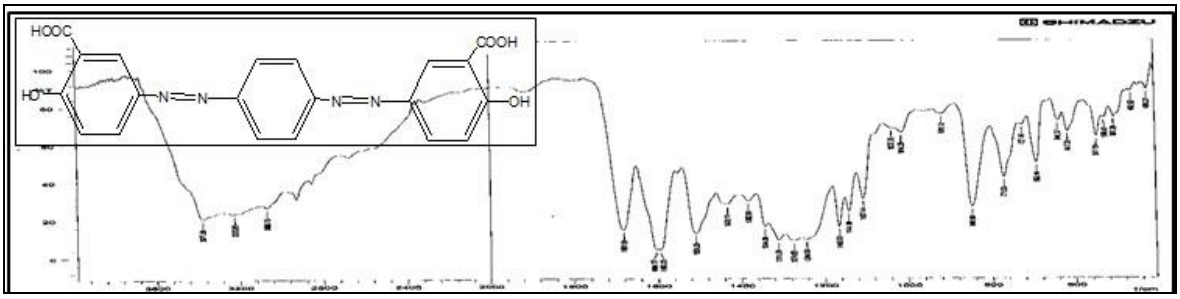


Figure 1: FT.IR spectrum of azo compound (H)

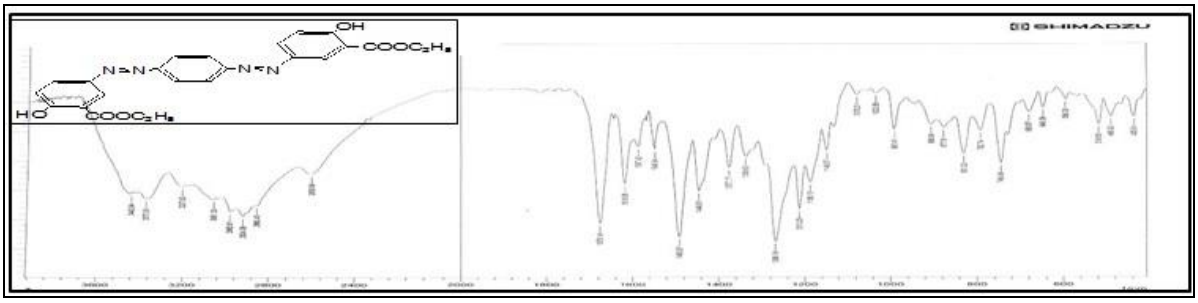


Figure 2: FT.IR spectrum of ester compound (H_1)

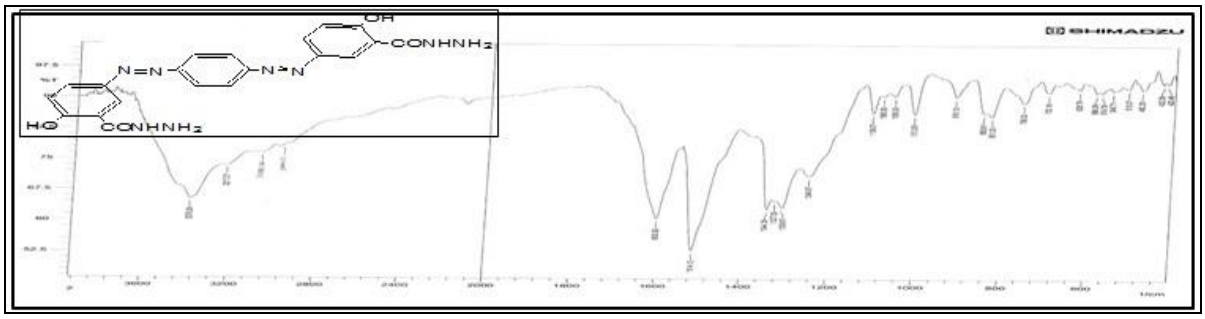


Figure 3: FT.IR spectrum of hydrazide compound (H_2)

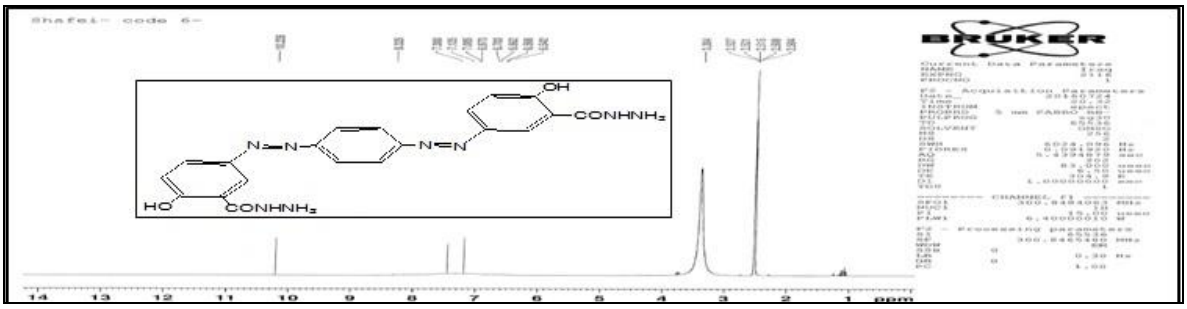


Figure 4: ^{1}HNMR spectrum of hydrazide compound (H_2)

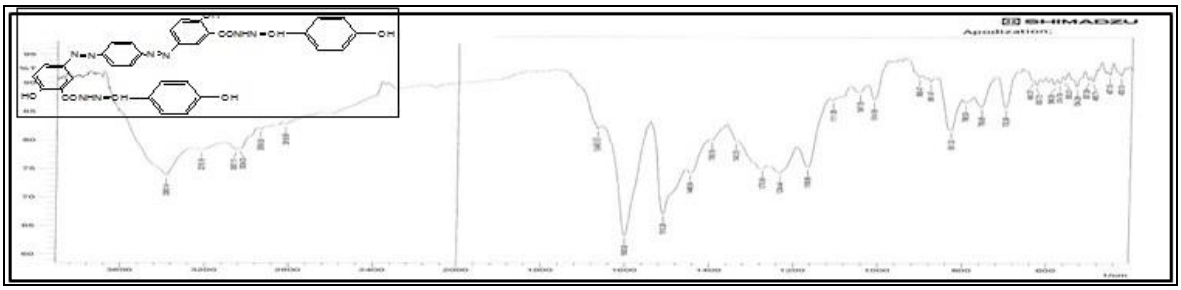


Figure 5: FT.IR spectrum of Schiff base compound (H_5)

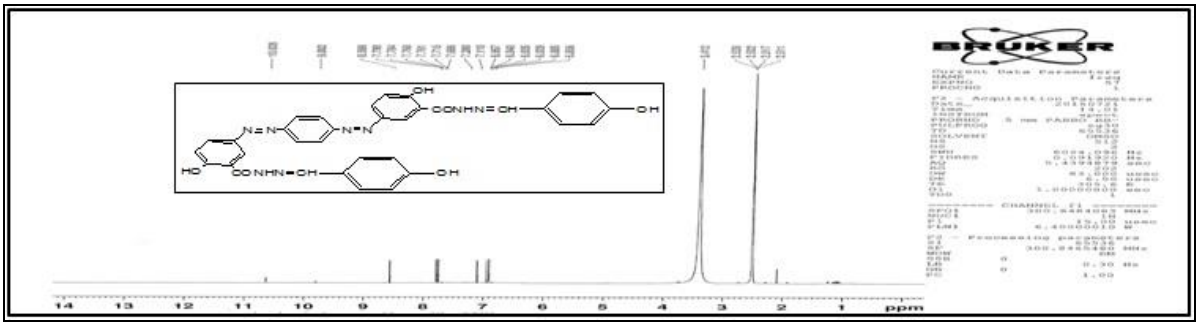


Figure 6: ^{1}HNMR spectrum of Schiff base compound (H_5)

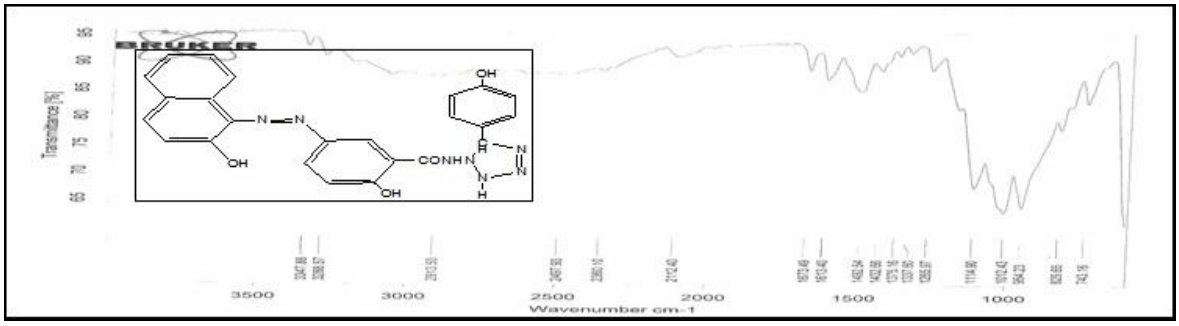


Figure 7: ^{1}HNMR spectrum oftetrazolecompound (H_{10})

CONCLUSION

In the present reserch synthesized som of tetrazole derivatives may be the derivatives have biological activity towerd the bacteria (postive or nagtive).

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