Preparation and Characterization of some new Azo Compounds and evaluation of their biological activity

تحضير وتشخيص بعض مركبات الآزو الجديدة وتقييم فعاليتها البايولوجية

هلال مسعود عبدالله * محمد عبد العباس حافظ * عماد عبد الوهاب عبد الله*
* قسم الكيمياء /كلية التربية ابن الهيثم/جامعة بغداد / العراق

Abstract

A new series of azo compounds (4_{a-e}) and (5_{a-e}) were prepared and their physical properties were recorded .The prepared compounds were characterized using Uv, FTIR, and H^1 NMR spectra .and their biological activity was investigated.

الخلاصة :-

تم في هذه الدراسة تحضير وتشخيص بعض مركبات الازو الجديدة(4a-e) و(5a-e) وتثبيت خةاصها الفيزياوية زوتم تشخيص المركبات المحضرة بواسة مطيا فية الاشعة الفوق البنفسجية والتحت الحمراء ومطيا فية الرنين االنووي المغناطيسي للبروتون كما درست فعاليتها البايولوجية ضد بعض انواع البكتريا.

Keyword **:** Azo Compound; Biological Activity; Spectroscopy .

Introduction

Aromatic amines are good starting materials for synthesizing a large numbers of deferent useful organic compounds such as hetero cyclic compounds [(1)] ,Schiff bases[(2)] ,and azo compounds.[(3)]

These compounds have been used in many important applications specially as antibiotics[(4)] and industrial applications[(5)] .Also azo compounds derived from aromatic amines are very important raw materials in dyes [(6)] and medical applications[(7)] .

Aromatic amines are converted to enolates through a reaction with α,β – unsaturated acetoacetate ,while enamines are producing heterocompounds such as indoles and quinoline derivatives[(8-10)]by heating them in acidic media. When enolates react with urea ,thiourea ,hydrazine and hydroxyl amine in strong alkaline media the products are five and six heterocyclic compounds[(11,12)] .

This paper covers the preparation of new azo-compounds from aromatic enamines derivatives and their biological activity was investigated.

Experimental

All the chemicals used from their sources (BDH. Co. and Fluka Co.) without any more purification. The prepared compounds were characterized with Uv., FT-IR., and H^1 NMR spectra, and their melting points were recorded uncorrected.

1- Preparation of Dimethyl (-3,3'-{1,4-phenylene bis-(azanediyl)}dibut-2-enoate(1):-

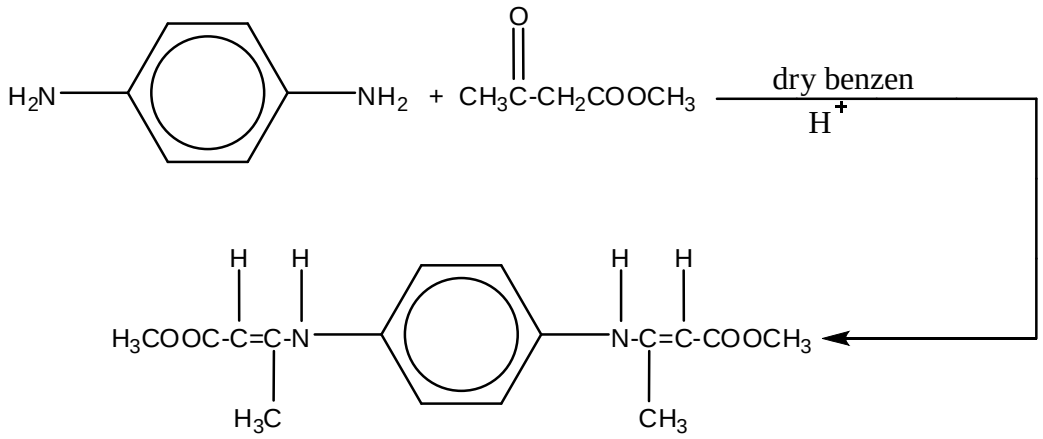
1,4-Phenylenediamine(0.05mol, 5.4 gm.) was dissolved in dry benzene (50mL) ,and to this solution methyl acetoacetate (0.18mol, 15 mL)was added with few drops of glacial acetic acid .The reaction mixture was refluxed for 60 min. Then cooled and filtered and the solid product was collected and recrystelized with benzene (m.p.=182^0C,yield; 90%).

2-Preparation of 6,6'-[1,4-phenylene bis(azanediyl) bis (6-methyl-2-amino-6H-1,3-oxazin-4-ol)]:-

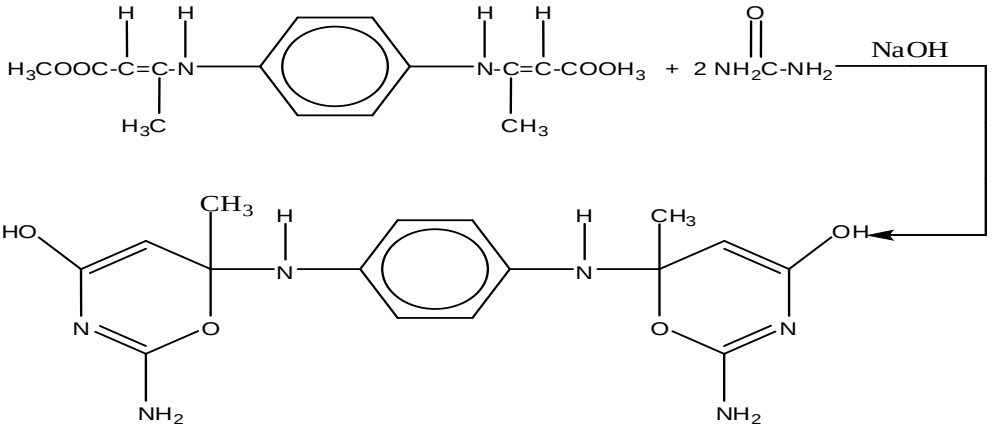
Compound (1) (0.003mol, 1.52gm.) was dissolved in (20mL)of alcoholic sodium hydroxide (40%) . To this mixture urea (0.01mol,0.6gm.)was added .The reaction mixture was stirred at (0-10 ^{0}C) in ice bath for 2hrs.and then kept over night in refrigerator ,it was then filtered and the precipitate was dried to give compound (2),(mp=188-190^{0}C,yield;77%).

3- Preparation of 6,6'-[1,4-phenylene bis(azanediyl) bis (6-methyl-2-amino-6H-1,3-thiazin-4-ol)](3):-

This compound was prepared by the same procedure in (2) despite using thiourea (0.01mol. ,0.76gm) instead of urea to obtain compound (3) (mp=195-197^{0}C, yield 71%).



(1)



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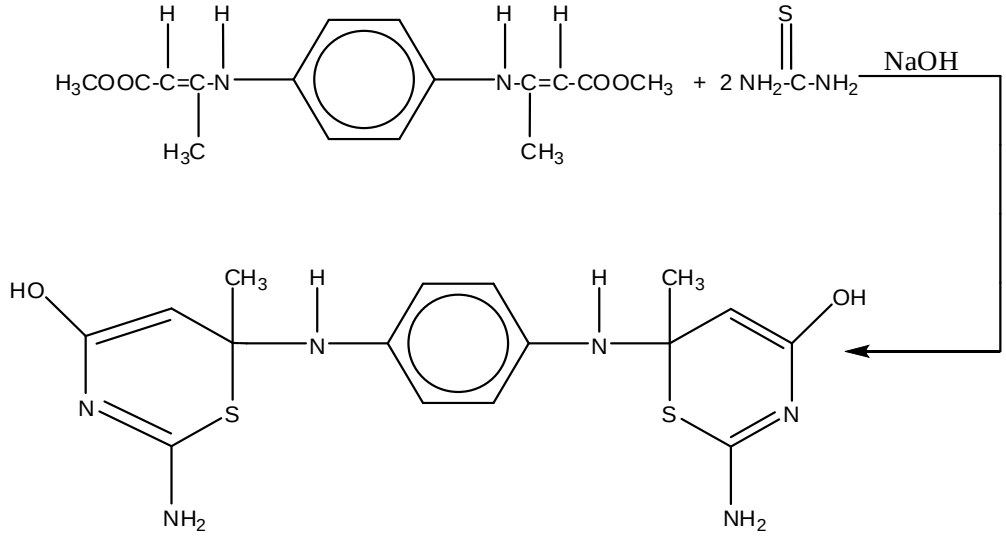

(3)

4-Preparation of azo compounds (4a-e) and (5a-e):-

These compounds were prepared in two steps

A)-Diazonium salts :

Compound (2)or(3) (0.001mol) was dissolved in diluted hydrochloric acid (1:1) ,then cooled in ice bath(0-5^{0}C).Sodium nitrite (0.001mol,0.070gm) was dissolved in small amount of distilled water and cooled in ice bath(0-5^{0}C) then mixed slowly with acidic solution above .the mixture was kept stirring at same temperature.

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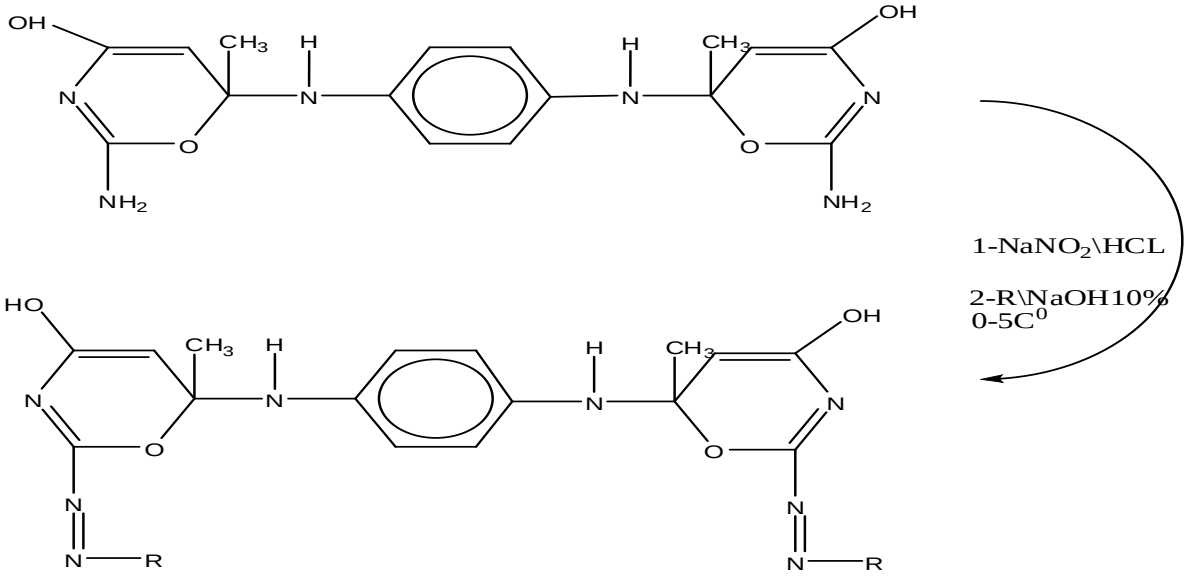
B- The appropriate Naphthol or phenol derivative (0.002mol.), was dissolved in sodium hydroxide solution (20 mL,10%) stirred at (0-5^{0}C) ;solution (A)was then added slowly to that solution with stirring at (0-5^{0}C).The reaction mixture was then left stirring till it reached room temperature, filtered , the solid product was collected. Physical properties of compounds (4a-e) and(5a-e) are listed in table-1-.



Where R=4-Nitro Phenol , 1- Naphtol, 2- Naphtol,4-Amino phenol,phenol

Schem -1-

Table -1- : Contains the physical properties of compounds (4a-e)and(5a-e).

No.	Chemical formula	M.P^{0}C	color	yield
4_a	$C_{28}H_{18}O_{10}N_8$	245	Gray	84%
4_b	$C_{35}H_{18}O_6N_6$	304	Deep green	92%
4_c	$C_{35}H_{18}O_6N_6$	297	Deep green	90%
4_d	$C_{28}H_{22}O_6N_8$	252	Brown	80%
4_e	$C_{28}H_{18}O_6N_6$	267	Deep Gray	87%
5_a	$C_{28}H_{18}O_8N_8S_2$	250	Gray	72%
5_b	$C_{35}H_{18}O_4N_6S_2$	320	Deep Green	80%
5_c	$C_{35}H_{18}O_4N_6S_2$	335	Deep Red	85%
5_d	$C_{28}H_{22}O_4N_8S_2$	270	Brown	90%
5_e	$C_{28}H_{18}O_4N_6S_2$	240	Deep Gray	88%

Results and Discussion

Compound (1) was prepared by the condensation of 1,4-penylendiamine with methyl aceto acetate in (1:2) mol ratio .This compound was characterized with its melting point ,FT-IR spectra and H^1 NMR spectra. Table -2-contians the FT-IR spectral data of compound (1)which confirmed its suggested structure , while the H^1NMR spectra showed singlet peaks as follows ; (δ= 1.97 ppm)for($6H^1$) protons of methyl groups on β-C-atom (δ=3.67 ppm)for (6 H^1) ester –methyl group protons; (δ= 4.69 ppm) for α C-atom ($2H^1$) protons , ($4H^1$) aromatic protons at(δ= 7.69 ppm) and (δ= 10.30 ppm) for ($2H^1$)protons on nitrogen atoms.

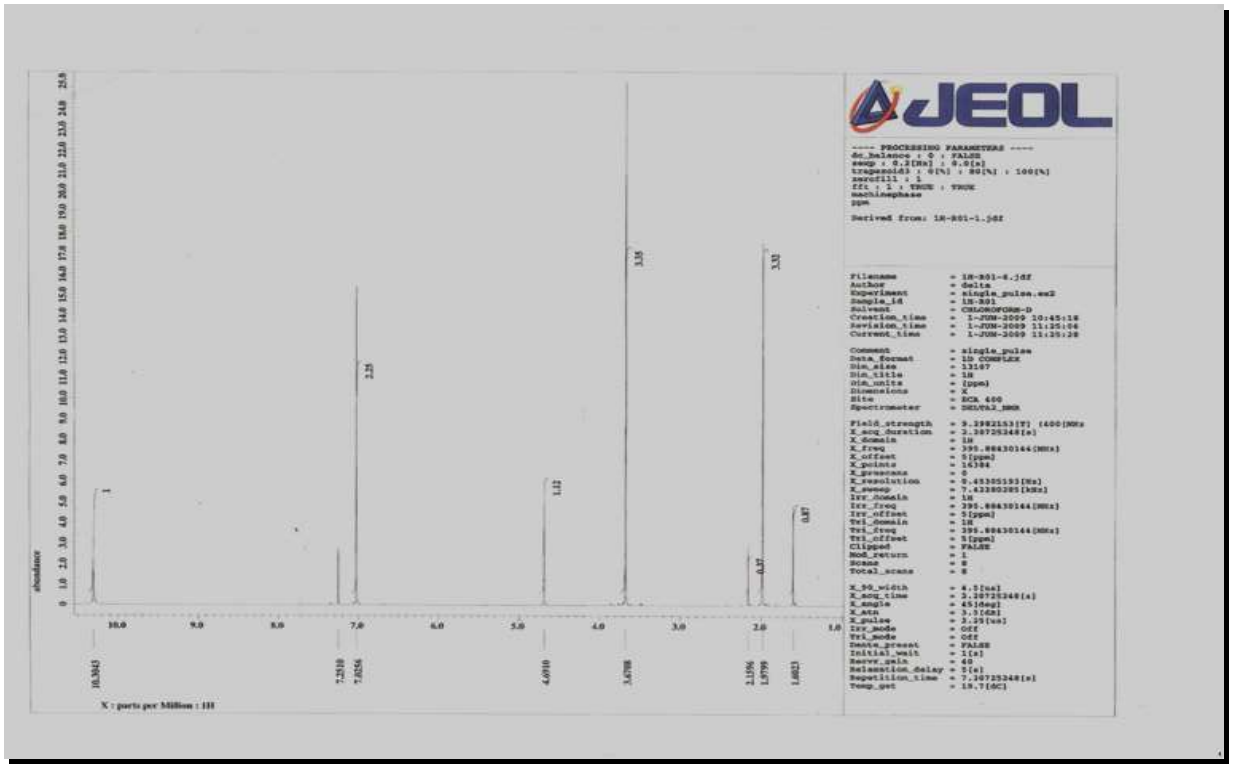


Figure-1: H^1 NMR spectra of compound -1-

Compound (2) was prepared by the reaction of compound (1) with urea in strong alkaline media at low temperature ,and it was characterized with its melting point and, FT-IR (Table-2-) and H^1 NMR spectra (Figure-2-);

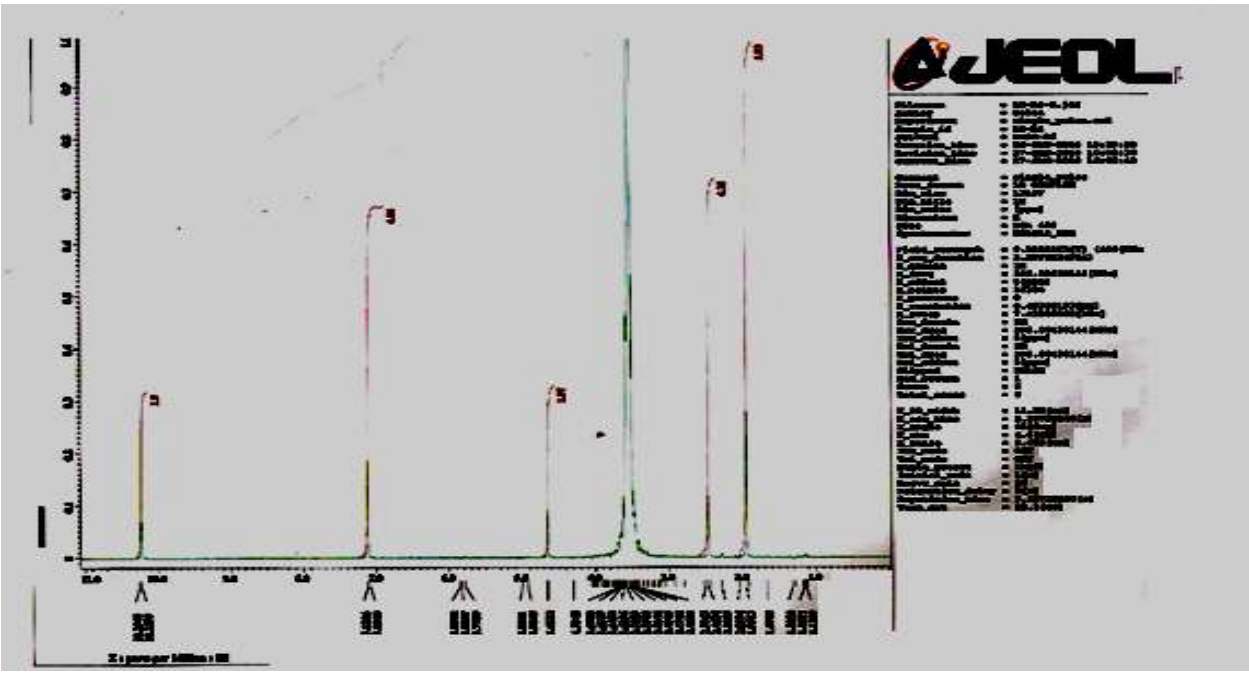


Figure-2- H^1 NMR spectra of compound-2-

Two new azo compounds series (4a-e)&(5a-e) were prepared and characterized with their melting points VU,and FT-IR spectra (Table-2-) and (Table-3-) contained their data .The spectral data confirmed the sugested structural fomulas of the prepared compounds.(Figures 3-6)showing the FT-IR spectra of some of prepared compounds .

The biological activities of the prepared compounds are listed in Table-4-. The azo compounds showing defferent inhibition effects to severals types of bacteria.

Table -2- : Data of UV spectra of compounds 4_{a-e}&5_{a-e}

Compound No.	λ_{max}
4a	442
4b	520
4c	605
4d	500
4e	498
5a	588
5b	480
5c	520
5d	560
5e	572

Table-3- : The FT-IR data for compounds1,2,34a-eand5a-e

No.	**N-H Cm^{-1}**	**O-H Cm^{-1}**	**C-H Cm^{-1}**	**C-O-C Cm^{-1}**	**C-S-C Cm^{-1}**	**Ar(C=C) Cm^{-1}**	**C=N Cm^{-1}**	**N=N Cm^{-1}**	**Others Cm^{-1}**
1	3255	3340	2970	1158	----------	1512-1600	-------	------	------------
2	3271	3360	2993	1161	----------	1512-1600	1662	-------	---------
3	3271	3430	2985	1261	1257	1521-1600	1657	----------	--------
4a	3329	3429	2966	1262	-------	1519-1597	1627	1496	1327 NO_2
4b	3282	3410	2984	1267	-------	1508-1589	1612	1477	1320(bending OH) naphthalic
4c	3255	3382	2916	1263	-------	1504-1593	1657	1480	840(bending OH) phenolic
4d	3210	3410	2854	1273	-------	1513-1600	1638	1469	2588 NH_2
4e	3286	3417	2924	1269	-------	1504-1598	1616	1488	833(bending OH) phenolic
5a	3244	3447	2920	-------	1288	1528-1602	1622	1490	NO_2
5b	3266	3415	2968	-------	1276	1530-1600	1613	1477	1319(bending OH) naphthalic
5c	3244	3416	2960	-------	1271	1522-1998	1620	1467	1311((bending OH) naphthalic
5d	3255	3400	2934	-------	1273	1513-1589	1598	1486	2500 NH_2
5e	3320	3437	2868	--------	1270	1519-1600	1616	1477	820(bending OH) phenolic

Table-4- : Biological activity of the prepared compounds

Compound Number	St.aureus	E.coli	Sal. Typhi
1	+	+	±
2	+	_	+
3	±	+	_
4_a	±	+	±
4b	+	+	+
4_d	+	±	_
4_e	++	±	_
5_a	+	+	±
5_b	±	+	±
5_c	+	±	_
5_d	+	+	±
5_e	++	±	_

Note: (-)= No-inhibition ,7-10mm ,(+)11-20mm,(++)=more than20mm

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