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Synthesis and characterization of some new Azo compounds From coupling of substituted 2-aminothiazolume salts with pyrrole

Entissar O. Al-Tamimi and Hussein F. Abdul Mahdi

Chemistry department, College of Science, University Of Baghdad, Iraq

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Abstract: The presented work involved the preparation of new Azo compounds containing aromatic heterocyclic (thiazole ring) derived from substituted aminobenzoic acid. The preparation procedure involves a series of steps. The first step includes the reaction of synthesized 2-aminothiazol compounds with nitrous acid at (0)°C to form the corresponding diazonium salts. The second step involved coupling the newly synthesized diazonium salts with pyrrole. All the prepared compounds in this work were characterized by melting point and softening points with other physical properties, FTIR and H^1-NMR spectra.

Keywords: Diazonium salts, Azo compound, Aminothiazole ring, pyrrole

INTRODUCTION

Thiazoles are one of the most intensively investigated classes of aromatic five-membered heterocyclic. It was first described by Hantzsch and Weber[1]**.** This five-membered ring system containing sulfur and nitrogen heteroatoms at positions-1 and -3, respectively is involved in many of the natural products. For example, the thiazolium ring present in vitamin B1 serves as an electron sink, and its coenzyme form is important for the decarboxylation of α-keto acids[2]. Thiazole and its derivatives are very useful compounds in various fields of chemistry including medicine and agriculture. In addition, thiazoles are

also synthetic intermediates and common substructures in numerous biologically active compounds such as various derivatives of penicillins and antibacterial Thiazoles[3]. Thiazolyl azo dyes are natural compounds effectively arranged by the diazotization of 2-aminothiazole and its derivatives. The diazuniom salt of the aminothiazole derivative must be combined with phenolic or other aromatic substances in acidic solutions at low temperature (0 °C to - 5 °C) to yield thiazolyl azo colors. General appearances of thiazolyl azo colors are red, violet or caramel hues in their crystalline state. A large portion of these compounds are just incompletely solvent or water insoluble. All things considered, their dissolvability can be expanded by the expansion of natural dissolvable, for example, chloroform, methanol, ethanol, dichloromethane, dimethylformamide tetrahydrofuran and acetone[4]**.**

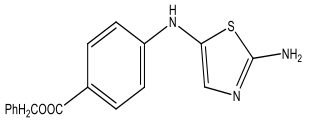
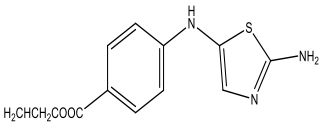
EXPERIMENTAL

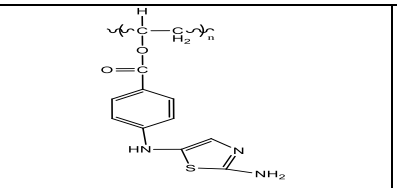
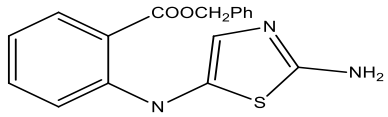
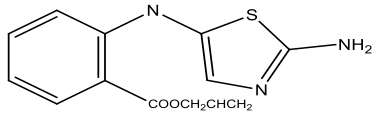
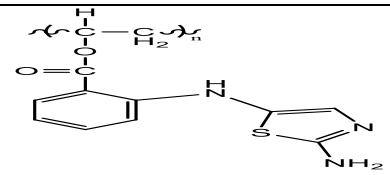
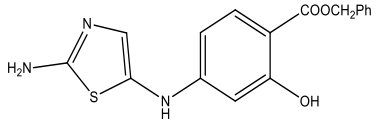
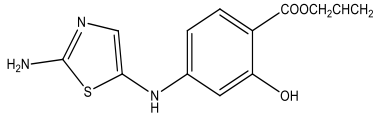
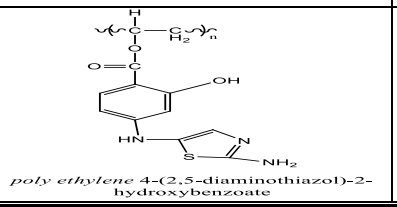
Material: All the chemicals were used of analytical grade and there were available from CDH, BDH and Fluka companies.

Instrument: Melting points were measured on Gallen Kamp capillary melting point apparatus (University of Baghdad college of science) and were uncorrected. FTIR spectra were recorded on Shimadzu FT-IR 8400 Fourier Transform Infrared Spectrophotometer (University of Baghdad college of science).Softening points were determined on Thermal Microscope Reichert Thermover 160 (University of Baghdad college of science). ^{1}H-NMR were measured in DMSO Solutions on a Bruker-500 MHz spectrophotometer (University of Isfahan) using TMS as an internal standard (chemical shifts in ppm)

General procedure for the preparation of amino thiazole compounds[5]: Literature procedure was used with modifications**.** In 100 ml R.B.F (0.02 mol) of chloroacetyl substituted amides and (0.02 mol) of thiourea were dissolved in 20 ml DMF and the blend were refluxed for 2 hours. Upon the finish, the blend was poured into water and the dry unrefined item was recrystallized from ethanol (Except the polymers were cleansed by dissolving them in DMSO and reprecipitating them from water). The physical properties of the prepared compounds are listed in the **Table (1).**

Table 1: physical properties of the prepared substituted 2-aminothiazole compounds

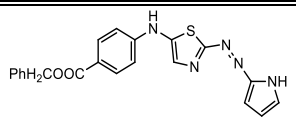
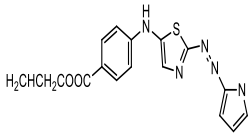
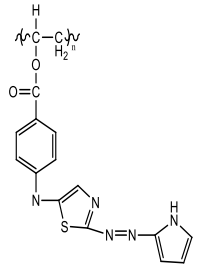
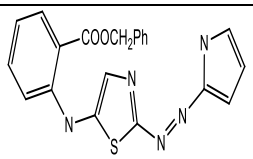
Comp. NO.	Structure and name	M.wt	M.P °C	S.P °C	Chemical formula	Color	Yield %	Recry. Solvent
19	 benzyl 4-((2,,5-diaminothiazol))benzoate	325	190	-	$C_{17}H_{15}N_3O_2S$	Dark red	73	Acetone
20	 allyl 4-(2,5-diaminothiazol)benzoate	275	172	-	$C_{13}H_{13}N_3O_3S$	Brown	78	Acetone

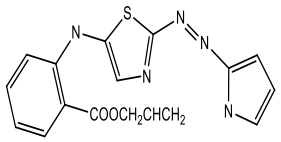
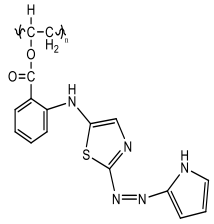
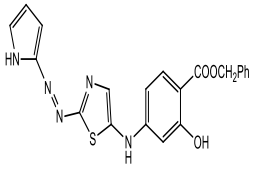
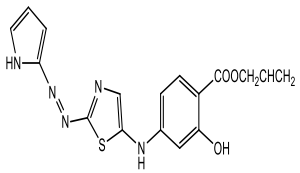
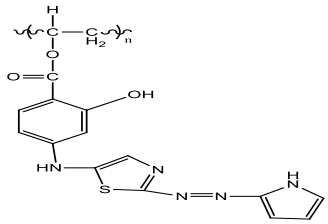
21	 *poly ethylene* 4-(2,5-diaminothiazol)benzoate	245	-	145	$C_{14}H_{17}N_3O_2S$	Brown	87	DMSO + H2O
22	 benzyl 2-(2,5-diaminothiazol)benzoate	325	108	-	$C_{17}H_{15}N_3O_2S$	Dark Red	76	Acetone
23	 allyl 2-(2,5-diaminothiazol)benzoate	275	101	-	$C_{13}H_{13}N_3O_2S$	Brown	79	Acetone
24	 *poly ethylene* 2-(2,5-aminothiazol)benzoate	245	-	107	$C_{14}H_{17}N_3O_2S$	Brown	63	DMSO + H2O
25	 benzyl 4-((2,5-diaminothiazol)-2-hydroxybenzoate	341	97	-	$C_{17}H_{15}N_3O_3S$	Dark red	80	Acetone
26	 allyl 4-(2,5-diaminothiazol)-2-hydroxybenzoate	291	120	-	$C_{13}H_{13}N_3O_3S$	Brown	87	Acetone
27	 *poly ethylene* 4-(2,5-diaminothiazol)-2-hydroxybenzoate	261	-	111	$C_{14}H_{17}N_3O_3S$	Dark Brown	72	DMSO + H2O

General procedure for the coupling 2-aminothiazol compounds with pyrrole[6]: Literature procedure was used with some modifications. The aminothiazole compounds (0.01 mol) were broken down in (6 mL, 50% HCl) and cooled at (0–5)°C. A solution of sodium nitrite (0.01 mol, 0.69 gm) in water (4 ml) beforehand cooled at 0°C was included dropwise keeping up the temperature at 0–5°C; stirring proceeded for 60 minutes, the readied diazonium compounds were utilized for coupling reaction . The pyrrole (0.01 mol) were broken down in GAA (30 mL) and cooled underneath 5°C. At that point was added dropwise

to the previously mentioned diazonium chloride solution with persistent stirring for 3 hours at 0–5°C. at that point reaction mixture was poured on ice to acquire the dyes, these dyes were filtered and dried at 70°C and were recrystallized from GAA (Except the polymers were purified by dissolving them in DMSO and reprecipitating them from water), the physical properties of the prepared compounds are listed in the **Table (2).**

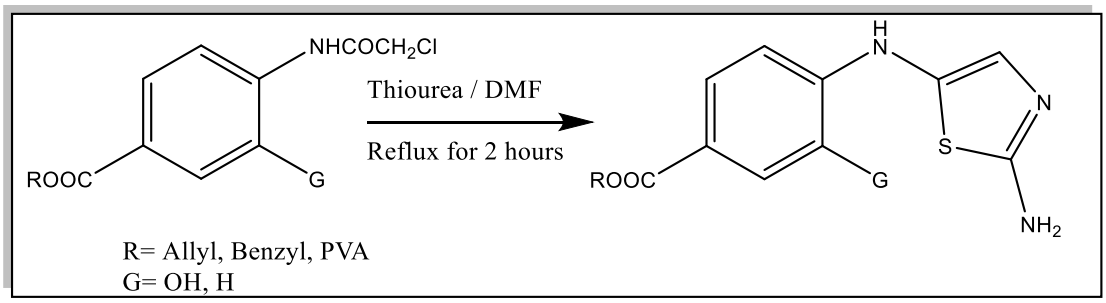
Table 2: Physical properties of the prepared Azo compounds

Comp. NO.	Structure and name	M.wt	M.P °C	S.P °C	Color	Chemical formula	Recrys. solvent	Yield %
28	 benzyl 4-[2-(1*H*-pyrrol-2-diazenyl)5-amino thiazole)benzoate	403	207 Dec.	-	Blue	$C_{21}H_{17}N_5O_2S$	GAA	95
29	 allyl 4-[2-(1*H*-pyrrol-2-diazenyl)-5-aminothiazole)benzoate	353	240 Dec.	-	Blue	$C_{17}H_{15}N_5N_2O$	GAA	92
30	 *poly ethyl* 4-[2-(1*H*-pyrrol-2-diazenyl-5-aminothiazol]benzoate	369	-	162	Blue	$C_{18}H_{19}N_5O_2S$	GAA	83
31	 benzyl 2-[2-(1*H*-pyrrol-2-diazenyl)-5-aminothiazol]benzoate	403	152 Dec.	-	Blue	$C_{21}H_{17}N_5O_2S$	GAA	86

32	 allyl 2-[2-(1*H*-pyrrol-2-diazenyl)-5-aminothiazol]benzoate	353	146 Dec.	-	Blue	$C_{17}H_{15}N_5O_2S$	GAA	74
33	 poly ethyl 2-[2-(1*H*-pyrrol-2-diazenyl-5-aminotiazol]benzoate	369	-	152	Blue	$C_{18}H_{19}N_5O_2S$	GAA	78
34	 benzyl 4-[2-(1*H*-pyrrol-2-diazenyl)-5-amino thiazol]-2-hydroxybenzoate	419	223 Dec.	-	Blue	$C_{21}H_{17}N_5O_3S$	GAA	85
35	 allyl 4-[2-(1*H*-pyrrol-2-diazenyl-5-aminothiazol]-2-hydroxybenzoate	369	215 Dec.	-	blue	$C_{17}H_{15}N_5O_3S$	GAA	94
36	 *poly ethyl* 4-[2-(1*H*-pyrrol-2-diazenyl-5-aminothiazol]-2-hydroxybenzoate	385	-	169	Blue	$C_{18}H_{19}N_5O_3S$	GAA	72

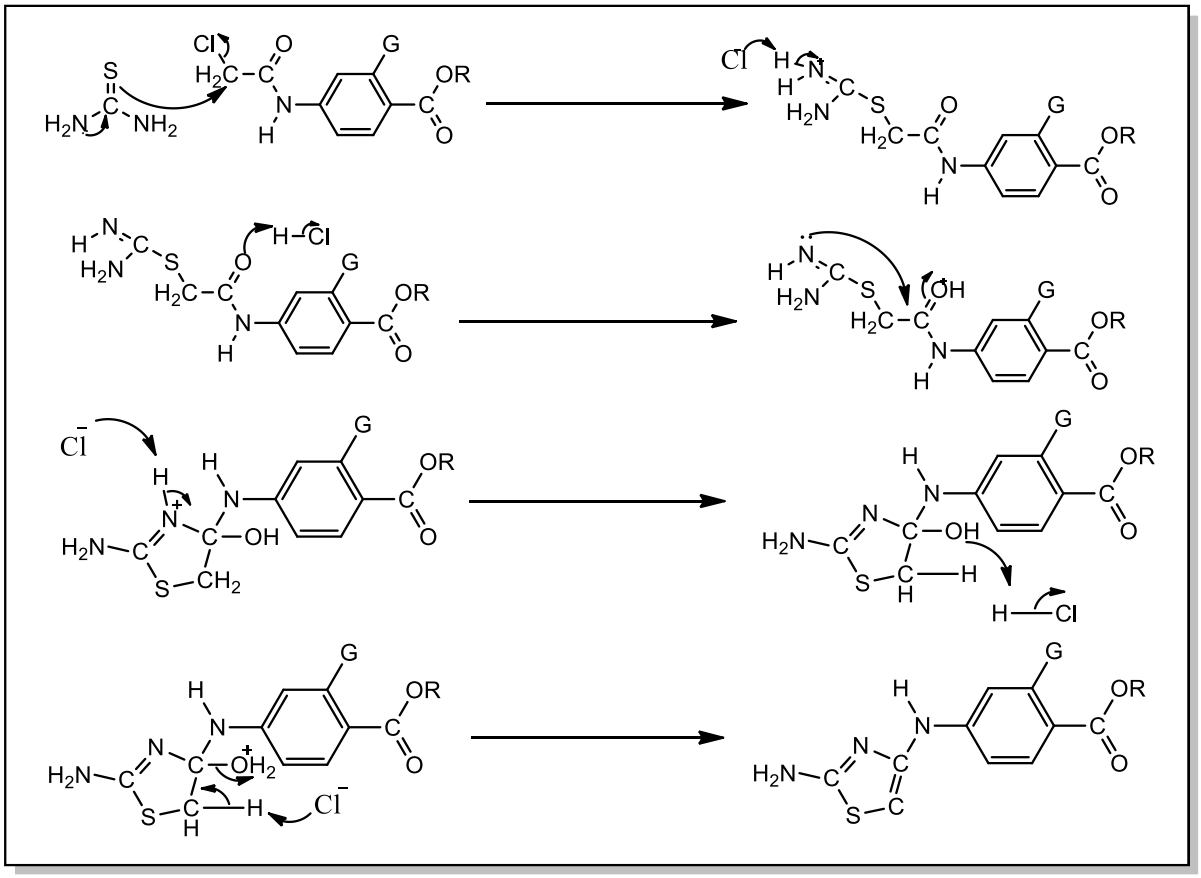
RESULT AND DISCUSSION

Preparation of compounds containing aminothiazole ring: Compounds {19, 20, 21, 22, 23, 24, 25, 26 and 27} were prepared by reaction of chloroacetyl substituted amides with thiourea in DMF. As shown in equation (1).



Equation (1): Preparation of aminothiazole ring containing compound

And the mechanism of the reaction goes like[7].



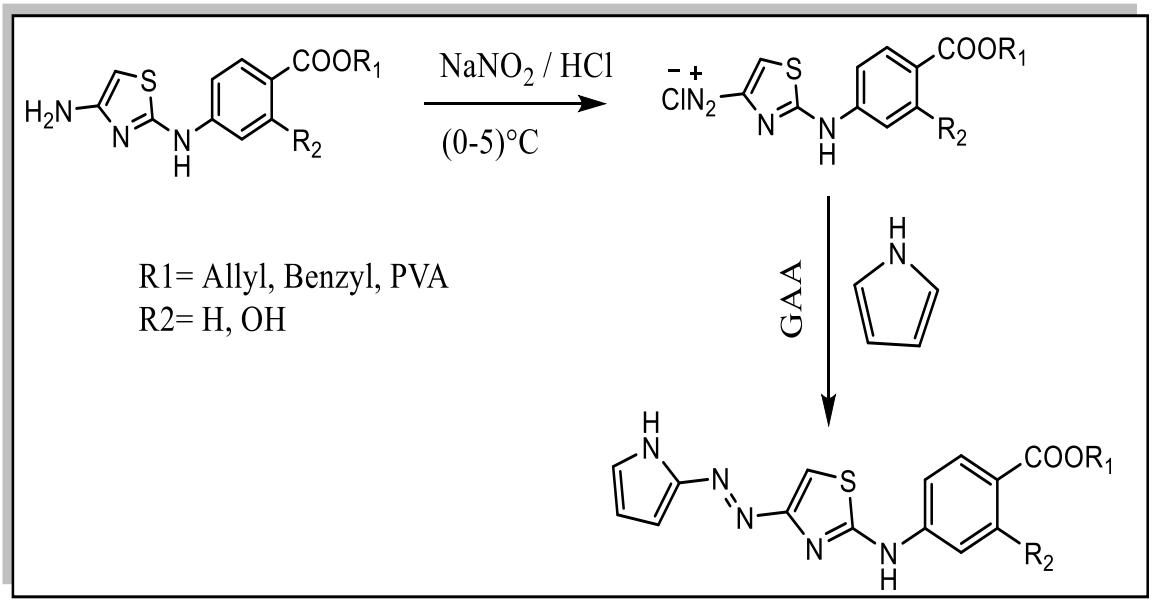
Scheme (1): mechanism for the formation of aminothiazole ring

Compounds {19, 20, 21, 22, 23, 24, 25, 26 and 27} were prepared by the reflux of chloroacetyl substituted amides and thiourea in DMF for 2 hours. The melting and softening point's ranges were (97-172) and the yield percentages were (63-87) %. All the physical properties of the prepared compounds are listed in the **Table (1).**

FTIR of compounds (19-27) showed the disappearance of the absorption band of (υC=O) amide at (1646-1681) cm^{-1}, absorption band of the (υC-Cl) group at (756-781) cm^{-1} which confirms the conversion to the final product, and the appearance of new band at (3420-3456) cm^{-1} of (NH_2) group and new absorption at (1630-1650) cm^{-1} of (υC=N) group and the other associations are listed in **Table (3)** .

^{1}H-NMR spectrum of compound 25 showed signal at δ10.1ppm for (s,1H,OH), δ9.3ppm for (s,2H,NH_2), δ8.6ppm for (s,1H,NH), 7.3ppm for (m,4H,Ar-H),δ 4.5ppm (s,1H,CH thiazole ring) as shown in **Table (4)** and **Figure (1) .**

All the Azo compounds were prepared by the diazotization reaction of the prepared substituted aminothiazole ring with pyrrole in the presence of nitrous acid at (0-5)°C . And the reaction is explained in scheme 1

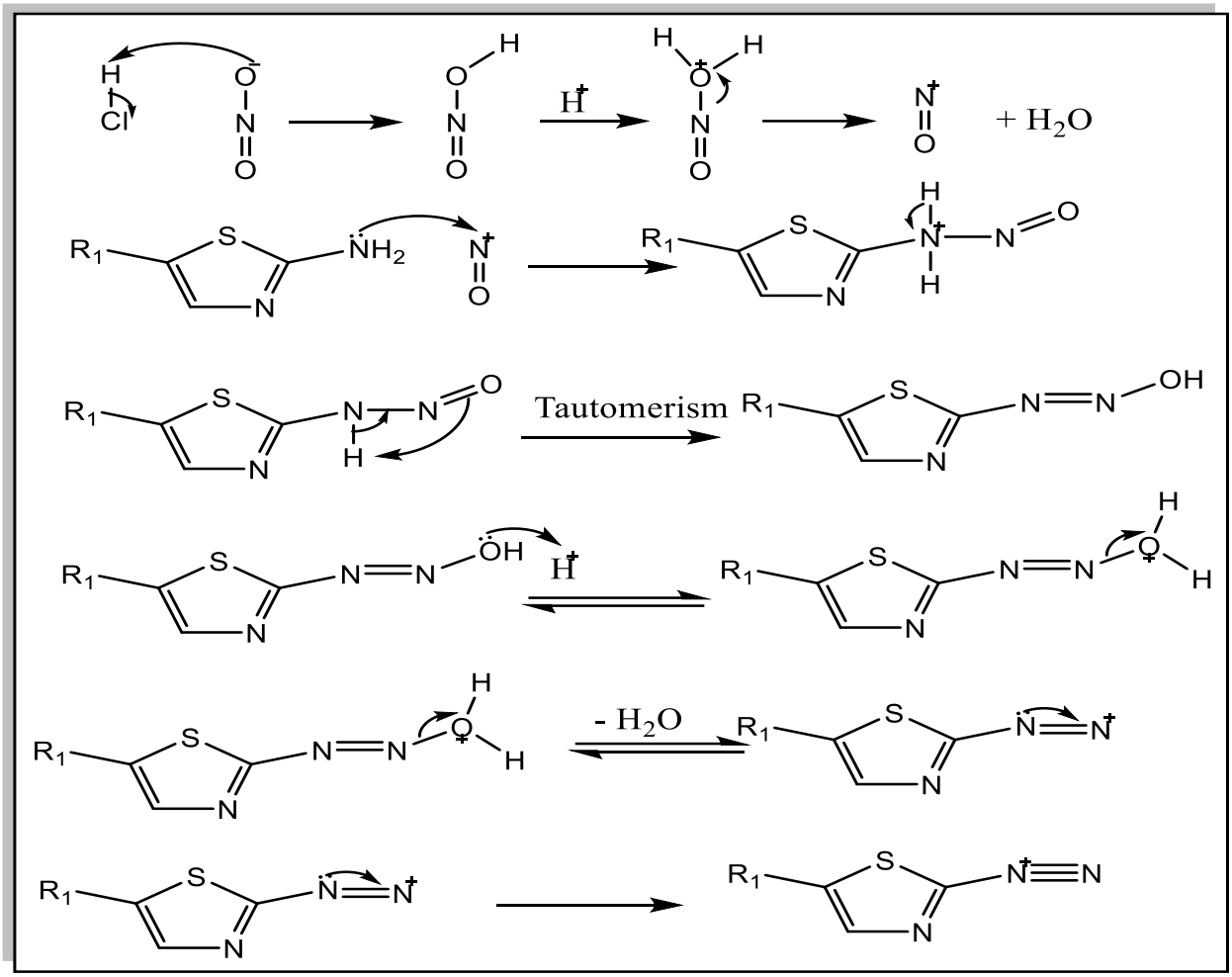


Scheme 2: Synthesis of azo compounds

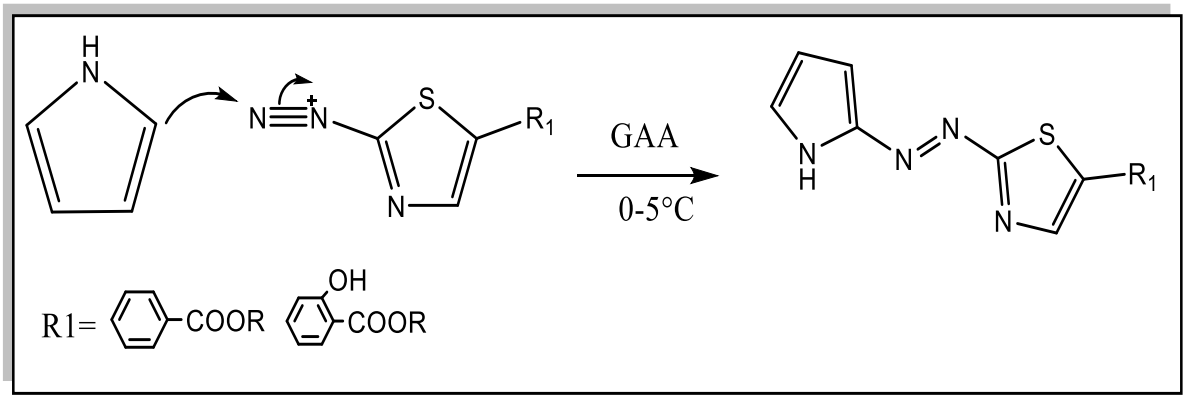
The mechanism of the reaction involves two steps[8, 9]:

Step 1: Formation of diazonium salt on the aromatic amine group attached to the aminothiazole ring as explained in the scheme (3).

Step 2: Then the coupling reaction of the produced diazonium salt with pyrrole as shown in scheme 4



Scheme (3): Formation of diazonium salt



Scheme 4: Coupling of pyrrole with aminothiazolume ring

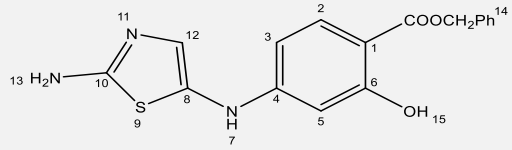
Compounds (28-36) were prepared by the coupling reaction of Pyrrole with the substituted aminothiazole ring in the presence of Nitrous acid at (0-5)°C, The melting, and softening point's ranges were (146-240)°C and the yield percentages were (95-72) %. all the produced compounds were confirmed by the physical properties listed in the table (2). FTIR spectra showed the formation of new absorption region at (1400-1452) cm^{-1} of υN=N group and some compounds (34, 35, 36) have an additional absorption region at (3524-3576) cm^{-1} of υO-H phenol and (1624-1632) cm^{-1} due to υC=C group all the other spectral data were listed in **table (5)** .^{1}H-NMR spectrum of compound 28 showed signal at δ 10.2ppm for (s, H, NH aromatic ring), δ 8.2 ppm for (s,1H,NH), 7.4 ppm for (m,4H,Ar-H), , δ 3.6 ppm for (s,1H, thiazole ring). As for compound 29 it showed signal at δ 11.5 ppm for (s,1H, Ar-OH), δ 8.5 ppm for (s,1H,NH), δ 7.3 ppm due to (m,4H, Ar-H), δ 6.6 ppm for the (d,2H,CH_2=CH-CH_3), δ 5.2 ppm for the (t,1H,CH_2=CH-CH_3) , δ 3.8 ppm of (d,3H,CH_2=CH-CH_3), δ 3.1 ppm for (s,1H, thiazole ring). All the spectral data are shown in table (6) and figures (2, 3)

Table 3: FTIR spectral data of 2-aminothiazole compounds

Comp.No.	υNH_2 1°amine	υNH 2°amine	υC-H aromatic	υC-H Aliphatic	υC=O ester	υC=N	υC=C aromatic	υC-N	υC-O	others
19	3450	3210	3049	2923 2832	1785	1632	1602 1550	1368	1244	-
20	3332	3190	3025	2921 2845	1781	1630	1601 1514	1374	1263	υC=C Olef. 1600
21	3452	3224	3010	2900 2834	1766	1637	1608 1543	1373	1242	-
22	3444	3230	3064	2927 2845	1762	1634	1606 1598	1375	1238	-
23	3456	3234	3064	2923 2852	1775	1640	1604 1536	1323	1160	υC=C Olef.1608
24	3450	3192	3046	2916 2856	1770	1639	1608 1598	1369	1180	-

25	3450	3210	3085	2954 2823	1776	1650	1612 1598	1373	1155	υO-H Phenol 3550
26	3420	3200	3069	2989 2846	1755	1642	1620 1576	1370	1223	υO-H Phenol 3540
27	3422	3199	3062	2916 2846	1760	1648	1604 1574	1372	1265	υO-H Phenol 3542

Table-4: Chemical shifts of compound 25

Compound	^{1}HNMR chemical shifts
	δ10.1ppm for (s,1H,OH), δ9.3ppm for (s,2H,NH_2), δ8.6ppm for (s,1H,NH), 7.3ppm for (m,4H,Ar-H),δ 4.5ppm (s,1H,CH thiazole ring)

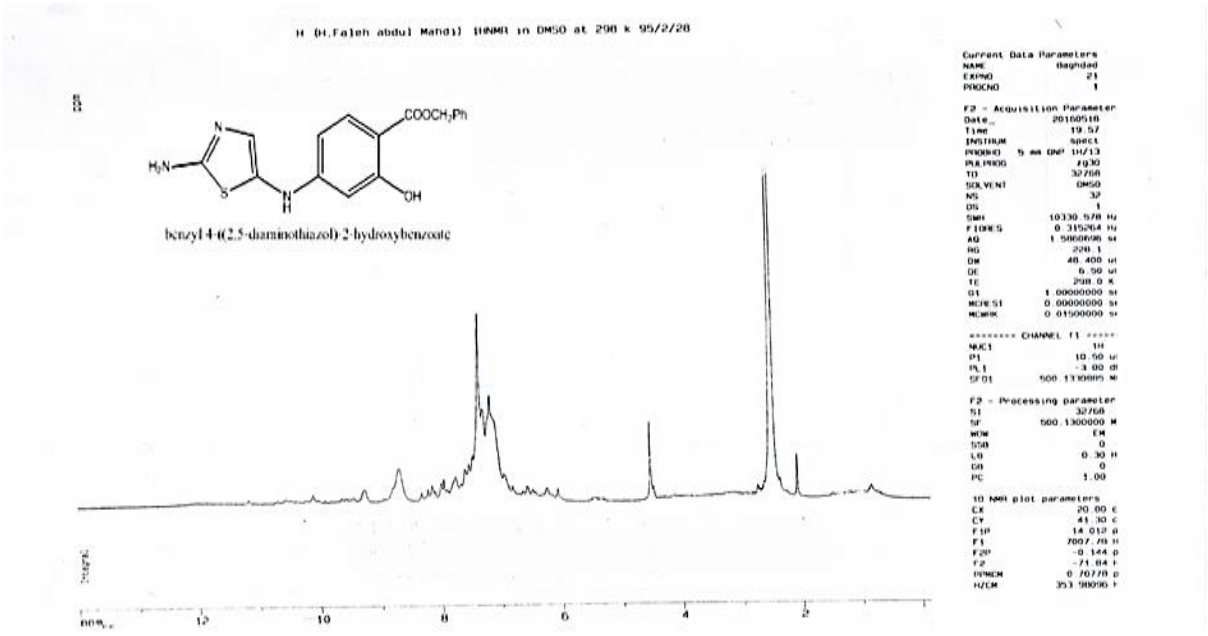
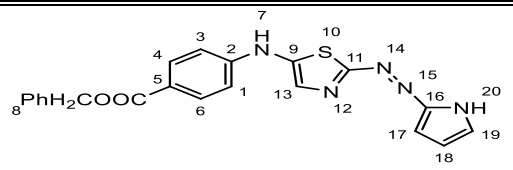
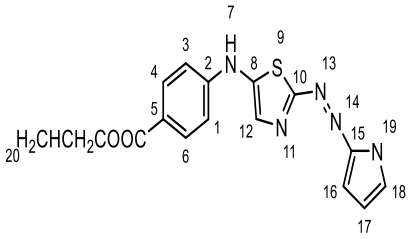


Figure 1: ^{1}HNMR spectra of compound 25

Table- 5: FTIR spectral data of the prepared azo compounds (28-36)

Comp.	υO-H phenol	υN-H 2°amine	υC-H aromatic	υC-H Aliphatic	υC=O ester	υC=C aromatic	υN=N Azo	υC-N	υC-O	others
28	-	3223	3023	2941 2855	1782	1607 1532	1450	1345	1245	-
29	-	3235	3087	2900 2865	1778	1604 1578	1421	1367	1243	υC=C Olef. 1627
30	-	3265	3034	2914 2856	1756	1600 1587	1417	1382	1232	-
31	-	3223	3012	2901 2834	1737	1627 1589	1400	1353	1223	-
32	-	3254	3042	2908 2834	1798	1620 1567	1452	1332	1243	υC=C Olef. 1632
33	-	3257	3022	2953 2832	1765	1618 1573	1412	1346	1265	-
34	3575	3221	3034	2910 2814	1788	1600 1589	1402	1326	1246	-
35	3524	3265	3026	2920 2856	1787	1601 1594	1400	1387	1275	υC=C Olef. 1624
36	3576	3212	3012	2902 2854	1784	1608 1543	1404	1343	1246	-

Table -6: Chemical shifts of compounds 28 and 29

Compound	^{1}HNMR chemical shifts
	δ 10.2ppm for (s, H, NH aromatic ring), δ 8.2 ppm for (s,1H,NH), 7.4 ppm for (m,4H,Ar-H), δ 3.6 ppm for (s,1H, thiazole ring).
	at δ 11.5 ppm for (s,1H, Ar-OH), δ 8.5 ppm for (s,1H,NH), δ 7.3 ppm due to (m,4H, Ar-H), δ 6.6 ppm for the (d,2H,CH_2=CH-CH_3), δ 5.2 ppm for the (t,1H,CH_2=CH-CH_3) , δ 3.8 ppm of (d,3H,CH_2=CH-CH_3), δ 3.1 ppm for (s,1H, thiazole ring).

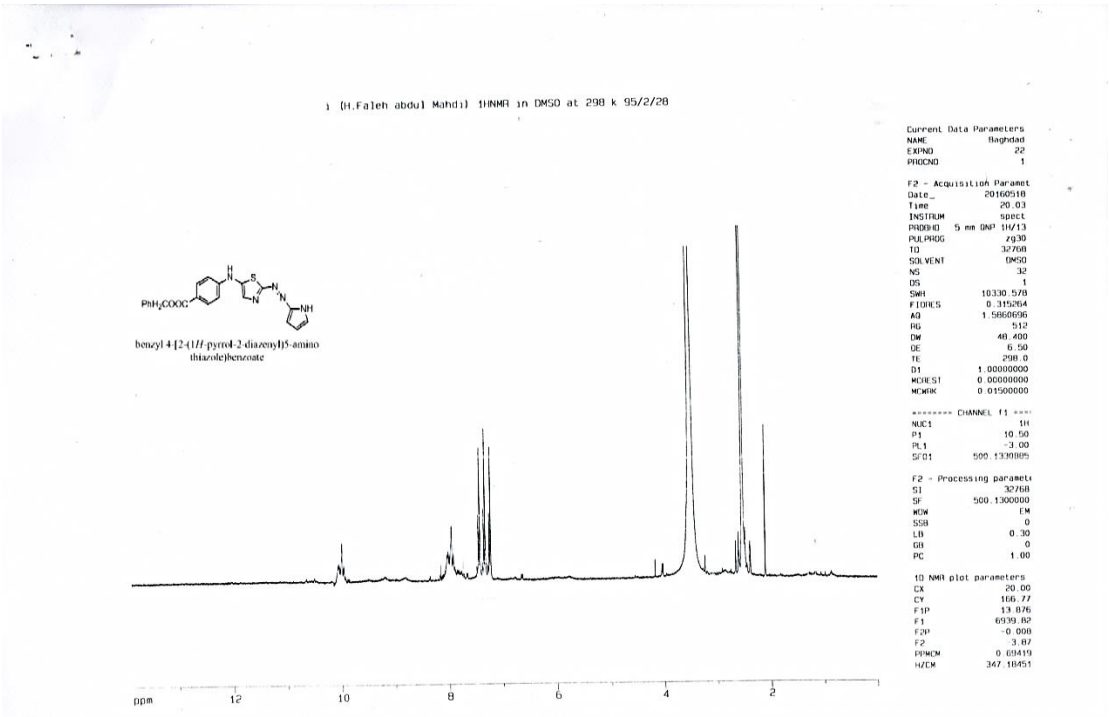


Figure-2: ^{1}HNMR spectra of compound 28

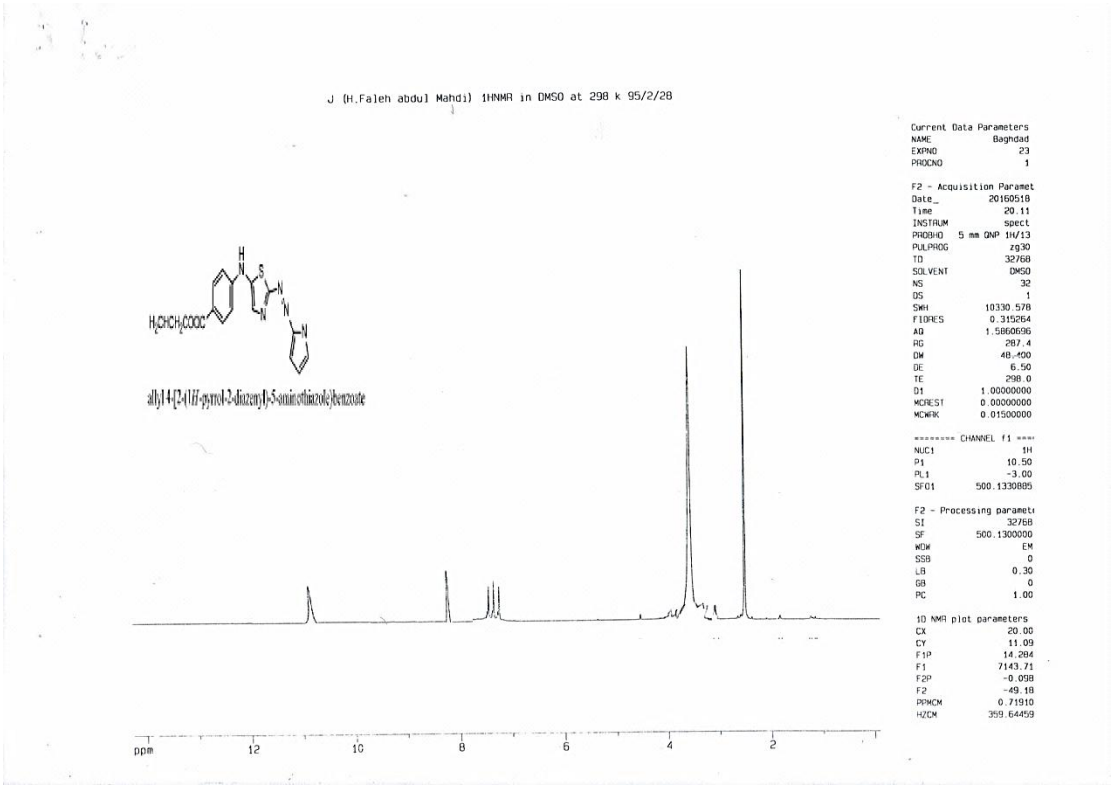


Figure 3: [1]HNMR spectra of compound 29.

The prepared compounds were tested for anti-bacterial activity and the results are listed in details in the articles[10]

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Corresponding author: Entissar O. Al-Tamimi,

Chemistry department, College of Science, University of Baghdad, Iraq

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