SYNTHESIS AND CHARACTERIZATION OF 2-HYDROXY-4-SUBSTITUTED–3(4,6-DISUBSTITUTED BENZOTHIAZOLYL-2- AZO)-BENZOIC ACID

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ABSTRACT

Diazotization of 4,6-disubstituted -2- amino benzothiazol with mixture of sodium nitrite and 50% sulphuric acid solution at (0-5)C gave 4,6-disubstituted-2 -benzothiazoldiazonium sulphate , upon coupling with 2-hydroxy-4-substituted -5-benzoic acid gave 2-hydroxy -4-substituted 3 (4,6-disubstituted –benzothiazolyl)azo benzoic acid derivatives which charactarized by their melting points , elemental analysis , FT-IR,UV-visible , and H-NMR spectra structure formula of the prepared compounds were confirmed depending on identification results.

Acidity constants were detrmined for both carboxylic and phenolic protons .

INTRODUCTION:-

Aryl diazonium salts are valuble intermediates in the synthesis of substituted arenas , aryl azo compounds and triazenes . Diazotization process is limited to the reactive primary amines and stabilized alkyl amines to produce essentially the diazonium salts such as chlorides, tri fluoro acetates , and fluoroborates . Diazo coupling of reactive phenols in slightly alkaline medium and reactive amines in an acidic medium produces diazo compounds which have long been used as disperse dyes and analytical ligands [1-5]

The pka s values for some phenylazo and naphthylazo dyes were determined and found to show linear relation with Hammet function [6,7]

O-acetyl benzenediazonium chloride , coupled with substituted phenols and phenolic carboxylic acids to give 2-(O-acetyl phenyl azo)-phenols and 2-(O-acetyl phenyl azo)-phenolic carboxylic acids [8]

Diazotization of 5-amino acridine with sodium nitrite in aqeous hydrochloric acid at(0-5)C gave acridinediazonium chloride , coupling of the resulting acridine diazonium chloride with reactive mono and di-substituted phenols produced acridine azo phenol [9]

Azo dyes of heterocyclic compound have been used to colour gasoline , fuel and diesel oils . due to their manifestation of novel structural , and relevance to biological processes [10]

EXPERIMENTAL :

Melting points , Rf,Yields and pka values of the prepared 2-hydroxy -4-substituted 3 (4,6-disubstituted –benzothiazolyl)azo benzoic acid derivatives were recorded and given in table (1); their elemental analysis and UV data are given in table (2) IR spectra are recorded as KBr disc

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with FT-IR spectrophotometer in Mutah University and listed in table (3).

The UV spectra are recorded on Shimadzu – Recc uv – 160 spectrophotometer using ethanol as (Solvent) and are given in table (2). Their H-NMR spectra were recorded with BRUKER – AC – 200MHZ FT-NMR and given in table (4).

Preparation of 4,6-disubstituted-2 -benzothiazoldiazoium sulphate:

Solution of 4,6-disubstituted-2-amino benzothiazol (0.02 mole) in 50%w:v of sulphuric acid was diazotized with sodium nitrite (0.02 mole , in 20 ml water) at (0-5 c).

The resulting 4,6-disubstituted-2 -benzothiazoldiaznium sulphate was fairly stable in liqued for 24h at 10c .

Preparation of 2-hydroxy -4-substituted 3 (4,6-disubstituted – benzothiazolyl)azo benzoic acid derivatives.

To (0.02 mole) of 4,6-disubstituted-2-benzothiazoldiazonium salt (0.02 mole) of the –2-hydroxy-5-methyl-benzoic acid in 40 ml of 10% NaOH was added with stirring for 1h at 0-5c. The precipitation product was filtered off and recrystalized twice from dry dioxane to give red crystals of 2-hydroxy -4-substituted 3 (4,6-disubstituted –benzothiazolyl)azo benzoic acid derivatives.

Calculation of Ionization constants:-

The potentiometric method was used to obtain the ionization constants for the prepared compounds , Afour-outlets round bottom flask was used. In the first outlet thire is the standardized H-pole , in the second a thermometer, the third used to inter the nitrogen gas whereas a Burite is fixed in the fourth outlet which is filled with sodium hydroxide solution (0.01) molar . A 25 mm of this solution is put in the flask to obtain its ionization constant.

Calculation

The constration of the solution is (0.0001) molar of the reducing it PH to the value of PH=1 . The process of filtration is carried then by using perchloric acid with the help of nitrogen which stirs the solution.

The Gauss mathematical program is used to register the values of PH to measure the value of $_{P}Ka$

DISCUSSION :

Table (1) contain some physical and expermintal properties of compounds (1-16).

Table (2) give C.H.N analysis results besides ultraviolet absorption spectra Uv-spectra of the prepared compounds revealed the following absorption bands ; (385-466) nm due to the thiazol skeleton , (300-377) nm due to N=N, the substituted phenyl ring (222- 299)nm.

Table (3) gives IR-spectra of these azo compounds , which revealed and the following absorption bands ; OH at (3421-3469)cm-1 , C=N and C=C at (1500-1522)cm^{-1} , N=N at (1433-1456)cm^{-1} and NO2 at(1545), (1366) cm^{-1} The chemical shifts of individual protons of all prepared compounds were assigned and given in table (4) . from this table the observed signals are (CH_3)group protons at δ = (2-2.5) ppm, protons of

phenyl ring (aromatic protons) at δ = (6.6-8.6)ppm , carboxylic group proton at (10.85-11.3)ppm and proton of phenolic OH atδ =(5.0-5.2)ppm .

Acid dissociation scheme for the prepared azo compounds can be represented as follows;

$$HL \rightleftharpoons L^- + H^+$$

The values of pkaS reflect the stability of the azo compounds which significantly affected by the nature of the substituents on the benzene ring .

Aryldiazonium ions are generated by diazotization of aromatic amines . They are stable in solution only near room temperature or below , and this limits the range of compounds that can be successfully coupled with diazonium salts .

Kenitic investigation have reveald second order limited kinetic behavior for diazonium coupling in a number of instances . It showed also that in the case of phenols , the conjugate base is attacked . This finding is entirely reasonable , since the deprotonated oxy group is abetter electron donor than the neutral hydroxy group . The reactivity increased by electron attracting groups and decreased by electron donor substituents [11]

The most unique feature of the mechanism for diazonium coupling is that proton loss can clearly be de monstrated tobe the rate determining step in certain cases . This feature is revealed in two ways , first , diazonium coupling of several sulphinate ions exhibit primary isotop effects in the rang of (4-6) when deuterium is present at the site of substituent , which is indicating that the cleavage of the C-H bond is occurring in the rate – determining step.

Second , the diazonium coupling reactions can be shown to be general base catalysed . This , too implies that the proton removal is rate – determining step [12]

Because of the limited range of aromatic compounds that react with diazonium ions , selectively data comparable to those discussed for other electrophilic substituent are not available . Presumable . Diazotization , since it involves a weak electrophile would reveal high substrate and position selectivity .

The reaction mechanism of the 4,6-disubstituted-benzothiazoldiazonium ions formation and coupling can be outlined as follows:

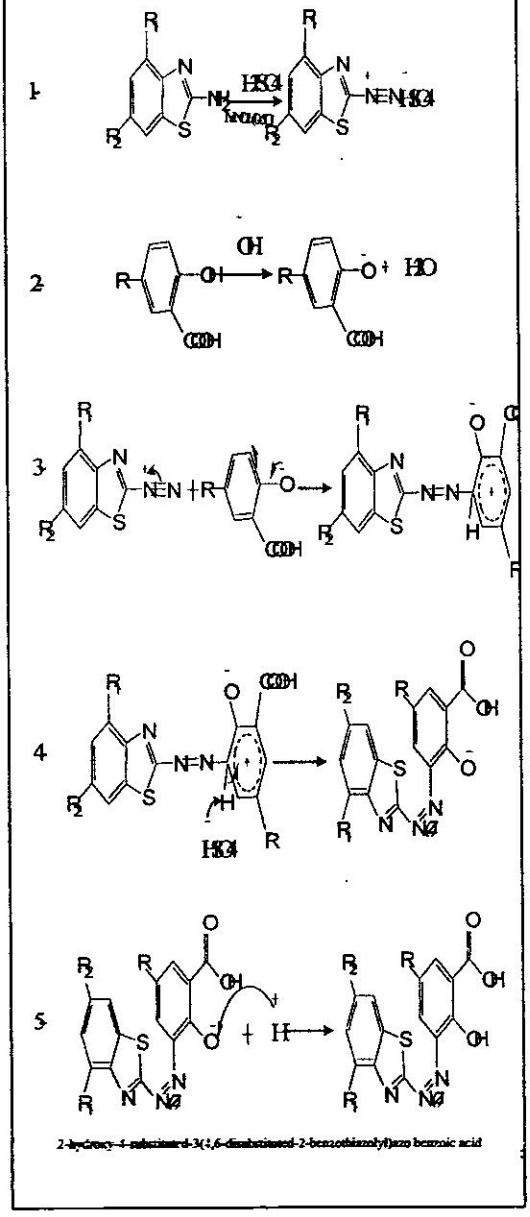
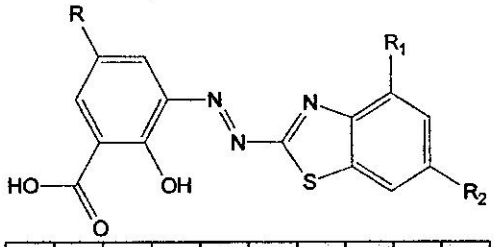
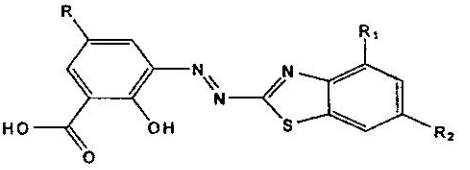


Table (1):Physical properties of 2-hydroxy -4-substituted 3 (4,6-disubstituted – benzothiazolyl)azo benzoic acid derivatives.



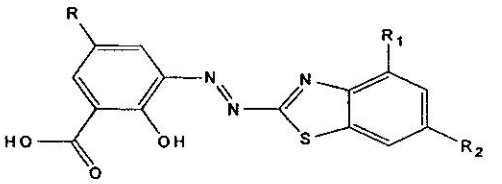
No.	R_1	R_2	R_3	M.F./C	Yield%	R_f	Plate	Plate	Plate
-	CH_3	H	CH_3	155-157	77	0.950	3.13	9.93	
-	-	H	Cl	165-165	78	0.955	2.87	9.42	
-	-	H	Br	158-160	75	0.891	2.77	9.61	
-	-	H	NO_2	173-175	81	0.903	2.38	9.69	
-	-	H	SO_3H	138-140	51	0.958	2.73	8.89	
-	-	CH_3	4,6di-CH3	145-147	57	0.955	2.73	8.79	
-	-	H	$NHCOCH_3$	157-159	72	0.922	3.27	9.91	
-	-	H	COOH	146-148	61	0.933	4.1	3.05	9.36
-	NO_2	H	CH_3	161-163	81	0.900	2.61	9.36	
-	-	H	Cl	174-176	90	0.871	2.42	9.35	
-	-	H	Br	165-167	79	0.921	2.53	9.35	
-	-	H	NO_2	181-183	77	0.957	2.32	9.60	
-	-	H	SO_3H	140-142	68	0.924	2.51	8.79	
-	-	CH_3	4,6-di-CH3	177-179	85	0.944	3.0	9.82	
-	-	H	$NHCOCH_3$	143-143	66	0.922	2.50	8.51	
-	H	COOH	$NHCOCH_3$	160-172	60	0.899	3.8	2.82	9.1

Table (2): C.H.N. analysis and UV-Spectral Data of 2-hydroxy -4-substituted 3 (4,6-disubstituted –benzothiazolyl)azo benzoic acid derivatives.



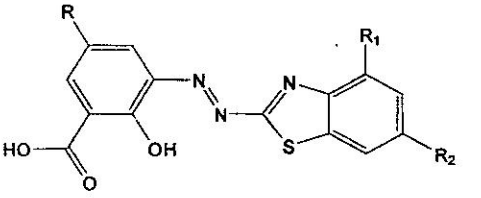
No.	R_1	R_2	R_3	Calc.			Found			UV-Spectra λ_{max} in Ethanol
				C	H	N	C	H	N	
-	CH_3	H	CH_3	58.70	4.00	12.84	59.00	3.99	12.69	
-	-	H	Cl	51.60	2.90	12.05	51.90	2.83	12.11	
-	-	H	Br	45.93	2.57	10.71	46.00	2.55	10.79	
-	-	H	NO_2	50.28	2.81	15.64	50.35	2.90	15.77	
-	-	H	SO_3H	55.13	3.81	15.13	55.22	3.66	15.00	
-	-	CH_3	4,6di-CH3	45.80	2.82	10.68	46.00	2.80	10.75	
-	-	H	$NHCOCH_3$	59.81	4.45	12.31	60.12	4.68	12.5	
-	-	H	COOH	53.78	3.10	11.76	54.00	3.00	11.92	
-	NO_2	H	CH_3	50.28	2.81	15.64	50.95	2.66	15.70	
-	-	H	Cl	44.40	1.86	14.79	44.22	1.63	14.58	
-	-	H	Br	39.73	1.67	13.24	40.09	1.80	13.25	
-	-	H	NO_2	43.19	1.81	17.99	43.26	2.01	18.22	
-	-	H	SO_3H	47.88	2.76	17.45	48.0	2.66	17.60	
-	-	CH_3	4,6-di-CH3	39.62	1.90	13.20	39.49	2.03	13.35	
-	-	H	$NHCOCH_3$	51.61	3.33	15.05	51.80	3.33	15.11	
-	H	COOH	$NHCOCH_3$	49.40	2.08	14.43	46.31	2.01	14.25	

Table (3): IR. Spectra /cm^{-1} in KBr disc of 2-hydroxy -4-substituted 3 (4,6-disubstituted –benzothiazolyl)azo benzoic acid derivatives.



No.	R	R_1	R_2	OH str.	C=Ostr.	C=N,C=Cstr.	N=N str.	C-S str.	other
			CH_3	3442	1658	1509	1450	1252	
			Cl	3443	1651	1502	1446	1248	
			Br	3426	1655	1503	1438	1245	
			NO_2	3421	1653	1520	1456	1251	
			SO_3H	3460	1643	1509	1447	1244	
			4,6di-CH_3	3421	1635	1500	1433	1257	
			$NHCOCH_3$	3421	1637	1506	1448	1248	3462, 3266 NH
			CH_3	3440	1649	1506	1443	1248	
			Cl	3436	1645	1510	1446	1239	
			Br	3428	1642	1513	1442	1238	
			NO_2	3452	1633	1520	1446	1242	
			SO_3H	3429	1638	1508	1443	1238	
		CH_3	4,6-di-CH_3	3463	1643	1511	1448	1235	
		H	$NHCOCH_3$	3439	1649	1522	1443	1246	3470,3251 NH
	H		CH_3	3469	1638	1510	1453	1245	
	COOH								

Table (4): H.N.M.R. Data of 2-hydroxy -4-substituted 3 (4,6-disubstituted – benzothiazolyl)azo benzoic acid derivatives.



الإزاحة الكيميائية بوحدات PPm

No.	R	R_1	R_2	Benzothiazol ring			benzene ring				R-H
				H_4	H_6	H_7	H_3	H_5	COOH	OH	CH_3	
			CH_3	8.15	6.7	7.7	7.65	6.65	10.85	5.1	2.3	2.5
			Cl	8.1	7.7	8.0	7.8	7.2	11.2	5.0	2.4	—
			Br	8.2	7.5	8.1	7.5	7.1	11.3	5.0	2.35	—
			NO_2	8.9	8.35	8.7	7.7	7.0	11.1	5.2	2.35	—
			SO_3H	7.65	7.7	7.7	6.8	6.75	11.15	5.15	2.4	2.1
			4,6di-CH_3	7.7	8.3	8.7	6.8	6.8	11.0	5.1	2.5	2.25
			$NHCOCH_3$	2.35	7.6	7.7	7.4	7.3	11.2	5.0	2.25	2.3
			CH_3	8.1	6.7	8.0	7.7	6.9	11.2	5.15	—	2.4
			Cl	8.0	7.8	7.9	7.9	7.3	11.1	5.0	—	—
			Br	8.1	7.6	8.0	7.9	7.5	11.3	5.2	—	—
			NO_2	8.2	7.7	8.1	7.8	7.9	11.2	5.15	—	—
			SO_3H	7.6	7.8	7.5	7.0	7.1	11.0	5.0	—	2.1
		CH_3	4,6-di-CH_3	7.8	8.4	8.5	7.2	7.1	11.2	5.15	—	2.0
		H	$NHCOCH_3$	2.35	7.7	7.8	7.6	7.5	11.3	5.1	—	2.2
	H		CH_3	7.8	8.4	8.5	7.2	7.0	11.0	5.0	—	2.1
	COOH											

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تحضير وتشخيص مركبات 2-هيدروكسي -4-معوض -3-ثنائي – معوض – بنزوثيازوليل -2-أزو) -حامض البنزويك

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الخلاصة :

إن دياَزة مركبات (4,6- معوض – 2 – امينوبنزوثايازول) بواسطة نتريت الصوديوم في مـزيج 50 % حامض الكبريتيك في (0 – 5)م أعطت أملاح الدايازونيوم لهذه المركبات.

إن ازدواج أملاح الدايازونيوم هذه مع 2 – هيدروكسي -4- معوض-5- – حامض البنزويك أعطى مشتقات 2 – هيدروكسي -4-معوض- 3 (4,6- معوض-2 – بنزوثايازوليل) أزو حامض البنزويك . وقد شخصت المركبات المحضرة بتعيين درجات انصهارها، تحليل العناصر، أطياف الأشعة فوق البنفسجية أطياف الأشعة تحت الحمراء أطياف الرنين النووي المغناطيسي وقد أسهمت نتائج التشخيص بالطرق المختلفة في إثبات الصيغ التركيبية للمركبات المحضرة . كما تم قياس قيم (Pka) .