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## Highlights

-chloro-4-hydroxyquinoline-2(1*H*)-one was used as a coupling component > solvatochromism of the azo dyes was studied > acidic dissociation constants were measured and correlated with Hammet substitution constants

Synthesis, structural elucidation, solvatochromism and spectroscopic properties of some azo dyes derived from 6-chloro-4-hydroxyquinoline-2(1*H*)-one

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#### Abstract

Malondianilide (I) derived from *p*-chloroaniline was cyclized to 6-chloro-4-hydroxyquinoline-2(1H)-one (II) in moderately good yield using polyphosphoric acid as catalyst. This compound was then coupled with some diazotized aromatic amines to give the corresponding azo disperse dyes 1-12. A systematic study of the effect of solvent, acid, base and pH upon the electronic absorption spectra of the dyes 1-12 was carried out. In DMSO, DMF, CH<sub>3</sub>CN, CHCl<sub>3</sub>, EtOH and acidic media (CH<sub>3</sub>COOH, acidified EtOH) these dyes that theoretically may be involved in azo-hydrazone tautomerism have been detected only as hydrazone tautomers T<sub>1</sub> and T<sub>2</sub>. The acidic dissociation constants of the dyes were measured in 80 vol% ethanol-water solution at room temperature and ionic strength of 0.1. The results were correlated by the Hammett-type equation using the substituent constants  $\sigma_x$ .

Key words: azo dye, tautomerism, pH, solvatochromism, pKa, hydrazone

#### **1. Introduction**

Dyes can be classified as azo, anthraquinone, arylmethane, acridine, cyanine, phthalocyanine, nitro, nitroso, quinoneimine, thiazole or xanthene dyes according to the type of chromophore group on the dye molecule. Azo dyes contain one or more azo groups (N=N) having aromatic rings. They are the largest dye class of synthetic dyes [1-3]. Azo dyes have been extensively used in various fields, such as dyeing of textile fibers, colouring of different materials, advanced applications in organic synthesis and many non textile applications [4-6]. Striking examples in this respect are those of containing quinolone moieties that deserve special attention due to their applications as disperses dyes [7, 8]. Moreover, the hydroxyl-quinolone compounds are very useful as enol-type precursors for the synthesis of some heterocyclic dyestuffs in color chemistry [9-11].

The presence of one hydroxyl group in conjugation to the azo bridge makes these compounds the main source of azo-hydrazone tautomeric structural requirement [12, 13]. In addition, the spectral data generally led to the conclusion that in some solvents, the tautomeric equilibrium of the arylazoquinolone dyes is a mixture of two hydrazone-keto forms [14-17].

Although several studies concerning the azo-hydrazone tautomeric equilibrium of dyes having azo-enol moieties have been reported, very few investigations have been devoted on the structures, precise characterization and spectroscopic properties of substituted 3-arylazo-4-hydroxyquinoline-2(1H)-ones.

Herein, some 3-aryl azo-quinolone dyes were prepared by coupling 6-chloro-4hydroxyquinoline-2(1H)-one with diazotized aniline derivatives. The visible absorption spectra of these dyes were evaluated with respect to the influence of solvents and substituents on the phenyl ring of the diazo components. The effects of acid and base on the visible absorption maxima of the dyes are reported. The pH effects along with the acid dissociation constants of the dyes are also included with the aim of elucidating the absorption behaviors of the compounds under investigation. The structures of coupling component and prepared dyes are depicted in Schemes 1 and 2.

#### 2. Experimental

#### 2.1. Materials and instrumentation

All the chemicals used in dye synthesis were of laboratory grade and were used without further purification. Elemental analyses were performed at the Microanalytical Center using CHNS- EL III Vario Elemental Analyzers and the results were within the accepted range ( $\pm 0.40$ ) of the calculated values. All melting points were measured on a Barnstead Electrothermal 9100 melting point apparatus and were uncorrected. IR spectra were recorded for KBr disc on a

PerkinElmer FT-IR spectrometer. Electronic absorption spectra were recorded on Cary UV–Vis double-beam spectrophotometer (Model 100). <sup>1</sup>H NMR spectra were measured on a FT-NMR (500 MHz) Brucker apparatus in CDCl<sub>3</sub> or DMSO as a solvent, using TMS as an internal standard, chemical shifts are expressed as  $\delta$ /ppm, and J values are given in Hz. Thin-layer chromatography (TLC) analysis was carried out on plates coated with silica gel 60 F<sub>254</sub>.



Scheme1. Preparation of 6-chloro-4-hydroxyquinolin-2(1H)-one.

## 2.2. Preparation of N, N'-bis (p-chlorophenyl) malonamide (I)

A mixture of *p*-chloroaniline (100 mmol, 12.80 g) with diethylmalonate (50 mmol, 7.62 ml) was refluxed in a round bottom flask equipped with an air condenser for 2 h so that the ethanol evolved and escaped from the top of the condenser. After cooling, the precipitate was filtered by

suction and recrystallized from ethanol giving the malonamide (I) (13.25g, 82%) as white crystals, m.p. 218–220  $^{\circ}$ C (reported 217  $^{\circ}$ C [10]).

2.3. Synthesis of 6-chloro-4-hydroxyquinolin-2(1H)-one (II)

*N*, *N*'-bis (*p*-chlorophenyl) malonamide (I) (3.23 g, 10.0 mmol) at 80°C was thoroughly mixed with 22 g polyphosphoric acid (PPA, sp.gr. 2.08) and then heated in an oil bath for 5 h at 150-160°C. The dark viscous solution was allowed to cool, water was added and the resultant gum solidified on prolonged standing. The precipitate so formed was filtered off, washed several times with water and dried in air. The crude product was dissolved in 100 ml of sodium hydroxide solution (0.5 mol·L<sup>-1</sup>) and undissolved material was filtered. The filtrate was carefully neutralized with concentrated hydrochloric acid and the precipitate was recrystallized from ethanol to afford 6-chloro-4-hydroxyquinolin-2(1*H*)-one (**II**) (1.47 g, 75%) as white powder: mp> 350 °C, FT-IR (KBr): v (cm<sup>-1</sup>): 3400-3150 (OH, NH), 1654(C=O), 1600(C=C), 1116(C-O), <sup>1</sup>H NMR(500 MHz,DMSO-d<sub>6</sub>, 25°C):  $\delta$ = 5.8 (s, 1H), 7.69(s, 1H), 7.26 (dd, J=8.6, 4.8 Hz,1H), 7.51(d, J=8.6Hz, 1H), 11.35(NH).

## 2.4. Preparation of arylazo quinolone dyes 1-12

A cold solution of aryldiazonium salt (2.0 mmol) was prepared by adding a solution of NaNO<sub>2</sub> (2.2 mmol, 0.15 g into 1.0 mL H<sub>2</sub>O) to a cold solution of arylamine hydrochloride (2.0 mmol of arylamine in 1.5 mL conc. HCl). The resulting solution of aryl diazonium salt was added drop wise to a mixture of compound (**II**) (2.0 mmol, 0.43g) in water (15 mL) containing NaOH (25 mmol, 1.0 g) at 0- 5°C. The pH of the reaction mixture was maintained at 9-10 by adding 2.5 % sodium hydroxide solution. Then, the reaction mixture was stirred for 2 h at the same temperature and the precipitate was filtered off and the resulting solid was washed with cold ethanol and dried at 50 °C in an oven. The crude product was purified using the

recrystallization method as mentioned in Table 1. Under the same reaction conditions, a series substituted arylazo quinolone dyes were obtained in satisfactory yields (Table 1, Scheme 2).



Scheme 2. Structures of dyes 1-12.

#### 3. Results and discussion

#### 3.1. Synthesis and characterization

As depicted in Scheme 1, malonamide (**I**) was prepared by refluxing 4-chloro aniline with diethyl malonate (2:1 molar ratio) in good yield. *N*, *N'*- di(4-chlorophenyl)malonamide (**I**) was then heated in polyphosphoric acid (PPA) at 150-160°C to afford the 6-chloro-4-hydroxyquinolin-2(1*H*)-one (**II**) [10, 18]. The crude products were purified by recrystallization from ethanol–water and were characterized by the FT-IR and <sup>1</sup>H NMR spectral analysis. For compound (**II**), the peak at 5.83 ppm (=CH) confirmed the formation of the desired quinolone ring.

The arylazo-quinolone dyes 1-12 were synthesized by coupling reaction of 6-chloro-4hydroxyquinolin-2-(1*H*)-one with diazotized *p*-substituted aniline derivatives in alkaline solution. The purified products can be obtained through recrystallization of the crude dyes in hot DMF/water (Table 1, Scheme2). The chemical structures of these dyes were confirmed by FT-IR, NMR and UV-vis spectroscopic methods and elemental analysis. The infrared spectra of all the compounds (in KBr) showed intense carbonyl bands at 1691–1655 cm<sup>-1</sup>, broad hydroxyl (- OH) and amide (NH-C=O) bands at 3500-3350 cm<sup>-1</sup> and 3291-3193 cm<sup>-1</sup>, respectively. The aromatic C-H  $v_{\text{max}}$  values at 3097–3051 cm<sup>-1</sup> were also recorded. The actual tautomeric forms of the azo dyes 1-12 were experimentally examined by their UV-vis absorption and <sup>1</sup>H NMR spectroscopy. It can be assumed that the prepared azo dyes may exist in one or more of seven tautomeric structures  $T_1$ - $T_7$  (Scheme3). The absence of a methine (>CH-) proton signal at about 6.4 ppm precludes the existence of structures  $T_4$  and  $T_6$  [19].

The physical properties of the dyes synthesized in this study.											
Dye	Color	Mp(°C)	Recrystalization	%C		%H		%N		Yield (%)	
				Calcd. Found		Calcd. Found		Calcd. Found			
1	Dark red	327-329	DMF	52.26	52.71	2.63	2.69	16.25	16.33	65	
2	Reddish brown	305-307	DMF/H <sub>2</sub> O	52.26	52.69	2.63	2.67	16.25	16.36	65	
3	Orange	325-327	DMF/H <sub>2</sub> O	59.18	58.96	2.79	2.83	17.25	17.32	70	
4	Dark orange	288-290	DMF/H <sub>2</sub> O	52.26	52.54	2.47	2.49	11.43	11.55	70	
5	Clear yellow	320-322	DMF/H <sub>2</sub> O	52.26	52.58	2.47	2.52	11.43	11.56	75	
6	Brown	288-290	DMF/H <sub>2</sub> O	56.71	56.89	2.86	2.89	13.23	13.74	77	
7	Gold	315-317	DMF/H <sub>2</sub> O	53.91	54.13	2.71	2.74	12.57	12.66	75	
8	Yellow	348-350	DMF/H <sub>2</sub> O	47.58	47.71	2.40	2.38	11.10	11.25	70	
9	Dark brown	278-280	DMF/H <sub>2</sub> O	42.33	42.56	2.13	2.15	9.87	10.06	68	
10	Clear brown	286-288	DMF/H <sub>2</sub> O	60.11	61.35	3.36	3.29	14.02	14.34	74	
11	Dark orange	295-297	DMF/H <sub>2</sub> O	61.25	61.64	3.86	3.84	13.39	13.48	80	
12	Orange	288-290	DMF/H <sub>2</sub> O	58.28	58.63	3.67	3.70	12.74	12.73	85	

Table 1

The existence of tautomeric forms  $T_3$ - $T_5$  involving quinolone NH proton rearrangement can be eliminated by studying the <sup>1</sup>H NMR spectrum of the compounds in the appropriate region. The <sup>1</sup>H NMR spectrum of the dyes in DMSO-d<sub>6</sub> showed two singlets at  $\delta$  11.56–11.33ppm and  $\delta$ 11.51–11.12ppm. The presence of these two broad singlets provides firm evidence for presence of the amide (-NH-C=O) bonds and is related to amide protons of two types of tautomeric forms  $T_1$  and  $T_2$ . In addition, the <sup>1</sup>H NMR spectra of the compounds show the significantly downfieldshifted resonances in range between 14 to 17 ppm corresponding to protons that are engaged in strong hydrogen bonding. According to results previously published in literature [13, 20], the hydrazone NH proton resonance appears approximately between 13.0 and 16.0 ppm in *o*- and *p*-hydroxyazo dyes. <sup>1</sup>H NMR spectra measured in DMSO-d<sub>6</sub> at 25 °C are given in Table 2. In addition to known aromatic and aliphatic protons, all the prepared azo dyes showed two broad peaks at  $\delta$  15.05–14.95ppm and  $\delta$  15.53–14.78ppm assigned to hydrazone proton signals (=N–NH–). These signals can be attributed to the hydrazone NH proton resonance related to hydrazone-keto forms T<sub>1</sub> and T<sub>2</sub> and evident that these azo dyes do not exist in tautomeric form T<sub>7</sub>. This downfield position of the NH proton is evidence for intramolecular chelation with the carbonyl group (Scheme 4). For example, the <sup>1</sup>H NMR spectrum of dye **10** (Fig. 1) in DMSO-d<sub>6</sub> at room temperature showed two peaks at 15.90 ppm and 15.16 ppm for hydrazone NH protons and 11.47 ppm and 11.31ppm for amide NH protons. It can be validly concluded that azo dyes **1–12** are present in hydrazone structures which can exist as a mixture of two tautomeric forms, namely the hydrazone-keto (**T**<sub>1</sub>) and hydrazone-keto (**T**<sub>2</sub>) as shown in Scheme 3.



Fig. 1. Partial <sup>1</sup>H NMR spectra of dye 10 (X=-H) in DMSO in which peaks are assigned to the presence of the two isomers of  $T_1$  and  $T_2$ .

Further evidence for this assignment was provided by the observation that the quinolone ring NH was extremely affected by solvent species, but the hydrazone NH was not affected so much. For example, <sup>1</sup>H NMR spectrum of dye **12** was measured in CDCl<sub>3</sub>. It was observed that the quinolone ring NH peak appears at higher field in chloroform than in DMSO. The quinolone rings NHs of dye **12** were observed at  $\delta$  8.38ppm and  $\delta$  8.04ppm in CDCl<sub>3</sub>, whereas the corresponding protons in other dyes were observed at  $\delta$  11.54ppm to  $\delta$  11.07ppm in DMSO-d<sub>6</sub>. The downfield chemical shift of the NH proton signal in DMSO-d<sub>6</sub> is larger than in CDCl<sub>3</sub>, because of the intermolecular hydrogen bonding between the NH and DMSO. Inspection of the hydrazone NHs chemical shifts of those azo dyes in both CDCl<sub>3</sub> and DMSO-d<sub>6</sub> showed that there was no significant difference in the chemical shifts in the two solvents, provided that the molecules are involved in a strong intramolecular hydrogen bond as shown in Scheme 4.



Scheme 3. Possible tautomeric forms for the synthesized azo dyes.

Dye		$IR(KBr, cm^{-1})$				<sup>1</sup> H NMR (δ, ppm)	N-H		
					Other				
	$v_{\text{O-H}}$	$v_{\text{N-H}}$	$v_{\rm C=O}$	$v_{c=c}$	functional	Aro. and AliphH's	Hydrazone	amide	
					groups				
1	3415	3266	1690	1610	1529 and	8.32(2H, d, J= 9.2 Hz), 7.86(2H, d, J= 9.2 Hz), 7.84	14.78	11.07	
					1348(NO <sub>2</sub> )	(1H, d, J= 2.8 Hz), 7.70-7.65(2H, m, overlapped)	15.07	11.44	
2	3417	3291	1691	1612	1531 and	8.52(1H, s),8.12-8.07(2H,m, overlapped), 7.85(1H,	14.92	11.41	
					1347(NO <sub>2</sub> )	d, J=2.4 Hz), 7.76(1H,t,J=8 Hz), 7.67(1H, dd, J=	15.47	11.53	
					,	8.6, 2.6 Hz), 7.21(1H, d, J=8.8Hz)		Y	
3	3416	3257	1690	1607	2229(CN)	7.92(2H,d, J=8.4 Hz), 7.85-7.83(3H,m,	14.82	11.35	
						overlapped), 7.66(1H, dd, J=9, 2.4 Hz), 7.20(1H,	15.34	11.54	
-						d, J=9Hz)			
4	3418	3288	1694	1606	1316(C-F)	7.91-7.76 (5H, m, overlapped), 7.58(1H, dd, J= 8.8	14.93	11.34	
						, 2.4Hz), 7.15 (1H, d, J=8.8 Hz)	15.50	11.54	
5	3415	3321	1685	1609	1317(C-F)	8.01(1H, s), 7.94(1H, d, J=5.2 Hz), 7.80(1H,s),	15.53	11.16	
						7.70(1H, t, J= 8 Hz), 7.64-7.60 (2H, m,	14.95	11.34	
						overlapped), 7.19(1H, d, J=8.8Hz)			
6	3413	3246	1655	1600	1231(C-F)	8.31(2H, d, J= 9.2 Hz), 7.84-7.18(5H, m,	15.12	11.45	
						overlapped)	15.87	11.55	
7	3417	3227	1689	1614	823(C-Cl)	7.86(1H, d, J= 2Hz), 7.70(2H, d, J=7 Hz),	15.15	11.10	
						7.58(1H,dd, J= 8.4, 2.4 Hz), 7.49(2H, d, J= 7 Hz),	15.89	11.34	
						7.20(1H, d, J=8.8Hz)			
8	3414	3272	1626	1591	534(C-Br)	7.89(1H, d, J= 2.4Hz), 7.59(2H, d, J=8.8 Hz),	14.80	10.26	
						7.50(2H,d, J= 8.8Hz), 7.33(1H, dd, J= 5.6, 2.4 Hz),	15.48	10.43	
						7.10(1H, d, J=8.8Hz)			
9	3418	3203	1657	1610	510(C-I)	7.84(2H, d, J= 8.4 Hz), 7.73-7.17(5H, m,	15.00	11.31	
						overlapped)	15.68	11.49	
10	3413	3161	1630	1595	-	7.85(1H, s), 7.69-7.63 (3H, m, overlapped),	15.16	11.31	
						7.50(2H, t, J = 7.6 Hz), 7.32-7.22 (2H, m, m)	15.91	11.47	
						overlapped)	12.00	44.00	
11	3415	3193	16/5	1611	2921(C-H)	7.50(1H, d, J=2.4Hz), 7.65(1H, dd, J= 8.8, 2.4 Hz),	15.23	11.09	
						7.58(2H, d, J=8.5 Hz), 7.31(2H, d, J=8.0 Hz), 7.21(1H, d, J=8.0 Hz), 7.21(1H, d, J=8.0 Hz), 7.21(2H, d, J=8.0 Hz), 7.2(2H, d, J=8.0 Hz), 7.2(2H, d, J=8.0 Hz), 7.2(2H, d, J=8.0 Hz),	16.05	11.30	
1.03	2421	2244	1 (00	1.000	1252/0 0	$/.21(1H, d, J=8.4 Hz), 2.50(3H, s, -CH_3)$	15.40	0.04	
12"	3421	5244	1689	1609	1253(C-O)	8.02 (1H, d, J=2.4Hz), 1.02 (2H, d, J=9.0 Hz),	15.40	8.04	
						(.45) (1H, ad, J=8.0, 2.4 HZ), $(.44-7.40)$ (3H, m,	16.02	8.38	

## Table 2. Characterization data of azo dyes 1-12.

<sup>a</sup> Recorded in CDCl<sub>3</sub>



Scheme4. Intramolecular hydrogen bonding in tautomers  $T_1$  and  $T_2$ .

#### 3.2. UV-Visible Spectroscopic Study

#### 3.2.1. Solvatochromism

The UV-Vis absorption spectra of dyes 1-12 were measured in four polar aprotic (DMSO, DMF, CH<sub>3</sub>CN and CHCl<sub>3</sub>) and two protic (EtOH and AcOH) solvents in a concentration range of  $10^{-8}$  to  $10^{-6}$  mol. L<sup>-1</sup> in the wavelength range 300-600 nm. The dyes have a very low solubility in all used solvents except DMSO and DMF. Therefore, each dye was dissolved in 100% DMSO to create stock solutions of  $10^{-3}$  mol. L<sup>-1</sup>. Then the necessary amounts of dyes were removed from its DMSO stock and dilutions were made in six above mentioned solvents for absorption measurements in the visible region. The results are given in Table 3.

The UV-vis absorption spectra of all the dyes showed two absorption bands in the visible region (Table 3). It can be suggested that the prepared azo dyes may exist as a mixture of two tautomeric forms in various solvents. These results are in accordance with NMR conclusions and can be assigned to the hydrazone tautomeric forms  $T_1$  and  $T_2$  (Scheme 4). It was observed that, although slightly positive solvatochromism is evident, the absorption spectra of dyes **1-12** did not change significantly in all the employed solvents and the absorption maxima did not correlate with the polarity of the solvent. This little absorption changes in  $\lambda_{max}$  strongly suggest the intramolecular hydrogen bonding in the compounds. As an example, dye **10** showed two absorbances at 391 nm and 430 nm (in DMSO), 392 and 422 (in DMF), 390 and 420 (in acetonitrile), 382 and 429 (in chloroform), 392 and 429 (in ethanol), and 389 and 431 (in acetic acid). The relatively small difference observed is assumed to be caused by solute - solvent interaction. Fig. 2 shows the electronic absorption spectra of dye **4**, as a typical example of series prepared, in the used solvents.



Fig.2. Absorption spectra of dye 4 in different solvents.

The difference in the  $\lambda_{\text{max}}$  values for the dye solutions can be explained by electron withdrawing and donating properties of the substituents in the benzenoid ring. The wavelengths of maximum absorption spectra in the visible region of the synthesized arylazo-quinolone dyes containing electron-accepting and electron-donating substituents are shown in Table 3. As it is apparent, the introduction of electron donating methyl and/or methoxy group in the benzene ring resulted in bathochromic shifts in all solvents with respect to electron-accepting nitro-, cyano, trifluoromethyl and halogen groups (e.g. for dye 12  $\Delta\lambda$ =+36 nm relative to dye 1,  $\Delta\lambda$  = +30 nm relative to dye 2,  $\Delta\lambda$  = +58 nm relative to dye 3,  $\Delta\lambda$  = +30 nm relative to dye 4,  $\Delta\lambda$  = +39 nm relative to dye 5,  $\Delta\lambda$ =+37 nm relative to dye 6,  $\Delta\lambda$ =+24nm relative to dye 7,  $\Delta\lambda$ =+27nm relative to dye 9,  $\Delta\lambda$ =+31nm relative to dye 10,  $\Delta\lambda$ =+22nm relative to dye 11 in chloroform). The introduction of electron-donating methoxy and methyl groups in the benzene rings resulted in bathochromic shifts in all solvents in comparison with unsubstituted dye 10. Fig. 3 shows the absorption spectra of some of the dyes with different substituents in chloroform.

	1						
Dye	Х	DMSO	DMF	CH <sub>3</sub> CN	CHCl <sub>3</sub>	EtOH	CH <sub>3</sub> COOH
1	p-NO <sub>2</sub>	404s, 421	402s, 417	404s, 416	406, 424s	400s, 418	403s , 425
2	$m-NO_2$	399s, 439	401s, 437	402s, 433	392, 430s	396s, 440	395s, 440
3	<i>p</i> -CN	403s ,418	403s ,414	395s , 408	388s , 402	397s, 418	393s , 420
4	<i>p</i> -CF <sub>3</sub>	397, 432s	396, 431s	391, 427s	375, 430s	396, 431s	396, 430s
5	<i>m</i> -CF <sub>3</sub>	407, 433s	402, 427s	398, 422s	400, 421s	392s, 408	391s, 417
6	<i>p</i> -F	320s, 413	340s, 400	340s, 400	357, 423s	340s, 416	335s, 429
7	<i>p</i> -Cl	392s,432	391s ,414	388s ,423	384s , 436	388s, 434	384s , 433
8	<i>p</i> -Br	407s ,458	406s,454	393s, 449	396s , 460	396s, 455	394s , 434
9	<i>p</i> -I	401s ,434	402s,432	393s, 430	378s , 433	390s, 434	383s , 432
10	<i>р</i> -Н	391s ,430	392s,422	390s, 420	382s , 429	392s, 429	389s, 431
11	<i>p</i> -CH <sub>3</sub>	401s ,438	395s,438	394s , 432	400s, 438	396s, 438	398s , 438
12	<i>p</i> -OCH <sub>3</sub>	404s ,454	403s ,454	388s , 449	389s , 460	389s, 459	389s, 455

Table3. Absorption maxima (in nm) of dyes 1–12 in different solvents.

<sup>s</sup>=shoulder



Fig 3. The effects of substituents on the absorption spectra of some of the prepared azo dyes.

# 3.2.2. Determination of pK<sub>a</sub> value of the dyes in ethanol-aqueous buffer solution

In order to investigate the role of pH of the media on the spectral changes in the structure of the studied dyes, their absorption characteristics as a function of pH in the pH range 1.1-13.6, in ethanol-water solution were studied. Buffer standard solutions with different pH values were

prepared with traditional procedure from distilled deionized water and ethanol with HCl, NaOH, H<sub>3</sub>PO<sub>4</sub>, KHC<sub>8</sub>H<sub>4</sub>O<sub>4</sub>, KH<sub>2</sub>PO<sub>4</sub>, H<sub>2</sub>B<sub>4</sub>O<sub>7</sub>, NaHCO<sub>3</sub>, KCl, and Na<sub>2</sub>CO<sub>3</sub>. In most cases, the pH needed to be adjusted using a pH meter and the drop wise addition of either 1.0 mol.L<sup>-1</sup> HCl or 1.0 mol.L<sup>-1</sup> NaOH to 1.0 L of solution. The accurate pH for each buffer solution was measured with a Jenway model 3505 digital pH meter.

It was observed that the absorption curves of the dyes were not sensitive to acid but were very sensitive to base. Absorption spectra of the compounds in 80 vol% ethanol-water solution did not change significantly when 0.1 mol.L<sup>-1</sup> HCl solution was added, being nearly the same as those observed in high proton donating solvents such as ethanol and acetic acid. In contrast, the  $\lambda_{max}$  of the dyes **1–12** shifted considerably when a few drops of 0.1 mol·L<sup>-1</sup> NaOH solution were added to their ethanolic solutions. In the ethanolic solution of the dyes containing a trace amount of NaOH, both a shoulder and a maximum in the longer wavelength region disappeared and a new maximum at short wavelength region was observed. A typical example is shown in Fig. 4. These hypsochromic shifts in basic media arise from the deprotonation of the enolic OH or hydrazone NH of the dye molecules, which lead to anionic forms of dyes with the predominant azo structure A<sup>-</sup> as is shown in Scheme 5.



Fig. 4. The UV-Vis absorption spectra of the dye **3** in acidic and basic solutions.



Scheme 5. Deprotonation of the studied azo dyes.

The absorption spectra of the studied azo dyes are very sensitive to pH values in the range of 6–10. The absorbance of a solution of each dye in 80 vol% ethanol-water was measured as the solution's pH was varied from acidic to basic conditions. There was no significant change in the spectra of all the synthesized dyes in acidic to medium (pH<6.0) and the absorption curves are resembled those in high proton donating solvents such as ethanol and acetic acid. As the solution pH was changed to basic, both a shoulder and a maximum in the longer wavelength region disappeared and a new maximum at shorter wavelength region was observed. These hypsochromic shifts in basic solvents are due to deprotonation of dye molecules, which lead to anionic forms of dyes (Scheme 5).

The acid dissociation constants for the hydroxy-azo quinolones dyes were determined spectrophotometrically at 25 °C in 80% ethanol-water mixture (v/v) [17]. Each compound exhibits two bands in the region of 353- 460 nm and 350–419 nm for molecular and the anionic species, respectively. As the pH value of the solution increases, the height of the former band decreases and simultaneously that of the latter band increases (Fig.5 for dye 10). From the optical spectra, in each case, the isobestic points indicate that two species are in equilibrium. For all the compounds under study, the dependence of the absorbance on the pH value gives sigmoid curves. Typical absorbance-pH curve is shown in Fig. 6. For all of these dyes, the changes of absorbance were extremely sharp and clear in the pH range of 6-10. The value of pK<sub>a</sub> was calculated from each measurement using the equation:

$$pK_a = pH_i + log[(A_b - A_i)/(A_i - A_a)]$$

Where  $A_i$  is the absorbance of the solution at intermediate  $pH_i$  and  $A_a$  and  $A_b$  are the absorbance values of the strongest acidic and alkaline buffer solutions of each compound. The  $pK_a$  values of the dyes were estimated by analysis of the spectral changes and listed in Table 4.

Sensitive acid–base property of the compounds can be explained by the formation of a  $\pi$  system within the whole dye structures. Since the electron density on the aromatic rings can be reduced by the electron withdrawing groups such as -NO<sub>2</sub>, -CN and -CF<sub>3</sub>, the pK<sub>a</sub> values show that the acidity of the hydroxyl group increases (6.90 for dye 1, 7.77 for dye 3, 7.70 for dye 4 and 7.57 for dye 5). While -OCH<sub>3</sub> group attached to phenyl ring of the dye 12 decrease the acidic character, due to its electron donating ability which destabilizes anionic forms of the azo dyes (Scheme 5).

				pH									
				1.56	2.56	4.36	6.32	8.67	9.54	10.58	12.61	13.63	
Dye	Х	$\sigma_p^{-a}$	$\sigma^{a}$		$\lambda_{max}(nm)$								pK <sub>a</sub>
1	p-NO <sub>2</sub>	1.27	0.78	425	426	425	360, 413	419	414	418	414	419	6.90
2	m-NO <sub>2</sub>	-	0.71	372	372	391	353, 427	351	351	351	351	352	7.83
3	<i>p</i> -CN	1.00	0.66	422	422	424	357, 423	351	393	396	353	352	7.77
4	p-CF3	0.65	0.54	416	416	411	354, 439	351	372	376	351	389	7.70
5	m-CF <sub>3</sub>	-	0.43	394	394	395	360, 398	355	352	352	353	352	7.57
6	<i>p</i> -F	-0.03	0.06	427	427	427	354, 427	350	350	351	351	351	7.84
7	p-Cl	0.23	0.23	438	440	446	360, 441	352	352	353	352	352	7.91
8	<i>p</i> -Br	0.25	0.23	441	442	443	355, 436	354	355	353	354	350	8.15
9	p-I	0.27	0.23	372	374	374	359	352	355, 425	385	351	352	8.74
10	<i>р</i> -Н	0.0	0.0	430	430	430	430	350, 435	350	350	350	350	8.43
11	p-CH <sub>3</sub>	-0.17	-0.17	395	395	395	355, 431	351, 457	351	351	351	352	8.64
12	p-OCH3	-0.24	-0.28	434	460	450	428	355,452	351, 435	380	353	352	9.63

Table 4. Absorption maxima ( $\lambda_{max}$ ) in different pH values and acidic dissociation constants (pK<sub>a</sub>) of prepared azo dyes.

<sup>a</sup> Taken from Ref.[22]



Fig. 5. The dependence of the spectra of the dye **10** by the pH of its  $2.0 \times 10^{-5}$  mol. L<sup>-1</sup> solutions in 80 vol% EtOH-water at ionic strength 0. 1 mol. L<sup>-1</sup> NaCl at 25 °C.



Fig. 6. Effect of pH on the maximum absorption intensity of 3-(4-trifluoromethylphenylazo)-6-chloro-4-hydroxyquinolin-2-(1H)-one (dye 4) in different80% ethanol-water buffer solutions.

Correlation of the  $pK_a$  data with the Hammett substituent constants  $\sigma_x$  resulted in the following equations:

$$pK_a = 8.56 - 1.66 \sigma$$

Plotting these  $pK_a$  data against  $\sigma_x$  values yields the graph shown in Fig. 7. It is obvious that all the substituents fall nearly on one correlation except the substituents with resonance effect such as *p*-OCH<sub>3</sub> and *p*-NO<sub>2</sub>, which are capable of direct interaction with the negatively charged sites in H<sup>-</sup> and A<sup>-</sup> (Scheme 5). Since the electron density on the aromatic rings can be reduced by the electron withdrawing groups such as -NO<sub>2</sub>, -CN and -CF<sub>3</sub>, the pK<sub>a</sub> values show that the acidity of the hydroxyl group increases. While -CH<sub>3</sub> and -OCH<sub>3</sub> groups attached to the compounds **11** and **12** will decrease the acidic character. This can be explained by the fact that the electron density on the aromatic rings can be increased by the electron releasing groups such as -OCH<sub>3</sub> due to their electron donating ability which destabilizes anionic forms of the dyes.



Fig. 7. Plot of the  $pK_a$  values against the Hammett constant ( $\sigma$ ) for the prepared azo dyes. 4. Conclusion

In conclusion, 6-chloro-4-hydroxyquinolin-2-(1H)-one was prepared by thermal cyclocondensation reaction of *N*, *N*'-di(4-chlorophenyl) malonamide in polyphosphoric acid.

Then, this compound was applied as a coupling component for preparation of 3-arylazo-6chloro-4-hydroxyquinolin-2-(1H)-ones in good yield. The structures of the newly synthesized compounds **1-12** were confirmed by spectral and elemental analyses data.

The investigation of the effect of solvent, acid and alkali addition, along with pH upon the electronic absorption spectra of the dyes **1-12**, together with spectrophotometric  $pK_a$  values determination were performed. The acid dissociation constants ( $pK_a$ ) of these dyes showed a good correlation with Hammett  $\sigma$ -constants of substituents on the diazo components. These results agreed with those from our previous study showing that the 6-chloro substituted aryl-azo quinolone dyes are more acidic than our previously published reports [17] due the negative inductive effect of chlorine, which reduces the negative charge, located on the oxygen or nitrogen of the anionic forms of the azo dyes.

The results have proved that in all the used solvents (DMSO, DMF, CHCl<sub>3</sub>, CH<sub>3</sub>CN and EtOH) and in acidic media (AcOH or acidified EtOH) the structures of dyes correspond to hydrazone tautomers  $T_1$  and  $T_2$ , whilst by increasing of pH or in alkalinized EtOH, these can be in equilibrium with deprotonated azo structures A<sup>-</sup>.

Additionally, both <sup>1</sup>H NMR spectral data and absorption spectroscopy in the visible region of the newly synthesized azo dyes indicate collectively that compounds 1 to 12 exist predominantly in hydrazo-keto structure  $T_1$  and  $T_2$ .

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