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Synthesis, characterization and spectroscopic properties of some new azo disperse dyes derived from 4-hydroxybenzo[*h*]quinolin-2-(1*H*)-one as a new synthesized enol type coupling component

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ABSTRACT

4-Hydroxybenzo[*h*]quinolin-2-(1*H*)-one (**IV**) was synthesized from the cyclocondensation of 3-(naphthalen-1-ylamino)-3-oxopropanoic acid (**I**) or *N*,*N*′-di(naphthalen-1-yl)malonamide (**II**) and subsequently coupled with diazotized *p*-substituted aniline derivatives. The structures of the synthesized dyes were determined by spectroscopic and analytical methods. Solvent effects on the ultraviolet–visible absorption spectra of these novel azo dyes were studied in six pure organic solvents with different polarities. The color of the dyes is discussed with respect to the nature of substituents on the benzene ring. The tautomeric structures of the azo compounds were studied by ^{1}H NMR spectroscopy in DMSO-d_6 and $CDCl_3$. The effects of acid and base on the visible absorption spectra of the dyes were also reported. Ionization constants, pK_a, for these dyes were determined in 80 vol. % ethanol–water medium at room temperature and correlated with the substituent constant, σ_p.

1. Introduction

Azo dyes and pigments constitute by far the most important chemical class of organic colorant owing to their versatile application in various fields of dye and organic chemistry [1,2]. Azo dyes synthesized from heterocyclic compounds have attracted much attention for their bright and strong color shades ranging from yellow to greenish blue on synthetic and natural fabrics [3,4]. In the last fifty years a number of studies have been carried out on synthesis, spectroscopic properties and dyeing performance of these compounds [5–10].

Enol type coupling components are among the most useful precursors for a wide variety of heterocyclic azo dyes [11]. The azo dyes derived from enol type coupling components constitute an interesting type of compound since they potentially have several tautomeric forms (enol-azo, keto-azo, hydrazo) in solution and solid state [12–15]. Azo-hydrazone tautomerism in azo dyes synthesized from enol type coupling components has been known for many years and has been reviewed several times [16,17]. Many studies dedicated to synthesis and spectroscopic characterization of these dyes for evaluating and improving their physical and chemical features [18–22]. Some important investigations have been carried out on the synthesis and spectroscopic behavior of arylazo dyes based on 4-hydroxy coumarin as an enol type coupling component by Shawali and coworkers [23,24]. In particular, the synthesis and tautomerism of heteroaryl azo dyes derived from 4-hydroxyquinolone and its derivatives have been explored by several authors [25–27].

In view of these encouraging reports, in this study we report the synthesis of 4-hydroxybenzo[*h*]quinolin-2-(1*H*)-one (**IV**) (Scheme 1) and using it as coupling component in reaction with some diazotized aromatic amines as diazo components (Scheme 2). The effects of solvents, substituents, acid and base on the visible absorption maxima of the dyes are also reported along with the acid dissociation constants of the dyes.

2. Experimental

2.1. General

All chemicals used for the synthesis of the studied compounds were obtained from Merck and Aldrich chemical companies and used without any purification process. Solvents used were of

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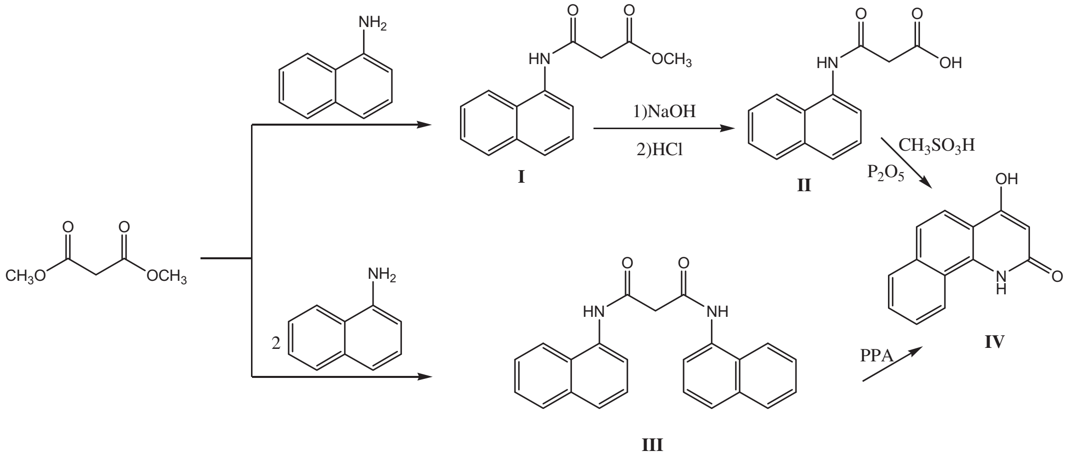


Scheme 1. Procedures used for synthesis of the 4-hydroxybenzo[*h*]quinolin-2-(1*H*)-one (**IV**).

spectroscopic grade. Melting points were determined with a Barnstead Electrothermal 9100 melting point apparatus in open capillary tubes and uncorrected. ^{1}H and ^{13}C NMR spectra measured on a Bruker 400 MHz spectrometer in DMSO-d$_6$ and CDCl$_3$ using TMS as an internal reference. The absorption spectra of the compounds were scanned on a Cary UV–vis Double-beam spectrophotometer (Model 100). Infrared spectra (in KBr pellets) were recorded on a Shimadzu-8400 FT-IR spectrometer. Microanalyses for C, H and N were performed on a Perkin–Elmer 2400(II) elemental analyzer.

2.2. Preparation of methyl 3-(1-naphthylamino)-3-oxopropanoate (I)

2-Naphthyl amine (10.0 mmol, 1.432 g) was dissolved in dimethyl malonate (100.0 mmol, 11.5 ml) and the mixture was refluxed in a 100 ml round bottom flask equipped with an air condenser for 1 h so that the methanol evolved and escaped from the top of the condenser. The solution was cooled and the volume was reduced to one third. On cooling in an ice bath a white solid product was obtained. Recrystallization from dibutylether afforded the white solid of methyl 3-(naphthalen-1-ylamino)-3-oxopropanoate (**I**) (1.71 g, 71%): mp 103–105 °C; FT-IR (KBr): ν 3415 (NH), 3050 (Aro-H), 2965 (Aliph-H), 1745 (C=O), 1644 (C=O) 1110 (C–O) cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 9.94 (1H, b, NH), 8.15 (1H, d, $J = 7.5$ Hz), 8.04 (1H, d, $J = 8.5$ Hz), 7.90 (1H, d, $J = 8.0$ Hz), 7.72 (1H, d, $J = 8.2$ Hz), 7.62–7.50 (3H, m, overlapped), 3.91 (3H, s, –OCH$_3$), 3.67 (2H, s, –CH$_2$–) ppm.

2.3. Preparation of 3-(1-naphthylamino)-3-oxopropanoic acid (II)

Compound (**I**) (10.0 mmol, 2.43 g) was stirred with a 1.0 mol L^{-1} NaOH (100 ml) at room temperature for 2.0 h, after which time the entire solid had dissolved. The solution was filtered and acidified with 10% HCl to yield a white precipitate which was filtered and washed well with water and dried. Recrystallization from chloroform giving the acid (**II**) (1.65 g, 72%) as white crystals: mp 138–139.5 °C, FT-IR (KBr): ν 3500 (OH), 3414 (NH), 3050 (Aro-H), 2962 (Aliph-H), 1720 (C=O), 1641 (C=O) cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 9.01 (1H, b, NH), 7.92–8.00 (3H, m, overlapped, Ar-H), 7.79 (1H, d, $J = 6.5$ Hz), 7.46–7.68 (3H, m, overlapped), 3.72 (2H, s, –CH$_2$–) ppm.

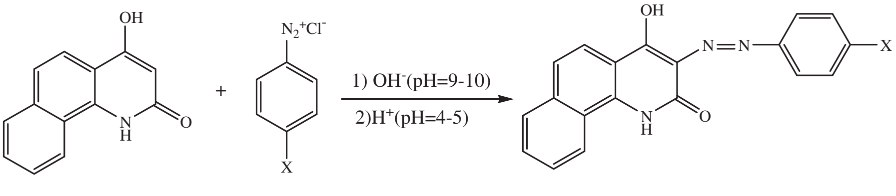
2.4. Preparation of N,N′-di(1-naphthyl)malonamide (III)

A mixture of 1-naphthyl amine (100 mmol, 14.32 g) with diemthyl malonate (50 mmol, 5.75 ml) was refluxed for 4 h in an oil bath. After cooling, the mixture was digested with diethylether, filtered by suction and recrystallized from ethanol giving the malonamide (**III**) (14.23 g, 81%) as creamy solid: mp 229–230 °C, FT-IR (KBr): ν 3414 (NH), 3053 (Aro-H), 2965 (Aliph-H), 1640 (C=O) cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 10.31 (2H, b, NH), 8.00 (2H, d, $J = 9.0$ Hz), 7.90 (2H, d, $J = 7.6$ Hz), 7.77 (2H, d, $J = 9.0$ Hz), 7.63 (2H, d, $J = 8.0$ Hz), 7.43–7.37 (3H, m, overlapped), 3.79 (2H, s, –CH$_2$–) ppm.

2.5. Synthesis of 4-hydroxybenzo[h]quinolin-2-(1H)-one (IV)

2.5.1. Method A: from 3-(1-naphthylamino)-3-oxopropanoic acid (II)

A mixture of (**II**) (10 mmol, 2.3 g) was dissolved in 18.0 ml methanesulfonic acid, which contains 10% of phosphorus pentoxide, and then heated at 120 °C for 30 min. The dark viscous solution was allowed to cool, water was added and the resultant gum solidified on prolonged standing. The solid was filtered, and then dissolved in 100 ml 10% sodium hydroxide. The aqueous solution was filtered to remove insoluble material and slowly acidified to pH < 4 with 20% hydrochloric acid. The resulting crude precipitates were collected, washed with water and dried to afford



(**1**):X=-NO$_2$ (**2**):X= -CN (**3**):X= -CF$_3$ (**4**):X= -F (**5**):X= -Cl
(**6**):X= -Br (**7**):X= - I (**8**): X= -H (**9**):X= -CH$_3$ (**10**):X= -OCH$_2$CH$_3$

Scheme 2. Synthesis of azo dyes **1**–**10**.

4-hydroxybenzo[*h*]quinolin-2-(1*H*)-one (**IV**) (1.4 g, 66%) as a deep pink powder.

2.5.2. Method B: from N,N′-di(1-naphthyl)malonamide (III)

N,*N*′-di(1-naphthyl)malonamide (**III**) (3.540 g, 10.0 mmol) was thoroughly mixed with 11.5 g polyphosphoric acid (PPA, sp. gr. 2.08) in 80 °C and was then heated in an oil bath for 5 h at 150 °C. The dark viscous solution was allowed to cool, water was added and the precipitated compound was filtered off, washed with water and dried in air. The crude product was dissolved in 100 ml of sodium hydroxide solution 0.1 mol L^{-1} and undissolved material was filtered. The filtrate was neutralized with concentrated hydrochloric acid and the precipitate was recrystallized from ethanol to afford 4-hydroxybenzo[*h*]quinolin-2-(1*H*)-one (**IV**) (1.65 g, 78%) as deep pink powder: mp 318–320 °C, FT-IR (KBr): ν 3500 (OH), 3402 (NH), 3050 (Aro-H), 1637 (C=O) cm^{-1}; ^1H NMR (DMSO-d$_6$): δ 11.58 (1H, b, OH), 11.42 (1H, b, NH), 8.83 (1H, d, *J* = 8.2 Hz), 7.96 (1H, d, *J* = 8.7 Hz), 7.66–7.59 (3H, m, overlapped), 5.89 (1H, s), ^{13}C NMR (DMSO-d$_6$): δ 164.8, 164.1, 135.0, 129.7, 129.3, 128.7, 127.2, 123.41, 122.4, 122.2, 120.5, 111.5, 99.1 ppm.

2.6. Preparation of arylazobenzoquinolone dyes 1–10

A cold solution of aryldiazonium salt (2.0 mmol) was prepared by adding a solution of $NaNO_2$ (2.2 mmol, 0.15 g into 1.0 mL H_2O) to a cold solution of arylamine hydrochloride (2.0 mmol of arylamine in 1.5 mL conc. HCl). The resulting solution of aryldiazonium salt was added drop wise to a mixture of compound (**IV**) (2.0 mmol, 0.42 g) in water (15 mL) containing NaOH (25 mmol, 1.0 g) at 0–5 °C. 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. The crude product was purified using the recrystallization method as mentioned in Table 1. Under the same reaction conditions, a series substituted arylazobenzoquinolone dyes were obtained in satisfactory yields (Table 1, Scheme 2). When aryldiazonium salts bearing an electron-withdrawing group such as nitro and trifluoromethyl or halogen atom were employed, corresponding arylazobenzoquinolone dyes were obtained with satisfied yields from 60 to 75% (Table 1, entries 1–6). However, when substrates bore an electron donating group such as methyl or ethoxy, the corresponding diazonium salts were very unstable in the reaction mixture and evolution of nitrogen gas was observed during the reaction process, thus only a small quantity of products were isolated in 30–42% yields (Table 1, entries 8–10).

3. Results and discussion

3.1. Synthesis and characterization

As depicted in Scheme 1, 4-hydroxybenzo[*h*]quinolin-2-(1*H*)-one (**IV**) was prepared via two different methods A and B. In method A malonamide ester (**I**) was converted to half malonic acid (**II**) which subsequently was treated with phosphorous pentoxide in methanesulfonic acid to give compound (**IV**). In method B, malonamide (**III**) was prepared by refluxing 2-naphthyl amine with dimethyl malonate (2:1 molar ratio) in good yield. Heating *N*,*N*′-di(1-naphthyl)malonamide (**III**) in polyphosphoric acid (PPA) at 140–150 °C afforded the 4-hydroxybenzo[*h*]quinolin-2-(1*H*)-one (**IV**). All of the compounds were characterized by the FT-IR and NMR spectral analysis. ^1H NMR spectra recorded for the prepared compounds clearly supported the proposed structures. The protons belonging to the aromatic system were observed at the expected chemical shifts and integral values. The peak at 5.89 ppm (=CH) also confirmed the formation of the desired quinolone ring in compound (**IV**).

The arylazoquinololin-2-one dyes **1**–**10** were prepared by coupling reaction of 4-hydroxybenzo[*h*]quinolin-2-(1*H*)-one with diazotized *p*-substituted aniline derivatives in basic solution (Scheme 2). The chemical structures of these dyes were confirmed by some spectroscopic methods and elemental analysis. The physical and spectral data of the dyes are summarized in Tables 1 and 2. As shown in Scheme 3, the four possible tautomeric forms enol-azo-keto (**EAK**), two keto-hydrazo-keto (**KHK1** and **KHK2**) and keto-azo-enol (**KAE**) can be written for the synthesized azo dyes.

Spectral investigations of the new synthesized azo dyes showed good agreement with proposed structures. FT-IR spectrum of compounds **1**–**10** showed broad OH and NH bands at 3434–3176 cm^{-1} and carbonyl group peaks at 1670–1640 cm^{-1}.

The ^1H NMR spectra measured in DMSO-d$_6$ at 25 °C revealed a multiplet from 8.88 to 7.01 ppm for aromatic protons, a singlet at 2.37 ppm (CH_3, **9**), a quartet at 4.12 ppm ($-OCH_2-$, **10**) and a triplet at 1.36 ppm ($-CH_3$, **10**). The results also showed that in DMSO-d$_6$ such dyes exist as a mixture of keto-hydrazo-keto forms **KHK1** and **KHK2** with nearly equal integration ratio. The spectra showed in each case two hydrazone proton signals (=N–NH–) at 16.85–14.97 ppm. These signals undoubtedly correspond to the hydrazone NH proton resonance related to hydrazone-keto forms **KHK1** and **KHK2** [19–22]. Further evidence for this assignment is provided by the observation that the ^1H NMR spectrum of the ^{15}N-phenylhydrazone derivatives of some azo heterocycles were reported to show two doublets centered at similar regions with *J* = 93–100 Hz indicating that the proton is attached to nitrogen atom [20]. It was reported that the hydroxyazo OH proton resonance comes 3–5 ppm higher than NH proton resonance; hence, the OH proton resonance signal of enol forms is expected to be in region 9–12 ppm [20,21]. The possibility of tautomers involving ring NH rearrangement can be eliminated by studying the ^1H NMR spectrum of the compounds in DMSO-d$_6$ and $CDCl_3$. The ^1H NMR spectrum of all the dyes showed two singlets at 11.34–11.53 and 11.45–11.60 ppm. The presence of these two broad singlets provides firm evidence for presence of the amide N–H bonds and is

Table 1
The physical properties of the dyes used in this study.

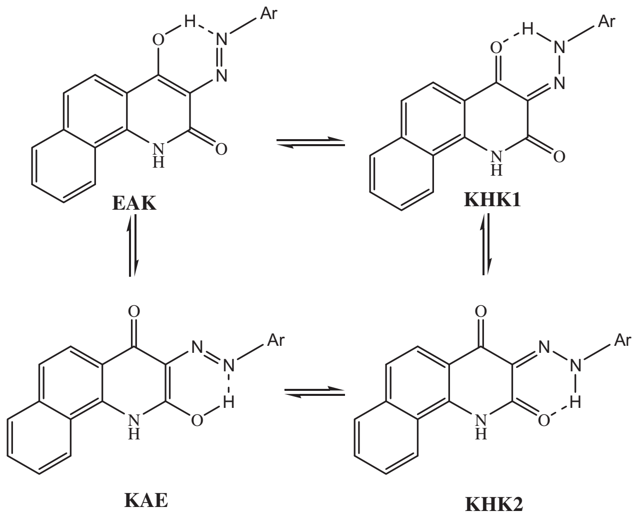
Dye	Color	Mp (°C)	Recrystalization	%C		%H		%N		Yield (%)
				Calcd.	Found	Calcd.	Found	Calcd.	Found	
1	Dark red	>370	DMF	63.33	64.02	3.36	3.29	15.55	15.19	60
2	Dark red	>370	DMF	70.58	70.81	3.55	3.59	16.46	16.92	65
3	Bright red	354–357	DMF	62.67	61.98	3.16	3.11	10.96	10.02	64
4	Orange	365–368	DMF	68.46	68.01	3.63	3.69	12.61	12.74	68
5	Dark red	340–342	DMF	65.24	64.80	3.46	3.51	12.01	12.25	69
6	Clear red	356–358	DMF/H_2O	57.89	56.91	3.07	3.14	10.66	10.02	75
7	Dark brown	307–308	DMF/H_2O	51.72	50.91	2.74	2.78	9.52	9.23	73
8	Brown	310–312	DMF/H_2O	72.37	72.96	4.16	4.21	13.33	13.01	70
9	Dark red	325–327	DMF/H_2O	72.94	72.11	4.59	4.64	12.76	12.16	52
10	Clear red	297–299	DMF/H_2O	70.18	69.94	4.77	4.84	11.69	11.62	46

Table 2
Spectral data for dyes **1**–**10**.

Dye	IR (KBr, cm^{-1})				^1H NMR (δ, ppm)				
	ν_{O-H}	ν_{N-H}	$\nu_{C=O}$	$\nu_{C=N}$	Other functional groups	Aro-H	Alip.-H	N–H	
								Hydrazo	Amide
1	3419	3200	1658	1590	1520 and 1261 (NO_2)	8.85 (1H, d, $J = 6.4$ Hz), 8.39 (2H, d, $J = 6.8$ Hz) 7.99–7.69 (7H, m, overlapped)	–	14.97 15.77	11.53 11.60
2	3416	3155	1641	1596	2254 (CN)	8.83 (1H, d, $J = 8.4$ Hz), 8.01–7.88 (6H, m, overlapped), 7.75 (1H, t, $J = 6.8$ Hz), 7.67 (2H, d, $J = 8$ Hz)	–	15.76 16.85	11.50 11.55
3	3434	3188	1670	1600	1320 (C–F)	8.85 (1H, d, $J = 8.4$ Hz), 8.01 (2H, d, $J = 8.0$ Hz), 7.94–7.88 (3H, m, overlapped), 7.75 (2H, t, $J = 7.2$ Hz), 7.68 (2H, d, $J = 8.4$ Hz)	–	15.08 15.94	11.49 11.54
4	3405	3186	1654	1600	1325 (C–F)	8.84 (1H, d, $J = 8.4$ Hz), 8.00 (2H, d, $J = 7.6$ Hz), 7.83–7.67 (5H, m, overlapped), 7.40 (2H, t, $J = 8.5$ Hz)	–	15.24 16.30	11.45 11.56
5	3415	3180	1648	1596	765 (C–Cl)	8.83 (1H, d, $J = 8.4$ Hz), 7.94 (2H, d, $J = 8.4$ Hz), 7.80 (1H, d, $J = 8.8$ Hz), 7.74 (2H, t, $J = 7.6$ Hz), 7.67 (2H, d, $J = 8.0$ Hz), 7.60 (2H, d, $J = 8.4$ Hz)	–	15.16 16.14	11.48 11.54
6	3411	3187	1644	1602	654 (C–Br)	8.84 (1H, d, $J = 8.8$ Hz), 8.01–7.66 (9H, m, overlapped)	–	15.15 16.10	11.34 11.45
7	3417	3176	1644	1601	534 (C–I)	8.83 (1H, d, $J = 8.4$ Hz), 7.99 (2H, d, $J = 8.4$ Hz), 7.88 (2H, d, $J = 8.4$ Hz), 7.74 (1H, t, $J = 7.2$ Hz), 7.66 (2H, d, $J = 8.4$ Hz), 7.58 (2H, d, $J = 8.4$ Hz)	–	15.12 16.08	11.43 11.49
8	3422	3212	1640	1600	–	8.85 (1H, d, $J = 7.9$ Hz), 8.01 (2H, t, $J = 8.2$ Hz), 7.77–7.56 (7H, m, overlapped), 7.37 (1H, t, $J = 8.5$ Hz)	–	15.27 16.33	11.45 11.50
						[a]8.16 (1H, d, $J = 8.4$ Hz), 8.05 (1H, d, $J = 7.6$ Hz), 7.95 (1H, d, $J = 7.6$ Hz), 7.78–7.50 (8H, m, overlapped))	–	15.33 16.90	8.55 8.87
9	3424	3210	1645	1600	2966 (C–H)	8.83 (1H, d, $J = 8.4$ Hz), 8.00 (2H, t, $J = 6.8$ Hz), 7.76–7.61 (5H, m, overlapped), 7.36 (2H, d, $J = 8.4$ Hz)	2.37 (3H, s)	15.34 16.46	11.43 11.48
10	3422	3196	1642	1600	1266 (C–O)	8.85 (1H, d, $J = 8.8$ Hz), 8.02 (2H, t, $J = 8.8$ Hz), 7.76–7.66 (5H, m, overlapped), 7.11 (2H, d, $J = 9.2$ Hz)	4.11 (2H, q), 1.37 (3H, t)	15.49 16.72	11.43 11.51
						[a]8.16 (1H, d, $J = 8.8$ Hz), 8.08 (1H, d, $J = 7.6$ Hz), 7.94 (1H, d, $J = 7.6$ Hz), 7.74–7.55 (5H, m, overlapped), 7.02 (2H, d, $J = 8.8$ Hz)	4.12 (2H, q), 1.48 (3H, t)	15.55 17.30	8.99 9.05

[a] ^1H NMR recorded in $CDCl_3$.

related to amide protons of two types of tautomeric forms **KHK1** and **KHK2**. The quinolone ring NH was extremely affected by solvent species, but the hydrazone NH was not affected so much. For example, in the ^1H NMR spectra of dyes **8** and **10**, the quinolone ring NH peak was observed at higher field in chloroform than in DMSO. The quinolone rings NHs of dye 10 were observed at 8.98 and 9.05 ppm in $CDCl_3$. whereas the corresponding protons were observed at 11.43 and 11.51 ppm in DMSO. The downfield chemical shift of the NH proton signal in DMSO-d_6 is larger than in $CDCl_3$, because of the intermolecular hydrogen bonding between the NH and DMSO (Table 1, entries 8 and 10).



Scheme 3. Tautomeric forms for the prepared azo dyes.

3.2. UV–visible study of the prepared azo dyes

The absorption spectra of arylazobenzoquinolone dyes **1**–**10** were measured in six organic solvents with different polarities (chloroform, ethanol, acetic acid, acetonitrile, dimethyl formamide and dimethyl sulfoxide) in the wavelength rang 300–600 nm at a concentration $\sim 10^{-5}$ mol L^{-1}. The results are given in Table 3. The dyes are hardly soluble in some of the used solvents but are completely soluble in DMSO. Therefore, stock solutions of each dye with a concentration of $\sim 10^{-3}$ mol L^{-1} were accurately prepared in DMSO and dilutions of these stocks were used for absorption measurements.

The electronic absorption spectra of the dyes in all used solvents (Table 3) revealed, in each case, two bands in the regions of 396–417 and 418–476 nm (e.g. Fig. 1 for dye **7**). It can be suggested that the dyes may exist as a mixture of two tautomeric forms in various solvents. The visible absorption spectra of the dyes didn't show regular variation with the polarity of solvents, therefore, it can be considered as a result of several solvent characteristics such as polarity, basicity and H-bond-accepting or -donating ability. Furthermore the spectra of unsubstituted derivatives **8** in different solvents showed small changes in maximum absorption wavelength (λ_{max}). The little absorption changes in λ_{max} strongly suggest the intramolecular hydrogen bonding in the compound. These results seem to be compatible with the hydrazone forms **KHK1** and **KHK2** rather than azo forms **EAK** and **KAE**, as they are similar to that of related hydrazone compounds [20–22]. The small shifts in λ_{max} of **8** in different solvents are due to solvent–solute interactions and are consistent with the assigned tautomeric structures. In agreement with this conclusion is the observation that the spectra of arylazo dyes derived from the reaction of similar enol type coupling components with diazotized aniline derivatives are largely independent of the solvent polarity [28–30].

Table 3
Absorption maxima (in nm) of dyes **1**–**10** in different solvents.

Dye	DMSO	DMF	CH_3CN	$CHCl_3$	EtOH	CH_3COOH
1	438, 417s	426, 415s	420, 410s	429, 406s	422, 413s	430, 411s
2	413s, 422	407, 427s	403, 425s	410s, 422	408, 426s	411s, 426
3	410, 422s	401, 432s	396, 428s	402s, 417	400, 427s	402s, 418
4	409s, 431	399, 461s	401s, 425	400s, 434	399, 436s	404s, 432
5	433, 412s	462s, 399	427, 404s	438, 402s	419, 404s	436, 403s
6	414s, 432	409s, 424	409s, 428	411s, 439	405s, 434	407s, 437
7	414s, 440	408, 476s	408s, 432	409s, 443	405s, 438	405s, 441
8	412s, 431	410s, 427	406s, 424	407s, 434	408s, 429	404s, 431
9	440, 410s	437, 411s	434, 406s	443, 411s	437, 406s	441, 407s
10	412s, 459	406s, 467	409s, 453	412s, 462	409s, 459	404s, 461

s = shoulder.

The difference in the λ_{max} values for the dye solutions can be assessed in terms of the electronic power of the substituents in the benzenoid system. Details of the visible absorption spectra of arylazobenzoquinolone dyes containing electron-accepting and electron-donating substituents are shown in Table 3. As it is apparent in Table 3, the introduction of electron donating ethoxy group in the benzene ring resulted in bathochromic shifts in all solvents with respect to electron-accepting nitro, cyano, trifluoromethyl and fluoro groups (e.g. for dye **10** $\Delta\lambda = 37$ nm relative to dye **1**, $\Delta\lambda = 51$ nm relative to dye **2**, $\Delta\lambda = 59$ nm relative to dye **3**, $\Delta\lambda = 60$ nm relative to dye **4** in ethanol). The introduction of electron-donating methyl and iodo (*p*-) groups in the benzene rings resulted in bathochromic shifts in all solvents in comparison with unsubstituted dye **8**. Similar significant changes were not observed for the dyes with *p*-Cl and *p*-Br substituents on diazo components (e.g. for dye **6** $\Delta\lambda = 1$ nm in DMSO, $\Delta\lambda = 3$ nm in DMF, $\Delta\lambda = 4$ nm in CH_3CN, $\Delta\lambda = 5$ nm in $CHCl_3$, $\Delta\lambda = 5$ nm in EtOH and $\Delta\lambda = 6$ nm in CH_3COOH relative to dye **8**). Fig. 2 compares the absorption spectra of some of the dyes with different substituents in chloroform.

Absorption maxima of the prepared dyes **1**–**10** were also measured in acidic and basic media. It was observed that the absorption curves of the dyes were not sensitive to acid but is very sensitive to base. There was no significant change in the spectra of all the synthesized dyes when a small amount of 0.1 mol L^{-1} HCl was added to their ethanolic solutions and the absorption curves are resembled those in high proton donating solvents such as ethanol and acetic acid. When 0.1 mol L^{-1} KOH was added to ethanolic solution of the dyes, both a shoulder and a maximum in the longer wavelength region were decreased and a new maximum at short 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 4). This indicates that arylazobenzoquinolone dyes **1**–**10** exist partly in a dissociated form and there is equilibrium between neutral and anionic forms. A typical example is shown in Fig. 3.

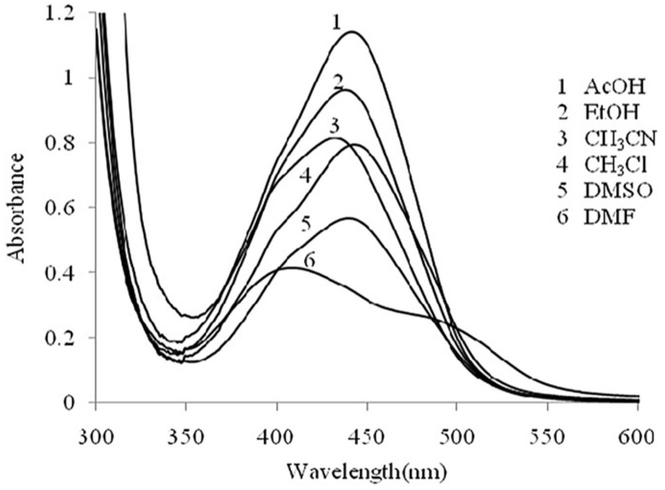


Fig. 1. Absorption spectra of **7** in different solvents.

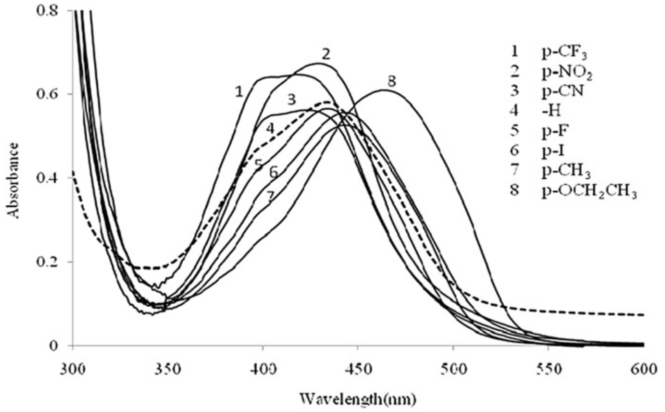
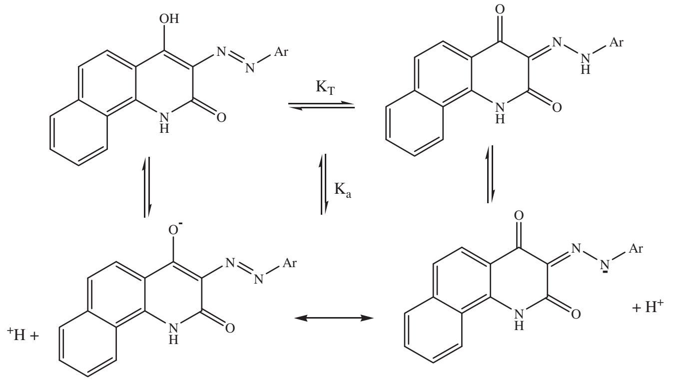


Fig. 2. Absorption spectra of the arylazobenzoquinolone dyes with different substituents on the benzenoid system.



Scheme 4. Acidic dissociation equilibrium of the prepared azo compounds.

3.3. *Determination of pK$_a$ values of the azo dyes*

The ionization constants (pK_a) of **1** to **10** were determined in 80 vo1% ethanol–water medium at room temperature and a μ of 0.1

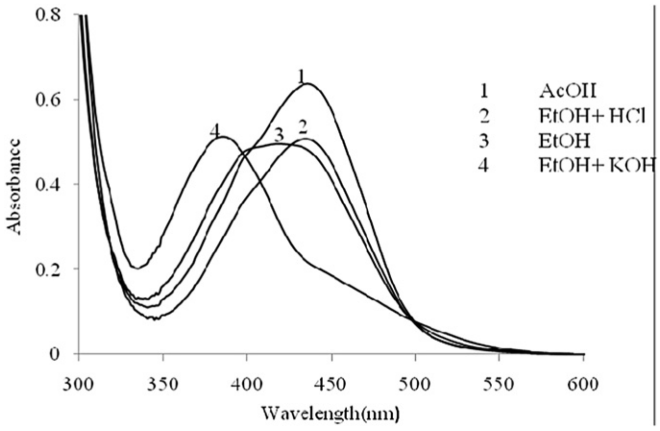


Fig. 3. Absorption spectra of dye **5** in acidic and basic solutions.

Table 4
Acidic dissociation constants (pK_a) and absorption maxima (λ_{max}) of prepared azo dyes in different pH values.

Dye	X	σ_p[a]	pH									pK_a
			1.77	6.43	6.78	7.50	8.03	9.53	10.40	12.15	13.19	
			λ_{max}									
1	p-NO_2	0.81	426	427	427	427	426	425	426	425	427	4.98
2	p-CN	0.70	420	415	420	422	403	401	400	401	400	6.66
3	p-CF_3	0.53	414	413	414	412	392	391	388	388	388	6.78
4	p-F	0.15	431	431	431	431	429	395	378	377	378	7.53
5	p-Cl	0.24	434	434	434	434	390	396	385	384	384	7.94
6	p-Br	0.26	435	430	434	435	406	396	387	387	385	7.66
7	p-I	0.28	439	438	440	439	427	400	389	387	388	8.16
8	p-H	0.0	431	432	431	431	431	431	387	380	380	8.61
9	p-CH_3	−0.14	440	440	440	441	440	441	391	380	379	8.78
10	p-OCH_2CH_3	−0.28	461	461	460	460	461	448	383	382	382	9.02

[a] Taken from Ref. [28].

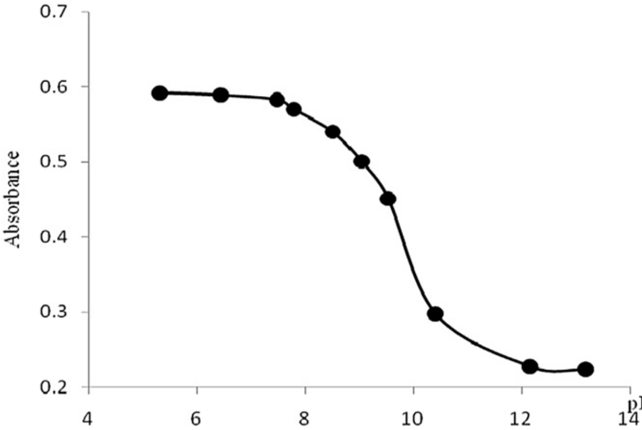


Fig. 5. Absorbance–pH curve for dye **8** at λ = 431 nm.

using a spectrophotometric titration method and given in Table 4. Each compound exhibited two bands in region of 379–427 nm for anionic and 412–462 nm for the molecular species. In all cases, as the pH value of the solution increased, the height of the former band increased and simultaneously that of the latter decreased. From the optical spectra (Fig. 4), in each case, the isobestic points indicate that anionic and neutral species are in equilibrium. Typical absorbance–pH curve is also showed in Fig. 5.

A digital pH meter Genway model 3505 was employed for determination of pH. It was calibrated using two standard Genway buffer solutions at pH 4.01 and 7.00. The pH meter readings (B) recorded in ethanol–water solutions were converted to hydrogen ion concentration $[H^+]$ by means of the widely used relation of Van Uitert and Haas [31], namely where log U_H, is the correction factor for the solvent composition and ionic strength for which B is read. For this purpose, readings were made on a series of solutions containing known amounts of hydrochloric acid and sodium chloride in a way that the ionic strength was equal to 0.1 in 80 vol.% ethanol–water at room temperature. The value of log U_H, was found to be −0.235.

$$-\log[H^+] = B + \log U_H$$

The acid dissociation constants of **1** to **10** were evaluated spectrophotometrically. An aliquot of a stock solution of the appropriate dye in dimethyl sulfoxide was diluted with aqueous hydrochloric acid and ethanol so that the final solution was 5×10^{-5} M in the azo dye, 0.1 M in HCl, and contained 80% volume ethanol. The test solution (50 ml) was then transferred to a 100 ml Erlenmeyer flask and the pH of the solution was measured and the spectrum was recorded using either the ionic medium or the corresponding aqueous ethanol as a blank. In both cases identical absorbance values in the employed wavelength range were obtained. The pH of the test solution was increased by addition of small volume of concentrated carbonate-free sodium hydroxide made up from the same solvent. Since the total change in volume did not exceed 1.0% no correction was made for dilution. After each spectral measurement, the pH was checked, and in all cases, the two values before and after the spectral measurement were found to be the same within the limits of the accuracy of the pH meter. In each run10–15 pH readings were taken and the value of pK_a was calculated from each reading 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 pH_i and A_a and A_b are the absorbance values of the strong acidic and alkaline solutions of each compound. Each compound was subjected to three pK_a determinations, and the average values, given in Table 4 are within ±0.05 pK_a units. Plotting pK_a values against Hammet constants (σ_p) yields the graph shown in Fig. 6. The equation of such a correlation is:

$$pK_a = 8.4377 - 3.2381\ \sigma_p$$

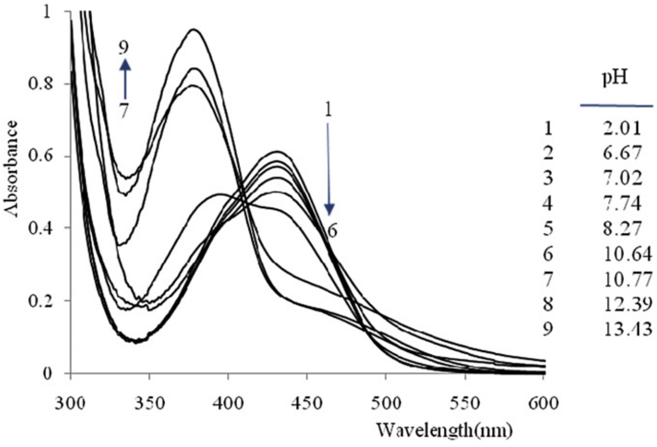


Fig. 4. Absorption spectra of dye **4** in different pH values.

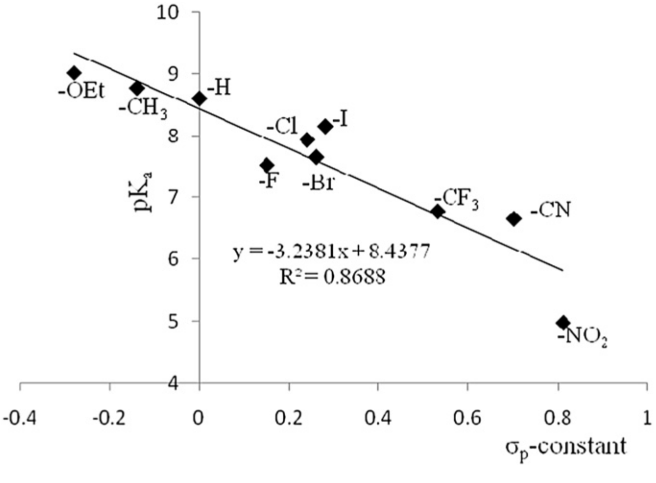


Fig. 6. Relation between Hammet constant (σ_p) and pK_a values for the prepared dyes.

Since the electron density on the aromatic rings can be reduced by the electron withdrawing groups such as $-NO_2$, $-CN$ and $-CF_3$, the pK_a values show that the acidity of the hydroxyl group increases. While $-OEt$ and $-CH_3$ groups attached to the compounds **9** and **10** decrease the acidic character, due to their electron donating ability which destabilizes anionic forms of the azo dyes (Scheme 4).

4. Conclusions

In this study, the enol type coupling component 4-hydroxybenzo[*h*]quinolin-2-(1*H*)-one was synthesized by cyclocondensation reaction in good yield via two different methods. This compound was coupled with diazotized aniline derivatives to give the corresponding arylazo-benzoquinolone dyes **1**–**10** in moderate to good yields. The dyes exhibited orange to red hues. All synthesized compounds were characterized by IR, ^{1}H NMR, UV–vis spectroscopy and elemental analysis.

All the azo dyes displayed two bands in their electronic absorption spectra in various organic solvents. The absorption spectra of these dyes were in consistent with ^{1}H NMR results and revealed that these compounds do exist in forming hydrazone-keto form species. The absorption curves of the dyes were very sensitive to small amounts sodium hydroxide solution, leading to new bands appearing at shorter wavelengths.

The acid dissociation constants (pK_a) of these azo dyes were also measured and showed a good correlation with Hammet σ-constants of substituents on diazo components.

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