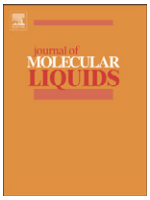
Journal of Molecular Liquids 160 (2011) 160–165

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq



A study of Solvatochromism in diazonium coupling products of 6-flouro 4-hydroxyl-2-quinolone

Enayat O'llah Moradi-e-Rufchahi [a,*], A. Ghanadzadeh [b]

[a] Department of Chemistry, Faculty of Science, Islamic Azad University, Lahijan Branch, Lahijan, Iran
[b] Department of Chemistry, Faculty of Sciences, Guilan University, Rasht, Iran

ARTICLE INFO

Article history:
Received 20 January 2011
Received in revised form 17 February 2011
Accepted 17 March 2011
Available online 23 March 2011

Keywords:
Azo dyes
Heterocyclic coupling components
Solvatochromism
Diazotization
Hydroxyl quinolone
Substituent effects

ABSTRACT

6-flouro 4-hydroxyl-2-quinolone was synthesized from cyclocondensation of corresponding dianilide and subsequently used as a potent coupling component with some diazotized aromatic amines. The prepared azo dyes were characterized by UV–vis, FT-IR, ^{1}H NMR spectroscopic techniques and elemental analysis. The solvatochromism of dyes was evaluated with respect to wavelength of maximum absorption (λ_{max}) in six solvents: acetic acid, methanol, chloroform, acetonitrile, dimethyl sulfoxide and dimethyl formamide. The color of the dyes is discussed with respect to the nature of substituents on the benzene ring. 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_x.

1. Introduction

Heterocyclic azo dyes have attracted considerable interest and have played an important role in the development of the chemistry of dyes and dyeing process [1–6]. In this regard, azo dyes based on heterocyclic coupling components have been developed and reported in many patents and papers [7–12]. The resultant dyes have higher tinctorial strength and give brighter dyeing than those derived from benzene based coupling components [13–17]. Of these compounds, very few comparable investigations were carried out using hydroxyl quinolone derivatives. These derivatives afford very electron rich coupling components and consequently can provide a pronounced bathochromic effect compared to the corresponding benzenoid compounds. Izzet sener et al. by using some heterocyclic amine derivatives as diazo components, investigated preparation and the tautomerism in azo dyes synthesizes from 4-hydroxy-2-quinolone [18]. According to the importance of these compounds, the present work reports the synthesis of 6-flouro-4-hydroxyl-2-quinolone and using it as coupling component in reaction with some diazotized aromatic amines as diazo components. The effects of solvents, substituents, acid and base on the visible absorption maxima of the dyes were also reported. The acid dissociation constants of the dyes were determined using electronic spectroscopic method in 80% (v/v) ethanol–water mixtures at 25 ± 2 °C. The ionic strength of the solutions was controlled to be 0.1 using a NaCl solution. The structures of coupling component and prepared dyes are depicted in Schemes 1 and 2.

2. Results and discussion

2.1. Synthesis and characterizations

6-flouro-4-hydroxyl-2-quinolone (**I**) were prepared by refluxing 2 equiv of 4-flouro aniline with dimethyl malonate and cyclocondasation of resulting dianilide in methane sulfunic acid containing 10% of phosphorus pentoxide (instead of $AlCl_3$ used by Zeigler) [19] (Scheme 1).

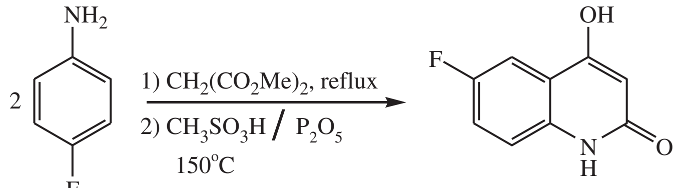
The IR spectra of compound (**I**) showed strong absorptions at 3500–3150 cm^{-1} for the OH and amide (NH) groups, and at 1637 cm^{-1} for the C=O group. The ^{1}H NMR spectrum (DMSO-d_6) of compound (**I**) revealed a broad peak at 11.29 ppm (1 H, b, NH), a singlet at 5.77 ppm (1H) for the C=C–H of pyridone ring, a dd at 7.27 ppm (1H, J = 8.9, 4.7 Hz), a multiplet at 7.38–7.45 ppm (2H) for the aromatic protons (Aro.-H). The proton decoupled ^{13}C NMR of this compound exhibited 9 distinct resonances at 164.16 ppm (C=O), 162 ppm (C–OH), 157 ppm (C–F), 136 ppm (C), 119 ppm (CH), 117 ppm (CH), 116 ppm (C), 108 ppm (CH) and 99.5 ppm (CH) in agreement with the quinolone structure.

The phenylazoquinolone dyes **1**–**14** were prepared by coupling 6-flouro-4-hydroxyl-2-quinolone with diazotized aniline derivatives (Scheme 2). The dyes may exist in six possible tautomeric forms, named as azo-enol-keto (T_1), azo-enol (T_2), azo-enol (T_3), hydrazone-

---

* Corresponding author. Tel./fax: +98 1312250309.
E-mail address: ena_moradi@yahoo.com (E.O. Moradi-e-Rufchahi).

0167-7322/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.molliq.2011.03.011



I

Scheme 1. Preparation of 6-flouro-4-hydroxyl-2-quinolone (**I**).

keto-enol (T_4), hydrazone-keto (T_5) and hydrazone-keto (T_6) as shown in Scheme 3.

As it can be seen in Table 1, the infrared spectra of all the dyes (in KBr) showed broad intense amide (NH–C=O) and hydroxyl (OH) bands at 3436–3288 cm^{-1}. The IR spectra also showed an intense band at 1680–1635 cm^{-1}, which was assigned to amide carbonyl group.

The ^1H NMR spectrum of all the dyes measured in DMSO-d_6 at 25 °C (Table 1) showed a multiplet from 7.18–8.50 ppm for aromatic protons, a singlet at 2.50 ppm (–CH_3, **3**), a singlet at 2.43 ppm (–CH_3, **12**), 2.49 ppm (–CH_3, **13**) and 3.82 ppm (–CH_3, **14**). The broad peaks at 16.34–14.84 ppm were assigned to tautomeric hydrazone proton (=N–NH–).The spectra of the studied compounds **1**–**14** provide additional evidence that they have the Hydrazone-keto structures T_5 and T_6 rather than the enol structures T_1–T_4. For example ^1H NMR spectrum of **10** in deuterated dimethyl sulfuxide exhibits two signals at 15.01 and 15.60 ppm with nearly equal integration ratio. Other compounds in these series show similar patterns (Table 1). These signals undoubtedly correspond to the hydrazone NH proton resonance related to hydrazone-keto forms T_5 and T_6. Further evidence for this assignment is provided by the observation that ^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 [20] indicating that the proton is attached to nitrogen atom. 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 [21,22].Two attributed broad singlet peaks at 11.22–11.36 and 11.40–11.56 ppm for amide (–NH) groups are related to amide protons of two types of tautomeric forms T_5 and T_6.

2.2. Solvent effect

The absorption spectra of the prepared dyes were measured in various solvents at a concentration of approximately10^{-5} to 10^{-6} Mol. L^{-1} and were run at different concentrations. The dyes were completely soluble in DMSO. Therefore, more dilute solutions were prepared, and it was found in all cases that λ_{max} was unaffected by the dye concentration. The stock solutions of each dye were accurately prepared in DMSO and dilutions of these stocks were used for absorption measurements. The results are given in Table 2. The visible absorption spectra of the dyes did not show regular variation with the polarity of solvents.

The electronic absorption spectra of the compounds **1**–**14** in all used solvents revealed a shoulder in the region 347–411 and a band in 396–458 nm (e.g. Fig. 1 for dye **13**). It can be suggested that dyes may exist as a mixture of two tautomeric forms which are in equilibrium. These results seem to be compatible with the hydrazone rather than the azo forms depicted in Scheme 3 and are consistent with the findings on tautomerism from ^1H NMR conclusions. It was also observed that the λ_{max} values of dyes didn't change significantly in various solvents. This behavior of dyes suggests that the molecules are involved in strong intramolecular hydrogen bond.

It was also observed that the absorption curves of the dyes were not significantly sensitive to acid but is sensitive to base. The absorption spectra of the dyes in methanol didn't change significantly when 0.1 M HCl was added and the absorption curves of the dyes resembled those in acetic acid. The λ_{max} of the dyes showed hypsochromic shifts when 0.1 M KOH was added to each of the dye solutions in methanol. A typical example is shown in Fig. 2.

2.3. Substituent effects

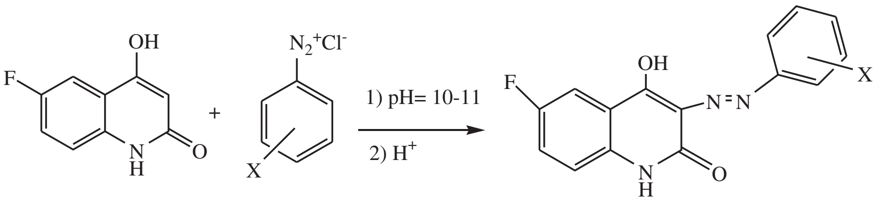
As far as absorption maxima are concerned, λ_{max} values are directly proportional to the electronic power of the substituents in the benzenoid system. As Fig. 3 depicts, a reasonable linear correlation exists between the difference in wavelength ($\Delta\lambda_{max}$) relative to that of unsubstituted dye **11** and the Hammett substituent constants (σ_m and σ_p) for relevant groups.

As it is apparent in Table 2, the introduction of electron donating methoxy group in the benzene ring resulted in bathochromic shifts in all solvents with respect to electron-accepting nitro, cyano and flouro groups (e.g. for dye **14** $\Delta\lambda = 35$ nm relative to dye **1,** $\Delta\lambda = 41$ nm relative to dye **2** in methanol). The introduction of electron-donating methyl (*m*-, *p*-) groups in the benzene rings resulted in bathochromic shifts in all solvents. The iodo (*p*-) group in the benzene ring resulted in bathochromic shifts in all solvents.

The introduction of electron-withdrawing nitro (*m*-) group in the benzene ring resulted in hypsochromic shifts in all solvents. The nitro (*p*-) group in the benzene ring resulted in bathochromic shifts in acetic acid and chloroform but did not change significantly in the other solvents. The position of all groups did not show a regular variation in all solvents. Fig. 4 compares the absorption spectra of some of the dyes with different substituents in chloroform.

2.4. Determination of pKa values of the azo dyes

The ionization constants (pK_a's) of **1** to **14** were determined in 80 vo1.% ethanol–water medium at 25 ± 2 °C and a μ of 0.1 using spectrophotometric titration method and are given in Table 3. Each compound exhibits two bands in region of 347–411 nm for anionic and 396–458 nm for the molecular species. As the pH value of the

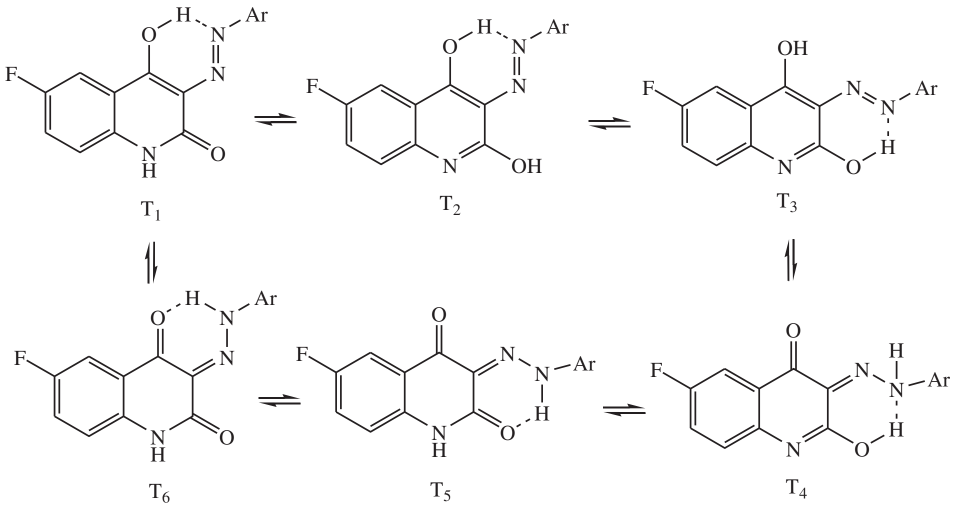


I

1-14

(**1**):X= *p*-NO_2	(**2**):X= *p*-CN	(**3**):X= *p*-$COCH_3$	(**4**):X= *p*-F	(**5**):X= *m*-NO_2
(**6**):X= *p*-Cl	(**7**):X= *p*-Br	(**8**):X= *m*-Cl	(**9**):X= *m*-CF_3	(**10**):X= *p*-I
(**11**):X= -H	(**12**):X= *m*-CH_3	(**13**):X= *p*-CH_3	(**14**):X= *p*-OCH_3	

Scheme 2. Synthetic routes for the preparation of azo dyes **1**–**14**.



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

solution increased, the height of the former band increases and simultaneously that of the latter decreased. From the optical spectra (Fig. 5), in each case, the isobestic points indicate that two species are in equilibrium (Scheme 4).

A digital pH meter Genway model 3505 was employed for determination of pH. The instrument was accurate to ±0.01pH unit. 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 [23], namely where log *U*, 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 25 ± 2 °C. The value of log *U*, was found to be −0.235.

$$-\log\,[\mathrm{H}]^{+} = \mathrm{B} + \log\ \mathrm{U_H}$$

The acid dissociation constants of **1** to **14** 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 water-jacketed thermostatted cell. The pH of the solution was measured and the spectrum was recorded

Table 1
Spectral data for dyes **1**–**14**.

Dye no.	FT-IR (cm^{-1}, in KBr)				^{1}H NMR (δ, ppm)			
	$\nu_{\mathrm{O-H}}$	$\nu_{\mathrm{N-H}}$	$\nu_{\mathrm{C=O}}$	$\nu_{\mathrm{Aro.-H}}$	Aro.-H	N—H		
						Alip.-H	Hydrazone	amide
1	3429	3191	1687	3033	8.34 (2H , d, J = 5 Hz), 7.85 (1 H, d, J = 5 Hz), 7.92 (1 H, d, J = 5 Hz), 7.64–7.26 (3H, m, overlapped)	–	14.48 15.30	11.36 11.57
2	3467	3193	1680	3042	7.92 (2H , d, J = 8.4 Hz), 7.82–7.22 (5H, m, overlapped)	–	14.88 15.38	11.28 11.47
3	3422	3188	1676 1720	3031	8.10–7.21 (7H, m, overlapped)	2.50 (3H, s)	15.07 15.64	11.28 11.49
4	3410	3188	1683	3056	7.75 (2H, dd,J = 9, 11.5 Hz), 7.64–7.34 (4H, m, overlapped), 7.25(1H, m)	–	15.19 15.92	11.23 11.42
5	3405	3186	1692	3044	8.50 (1H, s), 8.08 (2H, m, overlapped), 7.75 (1H, t, J = 8.2 Hz), 7.63–7.21 (3H, m, overlapped)	–	14.96 15.48	11.30 11.41
6	3411	3187	1688	3041	7.73 (2H, d,J = 8.6 Hz), 7.64–7.52 (4H, m, overlapped), 7.27 (1H, m)	–	15.10 15.76	11.25 11.45
7	3407	3186	1689	3033	7.69–7.63 (5H, m, overlapped), 7.53(1H, dd, J = 3, 11 Hz), 7.23(1H, m)	–	15.72 15.07	11.23 11.43
8	3435	3200	1670	3060	7.80–7.21(7H, m, overlapped)	–	15.58 14.97	11.26 11.45
9	3420	3190	1684	3056	8.09 (1H, s), 8.03–7.21 (6H, m, overlapped)	–	15.02 15.60	11.29 11.48
10	3422	3196	1674	3042	7.86–7.20 (7H, m, overlapped)	–	15.73 15.07	11.23 11.44
11	3423	3204	1678	3054	7.73–7.21(8H, m, overlapped)	–	15.22 15.95	11.23 11.42
12	3418	3211	1666	3020	7.70–7.22 (7H, m, overlapped)	2.43 (3H,s)	15.31 16.05	11.20 11.38
13	3422	3150	1680	3065	7.66–7.20 (7H, m, overlapped)	2.38 (3H, s)	15.30 16.08	11.21 11.40
14	3417	3145	1665	3064	7.71–7.10 (7H, m, overlapped)	3.80 (3H, s)	15.44 16.34	11.24 11.44

Table 2
Influence of solvents on λ_{max}(nm) of the prepared dyes.

Dye	X	DMSO	DMF	CH_3CN	CH_3OH	CH_3COOH	$CHCl_3$
1	p-NO_2	408s, 424	411s, 422	405s, 419	406s, 421	402s, 425	405s, 423
2	p-CN	410s, 419	407s, 426	397s , 403	397s, 415	399s, 421	400s, 416
3	p-$COCH_3$	390s, 409	401s, 416	397s, 418	402s, 427	404s, 433	401s, 433
4	p-F	396s, 416	397s, 424	393s, 419	397s, 426	398s, 430	398s, 432
5	m-NO_2	383s, 404	380s, 400	374s, 393	390s, 395	388s, 413	379s, 396
6	p-Cl	391s, 424	403s, 425	391s, 423	396s,430	395s, 433	394s, 435
7	p-Br	391s, 427	394s, 428	394s, 425	395s, 432	394s, 435	392s, 438
8	m-Cl	398s, 424	395s, 402	392s, 407	391s, 419	392s, 424	390s, 426
9	m-CF_3	398s, 416	398s, 420	395s, 419	400s, 418	400s, 413	397s, 430
10	p-I	396s, 436	399s, 432	395s, 431	399s, 436	398s, 441	394s, 441
11	-H	389s, 419	391s, 424	393s, 421	391s, 425	390s, 429	390s, 432
12	m-CH_3	405s, 431	404s, 429	392s, 427	400s, 431	396s, 433	402s, 436
13	p-CH_3	397s, 438	392s, 435	392s, 433	392s, 437	391s, 438	400s, 442
14	p-OCH_3	398s, 452	401s, 452	391s, 450	400s, 456	396s, 458	396s, 459

s = shoulder.

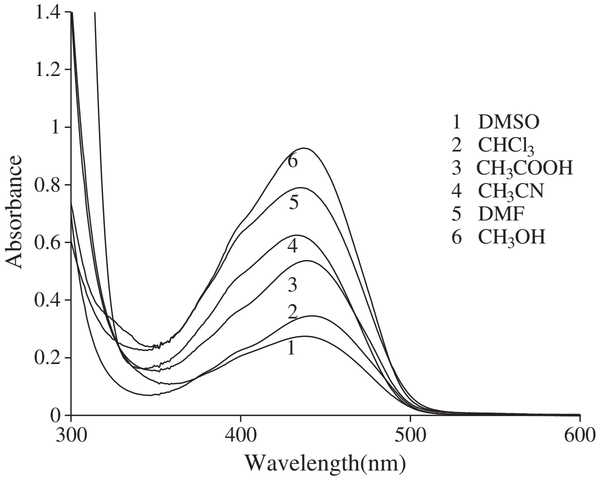


Fig. 1. Absorption spectra of dye **13** in various solvents.

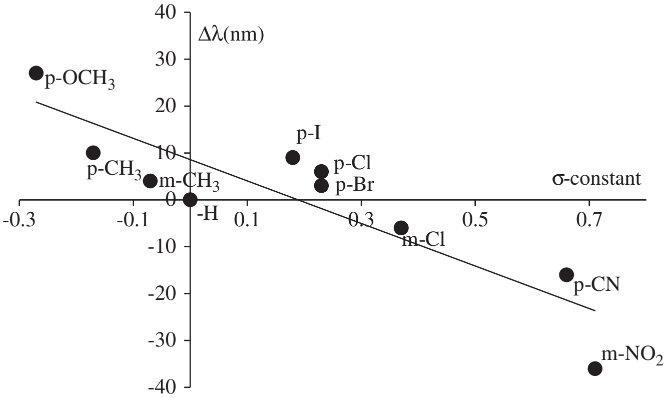


Fig. 3. Relation between Hammett constant (σ_m and σ_p) and $\Delta\lambda_{max}$ for the prepared azo dyes in $CHCl_3$.

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 run 10–15 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 Hammett constants (σ_m and σ_p) yields the graph shown in Fig. 6. The equation of such a correlation is:

$$pK_a = 8.00 - 1.95\ \sigma$$

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 —OMe and —CH_3 groups attached to the compounds **12**–**14** can decrease the acidic character, due to their electron donating ability which destabilizes anionic form of the azo dyes.

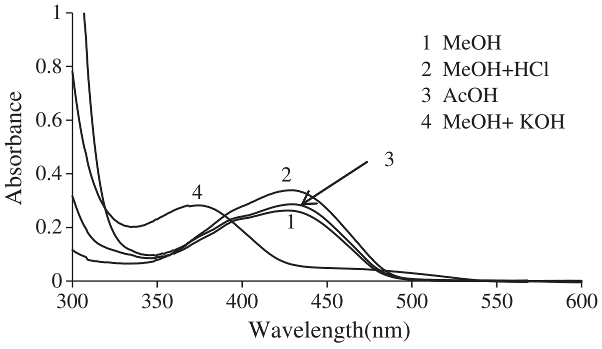


Fig. 2. Absorption spectra of dye **11** in acidic and basic solutions.

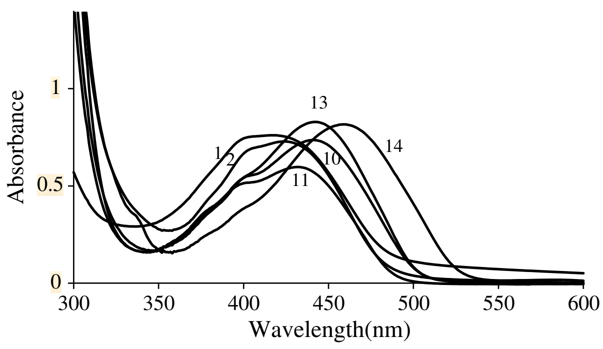


Fig. 4. Absorption spectra of dyes **1**, **2**, **10**, **11**, **13** and **14** in chloroform.

Table 3
Acidic dissociation constant (pK_a) and absorption maxima (λ_{max}) of prepared azo dyes in different pH values.

Dye no.	pH = 1	pH = 3	pH = 5	pH = 7	pH = 9	pH = 11	pH = 13	pK_a (±0.05)
1	425	425	425	425	420	412	399	6.75
2	419	419	419	420	401	399	400	7.21
3	430	429	429	430	405	399	399	7.80
4	431	428	430	431	484	375	376	6.79
5	404	408	410	412	385	382	383	6.99
6	433	432	433	433	390	382	381	6.86
7	434	434	433	434	433	391	384	7.49
8	420	423	423	423	387	380	376	6.93
9	412	412	416	416	386	379	380	6.83
10	438	436	439	435	393	386	386	7.03
11	430	429	431	429	431	426	374	7.68
12	437	432	434	433	433	433	377	7.86
13	440	439	438	440	439	438	376	8.85
14	456	458	457	457	457	380	380	9.54

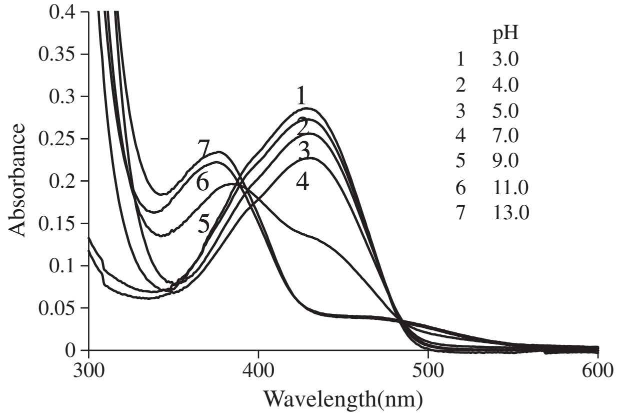


Fig. 5. Absorption spectra of the dye **4** (R = *p*-F) at different pH values.

3. Experimental

3.1. General

The chemicals used in the synthesis of all dyes were obtained from Merck Chemical Company and Aldrich Chemical Company and were used without further purification. 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. ^1H and ^{13}C NMR spectra were recorded on a Bruker 500 MHz spectrometer in DMSO-d_6 using TMS as an internal reference. Microanalyses for C, H and N were performed on a PerkinElmer 2400(II) elemental analyzer. Melting points were determined on a Barnstead Electrothermal 9100 melting point apparatus and uncorrected.

3.2. Preparation of N, N′-Di-(4-flourophenyl)malonamide

A mixture of 4-flouroaniline (100 mmol, 9.6 ml) with dimethylmalonate (50 mmol, 5.7 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. Yield 91%, white solid, m.p. 214–216 °C (reported 212 °C [19]).

3.3. Synthesis of 6-flouro-4-hydroxyquinoline-2-(1H)-one

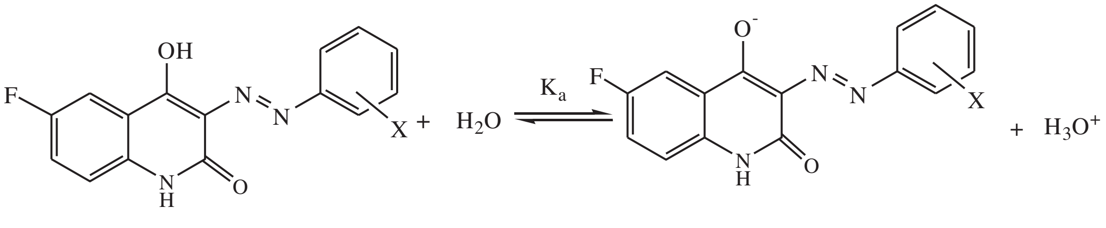
N, N′-Di-(4-flourophenyl)malonamide (0.576 g, 2 mmol) was dissolved in 3.5 ml methanesulfunic acid, which contains 10% of phosphorus pentoxide, and was then heated in an oil bath for 90 min at 150 °C. The dark viscous solution was allowed to cool, water was added and the precipitated compound was filtered off, washed with water and dried in air. The crude product was dissolved in 20 ml of sodium hydroxide solution 0.1 $mol \cdot L^{-1}$ and undissolved material was filtered. The filtrate neutralized with concentrated hydrochloric acid and the precipitate was recrystallized from ethanol to afford 6-flouro-4-hydroxyquinoline-2-(1H)-one as creamy crystals.

3.4. Preparation of phenylazohydroxyquinolone dyes

To a suspension of the aromatic amine (5.0 mmol) in water (10 mL) concentrated hydrochloric acid (24 mmol, 2 mL) was added until the mixture was homogeneous. The solution was cooled and kept at 0–5 °C in an ice bath and diazotized by addition of a solution of sodium nitrite (5.2 mmol, 0.345 g) in water (3 mL), followed by stirring for 30 min at 0–5 °C. To a solution of 6-flouro-4-hydroxyquinoline-2-(1H)-one (0.895 g) in sodium hydroxide (20 mmol) and water (15 mL) a solution of the diazonium salt at 0–5 °C was slowly added. The pH of the reaction mixture was maintained at 10–11 by adding 2.5% sodium hydroxide solution. The resulting mixture was stirred for 2 h at 0–5 °C. The progress of the reaction are followed by TLC, using DMF as developing solvent and silica gel TLC plates as the stationary phase. In the end of procedure the pH of reaction mixture was regulated at 4–5 by addition of 10% hydrochloric acid solution. The resulting solid was filtered, washed with cold ethanol and dried. The crude product was purified using the recrystallization method. The selected physical properties of dyes were measured and listed in Table 4.

4. Conclusion

In this research 6-flouro 4-hydroxyl-2-quinolone and its disperse azo dyes have been synthesized. Characterization and absorption ability of 14 novel phenylazoquinolone based dyes (**1**–**14**) were studied. Absorption spectra results of these dyes revealed that these compounds do exist in forming hydrazone-keto form species. The dyes exhibited yellow to red hues. The spectrophotometric results showed that in quinolone section, in spite of hydroxyl group as an electron donor, the stronger electron withdrawing nature of lactame



Scheme 4. Acidic dissociation equilibrium of the prepared compounds.

Table 4
The physical properties of the dyes used in this study.

Dye	Color	mp (°C)	Recrystallization	% C		% H		% N		Yield (%)
				Calcd.	Found	Calcd.	Found	Calcd.	Found	
1	Orange	>350	DMF	54.89	54.82	2.74	2.69	17.07	17.19	70
2	Reddish orange	327–328	DMF	62.34	62.61	2.92	2.99	18.18	17.92	75
3	Brown	294–296	DMF	62.77	61.98	3.72	3.61	12.92	13.02	77
4	Dark yellow	296–297	DMF	59.80	60.01	3.01	2.91	13.95	13.74	88
5	Clear yellow	314–316	DMF	54.89	54.80	2.74	2.71	17.07	17.25	79
6	Luster yellow	>350	DMF/H_2O	56.72	56.91	2.85	2.74	13.23	13.02	75
7	Luster yellow	336–338	DMF/H_2O	49.75	49.61	2.50	2.42	11.60	11.43	80
8	yellow	300 (dec.)	DMF/H_2O	56.72	56.96	2.85	2.76	13.23	13.01	70
9	Yellow	286–288	DMF/H_2O	54.71	54.11	2.58	2.64	11.96	11.76	90
10	Brown	346–347	DMF/H_2O	44.0	44.52	2.22	2.09	10.27	10.05	72
11	Dark brown	>350	Ethanol	63.60	64.74	3.56	3.47	14.84	14.22	73
12	Brown	260–262	Ethanol	64.64	64.52	4.07	4.12	14.14	14.22	74
13	Brown	270 (dec.)	Ethanol	64.64	64.18	4.07	4.11	14.14	14.22	68
14	Red	>350	Ethanol	61.34	60.98	3.86	3.78	13.41	13.11	66

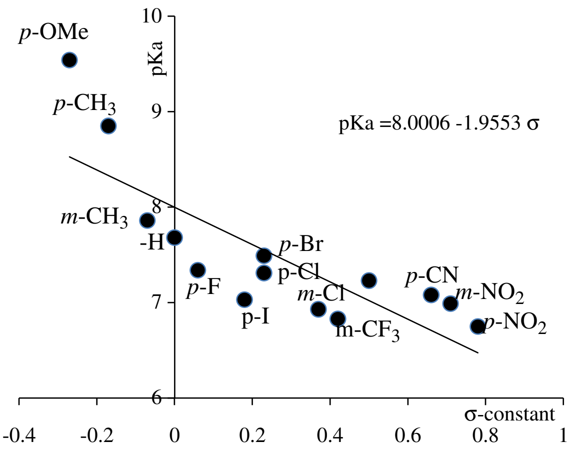


Fig. 6. Relation between Hammett constant (σ_m and σ_p) and pK_a values for the prepared dyes.

moiety is predominated. Hence, in compounds with electron releasing groups on diazo component the push–pull effect is better than others. 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.

References

[1] M.A. Weaver, L. Shuttleworth, Heterocyclic diazo components, Dyes and Pigments 3 (1982) 81–121.
[2] Q. Peng, M. Li, K. Gao, L. Cheng, Hydrazone-azo tautomerism of pyridone azo dyes: part 1-NMR spectra of tautomers, Dyes and Pigments 14 (1990) 89–99.
[3] Q. Peng, M. Li, K. Gao, L. Cheng, Hydrazone-azo tautomerism of pyridone azo dyes: part II: relationship between structure and pH values, Dyes and Pigments 15 (1991) 263–274.
[4] M.R. Yazdanbakhsh, A. Ghanadzadeh, E. Moradi, Synthesis of some new azo dyes derived from 4-hydroxy coumarin and spectrometric determination of their acidic dissociation constants, Journal of Molecular Liquids 136 (2007) 165.
[5] G. Zhang, S. Wang, Q. Gan, Y. Zhang, G. Yang, J. Ma, A stable trinuclear zinc cluster assembled from a thiazolylazo dye and zinc acetate: preparation, structural characterization and spectroscopic studies, European Journal of Inorganic Chemistry 20 (2005) 4186–4192.
[6] M.S. Yen, I.J. Wang, Synthesis and absorption spectra of hetarylazo dyes derived from coupler 4-aryl-3-cyano-2-aminothiophenes, Dyes and Pigments 61 (2004) 243–250.
[7] G.J. Lestina, T.H. Regan, Determination of the azo-hydrazono tautomerism of some 2-pyrazolin-5-onedyes by means of nuclear magnetic resonance spectroscopy and ^{15}N-labeled compounds, Journal of Organic Chemistry 34 (1969) 1685–1686.
[8] C. Lubai, C. Xing, G. Kunyu, H. Jiazhen, J. Griffiths, Colour and constitution of azo dyes derived from 2-thioalkyl-4,6-diaminopyrimidines and 3-cyano-1,4-dimethyl-6-hydroxy-2-pyridone as coupling component, Dyes and Pigments 7 (1986) 373–378.
[9] Q. Peng, M. Li, K. Gao, L. Cheng, Hydrazone-azo tautomerism of pyridone azo dyes: part II: relationship between structure and pH values, Dyes and Pigments 15 (1991) 263–274.
[10] N. Ertan, Synthesis of some hetarylazopyrazolone dyes and solvent effects on their absorption spectra, Dyes and Pigments 44 (1999) 41–48.
[11] F. Karcı, A. Demircalı, Synthesis of 4-amino-1H-benzo [4,5]imidazo[1,2-a] pyrimidin-2-one and its disperse azo dyes. Part 2: Hetarylazo derivatives, Dyes and Pigments 71 (2006) 97–102.
[12] S.A. Basaif, M.A. Hassan, A.A. Gobouri, $AlCl_3$-Catalyzed diazocoupling of 1-(aryl/hetaryl)-3-phenyl-1H-pyrazol-2-in-5-ones in aqueous medium: Synthesis of hetaryl-azopyrazolones and their application as disperse dyes, Dyes and Pigments 72 (2007) 387–391.
[13] E. Moradi-e-Rufchahi, Synthesis of 6-chloro and 6-fluoro-4-hydroxyl-2-quinolone and their azo disperse dyes, Chinese Chemical Letters 21 (2010) 542–546.
[14] Ali A. Abdel Hafez, Ibrahim M.A. Awad, Azo-dyes related to 5-sulphonylpiperidino and/ or morpholino-8-quinolinol, Dyes and Pigments 20 (1992) 197–209.
[15] R. Krishnan, S. Seshadril, Synthesis of azoic dyes from 7-Hydroxyd-phenyl quinoline derivatives, Dyes and Pigments 7 (1986) 69–77.
[16] Yun-Fei Cheng, Da-Tong Zhao, Meng Zhang, Zhi-Qiang Liu, Yi-Feng Zhou, Tian-Min Shu, Fu-You Li, Tao Yi, Chun-Hui Huang, Azo 8-hydroxyquinoline benzoate as selective chromogenic chemosensor for Hg^{2+} and Cu^{2+}, Tetrahedron Letters 47 (2006) 6413–6416.
[17] Aytul Saylam, Zeynel Seferoglu, Nermin Ertan, Synthesis and spectroscopic properties of new hetarylazo 8-hydroxyquinolines from some heterocyclic amines, Dyes and Pigments 76 (2008) 470–476.
[18] I. Sener, F. Karci, N. Ertan, E. Kilic, Synthesis and investigations of the absorption spectra of hetarylazo disperse dyes derived from 2,4-quinolinediol, Dyes and Pigments 70 (2006) 143–148.
[19] E. Ziegler, R. Wolf, R. Kappe, Eine einfache synthese des 4-hydroxycarboxytyrils und seiner derivate, Monatshefte für Chemie 96 (1965) 418–422.
[20] F.A. Snavely, C.H. Yoder, A study of tautomerism in arylazopyrazolones and related heterocycles with nuclear magnetic resonance spectroscopy, J. Org. Chem. 33 (1968) 513–515.
[21] G.L. Lestina, T.H. Regan, The determination of the azo-hydrazone tautomerism of some 2-pyrazolin-5-one dyes by means of nuclear magnetic resonance spectroscopy and ^{15}N-labeled compounds, Journal of Organic Chemistry 34 (1969) 1685–1686.
[22] C.H. Yoder, R.C. Barth, W.M. Richter, F.A. Snavely, A nuclear magnetic resonance study of some nitrogen-15 substituted azo heterocycles, Journal of Organic Chemistry 37 (1972) 4121–4123.
[23] L.G. Van Uitert, C.G. Haas, A method for determining thermodynamic equilibrium constants in mixed solvents, Journal of American Chemical Society 75 (1953) 451–455.