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Azo-8-hydroxyquinoline dyes: The synthesis, characterizations and determination of tautomeric properties of some new phenyl- and heteroarylazo-8-hydroxyquinolines

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ABSTRACT

Two series of new heterocyclic and carbocyclic disperse azo dyes based on 8-hydroxyquinoline were prepared and characterized by FT-IR, ^{1}H NMR, mass spectroscopic techniques and elemental analysis. Their solvatochromic properties in different solvents were investigated and their absorption spectra were strongly solvent dependent. The acid and base effects on this equilibrium were also examined. In addition, the colors of dyes were discussed with respect to the nature of the carbocyclic and heterocyclic rings and substituent therein. To determine the tautomeric forms of the prepared dyes in solid state, X-ray data for 5-(5-methylthiazol-2-yldiazenyl)-8-hydroxyquinoline were recorded. The X-ray results showed that the dye exists as an azo tautomer in the solid state.

1. Introduction

It is well known that, because of their versatile application in various fields such as the dyeing of textile fibers, the coloring of different materials and biological–medicinal studies, the azo compounds are the most widely used class of dyes. They are also used in the fields of non-linear optics (NLO), optical data storage, advanced applications in organic synthesis and analytical chemistry as acid–base, redox and metallochromic indicator [1–5].

In recently, monoazo dyes have became the most important type of azo dyes. The monoazo dyes based on heterocyclic amines have been developed and the resultant dyes have higher tinctorial strength and give brighter than those derived from aniline-based diazo components. For instance, amino-substituted thiazole, benzothiazole, isothiazole, thiadiazole, and thiophene compounds afford very electronegative diazo components and consequently, provide a pronounced bathochromic effect compared to the benzenoid compounds [6–12]. In addition, heterocyclic coupling component such as pyridone, pyrazolone, pyrimidine, thiophene, quinoline, and indole derivatives is also very important for industrial and other advanced applications [1]. Therefore, the synthesis and investigation of spectroscopic properties of many monoazo dyes containing one or two heterocyclic rings in molecule have been studied in the past decades [7–22].

The chemical properties of quinoline and its derivatives have been widely discussed because of their biological relevance, coordination capacity and their use as metal extracting agent [23]. They have attracted special interest due to their therapeutic properties. On the other hand, quinoline sulfonamides have been used in the treatment of cancer, tuberculosis and malaria [24]. Several quinoline derivatives possess chemotherapeutic activity and act as antimalaria and antiallergic agents [25]. They show broad-spectrum efficiency against multiple herpes viruses and they have a potential role for the treatment of a variety of infections [26]. 8-Hydroxyquinoline is one of the most important derivatives of quinoline because of its chelator properties for important metal ions [27]. 8-Hydroxyquinoline and its derivatives have high antibacterial activities [28,29]. Some of the 8-hydroxyquinoline derivatives and their complexes with transition metals were reported to be active against some bacteria and DNA [30,31]. In addition, azo compounds based on 8-hydroxyquinoline derivatives play a central role as chelating agents for a large number of metal ions [1,2,5,30–42]. Although 8-hydroxyquinoline azo dyes have bacteriostatic action, they have not been an indication of commercial value as textile dyes [43]. On the other hand, 8-hydroxyquinoline azo dyes derived from the sulfonamide derivatives were employed on textiles. Mordant dyeing with these acid azo dyes showed very good fastness properties on wool and nylon fibers [44]. In addition, some 8-hydroxyquinoline and azo derivatives found numerous applications in analytical chemistry as chromophoric and metallochromic indicators [45]. Although many papers were described in the synthesis and some properties of phenylazo-8-

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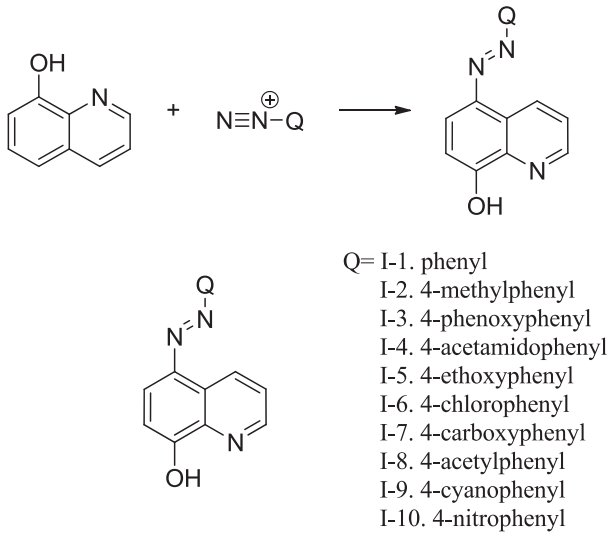

Fig. 1. Synthetic pathway and structure of phenylazo-8-hydroxyquinolines (**I 1–10**).

hydroxyquinolines [37,39,40,43,45], only few heteroarylazo-8-hydroxyquinolines were synthesized [38,46–49]. However, the solvatochromic properties of these dyes were not investigated in detail.

In our previous paper, we synthesized some new heteroarylazo 8-hydroxyquinoline dyes and evaluated their tautomeric equilibria in solution. In continuation of our work, we aimed to find new data for supporting tautomeric equilibria of these dyes. For this purpose, some novel various substituted heteroarylazo-8-hydroxyquinoline dyes were synthesized and their absorption spectra were compared with the absorption spectra of substituted phenylazo-8-hydroxyquinolines in various solvents. The color of the dyes was discussed in relation to the nature of the carbocyclic and heterocyclic rings and the substituents therein. Acid–base effects on the absorption spectra of the dyes were also studied in detail. The molecular structures of 5-(5-methylthiazol-2-yldiazenyl)-8-hydroxyquinoline obtained by X-ray diffraction analysis were also evaluated. 5-(2-carboxyphenyldiazenyl)-8-hydroxyquinoline was also used as a model compound for the determination of tautomeric equilibria of phenylazoquinoline dyes.

2. Results and discussion

The phenylazoquinoline dyes (**I 1–10**) were prepared by coupling 8-hydroxyquinoline with diazotized aniline derivatives with $NaNO_2$ in HCl/H_2O mixture (Fig. 1). The heteroarylazoquinoline dyes (**II 1–12**) were prepared by coupling 8-hydroxyquinoline with diazotized 2-aminothiazole, 2-aminobenzothiazole derivatives and 2-aminobenzimidazole in nitrosyl sulfuric acid (Fig. 2). The structures of prepared dyes have been confirmed by FT-IR, ^1H NMR, mass spectral data and elemental analysis. The all prepared

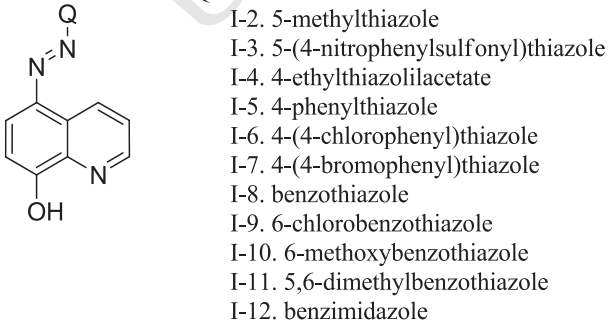

Fig. 2. Structure of heteroarylazo-8-hydroxyquinolines (**II 1–12**).

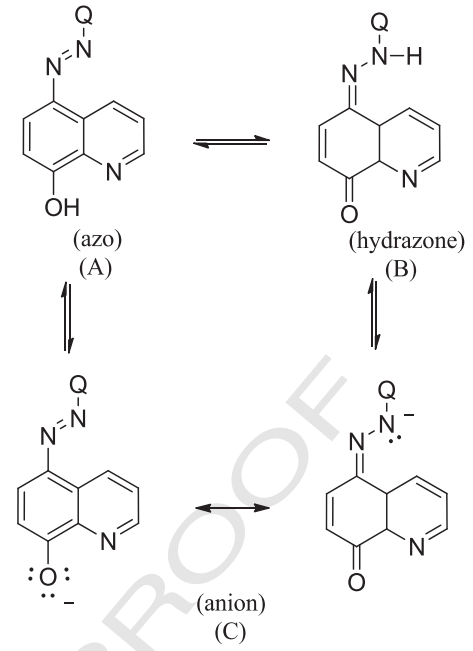

Fig. 3. Azo-hydrazone tautomeric and anionic form of phenyl- and heteroarylazo-8-hydroxyquinolines.

dyes may exist in two possible tautomeric forms, namely azo form A and hydrazone B as depicted in Fig. 3. The deprotonation of two tautomers leads to common anion C (Fig. 3).

The infrared spectra of the prepared dyes (**I 1–10** and **II 1–12**) (in KBr) showed strong and broad band within the range 3448–3147 cm^{-1} corresponding to quinoline ν_{O-H}. The broad value reveals that the –OH group was involved in intra- and intermolecular H-bonding. Some researcher suggested that 8-hydroxyquinolines and their phenylazo derivatives contain intramolecular H-bond in solid state [50,51]. The other study showed that they were stable in azo form because of intermolecular H-bond in solid state [37,52,53]. On the other hand, Basu Baul and co-workers suggested that phenylazo-8-hydroxyquinoline dyes were in azo form and may contain intra- and intermolecular H-bond in solid state [40].

In this work, to determine the tautomeric forms of the dyes in solid state, X-ray data for 5-(5-methyl-2-thiazolylazo)-8-hydroxyquinoline (**II-2**) (Figs. 4 and 5) were recorded. Suitable single crystals were obtained by slow evaporation from ethanol/H_2O in one week. The crystal structure of this dye showed only strong intramolecular H-bond between the hydroxy H and the quinoline N atoms (O–H–N = 2.212 Å). This result suggests that the synthesized dyes can be stable as azo in solid state. The other ν_{max} values at 3077–3040 (aromatic CH), at 2986–2851 (aliphatic CH) were recorded.

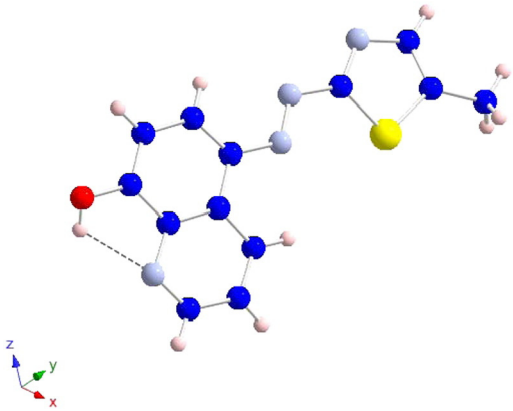

Fig. 4. Structure of a molecule of dye **II-2** in the crystal.

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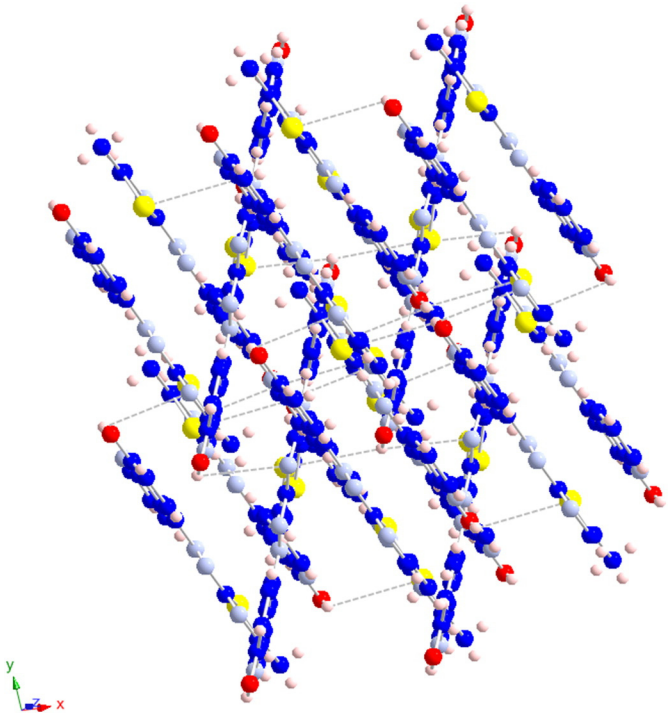

Fig. 5. A partial packing diagram of dye **II-2**.

The ^{1}H NMR spectra of aromatic protons of dyes in the 8-hydroxyquinoline ring appeared at δ 9.40–9.20 doublet, δ 9.00–8.90 doublet, δ 8.30–7.90 doublet, δ 7.80–7.60 multiplet and δ 7.30–7.10 doublet. The –OH protons of 8-hydroxyquinoline ring were not observed in DMSO-d_6 or DMSO-d_6 and $CDCl_3$ mixtures at 25 °C except of dyes **I-2**, **I-6**, **II-5**, and **II-10** [37]. These dyes showed a broad peak at δ 10.80, 10.80, 9.40, and 8.00 for quinoline –OH respectively. Dye **I-4** showed a broad peak at δ 9.70 for $-NHCOCH_3$. Dye **I-7** showed a broad peak at δ 12.50 for –COOH. Dye **II-12** showed a broad peak at δ 12.32 for benzimidazole –NH. The other ^{1}H NMR, IR and mass data of the dyes prepared are shown in the Experimental section.

2.1. Solvent effect on absorption spectra of compounds in various solvents

Although many papers on azo-hydrazone tautomerism of hydroxyazo dyes have been published, the determination of the tautomeric structure is important because the tautomeric equilibrium strongly depends on the nature of the corresponding medium [54–58]. In order to investigate the tautomeric equilibria of phenylazo- and heteroarylazo-8-hydroxyquinoline dyes (**I 1–10** and **II 1–12**) in detail, we prepared

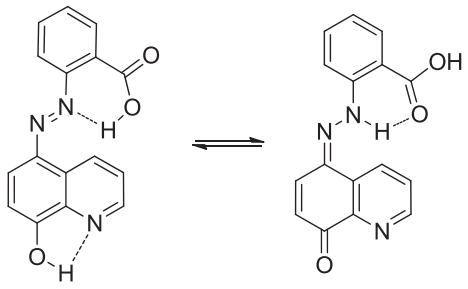

Fig. 6. Azo-hydrazone tautomeric equilibrium of 5-(2-carboxyphenyldiazenyl)-8-hydroxyquinoline (**I-7-o**).

disperse azo dyes and compared absorption maxima of the dyes in different solutions.

8-Hydroxyquinoline based azo dyes theoretically may be involved in azo-hydrazone tautomerism (Fig. 3). The visible absorption spectra of the phenylazo-8-hydroxyquinoline dyes **I 1–9** showed one absorption maximum in chloroform with the exception of the dye **I-10**. These results showed that the dyes were in favor of the predominantly single tautomeric form in chloroform. The absorption spectra of dye **I-10** exhibit one absorption maximum at 478 in methanol, at 445 in DMSO and one absorption maximum with shoulder in chloroform, acetic acid and acetonitrile and two absorption maxima in DMF (Table 1). The appearance of two absorption maxima in some solvents attributed two forms of the dyes in these solvents. In DMF, the phenylazo-8-hydroxyquinolines dyes exhibit two absorption maxima or one absorption maximum with a shoulder. Similar results were also observed in DMSO. These results suggest that dyes prepared exist as mixture of two tautomeric forms in DMSO and DMF. The determination of the most stable tautomeric form for 8-hydroxyquinoline type azo dyes is quite important for potential using field such as textile industry, optical data storage, molecular probe etc. In our study, in order to determine the most stable tautomeric form of the phenylazo-8-hydroxyquinoline dyes in solution, 5-(2-carboxyphenyldiazenyl)-8-hydroxyquinoline (**I-7-o**) has been used as model compound for dye **I-7**. This model compound was synthesized by the reaction of 2-aminobenzoic acid with 8-hydroxyquinoline. The dye **I-7-o** may contain intramolecular H-bond between COOH with hydrazone NH (Fig. 6) or COOH with azo group. The absorption spectra of dye **I-7-o** and dye **I-7** were compared to decide the most stable tautomeric form of dyes. The absorption spectra of dye **I-7-o** exhibit one absorption maximum at 521 nm in DMF (Fig. 7a), at 490 nm in methanol (Fig. 7b). On the other hand, the dye **I-7** exhibit two absorption maxima at 408 and 523 nm in DMF. Dye **I-7-o** exhibited significantly larger bathochromic shifts compared to dye **I-7** in DMF and methanol. For instance, $\Delta\lambda_{max}$ value of **I-7-o** is 90 nm in methanol relative to **I-7** in the same solvent (Fig. 7a and b). These large bathochromic shifts are attributed to azo-

Table 1
Influence of solvent on λ_{max} (nm) of phenylazoquinoline dye **I** (**1–10**).

	λ_{max} (nm)						
Dye no.	Q	Chloroform	Acetic acid	Methanol	Acetonitrile	DMF	DMSO
I-1	Phenyl	384	383	385, 465s	382	392, 499	396
I-2	p-CH_3	386	384	388, 468s	384	398, 501	397
I-3	p-OPh	391	376	390	390, 493s	401, 512s	407, 508
I-4	p-$NHCOCH_3$	394	395	403, 475s	395	416, 518	417, 517s
I-5	p-OC_2H_5	394	375, 427s	390	390	403, 496s	410, 508s
I-6	p-Cl	390	390	394, 474s	388, 492s	403, 524	406
I-7	p-COOH	397	401, 481s	400	395	408, 523	413
I-7o	o-COOH	426, 453, 542s	469	490	503	521	397, 510
I-8	p-$COCH_3$	402	399, 494	405	398	413, 569	417, 560
I-9	p-CN	405	400, 482	410	401	416, 562	425, 570
I-10	p-NO_2	414, 515s	417, 469s	478	413, 495s	433, 633	445

s: shoulder.

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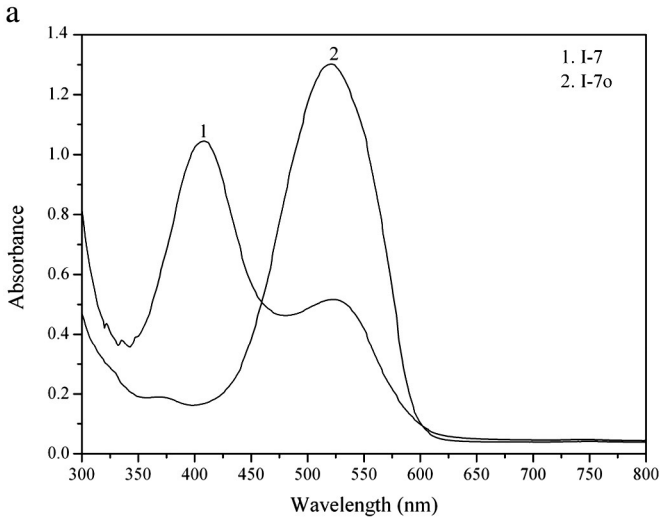

Fig. 7. Absorption spectra of dye **I-7** and **I-7-o** a) in DMF, b) in methanol.

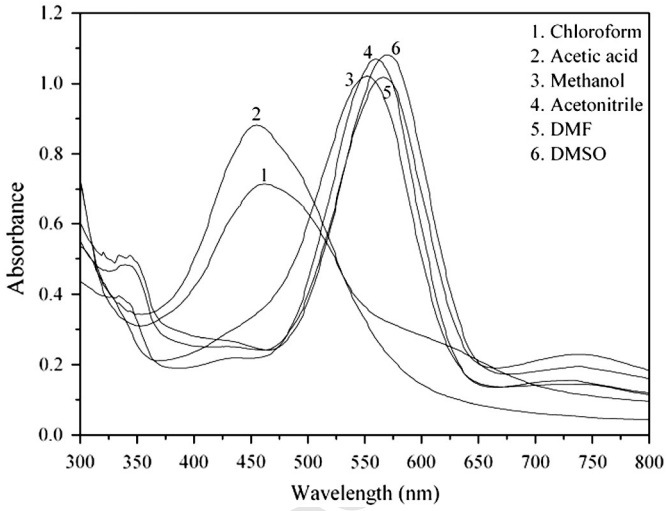

Fig. 8. Absorption spectra of dye **II-7** in various solvents.

hydrazone tautomerism. Thus it can be explained that **I-7-o** is stable as hydrazone form in DMF and methanol due to intramolecular H-bond between COOH with hydrazone NH. Similar results were also observed by Sawicki in 5-(2-methoxycarbonylphenyldiazenyl)-8-hydroxyquinoline [59]. On the other hand, it is known that the hydrazone form generally absorbs at a longer wavelength than azo form for these type compounds. Therefore, at the shorter wavelength band may be assigned to the azo form and at the longer wavelength band may be assigned to the hydrazone form for the phenylazo-8-hydroxyquinolines. These observations are in agreement with previous works [6,13,54–56].

Mono- or bis heteroarylazo disperse dyes tend to show larger solvatochromic and bathochromic effects than phenylazodyes because of the increased polarity of the dye system, especially in the excited state. Thus, they are preferred more than phenylazo analogs especially in industrial applications [1]. The absorption spectra of heteroarylazo-8-hydroxyquinoline dyes prepared (except of dye **II-3**) showed one absorption maximum in chloroform whereas they showed two absorption maxima or one absorption maximum with a shoulder in other solvents used (Table 2). In addition, dyes **II-5** and **II-6** have a broad band at long wavelength with low intensity in acetonitrile, DMSO and DMF. This broad band attributed the CT bands (charge-transfer). Dye **II-7** has also CT band at long wavelength in methanol, acetonitrile, DMSO and DMF (Fig. 8). Although the dyes **II-3**, **II-11** and **II-12** exhibit two absorption maxima in acetic acid, other dyes exhibit one absorption maximum in this solvent. These results suggest that these dyes (**II-3**, **II-11** and **II-12**) may exist as a mixture of two tautomeric forms in acetic acid (azo-hydrazone). The spectra of dye **II-4** in chloroform and acetic acid show one maximum at 438 nm and 441 nm respectively, whereas in DMSO and DMF the intensity of this band is decreased and a new more intensive band is appeared at the 565 and 562 nm and also two absorption bands are observed at 432 and 554 nm and at 444 and 544 nm in acetonitrile and methanol. Thus, the absorption curves almost pass through an isosbestic point approximately 505 nm characteristic of equilibria (Fig. 9). Similar results were observed for dye **II-10** (Fig. 10). This equilibrium may exist between the tautomeric forms

Table 2
Influence of solvent on λ_{max} (nm) of heteroarylazoquinoline dye **II** (**1**–**12**).

	λ_{max} (nm)						
Dye no.	Q	Chloroform	Acetic acid	Methanol	Acetonitrile	DMF	DMSO
II-1	Thiazole	428	435	434, 517s	425, 548	445s, 556	443
II-2	5-Methylthiazole	436	440	439	434, 551	444, 557	448, 563
II-3	5-(4-Nitrophenyl sulfonyl)thiazole	491, 589s	457, 542	581	582	591	593
II-4	4-Ethylthiazolacetate	438	441	444, 544	432, 554	434s, 562	432s, 565
II-5	4-Phenylthiazole	516	501	539	546, 716	565, 721	570, 732
II-6	4-(4-Chlorophenyl)thiazole	456	457	550	449, 548, 730	566, 731	569, 737
II-7	4-(4-Bromophenyl)thiazole	462	455	552, 741	560, 733	567, 740	570, 739
II-8	Benzothiazole	442	444	444s, 552	428s, 560	562	489, 572s
II-9	6-Chlorobenzothiazole	450	452	464, 568s	447, 559	564	461s, 564
II-10	6-Methoxybenzothiazole	461	469	518	457, 561	570	506
II-11	5,6-Dimethylbenzothiazole	456	457, 562	492	449, 573s	569	570
II-12	Benzimidazole	437	441, 554	430s, 526	431, 547	427s, 555	430s, 558

s: shoulder.

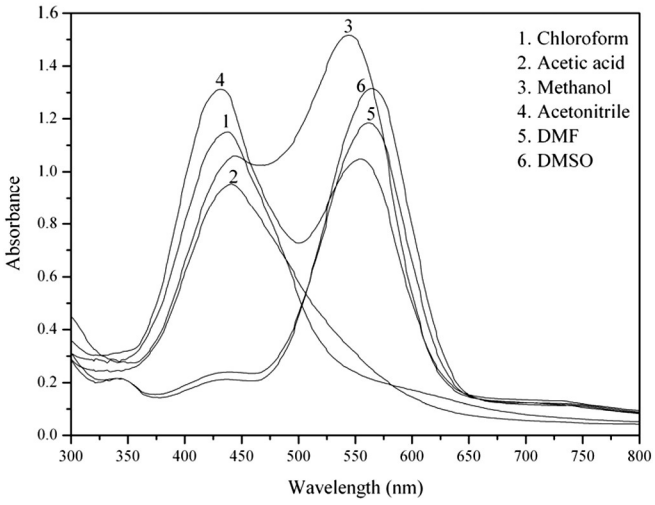

Fig. 9. Absorption spectra of dye **II-4** in various solvents.

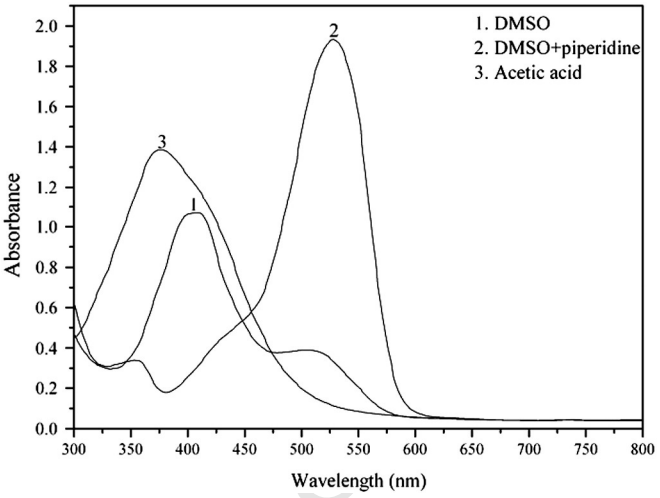

Fig. 11. Absorption spectra of dye **I-3** in acidic and basic solvents.

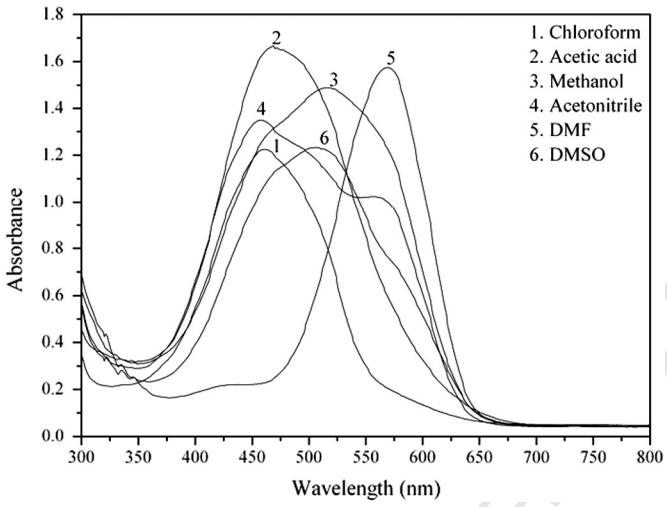

Fig. 10. Absorption spectra of dye **II-10** in various solvents.

(azo and hydrazone) or between one tautomeric form and anionic form because the equilibrium depends on the solvents used. In proton donating solvents such as acetic acid and chloroform, the dye give a hypsochromic shift of λ_{max} and are basically in the neutral form (azo or hydrazone). In proton-accepting solvents, such as DMSO and DMF, the dye gives a bathochromic shift of λ_{max} and may exist mainly in the common anion form, or the other tautomer. In the other solvents, the dyes exhibit equilibria (azo-hydrazone or azo-anion).

To determine the observed equilibrium, we examined the absorption spectra of the dyes prepared in acidic and basic media. The dyes prepared from carbocyclic amines (**I 1–10**) exhibit significant change at the absorption maxima, when a small amount of piperidine was added to the solutions in DMF, DMSO and chloroform (Table 3). In the case of dyes **I 3–5**, **I–8** and **I–9**, the addition of piperidine to their dye solutions in DMSO, maxima at the shorter wavelength disappeared and λ_{max} values at longer wavelength did not significantly change or shift to bathochromic region (Fig. 11). Similar effects were observed in the addition of piperidine in DMF solution of all phenylazo-8-hydroxyquinolines. These results indicate that the phenylazo-8-hydroxyquinoline dyes (**I 1–10**) in DMF and the dyes **I 3–5**, **I-8** and **I-9** in DMSO exist in a partly dissociated state. Therefore, the absorption maxima of these dyes in basic solutions are assigned to common anion form. The absorption maxima of prepared phenylazo-8-hydroxyquinoline dyes in chloroform are also sensitive to the addition of piperidine and λ_{max} of the dyes shifts to bathochromic and two absorption maxima appeared with the addition of piperidine in chloroform solution except for dye **I-10**. This equilibrium may exist between azo and common anion forms. The dye **I-10** exhibits one absorption maximum at short wavelength (414 nm) and shoulder at long wavelength (515 nm) in chloroform. The shoulder has very low intensity. When 0.2 mL piperidine was gradually added to the dye solution in chloroform, firstly the intensity of shoulder increased and turned to a maximum, the intensity of absorption band at short wavelength decreased at the same time. And then, the absorption maximum at short

Table 3
Absorption maxima of phenylazoquinoline dyes **I** (**1–10**) in acidic and basic solution.

	λ_{max} (nm)									
Dye no.	Q	DMSO	DMSO + piperidine	DMF	DMF + piperidine	Methanol	Methanol + KOH	Methanol + HCl	Chloroform	Chloroform + piperidine
I-1	Phenyl	396	526	392, 499	515	385, 465s	480	366	384	387, 473s
I-2	p-CH_3	397	522	398, 501	516	388, 468s	478	368	386	390, 478s
I-3	p-OPh	407, 508	528	401, 512s	520	390	484	374	391	401, 479s
I-4	p-$NHCOCH_3$	417, 517s	531	416, 518	522	403, 475s	486	381	394	405, 481
I-5	p-OC_2H_5	410, 508s	523	403, 496s	513	390	482	377	394	402, 468s
I-6	p-Cl	406	534	403, 524	530	394, 474s	490	375	390	395, 484s
I-7	p-COOH	413	531	408, 523	525	400	493	389	397	391, 491s
I-8	p-$COCH_3$	417, 560	573	413, 569	572	405	525	394	402	421, 516
I-9	p-CN	425, 570	571	416, 562	568	410	521	396	405	432s, 520
I-10	p-NO_2	445	636	433, 633	634	478	550	396, 546	414, 515s	541

s: shoulder.

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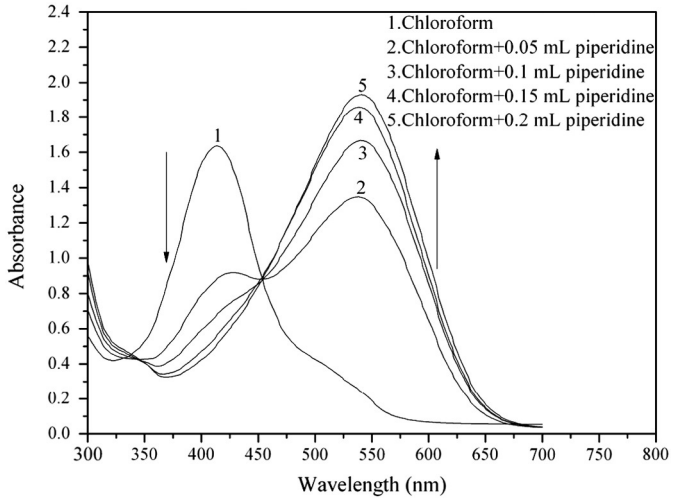

Fig. 12. Absorption spectra of dye **I-10** in chloroform and in addition of piperidine (0.05–0.2 mL).

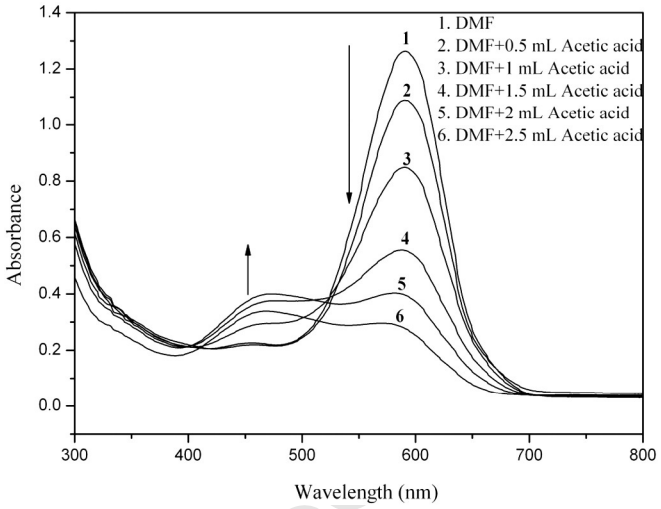

Fig. 13. Absorption spectra of dye **II-3** in DMF and in addition of acetic acid solvents (0.5–2.5 mL).

wavelength converts to shoulder. Finally, this shoulder disappeared and the absorption maximum at long wavelength appeared at 541 nm (Fig. 12). This result showed that the dye **I-10** exists predominantly one tautomeric form (azo or hydrazone) in chloroform and common anion form in basic chloroform solution.

Similarly, when 0.1 mL KOH was added to methanolic solutions of the phenylazo-8-hydroxyquinoline dyes, the absorption maxima of the dyes shifts bathochromically (for dye **I-1** $\Delta\lambda_{max} = 95$ nm, for dye **I-8** $\Delta\lambda_{max} = 120$ nm relative to their methanolic solution). These bands are assigned to anionic form. On the other hand, λ_{max} values of the dyes in methanol showed small hypsochromic shifts when 0.1 M HCl was added (for dyes **I-1** and **I-6** $\Delta\lambda_{max} = 19$ nm, for dye **I-2** $\Delta\lambda_{max} = 20$ nm and for dye **I-4** $\Delta\lambda_{max} = 22$ nm). These data indicate that the phenylazo-8-hydroxyquinolines may be converted into a cationic form or the other tautomeric forms in acidic medium.

The effects of the acid and base on the absorption maxima of the heteroarylazo-8-hydroxyquinolines were also investigated and the results are shown in Table 4. There was a significant change in the spectra of the dyes **II-1**, **II-2**, **II-4**, **II 8–10** and **II-12** when a small amount of piperidine was added to their solutions in DMSO. The absorption spectra of the other dyes didn't exhibit significant change. Similar effects were observed when the addition of piperidine to their solutions in DMF except of dyes **II-1**, **II-2**, **II-4** and **II-12**. This indicates that some heteroarylazo-8-hydroxyquinolines exist in partial or full dissociated state in DMSO and DMF. For example, the absorption spectra of dye **II-3** didn't change with the addition of piperidine to its solutions in DMSO and DMF and therefore it assigned to anionic form in DMSO and DMF. In addition, the absorption band of this dye shifted hypsochromically and two absorption bands appeared with the addition of acetic acid to its DMF solution. When 2.5 mL acetic acid was gradually added to the dye solution in DMF, two absorption maxima were observed (Fig. 13). This absorption curve is similar to the ones in acetic acid. These results show that the dye **II-3** exists in anionic form in DMF ($\lambda_{max} = 591$ nm) and in both tautomeric forms in acetic acid ($\lambda_{max} = 457, 542$ nm).

The absorption bands of heteroarylazo dyes prepared in chloroform are sensitive to the addition of piperidine and the absorption maxima of the dyes shift to bathochromic. Two absorption maxima (for dye **II-5**), one absorption maximum with a shoulder (for dye **II-2**) or one absorption maximum (for dyes **II-1**, **II-3**, **4** and **II 6–12**) appeared with the addition of piperidine in chloroform solution. The longest wavelength absorption maximum is attributed to the anionic form. Similar effects were observed when a small amount of 0.1 M KOH was added to methanolic solutions of the dyes. In the case of dyes **II-1** and **II-4**, the addition of 0.1 M KOH to their methanolic solution, maximum (dyes **II-1** and **II-4**) at the shorter wavelength disappeared. λ_{max} value at the longest wavelength did not significantly change for dye **II-4**. But the absorption maximum of dye **II-1** at longer wavelength shifts to bathochromic. The other dyes showed one absorption maximum at long wavelength in basic methanolic solution. When 0.1 M HCl was added to methanolic solutions of the dyes, λ_{max} values of the dyes showed hypsochromic shifts except of **II 1**, **2**, **II-9**, **II-11** and **II-12**. The

Table 4
Absorption maxima of heteroarylazoquinoline dyes **II** (**1–12**) in acidic and basic solution.

	λ_{max} (nm)									
Dye no.	Q	DMSO	DMSO + piperidine	DMF	DMF + piperidine	Methanol	Methanol + KOH	Methanol + HCl	Chloroform	Chloroform + piperidine
II-1	Thiazole	443	562	445s, 556	556	434, 517s	542	423, 548	428	535
II-2	5-Methylthiazole	448, 563	564	444, 557	560	439	544	434, 564s	436	446s, 535
II-3	5-(4-Nitrophenyl sulfonyl)thiazole	593	592	591	589	581	581	430	491,589 s	594
II-4	4-Ethylthiazolacetate	432s, 565	565	434s, 562	562	444, 544	547	431, 557s	438	540
II-5	4-Phenylthiazole	570, 732	574, 722	565, 721	570, 727	539	547	431, 540s	516	534, 695
II-6	4-(4-chlorophenyl)thiazole	569, 737	571	566, 731	567, 735	550	553	469	456	540
II-7	4-(4-Bromophenyl)thiazole	570, 739	572	567, 740	567, 736	552, 741	553	458	462	547
II-8	Benzothiazole	489, 572s	566	562	561	444s, 552	561	538	442	552
II-9	6-Chlorobenzothiazole	461s, 564	566	564	563	464, 568s	564	444, 525	450	563
II-10	6-Methoxybenzothiazole	506	573	570	569	518	563	472	461	557
II-11	5,6-Dimethylbenzothiazole	570	572	569	568	492	563	455, 551	456	557
II-12	Benzimidazole	430s, 558	559	427s, 555	556	430s, 526	532	462, 552	437	528

s: shoulder.

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dyes **II-9**, **II-11** and **II-12** have two absorption maxima with the addition of HCl to methanolic solution. It can be suggested that these dyes exist in the mixture of azo and hydrazone forms in acidic methanolic solution. On the other hand, the charged transfer band of dye **II-7** disappeared with the addition of HCl to methanolic solution of the dye. At the same time the absorption maximum of this dye at 552 nm shifts to 458 nm. The absorption spectra of **II-7** in methanolic HCl solution, being nearly the same as those observed in acetic acid and chloroform. The results indicate that heteroarylazo-8-hydroxyquinoline dyes may exist as one tautomeric form or mixture of two tautomeric forms in acidic methanolic solution.

2.2. Substituent effect on absorption spectra of dyes in various solvents

It is well known that λ_{max} values of dyes tend to be related to the electronic effects in chromophoric system. The bathochromic shifts can be obtained by enhancing the electron acceptor properties of the diazo component. In our obtained results, this bathochromic shifts was seen by enhancing the electron acceptor properties of substituents (Table 1). In the carbocyclic series, the introduction of electron-accepting substituents, such as NO_2, CN, $COCH_3$ and COOH in the para position of the phenyl ring results in a significant bathochromic shifts according to unsubstituted analog (for dye **I-7** $\Delta\lambda_{max} = 15$ nm, for dye **I-8** $\Delta\lambda_{max} = 20$ nm, for dye **I-9** $\Delta\lambda_{max} = 25$ nm and for dye **I-10** $\Delta\lambda_{max} = 93$ nm in methanol relative to dye **I-1**). Similarly, with the introduction of electron-donating substituents such as CH_3, OC_2H_5 at the para position into phenyl ring, absorption maxima shift bathochromically according to unsubstituted analogs (for dye **I-5** $\Delta\lambda_{max} = 14$ nm in DMSO, $\Delta\lambda_{max} = 10$ nm in chloroform, $\Delta\lambda_{max} = 8$ nm in acetonitrile relative to dye **I-1**; for dye **I-2** $\Delta\lambda_{max} = 1$ nm in DMSO, $\Delta\lambda_{max} = 3$ nm in methanol, $\Delta\lambda_{max} = 2$ nm in chloroform, relative to dye **I-1**). On the other hand, the introduction of electron-donating or electron-accepting substituents at the para position into phenyl ring, one absorption maximum was observed in chloroform except p-NO_2 derivative. This shows that, these dyes exist predominantly in one tautomeric form (azo) in chloroform. These results are in agreement with those obtained for 4-phenylazo-1-naphthol and 5-phenylazo-8-hydroxyquinolines [6,55,57,58]. In addition, the introduction of electron-accepting substituents into phenyl ring caused the absorption maxima of the dyes to shift more bathochromically than electron-donating substituted dyes.

In the heterocyclic series, the introduction of 4-nitrophenylsulfonyl group into the thiazole ring at the 5-position gives the largest bathochromic shift compared with the other heteroarylazo-8-hydroxyquinoline dyes in all solvents used (for dye **II-3** $\Delta\lambda_{max} = 150$ nm in DMSO, $\Delta\lambda_{max} = 63$ nm in chloroform, $\Delta\lambda_{max} = 34$ nm in acetonitrile relative to dye **II-1**; $\Delta\lambda_{max} = 23$ nm in DMSO, $\Delta\lambda_{max} = 26$ nm in DMF, $\Delta\lambda_{max} = 42$ nm in methanol, relative to dye **II-5**). On the other hand, the presence of a phenyl substituent in the 4-position of the thiazole ring gives rise to a bathochromic shift relative to thiazole (**II-1**) and 4-ethylthiazolacetate (**II-4**) in all solvents used (for dye **II-5** $\Delta\lambda_{max} = 127$ nm in DMSO, $\Delta\lambda_{max} = 88$ nm in chloroform, $\Delta\lambda_{max} = 66$ nm in acetic acid relative to dye **II-1**; $\Delta\lambda_{max} = 5$ nm in DMSO, $\Delta\lambda_{max} = 60$ nm in acetic acid, $\Delta\lambda_{max} = 78$ nm in chloroform, relative to dye **II-4**). In addition, the dyes **II 5–7** showed intramolecular CT band at the NIR (for dye **II-7** $\lambda_{max} = 741$ nm in methanol, 733 nm in acetonitrile, 740 nm in DMF and 739 in DMSO) in methanol, acetonitrile, DMSO and DMF due to π-donating properties of phenyl substituent. The introduction of electron-donating and accepting substituents into benzothiazole ring, absorption maxima shift to bathochromic in chloroform and acetic acid but in the other solvents did not significantly change (for dye **II-9** $\Delta\lambda_{max} = 2$ nm in DMF, $\Delta\lambda_{max} = 8$ nm in chloroform, $\Delta\lambda_{max} = 8$ nm in acetic acid relative to dye **II-8**, for dye **II-10** $\Delta\lambda_{max} = 8$ nm in DMF, $\Delta\lambda_{max} = 19$ nm in chloroform, $\Delta\lambda_{max} = 25$ nm in acetic acid relative to dye **II-8**).

3. Experimental

3.1. General

The chemicals used in the synthesis of all compounds were purchased from Sigma-Aldrich Chemical Company and used without further purification. The solvents used were of spectroscopic grade. IR spectra were recorded on a Mattson 1000 FT-IR spectrophotometer in KBr (ν are in cm^{-1}). ^1H NMR spectra were recorded on a Bruker-Spectrospin Avance DPX 400 Ultra-Shield in DMSO-d_6. Chemical shifts are expressed in δ units (ppm). Ultraviolet–visible (UV–vis) absorption spectra were recorded on a Analytik Jena Specord 200 spectrophotometer at the wavelength of maximum absorption (λ_{max}, in nm) in the solvents specified. λ_{max} values of the dyes were investigated when 0.1 mL piperidine was added to 1 mL of dye solutions in DMSO and DMF. The methanolic solutions of the dyes were examined, when 0.1 mL KOH (0.1 M) or 0.1 mL HCl to 1 mL of the dye solutions was added. In addition, λ_{max} was investigated when the solution of dyes in DMSO and DMF was examined over the temperature range 25–70 °C.

Elemental analyses were recorded on LECO CHNS 932 by Turkish Research Council Laboratories (Center of Science and Technology Research of Turkey). Mass spectra were recorded on an Agilent 5973 Network Mass Selective Detector, SIS (Direct Insertion Probe) and AGILENT 1100 MSD (electron impact 70 and 100 eV).

3.2. Crystallography

The X-ray diffraction data collection was performed on a Bruker-AXS SMART CCD Detector diffractometer equipped with MoK\a (λ = 0.71073 Å) radiation using w-scans. The intensity data were corrected for Lorentz polarization [60] and absorption [61] effects. The structure was analyzed by Crystal Maker 3D data visualization program. Crystallographic data are obtained from the Cambridge Crystallographic Data Centre with CCDC 725346.

3.3. Preparation of phenylazo-8-hydroxyquinoline dyes (*I 1–9*)

2 mmol carbocyclic amine was dissolved in HCl (1.5 mL) and water (4 mL). The solution was cooled in an ice-salt bath and a cold solution of $NaNO_2$ (0.15 g, 2 mmol) in water (3.0 mL) was added dropwise with stirring. The resulting diazonium salt was also cooled in an ice-salt bath. Excess nitrous acid was destroyed by the addition of urea. And then added dropwise with stirring to 8-hydroxyquinoline (0.29 g, 2 mmol) in KOH, cooled in an ice-salt bath. The solution was stirred at 0–5 °C for 1 h and the pH of the reaction mixture was maintained at 4–6 by the simultaneous addition of saturated sodium acetate solution (15–20 mL). The mixtures were stirred for further 1 h. The resulting solid was filtered off, washed with cold water and dried. The obtained compounds were purified by crystallization using ethanol and then analyzed. The yields of the dyes are in the range of 75–85%. Characterization data are below.

3.3.1. Preparation of 5-(phenyldiazenyl)-8-hydroxyquinoline (*I-1*)

This dye was obtained from aniline and 8-hydroxyquinoline as yellow crystalline (yield: 0.39 g, 78%; m.p. 186–187 °C, lit: 182–183 °C [40]; 185–185.5 °C [50]). IR(KBr): ν_{max}: 3409–3147 (quinoline OH), 3063 (aromatic CH), 1580, 1510 (C=C), 1240 (C–O) cm^{-1}; ^1H NMR (DMSO-d_6/$CDCl_3$): δ 9.40 (d,1H), 8.95 (d,1H), 8.10 (d,1H), 7.95 (d,2H), 7.70 (m,1H), 7.55 (m,2H), 7.50 (m,1H), 7.30 (d,1H). Anal. calcd. for $C_{15}H_{11}N_3O$ (249.27): C, 72.28; H, 4.45; N, 16.86. Found C, 71.97; H, 4.59; N, 16.76.

MS: (m/z, 100 eV): 250 $(M + 1)^+$, 172, 144.

3.3.2. Preparation of 5-(4-methylphenyldiazenyl)-8-hydroxyquinoline (*I-2*)

This dye was obtained from 4-aminotoluidine and 8-hydroxyquinoline as yellow crystals (yield: 0.39 g, 75%; m.p: 188–

189 °C, lit: 188–189 °C [40]). IR (KBr): ν_{max}: 3435–3242 (quinoline OH), 3063 (aromatic CH), 2960 (aliphatic CH), 1573, 1510 (C═C), 1227 (C–O) cm^{-1}; ^1H NMR (DMSO-d_6): δ 10.80 (br, OH), 9.30 (d,1H), 9.00 (d,1H), 8.00 (d,1H), 7.90 (d,2H), 7.80 (m,1H), 7.40 (d,2H), 7.20 (d,1H), 2.40 (s,3H)). Anal. calcd. for $C_{16}H_{13}N_3O$ (263.29): C, 72.99; H, 4.98; N, 15.96. Found C, 72.97; H, 4.84; N, 16.05.

MS: (m/z, 70 eV): 264 $(M+1)^+$, 263 (M^+), 179, 146.

*3.3.3. Preparation of 5-(4-phenoxyphenyldiazenyl)-8-hydroxyquinoline (**I-3**)*

This dye was obtained from 4-phenoxyaniline and 8-hydroxyquinoline as orange powder (yield: 0.58 g, 85%; m.p: 156–157 °C). IR (KBr): ν_{max}: 3268 (quinoline OH), 3056 (aromatic CH), 1573, 1510 (C═C), 1240 (C–O) cm^{-1}; ^1H NMR (DMSO-d_6): δ 9.20 (d,1H), 8.90 (d,1H), 8.00 (d,2H), 7.90 (d,1H), 7.70 (m,1H), 7.40 (m,2H), 7.20–7.00 (m,6H)). Anal. calcd. for $C_{21}H_{15}N_3O_2$ (341.36): C, 73.89; H, 4.43; N, 12.31. Found C, 74.04; H, 4.40; N, 12.41.

MS: (m/z, 100 eV): 342 $(M+1)^+$, 172, 144.

*3.3.4. Preparation of 5-(4-acetamidophenyldiazenyl)-8-hydroxyquinoline (**I-4**)*

This dye was obtained from 4-acetamidoaniline and 8-hydroxyquinoline as orange powder (yield: 0.48 g, 78%; m.p: 265–266 °C). IR (KBr): ν_{max}: 3275 (acetamido NH), 3070 (aromatic CH), 2960 (aliphatic CH), 1696, 1670, 1592, 1510 (C═C), 1240 (C–O) cm^{-1}; ^1H NMR (DMSO-d_6/$CDCl_3$): δ 9.70 (b, NH-$COCH_3$), 9.30 (d,1H), 8.90 (d,1H), 8.00 (d,1H), 7.90 (d,2H), 7.80 (d,2H), 7.60 (m,1H), 7.20 (d,1H), 2.20 (s,3H). Anal. calcd. for $C_{17}H_{14}N_4O_2$ (306.32): C, 66.66; H, 4.61; N, 18.29. Found C, 66.70; H, 4.58; N, 18.47.

MS: (m/z, 100 eV): 307 $(M+1)^+$, 263, 146.

*3.3.5. Preparation of 5-(4-ethoxyphenyldiazenyl)-8-hydroxyquinoline (**I-5**)*

This dye was obtained from 4-ethoxyaniline and 8-hydroxyquinoline as red powder (yield: 0.45 g, 85%; m.p: 182–183 °C, lit: 180–181 °C [40]). IR (KBr): ν_{max}: 3275 (quinoline OH), 3075 (aromatic CH), 2979, 2928 (aliphatic CH), 1606, 1573, 1510 (C═C), 1246 (C–O) cm^{-1}; ^1H NMR (DMSO-d_6): δ 9.30 (d,1H), 9.00 (d,1H), 8.00 (d,2H), 7.90 (d,1H), 7.70 (m,1H), 7.20 (d,1H), 7.10 (d,2H), 4.20 (q,2H), 1.40 (t,3H). Anal. calcd. for $C_{17}H_{15}N_3O_2$ (293.32): C, 69.61; H, 5.15; N, 14.33. Found C, 69.66; H, 5.28; N, 14.53.

MS: (m/z, 100 eV): 294 $(M+1)^+$, 279, 145.

*3.3.6. Preparation of 5-(4-chlorophenyldiazenyl)-8-hydroxyquinoline (**I-6**)*

This dye was obtained from 4-chloroaniline and 8-hydroxyquinoline as yellow powder (yield: 0.46 g, 81%; m.p: 229–230 °C, lit: 220–221 °C [39]). IR (KBr): ν_{max}: 3268 (quinoline OH), 3056 (aromatic CH), 1573, 1510 (C═C), 1234 (C–O) cm^{-1}; ^1H NMR (DMSO-d_6): δ 10.80 (br, quinoline OH), 9.30 (d,1H), 9.00 (d,1H), 8.10 (dd,3H), 7.80 (m,1H), 7.60 (d,2H), 7.25 (d,1H). Anal. calcd. for $C_{15}H_{10}ClN_3O$ (283.71): C, 63.50; H, 3.55; N, 14.81. Found C, 63.27; H, 3.46; N, 14.77.

MS: (m/z, 70 eV): 283 (M^+), 172, 144.

*3.3.7. Preparation of 5-(4-carboxyphenyldiazenyl)-8-hydroxyquinoline (**I-7**)*

This dye was obtained from 4-aminobenzoic acid and 8-hydroxyquinoline as red powder (yield: 0.47 g, 80%; m.p: 281–282 °C). IR (KBr): ν_{max}: 3210–2530 (COOH, OH), 3056 (aromatic CH), 1689 (C═O), 1573, 1606, 1510 (C═C), 1246 (C–O) cm^{-1}; ^1H NMR (DMSO-d_6/$CDCl_3$): δ 12.50 (br, COOH), 9.30 (d,1H), 8.90 (d,1H), 8.20 (d,2H), 8.10 (d,1H), 8.00 (d,2H), 7.70 (m,1H), 7.30 (d,1H). Anal. calcd. for $C_{16}H_{11}N_3O_3$ (293.28): C, 65.53; H, 3.73; N, 14.33. Found C, 65.46; H, 3.70; N, 14.26.

MS: (m/z, 70 eV): 293 (M^+), 172, 144.

*3.3.8. Preparation of 5-(4-acetylphenyldiazenyl)-8-hydroxyquinoline (**I-8**)*

This dye was obtained from 4-aminoacetophenone and 8-hydroxyquinoline as orange powder (yield: 0.49 g, 85%; m.p: 228–229 °C). IR (KBr): ν_{max}: 3281 (quinoline OH), 3050 (aromatic CH), 2979, 2928 (aliphatic CH), 1676 (C═O), 1573, 1510 (C═C), 1227 (C–O) cm^{-1}; ^1H NMR (DMSO-d_6): δ 9.20 (d,1H), 8.90 (d,1H), 8.07 (d,2H), 7.90–8.00 (m,3H), 7.70 (m,1H), 7.10 (d,1H), 2.57 (s,3H). Anal. calcd. for $C_{17}H_{13}N_3O_2$ (291.3): C, 70.09; H, 4.50; N, 14.42. Found C, 69.98; H, 4.52; N, 14.35.

MS: (m/z, 70 eV): 291 (M^+), 292 $(M+1)^+$, 146.

*3.3.9. Preparation of 5-(4-cyanophenyldiazenyl)-8-hydroxyquinoline (**I-9**)*

This dye was obtained from 4-cyanoaniline and 8-hydroxyquinoline as orange powder (yield: 0.44 g, 80%; m.p: 261–262 °C). IR (KBr): ν_{max}: 3256 (quinoline OH), 3063 (aromatic CH), 2222 (C ≡ N), 1573, 1510 (C═C), 1234 (C–O) cm^{-1}; ^1H NMR (DMSO-d_6): δ 9.20 (d,1H), 8.90 (d,1H), 7.90–8.05 (m,5H), 7.70 (m,1H), 7.10 (d,1H). Anal. calcd. for $C_{16}H_{10}N_4O$ (274.28): C, 70.06; H, 3.67; N, 20.43. Found C, 69.94; H, 3.60; N, 20.36.

MS: (m/z, 100 eV): 275 $(M+1)^+$, 145.

*3.3.10. Preparation of 5-(4-nitrophenyldiazenyl)-8-hydroxyquinoline (**I-10**)*

This dye was obtained from 4-nitroaniline and 8-hydroxyquinoline as violet powder (yield: 0.49 g, 83%; m.p: 274–275 °C). IR (KBr): ν_{max}: 3433 (quinoline OH), 3077 (aromatic CH), 1560, 1539 (C═C), 1217 (C–O) cm^{-1}; ^1H NMR (DMSO-d_6/$CDCl_3$): δ 9.30 (d,1H), 8.95 (d,1H), 8.45 (d,2H), 8.20 (d,1H), 8.10 (d,2H), 7.80 (m,1H), 7.15 (d,1H). Anal. calcd. for $C_{15}H_{10}N_4O_3$ (294.26): C, 61.22; H, 3.43; N, 19.04. Found C, 61.18; H, 3.35; N, 18.97.

MS: (m/z, 100 eV): 294 $(M)^+$, 145.

*3.4. Preparation of heteroarylazo-8-hydroxyquinoline dyes (**II 1–12**)*

2 mmol heterocyclic amines were dissolved in hot glacial acetic acid–propionic acid mixture (2:1, 6.0 mL) and was rapidly cooled in an ice-salt bath to −5 °C. The liquor was then added in portions during 30 min to a cold solution of nitrosyl sulfuric acid (prepared from sodium nitrite (0.15 g) and concentrated sulfuric acid, 98% (3 mL at 50 °C)). The mixture was stirred for an additional 2 h at 0 °C. Excess nitrous acid was destroyed by the addition of urea. The resulting diazonium salt was cooled in ice–salt bath. After diazotization was complete the azo liquor was slowly added to vigorously stirred solution of 8-hydroxyquinoline (2 mmol, 0.29 g) in potassium hydroxide (2.0×10^{-3} mol, 0.112 g) and water (2 mL). The solution was stirred at 0–5 °C for 2 h. After that the pH of the reaction mixture was maintained at 4–6 by the simultaneous addition of saturated sodium carbonate solution. The mixture was stirred for 1 day at room temperature. The resulting solid was filtered, washed with cold water and dried. The obtained compounds were purified by crystallization using ethanol and then analyzed. The yields of the dyes are in range of 54–78%. Characterization data are shown below.

*3.4.1. Preparation of 5-(thiazol-2-yldiazenyl)-8-hydroxyquinoline (**II-1**)*

This dye was obtained from 2-aminothiazole and 8-hydroxyquinoline as dark violet claret brown powder (yield: 0.29 g, 56%; m.p: 155–156 °C). IR(KBr): ν_{max}: 3448 (quinoline OH), 3070 (aromatic CH), 1573, 1510 (C═C), 1214 (C–O) cm^{-1}; ^1H NMR (DMSO-d_6/$CDCl_3$): δ 9.28 (d,1H), 8.94 (dd,1H), 8.28 (d,1H), 8.00 (d,1H), 7.70 (m,1H), 7.45 (d,1H), 7.35 (d,1H). Anal. calcd. for $C_{12}H_8N_4OS$ (256.28): C, 56.24; H, 3.15; N, 21.86; S, 12.51. Found C, 56.27; H, 3.28; N, 21.87; S, 12.80.

MS: (m/z, 70 eV): 256 (M^+), 144.

*3.4.2. Preparation of 5-(5-methylthiazol-2-yldiazenyl)-8-hydroxyquinoline (**II-2**)*

This dye was obtained from 2-amino-5-methylthiazole and 8-hydroxyquinoline as dark violet crystals (yield: 0.32 g, 60%; m.p: 232–233 °C). IR (KBr): ν_{max}: 3416–3268 (quinoline OH), 3070 (aromatic CH), 2928, 2870 (aliphatic CH), 1573, 1510 (C═C), 1208 (C–O) cm^{-1}; ^1H NMR (DMSO-d_6): δ 9.10 (d,1H), 9.00 (d,1H),

8.10 (d,1H), 7.80 (m,2H), 7.30 (d,1H), 2,55 (s,3H). Anal. calcd. for $C_{13}H_{10}N_4OS$ (270.31): C, 57.76; H, 3.73; N, 20.73; S, 11.86. Found C, 57.68; H, 3.68; N, 20.71; S, 11.48.

MS: (m/z, 70 eV): 270 (M^+), 144.

3.4.3. Preparation of 5-[5-(4-nitrophenylsulfonyl)thiazol-2-yldiazenyl]-8-hydroxyquinoline (**II-3**)

This dye was obtained from 2-amino-5-(4-nitrophenylsulfonyl) thiazole and 8-hydroxyquinoline as dark brown powder (yield: 0.64 g, 72%; m.p: 246–247 °C). IR (KBr): ν_{max}: 3416 (quinoline OH), 3070 (aromatic CH), 1535, 1490 (C═C), 1252 (C–O) cm^{-1}; ^1H NMR (DMSO-d_6/$CDCl_3$): δ 9.20 (d,1H), 8.90 (d,1H), 8.50 (s,1H), 8.40 (d,2H), 8.30 (d,2H), 8.10 (d,1H), 7.90 (m, 1H), 7.00 (d,1H).). Anal. calcd. for $C_{18}H_{11}N_5O_5S_2$ (441.44): C, 48.97; H, 2.51; N, 15.86; S, 14.53. Found C, 48.65; H, 2.42; N, 15.57; S, 14.35.

MS: (m/z, 70 eV): 442 $(M + 1)^+$, 146.

3.4.4. Preparation of ethyl[2-(8-hydroxyquinoline-5-yldiazenyl)-1,3-thiazol-4-yl]acetate (**II-4**)

This dye was obtained from 2-amino-4-ethylthiazoleacetate and 8-hydroxyquinoline as dark brown powder (yield: 0.54 g, 64%; m.p: 145–146 °C). IR (KBr): ν_{max}: 3377–3133 (quinoline OH), 3050 (aromatic CH), 2986, 2877 (aliphatic CH), 1740 (C═O), 1573, 1510 (C═C), 1227 (C–O) cm^{-1}; ^1H NMR (DMSO-d_6): δ 9.20 (d,1H), 9.05 (d,1H), 8.20 (d,1H), 7.70 (m,1H), 7.60 (s,1H), 7.20 (d,1H), 4.20 (q,2H), 3.90 (s, 2H), 1.80 (t, 3H).). Anal. calcd. for $C_{16}H_{14}N_4O_3S$ (328.35): C, 56.13; H, 4.12; N, 16.36; S, 9.37. Found C, 55.99; H, 4.08; N, 16.38; S, 9.49.

MS: (m/z, 100 eV): 343 $(M + 1)^+$, 342 $(M)^+$, 172, 144.

3.4.5. Preparation of 5-(4-phenylthiazol-2-yldiazenyl)-8-hydroxyquinoline (**II-5**)

This dye was obtained from 2-amino-4-phenylthiazole and 8-hydroxyquinoline as dark brown powder (yield: 0.45 g, 68%; m.p: 218–219 °C). IR (KBr): ν_{max}: 3486–3056 (quinoline OH), 3040 (aromatic CH), 1650, 1522 (C═C), 1271 (C–O) cm^{-1}; ^1H NMR (DMSO-d_6): δ 9.37 (br, quinoline OH), 9.18 (d,1H), 9.04 (d,1H), 8.25 (d,1H), 7.98 (d,1H), 7.85 (m,1H), 7.63–7.45 (m,6H), 7.30 (d,1H).). Anal. calcd. for $C_{18}H_{12}N_4OS$ (332.38): C, 65.04; H, 3.64; N, 16.86; S, 9.65. Found C, 64.97; H, 3.56; N, 16.88; S, 9.66.

MS: (m/z, 100 eV): 333 $(M + 1)^+$, 172, 144.

3.4.6. Preparation of 5-[4-(4-chlorophenyl)thiazol-2-yldiazenyl]-8-hydroxyquinoline (**II-6**)

This dye was obtained from 2-amino-4-(4-chlorophenyl)thiazole and 8-hydroxyquinoline as dark brown powder (yield: 0.55 g, 75%; m.p: 203–205 °C). IR (KBr): ν_{max}: 3428–3075 (quinoline OH), 3045 (aromatic CH), 1592, 1510 (C═C), 1240 (C–O) cm^{-1}; ^1H NMR (DMSO-d_6): δ 9.20 (d,1H), 9.03 (d,1H), 8.35 (d,1H), 8.08 (s,1H), 7.86 (m,1H), 7.64 (d,2H), 7.53 (d,2H), 7.30 (d,1H).). Anal. calcd. for $C_{18}H_{11}ClN_4OS$ (366.82): C, 58.94; H, 3.02; N, 15.27; S, 8.74. Found C, 58.65; H, 2.96; N, 15.15; S, 8.57.

MS: (m/z, 100 eV): 367 $(M + 1)^+$, 172, 144.

3.4.7. Preparation of 5-[4-(4-bromophenyl)thiazol-2-yldiazenyl]-8-hydroxyquinoline (**II-7**)

This dye was obtained from 2-amino-4-(4-bromophenyl)thiazole and 8-hydroxyquinoline as dark brown powder (yield: 0.64 g, 78%; m.p: 227–228 °C). IR (KBr): ν_{max}: 3448–3095 (quinoline OH), 3056 (aromatic CH), 1592, 1510 (C═C), 1240 (C–O) cm^{-1}; ^1H NMR(DMSO-d_6/$CDCl_3$): δ 9.20 (m,1H), 9.04 (d,1H), 8.15 (d,1H), 8.08 (s,1H), 7.95 (d,2H), 7.65 (d,2H), 7.85 (m,1H), 7.30 (d,1H).). Anal. calcd. for $C_{18}H_{11}BrN_4OS$ (411.28): C, 52.57; H, 2.70; N, 13.62; S, 7.80. Found C, 52.45; H, 2.65; N, 13.46; S, 7.76.

MS: (m/z, 100 eV): 410 $(M-1)^+$, 172, 144.

3.4.8. Preparation of 5-(benzothiazol-2-yldiazenyl)-8-hydroxyquinoline (**II-8**)

This dye was obtained from 2-aminobenzothiazole and 8-hydroxyquinoline as claret red powder (yield: 0.35 g, 57%; m.p: 191–192 °C, lit: 238–240 °C [49]). IR (KBr): ν_{max}: 3288–3089 (quinoline OH), 3050 (aromatic CH), 1567, 1510 (C═C), 1227 (C–O) cm^{-1}; ^1H NMR (DMSO-d_6): δ 8.74 (dd,1H), 8.14 (dd,1H), 8.10 (d,1H), 7.40 (m,3H), 7.28 (d,2H), 7.10 (d,1H). Anal. calcd. for $C_{16}H_{10}N_4OS$ (306.34): C, 62.73; H, 3.29; N, 18.29; S, 10.47. Found C, 62.65; H, 3.31; N, 18.18; S, 10.34.

MS: (m/z, 70 eV): 306 $(M)^+$, 144.

3.4.9. Preparation of 5-(6-chlorobenzothiazol-2-yldiazenyl)-8-hydroxyquinoline (**II-9**)

This dye was obtained from 2-amino-6-chlorobenzothiazole and 8-hydroxyquinoline as brown powder (yield: 0.37 g, 54%; m.p: 267–268 °C). IR (KBr): ν_{max}: 3428–3191 (quinoline OH), 3063 (aromatic CH), 1567, 1510 (C═C), 1246 (C–O) cm^{-1}; ^1H NMR (DMSO-d_6/$CDCl_3$): δ 9.20 (d,1H), 8.90 (d,1H), 8.25 (d,1H), 7.90–7.80 (m,3H), 7.65 (m,1H), 7.15 (d,1H). Anal. calcd. for $C_{16}H_9ClN_4OS$ (340.79): C, 56.39; H, 2.66; N, 16.44; S, 9.41. Found C, 56.25; H, 2.71; N, 16.42; S, 9.26.

MS: (m/z, 100 eV): 341 $(M + 1)^+$, 172, 144.

3.4.10. Preparation of 5-(6-methoxybenzothiazol-2-yldiazenyl)-8-hydroxyquinoline (**II-10**)

This dye was obtained from 2-amino-6-methoxybenzothiazole and 8-hydroxyquinoline as greenish yellow powder (yield: 0.42 g 63%; m.p: 250–251 °C). IR (KBr): ν_{max}: 3050 (aromatic CH), 2940 (aliphatic CH), 1567, 1510 (C═C), 1227 (C–O) cm^{-1}; ^1H NMR (DMSO-d_6/$CDCl_3$): δ 9.25 (d,1H), 8.75 (d,1H), 8.30 (dd,1H), 8.00 (br, quinoline OH), 7.70 (m,1H), 7.44 (s,1H), 7.40 (d,1H), 7.30 (d,1H), 7.10 (d,1H), 3.90 (s,3H). Anal. calcd. for $C_{17}H_{12}N_4O_2S$ (336.37): C, 60.70; H, 3.60; N, 16.66; S, 9.53. Found C, 60.55; H, 3.61; N, 16.35; S, 9.38.

MS: (m/z, 100 eV): 337 $(M + 1)^+$, 144.

3.4.11. Preparation of 5-(5,6-dimethylbenzothiazol-2-yldiazenyl)-8-hydroxyquinoline (**II-11**)

This dye was obtained from 2-amino-5,6-dimethylbenzothiazole and 8-hydroxyquinoline as claret red powder (yield: 0.36 g, 54%; m.p: 264–265 °C). IR (KBr): ν_{max}: 3288 (quinoline OH), 3050 (aromatic CH), 2921, 2851 (aliphatic CH), 1573, 1510 (C═C), 1234 (C–O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 9.25 (d,1H), 8.85 (d,1H), 8.28 (d,1H), 7.85 (s,1H), 7.62 (m,1H), 7.57 (s,1H), 7.24 (d,1H), 2.33 (s,6H). Anal. calcd. for $C_{18}H_{14}N_4OS$ (334.39): C, 64.65; H, 4.22; N, 16.75; S, 9.59. Found C, 64.37; H, 4.18; N, 16.70; S, 9.46.

MS: (m/z, 70 eV): 335 $(M + 1)^+$.

3.4.12. Preparation of 5-(benzimidazol-2-yldiazenyl)-8-hydroxyquinoline (**II-12**)

This dye was obtained from 2-aminobenzimidazole and 8-hydroxyquinoline as dark brown powder (yield: 0.32 g, 56%; m.p: 214–215 °C). IR (KBr): ν_{max}: 3409–3070 (quinoline OH, benzimidazole NH), 3055 (aromatic CH), 1567, 1458 (C═C), 1246 (C–O) cm^{-1}; ^1H NMR (DMSO-d_6): δ 12.32 (br, NH), 8.60 (d,1H), 8.40 (d,1H), 7.74–7.51 (m,4H), 7.30–7.10 (m,3H), 6.80 (s,1H). Anal. calcd. for $C_{16}H_{11}N_5O$ (289.29): C, 66.43; H, 3.83; N, 24.21. Found C, 66.52; H, 3.74; N, 24.18.

MS: (m/z, 100 eV): 290 $(M + 1)^+$, 172, 144.

4. Conclusions

In this study, some new heterocyclic and carbocyclic disperse azo dyes based on 8-hydroxyquinoline have been prepared. The absorption maxima of heteroarylazo-8-hydroxyquinolines shifted more to bathochromic than phenylazo-8-hydroxyquinolines in all solvents used except of dye **I-10**. Heterocyclic based azo disperse dyes showed larger solvatochromic effects than azo-benzene based dyes. The solvent

effects on the absorption spectra of the dyes indicated that the different tautomeric structures were exhibited. On the other hand, all dyes were of pure anionic form or exhibited azo-common anion equilibrium in DMF. It was also observed that the absorption curves of the dyes were very sensitive to acids and bases. The bathochromic shifts were obtained by enhancing the electron acceptor properties of the carbocyclic and heterocyclic diazo components. In addition, the crystal structure of the dye (**II-2**) showed that the dye exists azo structure in solid state due to strong intramolecular H-bond.

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Appendix A. Supplementary material

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as the supplementary publication no. CCDC 725346. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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