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# Synthesis and spectroscopic properties of new hetarylazo 8-hydroxyquinolines from some heterocyclic amines

Aytül Saylam, Zeynel Seferoğlu, Nermin Ertan*

*Gazi University, Faculty of Arts and Science, Department of Chemistry, 06500 Teknikokullar, Ankara, Turkey*

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## Abstract

A series of new heterocyclic disperse azo dyes based on 8-hydroxyquinoline have been prepared. The structures of these dyes were confirmed by UV–vis, FT-IR, $^1$H NMR and LC–MS spectroscopic techniques. Their solvatochromic properties in different solvents were investigated; the dyes are strongly solvent dependent and exhibited azo–common anion equilibrium in DMSO and DMF. The acid and base effects on this equilibrium are also examined. The colour of dyes is discussed with respect to nature of the heterocyclic ring and substituent therein. Absorption maxima of the dyes showed large bathochromic effects in comparison with analogous dyes containing carbocyclic amine residues and also the thiadiazolylazo dyes absorb bathochromically compared with their triazolyl analogues.

*Keywords:* Hetarylazo quinoline dyes; Heterocyclic disperse dyes; Quinoline derivatives; Absorption spectra; Solvent effect; Substituent effect

## 1. Introduction

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 [1]. They have attracted special interest due to their therapeutic properties. On the other hand, quinoline sulphonamides have been used in treatment of cancer, tuberculosis and malaria [2]. Several quinoline derivatives possess chemotherapeutic activity and act as antimaleria and antiallergic agents [3]. They show broad-spectrum efficiency against multiple herpes viruses and they have a potential role for the treatment of a variety of infections [4]. 8-Hydroxquinoline is one of the most important derivatives of quinoline. 8-Hydroxquinoline and its derivatives have high antibacterial activities [5,6]. Some of the 8-hydroxquinoline derivatives and their complexes with transition metals were reported to be active against some bacteria [7]. In addition azo compounds based on 8-hydroxquinoline derivatives play a central role as chelating agents for a large number of metal ions [1,2,5,7–14]. In recent years a number of novel merocyanine dyes have been synthesized which contain the 8-hydroxyquinoline nucleus and these dyes exhibit strong metallochromic behavior against some heavy and transition metal ions [15,16]. Although 8-hydroxyquinoline azo dyes have bacteriostatic action, they have not been indicated of having commercial value as textile dyes [17]. On the other hand, 8-hydroxquinoline azo dyes derived from the sulphonamide derivatives were employed in textile industry. Mordant dyeing with these acid azo dyes showed very good fastness properties on wool and nylon fibers [18]. In addition some 8-hydroxyquinoline and azo derivatives found numerous applications in analytical chemistry as chromophoric and metallochromic indicators [19]. Although many papers described the synthesis and some properties of carbocyclic azo 8-hydroxquinoline dyes [17,19], only few hetarylazo 8-hydroxquinoline compounds were synthesized [14,20–22]. However, the solvatochromic properties of these dyes were not investigated. Therefore in our work, we report here the synthesis of some new hetarylazo 8-hydroxquinoline dyes (**1–9**) using 8-hydroxquinoline as coupling component, and

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* Corresponding author. Tel.: +90 312 2126030x3060; fax: +90 312 2323226.

*E-mail address:* nertan@gazi.edu.tr (N. Ertan).

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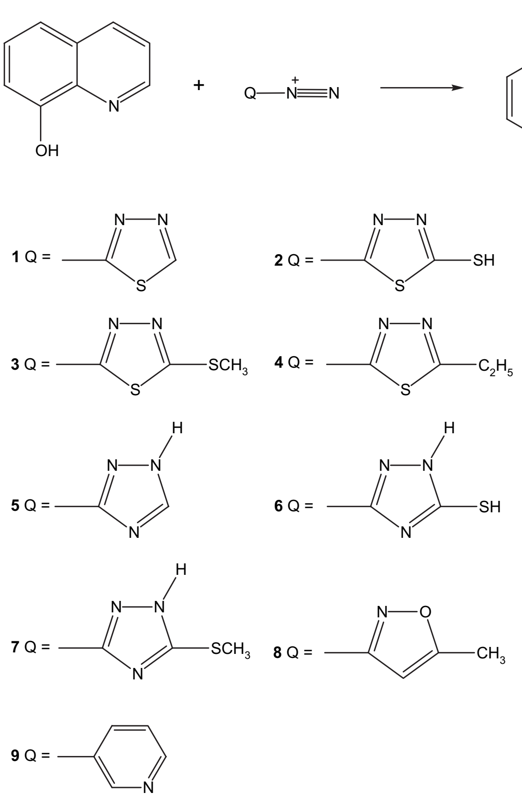
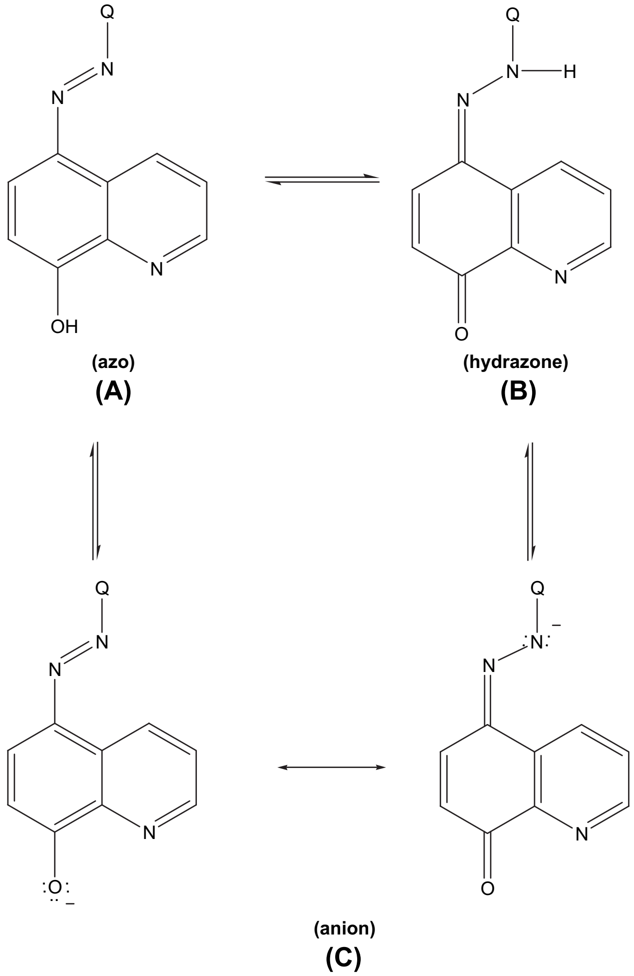
evaluation of their UV–vis absorption spectra with respect to the influence of solvent. The colour of the dyes is discussed with respect to the nature of the heterocyclic ring and substituent therein. The effect of acid and base on UV–vis absorption maxima of the dyes is also reported.

## 2. Results and discussion

The hetarylazoquinoline dyes (**1**–**9**) were prepared by coupling 8-hydroxyquinoline with diazotized 2-aminothiadiazole, 2-amino-5-ethyl-1,3,4-thiadiazole, 5-amino-1,3,4-thiadiazole-2-thiole, 2-amino-5-(methythio)-1,3,4-thiadiazole, 3-amino-1,2,4-triazole, 3-amino-5-mercapto-1,2,4-triazole, 3-amino-5-methythio-1*H*-1,2,4-triazole, 3-amino-5-methylisoxazole and 3-aminopyridine in nitrosyl sulphuric acid (Scheme 1). The structures of dyes prepared have been confirmed by FT-IR, $^1$H NMR and mass spectral data. The dyes prepared from 8-hydroxyquinoline (**1**–**9**) may exist in two possible tautomeric forms, namely azo form **A** and hydrazone **B** as depicted in Scheme 2. The deprotonation of two tautomers leads to common anion **C**.



Scheme 1. Structure of dyes **1**–**9**.



Scheme 2. Azo–hydrazone tautomerism and anionic form of hetarylazo 8-hydroxyquinolines.

The infrared spectra of the all the dyes (**1**–**9**) (in KBr) showed a strong, broad band within the range 3448–3236 cm$^{-1}$, due to intermolecular H-bonding. Recent works suggest that 8-hydroxyquinoline have intramolecular H-bonding [23], but Saylam et al. and La Deda reported the structures of some azoquinoline dyes and pointed out that the azo form existed in the crystal form of the dyes and intermolecular H-bonding in the solid state [13,24,25]. The other $\nu_{max}$ values at 3089–3056 (aromatic C–H) and at 2998–2858 (aliphatic C–H) were recorded.

The $^1$H NMR spectra of aromatic protons of dyes (**1**–**9**) in the 8-hydroxyquinoline ring appeared at $\delta$ 9.50–9.10 doublet, $\delta$ 9.06–8.90 doublet, $\delta$ 8.30–8.10 doublet, $\delta$ 7.90–7.60 multiplet and $\delta$ 7.30–7.20 doublet. The –OH protons of 8-hydroxyquinoline ring were not observed in DMSO-$d_6$ or DMSO-$d_6$ and CDCl$_3$ mixtures [13]. Dye **1** showed a singlet peak at $\delta$ 9.60 for aromatic proton at thiadiazole ring. Dye **2** showed a broad peak at $\delta$ 13.20 for –SH at thiadiazole ring. Dye **3** showed a singlet peak at $\delta$ 2.60 for methylmercapto group at thiadiazole ring. Dye **4** showed quartet peak at $\delta$ 3.10 and triplet peak at $\delta$ 1.40 for ethyl group at thiadiazole ring. Dye **5** showed a singlet peak at $\delta$ 8.20 for aromatic proton at triazole ring. Dye **6** showed broad peak at $\delta$ 15.10 for –NH at triazole ring. Dye **7** showed singlet peak at $\delta$ 2.70 for methylmercapto group at triazole ring. Dye **8** showed singlet peak at $\delta$ 6.40 for aromatic proton at isoxazole ring and singlet peak at $\delta$ 2.50 for methyl group at isoxazole ring. Dye **9** showed singlet peak at $\delta$ 9.10, doublet peak at $\delta$ 8.60 and 8.00, multiplet peak at 7.80 for aromatic protons at pyridine ring.

### 2.1. Solvent effect on absorption spectra of the dyes

Since the tautomeric equilibria strongly depend on the nature of media, the behavior of hetarylazoquinoline dyes in various solvents was studied. For this purpose, the absorption spectra of hetarylazoquinoline dyes (**1–9**) were measured in various solvents at a concentration approximately $10^{-6}$–$10^{-8}$ M and these are run at different concentrations because of solubility problems and the results are given in Table 1. It was found that the absorption maxima of these dyes are strongly solvent dependent and vary with solvent polarity. The dyes show generally bathochromic shifts as the polarity of the solvents is increased. The influence of solvents for the dyes increases in the order DMSO > DMF > acetonitrile ~ methanol > acetic acid > chloroform. The spectral shifts of dyes **2** and **8** in various solvents are shown in Figs. 1 and 2, respectively.

Dye **2** showed absorption maxima at 569 nm in DMSO, 563 nm in DMF, 554 nm in acetonitrile, 555 nm in methanol, 452 nm in acetic acid and 452 nm in chloroform; so dye **2** exhibits significantly larger bathochromic shifts in stronger polar solvents (DMSO and DMF) than the weaker polar solvents (acetic acid and chloroform). The same results were observed in absorption maxima of the dyes prepared (**1–9**) as shown in Table 1. For example, for dye **4**, $\Delta\lambda_{\max} = 123$ nm in DMSO, $\Delta\lambda_{\max} = 121$ nm in DMF, $\Delta\lambda_{\max} = 116$ nm in acetonitrile, $\Delta\lambda_{\max} = 113$ nm in methanol, $\Delta\lambda_{\max} = 2$ nm in acetic acid relative to those in chloroform.

Heterocyclic based azo disperse dyes tend to show larger solvatochromic effects than azo-benzene based dyes because of increased polarity of the dye system, especially in the excited state. Similar effects for the dyes containing benzothiazolyl, thiazolyl, thiadiazolyl and thienyl moieties have been reported for some derivatives of these types of dyes [26–32]. On the other hand, in hetarylazo dyes prepared from enol-type coupling components, their tautomeric equilibria need to be considered.

The absorption spectra of dye **2** showed only one absorption maximum in all of the solvents used whereas the other dyes prepared showed two absorption maxima or one absorption maximum with shoulder in all solvents used. It is known that two maxima are observed for compounds exhibiting azo–hydrazone tautomerism. These results suggest that the dyes prepared may exist as a mixture of two forms in solutions except for dye **2**. Especially for dyes **5–8**, which contain triazole, isoxazole and pyridine rings, were observed two absorption maxima in DMSO, DMF and methanol as shown in Fig. 2 and Table 1. On the other hand, the absorption spectra of the dyes in chloroform and acetic acid showed only one absorption maximum in the range 393–452 nm and 391–452 nm, respectively, except for dye **1**. The absorption spectra of dye **1** exhibit one absorption maximum at 503 nm with a shoulder at 434 nm in chloroform and one maximum at 425 nm with a shoulder at 496 nm in acetic acid. These results show that the dyes prepared are in favour of the predominantly single tautomeric form in chloroform and acetic acid except dye **1**. Dye **1** may exist as a mixture of two tautomeric forms in chloroform and acetic acid. Furthermore, the absorption patterns of the dyes are changed with solvents. The spectra of dye **8** in chlorofom and acetic acid show one maximum at 389 nm and 391 nm, respectively, whereas in DMSO, DMF, acetonitrile and methanol the intensity of this band is decreased and a new more intensive band is appeared in the range of 483–516 nm (Fig. 2). Thus, the absorption curves almost pass through an isosbestic point approximately 446 nm characteristic of equilibria. This equilibrium may exist between the tautomeric forms (azo and hydrazone) or between the one tautomeric form and the anionic form. Because the equilibrium depends on the acidity of the solvents used. The effect of solvents on the equilibria is somewhat different from that of solvents on azo–hydrazone tautomerism. In proton donating solvents such as acetic acid and chloroform, the

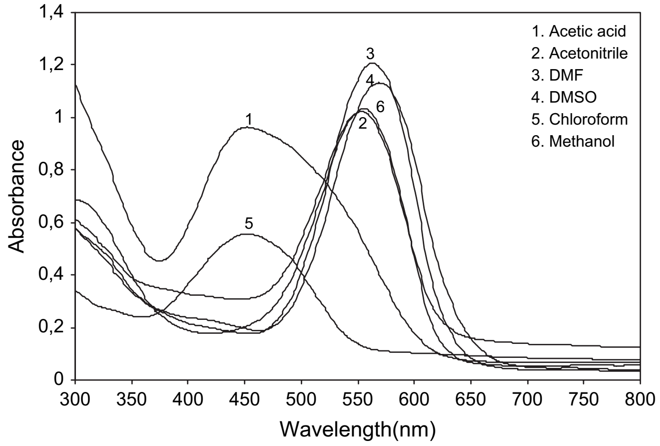


Fig. 1. Absorption spectra of dye **2** in various solvents.

Table 1
Influence of solvent on $\lambda_{\max}$ (nm) of dyes **1–9**

| Dye no | DMSO | DMF | Acetonitrile | Methanol | Acetic acid | Chloroform |
|---|---|---|---|---|---|---|
| **1** | 547 | 544 | 539 | 537 | 425,496s | 434s,502 |
| **2** | 569 | 563 | 554 | 555 | 452 | 452 |
| **3** | 560 | 556 | 433,553 | 553 | 442 | 441 |
| **4** | 549 | 547 | 419,542 | 428s,539 | 428 | 426 |
| **5** | 408,530 | 405,528 | 402,524 | 397,494 | 400 | 393 |
| **6** | 413,529 | 401,535 | 393 | 405,534s | 410 | 402 |
| **7** | 412,536 | 408,533 | 396 | 404,505 | 408 | 400 |
| **8** | 416s,516 | 405,514 | 387,500 | 393,483 | 391 | 389 |
| **9** | 538 | 537 | 388,513 | 397,490 | 403 | 396 |

s, shoulder.

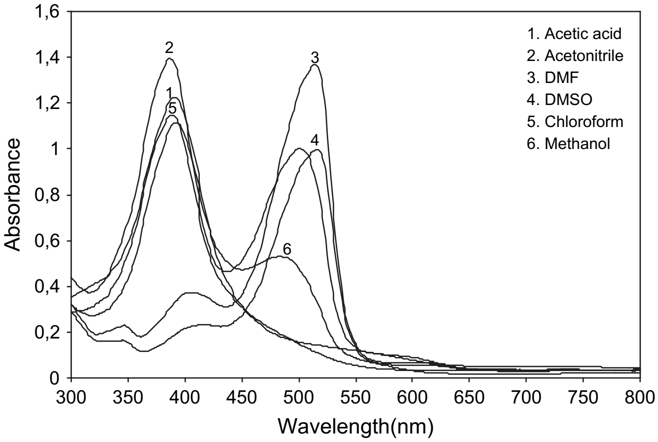


Fig. 2. Absorption spectra of dye **8** in various solvents.

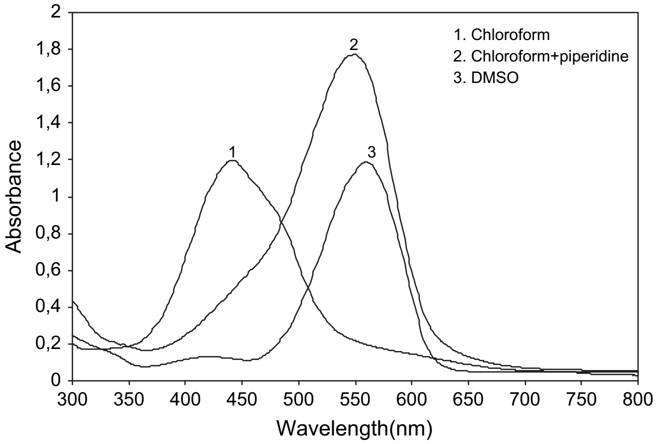


Fig. 3. Absorption spectra of dye **3** in neutral and basic solutions.

dyes give a hypsochromic shift of $\lambda_{max}$ and are basically in the neutral form. In proton-accepting solvents, such as DMSO, DMF, methanol, the dyes give a bathochromic shift of $\lambda_{max}$ and exist mainly in the common anion form. Such an order of the effect of solvents is consistent with the phenomenon of dissociation rather than azo–hydrazone tautomerism.

It was also observed that the absorption curves of the dyes (**1**–**9**) were very sensitive to acids and bases. $\lambda_{max}$ of the dyes showed large bathochromic shifts when a small amount of piperidine was added to each of the dye solutions in chloroform (Table 2), the absorption curves of the dyes resembled those in DMSO, DMF and methanol. A typical example is shown in Fig. 3. There was no significant change in the spectra of the dyes when a small amount of piperidine was added to their solutions in DMSO and DMF. Similar effects were observed when a small amount of 0.1 M KOH was added to methanolic solutions of dyes **1**–**3**. In the case of dyes **4**–**9**, the addition of 0.1 M KOH to their methanolic solutions, shoulder (dye **5**) or maxima at the shorter wavelength was disappeared and $\lambda_{max}$ values at longest wavelength did not significantly change. $\lambda_{max}$ values of the dyes in methanol showed large hypsochromic shifts when 0.1 M HCl was added, being nearly the same as those observed in acetic acid. This indicates that dyes **1**–**4** and dye **9** exist in dissociated state in DMSO, DMF and methanol with the exception of dyes **4** and **9** in methanol. In contrast, the dyes prepared exist in single tautomeric form in chloroform with the exception of dye **1**. These results also indicate that dyes **5**–**8** exist in a partly dissociated state in DMSO, DMF and methanol. Dyes **4** and **9** also exist in partly dissociated state in methanol.

These results are in agreement with those obtained for hetarylazopyridones and hetarylazopyrazolones in our previous works [26,27]. Peng et al. [33] also reported the same results for thiadiazolylazopyridones. Therefore, the structures of the dyes prepared were assigned to any of the tautomeric forms in acidic medium and to common anion form in basic form. These results also show that the thiadiazole ring facilitates the dissociation of hetarylazo dyes relative to 1,3,4-triazole, isoxazole and pyridine rings.

The effect of dye concentration and temperature on absorption maxima were examined, $\lambda_{max}$ values of dyes **1**–**9** did not change with dye concentration in all solutions. When solutions of the dyes in DMSO and DMF were examined over the temperature range 25–70 °C, $\lambda_{max}$ values of dyes **1**–**9** did not change significantly. These findings support the dissociation equilibrium of hetarylazoquinolines in proton-accepting solvents, which does not involve a change in energy.

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

Substituent effect of hetarylazo 8-hydroxyquinoline dyes was also studied. As apparent in Table 1, introduction of electron-donating $-SH$, $-SCH_3$, $-C_2H_5$ groups at the 5-position

Table 2
Absorption maxima of dyes **1**–**9** in acidic and basic solutions

| Dye no | $\lambda_{max}$ | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | DMSO | DMSO + piperidine | DMF | DMF + piperidine | Methanol | Methanol + KOH | Methanol + HCl | Chloroform | Chloroform + piperidine |
| **1** | 547 | 547 | 544 | 544 | 537 | 538 | 410,496 | 434s,502 | 535 |
| **2** | 569 | 573 | 563 | 566 | 555 | 555 | 458 | 452 | 551 |
| **3** | 560 | 560 | 556 | 557 | 553 | 553 | 438 | 441 | 548 |
| **4** | 549 | 550 | 547 | 547 | 428s,539 | 541 | 414,511 | 426 | 535 |
| **5** | 408,530 | 420s,530 | 405,528 | 405,526 | 397,494 | 487 | 385 | 393 | 401,506 |
| **6** | 413,529 | 426,531 | 401,535 | 418,535 | 405,534s | 496 | 404 | 402 | 407s,509 |
| **7** | 412,536 | 423s,536 | 408,533 | 415s,532 | 404,505 | 484 | 397 | 400 | 409,514 |
| **8** | 416s,516 | 421s,517 | 405,514 | 417s,513 | 393,483 | 490 | 379 | 389 | 401s,480 |
| **9** | 538 | 538 | 537 | 532 | 397,490 | 499 | 402 | 396 | 416,488 |

s, shoulder.

into the thiadiazole ring results in bathochromic shifts in all solvents used (for dye **2** $\Delta\lambda_{max} = 22$ nm in DMSO, $\Delta\lambda_{max} = 19$ nm in DMF, $\Delta\lambda_{max} = 15$ nm in acetonitrile, $\Delta\lambda_{max} = 18$ nm in chloroform relative to $\lambda_{max}$ of dye **1** in the same solvents; for dye **3** $\Delta\lambda_{max} = 13$ nm in DMSO, $\Delta\lambda_{max} = 12$ nm in DMF, $\Delta\lambda_{max} = 14$ nm in acetonitrile, $\Delta\lambda_{max} = 7$ nm in chloroform relative to $\lambda_{max}$ of dye **1** in the same solvents). Thus, the bathochromic shift can be obtained by enhancing the electron donor properties of the diazo component. Similarly, with the introduction of electron-donating $-$SH, $-SCH_3$ groups at the 5-position into the triazole ring, $\lambda_{max}$ showed bathochromic shifts in DMSO, DMF, methanol, acetic acid and chloroform but hypsochromic shift in acetonitrile (for dye **6** $\Delta\lambda_{max} = 5$ nm in DMSO, $\Delta\lambda_{max} = 9$ nm in chloroform, $\Delta\lambda_{max} = 9$ nm in acetonitrile relative to dye **5**; for dye **7** $\Delta\lambda_{max} = 6$ nm in DMSO, $\Delta\lambda_{max} = 5$ nm in DMF, $\Delta\lambda_{max} = 7$ nm in chloroform, relative to dye **5**). When sulphur atom was introduced into the five-membered heterocyclic triazole ring instead of nitrogen atom, $\lambda_{max}$ shifts bathochromically in all solvents (for dye **1** $\Delta\lambda_{max} = 17$ nm in DMSO, $\Delta\lambda_{max} = 41$ nm in chloroform relative to dye **5**; for dye **2** $\Delta\lambda_{max} = 40$ nm in DMSO, $\Delta\lambda_{max} = 42$ nm in acetic acid, $\Delta\lambda_{max} = 50$ nm in chloroform relative to dye **6**). On the other hand, the absorption spectra of the dyes in chloroform and acetic acid showed only one absorption maximum with the exception of dye **1**. In addition, when electron-donating group introduced into the 5-position of thiadiazole (dyes **2–4**) and triazole rings (dyes **6** and **7**), one tautomeric form is observed in acetic acid and chloroform. Moreover, while two tautomeric forms are observed in DMSO and DMF for dyes **6** and **7**, only single tautomeric form is observed for dyes **2–4** in DMSO and DMF. This shows that with the introduction of electron donor substituents to thiadiazole and triazole rings, the dyes exist predominantly in one tautomeric form in proton donating solvents.

## 3. Experimental

### 3.1. General

The chemicals used in the synthesis of all dyes were obtained from Aldrich Chemical Company and were used without further purification. The solvents used were of spectroscopic grade.

IR spectra were recorded on a Mattson 1000 FT-IR spectrophotometer in KBr. $^1$H NMR spectra were recorded on a Bruker-Spectrospin Avance DTX 400 Ultra Shield spectrophotometer in DMSO-$d_6$ and $CDCl_3$. Chemical shifts are expressed in $\delta$ units (ppm). Ultraviolet–visible (UV–vis) absorption spectra were recorded on Analytika Jena UV-200 spectrophotometer at the wavelength of maximum absorption ($\lambda_{max}$) in range of solvents, i.e. dimethylsulphoxide (DMSO), dimethylformamide (DMF), acetonitrile, methanol, acetic acid and chloroform. Change of $\lambda_{max}$ was investigated when 0.1 ml piperidine was added to 1 ml dye solutions in chloroform, DMSO and DMF, and similarly, when 0.1 ml base (potassium hydroxide, 0.1 M) or 0.1 ml hydrochloric acid (0.1 M) was added to 1 ml dye solutions in methanol. In addition, change of $\lambda_{max}$ was investigated when solution of dyes in DMSO and DMF were examined over the temperature range 25–70 °C. LC–MS analyses were recorded on Agilent 1100 MSD by Turkish Research Council Laboratories (Center of Science and Technology Research of Turkey). All melting points were uncorrected and are in degree Celsius.

### 3.2. Preparation of hetarylazo 8-hydroxyquinoline dyes (*1–9*)

Diazotisation of various heterocyclic amines was effected with $H_2SO_4$ and $NaNO_2$. A typical procedure that is described below is used for 2-aminothiadiazole; all other compounds were prepared in a similar manner. The yields of the dyes are in range of 57–83%. The obtained compounds were purified by crystallization using ethanol and then analyzed. Characterization data are given below.

#### 3.2.1. Preparation of 5-(2-thiadiazolylazo)-8-hydroxyquinoline (*1*)

2-Aminothiadiazole ($2.0 \times 10^{-3}$ mol, 0.202 g) was 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 sulphuric acid (prepared from sodium nitrite (0.15 g) and concentrated sulphuric acid (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 salt/ice mixture. After diazotisation was complete the diazo liquor was slowly added to vigorously stirred solution of 8-hydroxyquinoline ($2.0 \times 10^{-3}$ mol, 0.29 g) in Potassium hydroxide ($2.0 \times 1^{-3}$ mol, 0.112 g) and water (2 ml). The solution was stirred at 0–5 °C for 2 h. After 2 h, 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 one day at room temperature. After one day, the resulting solid was filtered, washed with cold water and dried. Recrystallisation from ethanol gave claret red crystalline 5-(2-thiadiazolylazo)-8-hydroxyquinoline (yield: 0.40 g, 78%; m.p: 111–113 °C). IR (KBr): $\nu_{max}$: 3442–3249 (quinoline −OH), 3056 (aromatic C−H), 1567 (C=N), 1510 (C=C), 1208 (C−O) cm$^{-1}$; $^1$H NMR (DMSO-$d_6$): $\delta$ 9.60 (s, 1H), 9.10 (d, 1H), 9.00 (d, 1H), 8.30 (d, 1H), 7.90 (m, 1H), 7.20 (d, 1H).

LC–MS: $(M+1)^+$ (*m/z*): 258 (6.7%), 172 (6.1%), 146 (100%), 144 (40.5%).

#### 3.2.2. Preparation of 5-(2-thiole-5-thiadiazolylazo)-8-hydroxyquinoline (*2*)

This dye was obtained from 5-amino-1,3,4-thiadiazole-2-thiole and 8-hydroxyquinoline as black crystals (yield: 0.46 g, 80%; m.p: 207 °C). IR (KBr): $\nu_{max}$: 3391–3275 (quinoline −OH), 3082 (aromatic C−H), 1599 (C=N), 1496 (C=C), 1220 (C−O) cm$^{-1}$; $^1$H NMR (DMSO-$d_6$): $\delta$ 13.20

(b, −SH), 9.10 (d, 1H), 9.00 (d, 1H), 8.20 (d, 1H), 7.90 (m, 1H), 7.20 (d, 1H).

LC−MS: $(M+1)^+$ (*m/z*): 290 (7.3%), 265 (46.0%), 172 (3.2%), 144 (6.6%).

### 3.2.3. Preparation of 5-(5-methylthio-2-thiadiazolylazo)-8-hydroxyquinoline (3)

This dye was obtained from 2-amino-5-methylthio-1,3,4-thiadiazole and 8-hydroxyquinoline as brown crystals (yield: 0.38 g, 63%; m.p: 224 °C). IR (KBr): $\nu_{max}$: 3448−3236 (quinoline −OH), 3056 (aromatic C−H), 2928 (aliphatic C−H), 1573 (C=N), 1510 (C=C), 1208 (C−O) $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$): δ 9.13 (d, 1H), 9.06 (d, 1H), 8.30 (d, 1H), 7.90 (m, 1H), 7.30 (d, 1H), 2.60 (s, 3H).

LC−MS: $(M+1)^+$ (*m/z*): 304 (8.7%), 172 (23.7%), 144 (100%).

### 3.2.4. Preparation of 5-(5-ethyl-2-thiadiazolylazo)-8-hydroxyquinoline (4)

This dye was obtained from 2-amino-5-ethyl-1,3,4-thiazole and 8-hydroxyquinoline as brown crystals (yield: 0.32 g, 57%; m.p: 222 °C). IR (KBr): $\nu_{max}$: 3428−3268 (quinoline −OH), 3075 (aromatic C−H), 2973 (aliphatic C−H), 1554 (C=N), 1490 (C=C), 1208 (C−O) $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$): δ 9.10 (d, 1H), 9.00 (d, 1H), 8.20 (d, 1H), 7.80 (m, 1H), 7.20 (d, 1H), 3.10 (q, 2H), 1.40 (t, 3H).

LC−MS: $(M+1)^+$ (*m/z*): 286 (19.8%), 172 (21.2%), 144 (100%).

### 3.2.5. Preparation of 5-(3-triazolylazo)-8-hydroxyquinoline (5)

This dye was obtained from 3-amino-1,2,4-triazole and 8-hydroxyquinoline as yellow crystals (yield: 0.38 g, 79%; m.p: 254 °C). IR (KBr): $\nu_{max}$: 3345−3275 (quinoline −OH), 3063 (aromatic C−H), 1580 (C=N), 1529 (C=C), 1201 (C−O) $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$−$CDCl_3$): δ 9.50 (d, 1H), 8.90 (d, 1H), 8.20 (s, 1H), 8.10 (d, 1H), 7.70 (m, 1H), 7.20 (d, 1H).

LC−MS: $(M+1)^+$ (*m/z*): 241 (81.7%), 172 (10.0%), 144 (100%).

### 3.2.6. Preparation of 5-(5-mercapto-3-triazolylazo)-8-hydroxyquinoline (6)

This dye was obtained from 3-amino-5-mercapto-1,2,4-triazole and 8-hydroxyquinoline as brown crystals (yield: 0.34 g, 62%; m.p: 140−148 °C). IR (KBr): $\nu_{max}$: 3428−3288 (quinoline −OH), 3063 (aromatic C−H), 1592 (C=N), 1510 (C=C), 1227 (C−O) $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$): δ 15.10 (b, triazole −NH) 9.40 (d, 1H), 9.00 (d, 1H), 8.20 (d, 1H), 7.90 (m, 1H), 7.30 (d, 1H).

LC−MS: $(M+1)^+$ (*m/z*): 273 (100%), 172 (38.5%), 144 (53.4%).

### 3.2.7. Preparation of 5-(5-methylthio-3-triazolylazo)-8-hydroxyquinoline (7)

This dye was obtained from 3-amino-5-methylthio-1*H*-1,2,4-triazole and 8-hydroxyquinoline as black crystals (yield: 0.45 g, 79%; m.p: 220 °C). IR (KBr): $\nu_{max}$: 3416−3314 (quinoline −OH), 3089 (aromatic C−H), 2858 (aliphatic C−H), 1561 (C=N), 1510 (C=C), 1240 (C−O) $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$−$CDCl_3$): δ 9.40 (d, 1H), 8.90 (d, 1H), 8.10 (d, 1H), 7.60 (m, 1H), 7.20 (d, 1H), 2.7 (s, 3H).

LC−MS: $(M+1)^+$ (*m/z*): 287 (65.0%), 172 (25.9%), 144 (100%).

### 3.2.8. Preparation of 5-(5-methyl-3-isoxazolylazo)-8-hydroxyquinoline (8)

This dye was obtained from 3-amino-5-methylisoxazole and 8-hydroxyquinoline as orange crystals (yield: 0.42 g, 83%; m.p: 219 °C). IR (KBr): $\nu_{max}$: 3268 (quinoline −OH), 3063 (aromatic C−H), 2960, 2935 (aliphatic C−H), 1573 (C=N), 1515 (C=C), 1220 (C−O) $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$−$CDCl_3$): δ 9.20 (d, 1H), 8.90 (d, 1H), 8.10 (d, 1H), 7.60 (m, 1H), 7.20 (d, 1H), 6.40 (s, 1H), 2.50 (s, 3H).

LC−MS: $(M+1)^+$ (*m/z*): 255 (100%), 172 (1.6%), 158 (5.2%), 144 (14.7%).

### 3.2.9. Preparation of 5-(3-pyridinylazo)-8-hydroxyquinoline (9)

This dye was obtained from 3-aminopyridine and 8-hydroxyquinoline as orange crystals (yield: 0.41 g, 81%; m.p: 210 °C). IR (KBr): $\nu_{max}$: 3326 (quinoline −OH), 3056 (aromatic C−H), 1573 (C=N), 1510 (C=C), 1201 (C−O) $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$): δ 9.30 (d, 1H), 9.10 (s, 1H), 8.90 (d, 1H), 8.60 (d, 1H), 8.20 (d, 1H), 8.00 (d, 1H), 7.80 (m, 1H), 7.70 (m, 1H), 7.20 (d, 1H).

LC−MS: $(M+1)^+$ (*m/z*): 251 (100%), 159 (3.8), 144 (6.8%).

## 4. Conclusions

In this study, a series of new heterocyclic disperse azo dyes were prepared by coupling 8-hydroxyquinoline with nine heterocyclic amines in nitrosyl sulphuric acid. Their solvatochromic properties in different solvents were investigated and the dyes are strongly solvent dependent, the dyes exhibited azo−common anion equilibrium in DMSO and DMF. The acid and base effects on this equilibrium are also examined. The colour of dyes is discussed with respect to nature of the heterocyclic ring and substituent therein. Absorption maxima of the dyes showed large bathochromic effects in comparison with analogous dyes containing carbocyclic amine residues and also the thiadiazolylazo dyes absorb bathochromically compared with their triazolyl analogues [24]. As a results of the introduction of electron-donating −SH, $-SCH_3$, $-C_2H_5$ groups at the 5-position into the thiadiazole ring, $\lambda_{max}$ shifts bathochromically in all solvents. Thus, the bathochromic shift can be obtained by enhancing the electron donor properties of the diazo component. Similarly with the introduction of electron-donating −SH, $-SCH_3$ groups at the 5-position into the triazole ring, $\lambda_{max}$ showed bathochromic shifts in DMSO, DMF, methanol, acetic acid and chloroform but hypsochromic shift in acetonitrile.

As a result, compounds **1**−**9** can be applied to wool and nylon fibers as mordant dyes. These compounds can also be used in biological–medical studies and analytic chemistry as pH indicators.

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