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Synthesis, spectral features and biological activity of some novel hetarylazo dyes derived from 8-chloro-4-hydroxyl-2-quinolone

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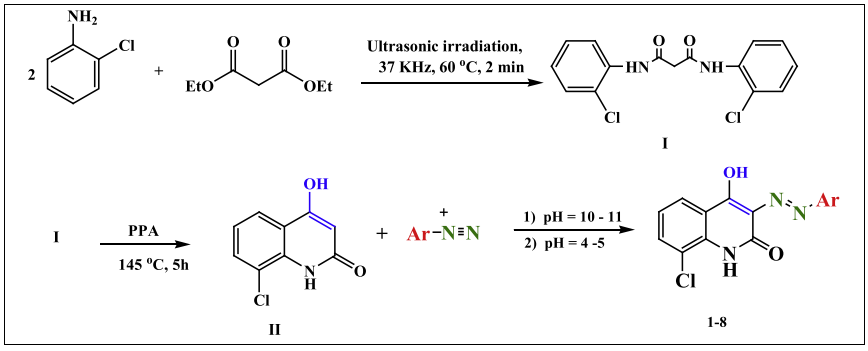
HIGHLIGHTS

- Preparation of some new azo dyes derived from 8-chloro-4-hydroxyl-2-quinolone.
- Characterization and evaluation of solvatochromic properties.
- Effects of concentration.
- Anti microbial activity of dyes were measured.

GRAPHICAL ABSTRACT

Synthetic routes for the preparation of hetarylazo dyes.



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ABSTRACT

In this study, 8-chloro-4-hydroxyl-2-quinolone was synthesized from cyclocondensation of corresponding dianilide and subsequently used as a potent coupling component with some diazotized heterocyclic amines. These compounds were characterized by UV–vis, FT-IR, ^{1}H NMR spectroscopic techniques and elemental analysis. Absorption spectra of these dyes were measured in six polar solvents and discussed with respect to the nature of solvents and substituted groups. The effects of acid, base, temperature and concentration on the visible absorption spectra of the dyes were reported. In addition, the antimicrobial activity of the dyes was explored in detail.

Introduction

Quinolones are one of the important classes of heterocyclic compounds, due to their unique biological and pharmacological activities, such as anti-thyroid, anticancer, anti-tubercular and antihypertensive, cardiotonic, diuretic and anti-inflammatory properties [1–7]. Furthermore, 4-hydroxyquinolone (4HQ) derivatives, for example L-701,324, L-703,717 and methoxy-MDL-104, 653 are one of the most potent and orally active antagonists for the glycine-binding site [8,9]. Some derivatives of quinolone are prepared by using 4-hydroxy quinolones as the starting material: for example, the reaction of 4-hydroxy-2(1*H*)-quinolones with α-acetyl-γ-butyrolactone in the presence of ammonium acetate gave pyrano[3,2-c]-quioline-2,5-diones [10]. As another example, treating 4-hydroxyquinolin-2(1*H*)-one with isatin and malononitrile in ethanol in an undivided cell in presence of sodium bromide,

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as an electrolyte, affords the spiro[indole-3,4′-pyrano [3,2-c]quinolines] that are useful for human cancer therapy and other biomedical applications [11]. Moreover, spiro[piperidine-4,4′-pyrano[3,2-c]quinolines] are prepared by the condensation of 4-hydroxyquinolone derivatives with α, β-unsaturated nitrile compounds [12].

Azo compounds are the most widely used class of dyes because of their versatile applications in various fields such as the dyeing, LCD color filters, chromophoric substrates for redox enzymes, design of optical data storage and advanced organic synthesis [13–21]. Among the azo dyes, heterocyclic azo compounds have brilliant color and chromophoric strength, excellent light, washing and sublimation fastness, as well as wide application as high level-dying agent in the dyestuff industry [22–24]. Furthermore, some heterocyclic azo compounds find application in biological and pharmacological studies [25,26]. For example, pyrazole and quinolone dyes have rich pharmaceutical applications due to antibacterial activity [27,28]. To the best of our knowledge, however, antimicrobial activity compounds containing hetarylazoquinolone dyes have not been studied so far. According to the importance of these compounds, and in continuation of our previous investigations, the synthesis of 8-chloro-4-hydroxy-2-quinolone and its application as coupling agent in reaction with some heterocyclic amines as diazo components are reported. The effects of solvents, substituent, acid and base on the visible absorption spectra of the dyes were investigated. In addition, the newly synthesised dyes were evaluated for their antimicrobial activity against *Escherichia coli*, *Bacillus subtilis*, *Micrococcus leuteus* and *Pseudomonas aeruginosa*. These dyes were active on both Gram-positive (*B. subtilis*, *M. leuteus*) and Gram-negative (*E. coli*, *Ps. aeruginosa*) bacteria. The structures of coupling component and prepared dyes are shown in Schemes 1 and 2.

Experimental

General

All starting materials were obtained from Merck Chemical Company and Aldrich Chemical Company and were used without further purification. IR spectra were recorded on a Shimadzu 8400 FT-IR spectrophotometer. ^{1}H and ^{13}C NMR spectra were obtained by FT-NMR 400 and 100 MHz Brucker apparatus in DMSO-d_6, using TMS as internal standard. The absorption spectra of the compounds were run on a Cary UV–vis double-beam spectrophotometer (Model 100). The elemental analysis was determined on a Leco CHNS-900 analyzer. Melting points were recorded with an electro-thermal apparatus and uncorrected.

Preparation of N, N′-di-(2-chlorophenyl)malonamide

2-Chloro aniline (2.55 g, 20 mmol), diethyl malonate (1.14 mL, 10 mmol) was properly mixed in a 25 mL beaker and well mixed. The obtained mixture was sonicated at frequencies of 37 kHz at 60 °C for 2 min. The crude product was recrystallized in a minimum amount of ethanol to give compound **I** as a white powder, Yield: 93%, Mp: 192–193 °C. FT-IR (KBr): ν (cm^{-1}) = 3100 (NH), 1685 (C=O); ^{1}H NMR (400 MHz, DMSO-d_6); δ 10.39 (NH), 7.80 (2H, d, J = 8.0 Hz), 7.50 (2H, d, J = 7.6 Hz), 7.20 (2H, dd, J = 8.0, 7.6 Hz), 7.02 (2H, dd, J = 7.6, 7.2 Hz), 3.58 (2H, s, –CH$_2$-).

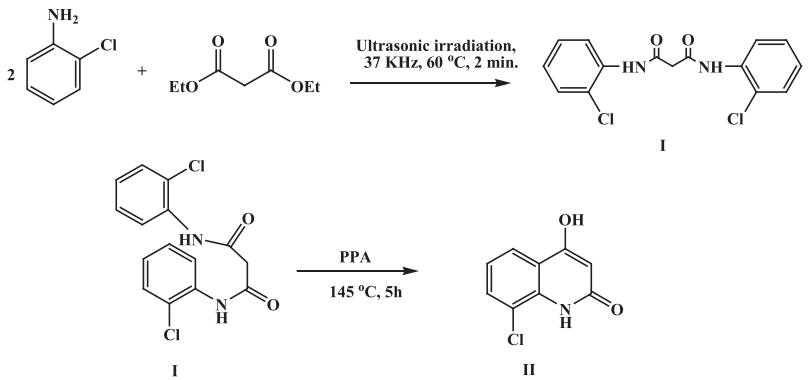
Synthesis of 8-chloro- 4-hydroxyquinoline -2-(1H)-one

The *N, N′*-di-(2-chlorophenyl)malonamide (0.65 g, 2.0 mmol) and polyphosphoric acid (3.55 g) were stirred in an oil bath for 5 h at 145 °C. Then the mixture was cooled, diluted with water and the resultant gum solidified by standing over night. The crude product was dissolved in 20 mL of sodium hydroxide solution 0.1 mol L^{-1} and the residual was filtered off. The filtrate was acidified with concentrated hydrochloric acid and the resulting precipitate was recrystallized in a minimum amount of ethanol to afford 8-chloro-4-hydroxyquinoline-2-(1*H*)-one (**II**) as creamy crystals, Yield 87%, Mp: 302–303 °C (reported 305 °C [29]). FT-IR (KBr): ν (cm^{-1}) = 3470 (OH), 3100 (NH), 1635 (C=O); ^{1}H NMR (400 MHz, DMSO-d_6); δ 11.86 (OH), 10.41 (NH), 7.81 (1H, d, J = 8.0 Hz), 7.67 (1H, d, J = 7.6 Hz), 7.18 (1H, dd, J = 8.0, 7.6 Hz), 5.83 (1H, s). ^{13}C NMR (100 MHz, DMSO-d_6):163.94 (C=O), 162.30 (C—OH), 138.22 (C), 135.32 (C—Cl), 129.12 (CH), 126.20 (C—H), 125.17 (CH), 119.10 (C), 99.19 (CH). Anal. Calcd. for $C_9H_6ClNO_2$: C, 55.26; H, 3.09; N, 7.16;. Found: C, 5.21; H, 3.06; N, 7.12.

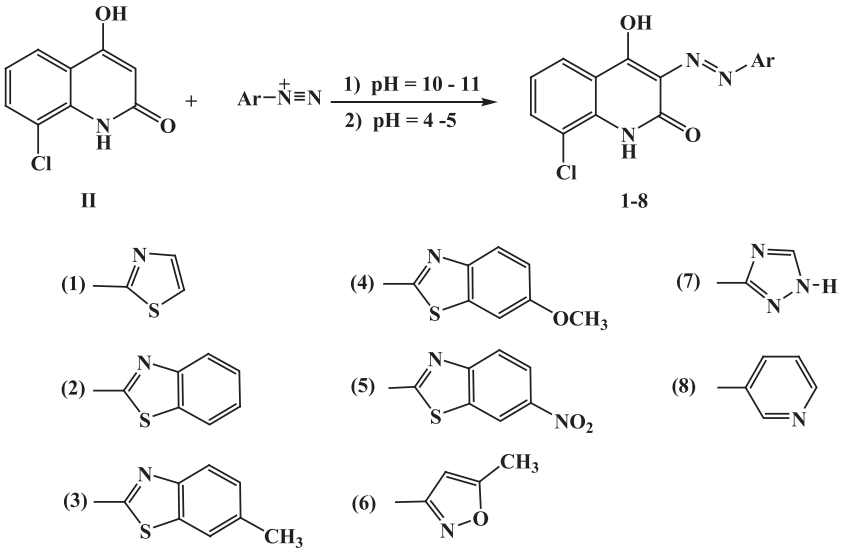
The general procedure for the synthesis and purification of disperse azo dyes

For the preparation of dyes **1–8**, the diazonium coupling reaction was employed. The route for synthesis of the dyes is presented in Scheme 2. A typical procedure used for preparation of dyes is described below.

Nitrosyl sulfuric acid solution was prepared from concentrated sulfuric acid (1.5 mL) and sodium nitrite (0.14 g, 2 mmol) at 70 °C and then cooled to 5 °C. This solution was added dropwise, with stirring, to 3 mL of (acetic acid + propionic acid) mixture (5:1v/v) containing 2.0 mmol of heterocyclic amines in an ice bath. The mixture was then stirred for 1.5 h at about 0–5 °C. After completion of diazotization procedure, the diazonium salt solution was added dropwise to the solution of 8-chloro 4-hydroxyquinoline -2-(1*H*)-one (0.39 g, 2.0 mmol) in sodium hydroxide (0.32 g,



Scheme 1. Preparation of 8-chloro-4-hydroxyl-2-quinolone (**II**).



Scheme 2. Synthetic routes for the preparation of hetarylazo dyes **1–8**.

8.0 mmol) and water (6.0 ml). The resulting solution was vigorously stirred at about 0–4 °C for 2 h, while the pH of the reaction mixture was maintained 10-11 by adding 2.5% sodium hydroxide solution. The progress of the reaction was followed by TLC, using (ethyl acetate + petroleum ether) mixture (5:1 v/v) as solvent. Afterwards, the pH of reaction mixture was regulated 4-5 by means of a 10% hydrochloric acid solution. At the end of the procedure, the resulting solid was filtered, washed thoroughly with cold ethanol and dried. Recrystallization from DMF-H_2O ended in pure crystals of the dye. The physical and spectral data of the purified dyes are as follows.

*Dye (**1**)*

Red crystals (Yield: 86%, Mp: 271–272 °C). FT-IR (KBr): ν (cm^{-1}) = 3440 (OH), 3202 (NH), 3075 (Aro.-H), 1698 (C=O); ^1H NMR (400 MHz, DMSO-d_6); δ 15.30 and 14.50 (b, hydrazone NH), 10.93 and 10.61 (b, amide NH), 7.98 (1H, d, J = 7.9 Hz), 7.82 (1H, d, J = 8.4 Hz), 7.68 (1H, d, J = 2.9 Hz), 7.55 (1H, d, J = 2.9 Hz), 7.23 (1H, dd, J = 8.4, 7.9 Hz). Anal. Calcd. for $C_{12}H_7ClN_4O_2S$: C, 46.99; H, 2.30; N, 18.27; S, 10.45. Found: C, 46.86; H, 2.33; N, 18.32; S, 10.50.

*Dye (**2**)*

Clear orange crystals (Yield: 84%, Mp: 315–316 °C). FT-IR (KBr): ν (cm^{-1}) = 3428 (OH), 3198 (NH), 3078 (Aro.-H), 1662 (C=O); ^1H NMR (400 MHz, DMSO-d_6); δ 15.32 and 14.41 (b, hydrazone NH), 10.85 and 10.52 (b, amide NH), 8.00 (1H, d, J = 8.2 Hz), 7.87 (1H, d, J = 7.2 Hz), 7.78 (1H, d, J = 7.6 Hz), 7.45–7.35 (3H, m, overlapped), 7.21 (1H, dd, J = 8.2, 7.6 Hz). Anal. Calcd. for $C_{16}H_9ClN_4O_2S$: C, 53.86; H, 2.54; N, 15.70; S, 8.99. Found: C, 53.82; H, 2.56; N, 15.66; S, 9.01.

*Dye (**3**)*

Orange crystals (Yield: 77%, Mp: 294–295 °C). FT-IR (KBr): ν (cm^{-1}) = 3436 (OH), 3211 (NH), 3054 (Aro.-H), 1682 (C=O); ^1H NMR (400 MHz, DMSO-d_6); δ 15.35 and 14.45 (b, hydrazone NH), 10.90 and 10.60 (b, amide NH), 7.98 (1H, d, J = 7.6 Hz), 7.88 (1H, s), 7.83 (1H, d, J = 7.6 Hz), 7.74 (1H, d, J = 8.4 Hz), 7.32 (1H, d, J = 7.6 Hz). 7.22 (1H, dd, J = 8.4, 7.6 Hz), 2.45 (3H, s). Anal. Calcd. for $C_{17}H_{11}ClN_4O_2S$: C, 55.06; H, 2.99; N, 15.11; S, 8.65. Found: C, 54.99; H, 3.02; N, 15.15; S, 8.71.

*Dye (**4**)*

Red crystals (Yield: 86%, Mp: 277–278 °C). FT-IR (KBr): ν (cm^{-1}) = 3432 (OH), 3206 (NH), 3053 (Aro.-H), 1672 (C=O); ^1H NMR (400 MHz, DMSO-d_6); δ 15.52 and 14.50 (b, hydrazone NH), 10.91 and 10.55 (b, amide NH), 8.10 (1H, d, J = 8.4 Hz), 7.82 (1H, d, J = 8.0 Hz), 7.76 (1H, d, J = 8.8 Hz), 7.70 (1H, s), 7.22 (1H, dd, J = 8.8, 8.0 Hz), 7.10 (1H, d, J = 8.4 Hz), 3.79 (3H, s). Anal. Calcd. for $C_{17}H_{11}ClN_4O_3S$: C, 52.79; H, 2.87; N, 14.48; S, 8.29. Found: C, 52.72; H, 2.82; N, 14.55; S, 8.31.

*Dye (**5**)*

Brown crystals (Yield: 75%, Mp: >350 °C). FT-IR (KBr): ν (cm^{-1}) = 3445 (OH), 3243 (NH), 3023 (Aro.-H), 1690 (C=O); ^1H NMR (400 MHz, DMSO-d_6); δ 15.22 and 14.43 (b, hydrazone NH), 11.10 and 10.60 (b, amide NH), 8.78 (1H, s), 8.39 (1H, d, J = 8.4 Hz), 7.80 (1H, d, J = 8.0 Hz), 7.64 (1H, d, J = 8.4 Hz), 7.40 (1H, d, J = 8.4 Hz), 7.14 (1H, dd, J = 8.8, 8.0 Hz). Anal. Calcd. for $C_{16}H_8ClN_5O_4S$: C, 47.83; H, 2.01; N, 17.43; S, 7.98. Found: C, 47.79; H, 2.04; N, 17.50; S, 7.92.

*Dye (**6**)*

Clear yellow crystals (Yield: 92%, Mp: 265–267 °C). FT-IR (KBr): ν (cm^{-1}) = 3430 (OH), 3210 (NH), 3014 (Aro.-H), 1652 (C=O); ^1H NMR (400 MHz, DMSO-d_6); δ 15.42 and 14.86 (b, hydrazone NH), 10.88 and 10.53 (b, amide NH), 7.98 (1H, d, J = 8.0 Hz), 7.82 (1H, d, J = 8.4 Hz), 7.23 (1H, dd, J = 8.4, 8.0 Hz), 6.60 (1H, s),), 2.65 (3H, s). Anal. Calcd. for $C_{13}H_9ClN_5O_3$: C, 51.25; H, 2.98; N, 18.39. Found: C, 51.19; H, 3.04; N, 18.29.

*Dye (**7**)*

Yellow crystals (Yield: 81%, Mp > 350 °C). FT-IR (KBr): ν (cm^{-1}) = 3415 (OH), 3198 (NH), 3068 (Aro.-H), 1681 (C=O); δ ^1H NMR (400 MHz, DMSO-d_6); 15.95 and 15.24 (b, hydrazone NH), 14.38 (NH), 10.87 and 10.48 (b, amide NH), 8.48 (1H, s), 8.10 (1H, d, J = 7.8 Hz), 7.60 (1H, d, J = 8.4 Hz), 7.25 (1H, dd, J = 8.4, 7.8 Hz). Anal. Calcd. for $C_{17}H_7ClN_6O_2$: C, 45.45; H, 2.43; N, 28.91. Found: C, 45.52; H, 2.46; N, 28.52.

*Dye (**8**)*

Yellow crystals (Yield: 79%, Mp: 260–262 °C). FT-IR (KBr): ν (cm^{-1}) = 3438 (OH), 3212 (NH), 3056 (Aro.-H), 1685 (C=O); ^1H NMR (400 MHz, DMSO-d_6); δ 15.67 and 14.90 (b, hydrazone NH),

10.70 and 10.46 (b, amide NH), 8.98 (1H, d, J = 1.6 Hz), 8.53 (1H, d, J = 4.2 Hz), 8.16 (1H, d, J = 8.4 Hz), 8.01 (1H, d, J = 7.6 Hz), 7.81 (1H, dd, J = 8.0, 1.6 Hz), 7.57 (1H, dd, J = 8.0, 4.2 Hz), 7.22 (1H, dd, J = 8.4, 7.6 Hz). Anal. Calcd. for $C_{14}H_9ClN_4O_2$: C, 55.92; H, 3.02; N, 18.63. Found: C, 55.86; H, 2.99; N, 18.68.

Determination of antimicrobial activity

Antimicrobial activity was determined against four bacteria: *E. coli*, *B. subtilis*, *M. leuteus* and *Ps. aeruginosa*. The test sample was dissolved in DMSO and added to the bacterial medium. A 100 µl suspension of bacterial growth in nutrient broth was transferred to 3 ml of the medium containing 125 µg/ml of the test dye. The culture was incubated at 37 °C overnight and the amount of growth determined spectrophotometrically at 600 nm. Control samples containing only the bacteria, bacteria and DMSO, and DMSO only, were used for comparison; Positive controls, including tetracycline, penicillin and vancomycin, were also used. The tests were repeated twice.

Result and discussion

Characterization of the synthesized dyes

The physical and spectral data of the dyes **1–8** are given in the experimental section. The dyes may exist in four possible tautomeric forms, namely the azo-enol-keto (T_1), hydrazone-keto (T_2), hydrazone-keto (T_3) and azo-enol-keto (T_4), as shown in Scheme 3.

The infrared spectra of the dyes **1–8** in (KBr) show intense hydroxyl (OH) band at 3445–3415 cm^{-1} and a band at 3243–3198 cm^{-1}, which can be assigned to amide group (NH—C=O). The other ν_{max} values of 3078–3014 cm^{-1} (aromatic C—H), 1698–1652 cm^{-1} (C=O) were recorded. It can be suggested that these dyes exist in azo-enol-keto form in solid state.

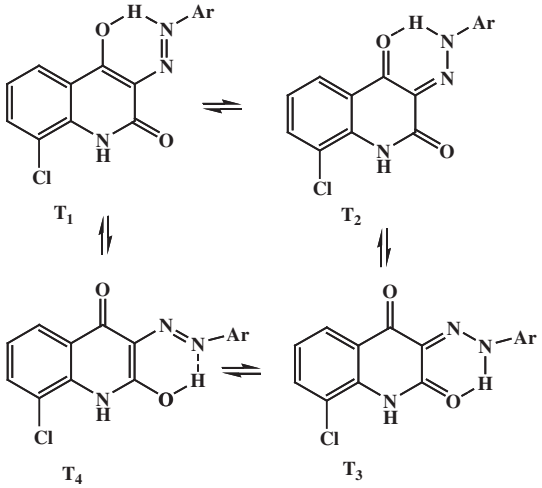
The ^{1}H NMR spectra measured in DMSO-d_6 at room temperature show a multiplate from 6.60 to 8.98 ppm for aromatic protons, a singlet at 2.45 ppm (–CH_3, **3**), a singlet at 3.79 ppm (–CH_3, **4**), and 2.65 ppm (–CH_3, **6**). The broad peaks at 14.40–15.92 ppm correspond to the tautomeric hydrazone proton (=N—NH). It was reported that the hydrazone NH proton resonance appears approximately between 13.0 and 16.0 ppm, in ortho and para-hydroxyazo dyes [30,31]. These results show that all the dyes may exist predominantly as the hydrazone-keto forms T_2 and T_3 in DMSO. Other notable signals were two broad singlet peaks at 10.46–10.61 ppm and 10.70–11.10 ppm attributed to amide (NH) groups, related to amide protons of two tautomeric forms (T_2 and T_3).

UV–visible and solvatochromic studies of the dyes

Absorption spectra of hetarylazoquinolone dyes **1–8** were recorded in various solvents at a concentration of about 10^{-8}–10^{-6} mol L^{-1}. The dyes were completely soluble in DMSO. Therefore, more diluted solution were prepared, and it was found in all cases that λ_{max} was unaffected by the concentration. The stock solutions of each dye were accurately prepared, and diluted samples of these stocks were used for absorption measurements. The results are summarized in Table 1 (see supplementary data).

The dyes show two absorption bands in all solvents. It can be suggested that the dyes may exist as a mixture of two tautomeric forms in various solvents. These results are in agreement with the results from ^{1}H NMR conclusions (e.g. Fig. 1 for dye **6**). The absorption spectra of the dyes (**1–4** and **8**) showed bathochromic shifts in methanol and acetic acid rather than in other solvents. These bathochromic shifts in proton-donating solvents were considered to be due to intermolecular hydrogen bonding between dye molecules and solvents, which are capable of stabilizing the ground state of the dyes leading to a resultant bathochromic shift (e.g. for dye **4** λ_{max} is 468 nm in methanol, 464 nm in acetic acid and 442 nm in DMSO) (Fig. 2). The λ_{max} of dyes **5–7** shows hypsochromic shifts in methanol and acetic acid with respect to the other solvents (e.g. for dye **6** λ_{max} is 369 nm in methanol, 368 nm in acetic acid and 390 nm in DMSO) (Fig. 3). It was also observed that the λ_{max} of dye **5** shifts considerably in DMSO and DMF with respect to the λ_{max} in other solvents (for dye **5** λ_{max} is 419 nm in DMSO, 417 nm in DMF and 383 nm in methanol) (see supplementary data Table 1). The obtained results in basic solvents might be attributed to partial deprotonation of hydroxyl group that enhances contribution of non-bonding electrons on the oxygen atom into the conjugated resonance structures.

It was also observed that the absorption curves of the dyes were a little sensitive to acid. The absorption maxima values of all dyes in methanol, on addition of 0.1 mol L^{-1} HCl, were nearly the same as those observed in acetic acid; but they are sensitive to bases except for that of dye **5**. The λ_{max} of the dyes showed a hypsochromic shift when a small amount of 0.1 mol L^{-1} KOH was added to their methanolic solutions. The λ_{max} of dye **5** does not change significantly when 0.1 mol L^{-1} KOH was added to the dye solution in methanol. In addition the absorption spectra of all the prepared dyes do not change significantly when a small amount of piperidine was added to their solutions in DMSO, DMF and chloroform



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

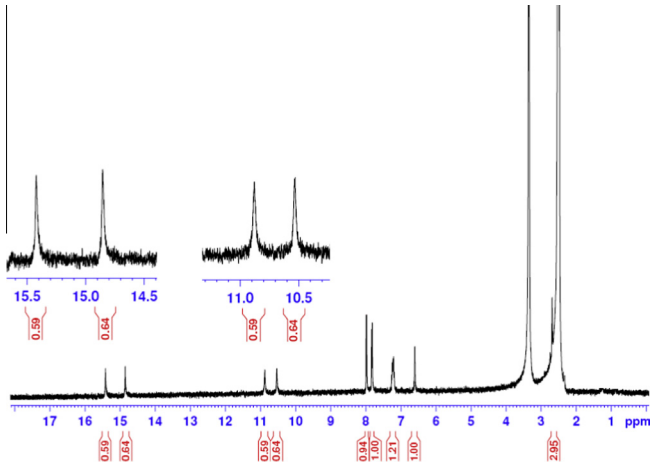


Fig. 1. ^{1}H NMR (400 MHz) spectrum of dye **6** in DMSO-d_6.

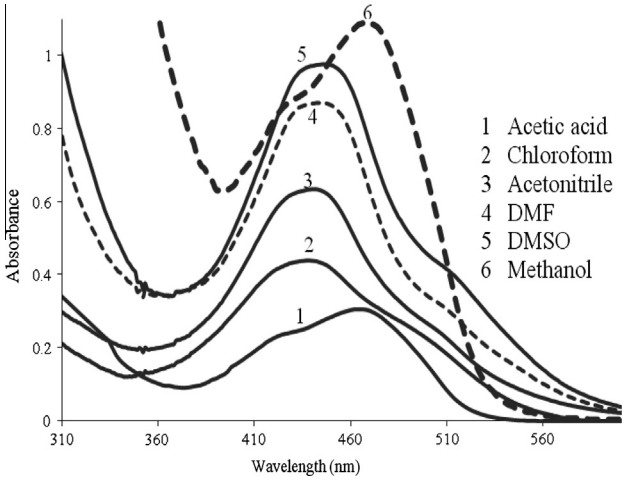


Fig. 2. Absorption spectra of dye **4** in various solvents.

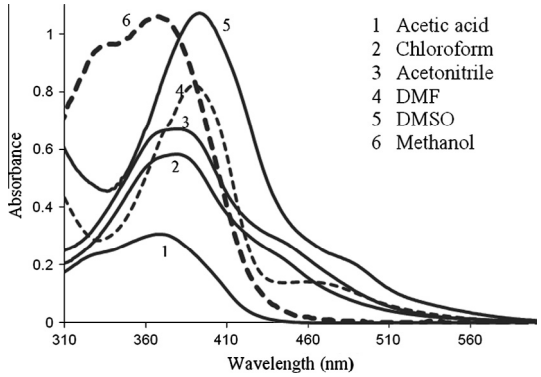


Fig. 3. Absorption spectra of dye **6** in various solvents.

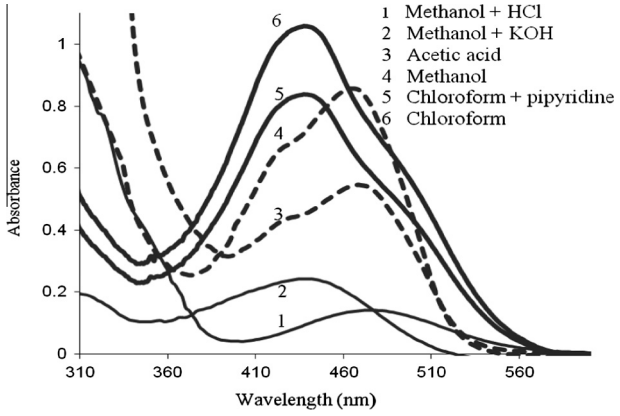


Fig. 4. Absorption spectra of dye **4** in acidic and basic solution.

(see supplementary data Table 2). A typical example is shown in Fig. 4.

The effects of concentration and temperature on the absorption maxima of the dyes were also examined and the results are listed in Table 3 (see supplementary data). The λ_{max} values of synthesized dyes do not vary considerably by altering the dye concentration in chloroform, acetonitrile, methanol, DMSO and DMF, except for that of dyes **3** and **4** in methanol, for which a red shift emerged when dye concentration was decreased. To evaluate the influence of temperature, a solution of each dye in chloroform, acetonitrile, methanol, DMSO and DMF was prepared and examined in a temperature range between 25 and 70 °C. The results indicate little change in λ_{max} values of dyes **1–8** on raising the temperature. These findings support the occurrence of a dissociation equilibrium related to hetarylazoquinolones in proton-accepting solvents in which no change in energy is involved.

Table 4
Percentage of bacterial growth in presence of dye (125 μg/ml) as compared to growth in the absence of the dye.

Comp.	*B. subtilis*	*E. coli*	*M. leuteus*	*Ps. aeruginosa*
1	0	0	0	0
2	46.8	0	59	74.6
3	57.1	0	49	51.8
4	54.5	0	0	4.0
5	18.0	14.0	23.8	26.8
6	53.3	41.0	54.2	70.6
7	0	37.0	0	0
8	42.2	66.9	54.6	60.5
Std[a]	0	0	0	0
Std[b]	0	35	0	0
Std[c]	0	0	68	0

[a] Tetracycline is used as standard.
[b] Penicillin is used as standard.
[c] Vancomycin is used as standard.

We evaluated the substituent and extension of resonance system effects on absorption maximum of synthesized heterocyclic azo dyes (see supplementary data Table 1). As it is apparent in Table 1, the introduction of electron- accepting nitro group into position 6 on benzothiazole ring results in hypsochromic shift in all solvents as compared to electron-donating, methyl and methoxy groups (for dye **3** $\Delta\lambda = 77$ nm; for dye **4** $\Delta\lambda = 85$ nm relative to dye **5** for spectra in methanol). Also dye **2;** including benzothiazole rings, show bathochromic shifts due to extended resonance system in comparison with dye **1** containing thiazolyl ring.

Antimicrobial activity

Control media containing DMSO, the bacterium only, and bacterium plus DMSO, showed that DMSO had no effect on absorbance or growth of the bacterium. The effect of the dyes on bacterial growth is shown in Table 4. All the dyes tested had an effect on bacterial growth, with the most effect being exhibited with, respectively, dyes number **1**, **7** and **4**. Dyes **6** and **8** had the least effect on bacterial growth. There was some growth by *E. coli* and *M. leuteus* in the presence of penicillin and vancomycin, respectively. Dye number **1** completely stopped growth by all four bacteria, as did tetracycline. Dye number **7** had a very similar effect to penicillin, stopping growth by all bacteria, except *E. coli*. showed a 37% growth in the presence of the dye and 35% growth in presence of penicillin. Dye number **4** stopped all growth by *E.coli* and *M. leuteus* and only 4% growth was shown by *Ps. aeruginosa*.

Conclusion

In summary eight dyes were prepared, in high yields, by diazotization of different heterocyclic amines and coupling with 8-chloro-4-hydroxyl-2-quinolone. The solvatochromic behaviors of these dyes in various solvents were evaluated. It was found that these azo dyes exist in azo-enol-keto forms in solid state, and in hydrazone-keto forms in solvents. It was also observed that the introduction of electron-accepting nitro group into position 6 on benzothiazole ring results in hypsochromic shift in all solvents, as compared to electron-donating, methyl and methoxy groups. All the dyes tested had some effect on bacterial growth, most potency being shown with dye number **1**. The antibacterial effects of the dyes demonstrate that these potentially valuable properties need to be examined in more detail.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2013.09.046.

References

[1] V. Ukrainets, S.G. Taran, O.V. Gorkhova, E.A. Taran, N.A. Jaradat, I.Y. Petokhova, Chem. Heterocycl. Compd. 36 (2000) 166–169.
[2] T.N. Glasnov, W. Stadlbauer, C.O. Kappe, J. Org. Chem. 70 (2005) 3864–3870.
[3] I.V. Ukrainets, A.A. Tkach, L.Y. Yang, Chem. Heterocycl. Compd. 44 (2008) 1347–1354.
[4] G. Leclerc, G. Marciniak, N. Decker, J. Schwartz, J. Med. Chem. 29 (1986) 2427–2432.
[5] J. Milecki, S.P. Baker, K.M. Standifer, T. Ishizu, Y. Chida, J.W. Kusiak, J. Med. Chem. 30 (1987) 1563–1566.
[6] I.V. Ukrainets, N.L. Bereznyakova, V.A. Parshikov, O.I. Naboka, Chem. Heterocycl. Compd. 44 (2008) 178–183.
[7] I.V. Ukrainets, N.L. Bereznyakova, E.V. Mospanova, Chem. Heterocycl. Compd. 43 (2007) 856–862.
[8] T. Hardahir, M.-R. Zhang, J. Maeda, T. Okauchi, T. Kida, K. Kawabe, S. Sasaki, T. Suhara, K. Suzuki, Chem. Pharm. Bull. 49 (2001) 147–150.
[9] T. Fuchigami, T. Haradahira, N. Fujimoto, Y. Nojiri, T. Mukai, F. Yamamoto, T. Okauchi, J. Maeda, K. Suzuki, T. Suhara, Bioorg. Med. Chem. 17 (2009) 5665–5675.
[10] R.B. Toche, M.N. Jachak, J. Heterocycl. Chem. 36 (1999) 467–471.
[11] M.N. Elinson, V.M. Merkulova, A.I. Ilovaisky, D.V. Demchuk, P.A. Belyakov, G.I. Nikishin, Mol. Diversity 14 (2010) 833–839.
[12] A. Dandia, S. Gautam, A.K. Jain, J. Fluorine Chem. 128 (2007) 1454–1460.
[13] H. Yousefi, A. Yahyazadeh, M.R. Yazdanbakhsh, M. Rassa, E.O Moradi-e-Rufchahi, J. Mol. Struct. 1015 (2012) 27–32.
[14] H. Yousefi, A. Yahyazadeh, Chin. Chem. Lett 23 (2012) 685–689.
[15] H. Yousefi, A. Yahyazadeh, E.O. Moradi-e-Rufchahi, M. Rassa, J. Mol. Liq. 180 (2013) 51–58.
[16] M.R. Yazdanbakhsh, M. Abbasnia, M. Sheykhan, L. Ma'mani, J. Mol. Struct. 97 (2010) 266–273.
[17] M.R. Yazdanbakhsh, A. Mohammadi, M. Abbasnia, Spectrochim. Acta A 77 (2010) 1084–1087.
[18] A. Mohammadi, M.R. Yazdanbakhsh, L. Farahnak, Spectrochim. Acta A 89 (2012) 238–242.
[19] C. Sakong, Y.D. Kim, J.-H. Choi, C. Yoon, J.P. Kim, Dyes Pigm 88 (2011) 166–173.
[20] M.H. Majles Ara, S.H. Mousavi, E. Koushki, S. Salmani, A. Gharibi, A. Ghanadzadeh, J. Mol. Liq. 142 (2008) 29–31.
[21] M. Kawasaki, H. Yamamoto, J. Am. Chem. Soc. 128 (2006). 16482-14683.
[22] G. Hallas, J.-H. Choi, Dyes Pigm. 40 (1999) 119–129.
[23] M.A. Weaver, L. Shuttleworth, Dyes Pigm. 3 (1982) 81–121.
[24] M.R. Yazdanbakhsh, A. Mohammadi, E. Mohajerani, H. Nemati, N. Hosain Nataj, A. Moheghi, E. Naeemikhah, J. Mol. Liq. 151 (2010) 107–112.
[25] M.R. Yazdanbakhsh, H. Yousefi, M. Mamaghani, E.O. Moradi, M. Rassa, H. Pouramir, M. Bagheri, J. Mol. Liq. 169 (2012) 21–26.
[26] P. Manojkumar, T.K. Ravi, S. Gopalakrishnan, Eur. J. Med. Chem. 44 (2009) 4690–4694.
[27] F. Karci, N. Sener, M. Yamac, I. Sener, A. Demircali, Dyes Pigm. 80 (2009) 47–52.
[28] A. Manvar, A. Bavishi, A. Radadiya, J. Patel, V. Vora, N. Dodia, K. Rawal, A. Shah, Bioorg. Med. Chem. Lett. 21 (2011) 4728–4731.
[29] D.R. Buckle, B.C.C. Cantello, H. Smith, B.A. Spicer, J. Med. Chem. 18 (1975) 726–732.
[30] A. Lycka, Z. Vrba, M. Vrba, Dyes Pigm. 47 (2000) 45–51.
[31] A. Lycka, Dyes Pigm. 43 (1999) 27–52.