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Some heterocyclic azo dyes derived from thiazolyl derivatives; synthesis; substituent effects and solvatochromic studies

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ABSTRACT

was investigated as well.

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1. Introduction

Thiazoles and their derivatives have attracted continuing interest over the years because of their versatile applications in various fields [1-4]. Thiazole derivatives also have been extensively used in the preparation of all kinds of dyes, especially azo dyes. Due to their sulfur and/or nitrogen content, these dyes provide bright and strong shades that range from red to green and blue [5-10]. In addition, five-membered heterocyclic azo dyes, such as azothiazoles, are of great importance since they have pronounced bathochromic absorptions compared to corresponding benzoid dyes and are environmentally friendly [6,11-14]. It is well known that azo dyes including thiazolyl components have been hugely utilized in the fields of nonlinear optics and optical data storage and have shown excellent optical properties in comparison with azo dyes derived from substituted anilines [8,9,15–17]. Recently, we have also demonstrated that azo dyes including thiazolyl component have many favorable features as nonlinear optical chromophores [6].

The present paper is concerned with the synthesis of some azo disperse dyes via coupling of heterocyclic aromatic diazonium salts with nucleophilic components. Furthermore, the effects of substituent, miscellaneous pH and solvatochromism features on these dyes were evaluated. The absorption maxima of these dyes changed significantly by the introduction of various substituents on the benzothiazolyl ring. Besides, the dyes 6 and 7 with methoxy group showed acid-base equilibrium in acidic solutions. The synthesized dyes were characterized by ¹H NMR, FT-IR and UV-Vis spectra and the chemical structures of these dyes are shown in Scheme 1.

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2. Results and discussion

2.1. Synthesis and characterization

A series of azo disperse dyes were synthesized by coupling reaction of N,N-diethylaniline, 2-

anilinoethanol and N-phenyl-2,2'-iminodiethanol with diazotized aminothiazolyl derivatives as diazo

components. These dyes have been prepared in good yields, and were characterized by UV-Vis, FT-IR

and ¹H NMR spectroscopic techniques. The effects of solvent polarity and various pH on dyes in the visible absorption spectra were evaluated. All dyes exhibit an excellent correlation coefficient (r > 0.92) for

the linear solvation energy relationship with π^* values calculated by Kamlet et al. The influence of the

pH on the dyes with electron-donating group implied that these dyes exist in acid-base equilibrium in

acidic environment. The effect of substituents of both coupler and diazo component on the color of dyes

Following the general procedure to prepare azo dyes, heterocyclic amines were first diazotized utilizing nitrosyl sulfuric acid and then treated with N-phenyl-2,2'-iminodiethanol, N,Ndiethylaniline and 2-anilinoethanol as coupling compounds dissolved in acetonitrile containing several drops of glacial acetic acid in an ice bath giving azo dyes 1–9 in good yields (Scheme 1). The structures of dyes were fully confirmed by their spectral data in deuterio-chloroform (CDCl₃) deuterio-dimethylsulfoxide (DMSO d_6), and the signals were reported at TMS as the internal reference. In ¹H NMR spectra, triplet appeared at 3.55, 3.48, 3.64 and 3.67 ppm are indicative of N-CH₂ protons and triplet or quartet appeared at 3.65, 3.60, 3.86 and 3.71 ppm represent O-CH₂ protons for dyes 1, 4, 6 and 8, respectively. Also a broad signal of OH protons can be seen at 4.62-4.94 ppm. For dyes 2, 5, 7 and 9 including N,Ndiethylaniline as coupler compound, and significant triplet signals of methyl protons (CH₃) were observed at 1.28, 1.31, 1.29 and 1.35 ppm, respectively. A clear quartet signals at 3.50, 3.55, 3.53 and 3.71 ppm were attributed to the methylene protons. Dye 3 showed two 2H triplet at 3.75 and 4.41 ppm, which were attributed to methylene protons in the coupling component. As well as these distinctive signals, the two broad signals at 5.07 and 7.28 ppm, seems to belong to the OH and NH protons, respectively. The aromatic

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protons for all compounds were observed from 6.65 to 9.04 ppm in the ¹H NMR spectrum. Therefore, all chemical shifts assigned to the spectrum clearly confirm the formation of these dyes.

2.2. UV–Visible and solvatochromic studies of dyes

It has long been known that UV-Vis/near-IR absorption spectra of chemical compounds especially azo dyes influenced by the surrounding medium and solvents can bring about a change in the position, intensity, and shape of absorption bands. In order to investigate the solvatochromic behaviour of synthesized disperse dyes we recorded their absorption spectra in 13 solvents with different polarities at a concentration of 10⁻⁵ to 10⁻⁶ M in the range of 300–700 nm (Table 1). The λ_{max} of all dyes were found to exhibit a strong solvent dependency, showing bathochromic effect (positive solvatochromism) in more polar solvents in comparison with solvents with less polarity characteristics. The higher values of λ_{max} were obtained in basic solvents such as DMSO, DMF for dyes including electron-withdrawing groups on benzothiazole rings while for dyes with electron-donating groups the higher values were gained in acidic solvents. The red shift in basic solvents is an account of these solvents interaction with non-bonding electron pair on nitrogen atom of coupler compounds that causes extended conjugation resonance system of dyes, while the significant red shift in glacial acetic acid (146 nm relative to cyclohexane for dye 6) is related to presence of these dyes in hydrazone form in acidic solutions as observed in our previous study [13,14]. As it is apparent in Table 1, λ_{max} of synthesized dyes shows a regular variation in different solvents. In particular, all dyes exhibit an excellent correlation coefficient (r) for the linear solvation energy relationship with π^* values calculated by Kamlet et al. [18]. Sample of such correlations are provided in Fig. 1 for dyes 6 and 8. For investigated solvents the correlation coefficient values (r) were as follows:

 Γ = 0.934 for Dye1, Γ = 0.933 for Dye2, Γ = 0.923 for Dye4, Γ = 0.923 for Dye5, Γ = 0.946 for Dye6, Γ = 0.932 for Dye7, Γ = 0.967 for Dye8 and Γ = 0.953 for Dye9.

These values obtained without acetic acid, chloroform and dichloromethane, which deviate from the regression line. In acidic media presence of acid–base equilibrium causes the deviation. It can be attributed to presence of two distinct species in the solvent medium. For two other solvents the deviation may be due to unique interactions between the polychlorinated solvents and the solute molecules. Such interactions can be accounted using another specific solvent polarity scale named as delta (δ) that generally is used in multi-parameter correlation. Therefore, these dyes with excellent correlation coefficient can be considered as solvent



Fig. 1. Variation of λ_{max} (nm) of dyes 6 and 8 as a function of π^* .

polarity indicator dyes. The influence of pH on the dye 6 with electron-donating group is taken into account by comparison of the absorption maxima of this dye in solutions with different pH, and shows that the dye exists in acid–base equilibrium (Scheme 2). Considering the λ_{max} in Fig. 2, this dye in acidic solutions shifts to higher wavelengths (614 nm for pH 1), which is probably related to the prominence of hydrazone form in acidic medium, while in neutral and basic solutions the dye exists in azo form (518 nm for pH 7 and 536 nm for pH 13). Therefore, dye 6 shows a slightly bathochromic shift in basic medium (18 nm) relative to neutral solutions. The UV–Vis spectroscopic study on dye 6 clearly indicates that the present dye exists in acid–base equilibrium forms in solution with pH 5 as shown in Fig. 2.



Fig. 2. Absorption of dye 6 in acidic, neutral and basic solutions at concentration of ${\sim}5\times10^{-5}$ M.



Scheme 2. Acid-base equilibrium of dye 6.

Base in mind those heterocyclic azo dves, especially those including sulfur and/or nitrogen, provide bright strong shades ranging from red to green and blue, which complement the yellow-orange colors of the nitrogen heterocyclic azo dyes so as to provide a complete coverage of the entire shade range [19,20]. In order to investigate the substituent effects, we recorded the spectral shifts of synthesized dyes in ethanol (Table 1). As expected, the donor-acceptor polarization of compounds 8 and 9 is increased by introducing an electron-accepting nitro group into the 6-position of benzothiazole ring, caused bathochromic shifts relative to similar dyes 6 and 7 including an electron-donating group. Also dyes 4 and 5, including benzothiazolyl ring, showed bathochromic shift due to extended resonance system in comparison with dyes 1, 2 and 3 containing thiazolyl ring as shown in Table 1. The maximum bathochromic absorption shifts along with the increase in the electron-accepting ability of substituents in the sequence of thiazole (dye 1) < benzothiaole (dye 4) < p-methoxybenzothiazole (dye</pre> 6) < *p*-nitrobenzothiazol (dye 8) are consistent with an increase in molecular donor-acceptor polarization.

2.3. Conclusions

In this study, a series of heterocyclic azo dyes based on thiazolyl derivatives with metallic shine were synthesized, good yields of these azo dyes were obtained via purification procedures. The structures of prepared dyes were confirmed by ¹H NMR, FT-IR and UV–Vis spectra. In order to determine the solvent polarity indicator dyes, we carried out a study of the absorption spectra for all dyes in selected solvents of different solvation characteristics. Also, the influence of the pH changes on the dye 6 with electron-donating group is considered by comparison of the absorption maxima of this dye in solutions with different pH, these fact directed us to the conclusion that the dye exist in acid–base equilibrium forms.

3. Experimental

3.1. Material and instrumentation

All reagents were of the highest purity available, purchased from Merck and Aldrich Chemical Companies and were used without further purification. All melting points were determined on

Table 1

Solvatochromic data [λ_{max} (nm)] for all synthesized dyes in 13 solvents with π^* values by Kamlet et al. [18].

an electrothermal melting point apparatus and were uncorrected. Infrared spectra were recorded on a Shimadzu 8400 FT-IR spectrophotometer. The ¹H NMR spectra were obtained on a FT-NMR (500 MHz) Bruker apparatus spectrometer, and the chemical shifts are expressed in δ ppm using TMS as an internal standard. UV–Vis absorption spectra were obtained using a Pharmacia Biotech Spectrophotometer.

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

For the preparation of dyes 1–9, the diazonium coupling reaction was employed. The route of synthesis of dyes is presented in Scheme 1. A typical procedure used for preparation of dyes is described below.

Nitrosyl sulfuric acid solution was prepared from concentrated sulfuric acid (8 mL) and sodium nitrite (0.21 g, 3 mmol) at 70 °C, and then cooled to 5 °C. This solution was added dropwise, with stirring, to 30 mL of acetic acid and propionic acid mixture (2:1) containing 3 mmol of heterocyclic amines (3 mmol) in an ice bath. The mixture was then stirred for an additional 1 h at 0–5 °C. After completion of diazotization procedure, the diazonium salt solution was added dropwise to the solution of coupler compounds (3 mmol) in acetonitrile (20 mL) and some drops of acetic acid. The resulting solution was vigorously stirred at 0-4 °C for 2 h, while the pH of the reaction mixture was maintained at 6-7 by simultaneous addition of sodium hydroxide solution (0.5 M). The progress of the reaction was evaluated by thin layer chromatography (TLC) and then crude dyes were filtered, washed with excess water and purified by recrystallization. The physical and spectral data of the purified dyes are as follows.

3.2.1. Dye (1)

Violet solid with metallic luster. Yield 82%. Mp 184–186 °C. Recrystallization from acetone/H₂O. IR (KBr): ν 3325 (OH), 2880–2980 (Aro.-H), 1508 (N=N). ¹H NMR (DMSO-d₆) δ 3.55 (t, 4H, N–CH₂, *J* = 5.43 Hz), 3.65 (t, 4H, O–CH₂, *J* = 5.43 Hz), 4.87 (t, 2H, OH, *J* = 5.12 Hz), 6.92 (d, 2H, Aro.-H, *J* = 9.33 Hz), 7.66 (d, 1H, Aro.-H, *J* = 3.35 Hz), 7.78 (d, 2H, Aro.-H, *J* = 9.33 Hz), 7.94 (d, 1H, Aro.-H, *J* = 3.35 Hz).

| | | - | - | | - | | | | | |
|---------------------|---------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|
| Solvents | π^* | Dye1 λ _{max} (nm) | Dye2 λ _{max} (nm) | Dye3 λ _{max} (nm) | Dye4 λ _{max} (nm) | Dye5 λ _{max} (nm) | Dye6 λ _{max} (nm) | Dye7 λ _{max} (nm) | Dye8 λ _{max} (nm) | Dye9 λ _{max} (nm) |
| Cyclohexane | 0.00 | 446 | 451 | 368 | 466 | 470 | 468 | 476 | 509 | 512 |
| Diethyl ether | 0.24 | 477 | 475 | 375 | 497 | 494 | 499 | 498 | 531 | 531 |
| Ethyl acetate | 0.45 | 477 | 477 | 379 | 496 | 496 | 497 | 499 | 533 | 534 |
| Dioxane | 0.49 | 479 | 483 | 376 | 497 | 500 | 500 | 503 | 531 | 534 |
| Ethanol | 0.54 | 490 | 495 | 374, 478 | 515 | 517 | 513 | 518 | 546 | 551 |
| Methanol | 0.60 | 490 | 496 | 375, 479 | 511 | 517 | 513 | 520 | 545 | 550 |
| Acetone | 0.62 | 484 | 487 | 371, 468 | 506 | 507 | 508 | 510 | 543 | 545 |
| Glacial acetic acid | 0.64 | 585 | 585 | 390, 569 | 600 | 596 | 614 | 610 | 584 | 581 |
| Acetonitrile | 0.66 | 486 | 491 | 371, 466 | 506 | 511 | 510 | 515 | 544 | 549 |
| Chloroform | 0.69 | 475 | 491 | 378 | 492 | 508 | 497 | 512 | 528 | 546 |
| Dichloromethane | 0.73 | 479 | 492 | 375 | 497 | 510 | 501 | 513 | 533 | 548 |
| Dimethylformamide | 0.88 | 497 | 498 | 378, 482 | 520 | 519 | 522 | 521 | 559 | 556 |
| Dimethylsulfoxide | 1.00 | 504 | 505 | 378, 491 | 525 | 525 | 530 | 529 | 569 | 564 |
| | | | | | | | | | | |

3.2.2. Dye (2)

Red–violet solid with metallic luster. Yield 85%. Mp 170–172 °C. Recrystallization from acetone/H₂O. IR (KBr): ν 2880–2980 (Aro.-H), 1505 (N=N). ¹H NMR (CDCl₃) δ 1.28 (t, 6H, CH₃, *J* = 7.11 Hz), 3.50 (q, 4H, N–CH₂, *J* = 7.11 Hz), 6.74 (d, 2H, Aro.-H, *J* = 9.26 Hz), 7.26 (d, 1H, Aro.-H, *J* = 3.35 Hz), 7.95 (d, 2H, Aro.-H, *J* = 9.26 Hz).

3.2.3. Dye (3)

Red solid with metallic luster. Yield 78%. Mp 120–122 °C. Recrystallization from EtOH/H₂O. IR (KBr): ν 3315 (OH) 3525 (NH), 1503 (N=N). ¹H NMR (DMSO-d₆) δ 3.75 (q, 2H, O–CH₂, *J* = 5.76 Hz), 4.41 (t, 2H, N–CH₂, *J* = 5.90 Hz), 5.07 (t, 1H, OH, *J* = 5.55 Hz), 7.28 (t, 1H, NH, *J* = 7.34 Hz), 7.44 (d, 1H, Aro.-H, *J* = 3.48 Hz), 7.48 (t, 2H, Aro.-H, *J* = 7.94 Hz), 7.62 (d, 2H, Aro.-H, *J* = 7.94 Hz), 7.71 (d, 1H, Aro.-H, *J* = 3.48 Hz).

3.2.4. Dye (4)

Violet solid with metallic luster. Yield 75%. Mp 220-222 °C. Recrystallization from acetone/H₂O. IR (KBr): ν 3335 (OH), 2900-2980 (Aro.-H), 1512 (N=N). ¹H NMR (DMSO-d₆) δ 3.48 (t, 4H, N-CH₂, *J* = 5.39 Hz), 3.60 (t, 4H, O-CH₂, *J* = 5.39 Hz), 4.62 (br, 2H, OH), 6.65 (d, 2H, Aro.-H, *J* = 9.31 Hz), 7.16 (t, 1H, Aro.-H, *J* = 7.14 Hz), 7.23 (t, 1H, Aro.-H, *J* = 7.10 Hz), 7.62 (d, 1H, Aro.-H, *J* = 7.69 Hz), 7.70 (d, 2H, Aro.-H, *J* = 9.31 Hz), 7.78 (d, 1H, Aro.-H, *J* = 7.99 Hz).

3.2.5. Dye (5)

Violet solid with metallic luster. Yield 80%. Mp 176–178 °C. Recrystallization from acetone/H₂O. IR (KBr): ν 2800–2950 (Aro.-H), 1510 (N=N). ¹H NMR (CDCl₃) δ 1.31(t, 6H, CH₃, *J* = 7.13 Hz), 3.55 (q, 4H, CH₂, *J* = 7.13 Hz), 6.78 (d, 2H, Aro.-H, *J* = 9.33 Hz), 7.42 (t, 1H, Aro.-H, *J* = 7.08 Hz), 7.50 (t, 1H, Aro.-H, *J* = 7.07 Hz), 7.86 (d, 1H, Aro.-H, *J* = 7.48 Hz), 8.02 (d, 2H, Aro.-H, *J* = 9.33 Hz), 8.10 (d, 1H, Aro.-H, *J* = 8.00 Hz).

3.2.6. Dye (6)

Dark violet solid with metallic luster. Yield 86%. Mp 216–218 °C. Recrystallization from DMF/H₂O. IR (KBr): ν 3300 (OH), 2850–3000 (Aro.-H), 1509 (N=N). ¹H NMR (DMSO-d₆) δ 3.64 (s, 8H, CH₂), 3.86 (s, 3H, OCH₃), 4.89 (t, 2H, OH, *J*=5.37 Hz), 6.96 (d, 2H, Aro.-H, *J*=9.30 Hz), 7.12 (d, 1H, Aro.-H, *J*=8.90 Hz), 7.61 (s, 1H. Aro.-H), 7.82 (d, 2H, Aro.-H, *J*=9.30 Hz), 7.88 (d, 1H, Aro.-H, *J*=8.90 Hz).

3.2.7. Dye(7)

Dark violet solid with metallic luster. Yield 90%. Mp 148–150 °C. Recrystallization from DMF/H₂O. IR (KBr): v 2920–2980 (Aro.-H), 1506 (N=N). ¹H NMR (CDCl₃) δ 1.29 (t, 6H, CH3, J = 7.14 Hz), 3.53 (q, 4H, CH2, J = 7.14 Hz), 3.95 (s, 3H, OCH₃), 6.77 (d, 2H, Aro.-H, J = 9.29 Hz), 7.10 (d, 1H, Aro.-H, J = 8.89 Hz), 7.32 (s, 1H, Aro.-H), 7.98 (d, 2H, Aro.-H, J = 9.29 Hz), 8.00 (s, 1H, Aro.-H).

3.2.8. Dye (8)

Violet–green solid with metallic luster. Yield 72%. Mp 240–242 °C. Recrystallization from DMF/H₂O. IR (KBr): ν 3380 (OH), 2910–2980 (Aro.-H), 1520 (N=N). ¹H NMR (DMSO-d₆) δ 3.67 (t, 4H, N–CH₂, *J* = 5.17 Hz), 3.71 (q, 4H, OCH₂, *J* = 5.17 Hz), 4.94 (t, 2H, OH, *J* = 5.24 Hz), 7.07 (d, 2H, Aro.-H, *J* = 9.44 Hz), 7.89 (d, 1H, Aro.-H, *J* = 9.32 Hz), 8.12 (d, 1H, Aro.-H, *J* = 8.95 Hz), 8.32 (d, 1H, Aro.-H, *J* = 8.95 Hz), 9.04 (s, 1H, Aro.-H).

3.2.9. Dye (9)

Violet–green solid with metallic luster. Yield 76%. Mp 236-238 °C. Recrystallization from DMF/H₂O. IR (KBr): ν 2930–2990 (Aro.-H), 1517 (N=N). ¹H NMR (CDCl₃) δ 1.35 (t, 6H, CH₃, *J* = 7.09 Hz), 3.56 (q, 4H, CH₂, *J* = 7.09 Hz), 6.81 (d, 2H, Aro.-H, *J* = 9.10 Hz), 8.03 (d, 2H, Aro.-H, *J* = 9.10 Hz), 8.13 (d, 1H, Aro.-H, *J* = 8.82 Hz), 8.35 (d, 1H, Aro.-H, *J* = 8.82 Hz), 8.78 (s, 1H, Aro.-H).

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