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Synthesis, structural characterization and tautomeric properties of some novel bis-azo dyes derived from 5-arylidene-2,4-thiazolidinone



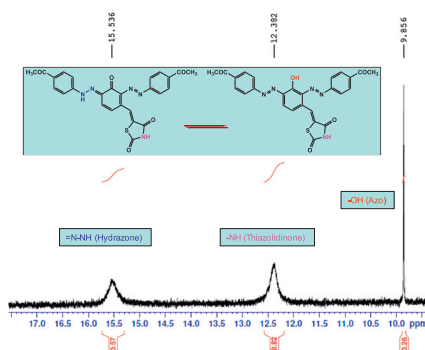
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HIGHLIGHTS

- Nine novel bis-azo dyes were synthesized and fully characterized.
- Spectroscopic properties were examined by UV-vis, FT-IR and NMR techniques.
- The azo-hydrazone tautomeric forms of prepared dyes were investigated.
- Effects of pH on the absorption spectrum of dyes were studied.

GRAPHICAL ABSTRACT

The partial ^1H NMR spectrum of synthesized dye in DMSO.

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ABSTRACT

Nine new bis-azo dyes derived from 5-arylidene-2,4-thiazolidinone have been synthesized in two steps using Knoevenagel condensation and diazotization-coupling reaction. The structures of the compounds were confirmed by UV-vis, IR, ^1H NMR and ^{13}C NMR spectroscopic techniques. The spectral characterizations demonstrate that there is an equilibrium between the azo (T1) and hydrazine (T2 and T3) tautomers for all prepared dyes in solutions. In addition, the solvatochromic behavior of the prepared dyes was evaluated using polarity/polarizability parameter (π^*) in various solvents. The UV-vis absorption spectra of dyes show a bathochromic shift with increasing polarity and base strength of the solvents. Finally, the effects of acid and base on the UV-vis absorption spectra of the dyes with different substituent in diazo component are reported.

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Introduction

Azo chromophores are a group of colorant materials characterized by the presence of an azo group ($-\text{N}=\text{N}-$) but can contain two (disazo), three (trisazo), or, more rarely, four (tetraakisazo) or

more (polyazo) azo groups. Since their discovery in the 19th century, azo compounds have been extensively used as colorants and accounting for over 50% of all commercial dyes [1,2].

In addition to their use as colorants, they have been employed for many applications, such as in ink jet printing [3], thermal transfer printing [4], photography [5], color additives [6], biomedical area [7], molecular recognition [8], light controlled polymers [9], liquid crystal industry [10].

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In addition, bis-azo dyes are a well known group of organic colorants, due to their versatile applications in various fields. Several synthetic ways have been developed to synthesis bis-azo derivatives. However, the common methods for synthesis of these classes of dyes are the using of diazotization-coupling reactions by aromatic diamines or phenols [11–13].

On the other hand, azo dyes with hydroxyl group at ortho to azo band display tautomerism depending on the proton transfer and azo-hydrazone tautomers of these compounds have been extensively studied. Determination and characterization of azo-hydrazone tautomers is interesting, since the tautomers have different technical properties [14–16].

Thiazolidine and its derivatives as bioactive heterocycles play a key role in medicinal chemistry and they have been extensively used as scaffolds for drug development [17–19]. Thiazolidinediones show a wide variety of biological activities such as antifungal, antibacterial, antiviral, antitumor, and antidiabetic potential [20–25]. Furthermore, thiazolidine derivatives represent useful synthetic building blocks in organic chemistry. However, there are very few reports on the synthesis of bisazo dyes bearing thiazolidinedione moiety in the literature. In addition, synthesis and application of such dyes is important in pharmaceutical, food, color and other industries and a foremost task for chemists. According to the above potent usefulness of the thiazolidinediones and in continuation of our studies on the synthesis of azo dyes [26], we report herein the synthesis of some novel bis-azo dyes bearing thiazolidine moiety in order to evaluate structure, solvatochromism and tautomeric properties (Scheme 1).

Experimental

Materials and apparatus

All compounds used in this study were obtained from Merck and Aldrich Chemical Companies and were used without further purification. All melting points were determined on an Electrothermal melting point apparatus and are uncorrected. Infrared spectra

were recorded on a Shimadzu 8400 FT-IR spectrophotometer. The Proton nuclear magnetic resonance (^1H NMR) spectra were obtained on a FT-NMR (400 MHz) Bruker apparatus spectrometer, and the chemical shifts are expressed in δ ppm using TMS as an internal standard. The visible spectra were measured using a Pharmacia Biotech Spectrophotometer. The purity determination of the substrates and reaction monitoring were accompanied by TLC using silica gel SIL G/UV 254 plates.

Synthesis of 5-(3-hydroxybenzylidene)-2,4-thiazolidinedione (**1**)

A mixture of m-hydroxy benzaldehyde (0.336 g, 3 mmol) and 2,4-thiazolidinedione (0.351 g, 3 mmol) with catalytic quantity of piperidine was refluxed in ethanol for 4–5 h and then cooled to 0 °C in an ice bath. After that HCl (0.5 M) and water are added and the precipitate is filtered and washed with water and petroleum ether. The solid product was isolated by recrystallization from EtOH/H₂O.

Light Yellow solid; yield 96%; m.p. 273–274 °C; IR (KBr) ν cm⁻¹: 3300 (OH), 3180 (NH), 3063 (=C–H), 1742 (C=O), 1686 (C=O), 1610 (C=C); ^1H NMR (400 MHz, DMSO-*d*₆), δ (ppm): 6.88 (d, 1H, *J* = 8.0 Hz, Ar–H), 6.99 (s, 1H, Ar–H), 7.04 (d, 1H, *J* = 8.0 Hz, Ar–H), 7.34 (t, 1H, *J* = 8.0 Hz, Ar–H), 7.70 (s, 1H, CH=C), 9.85 (s, 1H, OH), 12.61 (s, 1H, NH) ppm.

Synthesis of bis-azo dyes (**3a–i**)

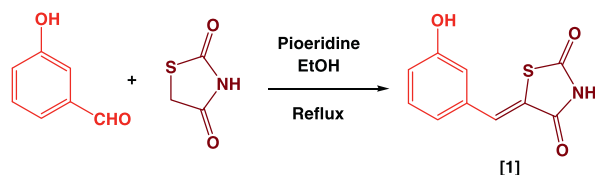
Diazotization

The aryl diazonium salts were prepared in good yield from equimolar mixture of aniline derivatives (**1a–i**) (6 mmol) and sodium nitrite (0.414 g, 6 mmol) according to previously described method [26].

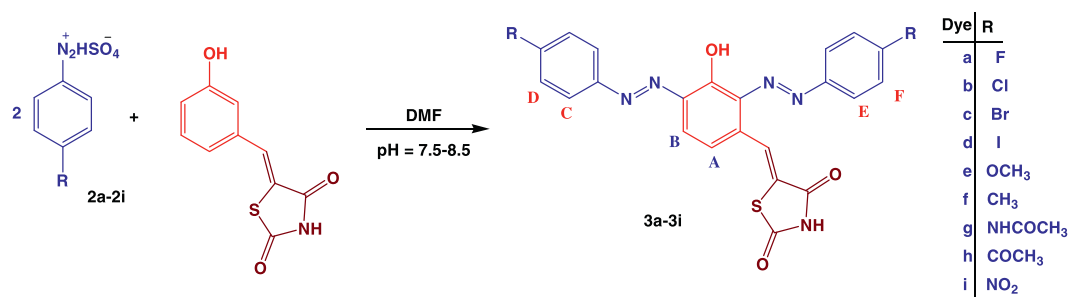
Coupling

The prepared diazonium salts solution was slowly added to a stirred solution of 5-(3 hydroxybenzylidene)-2,4-thiazolidinedione (**1**) (0.663 g, 3 mmol) as coupling component in alkali medium by

Step 1: Synthesis of intermediate **1** (Knoevenagel condensation)



Step 2: Synthesis of bis-azo dyes **3a–3i**.



Scheme 1. General synthetic route for synthesis of dyes **3a–3i**.

adjusting the pH at 8–9 and the temperature was maintained at 0–5 °C. The resulting solution was stirred for 2–3 h in an ice bath then allowed to reach room temperature. After 1 h, the pH value of the diazo liquor was adjusted to pH 4–4.5 by adding a diluted hydrochloric acid solution (0.5 M). The precipitated colored solids were filtered with suction, washed several times with cold water and purified by further recrystallization from DMF/H₂O, and finally dried in desiccator over anhydrous CaCl₂ to give the corresponding bis-azo dyes **3a–i** (Scheme 1). However, the amounts of formed by-products are trace, and cannot be isolated in the purification procedure. The purity and structure of prepared dyes was confirmed by physical and spectroscopic data.

Dye 3a. Red solid; yield 78%; m.p. 266–268 °C; IR (KBr) ν cm⁻¹: 3350 (OH), 3200 (NH), 3080 (=C–H), 1744 (C=O), 1690 (C=O), 1610 (C=C), 1505 (N=N); ¹H NMR (400 MHz, DMSO-*d*₆), δ (ppm): 6.70 (dd, 1H, *J* = 5.2 Hz, Ar–H, H_A), 7.29 (m, 2H, Ar–H, H_D), 7.47 (m, 2H, Ar–H, H_F), 7.63 (m, 4H, Ar–H, H_C and H_E), 7.87 (d, 1H, *J* = 9.6 Hz, Ar–H, H_B), 8.32 (s, 1H, CH=C), 9.86 (s, 0.44H, OH), 12.23 (s, 1H, NH), 15.73 (br s, 0.56H, N–NH). ¹³C NMR (DMSO-*d*₆), δ (ppm): 46.5, 116.8, 117.0, 119.6, 129.0, 129.1, 129.7, 131.4, 132.8, 134.9, 139.2, 144.6, 159.2, 161.6, 161.7, 164.1, 171.3, 172.6, 178.7, 179.0.

Dye 3b. Red solid; yield 82%; m.p. 239–240 °C; IR (KBr) ν cm⁻¹: 3300 (OH), 3184 (NH), 3060 (=C–H), 1746 (C=O), 1684 (C=O), 1610 (C=C), 1503 (N=N); ¹H NMR (400 MHz, DMSO-*d*₆), δ (ppm): 6.72 (dd, 1H, *J* = 4.8 Hz, Ar–H, H_A), 7.44 (d, 2H, *J* = 8.8 Hz, Ar–H, H_D), 7.59 (d, 4H, *J* = 8.4 Hz, Ar–H, H_C and H_E), 7.70 (d, 2H, *J* = 8.4 Hz, Ar–H, H_F), 7.88 (d, 1H, *J* = 9.6 Hz, Ar–H, H_B), 7.96 (s, 1H, CH=C), 9.86 (s, 0.21H, OH), 12.25 (s, 1H, NH), 15.63 (br s, 0.79H, N–NH). ¹³C NMR (DMSO-*d*₆), δ (ppm): 116.3, 119.1, 119.5, 129.4, 129.9, 130.4, 132.0, 134.8, 140.6, 144.2, 158.8, 160.2, 161.9, 164.1, 167.6, 170.3, 178.2, 179.1.

Dye 3c. Red solid; yield 86%; m.p. 233–234 °C; IR (KBr) ν cm⁻¹: 3114 (NH), 3045 (=C–H), 1744 (C=O), 1704 (C=O), 1608 (C=C), 1506 (N=N); ¹H NMR (400 MHz, DMSO-*d*₆), δ (ppm): 6.72 (dd, 1H, *J* = 4.4 Hz, Ar–H, H_A), 7.52 (d, 4H, *J* = 8.4 Hz, Ar–H, H_C and H_E), 7.59 (d, 2H, *J* = 8.4 Hz, Ar–H, H_D), 7.84 (d, 2H, *J* = 8.4 Hz, Ar–H, H_F), 7.90 (d, 1H, *J* = 10 Hz, Ar–H, H_B), 9.86 (s, 0.37H, OH), 12.29 (s, 1H, NH), 15.66 (br s, 0.63H, N–NH). ¹³C NMR (DMSO-*d*₆), δ (ppm): 115.9, 117.4, 118.6, 129.2, 129.3, 129.8, 130.9, 132.8, 135.1, 141.6, 143.6, 157.0, 157.6, 159.4, 161.1, 166.2, 170.9, 174.9, 178.5.

Dye 3d. Dark Red solid; yield 76%; m.p. 260–261 °C; IR (KBr) ν cm⁻¹: 3190 (NH), 3052 (=C–H), 1744 (C=O), 1700 (C=O), 1612 (C=C), 1512 (N=N); ¹H NMR (400 MHz, DMSO-*d*₆), δ (ppm): 6.70 (dd, 1H, *J* = 4.4 Hz, Ar–H, H_A), 7.52 (d, 4H, *J* = 8.4 Hz, Ar–H, H_C and H_E), 7.58 (d, 2H, *J* = 8.4 Hz, Ar–H, H_D), 7.70 (s, 1H, CH=C), 7.84 (d, 2H, *J* = 8.0 Hz, Ar–H, H_F), 7.89 (d, 1H, *J* = 9.6 Hz, Ar–H, H_B), 9.86 (s, 0.39H, OH), 12.28 (s, 1H, NH), 15.62 (br s, 0.61H, N–NH). ¹³C NMR (DMSO-*d*₆), δ (ppm): 110.3, 110.7, 116.0, 116.5, 118.2, 128.5, 129.8, 132.8, 134.2, 138.8, 144.6, 159.5, 166.3, 169.4, 169.9, 178.1, 178.7.

Dye 3e. Dark Red solid; yield 86%; m.p. 264–265 °C; IR (KBr) ν cm⁻¹: 3112 (NH), 3048 (=C–H), 1744 (C=O), 1700 (C=O), 1680 (C=O), 1605 (C=C), 1508 (N=N); ¹H NMR (400 MHz, DMSO-*d*₆), δ (ppm): 2.33 (s, 3H, OCH₃), 2.43 (s, 3H, OCH₃), 6.72 (dd, 1H, *J* = 5.2 Hz, Ar–H, H_A), 7.25 (d, 2H, *J* = 7.6 Hz, Ar–H, H_D), 7.42 (br s, 6H, Ar–H, H_C, H_E and H_F), 7.86 (d, 1H, *J* = 9.6 Hz, Ar–H, H_B), 12.23 (s, 1H, NH), 15.72 (br s, 0.44H, N–NH), 16.25 (br s, 0.56H, N–NH). ¹³C NMR (DMSO-*d*₆), δ (ppm): 59.1, 59.8, 119.1, 127.7, 128.2, 130.4, 132.2, 132.9, 136.9, 140.3, 145.4, 161.2, 161.6, 161.8, 164.8, 170.1, 178.0, 178.7.

Dye 3f. Dark Red solid; yield 83%; m.p. 244–245 °C; IR (KBr) ν cm⁻¹: 3300 (OH), 3112 (NH), 3040 (=C–H), 1744 (C=O), 1700 (C=O), 1680 (C=O), 1610 (C=C), 1504 (N=N); ¹H NMR (400 MHz, CDCl₃), δ (ppm): 2.39 (s, 3H, CH₃), 2.48 (s, 3H, CH₃), 6.75 (d, 1H, *J* = 9.6 Hz, Ar–H, H_A), 7.25 (d, 2H, *J* = 8.4 Hz, Ar–H, H_D), 7.36 (m, 4H, Ar–H, H_C and H_E), 7.45 (d, 2H, *J* = 8.0 Hz, Ar–H, H_F), 7.73 (d, 1H, *J* = 9.6 Hz, Ar–H, H_B), 12.26 (s, 1H, NH), 16.08 (br s, 0.67H, N–NH). ¹³C NMR (CDCl₃), δ (ppm): 26.7, 26.9, 119.8, 129.4, 130.0, 131.9, 133.5, 136.0, 141.4, 145.6, 161.4, 162.6, 164.3, 170.5, 171.9, 178.2, 178.7.

Dye 3g. Dark Red solid; yield 90%; m.p. 249–250 °C; IR (KBr) ν cm⁻¹: 3300 (OH), 3155 (NH), 3052 (=C–H), 1742 (C=O), 1715 (C=O), 1700 (C=O), 1680 (C=O), 1610 (C=C), 1502 (N=N); ¹H NMR (400 MHz, DMSO-*d*₆), δ (ppm): 2.08 (s, 3H, CH₃), 2.12 (s, 3H, CH₃), 6.75 (d, 1H, *J* = 9.2 Hz, Ar–H, H_A), 7.48 (m, 3H, Ar–H, H_D and CH=C), 7.70 (d, 2H, *J* = 8.8 Hz, Ar–H, H_F), 7.84 (m, 4H, Ar–H, H_C and H_E), 9.86 (s, 0.2H, OH), 10.14 (s, 1H, CONH), 10.31 (s, 1H, CONH), 12.12 (br s, 0.42H, CONHCO), 12.34 (br s, 0.50H, CONHCO), 15.77 (br s, 0.35H, N–NH), 16.36 (br s, 0.35H, N–NH). ¹³C NMR (DMSO-*d*₆), δ (ppm): 30.3, 31.2, 36.2, 117.0, 125.5, 126.0, 127.9, 130.3, 131.1, 134.4, 143.6, 147.5, 148.0, 162.7, 172.4, 182.6.

Dye 3h. Red solid; yield 88%; m.p. 253–254 °C; IR (KBr) ν cm⁻¹: 3300 (OH), 3118 (NH), 3050 (=C–H), 1744 (C=O), 1684 (C=O), 1610 (C=C), 1502 (N=N); ¹H NMR (400 MHz, DMSO-*d*₆), δ (ppm): 2.58 (s, 3H, CH₃), 2.68 (s, 3H, CH₃), 6.71 (d, 1H, *J* = 10 Hz, Ar–H, H_A), 7.66–7.75 (m, 4H, Ar–H, H_C and H_E), 7.93 (d, 1H, *J* = 9.6 Hz, Ar–H, H_B), 8.01 (d, 2H, *J* = 8.4 Hz, Ar–H, H_D), 8.19 (d, 2H, *J* = 7.6 Hz, Ar–H, H_F), 8.34 (s, 1H, CH=C), 9.85 (s, 0.26H, OH), 12.38 (br s, 1H, NH), 15.53 (br s, 0.57H, N–NH). ¹³C NMR (DMSO-*d*₆), δ (ppm): 37.0, 37.7, 121.4, 124.8, 128.0, 129.1, 130.8, 131.5, 136.4, 143.5, 147.9, 148.7, 161.0, 174.9, 181.3, 193.2, 193.6.

Dye 3i. Light Red solid; yield 79%; m.p. 299–300 °C; IR (KBr) ν cm⁻¹: 3200–3440 (OH, NH), 3066 (=C–H), 1740 (C=O), 1700 (C=O), 1680 (C=O), 1598 (C=C), 1510 (N=N); ¹H NMR (400 MHz, DMSO-*d*₆), δ (ppm): 6.70 (d, 1H, *J* = 9.6 Hz, Ar–H, H_A), 7.70 (d, 2H, *J* = 8.0 Hz, Ar–H, H_C), 7.88 (d, 2H, *J* = 8.8 Hz, Ar–H, H_E), 7.93 (d, 1H, *J* = 9.6 Hz, Ar–H, H_B), 7.96 (s, 1H, CH=C), 8.24 (d, 2H, *J* = 8.8 Hz, Ar–H, H_D), 8.49 (d, 2H, *J* = 8.8 Hz, Ar–H, H_F), 9.85 (s, 0.12H, OH), 12.39 (br s, 1H, NH), 15.23 (br s, 0.74H, N–NH). ¹³C NMR (DMSO-*d*₆), δ (ppm): 31.2, 36.2, 121.8, 122.7, 123.2, 124.8, 126.6, 127.2, 127.6, 133.1, 147.3, 150.1, 162.7.

Results and discussion

Synthesis

Knoevenagel condensation reaction of commercially available 2,4-thiazolidinedione as acidic component with 3-hydroxybenzaldehyde in refluxing ethanol in the presence of piperidine catalyst affords excellent yield of the 5-(3-hydroxybenzylidene)thiazolidine-2,4-dione (**1**) according to the literature methods [27] (Scheme 1, step 1).

The treatment of prepared different aryl diazonium salts with 5-(3-hydroxybenzylidene)thiazolidine-2,4-dione as key intermediate in alkaline medium provided novel bis-azo dyes **3a–i** in good yields (Scheme 1, step 2).

The structure of the synthesized intermediate **1** was confirmed by the IR, ¹H NMR spectroscopy. The infrared spectra of intermediate **1** showed the presence two carbonyl groups around 1722 cm⁻¹ and 1686 cm⁻¹ along with N–H and O–H groups at 3180–3300 cm⁻¹ region as overlapped. The ¹H NMR spectra of compound **1** displayed

the presence of vinyl, hydroxyl and amino protons around δ 7.70 (s, 1H, CH=C), 9.85 (br s, 1H, OH) and 12.61 (br s, 1H, NH) ppm, respectively.

The structures of the bis-azo dyes **3a–i** were confirmed by the IR, ^1H and ^{13}C NMR spectroscopy. The ^1H NMR spectra of all the dyes exhibited significant signals at δ 15.23–16.36 and around 9.85 ppm, which can be attributed to the imine N–H proton resonance (hydrazone form) and the hydroxyl O–H proton resonance (azo form), respectively. In addition, ^{13}C NMR spectra showed three and/or four C=O signals around at 170 ppm as a proof for the presence of a hydrazo group for all dyes in the solution. These data are in agreement with those previously reported for similar compounds [28]. Typical ^1H NMR spectra of dye **3a** is shown in Fig. 1.

On the other hand, IR and NMR spectra and UV–visible absorption spectroscopy indicated that the prepared bis-azo compounds existed in three tautomeric forms namely, azo-enol-azo (T1), hydrazo-keto-azo (T2) and azo-keto-hydrazo (T3), but the other tautomeric forms are possible. The tautomeric forms of dyes are shown in Scheme 2. Examination of all spectroscopic data reveals that the equilibrium between T1 and T2 or T3 tautomeric forms is predominantly shifted to the T2 and/or T3. For example, the dye **3h** exists in 65% in hydrazo form and 35% in azo form in solution of DMSO (Fig. 2).

The UV–vis absorption spectra of all the synthesized dyes showed two strong bands at about 280–360 and 450–550 nm, in which attributed to $n \rightarrow \pi^*$ and/or $\pi \rightarrow \pi^*$ electronic transitions of azo (T1) and hydrazo (T2 and T3) tautomeric forms, respectively. The UV–vis, IR, ^1H and ^{13}C NMR spectra also showed the important signals at their expected positions for all prepared bis-azo dyes. Thus, the chemical structures of bis-azo dyes were confirmed as shown in Scheme 1.

The UV–visible spectra and solvatochromic studies

In order to study of solvent effects on spectral features of the bis-azo dyes **3a–i**, we recorded their absorption spectra in twelve solvents with different polarity at a concentration of 10^{-4} – 10^{-5} M in the range of 200–800 nm at room temperature. The results are shown in Table 1. Typical UV–vis absorption spectra of dyes **3a** and **3h** in selected solvents are shown in Figs. 3 and 4, respectively.

As seen in Table 1, the two absorption maxima (λ_{max}) were observed in the range of 322–336 and 478–512 nm, in which attributed to T1 (azo) and T2 and/or T3 (hydrazone) tautomeric forms. However, the shape and intensity of both the azo and hydrazo tautomeric forms in all the dyes depend on the solvent–solute interactions and solvent nature as well as on the substituent type. As shown in Fig. 3, the UV–vis absorption spectra of the dye **3a** in polar and highly polar solvents such as DMF and DMSO showed a main band at about 280–380 nm, assigned to the azo tautomeric form and a very weak band at 440–540 nm, in which attributed to hydrazone tautomeric form. However, in protic and chlorinated solvents, the two main bands at about 280–380 nm and 440–540 nm were observed, assigned to the tautomeric azo-hydrazo equilibria.

The absorption spectra of all the investigated dyes except **3a** showed two main bands in the protic and non protic solvents as for the dye **3h** (Fig. 4). However, the intensity of bands in absorption spectra changes in relation to the type of substituent on the diazo component.

In addition, the UV–vis absorption spectra (λ_{max}) of the synthesized dyes are influenced by the solvents with different solvatochromic effects, which is due to the interaction between the

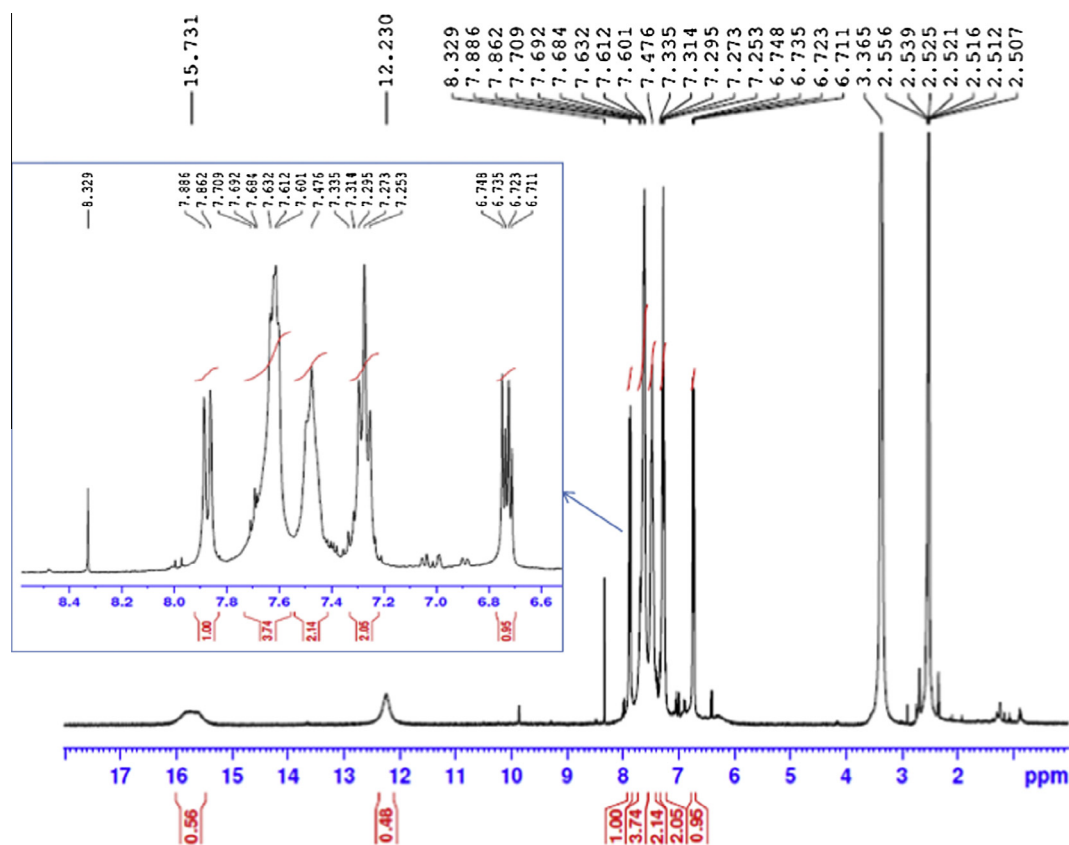
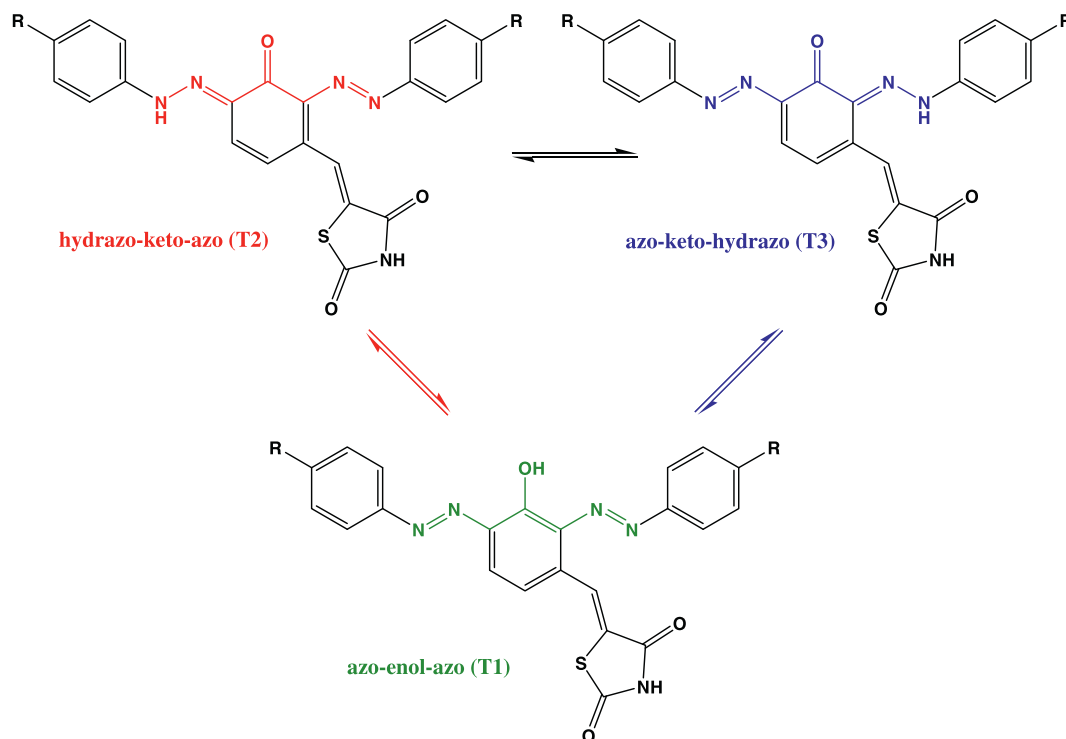


Fig. 1. ^1H NMR spectra of dye **3a**.



Scheme 2. The equilibrium between the azo form (T1) and the hydrazone forms (T2 and T3) of prepared dyes.

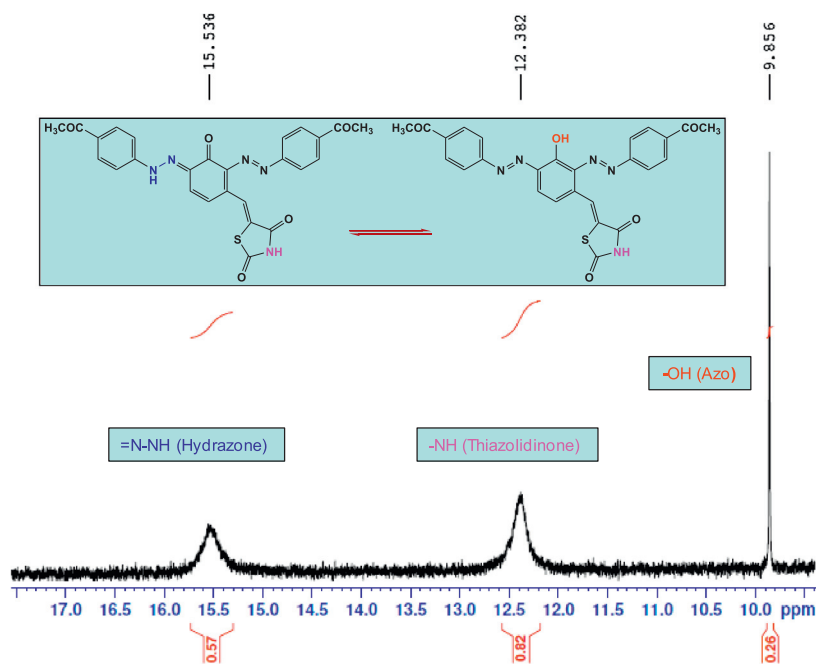


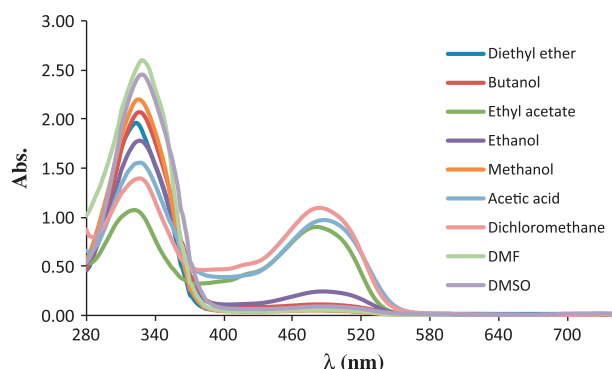
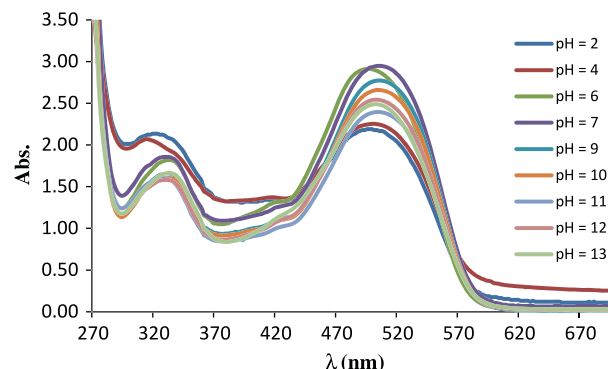
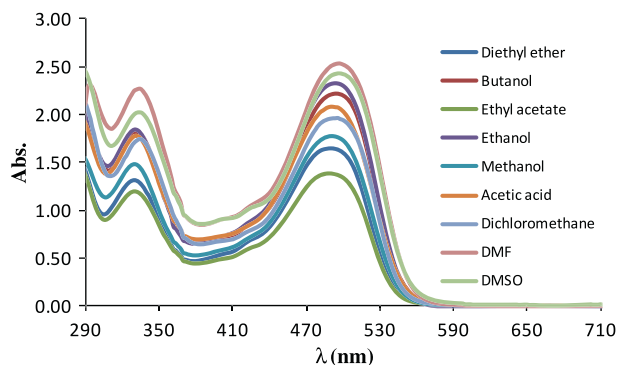
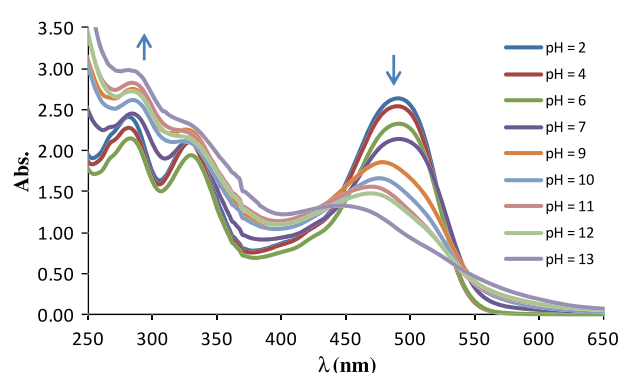
Fig. 2. The partial ^1H NMR spectrum of dye **3h** in DMSO.

solute and solvents. Therefore an increase in the polarity of selected solvents has caused a slightly positive bathochromic shift in the absorption maxima of dyes **3a–3i**. For example, in the absorption spectrum of dye **3a**, the λ_{max} is shifted from $\lambda_{\text{max}} = 478$ nm to $\lambda_{\text{max}} = 494$ nm ($\Delta\lambda_{\text{max}} = 10$ nm) by changing the solvent from diethyl ether ($\pi^* = 0.27$) to DMSO ($\pi^* = 1.00$). Besides the effects of the substituents and solvent polarity on the absorption spectra, azo-hydrazone tautomerism was studied and it was concluded that equilibrium depends on the substituents as well as the solvents.

In order to study of acid and base effects on the spectral characteristics, dyes **3e** with electron-donating group ($\text{R} = \text{OCH}_3$), and **3h** including electron-withdrawing group ($\text{R} = \text{COCH}_3$) were selected. The pH values of the selected dyes were also determined spectrophotometrically in 80% (v/v) methanol–water mixtures according to the previously described method [26a,29]. The absorption maxima and spectra recorded for dye **3e** and **3h** are given in Table 2 and Figs. 5 and 6. As shown in Table 2 and Fig. 5, there were no significant changes in shapes and wavelengths of dye **3e** with elec-

Table 1Experimental electronic absorption maxima for dyes **3a–i** and solvent dipolarity/polarizability parameter (π^*) [28].

Solvents	π^*	3a	3b	3c	3d	3e	3f	3g	3h	3i
Diethyl ether	0.27	322,478	320,486	322,486	322,490	326,492	324,486	324,500	330,490	332,488
Butanol	0.47	326,484	326,490	332,486	326,494	336,498	328,488	326,500	332,494	330,486
Ethyl acetate	0.54	322,482	324,486	332,480	324,492	328,492	324,486	324,502	330,488	334,486
Ethanol	0.54	326,488	326,490	330,484	326,494	334,502	328,490	326,504	330,494	334,490
Dioxane	0.55	324,484	324,488	332,484	326,492	326,496	326,490	324,502	332,492	332,484
Chloroform	0.58	328,486	328,490	334,486	330,494	330,494	330,490	326,504	334,492	332,492
Methanol	0.60	326,486	324,490	324,488	324,492	332,498	326,490	326,502	330,492	332,488
Glacial acetic acid	0.64	326,488	326,490	332,488	326,496	336,510	330,494	330,506	332,492	334,488
Acetone	0.71	324,492	324,500	326,478	326,504	334,508	328,484	328,504	330,490	330,490
Dichloromethane	0.82	326,484	328,490	336,484	328,492	332,498	328,488	328,504	334,496	334,492
DMF	0.87	328,488	322,498	326,494	328,496	332,500	328,494	330,512	334,498	330,492
DMSO	1.00	326,494	322,498	332,484	332,504	332,504	328,496	328,512	334,498	326,498

**Fig. 3.** Absorption spectra of dye **3a** in selected solvents.**Fig. 5.** Absorption spectra of dye **3e** at different pH values.**Fig. 4.** Absorption spectra of dye **3h** in selected solvents.**Fig. 6.** Absorption spectra of dye **3h** at different pH values.

tron-donating group within the pH range of 6.0–13.0. However, changes were observed in the intensity of bands in very acidic solutions. The shape, intensity and wavelengths of spectra for dye **3h** with electron-withdrawing group changed upon increasing the pH from 7.0 to 13.0, while no significant change in shape and absorption maxima of the spectra occurred from pH 1.0 to 7.0 (Table 2 and Fig. 6). As a result, significant changes were observed for dye **3h** including electron-withdrawing group between pH 7.0 and

8.0. Therefore, the prepared bis-azo dyes with electron-withdrawing substituent such as **3h** can be used as new pH indicators.

As seen in Table 1 and Fig. 7, the absorption spectra of dyes **3e** and **3g** with electron-donating groups ($R=\text{OCH}_3$, NHCOCH_3) show a bathochromic shift in all used solvents when compared with dye **3i** including electron-withdrawing group ($R=\text{NO}_2$). This result may be explained by the fact that the maximum absorption (λ_{max}) values of the hydrazone tautomeric form of azo dyes with electron-withdrawing groups show shorter wavelengths in relation to hydrazone

Table 2Absorption maxima (λ_{max}) of dyes **3e** and **3h** at different pH values.

Dye No.	λ_{max} (nm)									
	pH = 2	pH = 4	pH = 6	pH = 7	pH = 8	pH = 9	pH = 10	pH = 11	pH = 12	pH = 13
3e	322,500	318,500	334,498	332,506	334,502	334,504	332,504	328,506	330,504	332,504
3h	330,490	330,490	330,492	330,492	330,494	326,480	324,476	322,472	322,470	320,456

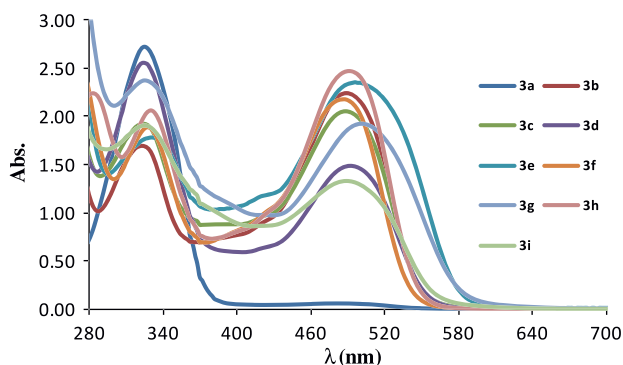


Fig. 7. Absorption spectra of dyes 3a–i in methanol.

form containing electron-donating groups in diazo components [30]. However, the introduction of electron-accepting or electron-donating groups into the diazo component produces slight bathochromic or hypsochromic effects.

Conclusions

In conclusion, nine novel bis-azo dyes were synthesized through Knoevenagel condensation and diazotization-coupling reaction based on 5-(3-hydroxybenzylidene)-2,4-thiazolidinedione. The UV–vis absorption spectra of the dyes in twelve protic and non protic solvents were studied. The spectral data showed that the prepared dyes exist in two azo-hydrazone tautomeric forms. It was demonstrated that the shape and intensity of both the azo and hydrazone tautomeric forms in the UV–vis absorption spectra of all the dyes depend on the nature of the studied substituent and solvent. The study of pH and substituent effects on the spectra of the synthesized dyes indicate that there are significant changes for dyes including electron-withdrawing group between pH 7.0 and 8.0. Therefore these dyes can be used as new pH indicators.

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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.2014.02.010>.

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