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Synthesis, solvatochromic properties and biological evaluation of some novel azo-hydrazone tautomeric dyes

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ABSTRACT

Five novel azo-hydrazone tautomeric dyes **3a**–**e** were synthesized in two steps using Knoevenagel condensation and azo coupling reaction. The structures of the new compounds were confirmed by UV–vis, IR and NMR spectroscopies. Spectral data indicated that these dyes exist predominantly in the hydrazone tautomeric form in solutions. In addition, the absorption ability of the dyes showed that the solvent effect on UV–vis absorption spectra is complex and effectively depends on the nature of the substituent on the diazo component. The effects of acidic and basic media on the visible absorption spectra of the dyes were also examined. The antibacterial and antioxidant activities of the dyes were characterized using the agar well diffusion and ferric reducing antioxidant power (FRAP) methods, respectively. The synthesized dyes exhibited both antioxidant and antibacterial activities.

1. Introduction

It has been known for many years that azo compounds are very important in the field of organic colorants and advanced materials. Azo compound consists of at least a conjugated chromophore azo (–N=N–) group in association with one or more aromatic or heterocyclic system. Since their discovery in the 19th century, azo compounds have been extensively used as colorants and account for over 50% of all commercial dyes [1–4]. In recent years, azo dyes have attracted wide interest and found many uses in various fields such as dyeing of textile fibers, coloring of different materials, biological–medical studies, organic synthesis and advanced applications including optical storage capacity, optical switching, holography and non-linear optical properties [5–10].

Furthermore, azo dyes with hydroxyl group at ortho to azo band display tautomerism depending on the proton transfer. Tautomers are structural isomers of the same chemical substance that usually have different technical properties. Small changes in molecular structure or solvent environment can considerably change the ratio of tautomers. Determination and characterization of tautomeric equilibrium are interesting and extensively studied during the recent decades using both theoretical calculations and experimental approaches [11–15].

Thiazolidine and its derivatives as bioactive heterocycles play a key role in medicinal chemistry and they have been widely used as scaffolds for drug discovery. On the other hand, thiazolidinediones show a wide range of biological activities such as antioxidant, antifungal, antibacterial, antiviral, antitumor, and antidiabetic potential [16–22]. In addition, thiazolidine derivatives represent useful synthetic building blocks in organic chemistry [23–25].

However, there are very few reports on the synthesis of bis-azo dyes with thiazolidinediones moiety in the literature. In addition, synthesis and application of such dyes are important in the 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 [15,26–28], we report herein the synthesis of some novel azo-hydrazone tautomeric dyes with thiazolidine moiety in order to evaluate structure, solvatochromism, tautomeric properties and biological activities (Scheme 1).

2. Experimental

2.1. 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

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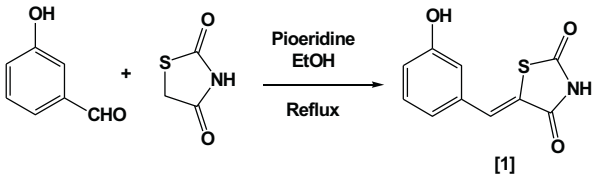
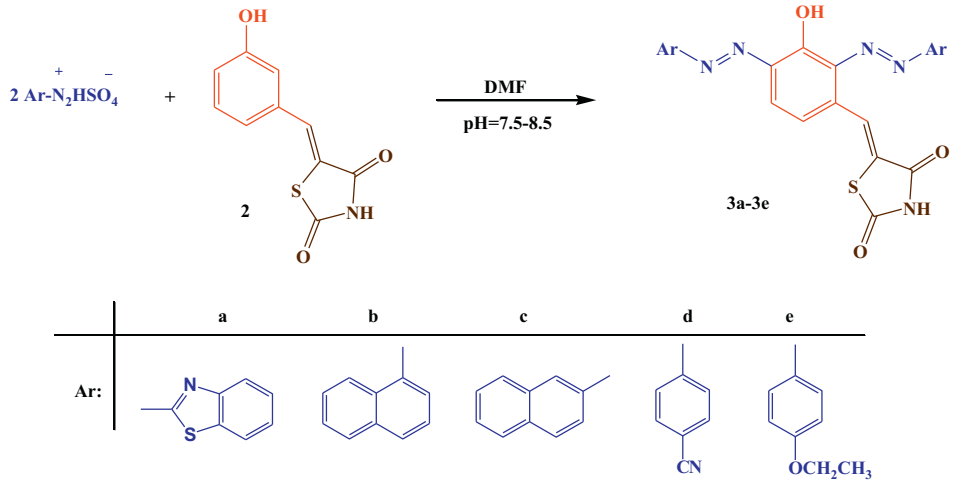
Step 1: Synthesis of intermediate 1 (Knoevenagel condensation)



Step 2: Synthesis of bis-azo dyes 3a-3e



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

resonance (^{1}H NMR) spectra were obtained on a FT-NMR (400 MHz) Brucker apparatus spectrometer, and the chemical shifts are expressed in δ ppm using TMS as an internal standard and *J* values are given in Hz. 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.

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

A mixture of m-hydroxy benzaldehyde (0.336 g, 3 mmol) and 2,4-thiazolidinonedione (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/H_2O.

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); and^{1}H 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), and 12.61 (s, 1H, NH).

2.3. Synthesis of bis-azo dyes (3a–e)

2.3.1. Diazotization and coupling

The diazonium salts were prepared in good yield from equimolar mixture of corresponding primary aromatic amines (1a–e) and nitrous acid according to previously described methods [26,27]. The prepared diazonium salt solution was slowly added to a stirred solution of 5-(3-hydroxybenzylidene)-2,4-thiazolidinedione (1) as coupling component in alkali medium by adjusting the pH at 8–9 and the temperature was maintained at 0–5 °C. The resulting mixture was stirred for 2–3 h in an ice bath then allowed to reach room temperature. The resulting mixture was acidified using dilute HCl (pH 4–5), and the solid product was collected by filtration and washed two times with water and ethanol. The crud products were purified by recrystallization from DMF/H_2O for dyes**3d–e** and column chromatography on silica gel, using ethyl acetate/petroleum (4:3) as eluent for dyes**3a–c**. The characterization data of prepared dyes are given below.

Dye **3a**: Dark purple solid; yield 75%; m.p. 292–294 °C; IR (KBr) ν cm^{-1}: 3320–3400 (NH), 3080 (═C–H), 1740 (C═O), 1700 (C═O), 1620 (C═C), 1528 (N═N); and^{1}H NMR (400 MHz, DMSO-d_6, 298 K), δ (ppm): 6.80 (d, 1H, *J* = 9.6 Hz, Ar–H), 7.12 (s, 0.86H, NH, benzothiazolyl ring, T3 or/and T33 tautomers), 7.36 (t, 1H, *J* = 7.2 Hz, Ar–H), 7.48 (t, 1H, *J* = 7.6 Hz, Ar–H), 7.54 (t, 1H, *J* = 8.0 Hz, Ar–H), 7.65 (t, 1H, *J* = 7.6 Hz, Ar–H), 7.79 (d, 1H, *J* = 8.4 Hz, Ar–H), 7.83 (d, 1H, *J* = 8.0 Hz, Ar–H), 7.96 (s, 1H, CH═C), 8.02 (d, 1H, *J* = 10.0 Hz, Ar–H), 8.10 (d, 1H, *J* = 7.6 Hz, Ar–H), 8.19 (d, 1H, *J* = 8.0 Hz, Ar–H), 12.69 (s, 1H, NH, thiazolidine), and 15.07 (br s, 0.14H, N–NH, hydrazone). ^{13}C 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, and 162.7.

Dye **3b**: Dark Red solid; yield 78%; m.p. 188–190 °C; IR (KBr) ν cm^{-1}: 3370 (NH), 1735 (C═O), 1700 (C═O), 1630 (C═C), 1495 (N═N); ^{1}H NMR (400 MHz, DMSO-d_6, 298 K), δ (ppm): 6.62 (d, 1H, *J* = 10 Hz, Ar–H), 7.61–7.68 (m, 6H, Ar–H), 7.77 (t, 2H, *J* = 8.0 Hz, Ar–H), 7.84 (d, 1H, *J* = 7.6 Hz, Ar–H), 7.97 (s, 1H, CH═C), 8.01 (d, 2H, *J* = 6.4 Hz, Ar–H), 8.04 (m, 4H, Ar–H), 12.23 (s, 1H, NH, thiazolidine), 15.72 (br s, 1H, N–NH, hydrazone).

Dye **3c**: Red solid; yield 80%; m.p. 184–186 °C; IR (KBr) ν cm^{-1}: 3310 (NH), 3045 (═C–H), 1720 (C═O), 1694 (C═O), 1608 (C═C), 1518 (N═N); and ^{1}H NMR (400 MHz, DMSO-d_6, 298 K), δ (ppm): 6.77 (d, 1H, *J* = 9.6 Hz, Ar–H), 7.48 (t, 1H, *J* = 8.0 Hz, Ar–H), 7.54 (t, 1H, *J* = 7.2 Hz, Ar–H), 7.68 (m, 4H, Ar–H), 7.91–7.94 (m, 2H, Ar–H), 7.95 (s, 1H, CH═C), 8.01 (d, 1H, *J* = 9.2 Hz, Ar–H),8.04–8.11 (m, 4H,