



Synthesis, spectroscopic, thermal and electrochemical studies on thiazolyl azo based disperse dyes bearing coumarin



Müjgan Özkütük^{a,*}, Ezgi İpek^a, Burcu Aydın^b, Serhat Mamaş^b, Zeynel Seferoğlu^b

^a Eskişehir Osmangazi University, Department of Chemistry, 26480, Eskişehir, Turkey

^b Gazi University, Department of Chemistry, 06500, Ankara, Turkey

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ABSTRACT

In this study, seven novel thiazolyl azo disperse dyes (**6a-g**) were synthesized and fully characterized by FT-IR, ¹H NMR, ¹³C NMR, and mass spectral techniques. The electronic absorption spectra of the dyes in solvents of different polarities cover a λ_{max} range of 404–512 nm. The absorption properties of the dyes changed drastically upon acidification. This was due to the protonation of the nitrogen in the thiazole ring, which in turn increased the donor-acceptor interplay of the π system in the dyes, and therefore increased the absorption properties of the prepared dyes. Thermal analysis showed that these dyes are thermal stable up to 269 °C. Additionally, the electrochemical behavior of the dyes (**6a-g**) were investigated using cyclic voltammetric and chronoamperometric techniques, in the presence of 0.10 M tetrabutylammonium tetrafluoroborate, in dimethylsulfoxide, at a glassy carbon electrode. The number of transferred electrons, and the diffusion coefficient were determined by electrochemical methods. The results showed that, for all the dyes, one oxidation peak and two reduction peaks were observed.

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1. Introduction

Nitrogen-containing heterocyclic compounds constitute an important class of aromatic heterocyclic structures due to their exceptional pharmacological properties [1]. These compounds have a variety of functional groups and form the backbone of bioactive compounds [2–6]. Thiazole ring plays an important role in the chemistry of heterocyclic compounds and exists in the structure of a number of biologically active molecules [7,8]. It is found in the structure of some natural products such as Vitamin B1 (thiamine), penicillin and carboxylase. Furthermore, 2-aminothiazole which is an important derivative of thiazole, is a leading precursor in the development of drug design [9]. 2-aminothiazole based compounds, which are derived by attaching different substituents at different positions on the ring, show some important pharmacological and biological activities [10–12]. Apart from the pharmacologically important field of use, 2-aminothiazole and its derivatives are widely used as coupling and diazo components in dye industry [13]. The increase in fiber production in the textile industry requires the development and synthesis of new disperse

dyes. Disperse azo dyes have attracted considerable attention in having good fastness properties, and due to their cheap production in recent years. Color, light, and wash fastness of heteroarylazo disperse dyes obtained by coupling with the diazo component of another heteroaryl component are better than the carbocyclic analogs, since both the diazo and the coupling components are heterocyclic compounds [14–16]. Therefore, in recent years, a number of azo dyes, which were obtained by using 2-aminothiazole as the coupling component and its derivatives as the diazo components, and their properties were investigated [17–20]. The synthesis of these new derivatives of 2-aminothiazole will particularly contribute to diversification, and will also lead to increase in color range.

Coumarin has a high fluorescence in visible light, a high quantum yield, and superior photo-stability [21–24]. Moreover, the absorption and emission characteristics, according to the characteristics of the solvent used, can be adjusted easily in coumarin derivatives, especially when having electron accepting or donating substituents at the 3- and 7-positions [25,26]. Coumarin derivatives obtained in these forms are potential materials for a wide field of applications such as optical brighteners, laser dyes, nonlinear optical chromophores (NLO), solar collectors, monitoring systems in medicine and biology, electroluminescence (EL) materials, fluorescent labels and chemosensors [27–36]. Furthermore, coumarin ring is readily available and functionalized. Therefore, we proposed

* Corresponding author.

E-mail addresses: mujgan@ogu.edu.tr (M. Özkütük), znseferoglu@gazi.edu.tr (Z. Seferoğlu).

that the integration of coumarin unit into thiazolyl azo disperse dye based structures, leads to novel dye structures with promising properties that may be considered for the development of functional dyes. Therefore, in this study, we report the syntheses of azo dyes bearing coumarin unit as the main structure. Due to its good photophysical properties we think that the synthesized azo dyes (**6a-g**) can exhibit better photophysical activity. Firstly, here we determined the photophysical properties of a series of newly synthesized thiazolyl azo disperse dyes in different solvents and then examined the azo-hydrazone tautomeric equilibria in the same solvents. The reduction-oxidation and thermal behavior of the azo dyes play an important role in biomedical research, dyeing textile fibers, liquid crystal displays, electro-optical devices, laser-inkjet printers, and treatment of azo dyes waste [37]. Therefore, the electrochemical properties of the synthesized azo dyes were also evaluated. For determination of thermal stability of the synthesized azo dyes, the thermal studies were done by using thermal gravimetric techniques (TGA).

2. Experimental

2.1. Materials and methods

All the chemicals used in this study were purchased from Sigma-Aldrich, and were used as without any further purification. Thin-layer chromatography was carried out using precoated aluminum-backed plates (Merck Silica Gel 60 F254) and visualised under UV light ($\lambda = 254\text{--}362\text{ nm}$). FT-IR (ATR) Spectra were recorded on a Perkin Elmer 100 FT-IR spectrometer (ν are in cm^{-1}). ^1H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz spectrometer in $\text{DMSO-}d_6$. Coupling constant (J) are given in hertz (Hz). Signals are abbreviated as follows: singlet, s; doublet, d; doublet-doublet, dd; triplet, t; multiplet, m. Chemical shifts (δ) are given in parts permillion (ppm) using the residue solvent peaks as reference relative to TMS. J values are given in Hertz (Hz). Mass analysis was obtained by using Waters 2695 Alliance ZQ Micromass LCMS working with ESI apparatus; in m/z (rel. %) (Department of Pharmacological Sciences, Ankara University Laboratories). The melting points were measured using Schmelzpunktbestimmer SMP II apparatus and are uncorrected. Thermal analyses (TG/DTA) were performed with a Perkin Elmer Diamond TG/DTA Thermal Analyzer at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ in a static atmosphere, at the temperature of $30\text{--}900\text{ }^\circ\text{C}$. Voltametric measurements were carried out using CHI 760d Electrochemical Workstation. Glassy carbon electrode (BAS MF-2012) and $11\text{ }\mu\text{m}$ -ultramicro carbon electrode (BAS MF-2007) were used as the working electrodes. The electrodes were polished with $1\text{ }\mu\text{m}$ and $0.05\text{ }\mu\text{m}$ alumina slurries made from dry Buehler alumina and ultra pure water, on polishing microcloth, before each use. A platinum wire was used as the auxiliary electrode (BAS MW-1032). The reference electrode was a silver wire in contact with 0.01 M AgNO_3 (BAS MF-2052). All the solutions were deaerated for 15 min with pure nitrogen. All measurements were taken at room temperature, $21 \pm 1\text{ }^\circ\text{C}$. In all the voltammetric measurements, the background currents were automatically subtracted from the original currents obtained. The number of transferred electrons, and the diffusion coefficients were determined by ultramicro electrode CV technique of Baranski method [38].

2.2. Preparation of dyes (**6a-g**)

Diazotization of various heterocyclic amines was affected using H_2SO_4 and NaNO_2 . A typical diazotization and coupling procedures are described below for 2-amino-4-(coumarin-3-yl)thiazole (**3**) and 1,2-dimethyl-1H-indole (**5a**), and all the other dyes were prepared

in a similar manner. All the compounds obtained were purified by crystallization from ethanol, and then analyzed.

2.2.1. Preparation of (E)-3-(2-((1,2-dimethyl-1H-indol-3-yl)diazenyl)thiazol-4-yl)-2H-chromen-2-one (**6a**)

2-amino-4-(coumarin-3-yl)thiazole (**3**) (0.49 g, 2.0 mmol) was dissolved in glacial acetic acid-propionic acid mixture (2:1, 6.0 mL) and was rapidly cooled in a salt/ice bath to $0\text{--}5\text{ }^\circ\text{C}$. The solution was placed in an ice-salt bath to cool. After that, cold solution of NaNO_2 (0.15 g, 2 mmol) in water (3.0 mL) was added dropwise while stirring. The mixture was stirred for an additional 1 h at $0\text{ }^\circ\text{C}$. Excess nitrous acid was removed by the addition of urea. The resulting diazonium salt (**4**) was cooled in a salt/ice mixture. The 1,2-dimethyl-1H-indole (**5a**) (0.29 g, 2.0 mmol) was also dissolved in a mixture of glacial acetic acid-propionic acid solution (3:1, 8 mL) and cooled in an ice bath. Cold diazonium solution was added to this cooled solution in a dropwise manner while stirring. The solution was then stirred at $0\text{--}5\text{ }^\circ\text{C}$ for 1 h. The pH of the reaction mixture was maintained at 4–6 by the intermittent addition of saturated sodium carbonate solution. The mixture was further stirred for 1 h at room temperature. The resulting solid was filtered, washed with cold water, and then dried. Recrystallization of the resulting dried solid from ethanol gave an orange powder (MW: 400.45 g/mol, $\text{C}_{22}\text{H}_{16}\text{N}_4\text{O}_2\text{S}$ yield: 0.649 g, 81%; m.p: $281\text{--}282\text{ }^\circ\text{C}$); FT-IR (ATR): ν_{max} : 3077 (aromatic C–H), 1712 (C=O), 1484, 1475, 1451 (C=C), 1399 (N=N), 1360, 1315, 1251 (C–N), 1169 (C–O–C) cm^{-1} ; ^1H NMR (300 MHz, $\text{DMSO-}d_6$): δ 8.94 (s, 1H), 8.36 (m, 1H), 8.29 (s, 1H), 8.00 (dd, $J = 7.8, 1.3\text{ Hz}$, 1H), 7.65 (m, 3H), 7.48–7.37 (m, 4H), 3.84 (s, 3H, -NCH₃), 2.79 (s, 3H, -CH₃); ^{13}C NMR (75 MHz, $\text{DMSO-}d_6$): δ 179.3, 159.4, 153.0, 151.9, 147.2, 139.7, 138.4, 132.6, 132.6, 132.4, 129.6, 125.0, 124.6, 122.3, 120.7, 119.7, 119.2, 119.1, 118.5, 116.3, 111.7, 31.0, 10.6; LC-MS: ($\text{M}+1$)⁺ (m/z): 401.24 (100%).

2.2.2. Preparation of (E)-3-(2-((1-methyl-2-phenyl-1H-indol-3-yl)diazenyl)thiazol-4-yl)-2H-chromen-2-one (**6b**)

This dye was obtained by coupling diazotized amine (**4**) with 1-methyl-2-phenyl-1H-indole (**5b**), as a tile red powder (MW: 462.52 g/mol, $\text{C}_{27}\text{H}_{18}\text{N}_4\text{O}_2\text{S}$, yield: 0.592 g, 64%; m.p: $261\text{--}262\text{ }^\circ\text{C}$). FT-IR (ATR): ν_{max} : 3055 (aromatic C–H), 1720 (C=O), 1489, 1468 (C=C), 1387 (N=N), 1323, 1252 (C–N), 1170 (C–O–C) cm^{-1} ; ^1H NMR (300 MHz, $\text{DMSO-}d_6$): δ 8.97 (s, 1H), 8.52–8.46 (m, 1H), 8.29 (s, 1H), 8.02 (dd, $J = 7.7, 1.2\text{ Hz}$, 1H), 7.85–7.76 (m, 3H), 7.70–7.60 (m, 4H), 7.55–7.39 (m, 5H), 3.91 (s, 3H, -NCH₃); ^{13}C NMR (75 MHz, $\text{DMSO-}d_6$): δ 159.4, 153.0, 139.8, 138.4, 132.4, 132.2, 130.4, 129.6, 128.6, 128.3, 125.8, 125.3, 125.2, 122.9, 120.6, 119.8, 119.7, 118.2, 116.3, 112.1, 32.7; LC-MS: ($\text{M}+1$)⁺ (m/z): 463.39 (100%), 485.19 ($\text{M}+\text{Na}$).

2.2.3. Preparation of (E)-3-(2-((2-phenyl-1H-indol-3-yl)diazenyl)thiazol-4-yl)-2H-chromen-2-one (**6c**)

This dye was obtained by coupling diazotized amine (**4**) with 2-phenyl-1H-indole (**5c**), as a red powder (MW: 448.50 g/mol, $\text{C}_{26}\text{H}_{16}\text{N}_4\text{O}_2\text{S}$, yield: 0.762 g, 85%; m.p: $272\text{--}273\text{ }^\circ\text{C}$) FT-IR (ATR): ν_{max} : 3305 (N–H), 3130 (aromatic C–H), 1717 (C=O), 1463, 1454 (C=C), 1393, 1349 (N=N), 1207 (C–N), 1168 (C–O–C) cm^{-1} ; ^1H NMR (300 MHz, $\text{DMSO-}d_6$): δ 13.00 (s, 1H, -NH), 8.98 (s, 1H), 8.50–8.42 (m, 1H), 8.38 (s, 1H), 8.16–8.09 (m, 2H), 8.02 (dd, $J = 7.9, 1.4\text{ Hz}$, 1H), 7.71–7.52 (m, 5H), 7.51–7.35 (m, 5H); ^{13}C NMR (75 MHz, $\text{DMSO-}d_6$): δ 179.3, 159.4, 153.0, 147.6, 146.8, 139.9, 137.0, 132.5, 130.7, 130.5, 129.7, 129.3, 126.0, 125.3, 124.7, 123.3, 120.6, 119.9, 119.7, 119.2, 116.3, 113.1; LC-MS: ($\text{M}+1$)⁺ (m/z): 449.31 (100%).

2.2.4. Preparation of (E)-3-(2-((4-(diethylamino)phenyl)diazenyl)thiazol-4-yl)-2H-chromen-2-one (**6d**)

This dye was obtained by coupling diazotized amine (**4**) with

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