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Solvatochromic and electrochemical properties of new thermally stable azo–azomethine dyes with $N_2S_2O_2$ donor set of atoms

Hamid Khanmohammadi *, Fatemeh Khodam

Department of Chemistry, Faculty of Science, Arak University, Arak 38156-8-8349, Iran

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ABSTRACT

A new series of azo–azomethine dyes with $N_2S_2O_2$ donor set of atoms have been synthesized via condensation reaction of α,α′-bis(2-aminoethylthio)-1,3-xylene and substituted azo-coupled salicylaldehyde. The dyes were characterized by IR, UV–Vis and ^{1}H NMR spectroscopic methods as well as elemental analysis. The solvatochromic behavior of the dyes was probed by studying their UV–Vis spectra in four pure organic solvents of different polarities and a meaningful correlation was observed. The electrochemical properties of the dyes have been also studied by cyclic voltammetry in DMSO. Moreover, thermal properties of the prepared dyes were examined by thermogravimetric analysis and results indicated that the framework of the dyes is stable up to 260 °C.

1. Introduction

Azo compounds are receiving continuous attention primarily due to their applications in synthesis of dyes, pigments and functional materials [1–6]. Attention was devoted also to the optical and physico-chemical properties of these compounds. For example, azo-containing photochromic organic compounds with liquid crystalline character and azo-conjugated metal complexes have been attracting much attention because of their possible applications in the area of photon-mode high density information storage, photo-switching devices and optical computing [7–9]. On the other hand, it is well known that the spectral and physico-chemical properties of azo dyes depend not only on the azo groups, but also on the presence of other coupling groups. Among many different types of coupled azo compounds, the azo–azomethine dyes have attracted particularly great researchers because of their structural properties and uses [10–13]. Azo–azomethine dyes are relatively robust and chemically stable and their spectral properties depend on the combination of electron-donating and -withdrawing moieties in the molecules [14–16].

Recently, considerable attention has been paid to the synthesis and spectral studies of azo–azomethine dyes containing hydroxyl groups [10,17–20]. The prototropic properties of hydroxyl groups of those dyes have important consequences on their electronic structure which can be exploited for their thermochromic and/or photochromic behavior [21] and also for the design of molecular electronic devices [22]. However, photo-physical and photo-chemical properties of polyhydroxy azo–azomethine dyes are in turn strongly influenced by several factors including temperature, substituent groups and solvent polarity [23–27]. Because of this, our interest has been focused in preparing new *o*-hydroxy azo–azomethine derivatives with various donor and acceptor groups [16,28,29]. We report here the synthesis and characterization of new acyclic azo–azomethines, **1a**–**5a**, by condensation reaction of azo-coupled salicylaldehyde derivatives, **1**–**5**, with α,α′-bis(2-aminoethylthio)-1,3-xylene, **a** (Fig. 1). All the prepared multifunctional compounds are air stable solids, intensely colored, soluble in DMF and DMSO and exhibited dye characteristic since the molar extinction coefficients (ε) were over 11,000 M^{-1} cm^{-1} in DMSO [30]. The solvatochromic behavior and substituent effect of the potentially polydentate prepared compounds in four pure organic solvents of different polarities were evaluated. Also, the thermal properties of the prepared compounds were examined by thermogravimetric analysis. The results indicated that the framework of the dyes is stable up to 260 °C.

2. Experimental details

2.1. Materials

All of the reagents and solvents involved in synthesis were of analytical grade and used as received without further purification. Salicylaldehyde, 4-nitroaniline, 4-chloroaniline, 4-ethylaniline, 4-bromaniline and 4-flouroaniline were obtained from Aldrich and Merck. Azo-coupled salicylaldehyde precursors (**4**, **5**) were prepared according to the well-known literature procedure [16,28,31].

* Corresponding author. Tel.: +98 861 2777401; fax: +98 861 4173406.
E-mail address: h-khanmohammadi@araku.ac.ir (H. Khanmohammadi).

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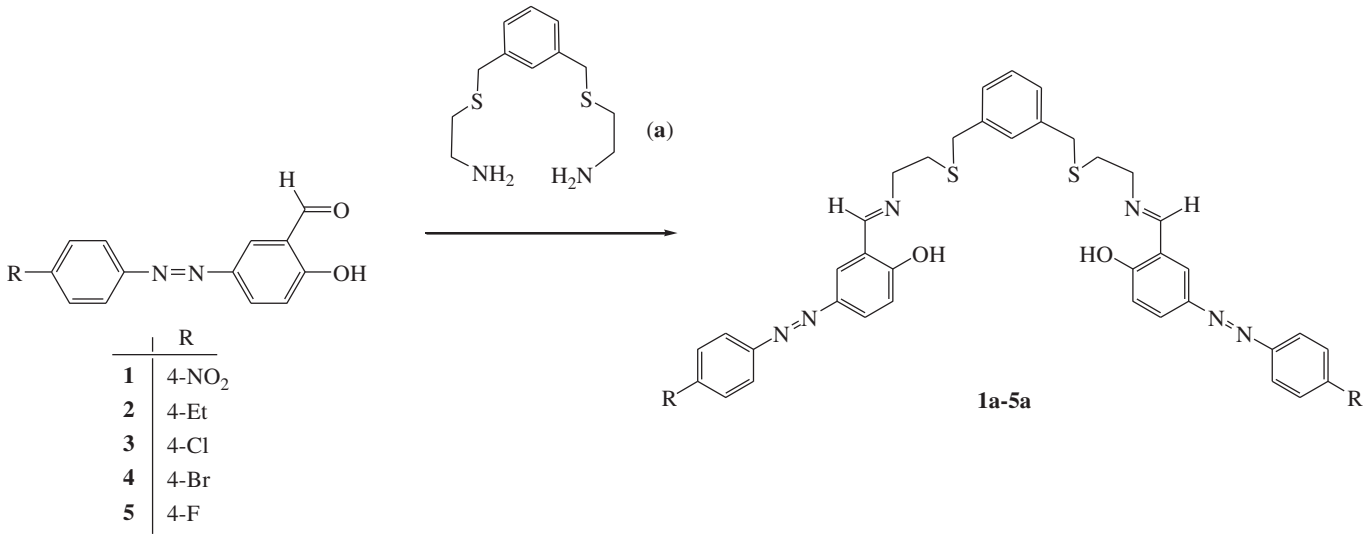

	R
1	4-NO_2
2	4-Et
3	4-Cl
4	4-Br
5	4-F

Fig. 1. Synthesized azo–azomethine dyes.

2.2. Instrumentation

The structure of all synthesized compounds was confirmed by ^{1}H NMR spectra, recorded on a Bruker Avance 300 MHz spectrometer. FT-IR spectra were recorded as pressed KBr disks, using Unicom Galaxy Series FT-IR 5000 spectrophotometer in the region of 400–4000 cm^{-1}. Melting points were determined on an Electrothermal 9200 apparatus. Electrochemical measurements were recorded on an Autolab 30 V potentiostat/galvanostat from the Eco Chemie company. All readings were taken using three electrode potentiostatic systems in DMSO with 0.1 mol cm^{-3} tetrabutylammonium bromide (TBAB) as supporting electrolyte. A three-electrode assembly composed of a platinum working electrode, a platinum auxiliary electrode, and calomel reference electrode was used with sample concentrations of 1×10^{-3} $molL^{-1}$. Thermal analyses were performed on TGA V5.1A DuPont 2000 and Perkin-Elmer thermogravimetric analyzer TG/DTA 6300 instruments. C. H. N. analyses were performed on a Vario EL III elemental analyzer. Electronic spectral measurements were carried out using Perkin-Elmer Lambda spectrophotometer in the range 200–700 nm.

2.3. Synthesis

2.3.1. Preparation of 1 α,α′-bis(2-aminoethylthio)-1,3-xylene, **a**

Sodium metal (0.92 g, 40 mmol) was dissolved in degassed absolute ethanol (50 mL) under N_2 and the solution was refluxed for 10 min. A solution of 2-aminoethanethiol hydrochloride (2.27 g, 20 mmol) in warm degassed absolute ethanol (20 mL) was then added, whereupon a white solid (NaCl) separated immediately. The reaction mixture was stirred at 70 °C for 30 min and a solution of 1,3-bis-(bromomethyl) benzene (2.64 g, 10 mmol) in degassed absolute ethanol (20 mL) was added dropwise, with stirring, over a period of 1 h. The reaction mixture was then refluxed for 6 h and left at room temperature overnight. The white solid was filtered off, the filtrate was concentrated to a volume of about 10 mL, and diethyl ether was added. After this the mixture was stored in a refrigerator. The separated yellow solid was filtered, washed with diethyl ether, and dried. Yield; 1.61 g (63%). ^{13}C NMR (D_2O, ppm): δ 31.27, 32.33, 38.69, 127.61, 130.80 and 136.05. IR (KBr, cm^{-1}); 1668 (CHO), 1620, 1572, 1476 (N═N), 1287 (C–O), 1167, 829 and 719.

2.3.2. General procedure for the synthesis of azo-coupled precursors, **4**, **5**

Salicylaldehyde (10 mmol) was dissolved in water (20 mL) containing 10 mmol of sodium hydroxide and 40 mmol of sodium carbonate for a period of 30 min at 0 °C. The resulting solution was added slowly to a solution of diazonium chloride (10 mmol) in water at 0–5 °C. The reaction mixture was stirred for 1 h at 0 °C and then allowed to warm slowly to room temperature. The product was collected by filtration and washed with 100 mL of NaCl solution (10%) under vacuum. The obtained solid was dried under vacuum at 80 °C overnight.

2.3.2.1. 1-(3-Formyl-4-hydroxyphenylazo)-4-bromobenzene, **4**. Yield: 2.77 g (91%), m.p. 206–207 °C. ^{1}H NMR (DMSO-d_6, 300 MHz, ppm): δ 7.19 (d, 1H, J = 8.86 Hz), 7.78 (br, s, 4H), 8.09 (dd, 1H, J = 8.86 Hz and 2.41 Hz), 8.18 (d, 1H, J = 2.41 Hz), 10.36 (s, 1H), 11.61 (br, 1H). IR (KBr, cm^{-1}); 1668 (CHO), 1620 (C═C), 1572 (phenol ring), 1475 (N═N), 1286 (C–O), 1167, 829 and 719.

2.3.2.2. 1-(3-Formyl-4-hydroxyphenylazo)-4-flourobenzene, **5**. Yield: 2.27 g (93%), m.p. 156–158 °C. ^{1}H NMR (DMSO-d_6, 300 MHz, ppm): δ 7.17 (d, 1H, J = 8.76 Hz), 7.37 (br, t, 2H), 7.88 (m, 2H), 8.04 (dd, 1H, J = 8.76 and 2.22 Hz), 8.14 (d, 1H, J = 2.22 Hz), 10.35 (s, 1H), 11.48 (br, 1H). IR (KBr, cm^{-1}); 1672 (CHO), 1620 (C═C), 1595 (phenol ring), 1574, 1501, 1479 (N═N), 1287 (C–O), 1226, 1152, 839 and 767.

2.3.3. General procedure for the synthesis of azo–azomethine compounds, **1a–5a**

A solution of diamine, **a** (1 mmol) in absolute EtOH (10 mL) was added to a stirring solution of azo-coupled precursors, **1–5**, (2 mmol) in absolute EtOH (50 mL) for a period of 10 min at 60–70 °C. The mixture was heated in a water bath for 4 h at 80 °C with stirring. The mixture was filtered while hot and the obtained solid was washed with hot ethanol (three times) and then with diethyl ether. The resulting product was dried in air.

2.3.3.1. 1,3-Bis(2-[2-sulfanyl-ethylimino)-methyl]-4-(4-nitro-phenylazo)-phenol)methylenbenzene, **1a**. Yield: 0.61 g (80%), m.p. 144–146 °C. ^{1}H NMR (DMSO-d_6, 300 MHz, ppm) δ_H: 2.77 (br, 4H, J = 5.58 Hz), 3.80 (br, 8H), 6.76 (d, 2H, J = 9.61 Hz), 7.25 (m, 4H), 7.91 (m, 6H), 8.05 (s, 2H), 8.33 (d, 4H, J = 8.53 Hz), 8.66 (s, 2H), 13.80 (vbr, 2H). IR (KBr, cm^{-1}); 1634 (C═N), 1614 (C═C), 1587 (phenol ring), 1516 (NO_2), 1491 (N═N), 1341 (NO_2), 1288 (C–O), 1105, 856. Anal. calcd. for $C_{38}H_{34}N_8O_6S_2$: C, 59.83; N, 14.69; H, 4.49; S, 8.41. Found: C, 59.74; N, 14.82; H, 4.53; S, 8.61%. λ_{max} (nm) (ε (M^{-1} cm^{-1})): 258 (6789), 417 (67,963) and 470 (6843) in DMSO.