Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 138 (2015) 643–647

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

The triazine-based azo-azomethine dyes; synthesis, characterization, spectroscopy, solvatochromism and biological properties of 2,2′-(((6-methoxy-1,3,5-triazine-2,4-diyl)bis(sulfanediyl)bis(2,1-phenylene))bis(azanylylidene)bis(methanylylidene))bis(4-(phenyldiazenyl)phenol)

Motaleb Ghasemian [a], Ali Kakanejadifard [a,*], Farideh Azarbani [b], Abedin Zabardasti [a], Somayeh Shirali [a], Zeinab Saki [a], Sahar Kakanejadifard [b]

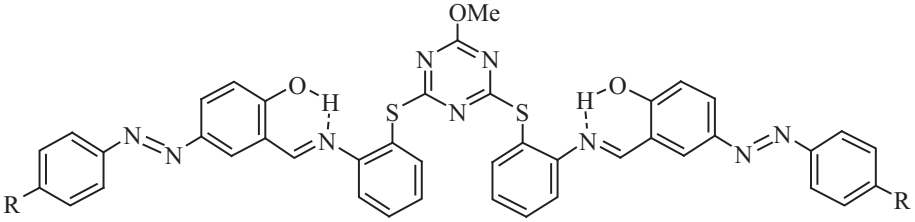
[a] Department of Chemistry, Faculty of Science, Lorestan University, Khorramabad, Iran
[b] Department of Biology, Faculty of Science, Lorestan University, Khorramabad, Iran

HIGHLIGHTS

- Azo-azomethine dyes with triazine based.
- The tautomerism between enol-amine, enaminone and hydrazone forms in organic solvent was studied.
- The solvatochromism is dependent on the substitution, solvent, pH and temperature.
- The azo-azomethine dyes has antioxidant activity, which are dependent on electron releasing of substituents.

GRAPHICAL ABSTRACT

The azo-azomethine dyes were prepared via condensation reaction of 2,4-dichloro-6-methoxy-1,3,5-triazine with azo couled 2-(2-mercaptophenylimino)methyl)-4-(aryldiazenyl)phenol.
The UV–vis spectra indicated positive solvatochromism in synthesized compound are dependent on the substitution, solvent, pH and temperature. Some compounds exhibited antibacterial, antioxidant activities.



ARTICLE INFO

Article history:
Received 2 August 2014
Received in revised form 11 November 2014
Accepted 20 November 2014
Available online 28 November 2014

Keywords:
Azo-azomethine schiff bases
Triazine
Enol–keto tautomeric
Antibacterial activity
Antioxidant activity

ABSTRACT

The macrocyclic azo-azomethine dyes 2,2′-(((6-methoxy-1,3,5-triazine-2,4-diyl)bis(sulfanediyl)bis(2,1-phenylene))bis(azanylylidene)bis(methanylylidene))bis(4-(phenyldiazenyl)phenol) and its derivatives were synthesized and characterized by elemental analysis, mass, FT-IR, UV–vis and NMR spectroscopy. The solvatochromism as well as effects of substitutions on the electronic absorption of these compounds have been studied in the DMSO, DMF, THF, CH_3CN, CH_3OH and CH_3COOH as solvents. Also they positive solvatochromism behaviors are explained on the basis of intramolecular hydrogen bonding, enol–keto tautomeric and dipole moment changes. Compounds having electron donating substituent on the phenyl ring showed good antioxidant activity. However, none of them has a considerable antibacterial activity.

* Corresponding author. Tel.: +98 661 6200610; fax: +98 661 6200612.
E-mail addresses: kakanejadi.a@lu.ac.ir, alikakanejadifard@Yahoo.com (A. Kakanejadifard).

http://dx.doi.org/10.1016/j.saa.2014.11.048
1386-1425/

Introduction

The azo dyes are one of the major groups of synthetic organic dyes; which their applications of high technology have been attracting much attention. They are used in various fields such as paper printing, electronic photography, color formers, dyeing, bleaching, polymers, liquid crystal displays, laser technology, data storage and solar energy conversion [1–10]. Recently, there is a rapidly growing interest in the potential of their biological–medical applications. They are known to have a broad range of biological activities such as antibacterial, antifungal, antitumor and antioxidant activities [11–14]. In addition, azo dyes also have an adverse impact in terms of total organic carbon (TOC), biological oxygen demand (BOD) and chemical oxygen demand (COD) [15]. It is worth to mention that many synthetic azo dyes and their metabolites are toxic, carcinogenic, and mutagenic [16]. The azo-azomethine compounds provide the possibility of forming different type of intra- and intermolecular hydrogen bond and allow the formation of an intramolecular proton transfer with the nitrogen atoms. This tautomerization can be induced either by light, heat or the solvent [17–22]. We are now interested on the tautomerization and solvatochromism of azo-azomethine compounds. On the other hand, s-triazines have found widespread applications in the pharmaceutical, textile, plastic, and rubber industries, and are used as pesticides, dyestuffs, optical bleaches, explosives, and surface active agents [23–29]. The azo dyes including s-triazines ring (i.e. Reactive Red 141 (RR141), Reactive Blue 171 (RB 171), Reactive Green 19 (RG19) have appropriate chemical behavior [30–33]. Therefore, the ultimate scope of our investigation is preparation of azo-azomethine dyes of **3a**–**d** with three objectives: (i) synthesis of 1,3,5-triazine-based azo-azomethine dyes, (ii) study of solvatochromic behavior and substituent effects of the prepared dyes in various solvents, (iii) study of antibacterial and antioxidant properties of synthesized compounds and comparison with similar known compounds.

Experimental

Materials and measurements

All chemical reagents were obtained from the Merck and used without further purification. For UV–vis measurements solvents with spectroscopic grade (>99.9%) were used, without any further purification. 2,4-Dichloro-6-methoxy-1,3,5-triazine,2-hydroxy-5-[(aryldiazenyl)]benzaldehydes (**1a**–**d**) and 2-((2-mercaptophenyl imino)methyl)-4-(aryldiazenyl)phenols (**2a**–**d**) have been prepared and purified according to the methods reported in the literature [34,17–22]. Elemental analyses were performed on an Elementar Vario EL III elemental analyzer. Mass spectra were recorded on a Agilent MS Model 5973. Melting points were measured with Electrothermal 9300 apparatus. FT-IR spectra were recorded on Shimadzu 8400S spectrometer with samples investigated as KBr discs. The electronic absorption spectra were recorded with a Shimadzu 1650 spectrophotometer. The structure of all synthesized compounds were confirmed by ^{1}H and ^{13}C NMR spectra, in DMSO-d_6 as solvent recorded on a Bruker AV 300 MHz spectrometer.

*General procedure for synthesis of 2,2′-(((6-methoxy-1,3,5-triazine-2,4-diyl)bis(sulfanediyl)bis(2,1-phenylene))bis(azanylylidene) bis(methanylylidene))bis(4-(phenyldiazenyl)phenol) (**3a**–**d**)*

2,4-Dichloro-6-methoxy-1,3,5-triazine [34] (10 mmol) was dissolved in THF (20 ml). K_2CO_3 (20 mmol) was added and the suspension mixture was cooled to 0–5 °C. Then 2-((2-mercaptophenylimino) methyl)-4-(aryldiazenyl)phenols (**2a**–**d**, 20 mmol) [21] in 30 ml THF was added portionwise to the mixture. The suspension mixture was allowed to increase to 25 °C and kept for 1 h then heated at 60–70 °C for 6 h. The mixture was filtered and the solvent of the filtrate was removed to give the crude product. Products are air stable and soluble in DMSO, DMF, CH_3OH, CH_3-COOH and THF. They were purified by recrystallization and their structures were characterized by elemental analysis, mass, FT-IR, UV–vis, ^{1}H and ^{13}C NMR spectroscopy.

*Compound **3a***

The orange product crystallized from CH_3CN. Yield, 4.49 g (58%), m.p. 239 °C. Anal. Calcd. for $C_{42}H_{31}N_9O_3S_2$: C, 65.18; H, 4.04; N, 16.29; S, 8.29. Found: C, 65.14; H, 3.96; N, 16.12; S, 8.16. The EI-MS: *m*/*z*; 775 $(M+1)^+$, 774 $(M)^+$, 669, 578, 558, 474, 442, 333, 301, 225, 198, 106. FT-IR (KBr, cm^{-1}): 3300–3500 υ(bs, OH), 3056 υ(Ar—H), 2943, 2848 υ(CH=N), 1612 υ(C=N), 1581 υ(N=N), 1490 υ(C=C), 1277, 1153 υ(C—N), 1217 υ(C—S), 1070 υ(C—O). ^{1}H NMR ppm: 11.11 (1H, OH, D_2O exchangeable), 9.92 (s, 1H, C<u>H</u>=N), 8.84–6.83 (m, 11H, Ar—H), 3.91 (s, 3H). ^{13}C NMR ppm: 190.98, 178.24, 163.63, 161.66, 161.58, 160.75, 152.89, 149.92, 144.99, 134.87, 132.99, 131.84, 128.99, 119.59, 119.52, 119.49, 118.94, 116.84, 116.78, 54.12.

*Compound **3b***

The yellow product crystallized from CH_3CN. Yield, 4.88 g (61%). m.p. 256 °C. Anal. Calcd. for $C_{44}H_{35}N_9O_3S_2$: C, 65.90; H, 4.40; N, 15.72; S, 8.00. Found: C, 65.78; H, 4.36; N, 15.66; S, 7.92. The EI-MS: 804 $(M+2)^+$, 802 $(M)^+$, 746, 685, 652, 626, 582, 559, 399, 239, 196, 92. FT-IR (KBr, cm^{-1}): 3300–3500 υ(bs, OH), 3070 υ(Ar—H), 2972, 2869 υ(CH=N), 1618 υ(C=N), 1575 υ(N=N), 1479 υ(C=C), 1286 υ(C—N), 1205 (C—S), 1174, 1089 υ(C—O). ^{1}H NMR ppm: 11.21 (1H, OH, D_2O exchangeable), 9.95 (s, 1H, C<u>H</u>=N), 8.64–6.42 (m, 11H, Ar—H), 3.95 (s, 3H), 2.28 (s, 3H). ^{13}C NMR ppm: 191.42, 175.98, 165.59, 154.92, 152.58, 142.26, 135.68, 131.86, 130.73, 128.84, 127.16, 123.09, 123.03, 122.53, 119.52, 119.46, 119.17, 116.89, 116.62, 53.49, 21.48.

*Compound **3c***

The yellow product crystallized from a mixture of THF/C_2H_5OH (1:1). Yield, 4.96 g (59%). m.p. 271–273 °C. Anal. Calcd. For $C_{42}H_{29}Cl_2N_9O_3S_2$: C, 59.86; H, 3.47; N, 14.96; S, 7.61. Found: C, 59.78; H, 3.40; N, 14.84; S, 7.52. The EI-MS: *m*/*z* 845 $(M+2)^+$, 843 $(M)^+$, 732, 704, 612, 585, 509, 367, 232, 102. FT-IR (KBr, cm^{-1}): 3300–3500 υ(bs, OH), 3058 υ(Ar—H), 2954, 2864 υ(CH=N), 1616 υ(C=N), 1583 υ(N=N), 1490 υ(C=C), 1274, 1217 υ(C—N), 1217 υ(C—S), 1108, 1066 υ(C—O), 831 (C—Cl). ^{1}H NMR ppm: 11.19 (1H, OH, D_2O exchangeable), 9.83 (s, 1H, C<u>H</u>=N), 8.85–7.30 (m, 11H, Ar—H), 3.90 (s, 3H). ^{13}C NMR ppm: 191.87, 178.38, 164.22, 161.83, 161.66, 160.75, 151.21, 149.93, 144.99, 134.87, 132.79, 132.27, 127.99, 119.59, 119.52, 119.49, 118.82, 116.69, 116.58, 54.46.

*Compound **3d***

The brown product crystallized from a mixture of THF/CH_3CN (1:1). Yield, 4.85 g (56%). m.p. 292–293 °C. FT-IR (KBr, cm^{-1}): 3300–3500 υ(bs, OH), 3068 υ(Ar—H), 2966, 2874 υ(CH=N), 1610 υ(C=N), 1581 υ(N=N), 1532 υ(N=O, Unsym. Stretching), 1488 υ(C=C), 1336 υ(N=O, Sym. Stretching), 1263, 1211 υ(C—N), 1205 υ(C—S), 1112 υ(C—O), 1076, 921 υ(N—O). ^{1}H NMR ppm: 11.18 (1H, OH, D_2O exchangeable), 10.43 (s, 1H, C<u>H</u>=N), 8.87 (m, 2H), 8.72 (m, 2H), 8.34, 8.18 (dd, 8H, J = 5.82 Hz), 7.39 (m, 2H), 7.35–7.23 (m, 8H), 3.93 (s, 3H). Anal. Calcd. For $C_{42}H_{29}N_{11}O_7S_2$: C, 58.39; H, 3.38; N, 17.84; S, 7.42. Found: C, 58.31; H, 3.34; N, 17.78; S, 7.38.The EI-MS: *m*/z 865 $(M+1)^+$, 864 $(M)^+$, 863 $(M-1)^+$, 818, 742, 714, 622, 595, 519, 487, 378, 346, 270, 243, 151, 123.