



Solvatochromic, acid–base features and time effect of some azo dyes derived from 1,3-benzothiazol-2-ylacetonitrile: Experimental and semiempirical investigations

Y.H. Ebead^{a,*}, M.A. Selim^a, S.A. Ibrahim^b

^a South Valley University, Faculty of Science, Chemistry Department, 83523 Qena, Egypt

^b Assiut University, Faculty of Science, Chemistry Department, 71516 Assiut, Egypt

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ABSTRACT

The solvatochromism and other spectroscopic properties of seven azo dyes were studied, with a particular respect to the role of the solvent basicity, and interpreted with the aid of experimental findings and semiempirical data. The electronic absorption spectra of the dyes examined in different solvents combined with theoretical calculations showed that most of the investigated compounds coexist in the hydrazone and/or azo-enamine-common anion equilibrium or in the solely anionic form depending upon the nature of the solvent employed. These interesting features open up possibilities for the use of these compounds in analytical chemistry as acid–base indicators. Furthermore, both of intermolecular and intramolecular charge transfer equilibria have been reflected by experimental absorption spectra of compounds **4** and **5**. The enthalpies of formation predicted at PM6 (COSMO) and PM6/CI (COSMO) for the ground (S_0) and excited (S_1) states, respectively have been successfully used for the explanation of the observed bathchromic shift in non-polar solvents. The effect of time on the longer wavelength visible band of compound **7** has been thoroughly investigated.

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1. Introduction

Electronic absorption spectroscopy is one of the most powerful tools available to chemists and widely used for the identification and determination of myriad inorganic and organic species, particularly for determining environmental pollutants [1,2]. Consequently, it is probably more widely used in chemical and clinical laboratories – because many substances can be selectively converted into a color derivative – throughout the world than any other single procedure [3]. However, synthesis of new azo compounds and studying their physicochemical properties are important subjects due to their fundamental role in biological, pharmaceutical and colorimetric chemosensors for metal ions [4–9]. Of particular interest are their widespread commercial applications in a textile dyeing industries as well as food, cosmetic and ink-jet printers [10,11]. Nevertheless, azo dyes are not renowned for recalcitrant to biodegradation and consequently they contribute to mutagenic activity of ground and surface waters pollution [12,13]. Considering their significant biological activity, pharmacological and physicochemical properties, azo dyes are extremely important. In a broader sense, the azo dyes constitute the largest group of all the synthetic

colorants [10,14,15]. Recently, the demand for such group of compounds especially those having sufficient large non-linear optics (NLO) have increased as a result of several new technological applications that have been found [16–18]. Furthermore, azo dyes have received considerable attention in the field of solvatochromic studies and in the design of polarity scale [19–21]. It is well-known that benzothiazole derivatives show a broad spectrum of biological activities [22–24]. Additionally, benzothiazole and its derivatives were investigated in azo push–pull systems [25]. In continuation of our earlier work on azo and other biologically active compounds [26–29], the present work focuses on the synthesis, spectroscopic properties of some novel azo dyes derived from 1,3-benzothiazol-2-ylacetonitrile using UV–vis and semiempirical molecular orbital PM3, PM6 methods. Furthermore, the effect of time on the low energy band of compound **7** appearing in the basic solvent (DMF) has been also investigated. A wide variety of organic solvents have been employed, aiming to evaluate which tautomeric form of these compounds is spectroscopically active, considering their possible applications as indicators or spectral probes.

2. Experimental

2.1. Synthesis of the azo compounds 1–7 (Scheme 1)

The azo compounds under investigation were prepared according to the procedure previously described in the literature [30,31].

* Corresponding author. Tel.: +20 108928365; fax: +20 96/5213383.

E-mail address: ebeadhassan88@yahoo.com (Y.H. Ebead).

Thus, to an ice cooled stirred solution of the proper primary aromatic amine (0.01 mol) dissolved in diluted HCl a cold solution of NaNO₂ (0.01 mol) was added gradually with stirring for 20 min. To a solution of 1,3-benzothiazole-2-ylacetonitrile (0.01 mol) [32] in ethanol in the presence of sodium acetate (0.01 mol), a solution of diazotized amine was added dropwise with vigorous stirring at 0–5 °C for 35 min. After the addition, stirring was continued for 1 h and the obtained precipitate was filtered off and washed with water and cold ethanol. The solid products were recrystallized from ethanol and dried in vacuo over silica gel. The chemical structures of compounds were assigned on the basis of their elemental analysis and spectral data (Table 1).

2.2. Measurements

The chemical composition of the products was proved by elemental analysis using Carlo-Erba (model EAGER 200) instrument. Melting points were determined by Electro-thermal melting point apparatus. Spectral measurements in the UV and visible regions were recorded on a Shimaduz 2401 PC spectrophotometer within the wavelength range 200–700 nm using 1-cm matched quartz cell. ¹H NMR (DMSO-d₆) spectra were taken on a Varian Mercury VX-300 MHz spectrometer. All solvents (methanol, ethanol, acetone, acetonitrile, carbon tetrachloride, chloroform, methylenechloride, dimethylsulfoxide and dimethylformamide) used in this investigation were analytically pure or spectroscopic grade and were used as purchased. Infrared spectra of the solids were performed on a FT-IR Bruker Vector 22 using the KBr technique. All the measurements were carried out at room temperature (25 °C).

2.3. Quantum chemical calculations

The fully geometry optimization of the isolated molecules **1–7** (Scheme 1) in ground (S₀) and first excited (S₁) states were optimized using the semiempirical PM6 and PM6/CI methods [33]. From which some physicochemical and structural parameters in gaseous phase for each tautomer were estimated. Solvent effects on tautomers were also investigated using PM6 (COSMO) model [33] as implemented in MOPAC 2007. PM3 method was employed for comparison when it was necessary [34]. The geometry data were obtained from MOPAC 2007—free license on internet [35]. The wavelengths of the electronic transitions in absorption spectra were calculated at AM1 with a 10 × 10 CI singly excited matrix [36]. Heats of formation, dipole moments and other parameters were extracted directly from the data files following the geometry optimizations. All calculations were done on a Pentium IV PC computer.

3. Results and discussion

3.1. Structural and physicochemical features of the molecules in the ground and excited states

Three different structures could be written corresponding to the molecular composition of each compound namely, azo, hydrazone and azo-enamine (Scheme 1). This is due to the migration of the hydrogen atom attached to C₁₀ to the benzothiazole nitrogen atom or to N₁₃. A further tautomeric structure is also possible in the case of compound **7** (R=OH) as a result of transfer of the phenolic OH proton to N₁₂. The latter tautomer is excluded from our discussion due to its high heat of formation. Azo, hydrazone and azo-enamine as well as the anionic forms have been geometrically optimized in the gaseous phase and in different media using PM6 and PM6 (COSMO), respectively. PM6 which has been recently released as a modification on NDDO formalism gave satisfactory estimates of

Table 1
Microchemical analysis data, melting points, color, IR and ¹H NMR spectra of the synthesized compounds.

Comp.	Formula	m.p. (°C)	Color	% Calculated (found)				IR ν (cm ⁻¹)		¹ H NMR (ppm)
				C	H	N	S	ν (NH)	ν (C≡N)	
1	C ₁₅ H ₁₀ N ₄ S	155–157	Green yellow	64.67 (64.10)	3.59 (3.48)	20.12 (19.87)	11.50 (11.77)	3449	2217	12.22 (s, 1H, NH), 7.12–8.09 (m, 9H, Ar-H)
2	C ₁₆ H ₁₂ N ₄ S	182–184	Dark yellow	65.67 (65.29)	4.10 (3.80)	19.15 (19.11)	10.95 (11.07)	3462	2216	12.16 (s, 1H, NH), 7.21–8.19 (m, 8H, Ar-H), 2.29 (s, 3H, CH ₃)
3	C ₁₆ H ₁₂ N ₄ O ₂ S	162–164	Orange	62.26 (61.75)	3.89 (3.50)	18.16 (18.17)	10.38 (10.32)	3456	2217	12.17 (s, 1H, NH), 7.00–8.07 (m, 8H, Ar-H), 3.80 (s, 3H, OCH ₃)
4	C ₁₆ H ₁₀ N ₄ O ₂ S	269–271	Yellow	59.56 (59.16)	3.10 (3.43)	17.37 (17.16)	9.93 (9.80)	3456	2223	13.80 (s, 1H, COOH), 12.15 (s, 1H, NH), 7.00–8.20 (m, 8H, Ar-H)
5	C ₁₅ H ₈ N ₄ O ₂ S	237–239	Dark yellow	55.67 (55.20)	2.78 (3.08)	21.65 (21.40)	9.89 (9.37)	3483	2230	12.60 (s, 1H, NH), 7.48–8.33 (m, 8H, Ar-H)
6	C ₁₅ H ₉ ClN ₄ S	174–176	Yellow	57.55 (57.17)	2.88 (2.77)	17.90 (17.93)	10.23 (10.12)	3436	2230	12.27 (s, 1H, NH), 7.45–8.10 (m, 8H, Ar-H)
7	C ₁₅ H ₁₀ N ₄ O ₂ S	221–223	Brown	61.16 (60.79)	3.39 (3.07)	19.03 (19.07)	10.87 (10.86)	3469	2209	14.40 (s, 1H, OH), 12.12 (s, 1H, NH), 6.81–8.25 (m, 8H, Ar-H)

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