

Experimental and computational studies on the electronic spectral properties of some 3-hydroxy, 4-arylozo [(Benzylidene) dithio] diacetic acids

Gamal A. Gohar*

Chemistry Department, Faculty of Science, Alexandria University, Ibrahimia PO Box 426, Alexandria, Egypt

J. Chem. Research (S),
2003, 188-190
J. Chem. Research (M),
2003, 0470-0488

The correlations between the electronic spectral properties of the title azo compounds and organic solvent parameters have been analysed also, their electronic transition energies have been calculated, using a semi empirical approach and the results were compared with the experimental measurements.

Keywords: azo-compounds; electronic spectra, regression analysis; AM1 and PM3

The structure of azo dyes has attracted considerable attention in recent times due to their wide applicability in light-induced photoisomerisation.⁴ The structural properties of azo compounds were elucidated by various spectroscopic and photochemical methods, including UV-visible absorption, femtosecond time resolved absorption,⁵ IR, Raman,⁶ NMR,⁷ as well as by theoretical modeling, utilising semi-empirical and ab initio methods.⁸

Accordingly, the main objectives for carrying out the present investigation are 3-fold: (1) The study of the UV-visible spectra of 4-(substituted phenylazo), 3-hydroxy [(benzylidene) dithio] diacetic acids, using solvents of various polarities and basicities; (2) analysing and understanding the contribution of different solvent parameters in affecting the electronic spectral properties of the substituted azo compounds, utilising a multiple regression technique; and (3) a critical comparison of the experimentally observed electronic spectra with the theoretical semi empirical computations.

The title compounds were synthesised and their structures identified by their infrared and ¹H NMR spectra and elemental analyses. The electronic spectra of the title compounds were recorded in different organic solvents within the wavelength range 200–800 nm on a Perkin Elmer Lambda 4B UV/VIS Spectrophotometer, using 1 cm match fused silica cells at 25°C. The solvent effects on the spectra of the investigated compounds in different organic solvents have been analysed by the multiple linear regression technique,^{14,15} using Eqns (1) and (2).

The electronic spectra of compounds under investigation showed a band that is attributed to the $\pi - \pi^*$ transition, within the aromatic nucleus and shifted in response to the solvent properties. The spectra also showed two bands; the first appeared at 345–395 nm, B₁, and the second at 381–487 nm, B₂. These two bands are ascribed to the absorption of hydrogen-bonded solvated complexes,²³ which include intra- and intermolecular charge transfer transition (CT). The solvent effect on the position of the CT bands (Table 1) reveals that this band acquires a red shift on changing the solvent from dioxane → EtOH → DMF → AN → EA → Ac → DMSO and EtOH → EA → DMF → Ac → AN → DMSO for B₁ and B₂ bands, respectively. The shorter wavelength band, B₁, is attributed to the absorption of the intramolecular hydrogen bonding structure. The longer one, B₂ is assigned to the intermolecular hydrogen bonding structure, as shown in Figure 2.

In order to account for the three types of dominant solute-solvent interactions from the cavity effect,²⁵ the available values of the solvent parameters and the electronic transition energies of the CT bands, E (eV), Table 2, were subjected to multiple linear regression analysis by applying Eqns (1) and (2). The important statistical correlation data were

selected and collected in Table 4. The data show that the shift in the experimental electronic transition energies of the B₁ bands of **1a c–j** compounds might be affected by the empirical solvent polarity, E^{*}; the permanent solvent dipole – permanent dipole interactions, N, as well as the solute permanent dipole – solvent induced dipole interaction, M. The dipolarity and HBD acidity of the solvent E_T^N, the solvent dipolarity – polarisability, π^* ; and the solvent hydrogen bond acceptor basicity, β , parameters constitute the fundamental influences of the total solvent effects on the electronic transition energies of the CT band B₂, of the title compounds.

Figure 3 represents the correlation between the solvent experimental proton affinities PA (eV)²⁸, and the electronic transition energies, E (eV) of the band, B₂, of the spectra **1c, d, i–j**. In this sense, it is quite interesting to note that the maximum point corresponds to EA solvent at PA = 8.7 eV. This maximum might be assigned to the critical behaviour, where a ca ~ 50% proton transfer complex exists.²⁹ The left hand side of the critical region represents the molecular complexes while the right hand side might be assigned to the proton transfer ones. These results indicate that the stated mode of the specific interactions of certain organic solvents with the investigated azo-compounds is in a good agreement with the general mechanistic features, previously reported.^{29,30}

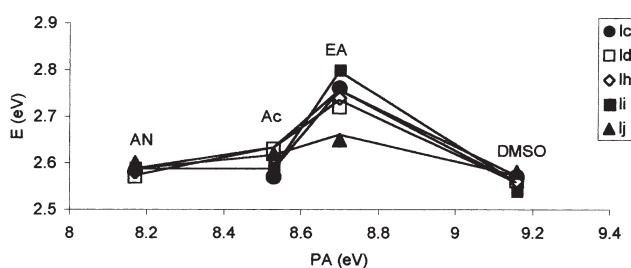


Fig. 3 The correlation between the solvent PA and E (eV) of B₂ band of compounds **1c, d, h–j** in different organic solvents

It has been found that the substituent influences on the position of band B₁, denotes a high conjugation in the molecule; *i.e.*, a planar form is apparent confirming the stability of the intramolecular hydrogen-bonding structures. Ideally, the fact is substantiated by correlating the E (eV) of B₁ bands against Hammett σ constants. Comparable good correlations are found for compounds having the substituent (X=4'-H; 4'-OH; 3'-OH; 4'-OCH₃; 4'-COOH and 4'-NO₂) in dipolar aprotic solvents, EA, (E (eV) = -0.043 σ + 3.21); Ac and DMSO. Linear correlations with negative slopes and correlation coefficients, R equal to 0.86; 0.82 and 0.82 in EA, Ac and DMSO, respectively, are obtained. This indicates that the resonance, as well as inductive effects of the ring substituent of phenylazo moiety, influenced the stability of the intramolecular hydrogen-bond-

* To receive any correspondence. E-Mail: gohar_g@link.net

predicting the proton transfer energy barriers of the equilibrium between azo- and hydrazo-like forms in the gas phase of the title compounds with a certain degree of accuracy.

Received; accepted 13 March 2003

Paper 02/1466

References

- 4 H. Rau *Photochromism: Molecules and Systems* Durr. H. Bouas-Laurant. H. Eds. Elsevier. Amsterdam, 1990, Chap. 4. P 165
- 5 K. Lednev, Tian-Qing Ye, R.E. Hester and N. Moore. *J. Phys. Chem.*, 1996, **100**, 1338.
- 6 H. Okamoto, H. Hamaguchi and M. Tasumi, *Chem. Phys. Lett.*, 1986 **130**, 185.
- 7 (a) V. Koleva, T. Dudev and I. Wawer, *J. Mol. Struct.*, 1997, **412**, 153; (b) G. McGeorge; R.K. Harris; A.M. Chippendale; J.F. Bullock, *J. Chem. Soc. Perkin Trans. 2*, 1996, **8**, 1733.
- 8 (a) N. Biswas; S. Unapathy, *J. Phys. Chem. A*, 2000, **104**, 2734; (b) N. Kurita; S. Tanaka and S. Itoh, *J. Phys. Chem. A*, 2000, **104** and 8114; (c) N. Biswas and S. Umpathy, *J. Phys. Chem. A*, 1997, **101**, 5555
- 14 F.W. Fowler and A.R. Katritzky *J. Chem. Soc. (B)*, 1971, 460.
- 15 (a) R.M.C. Goncalves, A.M.N. Simoes and L.M.P.C. Albuquerque, *J. Chem. Soc. Perkin Trans 2*, 1991, 825; (b) M. Dutkiewicz, *J. Chem. Soc. Faraday Trans*, 1990, **86(12)**, 2237-2241; (c) M.H. Abraham, R.M. Doherty, M.J. Kamlet, J.M. Harris and R.W. Taft, *J. Chem. Soc. Perkin Trans. II*, 1987, 913-920.
- 23 G.A. Goher, E.A. Hamed, A.A. El-Bardan and A.A. Abdallah, *Spectrochimica Acta*, 1993, **49A(7)**, 1021
- 25 M.H. Abraham, P.L. Grellier, J.-L.M. Abboud, R.M. Doherty and R.M. Taft *Can. J. Chem.*, 1988, **66**, 2673.
- 28 S.G. Lias, J.F. Liebman and R.D. Levin, *J. Phys. Chem. Ref. Data*, 1984, **13**, 695-808
- 29 G.A. Gohar, and M.M. Habeeb, *Spectroscopy*, 200, **14**, 99
- 30 M.M. Habeeb, and G.A. Gohar, *J. Chem. Res. (M)*, 2002, **3**, 316.
- 32 (a) J.O. Morely, *J. Chem. Soc. Faraday Trans.*, 1995, **91**, 2067-2069; (b) J.O. Morely, M.G. Hutchings, J. Zyss and I. Ledoux, *J. Chem. Soc. Perkin Trans. 2*, 1997, 1139-1141
- 33 (a) H.B. Broughon. S.M. Green and H.S. Rzepa, *J. Chem. Soc. Perkin Trans. 2*, 1995, 877; (b) J.O. Morely, I. Juranic, H.S. Rzepa and M. Yi, *J. Chem. Soc. Perkin Trans. 2*, 1990, 877.
- 34 A. Koll and I. Majerz, *Bull.Soc. Chim. Belg.*, 1994, **103**, 629.