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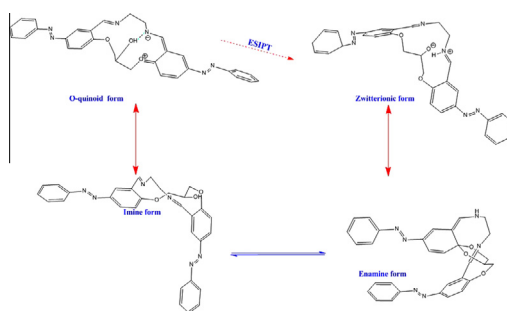
The interactional behaviors and photo-physical properties of azo-salicylaldehyde ligands in solvents media

M.S. Zakerhamidi ^{a,*}, K. Nejadi ^b, S. Alidousti ^a, M. Saati ^b^a Research Institute for Applied Physics and Astronomy, University of Tabriz, Tabriz, Iran^b Department of Chemistry, Payam Noor University, P.O. Box 19395-3697, Tehran, Islamic Republic of Iran

HIGHLIGHTS

- Solvatochromism of salicylaldehyde ligands strongly depend on the steric hindrance.
- Imine forms of salicylaldehyde show polar structural character than enamine forms.
- ES IPT and sterically hindered control salicylaldehyde ligands spectroscopic behavior.

GRAPHICAL ABSTRACT



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ABSTRACT

A quantitative study of solvent effects on photo-physical properties of some azo-salicylaldehyde Schiff Bases ligands, with various substituent and alkyl group, was carried out, at room temperature. The solvatochromic behavior of these substances and their solvent–solute interactions, both specific and non-specific, was analyzed using linear solvation energy relationship concept, suggested by Kamlet–Taft. The ground and excited state dipole moments of these substances and their molecular resonance structures were also evaluated via solvatochromic shift method.

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Introduction

Schiff Base compounds are very popular ligands which are widely used as synthetic intermediates for coordinating transition and inner transition metal ions [1,2]. Practical applications of Schiff Bases in coordination chemistry, sensing materials, catalysis, metallic deactivators, biology, pharmaceutical and enzymatic make study of these compounds interesting and essential [3–5].

The steric configuration and electronic structure of electron withdrawing or electron donating substituent in

salicylaldehyde-Based Schiff Base ligands alter photo-physical properties such as; electronic structure, ground and excited state dipole moments and intra- and inter-molecular interactions, in solutions [5]. Along with substitution changes, the solvent media have a significant effect on performance of chemical reaction and physical behaviors of these ligands [5–8].

Solvent effect is closely related to the nature and degree of solute–solvent interactions. The solvent dependent variation in photo-physical behaviors of solute can arise from either non-specific (dielectric enrichment) or specific solute–solvent interactions (e.g. hydrogen-bonding). Therefore, quantitative measurement of the solvent's effect can effectively determine the solute molecules' interaction and reactivity, for practical application [9–11].

* Corresponding author. Tel.: +98 411 3393003; fax: +98 411 3347050.

E-mail address: Zakerhamidi@tabrizu.ac.ir (M.S. Zakerhamidi).

Single and/or multi-parameter solvent polarity scales can be used for quantitative assessment of the solvent–solute interactions [12–15]. However, the selection of polarity parameters is very important in explaining the photo-physical behavior and molecular interactions between solvent and solute [16]. Due to the wide influence of solvents on solutes and various interactions between them, multi-parameter solvent polarity method is used to evaluate the exact behavior of solute in solvent media, and also obtain a more accurate diagnosis of the interactions [5,11,17].

Multi-parameter solvent polarity can be coupled using linear free-energy relationship concept. Kamlet–Abboud–Taft's formulated solvent's multitude effects on the spectral features of solute by means of linear solvation energy relationship (LSER) concept, Eq. (1), [18]:

$$v = v_0 + s\pi^* + b\beta + a\alpha \quad (1)$$

where π^* is a measure of the solvent's dipolarity/polarizability [19], β is the scale of solvent's hydrogen bond acceptor (HBA), basicities [20], α is the scale of solvent's hydrogen bond donor (HBD), acidities [21] and v_0 is the regression value of the solute property in the reference solvent, such as cyclohexane. The regression coefficients s , b and a in Eq. (1) measure the relative susceptibilities of the solvent-dependent solute property to the indicated solvent parameters.

In this work, some azo-salicylaldehyde Schiff Bases ligands, with various substituent and alkyl group, were studied in different solvents, in order to perform a correlation between their structural and spectroscopic behaviors, through estimation of singlet ground and excited-state dipole moments and multi-parameter solvent polarity scales. The acquired data identify the specific and non-specific interactions' effects on solvation of these Schiff Bases and reveal the structural configuration in ground and excited states, as well as activity of these ligands in different solvent media.

Experimental

Material

Salicylaldehyde-Based Schiff Bases ligands (Fig. 1) were synthesized and purified, according to the common procedure in our laboratory and used as solutes (guests) [1,2]. All solvents used in this study were of the highest available purity from Merck. The selected empirical polarity parameters, polarity functions and physical properties of the employed solvents are listed in Table 1.

Absorption and fluorescence spectroscopy

Double beam Shimadzu UV-2450 Scan spectrophotometer was used to record the absorption spectra, over a wavelength range between 300 and 800 nm, which is combined with a cell temperature controller. Fluorescence of substances' solutions were studied with a JASCO FP-6200. Quartz rectangular cuvettes with 1 cm path length were used for measurements in solution. The solute concentrations' were chosen to be 5×10^{-5} M, for all the samples.

Estimation of the dipole moments

The most common technique for determining the dipole moment is based on the solvent spectral shift method. In this method, through using the quantum mechanics second order perturbation method, and taking into account the Onsager model of reaction field for a polarizable dipole moment [22–24], expressions for difference and sum of absorption, $\tilde{\nu}_a$, and fluorescence, $\tilde{\nu}_f$, bands maxima are obtained:

$$\tilde{\nu}_a - \tilde{\nu}_f = m_1 f(\varepsilon, n) + const. \quad (2)$$

$$\tilde{\nu}_a + \tilde{\nu}_f = -m_2 [f(\varepsilon, n) + 2g(n)] + const. \quad (3)$$

where

$$m_1 = \frac{2(\mu_e - \mu_g)^2}{hca^3} \quad (4)$$

$$m_2 = \frac{2(\mu_e^2 - \mu_g^2)}{hca^3} \quad (5)$$

Parameters m_1 and m_2 for difference and sum of wave numbers, which are linear functions of solvent polarity functions $f(\varepsilon, n)$ and $g(n)$, can be determined from slopes of the straight lines. The solvent polarity parameters $f(\varepsilon, n)$ and $g(n)$ are as followed:

$$f(\varepsilon, n) = \frac{\frac{\varepsilon-1}{2\varepsilon+1} - \frac{n^2-1}{2n^2+1}}{\left(1 - \frac{2\alpha}{a^3} \frac{\varepsilon-1}{2\varepsilon+1}\right) \left(1 - \frac{2\alpha}{a^3} \frac{n^2-1}{2n^2+1}\right)^2} \quad (6)$$

$$g(n) = \frac{\frac{n^2-1}{2n^2+1} \left(1 - \frac{\alpha}{a^3} \frac{n^2-1}{2n^2+1}\right)}{1 - \frac{\alpha}{a^3} \frac{n^2-1}{2n^2+1}} \quad (7)$$

In these relations, ε denotes the dielectric permittivity and n is the refractive index. a and α represent the spherical cavity radius of the solute and average polarizability, respectively. For an isotropic polarizability of the solute, the condition $\frac{2\alpha}{a^3} = 1$ is usually satisfied [25–27] and the following relations were obtained by Bakhshiev:

$$f_{BK}(\varepsilon, n) = \frac{2n^2 + 1}{n^2 + 2} \left[\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right] \quad (8)$$

$$g_{BK}(n) = \frac{3}{2} \left[\frac{n^4 - 1}{(n^2 + 2)^2} \right] \quad (9)$$

Considering that the ground and excited state dipole moments are parallel, based on Eqs. (4) and (5), one obtains [27]:

$$\mu_g = \left| \frac{m_2 - m_1}{2} \right| \left[\frac{hca^3}{2m_1} \right]^{1/2} \quad (10)$$

$$\mu_e = \left| \frac{m_2 + m_1}{2} \right| \left[\frac{hca^3}{2m_1} \right]^{1/2} \quad (11)$$

$$\mu_e = \frac{m_1 + m_2}{m_1 - m_2} \mu_g \quad (m_1 > m_2) \quad (12)$$

h is Plank's constant and c is the velocity of light in vacuum. μ_e and μ_g are dipole moments in excited and ground states, respectively. Onsager cavity radii (a), for investigated samples, were determined theoretically, according to their optimized geometry [28]. The radius of spherical cavity for each solute, which is used in Onsager solvation model, was calculated from its optimized gas phase geometry. First, the geometry of the molecule was optimized by B3LYP hybrid-GGA functional and 6-31G(2df,2p) basis set in gas phase. Afterwards, the molecular volume was computed as the volume inside a contour of 0.001 electron/Bohr³ density and the radius of this spherical volume was calculated. All of the mentioned calculations were performed by Gaussian 03 program [29].

Result and discussion

The solvent effect on absorption and fluorescence spectra

The absorption and fluorescence emission spectra of studied Schiff Bases ligands (5×10^{-5} M) were obtained at room temperature (22 °C), in various organic solvents with different polarities. It should be noted that, the molecular structure of studied Schiff

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