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Solvatochromic behavior and electronic structure of some symmetric 2-aminophenol Schiff base derivatives

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ABSTRACT

The solvatochromic behavior and electronic structure of four symmetric 2-aminophenol Schiff base derivatives were investigated by using electronic absorption spectra in fourteen different spectroscopic grade solvents. The electronic transitions of these molecules have been interpreted. The electronic transition mechanisms and properties are investigated with four different linear solvation energy relationship (LSER) methods, which use different parameters such as Kamlet–Taft parameter (dielectric function $f(\varepsilon) = (\varepsilon - 1) / (\varepsilon + 2)$, refractive index function $f(n) = (n^2 - 1) / (n^2 + 1)$, hydrogen bond acceptor capacity (β) and hydrogen bond donor capacity(α)), Catalan parameters (polarity/polarizability (SPP), acidity of solvents (SA) and basicity of solvents (SB)), Marcus optical dielectric function and Reichardt–Dimroth E_T solvent parameter. Some electronic parameters, such as E_{HOMO}, E_{LUMO}, E_{HOMO-1}, E_{LUMO+1}, dipole moment, electron affinity, electronegativity and ionization potential, MEP (molecular electrostatics potential) and SAS (solvent accessibility surface) were calculated by using B3LYP/6-31G(d,p) method.

1. Introduction

Schiff base compounds having imine groups (CH–N) between two benzene rings and π-conjugate system can be used to design various molecular electronic devices because of having specific electronic structure process like ESIPT (excited state intra/inter-molecular proton transfer). This process occurs both in solvent medium and solid state phase. ESIPT eventuates to H-atom transfer from hydroxyl O atom to imines N atom in solid state [1–3]. In addition, the formation of ESIPT process leads Schiff base derivatives to have photochromism and thermochromism properties. These compounds have important characteristic properties and many application areas such as photochromic, thermochromic, optical sensor, molecular memory retention, measure and control of radiation intensity in optic computers and display systems [4–9]. These compounds are known to be one of the most important classes used for the synthesis of novel optical and conductor materials. Moreover, compounds including imine group are still an important research topic due to having various applications in optical communication, electronic, optoelectronic and photonic areas [10]. Many Schiff base compounds have been found to have liquid crystal properties in recent years [11,12]. It is reported that these compounds can be used as non-linear optic material due to exhibiting positive solvatochromism [13]. The Schiff base accommodates different metal centers involving various coordination modes thereby allowing successful synthesis of homo- and hetero-metallic complexes with varied stereochemistry [14].

The spectral behavior of any organic compound is considerably related to its structure in both the ground and excited states. The investigation of solvent–solute interactions is very important, when the solvent medium can substantially influence the chemical and physical properties of the solute. Solvatochromic behavior of molecules born out from the solvation of ground and excited states of the light-absorbing molecule, thus, provides a convenient tool to study the photophysical and related different properties [15–18].

These compounds are very usable in the design of new different electronic devices because symmetric Schiff base molecules have specific electronic structure. Thus, in this study, we have researched the solvatochromic behavior and electronic structure of four symmetric 2-aminophenol Schiff base derivatives. The electronic transitions of molecules were measured in fourteen solvents with various polarities. The solvatochromic behavior of investigated molecules was determined by using Kamlet–Taft Parameter (dielectric function $f(\varepsilon) = (\varepsilon - 1) / (\varepsilon + 2)$, refractive index function $f(n) = (n^2 - 1) / (n^2 + 1)$, hydrogen bond acceptor capacity (β) and hydrogen bond donor capacity(α)), Catalan parameters (polarity/polarizability (SPP), acidity of solvents (SA) and basicity of solvents (SB)), Marcus optical dielectric function and Reichardt–Dimroth E_T solvent parameter. DFT calculations on some electronic parameters in the ground state of the symmetric Schiff base derivatives were performed and discussed. In addition, solvent accessibility surface (SAS) and molecular electrostatic potential (MEP) were depicted and evaluated.

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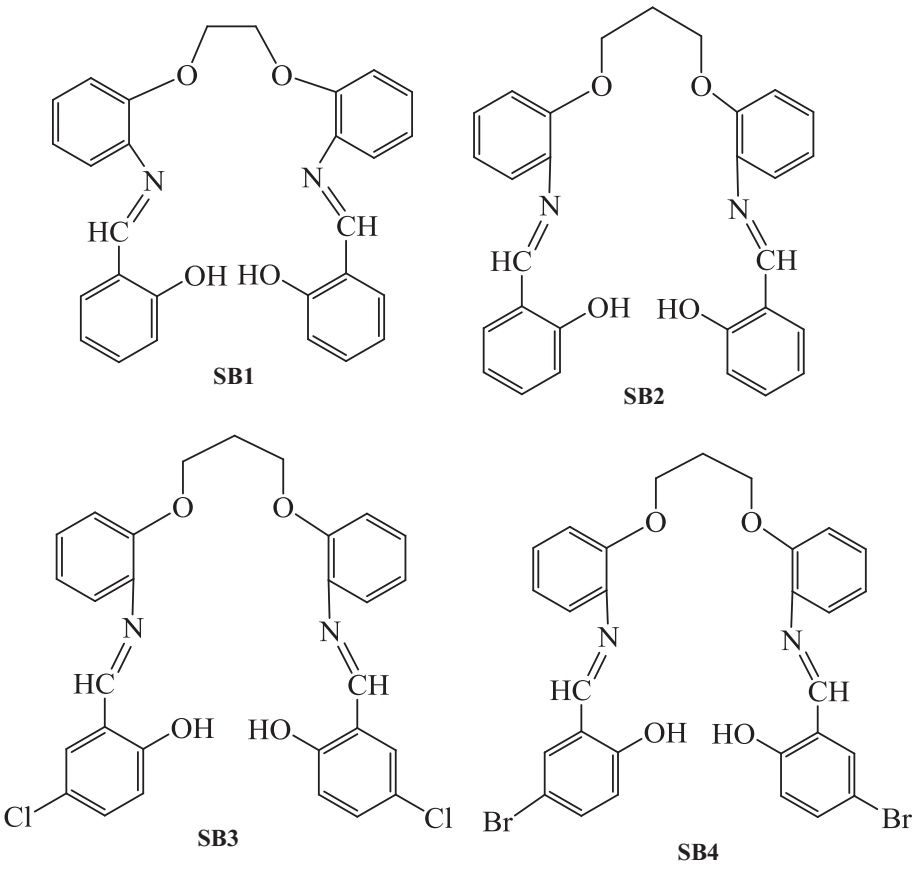

Fig. 1. Molecular structures of the studied SSBs.

2. Materials and methods

2.1. Experimental section

Synthesis and purification of the studied symmetric Schiff bases (SSB) are performed as given in the references [19,20]. The molecular structures of these molecules are depicted in Fig. 1. Moreover, IUPAC names are listed in Table 1. All of the used organic solvents purchased from Sigma & Aldrich are spectroscopic grade. The solutions have been prepared with the concentration of 10^{-5} M. The UV–visible spectra of the prepared solutions are recorded using Shimadzu UV2101 Pc series spectrometer in 1 cm quartz cell.

2.2. Quantum chemical calculations

Firstly, energy optimization was performed with AM1 [21]. method after molecules were drawn with ChemOffice03. Secondly, input files of molecules have been established in GaussView5 software [22]. In the last step, input files were created by using B3LYP/6-31G(d,p) [23–25] level of theory and transferred to Gaussian09W packet program [26] for calculation. Quantum chemical calculations were completed and some electronic parameters (E_{HOMO}, E_{LUMO}, E_{HOMO-1}, E_{LUMO+1}, dipole moment, electron affinity, electronegativity and ionization potential etc.), solvent accessibility surface (SAS), molecular electrostatic potentials (MEPs) were obtained.

2.3. Statistical methods

LSERs (linear solvation energy relationships), which effects the solvent polarity on the spectral features of solute, is used for determining to coefficients obtained from Kamlet–Taft [27] parameters with Eq. (1) and Catalan parameters [28] with Eq. (2) using multiple linear regression analysis (MLRA).

$$\nu_{max} = C_0 + C_1.f(n) + C_2.f(\varepsilon) + C_3.\beta + C_4 \cdot \alpha \quad (1)$$

$$\nu_{max} = C_5 + C_6 \cdot SPP + C_7 \cdot SA + C_8 \cdot SB. \quad (2)$$

In these equations, ν_{max} is defined as the maximum absorption band. In Eq. (1), dielectric function is characterized as $f(\varepsilon) = (\varepsilon - 1)/(\varepsilon + 2)$, refractive index function as $f(n) = (n^2 - 1)/(n^2 + 1)$ and where, β and α are Kamlet–Taft parameters. In Eq. (2), polarity/polarizability is characterized as SPP, acidity of solvents as SA and basicity of solvents as SB.

C_0 and C_5 coefficients describe the maximum absorption band in gaseous phase for Kamlet–Taft and Catalan solvatochromism, respectively.

Table 1
IUPAC names of the studied Schiff bases.

Molecule	IUPAC name
SB1	2,2′-(1E,1′E)-(2,2′-(ethane-1,2-diylbis(oxy))bis(2,1-phenylene))bis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)diphenol
SB2	2,2′-(1E,1′E)-(2,2′-(propane-1,3-diylbis(oxy))bis(2,1-phenylene))bis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)diphenol
SB3	2,2′-(1E,1′E)-(2,2′-(propane-1,3-diylbis(oxy))bis(2,1-phenylene))bis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)bis(4-chlorophenol)
SB4	2,2′-(1E,1′E)-(2,2′-(propane-1,3-diylbis(oxy))bis(2,1-phenylene))bis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)bis(4-bromophenol)