



Spectroscopic Investigation at Different pH and FMO Analysis of Unsymmetrical Schiff Bases

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Abstract

In this study N-(salicylidene)-N'-(2-hydroxy acetophenone)ethylenediamine (H_2L^1) and N-(2-hydroxy-5-methyl acetophenone)-N'-(2-hydroxy acetophenone)ethylenediamine (H_2L^2) Schiff bases have been subjected to spectroscopic investigation at different pH and theoretical studies by using Semi-empirical AM1 method. The molecular geometry, HOMO-LUMO energy gap, molecular hardness (η), ionization energy (IE) and electron affinity (EA) were analyzed.

Introduction

Tetradentate Schiff bases with N2O2 donor atoms are well known to coordinate with various metal ions and have attracted a great deal of interest in recent years due to their potential legating ability, structural flexibility, spectral and chemical properties as well as magnetic properties [1, 2]. The spectroscopic investigations of 2-hydroxy Schiff bases have eminent importance of intramolecular hydrogen bond as a consequence of intramolecular proton transfer between phenolic oxygen and imine nitrogen sites. The ultraviolet and visible spectrometer is an important analytical instrument in the modern day laboratory. It is used to understand the behavior of molecular electron when they are exposed to light having an energy that matches possible electronic transition within organic and inorganic molecule. The UV-Vis spectroscopic studies can be conducted in the solid state or in solution. The effect of solvent on the electronic spectra of the organic and inorganic molecule is well established [3]. The nature of solvent plays a major role in the position of the wavelength of a molecular electronic transition band. The molecular structure of the compound and nature of the solvent contribute to spectral behavior. In the present work, the electronic absorption spectra of hydroxyl aryl Schiff base ligands derived from salicyladehyde or 2-hydroxy-5-methyl acetophenone, 2-hydroxy acetophenone and ethylenediamine in organic solvent and buffer solution of 4.0, 7.0 and 9.2 pH.

Experimental

The Schiff base ligands were synthesized by condensation of the salicyladehyde or 2-hydroxy-5-methyl acetophenone, 2-hydroxy acetophenone with ethylenediamine by reported procedure [4] and confirmed by elemental analyses, UV-Vis, IR, ¹H and ¹³C NMR, FAB-Mass spectroscopy and decomposition





temperature. The stock solutions of 1×10^{-3} M of the Schiff base ligands N-(salicylidene)-N'-(2-hydroxy acetophenone)ethylenediamine (H₂L¹) (Figure 1) and N-(2-hydroxy-5-methyl acetophenone)-N'-(2-hydroxy acetophenone)ethylenediamine (H₂L²) (Figure 2) were prepared by dissolving the accurate weight of the solid compound in the ethanol using 100mL volumetric flask. A buffer solution is one which resists changes in pH when small quantities of an acid or alkali added to it. Stock solutions are prepared by using buffer Tablet of pH 4.0, 7.0 and 9.2 of Merck in distilled water. The pH of buffer solutions was check by using pH meter. The UV-Vis spectra of ligand (H₂L¹) and (H₂L²) (Figure 3) solutions were recorded at Government College of Pharmacy, Amravati.



Figure 1 3D optimized geometry of H_2L^1



Figure 2 3D optimized geometry of H_2L^2

Results and Discussion

Spectroscopic Investigation

The electronic absorption spectra of the Schiff base ligands H_2L^1 and H_2L^2 at different pH involve the absorption bands due to various electronic transitions liable to occur within the molecule such as:

- i) Bands due to excitation of π -electron within the aromatic moieties attached to the azomethine group which generally lies in the UV-region.
- ii) Bands corresponding to localized electronic transition within the azomethine group namely the excitation of the π and n-electron which lie in the visible region.

For an azomethine compound, the absorption spectrum should contain the bands due to electronic transitions within the aromatic moieties as well as the -N=CH- group. These spectra indicated that the bands due to localized electronic transitions are slightly influenced by the variation of pH.

Frontier Molecular Orbital Analysis

The frontier orbital (HOMO and LUMO) of the chemical species are very important in defining its reactivity [5, 6]. The HOMO represents the ability to donate an electron and LUMO as an electron acceptor. The HOMO and LUMO energies were calculated by Semi empirical AM1 method. An electronic system with a larger HOMO-LUMO gap should be less reactive than one having smaller gap [7]. The electronic transition absorption corresponds to the transition from the ground to the first excited state and is mainly described by an electron excitation from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The atomic compositions of the frontier





molecular orbital are shown in Figure 4. Relatively large LUMO–HOMO energy gap of the studied molecule indicates that it would not be kinetically sTable.



Figure 3 Absorption spectra of (a) H_2L^1 and (b) H_2L^2 .

The ionization energy (IE) can be expressed through HOMO orbital energies as $IE = -C_{HOMO}$ and electron affinity (EA) can be expressed through LUMO orbital energies as $EA = -C_{LUMO}$. The hardness (η) corresponds to the gap between the HOMO and LUMO orbital energies. The larger the HOMO-LUMO orbital energy gap, the harder the molecule. The hardness has been associated with the stability of the chemical system. In the present study, the HOMO-LUMO gap of the H₂L¹ and H₂L² molecules are 7.067 and 7.007 eV respectively (Table 1) obtained by semi-empirical AM1 method clearly indicates that the molecules are very sTable.[8] The ionization potential values obtained by this method were supports the stability of the molecules.



Figure 4 Molecular orbital surface and HOMO–LUMO energy gap for (a) H_2L^1 and (b) H_2L^2 by AM1 semi-empirical method.

Table 1. Comparison of HOMO-LUMO energies of H_2L^1 and H_2L^2 molecules.

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€ _{HOMO} (eV)	-9.304	-9.066
E _{LUMO} (eV)	-2.237	-2.059
ϵ_{HOMO} - ϵ_{LUMO}	7.067	7.007
Hardness $(\eta) = \frac{1}{2} (\mathcal{E}_{HOMO} - \mathcal{E}_{LUMO})$	3.534	3.504
$IE = - \epsilon_{HOMO}$	9.304	9.490
$EA = - \mathcal{E}_{LUMO}$	2.237	1.131

References

- [1]. Hunoor RS, Patil BR, Badiger DS, Vadavi RS, Gudasi KB, Chandrashekhar VM, Muchchandi IS. Spectroscopic, magnetic and thermal studies of Co(II), Ni(II), Cu(II) and Zn(II) complexes of 3acetylcoumarin-isonicotinoylhydrazone and their antimicrobial and anti-tubercular activity evaluation. Spectrochim Acta Part A. 2010; 77:838-844.
- [2]. Qingbao S, Xiaoli W, Yongmin L, Yongxiang MA. Acylferrocene 2-furoyl hydrazones and their transition metal(II) complexes. Polyhedron. 1994; 13 : 2395-2399.
- [3]. Basu S. Advances in quantum chemistry. Ist Ed. P. O. Lowdin Academic press, New York. 1964;145-169.
- [4]. Maldhure A.K. and Aswar A.S. Synthesis and Characterization of nickel (II), cobalt (II), manganese (II), copper (II), iron (III) and chromium (III) complexes of unsymmetrical salen-type ligand and their application as catalyst for the oxidation of styrene. J. Indian Chem. Soc. 2009; 86: 697-702.
- [5]. Fukui K., Yonezaw T., Shingu. A. Molecualr Orbital Theory of Reactivity in Aromatic Hydrocarbons, J. Chem. Phy. 1952; 20: 722-725.
- [6]. Huizar Luis Humberto-Mendoza and Reyes Clara Hilda Rios. Chemical Reactivity of Atrazine Employing the Fukui Function. J. Mex. Chem. Soc. 2011; 55: 142-147.
- [7]. Kurtaran Raif, Sinem O., Akin Azizoglu; Experimental and Computational study on [2,6-bis(3,5-dimethyl-N-pyrazolyl) pyridine] (dithiocyanato) mercury (II), Polyhedron.2007; 26, 5069-5074.
- [8]. Singh R., Kumar D., Goswami Y.C. and Sharma R. Synthesis, spectral studies and quantumchemical investigations on S-benzyl b-N-(4-NN biscynodi ethylamino phenyl methylene)dithiocarbazate. Arab. J. Chem. 2014 (doi:10.1016/j.arabjc.2014.10.022).