Synthesis and Theoretical Studies of Salicylidene-2,4-diaminophenol

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Schiff-base isomers derived from salicylaldehyde and 2,4-diaminophenol has been synthesized and characterized by FTIR and UV-visible spectroscopy. Theoretical calculations of Schiff-base were studied by quantum chemical calculations. The optimized structure of Schiff-base was obtained by density functional theory at B3LYP/6-31G level. Also total energy, heats of formation, dipole moment, point group, molecular orbital's energy of HOMO and LUMO, energy gaps (E_g) and ΔG reaction were calculated and here we suggested the better Schiff base structure may be form. According to theoretical study and based on the results of density function theory (DFT), L3 possesses higher stability state compared with other isomers studied.

Keywords: Synthesis, Salicylaldehyde-2,4-diaminophenol.

INTRODUCTION

Azomethines are generally known as Schiff bases to honour Hugo Schiff, who synthesized such compounds. These are the compounds containing characteristic -C=N- group. Several methods have been reported for the preparation of azomethines. Selvam *et al*.[1] have prepared sulfonamide and its derivatives as anti-HIV agents. More *et al*.[2] have marked the biological activity of Schiff bases synthesized from aminothiazoles. The field of Schiff bases has been fast developing on account of the wide variety of possible structures for the compounds depending upon the aldehydes and amines. Schiff bases are considered as a very important class of organic compounds, which have wide applications in many biological aspects[3].

Schiff bases have been widely used as compounds because of high stability of the coordination compounds of them[4]. The π-system in a Schiff-base often imposes a geometrical constriction and affects the electronic structure as well[5]. Electronic structure methods provide useful information on the molecular structure and charge distribution, so they are useful to understand and describe systems where electronic effects and molecular orbital interactions are dominant. Depending on the theoretical assumptions used for calculations, electronic structural was carried out using density functional theory/B3LYP 6-31G base method.

Our aim in this work is to give a deeper insight into the best structure effect on the stability of salicylidene-2,4-diaminophenol and to compare predictions made from theoretical observations using DFT calculations.

EXPERIMENTAL

Absolute ethanol, salicylaldehyde (B.D.H Company), 2,4-diaminophenol dihydrochloride from (Fluka Company). Physical measurements, FTIR-8400S Shimadzu in the range of 4000-200 cm⁻¹. Absorption Spectra in absolute ethanol with the concentration of (1×10^{-5}) M were determined on a UV-VIS-1650 PC Shimadzu spectrophotometer, at wavelength (200-1100) nm at 25 °C.

Synthesis of Schiff base compound: Salicylaldehyde (1.22 g, 10 mmol) and 2,4-diaminophenol dihydrochloride (1.97 g, 10 mmol) were separately dissolved in 25 mL ethanol absolute. The two solutions were mixed and refluxed for 2 h on a hot plate magnetic stirred (**Scheme-I**). The condensation product was filtered, washed with cold ethanol and recrystallized with ethanol, dried in oven to 2 h at 110 °C. Schiff base was characterized by FTIR and UV/visible spectra.

Computational methods: Theoretical calculations were done using the density functional theory (DFT) method implemented in the Gaussian 03 suite of programs[6] with the B3LYP functional using the 6-31G base set[7,8]. DFT/B3LYP combination is known to produce good estimate of molecular properties related to molecular reactivity[9].

RESULTS AND DISCUSSION

In this paper, we describe the synthesis of Schiff base in good yield. The compound is stable at room temperature and is non-hygroscopic. UV/visible spectra of Schiff base
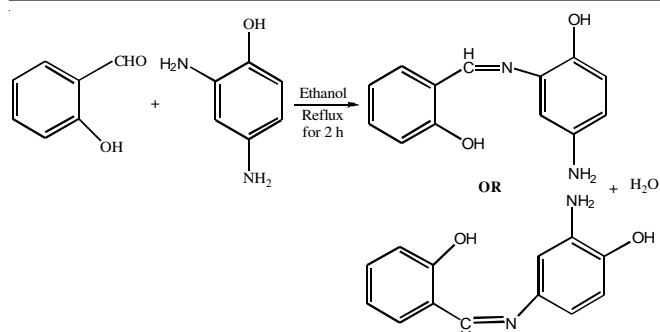
Scheme-I: Schematic route for the preparation of Schiff base

exhibited three absorption bands at (270) nm suggesting the presence of (π-π*) transition and absorption bands at (330, 461) nm suggesting the presence of (n-π*) transitions.

The Schiff base was identified by FTIR spectra in the range (4000-400) cm⁻¹. The NH group in compound was appeared

at (3375 cm⁻¹), OH group was appeared at (3350 cm⁻¹), the absorption band at (1633 cm⁻¹) corresponding to (C=N) compound, while absorption band at (1200 cm⁻¹) corresponding to (C-O). Table-1 shows some physical properties and spectroscopic data of compound.

Theoretical results: The quantum chemical calculations reported in this work are performed at the DFT B3LYP/ 6-31G level of theory using GAUSSIAN 03 series of programs[10].

Fig. 1 presents some of the optimized calculated of four molecule isomers, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the molecules under study are done.

Table-2 presents some of parameters calculated molecule isomers: total energies, heats of formation, dipole moment, point group, Gibbs energy (ΔG) of reaction and molecules orbitals energy: the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital

TABLE-1
PHYSICAL PROPRIETIES AND SPECTROSCOPIC DATA OF SALICYLIDENE 2,4-DIAMINOPHENOL

Compound	Colour	m.p.	ν(N-H) (cm⁻¹)	ν(O-H) (cm⁻¹)	ν(C=N) (cm⁻¹)	ν(C–O) (cm⁻¹)	UV-visible λ (nm)
Salicylidene 2,4-diaminophenol	Dark brown	330 Decomp.	3375	3350	1610 (1633)	1200	270 π- π* 330, 461 n-π*

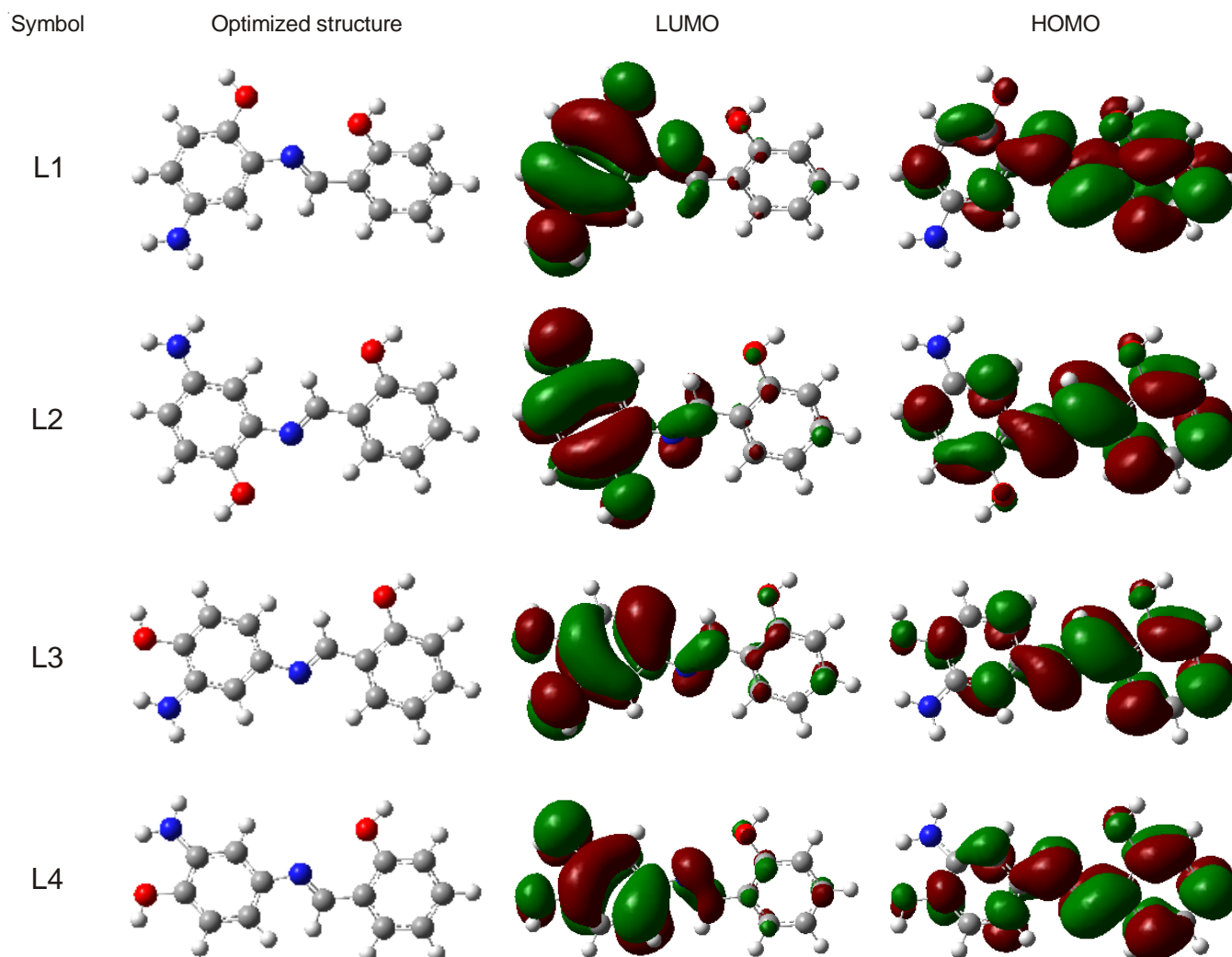| Symbol	Optimized structure	LUMO	HOMO

Fig. 1. Optimized structures, HOMO and LUMO for the studied isomers (performed at the B3LYP/6-31G)

TABLE-2
CALCULATED TOTAL ENERGY, HEAT OF FORMATION, DIPOLE MOMENT GIBBS ENERGY,
THE MO ENERGY OF HOMO, LUMO LEVELS AND ENERGY GAP

Symbol	Total energy (a.u.)	Heat of formation (Kcal/mol)	Dipole moment (Debye)	Point group	Gibbs energy (Kcal/mol)	HOMO (eV)	LUMO (eV)	ΔE (eV)
L1	-762.3166	26.690	1.6253	C_1	25.6848	-4.6077	-1.1880	3.4196
L2	-762.3271	26.883	2.7516	C_1	26.0956	-4.6806	-1.2843	3.3962
L3	-762.3367	27.106	1.9244	C_1	26.5129	-4.8594	-1.2996	3.5597
L4	-762.3270	26.944	0.9337	C_1	26.3190	-4.8218	-1.2160	3.6057

(LUMO) of the molecules under study. The heats of formation of all isomers under study are enothermic (positive charge). The isomer L3 has the highest total energy and heat of formation values, this mean this isomer (L3) may be the best structure isomer stability among these isomers under study, while the Gibbs energies are unspontaneously reaction in all isomers (positive charge). The greater value of Gibbs energy reaction found in isomer (L3). All isomers have same point group (C_1).

Table-2 also shows the quantum chemical parameters computed for the purpose of analyzing the reactivity of the molecules. The results show that the HOMO of isomers were highest value in L3 isomer, that is mean isomer has more stability compared with other isomers. Therefore theoretically we expect L3 is the chief product among other types. The shape and symmetry of the HOMO and the LUMO (Fig. 1) are important in predicting the reactivity of a molecule as well as predicting the direction of chemical reactions[11]. The analysis of the HOMO indicates the regions of the molecule that have a tendency to donate electrons to electrophilic species (metals), while the analysis of LUMO predicts the regions of molecule with high tendency to accept electrons from nucleophilic species.

The values of the difference between the HOMO and LUMO orbitals, known as energy gap (ΔE)[12,13] are also given in Table-2. The lowest energy gaps values of the isomers is found in L2 (3.3962), this means in any excitation process, that isomer need less energy than others[14]. All isomers under studied have C_1 point group.

Mulliken atomic charges were calculated of two amines in 2,4-diaminophenol and found the first amine at position (C_2) has total charge equal to (-0.828) Mulliken, while the second one at position (C_4) has total charge equal to (-0.821) Mulliken, this mean the first amine prefer reaction with carbonyl more than second one.

Conclusion

In this paper, we synthesized and characterized of Schiff base by reaction of 2,4-diaminophenol dihydrochloride with salicylaldehyde. The FTIR and UV-visible spectra suggest that the isomer have ratio 1:1 (amine-carbonyl) stoichiomtry. DFT based chemical reactivity descriptor analysis has provided valuable information about the reactive sites for various types of attacks and orientations for a selected arylamine. The quantum chemical DFT calculations can be successfully used for the prediction of making more active isomers and hence for the formation of more stable isomer among many types which have same isomers, as it is discussed here for Schiff base isomer. The results show that the amine in the position 2 has more chance to reaction with carbonyl group, therefore we will get only two isomers (L3 and L4) and from these two isomers, isomer L3 has total energy and HOMO (-762.3367, -4.8594) respectively more than the another isomer (L4), therefore we suggested this isomer is the main product.

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