

## Excited State Proton Transfer Process In The 2-hydroxy – N-Salicylidene Schiff Base

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### ABSTRACT

The Excited state reaction coordinates and the consequent energy profiles of a new Schiff Base N-Salicylidene-2-Bromoethylamine (NSBA) have been investigated at the CC2 level of theory. The electron-driven proton transfer and torsional deformation have been identified as the most important photochemical reaction coordinates. The potential energy profiles of the ground and the lowest excited singlet state are calculated. In contrast to the ground state, the excited state potential energy profile shows a barrier-less dissociation pattern along the O–H stretching coordinate which verifies the proton transfer reaction at the S1 ( $\pi\pi^*$ ) state. The calculations indicate S1/S0 conical intersections (CIs) which provide non-adiabatic gates for radiation-less decay to the ground state. At the CI, barrier-free reaction coordinates direct the excited system to the ground state of enol-type minimum. According to calculation results, a trans- keto type structure obtained from photoexcitation of the enol, can be responsible for the photo chromic effect of title compound. Furthermore, our results confirm the suggestion that aromatic Schiff Bases are potential candidates for optically driven molecular switches.

**Keywords:** Schiff Base, Intramolecular Proton Transfer, Photo chromism

## 1. Introduction

From the beginning of the 21st century, the research for molecular switches based on light-induced conformational changes has been a hot topic. Schiff Base molecules represent a class of advanced materials widely employed in photonic and optoelectronic applications [1–5]. Many of these belong to the family of photo- (PC) or thermo- chromic (TC) materials—that is, systems that change their color after photo- or thermo irradiation, respectively. It is also well established that the optical properties of Schiff base molecules are related directly to their photochromic nature, which is a reversible reaction between enol and keto forms, giving rise to the reversible photo coloration of a single chemical species between two states. Recently, the photochromic effect of salicyl aldehyde Schiff bases have been the subject of several papers, where it was demonstrated that the excited state intramolecular proton transfer (ESIPT) process after photo excitation is the most crucial step in excited state reaction dynamics of these molecules. Beyond this process, producing a keto structure as a new tautomeric form is responsible for photochromic effect with bathochromically shifted spectra. So far, the ESIPT has attracted massive research interest, both in theory and experiment [6-10].

Usually, ortho-hydroxy Schiff bases display two possible tautomeric forms, the enol-imine and the keto- amine forms. Depending on the tautomers, two types of intramolecular hydrogen bonds can exist in Schiff bases: O—H···N in enol-imine and N—H···O in ketoamine tautomers [11, 12].

## 2. Experimental

### Computational Details

The ab initio calculations have been performed with the TURBOMOLE program package [13, 14]. The Resolution of identity Møller–Plesset perturbation theory to

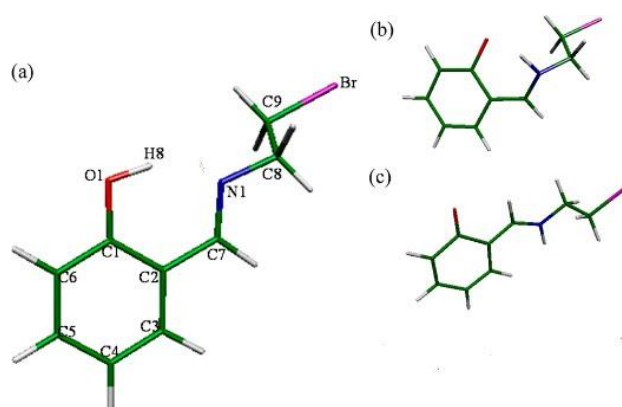
second-order (RI-MP2) [15, 16] calculations were performed to obtain the equilibrium geometry of the titled compound at the ground electronic state. Excitation energies and equilibrium geometry of the lowest excited singlet states have been determined at the resolution-of-identity second-order approximate coupled-cluster (RI-CC2) method. The calculations were performed with the correlation-consistent polarized valence double- $\zeta$  (cc-pVDZ) basis set.

### 3. Results and discussion

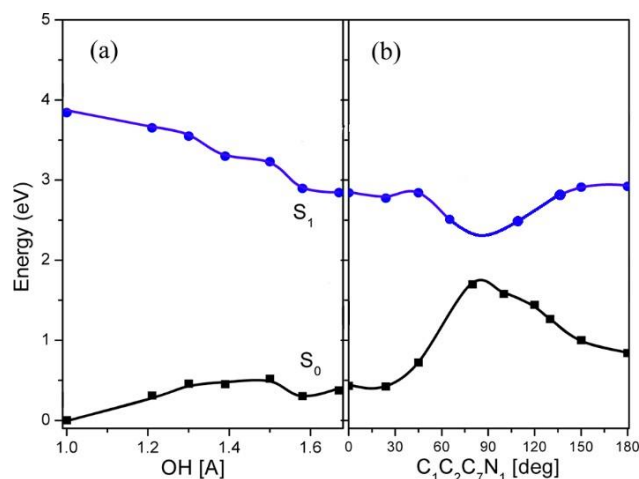
The first step of this work is looking for the most stable structure of title compound. The most stable structure in ground state ( $S_0$ ) at the MP2/cc-pVDZ level of theory is enol form (E). While the excited state proton transfer (ESPT) is mainly achieved after the  $S_1$  geometry optimization of the E form at the CC2 level as keto form (K), (see Fig. 1). The potential energy profiles calculated along the minimum energy paths (MEP) for hydrogen (or proton) transfer of the enol form of NSBA together with torsion of the ethylamine group ( $C_1-C_2-C_7-N_1$  dihedral angle) in the keto structure of NSBA in the  $S_0$  and  $S_1$  states are shown in Figure .2a, b. As shown, in the ground state, the local minimum is in the enol side, whereas in the  $S_1$ , the minimum is in the keto side. The minimum energetic level of the  $S_1$  state along the PT coordinate lies in the short distance to the long distance of OH, which corresponds to the new bond formation of H-N. In the ground state, the enol-keto transformation is not favored by considering the energy changes, but in the  $S_1$  state, the PES does not show a barrier, and this transformation will be favored by decreasing the internal energy of the system along the enol-keto transformation. Transfer of a proton between the oxygen and nitrogen atoms in the initial  $S_1$  state of enol leads to create the keto in its  $\pi\pi^*$  state. At this minimum, the  $S_0/S_1$  potential energy profiles touch each other and obtain new way to return enol form. Namely reversible structural

change along with spectral shift. This result indicates that the photochromism of certain ES IPT systems. The characteristic features of such systems are strong and broad absorption in the UV/vis range, and very fast radiation-less return to the ground state.

The  $S_0$  curve in Figure 2a exhibits a barrier for protontransfer in the  $S_0$  state of NSBA ( $E = 0.45$  eV), while the energy profile of the  $S_1$  state calculated along the  $S_1$  reaction path in Figure 2a indicates a barrierless reaction coordinate for proton transfer from oxygen toward the nitrogen atom. It verifies that spontaneous hydrogen transfer takes place, resulting in the formation of keto tautomer on the excited state potential energy surface. The keto-type  $S_1$  structure is estimated to lie 2.84 eV (CC2 result) above the global minimum of the ground state.



**Fig 1:** Optimized geometries and numbering pattern: (a) the most stable configuration of the enol form of NSBA (calculated at the MP2/cc-pVDZ level of theory); (b) the  $S_1$  optimized structure of cis-keto form of NSBA (determined at the CC2/cc-pVDZ geometry optimization of the E form); (c) the optimized geometry structure of trans-keto form of NSBA obtained at the MP2/cc-pVDZ level of theory.



**Fig 2:** Potential energy curves of the S0 state (squares) and the S1( $\pi\pi^*$ ) state (circles), as the functions of hydrogen transfer reaction path in the enol form of NSBA (a) and torsional reaction path in the keto form of NSBA (b). The energy origin is the energy of minimum enol in the ground state.

### ***Electronic Properties:***

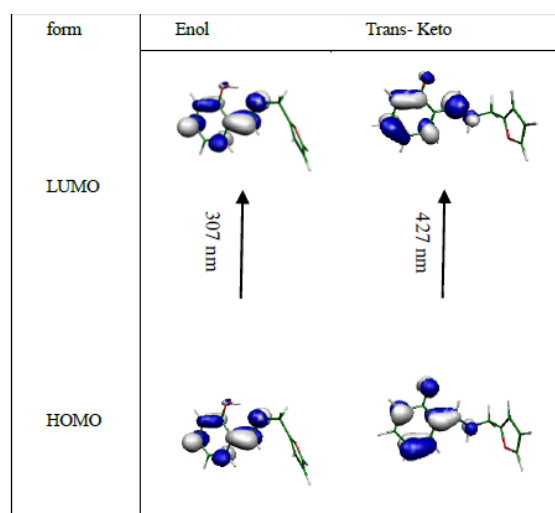
The vertical electronic transition energies of the most stable enol and keto forms of NSBA are presented in Table 1. The vertical excitation energy at the CC2/cc- pVDZ level on the S0 geometry of the E identifies two strong electronic transitions: The S1–S0 transition at 4.03 eV (307.7 nm) can be described as the  $\pi\pi^*$  (H–L) excitation, (H and L indicate to HOMO and LUMO, respectively). The oscillator strength of this transition is 0.125. The S3–S0 lies at 5.09 eV (243 nm) with the oscillator strength of 0.255, and can be described as the  $\pi\pi^*$  state.

The vertical excitation energies at the same level of theory on the MP2 ground state optimized geometry of trans-keto tautomer indicate two strong electronic transitions; the S2–S0 transition at the 3.07 eV (404.56 nm) can be described as the  $\pi\pi^*$  (H–L) excitation (see Table 1). The oscillator strength of this transition is 0.320. The S4–S0 transition also lies at 4.62 eV (268.8 nm) with the oscillator strength of 0.17 and can be described as the  $\pi\sigma^*$  since there is one electron excitation of H–(L+1).

Enol			Trans-Keto		
Transition	eV	f	Transition	eV	f
S1 ( $\pi\pi^*$ )	4.03	0.125	S1 ( $n\pi^*$ )	2.9	0.002
S2 ( $n\pi^*$ )	4.95	0.001	S2 ( $\pi\pi^*$ )	3.07	0.32
S3 ( $\pi\pi^*$ )	5.09	0.255	S3 ( $\pi\pi^*$ )	4.37	0.006
S4 ( $\pi\pi^*$ )	5.51	0.004	S4 ( $\pi\pi^*$ )	4.62	0.172

**Table 1.** Vertical Energy Gap (eV) and Oscillator Strength (f) of the E and trans-Keto Rotamers

The vertical electronic transition energies and molecular orbitals of the most stable enol and keto forms of NSBA are presented in Table 2. Calculations shows about 120 nm shift along the intramolecular proton transfer.



**Table 2.** Molecular Orbital and transition wavelength (S1–S0)

## 4. Conclusions

The computational results of the present work suggest the following features of the photophysics of NSBA. This molecule is transparent to visible radiation but strongly absorbent for UV radiation. The primary UV- induced reaction is proton transfer from the hydroxyl group to the imine group. This reaction is predicted to be essentially barrierless and thus extremely fast. The system switches from the S1 surface to the S0 surface via a non-adiabatic transition. It is thus possible that the global minimum structure of NSBA is restored with a probability very close to unity, which is a requirement for the function of SBEA as an effective photo stabilizer.

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