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Photo switching of Salicylidene methyl Furyl amine: A Theoretical Photo dynamics Study

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ABSTRACT

Potential energy surfaces (PES) for the ground and excited state intramolecular proton transfer (ESIPT) processes in N-salicilydene methyl furylamine(SMFA)have been studied usingCC2 level of theory. Our calculations suggest thenon-viability of ground state intramolecular proton transfer. Excited states PES calculations support the existence of ESIPT process in SMFA.The calculated results show that the intramolecular hydrogen bond were formed in the S0 state, and upon excitation, the intramolecular hydrogen bonds between - OH group and nitrogen atom would be strengthened in the S1 state, which can facilitate the proton transfer process effectively. The calculations indicate two S1/S0 conical intersections (CIs) which provide radiation-less decay to the ground state. At the CIs, two barrier-free reaction coordinates direct the excited system to the ground state of enol-type minimum.The keto-type S1 state attained by barrier less proton transfer is found to be unstable via a torsional motion, which provides fast access to a S1−S0 conical intersections. From the conical intersection, a barrier less reaction path directs the system back to the enol-type minimum of the S0 potential energy surface, thus closing the photocycle.

Keywords: Schiff Base, Intramolecular Proton Transfer, Photo chromism

1. Introduction

Excited-state reactions play important roles in the electronic properties of materials and biological systems, including their photo induced functions. Aromatic Schiff bases and their metal complexes have recently attracted considerable attention because of their interesting and important properties such as biological activities,chemodosimeter, molecular tweezers, photochemical behavior, ionophores, catalytic activities, and pH- responsive [1-6].Aromatic Schiff bases belong to a broad family of molecular systems whose photo physics is determined by the excited state intramolecular proton-transfer (ESIPT) reaction. Photochromic Schiff bases represent a special group of ESIPT systems, whose depopulation routes of the excited molecule are particularly complex. Besides the PT reaction cycle, returning the system to its original state through the back-PT, a large portion of molecules may be trapped in the ground state as metastable photochromic species. The photochromic and tautomerism features make extensive applications for Schiff bases in the laser dyes, molecular switches, nonlinear optical properties, and molecular electronic devices. The search for molecular switches based on light-induced conformational changes prompted by the ESIPT reaction is drawing special attention [10-12] since the theoretical proposition of a long- distance intramolecular hydrogen-atom transfer due to this phenomenon. According to significances of proton transfer and tautomer's processes in Schiff bases, so far, they have been the subject of numerous studies [11-15].

2. Experimental

Computational Details

With the TURBOMOLE program package [16, 17]. The Resolution of identity Møller−Plesset perturbation the oryto second-order(RI-MP2) [18,19] 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) [20, 21] method. The calculations were performed with the correlation-consistent polarized valence double-ζ (cc-pVDZ) basis set [17].

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 (S0) at the MP2/cc-pVDZ level of theory is enol form (E). While the excited state proton transfer (ESPT) is mainly achieved after the S1 geometry optimization of the E form at the CC2 level as keto form (K),(see Fig. 1). The minimum potential energy (MPE) profiles of E in the S0 state and in the lowest excited ππ* state, determined along the PT (OH distance) and along the torsion of the ethyl-furyl group (dihedral angle of θ (C2–C7–N1–C8)) and of the methylamine group (dihedral angle of θ(C1–C2– C7–N1)) are shown in Fig. 3.

The middle panel of Fig. 3, illustrates that the enol form isa typical excited-state intramolecular proton transfer (ESIPT) system. The minimum energy profiles were obtained by optimization of molecular geometry for fixed values of the reaction coordinate for ground and excited states, performed respectively at the MP2/cc-pVDZ or CC2/cc-pVDZ level of theory. The results showed that after optical excitation of E to the first excited singlet state (ππ*), a spontaneous (barrier-free) PT reaction occurs. Although the C2–C7 bond is a single bond in the enol form after the proton transfer, it changes into a double bond of cis-enol form. Considering the MPE curve of the ground state in Fig.

3(b), the enol–keto transformation is not favored any more in the ground state, while in the S1 (ππ*) 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. It verifies that spontaneous hydrogen transfer takes place on the S1 (ππ*) state, resulting in the formation of the keto tautomer on the excited state potential energy surface. The keto- type S1 structure is estimated to lie 2.80 eV (CC2 result) above the global minimum of the ground state (see Fig. 3(b)).calculations for PT systems shows that the torsion of the proton-accepting group relative to the proton donating group plays an essential role for the effective quenching of the electronic excitation in these systems. Although we didn’t find a ground state minimum for the case of cis-keto structure of SMFA.A barrier-less PE profile of the S1 (ππ*) state in the direction of the PT reaction and the small mass of the proton leads to the conclusion that the photo physics of SMFA is dominated by the ESIPT reaction which eventually may result in the formation of the photochromic trans-keto form. However, the reaction pathway leading to the CI-2, is also barrier-less and it plays an essential role in the photo chemical behavior of SMFA after excitation. Internal conversions through these CIs, from both sides of Fig. 3, populate the ground state of SMFA at the conformations near to CI1 and CI2.However, the reaction pathway leading to the CI2, is also barrier-less and it plays an essential role in the photochemical behavior of SMFA after excitation. Since a large steric hindrance exists when θ> 95, we didn’t find a local minimum for the ground state along with this reaction coordinate. Therefore, this reaction coordinate should only act as a radiation-less deactivation pathway of the S1 (ππ*) state to the ground state via the CI2.

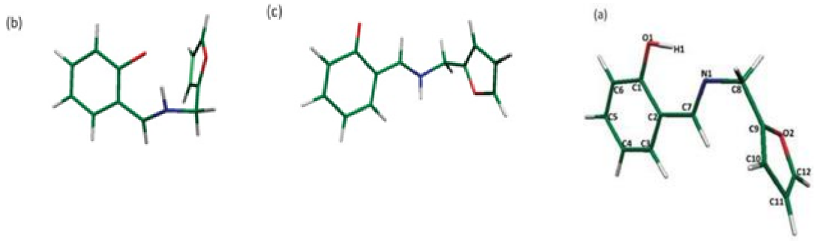

Fig.1: Optimized geometries and numbering pattern: (a) the most stable configuration of the enol formof SMFA (calculated at the MP2/cc-pVDZ level of theory); (b) the S1 optimized structure of cis-keto form of SMFA (determined at the CC2/cc-pVDZ geometryoptimization of the E form); (c) the optimized geometry structure of trans-keto form of SMFA obtained at the MP2/cc-pVDZ level of theory

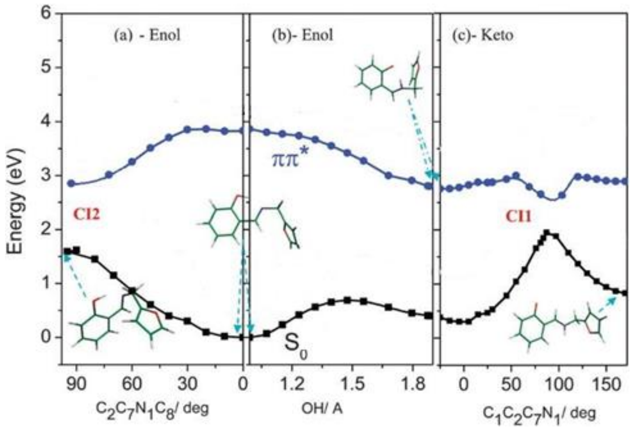

Fig.2: Potential energy curves of the S0 state (squares) and the S1($\pi\pi$*) state (circles), as the functions the torsional reaction path (a and c) and the hydrogen transferreaction path (b. The energy origin is the energy of minimum enol in the ground state.

Electronic Properties:

The vertical excitation energy at the CC2 level using cc-pVDZ basis sets on the S0 geometry of most stable enol form (E) and also trans- keto tautomer (K) are presented inTable1.Thevertical excitation energy at the CC2/cc-pVDZ level on theS0 geometry of the E identifies two strong electronic transitions: The S1−S0 transition at 4.19eV (295.7 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 0.118. The S3−S0 lies at 5.39eV (230 nm) with the oscillator strength of 0.181, 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 3.28eV (378 nm) can be described as the ππ* (H−L) excitation (see Table 1).The oscillator strength of this transition is 0.3. The S4−S0 transition also lies at 5.6eV (221 nm) with the oscillator strength of 0.155 with electron excitation of H−(L+1).

The vertical electronic transition energies and molecular orbitals of the most stable enol and keto forms of SMFA are presented in Table 2. Calculations shows about 80 nm shift along the intramolecular proton transfer and Trans-keto formation.

Enol			**Trans-Keto**		
Transition	eV	f	Transition	eV	f
S1 (ππ*)	4.19	0.1180	S1 (nπ*)	3.03	0.0034
S2 (nπ*)	5.09	0.0010	S2 (ππ*)	3.28	0.3004
S3 (ππ*)	5.39	0.1810	S3 (ππ*)	4.88	0.0050
S4 (ππ*)	6.07	0.0040	S4 (ππ*)	5.6	0.1552

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

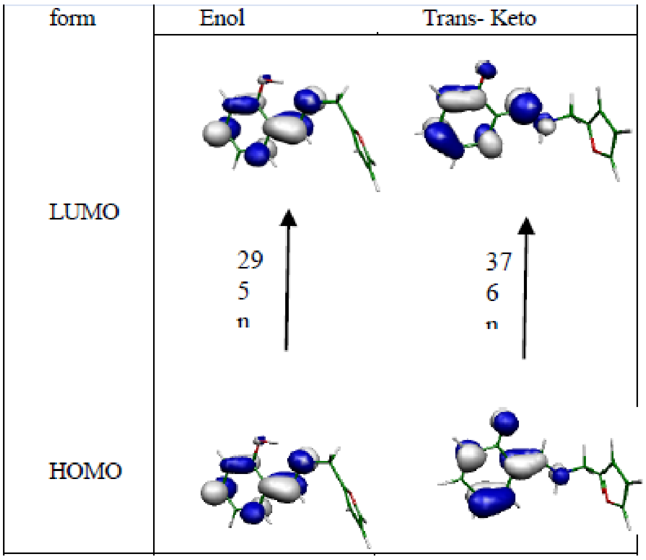

Table 2. Molecular orbital and transition wavelength (S1-S0)

4. Conclusions

The proton transfer is the main character of SMFA at the excited state. In contrast to the ground state, the PT process is significantly exoergic in the excited state. From the barrier less potential energy curve of the enol form at the excited state, one can conclude the fast dynamics for such ESIPT. The calculations indicate that the trans-keto form produced by UV excitation of enol form is a strong UV/vis absorber and should be highly photo stable. Upon strong UV irradiation, a significant concentration of the trans-keto form of SMFA can be produced. This form absorbs strongly in the visible range of the spectrum. The ground state of the trans-keto form is metastable (0.84eV). The thermal back reaction from trans-keto to the more stable E has to overcome a barrier of about 1.1 eV and is therefore expected to be rather slow. Thus, UV irradiation of SMFA may result in a mixture of enol and its photoproduct.

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