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REGULAR ARTICLE

A DFT/TDDFT Investigation of Excited-State Intramolecular Proton Transfer Mechanism of New Chromophore

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Abstract: Based on the time-dependent density functional theory (TDDFT), the excited state intramolecular proton transfer (ESIPT) mechanism of a new compound **3** chromophore synthesized and designed by Mukherjee *et al*. [Sensors and Actuators B: Chemical, 202 (2014), 1190-1199] has been investigated theoretically. The calculations of primary bond lengths, angles, the IR vibrational spectra and hydrogen bond energies between the S_0 state and the S_1 state vertified the intramolecular hydrogen bond was strengthened. The fact that reproduced the experimental absorbance and fluorescence emission spectra well theoretically demonstrates that the TDDFT theory we adopted is reasonable and effective. In addition, intramolecular charge transfer based on the frontier molecular orbitals demonstrated the indication of the ESIPT reaction. The constructed potential energy curves of ground state and the first excited state based on keeping the O-H distance fixed at a series of values have been used to illustrate the ESIPT process. A little barrier of 3.934 kcal/mol in the S_1 state potential energy curve (lower than that of 8.254 kcal/mol in the S_0 state) provided the transfer mechanism.

AMS subject classifications: 78M50, 74E40, 65D18

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1. Introduction

The hydrogen bond, as one of the most significant weak interactions, is omnipresent in nature, based on which life-cycle can be sustained in the world [1-5]. It plays important roles in crystal packing of many organic and organometallic molecules, stabilization of the secondary structure of biomolecules like proteins, nucleic acids and so forth [1-5]. In addition, a dual effect has been found in biological systems: on one hand, in the form of a collectively strong directional interaction it leads to stable supramolecular architectures which are inevitable for the construction of fundamental building blocks of life, and on the other hand, by virtue of its dynamic features, it serves as an active site for the occurrence of a vista of interactions [6]. Therefore, a thorough investigation of the interaction will be vital to delve into the critical evaluation of many phenomenon taking place not only in the crystal state, but also in solutions and living organisms [7-9]. Particularly, Han and co-workers have determined that intermolecular hydrogen bonds between solute and solvent molecules should be significantly strengthened in the electronic excited states after photo-excitation theoretically [10-18], since then, many investigations of mechanism respecting exited state hydrogen bonding need to be revisited in physics, chemistry and biology. Proton transfer (PT), as one fundamental class of photochemistry, has attracted more and more attentions along hydrogen bonding in recent years [15-33]. Especially, the excited state intramolecular proton transfer (ESIPT) reactions have been drawing great attention due to their unique photophysical and photochemical properties which facilitate novel optoelectronic applications such as fluorescence sensors, laser dyes and LEDs, UV filters, molecular switches and so forth [34-46]. Naturally, the attention focused on this phenomenon is both cognitive and applied, through which it crops up as a demanding subject of research even today.

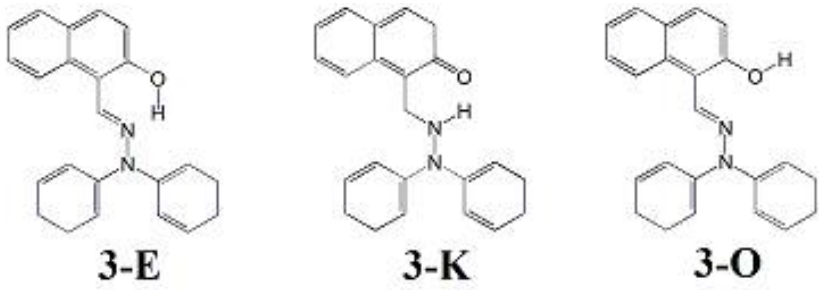

Figure 1: The structures of **3-E**, **3-K** and **3-O** at B3LYP/ TZVP theoretical level.

Recently, Mukherjee et al. reported a series of aromatic hydrazones (named **1**, **2**, **3** and **4**) that were synthesized and characterized based on the 2-hydrozy-1-naphthaldehyde and salicylaldehyde [47]. Based on these structures, fluoride anion fluorescence sensor in the aprotic polar solvent DMSO has been studied based on experiment [47]. However, the investigation about mechanism is very limited due to spectroscopic techniques, which can only provide indirect information about photo-physical properties, such as steady-state absorption spectroscopy, fluorescence spectroscopy, the time resolved fluorescence spectroscopy and so on. In fact, there are some questionable points worth investigating deeply. Therefore, in the present work, **3** chromophore, as a representative, is selected to investigate theoretically both the S_0 and the S_1 state relevant to the transfer mechanism based on the DFT and the TDDFT method in detail. The structures of **3-E** (3-enol form), **3-K** (3-keto form) and **3-O** (the non-hydrogen bonded **3** form) are shown in **Figure 1**.The configurations of S_0 state and S_1 state were optimized, and further vertical excitation energies, IR vibration spectra, the frontier molecular orbitals and homologous S_0, S_1 and S_2 states potential energy curces were calculated and analyzed to provide the direct information of the ESIPT process

2. Computational Details

All electronic structure calculations were carried out based on the Gaussian 09 program suite [48]. The geometric optimization of **3** was performed in the ground-state using DFT and in the electronic excited-state using TDDFT. The TDDFT method has become a very useful tool to theoretically investigate the hydrogen bonding interaction that occurs in the excited-state of hydrogen-bonded systems [11-18, 38-46]. Becke's three-parameter hybrid

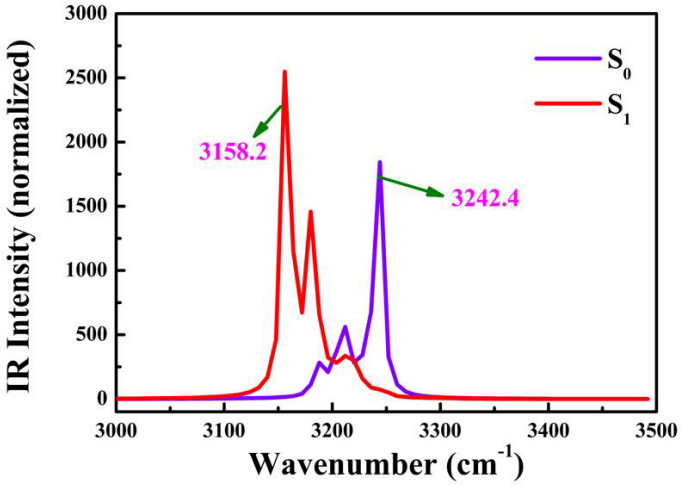

Figure 2: The calculated IR spectra of **3-E** structure in DMSO solvent at the spectral region of O-H stretching band at B3LYP/TZVP theoretical level.

exchange functional with Lee–Yang–Parr gradient-corrected correlation (B3LYP functional) was used in both the DFT and TD-DFT methods [49–51]. The triple-ζ valence quality with one set of polarization functions (TZVP) was chosen as the basis set throughout, which is an appropriate basis set for the system. No constrains for symmetry, bonds, angles or dihedral angles were applied in the geometric optimization calculations.

To evaluate the solvent effects, DMSO was selected as the solvent in the calculations dependent on the polarizable continuum model (PCM) using the integral equation formalism variant (IEFPCM). All the local minima were confirmed by the absence of an imaginary mode in the vibrational analysis calculations. The S_0, S_1 and S_2 potential energy curves have been scanned using constrained optimizations in their corresponding electronic states and keeping the O–H bond distance fixed at a series of values. Fine quadrature grids 4 were also employed. Harmonic vibrational frequencies in both the ground-state and excited-state were determined using diagonalization of the Hessian [52]. The excited-state Hessian was obtained by numerical differentiation of the analytical gradients using central differences and default displacements of 0.02 Bohr [53]. The infrared intensities were determined using the gradients of the dipole moment.

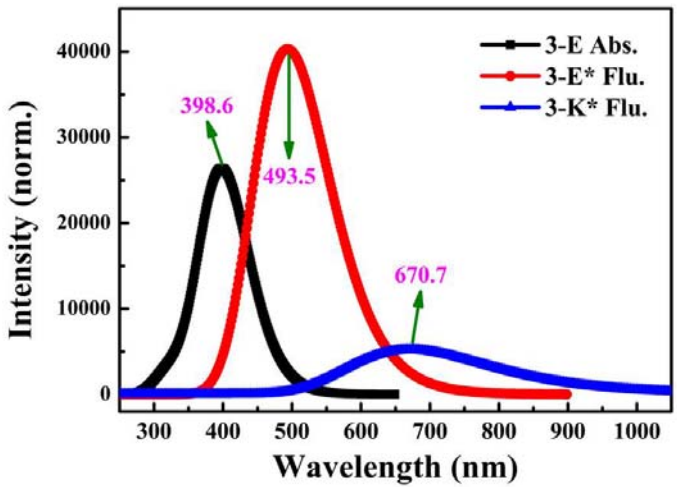

Figure 3: The calculated electronic spectra of **3-E** and **3-K** in DMSO solvent at TDDFT/B3LYP/TZVP level.

3. Results and discussion

3.1 Geometric structures

The ground-state and excited-state structures of the **3-E**, **3-K** and **3-O** were obtained based on the B3LYP function with the TZVP basis set and a subsequent vibrational frequency analysis to ensure the validity of the stationary points. To consider the solvent effects, DMSO

has been selected as the reaction solvent in the IEFPCM model. The most important structural parameters have been listed in **Table 1**. Especially, the bond length of O-H of the **3-O** structure was calculated to be 0.972 Å, however, it changed to be 0.994 Å in **3-E** form, which indicates the formation of hydrogen bond O-H···N in the S_0 state. In addition, it should be noted that the elongation of the O-H bond from 0.994 Å in the S_0 state to 0.998 Å in the S_1 state, and the shorting of N···H bond from 1.735 Å to 1.710 Å with the concomitant enlargement of O-H···N angle from 146.2º to 147.5º following the photo-excitation. And we also found that the N-N bond is elongated from 1.365 (S_0 state) to 1.373 (S_1 state) Å and the N-C bond is elongated from 1.301 to 1.368 Å, respectively. Based on these calculated results, the intramolecular hydrogen bond O-H···N is strengthened in the S_1 state. Furthermore, the hydrogen bond strengthening or weakening could also be revealed based on monitoring the spectral shifts of vibrational modes involved in the formation of hydrogen bonds [11-18, 38-46]. The vibrational spectra of **3** chromophore in the conjunct vibrational regions of the O-H stretching modes have been shown in **Figure 2**. It should be noted that the calculated O-H stretching vibrational frequency is located at 3242.4 cm^{-1} in the S_0 state, whereas it is located at 3158.2 cm^{-1} in the S_1 state. The about 84.2 cm^{-1} red-shift of O-H stretching frequency demonstrates intramolecular hydrogen bonds O-H···N was strengthened in the S_1 state. The strong and intuitional evidence, the hydrogen bond energy, has also been provided based on the method that the energy of **3-E** form minus the energy of **3-O** form. The calculated results demonstrates that the hydrogen bond energy is 8.52 kcal/mol in the S_0 state and 12.29 kcal/mol in the S_1 state, which further indicates the intramolecular hydrogen bond is strengthened. Therefore, the conclusion of strengthened hydrogen bond in the S_1 state may be a tendency of the ESIPT process.

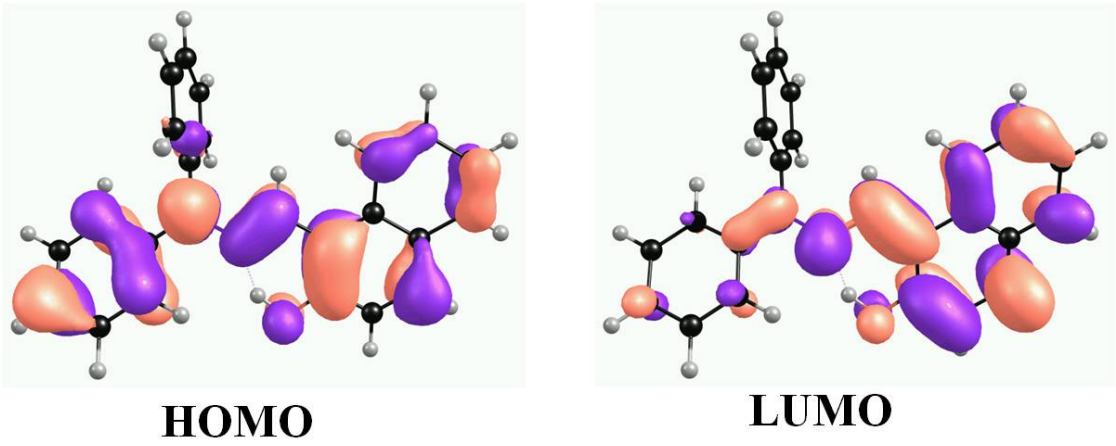

Figure 4: The calculated frontier molecular orbitals HOMO and LUMO for **3-E** chromophore based on TDDFT/B3LYP/TZVP theoretical level.

3.2 Electronic spectra and Frontier molecular orbitals (MOs)

Even though the experimental spectral characteristics of **3-E** have been reported in the previous work [47], the investigations based on the theoretical calculations are limited declaring the ambiguous mechanism still exists. The calculated absorption and fluorescence spectra of **3-E** and **3-K** are shown in **Figure 3**. To clearly visualize the shape of the spectra, we have shown the calculated absorption and fluorescence spectra in the range of λ = 250–1050 nm. The S_0–S_1 vertical excitation energy of the **3-E** was determined on the basis of the TDDFT calculations using the ground-state optimized geometric conformations. The strong absorption for the isolated **3-E** is clearly peaked at λ = 398.6 nm, which is consistent with the experimental value (about 375 nm) [47]. The S_1 state of the **3-E** form was fully optimized based on the TD-DFT method. In view of the excite state, there are two outcomes: i) the **3-E*** tautomer and ii) the **3-K*** tautomer, respectively. As can be seen from **Figure 3**, the theoretical result of the **3-E*** tautomer shows a normal Stokes shifted emission maximum at λ = 493.5 nm, which is also consistent with the experimental value [47]. In the case of the geometry-relaxed **3-K***, a large Stokes shift upon emissive relaxation can be found at λ = 670.7 nm, which is in good agreement with the experimental value [47]. The agreement with the experimental values justifies that the validity of our calculated methods can explain the excited-state properties of **3-E** chromophore well.

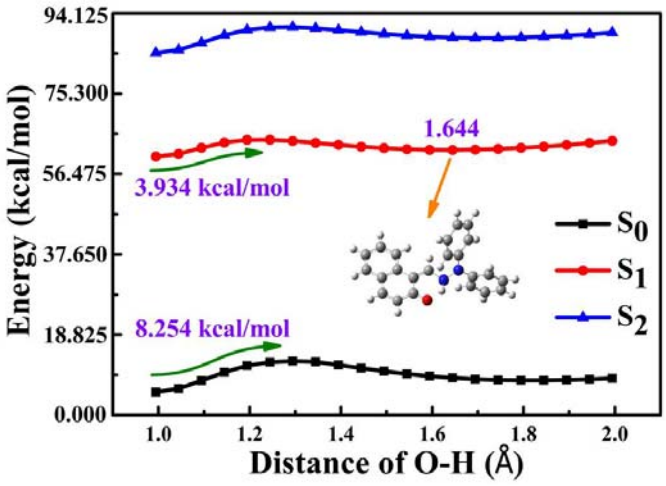

Figure 5: Potential energy curves of S_0, S_1 and S_2 states for **3-E** chromophore along with O-H bond length.

In fact, the phenomenon of ESIPT is percussion of the substantial adjustment of electronic charge density distribution on the heavy atoms induced by photo-excitation. The detailed investigation of the charge distribution over the atoms involved in intra- or inter-

molecular hydrogen bond can be used as a reasonable evidence to explore the proton transfer reaction based on the Mulliken's charge distribution analysis method. The one should be noted that the decrease of negative charge distributionon about O atom of the –OH moiety from -0.702 in the S_0 state to -0.666 in the S_1 state together with the increase on the N atom from -0.317 to -0.337 based on the B3LYP/TZVP theoretical level. Therefore, the ESIPT process can be predicted based on the above discussion. In order to qualitatively discuss the charge distribution and charge transfer, the frontier MOs of **3-E** are presented in **Figure 4**. Herein, we only show the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), since the S_1 state is only associated with these orbitals (see **Table 2**). Clearly, the S_1 state is a dominant $\pi\pi^*$-type transition from HOMO to LUMO due to the π character for the HOMO as well as the π^* character for LUMO. The one should be noted that the HOMO and LUMO are localized on different parts. Especially, the part involved in the intramolecular hydrogen bond O-H···N, the electron density of the hydroxide radical moiety changes after the transition from HOMO to LUMO. One can note that, the hydroxyl moiety and nitrogen atom make larger and little contribution to the HOMO, but these contributions are greatly decreases and increased, respectively, upon transition from the HOMO to the LUMO. That is to say, the first excited state involves the intramolecular charge transfer, and the change of electron density in the hydroxide radical moiety can directly influence the intramolecular hydrogen bonding O-H····O. As a consequence, the H····O bond length could be shorted upon excitation to the first excited state. So the ESIPT process could happen due to the intramolecular charge transfer.

Table 1. The calculated primary bond lengths (Å) and angles (º) of **3-E**, **3-K** and **3-O** forms in the S_0 and S_1 states based on the DFT and TDDFT methods, respectively.

	3-E		**3-K**		**3-O**	
Electronic state	S_0	S_1	S_0	S_1	S_0	S_1
O-H	0.994	0.998	1.817	1.635	0.972	0.973
N···H	1.735	1.710	1.030	1.059	-	-
δ(O-H···N)	146.2º	147.5º	130.1º	142.7º	-	-

3.3 Potential energy curves

For further understanding the ESIPT process, the potential energy curves of S_0, S_1 and S_2 states have been scanned. The scan was based on the constrained optimizations in their corresponding electronic states and kept the O-H bond distance fixed at a series of values. Although the TDDFT/B3LYP method may not be expected to be sufficiently accurate to surmount the correct ordering of the closely spaced excited-states, previous research has

indicated that this method is reliable as far as the shape of the hydrogen-transfer potential energy curves are concerned [54-56]. The potential energy curves of **3-E** chemosensor are shown in **Figure 5** with the variable parameter of O-H bond length limited from 0.99 to 2.1 Å in step of 0.1 Å. It is notable that the S_1 and S_2 potential energy curves for HBQ do not have any overlap. In addition, the energy of the S_1 state decreases after a low potential barrier 3.934 kcal/mol following the O-H bond length increases until it reaches a stable point at ~1.644 Å, which corresponds to the stable optimized geometry of the S_1 state. The energy of the corresponding S_0 state increases along with the O-H bond length across a barrier about 8.254 kcal/mol from the optimized length of ~0.99 Å. Up to now, our calculated results can successfully interpret the ESIPT process of HBQ, which is more likely to be happened in the S_1 state. And the mechanism of the ESIPT process can be described as: in the S_1 state, the N atom can capture the proton of the hydroxyl group solidly, subsequently, the ESIPT reaction takes place with the hydroxyl group acting as a proton donor and the neighboring N atom acting as a proton acceptor forming 3-K*. Subsequently, the **3-K*** decays to the ground state **3-K** form through radiating fluorescence.

Table 2. Electronic excitation energy (nm), corresponding oscillator strengths and the corresponding compositions of the low-lying singlet excited states for **3-E** chemosensor.

	Transition	λ(nm)	f	Composition	CI (%)
3-E	$S_0 \rightarrow S_1$	398.6	0.6453	H → L	98.46%
	$S_0 \rightarrow S_2$	336.7	0.0329	H →L+1	93.26%
				H → L+2	4.28%

4. Conclusion

In summary, we have investigated the ESIPT reaction mechanism of **3-E** chemosensor through calculating the geometries, photo-physical properties and the potential energy curves based on DFT and TDDFT methods. The absorption and fluorescence spectra are well represented by the vertical transition energies calculated using the optimized geometries of the S_0 and S_1 states. For our qualitative discussion on the charge distribution and charge transfer, the corresponding frontier MOs has been analyzed. The results have shown that the ESIPT process can occur via the intramolecular charge transfer process. Detailed analysis of these curves shows that the spontaneous ESIPT reaction can take place in the S_1 state easier than in the S_0 state with proton transfer from the O atom to the N atom.

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