Journal of Atomic and Molecular Sciences

Global Science Press

ISSN 2075-1303

Received Oct. 26, 2017,
Accepted Dec. 08, 2017,

DOI: 10.4208/jams.102617.120817a

http://www.global-sci.org/jams/

Excited state process of a novel NIR-BODI molecule in toluene and acetonitrile solvents: A theoretical study

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Abstract. In this work, using DFT and TDDFT methods, we investigated the excited-state intramolecular proton transfer (ESIPT) mechanism of a novel NIR-BODI system [*Org Biomol Chem* **15**:4072, 2017.] in both toluene and acetonitrile (CH_3CN) solvents theoretically. Comparing the prime structural variations of NIR-BODI involved in the intramolecular hydrogen bond, we can conclude that O-H···N should be strengthened in the S_1 state, which may facilitate the ESIPT process. Concomitantly, infrared vibrational spectra analysis further verify the stability of hydrogen bond. In good agreement with previous experimental results, NIR-BODI reveals two kinds of excited-state structures (NIR-BODI-enol* and NIR-BODI-keto*). Analysis about charge redistribution reveals the tendency of ESIPT process. Our scanned potential energy curves according to variational O-H coordinate demonstrates that the proton transfer process should be more likely to occur in the S_1 state due to the inappreciable potential energy barriers. In addition, due to the minute differences of potential energy curves contrasting toluene (the NIR-BODI-keto could be not located) and CH_3CN (the NIR-BODI-keto can be located) solvents in S_0 state, we deem that solvent effect could play roles NIR-BODI system. Given the S_1-state potential energy barriers, we confirm that the ESIPT process is easier in CH_3CN solvent.

1. Introduction

It is well known that hydrogen bonding plays important roles in many biological and chemical fields [1-4]. Based on the excitation of hydrogen-bonded systems, reorganizations of hydrogen acceptor and donor parts are inevitable due to the primary differences in charge distribution of different electronic states, which could lead to various photochemical and photophysical processes in the excited states [5-9]. Proton transfer (PT) reaction, as one of the most fundamental reactions interrelated with hydrogen bonding, exists in most biological systems such as RNA, DNA, protein environment, and so forth [10, 11]. PT processes have been investigated and explained broadly in the S_0 state, while we focus on the excited state proton transfer (ESPT) reaction, since broad scale applications about ESPT compounds have already become the hot topic via development of novel materials for chemical sensing [12-14], bio-sensing [15, 16], celling imaging [17], white light LED [18-20], and so on.

In general, the excited state intra- or inter- molecular proton transfer (ESIPT) starting from the ground state enol form and returning back to the same state after a so-called “four-level reaction cycle” is reversible [21-25]. Within the frame of ESIPT process, the S_0-state enol could be excited to the excited-state enol*. This form convers into the excited photoproduct (i.e. so-called photo-tautomer keto*), then by the translocation of proton and hence the alteration of the electronic structure. Keto* cold be recognized by the emission spectrum strongly shifted to longer wavelengths. Then the relaxation of keto* results in the S_0-state keto that undergo the reversed proton transfer with the recovery of enol structure to finish the reaction cycle. Experimentally, the fluorescence band of the initial enol* could exhibit a normal Stokes Shift (i.e. the difference between absorption and emission peaks of the enol structure). While the keto* could emit another fluorescence with longer wavelength. Basically, this kind of large Stokes Shift observed in experiment might be as large as 6000 ~ 12000 cm^{-1}.

It is known that the near-infrared (NIR) light could provide the advantages of minimum photodamage to biological samples, decreased interference from the background autofluorescence and deep tissue penetration [26]. The fluorescent dyes owning NIR emission are attributive for the construction of fluorescent imaging

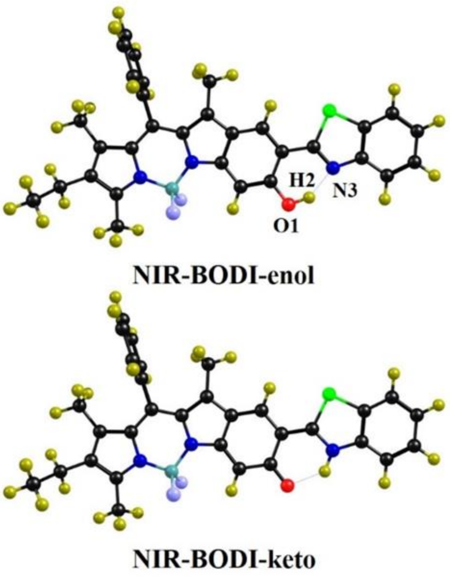

Figure 1: Views of the optimized structures of NIR-BODI-enol and the proton-transfer structure NIR-BODI-keto based on TDDFT/B3LYP/TZVP theoretical level.

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sensors. Recently, Fei *et al*. designed and reported a novel NIR fluorescent dye NIR-BODI (see **Figure 1**) system [27]. The significant chemical feature of NIR-BODI is the pre-existing intramolecular hydrogen bond, which could promote the ESIPT process and introduces the NIR fluorescence. Particularly, the free hydroxyl moiety of NIR-BODI could be readily modified to develop novel fluorescent sensors *in vitro* and *in vivo* applications [27]. However, the theoretical investigations about this novel NIR-BODI system is absent, peculiarly, the specific excited state dynamical process is missing in previous experimental work [27]. Furthermore, it is well known that experiments could only provide the indirect information about the photophysical and photochemical properties. The theoretical study about the novel fluorescent NIR-BODI sensor could further deepen the understanding its applications. Therefore, in-depth investigations about the ESIPT reaction of NIR-BODI is necessary. Given the most common theoretical level, the density functional theory (DFT) and time-dependent density functional theory (TDDFT) methods have been widely used to clarify fundamental aspects about different electronic states. In this present work, we mainly focus on studying the ESIPT mechanism based on DFT and TDDFT methods. Bond lengths and bond angles about the intramolecular hydrogen bond as well as homologous infrared (IR) vibrational spectra have been analyzed in detail. Based on the photoexcitation, the frontier molecular orbitals (MOs) and corresponding Mulliken's as well as NBO charge distribution analysis explore the charge redistribution, which reveals the tendency of ESPT reaction. At last, the constructed S_0 and S_1 states potential energy curves indicate the direct information about NIR-BODI sensor.

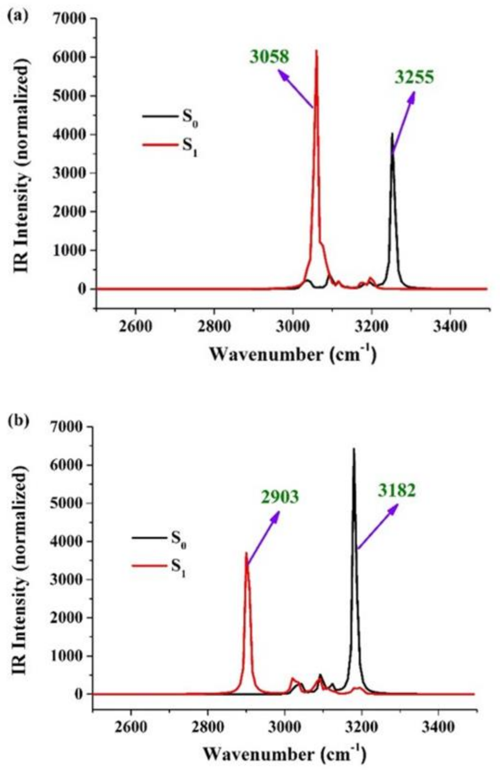

Figure2: The theoretical IR spectra of NIR-BODI-enol structure in both toluene (a) and CH_3CN (b) solvents at the spectral region of corresponding O1-H2 bond in both S_0 and S_1 states.

Our paper is organized such as that the next section describes the details of the Computational Details. Then the Results and Discussion part shows and discusses our theoretical results, and is organized by subsections that consider geometries, electronic spectra, frontier molecular orbitals and the analyses of mechanism. A final section summarizes and provide the conclusions of this present study.

2. Computational Details

In the present work, all the electronic structure calculations have been carried out depending on the Gaussian 09 program suite [28]. The geometric optimizations of the NIR-BODI were performed in the ground state using density functional theory (DFT) method and the electronic excited state was performed depending on time dependent DFT (TDDFT) method, respectively. Becke' three-parameter hybrid exchange functional with Lee-Yang-Parr gradient-corrected correlation (B3LYP functional) was used in both the DFT and TDDFT methods [29-31]. The triple-ζ valence quality with one set of polarization functions (TZVP) was chosen as basis sets throughout, which is an appropriate basis set for this system. There were no constraints to all the atoms, bonds, angles or dihedral angles during the geometric optimization. To evaluate the solvent effect, according to previous experiment [27], toluene and acetonitrile (CH_3CN) were used as solvent in the calculations depending on the model that the Polarizable Continuum Model (PCM) using the integral equation formalism formalism variant (IEFPCM) [32-34]. All the local minima were confirmed by the absence of an imaginary mode in vibrational analysis calculations. The S_0 and S_1 potential energy curves have been scanned by constrained optimizations in their corresponding electronic state, and keeping the O-H distances fixed at a serious of values.

3. Results and discussion

The structures of ground state and the first excited state of NIR-BODI chromophore have been obtained based on B3LYP functional with TZVP basis set level of theory, with a subsequent vibrational frequency analysis to ensure the validity of the stationary points. Both toluene and CH_3CN solvents were used in the IEFPCM model insuring consistency with previous experiment. After optimizations, we found two kinds of configurations of NIR-BODI sensor (i.e., NIR-BODI-enol (the normal NIR-BODI structure) form and NIR-BODI-keto (the proton-transfer NIR-BODI structure) form) in both S_0 and S_1 states (see **Figure 1**). Within the framework of AIM theory (manly based on the analysis of electron density at the specific point (ρ

Table 1: The calculated bond lengths (Å) and angles (º) for NIR-BODI-enol and NIR-BODI-keto forms in S_0 and S_1 states based on the DFT/TDDFT methods with IEFPCM (toluene and CH_3CN), respectively.

	Toluene				CH_3CN			
	NIR-BODI-enol		NIR-BODI-keto		NIR-BODI-enol		NIR-BODI-keto	
	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1
O1-H2	0.990	0.992	-	1.829	0.993	1.009	1.602	1.842
H2-N3	1.732	1.726	-	1.026	1.708	1.650	1.061	1.025
δ(O1-H2-N3)	146.29°	146.89°	-	131.4°	148.18°	148.62°	140.71°	130.85°