Theoretical study of excited-state proton transfer of 2,7-diazaindole·$(H_2O)_2$ cluster via hydrogen bonding dynamics

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ABSTRACT

A new chromophore, 2,7-diazaindole (2,7-DAI), has been designed to surpass the limitation of 7-azaindole (7AI). It exhibits remarkable water catalyzed proton-transfer properties. Excited-state proton transfer (ESPT) has been investigated based on the time-dependent density functional theory method. The calculated vertical excitation energies in the S_0 and S_1 states agree well with the experimental values. Proton transfer couples with hydrogen-bonding dynamics between the 2,7-diazaindole and the surrounding water molecules. Hydrogen bond strengthening has been testified in the S_1 state based on a comparison of primary bond lengths and hydrogen bond energy that is involved in the intermolecular hydrogen bond between the S_0 and S_1 states. Frontier molecular further suggest that the electron density changes between the ground and excited states serve as basic driving forces for proton transfer. We determined the potential-energy curves of the S_0 and S_1 states to characterize the ESPT process. This work explains that the ESPT process for 2,7-DAI·$(H_2O)_2$ clusters at the molecular level, and highlights the importance of hydrogen bonding in ESPT.

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1. Introduction

Excited-state reactions currently have gained increased attention because of their significant role in the electronic properties of material and biological systems [1–7]. Ultrafast hydrogen-bonding dynamics in the excited state are essential in photo-physics, photochemistry and photobiology [8–11], and have been investigated extensively by various experimental and theoretical methods [12–17]. The intermolecular hydrogen bonds are strengthened in the electronic excited states upon photo-excitation as proposed by Han and Zhao [18–24], and may play a significant role in numerous excited-state phenomena, including intramolecular charge transfer, excited-state proton transfer (ESPT) and photo-induced electron transfer [17,25–31]. Proton transfer (PT), another excited-state reaction, is a general hydrogen bonded dynamics in molecules with acidic and basic groups in the excited states, and serves as a fundamental chemical and biological reaction [32]. However, the mechanistic understanding of this process is limited, and includes proton transfer mechanisms in green fluorescent protein (GFP) [33]. Molecular level investigation of the ESPT is highly desirable [32,34–40].

7-azaindole (7AI), comprises both a proton donor (—NH) and a proton acceptor (—N—), can form a hydrogen bonded network upon complexation with protic solvents (H_2O, NH_3 or alcohols, etc.) and has been

investigated widely as an ESPT sensor in different systems. 7AI molecules have only one emission band in the water solvent, which contrasts sharply with the dual emission bands in alcohols. To overcome this limitation, Chou and coworkers [37] designed a 7AI analogue, 2,7-diazaindole (2,7-DAI) (as shown in Fig. 1). They replaced pyrrole with a pyrazole moiety, in which the N(2) atom acts as an efficient electron withdrawing group [41], and increases the N1-H proton acidity without disturbing the geometry. This result is in sharp contrast with the lack of tautomer emissions for 7AI in water. Using 2,7-DAI as a core moiety, they developed a new tryptophan analogue, 2,7-diazatryptophan, which exhibits remarkable water-catalyzed proton-transfer properties and a superior of water-molecule sensing in proteins, so research on 2,7-DAI is very useful. The bridge of solvent molecules (H_2O, NH_3 or alcohols, etc.) that are hydrogen-bonded to each other with two or three components is stable, the more would hinder its ability to deliver proton [42]. We have compared the 2,7-DAI between two H_2O and three H_2O molecules, and think that the 2,7-DAI with two H_2O molecules is ideal choice for studying ESPT dynamics. An investigation of the behavior of the hydrogen-bonded system in the excited state is important to determine the ESPT scenarios for 2,7-DAI·$(H_2O)_2$ cluster. Experiments have reported a water-catalyzed ESPT reaction in the 2,7-DAI·$(H_2O)_2$ cluster, based on steady state absorption and emission spectra [37]. We conducted density functional theory (DFT and TDDFT) calculations to investigate the ESPT of 2,7-DAI·$(H_2O)_2$ cluster, with a focus on hydrogen bond strengthening and weakening, a comparison of hydrogen bond

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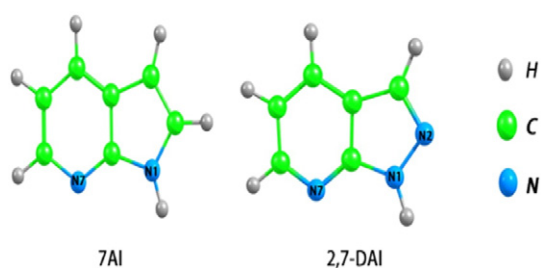
Fig. 1. The geometry comparison of 7AI and 2,7-DAI.

energy, the proton transfer energy barrier in the excited state, and we also simulated electronic spectra for comparison with experimental values. We could explain the ESPT pathway of the 2,7-DAI·(H₂O)₂ cluster.

2. Computational Details

All theoretical calculations have been accomplished based on the Gaussian 09 programs [43]. Geometry optimizations for the S_0 and S_1 states were finished based on the DFT and TDDFT methods with Becke's three-parameter hybrid exchange function, the Lee–Yang–Parr gradient-corrected correlation functional (B3LYP) [44–46] and the triple-ζ valence quality with one set of polarisation functions (TZVP) [47,48]. Considering the solvent effect in previous experimental work [37], water was selected as the reaction solvent in the integral equation formalism variant (IEFPCM) [49–51] model, to mimic the implicit solvent effect. All geometries of the S_0 and S_1 states were optimized without constraining bonds, angles and dihedral angles. The geometric structure of the ground state (S_0) and the excited state (S_1) for 2,7-DAI·(H₂O)₂ cluster have been optimized based on the B3LYP function with TZVP basis set. Vibrational frequency calculations have been used to analyze all the optimized structures to confirm that these structures correspond to the local minima on the S_1 PESs. Calculations of vertical excitation energies were performed from the ground-optimized structures based on the TDDFT methodology with IEFPCM, and our theoretical calculations predicted six low-lying absorbing transitions. The potential energy curves for 2,7-DAI·(H₂O)₂ in the S_1 states have been scanned by constrained optimizations by keeping the related bond lengths fixed at a series of values. Each point in the potential energy curves has been sufficiently optimized. Previous investigations have indicated that TDDFT/B3LYP method is reliable as far as the shape of the hydrogen transfer potential energy curves is concerned [13,54,55].

3. Results and Discussion

3.1. Geometric Structure and Hydrogen Bond Energy

Hydrogen-bonding dynamics may play the indispensible role in the excited-state proton transfer. The hydrogen-bonding induced PT
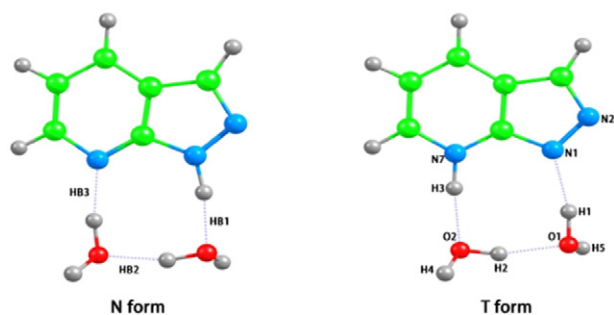

Fig. 2. The optimized geometric structures of N form and T form for 2,7-DAI·(H₂O)₂ cluster in S_1 state, as well as the denotations of hydrogen bonds and some atoms.

Table 1
The calculated bond lengths (Å) and dihedral angles (°) of N and T forms in S_0 and S_1 states. Hydrogen-bonded chain is summation of each hydrogen bond length. $\emptyset_1$ = $N_1C_1N_7C_2$ $\emptyset_2$ = $O_1N_1N_7O_2$.

	N		T
	S_0	S_1	S_1
N_1—H_1	1.028	1.052	1.880
H_1—O_1	1.838	1.685	0.984
O_1—H_2	0.985	0.991	1.782
H_2—O_2	1.776	1.730	0.984
O_2—H_3	0.990	1.001	1.843
H_3—N_7	1.842	1.757	1.028
Hydrogen-bonded chain	8.459	8.216	8.501
$\emptyset_1$	179.98	179.99	179.99
$\emptyset_2$	0.46	0.39	1.10

reaction of the 2,7-DAI·(H₂O)₂ cluster is dominated by the bond length and binding energy of the hydrogen bonds. An investigation of excited-state hydrogen bonding dynamics is the key to understand the PT mechanism. Fig. 2 lists all isomers of 2,7-DAI·(H₂O)₂, where N represents the normal form and T is the proton-transfer tautomer. The corresponding structural parameters involved in the hydrogen bonds are listed in Table 1. All hydrogen bonds of 2,7-DAI·(H₂O)₂ in the S_0 and S_1 states are strengthened upon the photo-excitation, and the length of the hydrogen-bonded chain (the bridge of water molecules that are hydrogen-bonded to 2,7-DAI) was shortened from 8.459 Å in the S_0 state to 8.216 Å in the S_1 state, which facilitates PT proceeding in the S_1 state [52]. When the T form was formed in the S_1 state after PT reaction, the chain length was increased to 8.501 Å, and approximated that of the N form in the S_0 state. The optimized structure of 2,7-DAI·(H₂O)₂ is planar, as indicated by a dihedral angle $\emptyset_1(N_1C_1N_7C_2)$ close to 180° for all complexes (Table 1). The hydrogen-bonded network is also almost planar, as indicated by $\emptyset_2(O_1N_1N_7O_2)$ with absolute values smaller than 1.5°.

The tightness of the hydrogen-bonded chain could facilitate proton transfer [52] of 2,7-DAI·(H₂O)₂, therefore, hydrogen-bonding dynamics in the excited state are important in the PT reaction. However, it is difficult to monitor the binding energies of the hydrogen bonds and the experiment [37] was not designed to elaborate on this point. Hydrogen-bond strengthening or weakening could be revealed by monitoring the stretching vibrations of the functional groups that were involved in hydrogen bonding, i.e., their shift with respect to wavenumber, their intensification, and broadening [18,20,22–24]. Moreover, the formation of hydrogen bonds would lead to a red-shift of stretching bands of functional groups involved in hydrogen bonding [42], which are listed in Table 2. The vibrational spectra of the 2,7-DAI·(H₂O)₂ cluster is shown in Fig. 3. The spectral region of the N_1-H_1, O_1-H_2, and O_2-H_3 stretching bands is red-shifted in the S_1 state compared with that in the S_0 state, which indicates that the strengths of the three intermolecular

Table 2
The stretching vibration (ω) of functional groups involved in hydrogen bonding, the downshifts due to the corresponding hydrogen bond (Δω).

Species	State	Stretching bands	ω (cm^{-1})	ω_{free} (cm^{-1})	$\Delta\omega$ (cm^{-1})
N form	S_0	N_1—H_1	3255	3660[a]	405 (HB1)
		O_1—H_2	3409	3793[c]	384 (HB2)
		O_2—H_3	3290	3793[c]	503 (HB3)
	S_1	N_1—H_1	2885	3572[b]	687 (HB1)
		O_1—H_2	3299	3793[c]	494 (HB2)
		O_2—H_3	3061	3793[c]	732 (HB3)
T form	S_1	H_1—O_1	3385	3793[c]	408 (HB1)
		H_2—O_2	3444	3793[c]	349 (HB2)
		H_3—N_7	3258	3656[d]	398 (HB3)

[a] The stretching vibration frequencies of free N—H of isolated 2,7-DAI (N form) in S_0 state.
[b] The stretching vibration frequencies of free N—H of isolated 2,7-DAI (N form) in S_1 state.
[c] The stretching frequencies of free O—H in grounded H₂O.
[d] The stretching vibration frequencies of free N—H of isolated 2,7-DAI (T form) in S_1 state.