Theoretical Investigation of Excited-State Intramolecular Double-Proton Transfer Mechanism of Substituent Modified 1, 3-Bis (2-pyridylimino)-4,7-dihydroxyisoindole in Dichloromethane Solution

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Research Article

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Abstract

Density functional theory (DFT) and time-dependent DFT (TDDFT) methods were used to investigate substituent effects and excited-state intramolecular double-proton transfer in 1, 3-bis (2-pyridylimino)-4, 7-dihydroxyisoindole (BPI-OH) and its derivatives. The results of a systematic study of the substituent effects of electron-withdrawing groups (F, Cl, and Br) on the adjacent sites of the benzene ring were used to regulate the photophysical properties of the molecules and the dynamics of the proton-transfer process. Geometric structure comparisons and infrared spectroscopic analysis confirmed that strengthening of the intramolecular hydrogen bond in the first excited state (S_1) facilitated proton transfer. Functional analysis of the reduction density gradient confirmed these conclusions. Double-proton transfer in BPI-OH is considered to occur in two steps, i.e., $\text{BPI-OH (N)} \rightarrow \text{BPI-OH (T}_1\text{)} \rightarrow \text{BPI-OH (T}_2\text{)}$, in the ground state (S_0) and the S_1 state. The potential-energy curves for two-step proton transfer were scanned for both the S_0 and S_1 states to clarify the mechanisms and pathways of proton transfer. The stepwise path in which two protons are consecutively transferred has a low energy barrier and is more rational and favorable. This study shows that the presence or absence of coordinating groups, and the type of coordinating group, affect the hydrogen-bond strength. A coordinating group enhances hydrogen-bond formation, i.e., it promotes excited-state intramolecular proton transfer.

1. Introduction

Proton transfer is an essential process in biology and chemistry. It can achieve interactions via formation of specific hydrogen bonds [1, 2]. Photochemical excited-state intramolecular proton transfer (ESIPT) of an enol to the proton-transferred keto isomer is usually accompanied by significant changes in the photophysical properties; this leads to a large Stokes shift [3–7]. Because of its distinct photophysical and photochemical effects, ESIPT has attracted much attention for use in various areas, e.g., white-light-emitting materials [8–10], fluorescence sensors [11], and biological probes [12–17]. Most reported physical processes involve single-proton transfer. However, in biological systems, multi-proton-transfer reactions also occur. For 2,5-bis(benzoxazol-2-yl)thiophene-3,4-diol, which has two proton-transfer sites, competitive mechanisms that involve S_1 state single and double-proton transfers have been proposed [18]. A series of theoretical calculations have indicated stepwise or coordination mechanisms for excited-state intramolecular double-proton transfer (ESIDPT) processes [19–21].

Hydrogen-bonding interactions are typically present in the microscopic frameworks of molecules and supramolecules, e.g., in proteins, DNA, and some polymers [22, 23]. Intramolecular hydrogen bonds are also formed between proton donors and acceptors, and are prerequisites for ESIPT reactions. The theory of excited-state hydrogen-bond strengthening, which was proposed by Han *et al.*, has attracted significant attention in recent years [24–29]. In addition to hydrogen bonding, the substituents on donor and acceptor units, solvent polarity, and pH values of the surrounding media can affect the ESIPT rate [30–33]. Some progress has been made in improving the photophysical properties of probes and sensors by using halogen atoms as coordinating groups. Piechowska's group reported that large Stokes shifts could

be obtained by introducing electron-donating and electron-accepting groups into pyridine rings, and investigated the effects of such groups on the ESPT behavior of 10-hydroxy-11H-benzo[b]fluoren-11-one (HBQ) [34]. Yu *et al.* reported that the photophysical properties could be adjusted by introducing electron-accepting or electron-donating substituents into a phenolic ring [35].

Recently, the photo-physical behavior of 5,6-dichloro-1,3-bis(2-pyridylimino)-4,7-dihydroxyisoindole and the absorption and emission properties of ten isomers have been reported [36]. However, in this previous study, the effects of substituents on the ESIDPT process were not considered. Here, we systematically investigated the effects of different electron-withdrawing substituents (F, Cl, and Br) in BPI-OH on proton transfer in the S_0 and S_1 states. We used DFT and TDDFT methods to explore the effects of electron-withdrawing groups (F, Cl, and Br); the geometric parameters, infrared (IR) spectra, and reduction density gradient (RDG) function were examined. The frontier molecular orbitals (FMOs) [37] and Mulliken's charge were used to predict the charge distribution. Most importantly, details of the ESIDPT mechanism were clarified by constructing the potential-energy curves (PECs) for the S_0 and S_1 states.

2. Computational Details

DFT/TDDFT calculations were performed using the Gaussian 16 program suite [38]. The geometric structures and reaction pathways were calculated without constraint by using the B3LYP function (Hybrid Becke, three-parameter, with 20% Hartree-Fock exchange energy) with the TZVP basis set [39, 40]. Dichloromethane (DCM) was selected as the solvent in all calculations on the basis of the integral equation formalism variant in the polarizable continuum model (IEFPCM) [41–43]. Vibration frequency calculations were performed to confirm each optimized structure corresponding to a local minimum (no imaginary frequency). The RDG function was introduced to investigate non-covalent interactions by using the Multiwfn program [44–46]. The PECs for the S_0 and S_1 states in double-proton transfer were obtained at the B3LYP/TZVP level.

3. Results And Discussion

3.1 Geometric structures and IR vibrational spectra

Calculations were performed at the B3LYP/TZVP level to determine the geometric configurations of BPI-OH (N), BPI-OH (T_1), and BPI-OH (T_2) in DCM; the results are shown in Fig. 1. The optimized geometric structures of BPI-OH-F, BPI-OH-Cl, and BPI-OH-Br are shown in Fig. 2. The optimized geometries of BPI-OH and its derivatives all have the same symmetry. The bond length of O_1-H_2 is the same as the bond length of O_4-H_5 , and the $O_1-H_2 \cdots N_3$ bond angle is the same as the $O_4-H_5 \cdots N_6$ bond angle. Table 1 lists the hydrogen-bond lengths in BPI-OH and its derivatives (normal structure) in the S_0 and S_1 states. The O_1-H_2 hydrogen bond length in BPI-OH (N) is 0.9813 Å in S_0 state, and 0.9975 Å in S_1 state. For BPI-OH-F (N), BPI-OH-Cl (N), and BPI-OH-Br (N), the O_1-H_2 bond lengths are 0.9832, 0.9843, and 0.9847 Å, respectively, in the S_0 state. These increase by 0.0189, 0.0189, and 0.0190 Å, respectively, to 1.0021, 1.0032, and 1.0037

Å, respectively, in the S_1 state. In BPI-OH-F (N), BPI-OH-Cl (N), and BPI-OH-Br (N), the distances between hydroxyl groups are greater than the corresponding distances in BPI-OH (N) in both the S_0 and S_1 states. This shows that the further apart the hydroxyl group is, the easier proton loss is; this is conducive to proton transfer. The H_2-N_3 hydrogen-bond length in BPI-OH (N) is 2.0590 Å in S_0 state and 1.9486 Å in S_1 state. For BPI-OH-F (N), BPI-OH-Cl (N), and BPI-OH-Br (N), the H_2-N_3 bond lengths are 2.0538, 2.0217, and 2.0104 Å, respectively, in the S_0 state. These decrease by 0.1263, 0.1172, and 0.1147 Å, respectively, to 1.9275, 1.9045, and 1.8957 Å, respectively, in the S_1 state. For the BPI-OH (N), BPI-OH-F (N), BPI-OH-Cl (N), and BPI-OH-Br (N), the $O_1-H_2\cdots N_3$ bond angles change from 143.77°, 143.42°, 144.59°, and 144.99° in the S_0 state to 147.27°, 147.32°, 148.21°, and 148.52°, respectively, in the S_1 state, i.e., they increase by 3.50°, 3.90°, 3.62°, and 3.53°, respectively. In BPI-OH-Br (N), BPI-OH-Cl (N), and BPI-OH-F (N), the bond angles tend to be larger than those in BPI-OH (N). This shows that the presence of a ligand increases the ability of the proton acceptor to capture a proton.

Table 1
Calculated primary bond lengths (Å) and angles (°) for BPI-OH (N), BPI-OH-F (N), BPI-OH-Cl (N), and BPI-OH-Br (N) in S_0 and S_1 states.

	BPI-OH(N)		BPI-OH-F(N)		BPI-OH-Cl(N)		BPI-OH-Br(N)	
parameter	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1
O_1-H_2	0.9813	0.9975	0.9832	1.0021	0.9843	1.0032	0.9847	1.0037
H_2-N_3	2.0590	1.9486	2.0538	1.9275	2.0217	1.9045	2.0104	1.8957
$\delta(O_1-H_2-N_3)$	143.77	147.27	143.42	147.32	144.59	148.21	144.99	148.52
O_4-H_5	0.9813	0.9975	0.9832	1.0021	0.9843	1.0032	0.9848	1.0038
H_5-N_6	2.0590	1.9486	2.0539	1.9275	2.0218	1.9044	2.0103	1.8968
$\delta(O_4-H_5-N_6)$	143.80	147.37	143.42	147.32	144.59	148.21	144.99	148.47

Table 2 shows the parameters for the BPI-OH (T_1), BPI-OH-F (T_1), BPI-OH-Cl (T_1), and BPI-OH-Br (T_1) structures, which were formed via ESIPT. In hydrogen-bonded $O_1-H_2\cdots N_3$, the O_1-H_2 bond lengths are 2.1388, 2.1723, 2.1320, and 2.1244 Å, respectively, in S_0 state, and 2.1637, 2.2158, 2.1838, and 2.1753 Å, respectively, in the S_1 state. The $H_2\cdots N_3$ bond lengths are 1.0218, 1.0207, 1.0217, and 1.0220 Å, respectively, in S_0 state, and 1.0206, 1.0188, 1.0194, 1.0196 Å, respectively, in the S_1 state. The $O_1\cdots H_2-N_3$ bond angle changes from 133.46°, 132.73°, 133.09°, and 133.14° in S_0 state to 132.48°, 131.43°, 131.46°, and 131.48°, respectively, in the S_1 state. This indicates that the hydrogen bond in $O_1\cdots H_2-N_3$ is stronger in the S_0 state. In hydrogen-bonded $O_4-H_5\cdots N_6$, the O_4-H_5 bond lengths increase from 0.9806,

0.9819, 0.9829, and 0.9835 Å in S₀ state to 0.9861, 0.9890, 0.9902, and 0.9908 Å, respectively, in the S₁ state. The H₅···N₆ bond lengths decrease from 2.0947, 2.0875, 2.0528, and 2.0372 Å, respectively, in the S₀ state to 2.0362, 2.0099, 1.9817, and 1.9696 Å, respectively, in the S₁ state. The O₄-H₅···N₆ hydrogen-bond angles in BPI-OH (T₁), BPI-OH-Br (T₁), BPI-OH-Cl (T₁), and BPI-OH-F (T₁) are 2.61°, 2.67°, 2.73°, and 2.88°, respectively, higher in the S₁ state than in the S₀ state. This data show that the bond angle increases with increasing electron absorption intensity after addition of a coordinating group. These observations indicate that the intramolecular hydrogen bonds become stronger with increasing electron absorption intensity, and are stronger in the S₁ state than in the S₀ state.

BPI-OH (T₂), BPI-OH-F (T₂), BPI-OH-Cl (T₂), and BPI-OH-Br (T₂) are formed via two ESIPT processes, along with two corresponding hydrogen bonds. The O₁···H₂-N₃ is discussed because of its symmetrical structure. The data in Table 3 show that in the S₀ state, the O₁···H₂ and H₂-N₃ bond lengths in BPI-OH (T₂), BPI-OH-F (T₂), BPI-OH-Cl (T₂), and BPI-OH-Br (T₂) are 2.2752, 2.2878, 2.2512, and 2.2406 Å, respectively, and 1.0155, 1.0152, 1.0157, and 1.0159 Å, respectively. These are 2.2184, 2.2380, 2.2104, and 2.2009 Å, respectively, and 1.0186, 1.0181, 1.0183Å, and 1.0185Å, respectively, higher in the S₁ state. The O₁···H₂-N₃ bond angles change from 128.70°, 128.88°, and 128.97°, respectively, in the S₀ state to 130.13°, 129.96°, and 130.00°, respectively, in the S₁ state. These changes in the bond parameters prove that two intramolecular hydrogen bonds are strengthened on photoexcitation. The effect of hydrogen-bond enhancement is clearest when the coordinating group contains F. ESIPT is therefore promoted by the presence of a coordinating base and excited states.

Table 2
Calculated primary bond lengths (Å) and angles (°) for BPI-OH (T₁), BPI-OH-F (T₁), BPI-OH-Cl (T₁), and BPI-OH-Br (T₁) in S₀ and S₁ states.

	BPI-OH(T ₁)		BPI-OH-F(T ₁)		BPI-OH-Cl(T ₁)		BPI-OH-Br(T ₁)	
parameter	S ₀	S ₁	S ₀	S ₁	S ₀	S ₁	S ₀	S ₁
O ₁ -H ₂	2.1388	2.1637	2.1723	2.2158	2.1320	2.1838	2.1244	2.1753
H ₂ -N ₃	1.0218	1.0206	1.0207	1.0188	1.0217	1.0194	1.0220	1.0196
δ(O ₁ -H ₂ -N ₃)	133.46	132.48	132.73	131.43	133.09	131.46	133.14	131.48
O ₄ -H ₅	0.9806	0.9861	0.9819	0.9890	0.9829	0.9902	0.9835	0.9908
H ₅ -N ₆	2.0947	2.0362	2.0875	2.0099	2.0528	1.9817	2.0372	1.9696
δ(O ₄ -H ₅ -N ₆)	142.84	145.45	142.52	145.40	143.81	146.54	144.26	146.93

Table 3
Calculated primary bond lengths (Å) and angles (°) for BPI-OH (T₂), BPI-OH-F (T₂), BPI-OH-Cl (T₂), and BPI-OH-Br (T₂) in S₀ and S₁ states.

	BPI-OH(T ₂)		BPI-OH-F(T ₂)		BPI-OH-Cl(T ₂)		BPI-OH-Br(T ₂)	
parameter	S ₀	S ₁	S ₀	S ₁	S ₀	S ₁	S ₀	S ₁
O ₁ -H ₂	2.2752	2.2184	2.2878	2.2380	2.2512	2.2104	2.2406	2.2009
H ₂ -N ₃	1.0155	1.0186	1.0152	1.0181	1.0157	1.0183	1.0159	1.0185
δ(O ₁ -H ₂ -N ₃)	128.99	130.46	128.70	130.13	128.88	129.96	128.97	130.00
O ₄ -H ₅	2.2750	2.2181	2.2882	2.2383	2.2512	2.2102	2.2407	2.2008
H ₅ -N ₆	1.0155	1.0186	1.0152	1.0180	1.0157	1.0183	1.0159	1.0185
δ(O ₄ -H ₅ -N ₆)	128.99	130.47	128.70	130.12	128.89	129.96	128.96	130.00

The IR vibrational spectra of BPI-OH and its derivatives were calculated. The stretching vibration frequencies on the S₀ and S₁ states for BPI-OH, BPI-OH-F, BPI-OH-Cl, and BPI-OH-Br are shown in Figs. 3 and 4. For BPI-OH (N), the O₁-H₂ stretching frequency is 3484 cm⁻¹ in the S₀ state and 3198 cm⁻¹ in the S₁ state. A red shift of 286 cm⁻¹ was observed for the S₁ state; this shows that enhanced hydrogen bonding results in a red shift. Similarly, the spectra of BPI-OH-F (N), BPI-OH-Cl (N), and BPI-OH-Br (N) show gradually increasing red shifts from the S₀ to S₁ state, namely 335, 333, and 333 cm⁻¹, respectively. Among the three derivatives of BPI-OH, BPI-OH-F (N) gives the highest red shift from the S₀ to the S₁ state. These data confirm an excited-state hydrogen-bond enhancing mechanism. The presence or absence of coordinating groups and different coordinating groups affect the hydrogen-bond strength. The presence of coordinating groups enhances hydrogen bonding, i.e., it promotes ES IPT.

Figure 3(b) shows that the O₁-H₂ vibration frequency red shifts by 120 cm⁻¹ from 3512 cm⁻¹ in the S₀ state to 3392 cm⁻¹ in S₁ state. This indicates that the O₁-H₂...N₃ hydrogen bond is enhanced in the S₁ state. The N₆-H₅ vibration blue shifts by 21 cm⁻¹ from 3409 cm⁻¹ in the S₀ state to 3430 cm⁻¹ in the S₁ state, i.e., the N₆-H₅...O₄ hydrogen bond is stronger in the S₀ state than in the S₁ state. Figure 4 (b) shows red shifts of the vibration frequency of 121, 122, and 124 cm⁻¹ in the spectra of BPI-OH-Br (T₁), BPI-OH-Cl (T₁), and BPI-OH-F (T₁), respectively. This shows that the red shift increases with increasing electron absorption intensity of the coordinating group. Figure 3(c) shows that the stretching vibration frequency of N₃-H₂ (N₆-H₅) in BPI-OH (T₂) clearly blue shifts by 24 cm⁻¹. Figure 4 (c) shows vibration frequency blue shifts of 2, 6, and 15 cm⁻¹ for BPI-OH-Br (T₂), BPI-OH-Cl (T₂), and BPI-OH-F (T₂), respectively. This shows that the N₃-H₂...O₁ (N₆-H₅...O₄) hydrogen bond is stronger in the S₀ state than in the S₁ state.

3.2 RDG analysis

Fig. 5 shows scatter plots of RDG versus sign (λ_2) ρ and the corresponding gradient isosurfaces. The RDG isosurface range is from -0.05 to 0.05; the hydrogen-bond isosurfaces are shown in blue. In the AIM theory, $\rho(r)$ at the critical point of a weak interaction is an important index in determining the interaction strength, and there is a positive correlation between its value and the bond strength. The larger $\rho(r)$ in the blue region is, the stronger and more attractive the weak interactions. In Fig. 5, the spikes in the small red circles correspond to attractive intramolecular hydrogen-bonding interactions. The spikes for BPI-OH-F (N), BPI-OH-Cl (N), and BPI-OH-Br (N) range from -0.04 to -0.03 a.u. The spikes for BPI-OH-F (N), BPI-OH-Cl (N) and BPI-OH-Br (N) are situated to the left of those for BPI-OH (N). This indicates stronger intramolecular hydrogen bonds. In summary, the presence of coordinating groups strengthens hydrogen bonds, and this increases the probability of ESIPT.

3.3 Electronic spectra, FMO analysis, and Mulliken's charge distributions

The first excited states of BPI-OH-Br, BPI-OH-Cl and BPI-OH-F molecules were fully optimized by TDDFT/B3LYP/TZVP on the basis of their S_0 state optimized structures. The absorption and emission spectra are shown in Fig. 6. The calculated absorption values for BPI-OH-Br (N), BPI-OH-Cl (N), and BPI-OH-F (N) are 410, 426, and 431 nm, respectively. The theoretical fluorescence values are 485, 505, and 512 nm for BPI-OH-Br (N), BPI-OH-Cl (N), and BPI-OH-F (N), respectively. These values are close to the experimental emission wavelengths. Figure 6 also shows the fluorescence spectra of BPI-OH-F (T_1 , T_2), BPI-OH-Cl (T_1 , T_2), and BPI-OH-Br (T_1 , T_2) in DCM. During ESIPT, double fluorescence emissions are observed, and large Stokes shifts are observed for BPI-OH-Br (N) (122 nm), BPI-OH-Cl (N) (133 nm) and BPI-OH-F (N) (136 nm). The red shifts of the emission wavelengths and large Stokes shifts favor ESIPT. The addition of an F functional group is therefore most effective in enabling use of BPI-OH as a probe.

Redistribution of the electron densities of proton donors and proton acceptors provide the driving force for electron-spin transfer after photoexcitation. The FMOs of BPI-OH-Br (N), BPI-OH-Cl (N), and BPI-OH-F (N) are shown in Fig. 7. This shows the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO); the S_0 - S_1 transitions can be described as predominantly $\pi\pi^*$ -type transitions. The data in Table 4 show that the contributions to the excited electronic states are BPI-OH-F (N), 98.7%; BPI-OH-Cl (N), 98.9%; and BPI-OH-Br (N), 99.0%. The order of the oscillator strengths in the S_1 state is BPI-OH (N), 0.3802; BPI-OH-Br (N), 0.5038; BPI-OH-Cl (N), 0.4659; and BPI-OH-F (N), 0.3832. The molecular optical polarizability and biological activity can be determined from the electron transition energy. The transition energies in the S_1 state for BPI-OH-Br (N), BPI-OH-Cl (N), and BPI-OH-F (N) are 2.901, 2.929, and 3.016 eV, respectively (Fig. 7). The calculations show that BPI-OH-Br (N), BPI-OH-Cl (N), and BPI-OH-F (N) all have low kinetic stability and high chemical reactivity in DCM. After light excitation, the electron density is redistributed from the proton donor oxygen (O_1) in the HOMO to the proton acceptor

nitrogen (N₃) in the LUMO. This enhances attraction to H and facilitates proton transfer from the enol structure to the keto structure in the S₁ state.

The data in Table 5 show that for BPI-OH-F (N), the Mulliken's charge on O₁ decreases from - 0.275 to -0.270 and that on N₃ increases from - 0.226 to -0.236. This indicates that the electronegativity of N₃ increases and that of O₁ decreases. The attraction between N₃ and H is enhanced, which promotes ES IPT. Similar results were obtained for BPI-OH-Cl (N) and BPI-OH-Br (N). The above discussion shows that ES IPT is affected by a change in charge density.

Table 4
Calculated of electronic excitation energies (nm), corresponding oscillator strengths (f) of low-lying electronically excited states for BPI-OH (N), BPI-OH-F (N), BPI-OH-Cl (N), and BPI-OH-Br (N), and orbital transition (OT) contributions to electronic excited states (Cl).

	transition	$\lambda(\text{nm/eV})$	f	OT	Cl (%)
BPI-OH (N)	S ₀ →S ₁	433/2.86	0.3802	H→L	99.2%
BPI-OH-F (N)	S ₀ →S ₁	410/3.02	0.3832	H→L	98.7%
BPI-OH-Cl (N)	S ₀ →S ₁	426/2.91	0.4659	H→L	98.9%
BPI-OH-Br (N)	S ₀ →S ₁	431/2.88	0.5038	H→L	99.0%

Table 5
Calculated Mulliken's charge distributions for BPI-OH (N) and its derivatives in S₀ and S₁ states.

Mulliken's charge						
	O ₁		H ₂		N ₃	
	S ₀	S ₁	S ₀	S ₁	S ₀	S ₁
BPI-OH-F (N)	-0.275	-0.270	0.320	0.328	-0.226	-0.236
BPI-OH-Cl (N)	-0.273	-0.268	0.318	0.325	-0.227	-0.236
BPI-OH-Br (N)	-0.277	-0.272	0.318	0.325	-0.228	-0.236

3.4 PEC analysis

PECs were constructed by step-by-step and point-to-point optimization to gain a deeper understanding of the effects of various ligands on ES IPT. As shown in Figs. 8 and 9, the PECs were constructed by keeping the O₁-H₂ and O₄-H₅ bond distances fixed at given values in steps of 0.05 Å, and optimizing the other

atoms in the system without any constraints. As shown in Fig. 8, the reaction barriers for ESIPT are 4.03, 2.82, 2.79, and 2.68 kcal/mol for BPI-OH, BPI-OH-Br, BPI-OH-Cl, and BPI-OH-F, respectively, in the S_1 state. The electronic energies of the keto products (T_1) are more stable than those of the enol reactants (N), which indicates that the ESIPT reactions are exothermic. The reaction barriers for molecules with coordinating group, i.e., BPI-OH-Br, BPI-OH-Cl, and BPI-OH-F, are much lower than that for BPI-OH, therefore their ESIPT reactions are easier. The energy barriers make proton transfer reactions of BPI-OH, BPI-OH-Br, BPI-OH-Cl, and BPI-OH-F in the S_0 state are 10.89, 9.22, 6.20, and 3.71 kcal/mol, respectively. These high energy barriers make proton transfer reactions of BPI-OH, BPI-OH-Br, and BPI-OH-Cl less likely in the S_0 state than in the S_1 state. Single-proton transfer is exothermic in the S_1 state but endothermic in the S_0 state. The results show that proton transfer may occur in S_1 state.

Previous studies have shown that two protons in the BPI-OH molecule are transferred step-by-step in the S_0 and S_1 states, i.e., proton transfer along the O_1-H_2 bond occurs only after completion of transfer of the first proton along the O_4-H_5 bond [47]. This represents a proton-relay process. Figure 9 shows that for $T_1 \rightarrow T_2$, the reaction barriers for ESIPT are 7.88, 6.62, 6.54, and 6.49 kcal/mol for BPI-OH, BPI-OH-Br, BPI-OH-Cl, and BPI-OH-F, respectively, in the S_1 state. Compared with the energy barriers for proton transfer along the O_1-H_2 bond in the first step, the corresponding values for the O_4-H_5 bond are much higher in both the S_0 and S_1 states. Reaction barrier is lowest for BPI-OH-F, therefore the ESIPT reaction occurs more easily. In summary, substituent modification facilitates ESIPT, and the higher the electron absorption intensity, the lower the energy barrier for a proton-transfer reaction.

4. Conclusions

In summary, new insights into substituent modification and the ESIDPT mechanism for symmetric structures of BPI-OH and its derivatives were obtained by using DFT/TDDFT methods. Comparisons of the changes in the primary bond parameters confirmed that substituent modification strengthened excited-state intermolecular hydrogen bonds. Analysis of PECs in the S_0 and S_1 states showed that proton transfer involved two steps in the S_1 state, and was difficult to achieve in the S_0 state. Our results suggest that strengthening of intramolecular hydrogen bonds can effectively decrease the energy barriers and promote the proton-transfer process. Modification with electron-withdrawing groups (F, Cl, and Br) favors proton-transfer reactions. These distinctive properties will enable control of ESIDPT processes and provide guidance for the design and synthesis of similar molecules.

5. Declarations

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Conflicts of interest

There are no conflicts of interest.

Availability of data and material Not applicable **Code availability** Not applicable **Authors' contributions**

Xiumin Liu: Investigation, Writing - original draft

Wenzhi Li: Investigation

Yuxi Wang: Data curation

Yaping Tao: Data curation

Yi Wang: Writing - review & editing, Funding acquisition

Yingmin Hou: Conceptualization, Writing - review & editing

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Figures

Figure 1

Structures of BPI-OH (N), BPI-OH (T₁) (single-proton transfer of BPI-OH), and BPI-OH (T₂) (double-proton transfer of BPI-OH). Atoms involved in two intramolecular hydrogen bonds are indicated in the BPI-OH structure.

Figure 2

Optimized structures of BPI-OH derivatives: (a) BPI-OH-F, (b) BPI-OH-Cl, and (c) BPI-OH-Br.

(a)

(b)

(c)

Figure 3

IR spectra (B3LYP/TZVP): (a) O1-H2 (O4-H5) in BPI-OH (N); (b) O1-H2 and N6-H5 in BPI-OH (T1); and (c) N3-H2 (N6-H5) in BPI-OH (T2).

Figure 4

IR spectra (B3LYP/TZVP): (a) O1-H2 (O4-H5) in BPI-OH-F (N), BPI-OH-Cl (N), and BPI-OH-Br (N); (b) O1-H2 and N6-H5 in BPI-OH-F (T1), BPI-OH-Cl (T1), and BPI-OH-Br (T1); and (c) N3-H2 (N6-H5) in BPI-OH-F (T2), BPI-OH-Cl (T2), and BPI-OH-Br (T2). (dotted lines: S0; solid lines: S1)

Figure 5

Plots of RDG versus electron density multiplied by sign of second Hessian eigenvalue and color-mapped RDG isosurfaces for BPI-OH (N) and its derivatives in S1 state.

(a)

(b)

(c)

Figure 6

Calculated absorption (abs) and fluorescence (flu) wavelengths for (a) BPI-OH-Br, (b) BPI-OH-Cl, and (c) BPI-OH-F; N: normal form; T1 and T2: tautomeric forms.

Figure 7

Calculated FMOs (HOMOs and LUMOs) for BPI-OH (N), BPI-OH-Br (N), BPI-OH-Cl (N), and BPI-OH-F (N) in S1 state and their transition energies.

Figure 8

PECs for S₀ and S₁ states of BPI-OH (N), BPI-OH-Br (N), BPI-OH-Cl (N), and BPI-OH-F (N), and O1-H2 bond lengths. The insets show corresponding optimized configurations (N $\rightarrow$ T₁): (a) BPI-OH, (b) BPI-OH-Br, (c) BPI-OH-Cl, (d) BPI-OH-F.

Figure 9

PECs for S₀ and S₁ states of BPI-OH (T1), BPI-OH-Br (T1), BPI-OH-Cl (T1), and BPI-OH-F (T1), and O4-H5 bond lengths. The insets show the corresponding optimized configurations (T1 → T2): (a) BPI-OH, (b) BPI-OH-Br, (c) BPI-OH-Cl, (d) BPI-OH-F.