

Modulating N-H-based Excited-State Intramolecular Proton Transfer by Different Electron-Donating/Withdrawing Substituents in 2-(2'-aminophenyl)benzothiazole Compounds

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Abstract. At the B3LYP/6-311+G(d, p)/IEFPCM (in dichloromethane) theory level, the N-H-based excited-state intramolecular proton transfer (N-H-based ESIPT) process of 2-(2'-aminophenyl)benzothiazole (PBT-NH₂) and its three derivatives 2-(2'-methylaminophenyl)benzothiazole (PBT-NHMe), 2-(2'-acetylaminophenyl)benzothiazole (PBT-NHAc) and 2-(2'-tosylaminophenyl) benzothiazole (PBT-NHTs) have been explored by the time-dependent density functional theory (TD-DFT) method. Our calculated hydrogen bond lengths and angles sufficiently confirm that the intramolecular hydrogen bonds N₁-H...N₂ formed at the S₀ states of the four compounds should be significantly strengthened in the S₁ state, which are further supported by the results obtained based on the analyses of infrared spectra shifts. The scanned potential energy curves reveal that the energy barriers of the first singlet excited state of the four titled compounds along the ESIPT reactions are predicted at 8.74, 8.98, 6.72 and 1.69 kcal/mol, respectively, suggesting that the inclusion of a strong electron-withdrawing tosyl (Ts) group can remarkably facilitate the occurrence of the ESIPT reaction, while the involvement of an electron-donating methyl group has slight opposite effect on the ESIPT process of the amino-type hydrogen-bonding system.

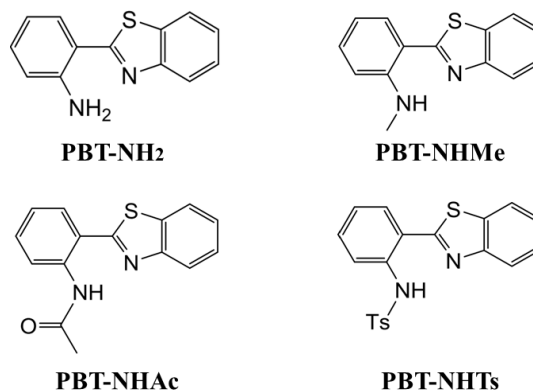
Keywords: N-H-based excited-state intramolecular proton transfer; electron-donating/withdrawing substituents; potential energy curves; TDDFT method.

1. Introduction

Excited state intramolecular proton transfer (ESIPT) reaction, as one of the most fundamental processes in both chemical and biological systems, has been receiving considerable attention in the past few decades. In recent years, considerable progress has been made in exploring the excited-state intramolecular proton transfer (ESIPT) reactions of the hydroxyl-type hydrogen-bonding (H-bonding) systems using hydroxyl as a proton donor [1-8]. It is well-known that the ESIPT reactions of the O-H-type H-bonding molecules are usually highly exergonic and remarkably ultrafast. Owing to its particular property, the O-H-type ESIPT chromophores has been extensively applied as molecular probes [9], fluorescence sensors [10, 11], luminescent materials [12-14] and so on.

In contrast to the many studies on O-H-type ESIPT [1-14], work about the amino-type H-bonding systems is much less reported [15-19]. A main reason is that the acidity of the amino proton is much weaker than that of the hydroxyl proton, thus leading to the much weaker intramolecular hydrogen bond (H-bond) associated with the amino N-H proton. To solve the problem, extensive efforts have been made by experimentalists and theorists to tune the ESIPT behaviors of

several amino-type H-bonding systems [20-22]. In 2015, Chou group designed and synthesized a new series of amino-type H-bonding compounds 2-(2'-aminophenyl)benzothiazole (PBT-NH₂) and its three derivatives 2-(2'-methylaminophenyl)benzothiazole (PBT-NHMe), 2-(2'-acetylaminophenyl)benzothiazole (PBT-NHAc) and 2-(2'-tosylaminophenyl) benzothiazole (PBT-NHTs), as shown in Scheme 1 [20]. It was found that ESIPT in the parent molecules PBT-NH₂ and PBT-NHMe is highly endergonic and thus prohibited, whereas introduction of electron-withdrawing group tosyl or acetyl (Ac) onto the amino nitrogen, could facilitate the ESIPT process [20]. In the presence of strong electron-withdrawing tosyl group that directly replaces one of



Scheme 1. Geometrical structures of PBT-NH₂, PBT-NHMe, PBT-NHAc and PBT-NHTs.

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the amino protons, complete and ultrafast ESIPT is resolved for **PBT-NHTs**. Upon the substitution of moderate strong electron-withdrawing group Ac, compound **PBT-NHAc** exhibit equilibrium type ESIPT, resulting in a remarkable dual emission.

Based on Chou's results, DFT and TD-DFT calculations at the B3LYP level of theory were performed by Zhang and coworkers to explore the photophysical behaviors of three amino-type **PBT-NH₂** derivatives (**PBT-NHMe**, **PBT-NHAc** and **PBT-NHTs**) [21]. Their calculated energy barriers of the first singlet excited state of the three amino-type H-bonding compounds **PBT-NHMe**, **PBT-NHAc** and **PBT-NHTs** along the ESIPT reactions are 0.39, 0.30 and 0.12 eV respectively, based on which they concluded that the inclusion of a strong electron-withdrawing tosyl group can remarkably facilitate the occurrence of the ESIPT reaction, while the involvement of an electron-donating methyl group has no effect on the ESIPT process of the amino-type hydrogen-bonding system.

Despite such significant efforts, there are still some key questions that remain to be unresolved for these amino-type H-bonding systems, for instance, both the forward and backward energy barriers of the excited-state proton-transfer reaction of all the four amino-type H-bonding compounds **PBT-NH₂**, **PBT-NHMe**, **PBT-NHAc** and **PBT-NHTs**, which are critical to reveal the detailed mechanism of the whole photophysical process. To gain the clear pictures of the ESIPT processes of these amino-type H-bonding systems bearing the benzothiazole scaffold, we chose **PBT-NH₂** together with its three derivatives **PBT-NHMe**, **PBT-NHAc** and **PBT-NHTs** as representative examples. A main objective of this work is to shed light on the impact of the introduction of an electron-donating methyl group, a weak electron-withdrawing Ac group or a strong electron-withdrawing Ts group on the photophysical behaviours of **PBT-NH₂**. By employing the density functional theory (DFT) and time-dependent DFT (TD-DFT) methods, we have investigated the potential energy surfaces of the four amino-type H-bonding compounds in both ground and excited states along the ESIPT reaction pathway. Great attentions should be paid to the changes of the forward

and backward energy barriers as one of the amine hydrogen atom is replaced by electron-donating group methyl, weak electron-withdrawing group Ac and strong electron-withdrawing group Ts. We truly expected that these theoretical calculations can improve our understanding of the basic photophysical properties of these amino-type H-bonding systems.

In the present work, all the electronic structure calculations were carried out with the Gaussian 16 program [23] suite. Using DFT and TDDFT methods with Becke's three-parameter hybrid exchange function with the Lee-Yang-Parr gradient-corrected correlation functional (B3LYP) [24-29] as well as the 6-311+G(d, p) basis set, we have theoretically studied the excited-state overall perspective of the proton transfer process of the four amino-type H-bonding compounds. Since previous experimental and theoretical works were carried out in dichloromethane [20, 21], we took dichloromethane into consideration in all calculations via Polarizable Continuum Model (PCM) using the integral equation formalism variant (IEF-PCM) [30-32] to be consistent with former works. No symmetry constraint is contained in all our calculations.

The geometrical structures of the four amino-type H-bonding compounds **PBT-NH₂**, **PBT-NHMe**, **PBT-NHAc** and **PBT-NHTs** in dichloromethane at ground state S_0 and the first singlet excited state S_1 have been optimized at the B3LYP/6-311+G(d, p)/IEFPCM and TD-B3LYP/6-311+G(d, p)/IEFPCM theory level, respectively. **Figure 1** shows the optimized ground-state geometrical structures of the four amino-type H-bonding compounds while related hydrogen bond lengths and angles in both ground state S_0 and first singlet excited state S_1 are listed in **Table 1**. For comparisons, we named the intramolecular hydrogen bonds within the four amino-type H-bonding compounds all as $N_1-H \cdots N_2$. From **Table 1**, it can be found that, from ground state S_0 to first singlet excited state S_1 , the bond lengths of N_1-H in all the four amino-type H-bonding compounds are all increased, whereas those of hydrogen bond $H \cdots N_2$ are all decreased. At the same time, the bond angles

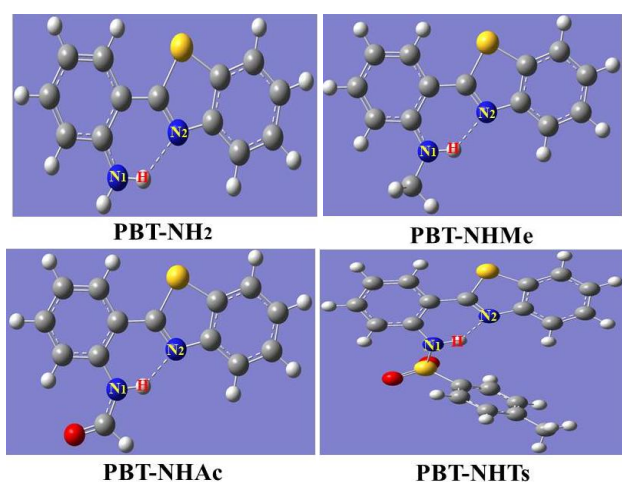


Figure 1: Optimized ground-state geometrical structures of **PBT-NH₂**, **PBT-NHMe**, **PBT-NHAc** and **PBT-NHTs** at B3LYP/6-311+G(d, p)/IEFPCM (dichloromethane) theory level.

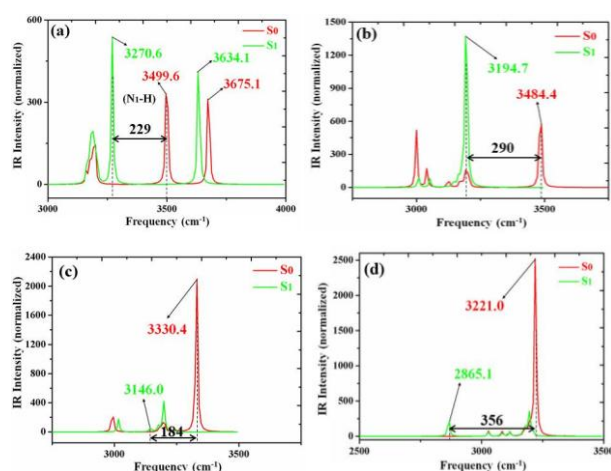


Figure 2: IR spectra of **PBT-NH₂** (a), **PBT-NHMe** (b), **PBT-NHAc** (c) and **PBT-NHTs** (d) at the spectral region of N_1-H stretching band in both S_0 and S_1 states at (TD)B3LYP/6-311+G(d, p)/IEFPCM (dichloromethane) theory level.

of $N_1-H\cdots N_2$ in the four amino-type H-bonding compounds are all increased. Both the decreases of the hydrogen bond lengths and the increases of the hydrogen bond angles indicate that the intramolecular hydrogen bonds $N_1-H\cdots N_2$ formed in the ground state S_0 of the four amino-type H-bonding compounds should be strengthened upon photoexcitation to the first singlet excited state S_1 .

We all know that detecting the infrared (IR) vibrational spectral shift is an effective way to explore the changes of hydrogen bonds upon photoexcitation [33–36]. Therefore, the vibrational spectra involved in intramolecular hydrogen bonding moiety of the four amino-type H-bonding compounds in the N_1-H vibrational stretching modes in both ground state S_0 and first singlet excited state S_1 have been displayed in Figure 2. From Figure 2 (a), it should be noticed that, in **PBT-NH₂**, the vibrational stretching mode of the N_1-H group that is involved in the formation of intramolecular hydrogen bond $N_1-H\cdots N_2$ is significantly redshifted by 229 cm^{-1} from 3499.6 cm^{-1} in ground state S_0 to 3270.6 cm^{-1} upon photoexcitation to first singlet excited state S_1 . On the contrary, the vibrational stretching mode of the $N-H$ group that is not involved in the formation of intramolecular hydrogen bond is just slightly redshifted by 41 cm^{-1} from 3675.1 cm^{-1} in ground state S_0 to 3634.1 cm^{-1} in first singlet excited state S_1 . Furthermore, the vibrational stretching mode of the N_1-H group is redshifted by 175.5 cm^{-1} to 3499.6 cm^{-1} from 3675.1 cm^{-1} in ground state S_0 . For N_1-H group in **PBT-NH₂**, the redshift of vibrational stretching mode in ground state S_0 (175.5 cm^{-1}) and that upon photoexcitation to first singlet excited state S_1 (229 cm^{-1}) should be mainly due to the formation of the intramolecular hydrogen bond in state S_0 and its strengthening upon photoexcitation to state S_1 , respectively. From Figure 2 (b), (c)

and (d), it can be found that, from ground state S_0 to first singlet excited state S_1 , the vibrational stretching mode of the N_1-H group in compounds **PBT-NHMe**, **PBT-NHAc** and **PBT-NHTs** are redshifted by 290, 184 and 356 cm^{-1} respectively, which all should be arisen from the strengthening of the intramolecular hydrogen bonds $N_1-H\cdots N_2$ upon photoexcitation to first singlet excited state S_1 . The above conclusions are consistent with those deduced from the calculated bond lengths and angles.

To further reveal the detailed N-H-type ESIPT mechanism, we have also constructed the S_1 -state potential energy curves of all the four amino-type H-bonding compounds with fixing H- N_2 bond lengths at a series of certain values in step of -0.05 Å , as shown in Figure 3. From Figure 3 (a), it can be found that, in compound **PBT-NH₂**, the forward (H^+ transferred from N_1 to N_2) and backward (H^+ transferred from N_2 back to N_1) proton transfer energy barrier are approximately the same, 8.74 kcal/mol , which is too high to allow the ESIPT process to happen. From Figure 3 (a) to Figure 3 (b), the forward proton transfer energy barrier is increased from 8.74 kcal/mol in compound **PBT-NH₂** to 8.98 kcal/mol in compound **PBT-NHMe**. This increase in forward proton transfer energy barrier is arisen from the introduction of the electron-donating group methyl at the amine site, which decreases the acidity of the N_1-H atom and hence hinders the ESIPT process. The above conclusions are consistent with the sole emission peak resulted from the excited-state normal form of compounds **PBT-NH₂** and **PBT-NHMe** observed in dichloromethane by Chou [20].

Compared with Figure 3 (a), it can be found from Figure 3 (c) that for compound **PBT-NHAc**, both the forward proton transfer energy barrier and the backward proton transfer

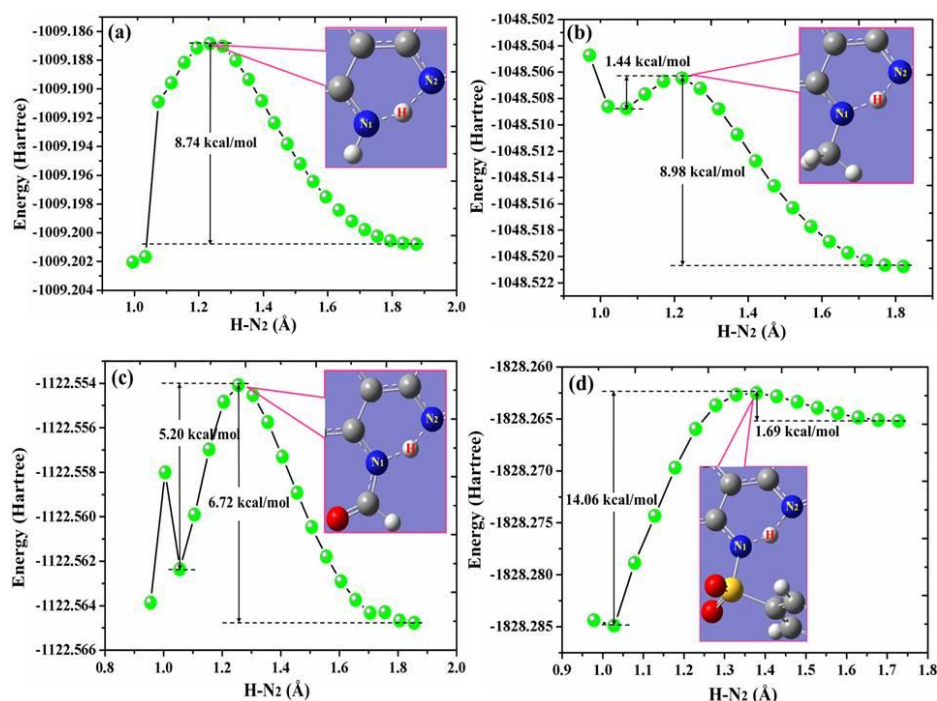


Figure 3: Calculated potential energy curves of S_1 state for **PBT-NH₂** (a), **PBT-NHMe** (b), **PBT-NHAc** (c) and **PBT-NHTs** (d) along with the H- N_2 bond distance at TD-B3LYP/6-311+G(d, p)/IEFPCM (dichloromethane) theory level.

energy barrier are decreased, from 8.74 kcal/mol to 6.72 and 5.20 kcal/mol, respectively. These moderate proton transfer energy barriers (6.72 and 5.20 kcal/mol) will allow both the forward and the backward ESIPT process to happen, which is consistent with the dual emission peaks resulted from excited-state normal and proton-transferred forms of compound **PBT-NHAc** respectively, as observed in dichloromethane by Chou [20]. From **Figure 3 (d)**, it can be found that, when one of the two amino hydrogen atoms is replaced with strong electron-withdrawing group tosyl (Ts) to form **PBT-NHTs**, the forward proton transfer energy barrier is sharply decreased to 1.69 kcal/mol whereas the energy barrier of the backward proton transfer is significantly increased to 14.06 kcal/mol. This quite low forward proton transfer energy barrier 1.69 kcal/mol will allow the proton transferred from N_1 to N_2 in ultrafast time scale, whereas the quite high backward proton transfer energy barrier 14.06 kcal/mol will hinder the proton transferred back from N_2 to N_1 , which is consistent with the sole emission peak resulted from the proton-transferred form of compound **PBT-NHTs** observed in dichloromethane by Chou [20].

In summary, we have theoretically studied the ESIPT process for the four amino-type H-bonding compounds **PBT-NH₂**, **PBT-NHMe**, **PBT-NHAc** and **PBT-NHTs** at the TD-B3LYP/6-311+G(d, p)/IEFPCM (dichloromethane) theory level. Analyses of hydrogen bond lengths and bond angles indicate that the intramolecular hydrogen bonds $N_1-H\cdots N_2$ formed within the four amino-type H-bonding compounds in ground state should be strengthened in the S_1 state, which is consistent with the results obtained based on infrared spectra shifts. To obtain the detailed excited-state proton transfer mechanism, we have scanned the excited-state potential energy curves for all the four compounds, which show the overall perspective of the ESIPT dynamics and provides a clear mechanism for previous experiment.

Acknowledgements

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