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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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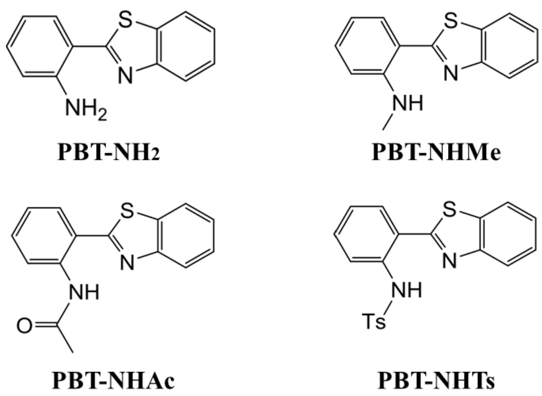
Abstract. At the B3LYP/6-311+G(d, p)/IEFPCM (in dichloromethane) theory level, the N-H-based excited-state intramolecular proton transfer (N-H-based ESIPT) process of 2-(2'-aminophenyl)benzothiazole (PBT-NH2) and its three derivatives 2-(2'-methylaminophenyl)benzothiazole(PBT-NHMe), 2-(2'-acetylaminophenyl)benzothiazole (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 N_1-H•••N_2 formed at the S_0 states of the four compounds should be significantly strengthened in the S_1 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], luorescence 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-NH_2**) 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-NH_2** 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-NH_2**, **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-NH$_2$** 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-NH$_2$**, **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-NH$_2$** 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-NH$_2$**. 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-NH$_2$**, **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•••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•••N_2 are all decreased. At the same time, the bond angles

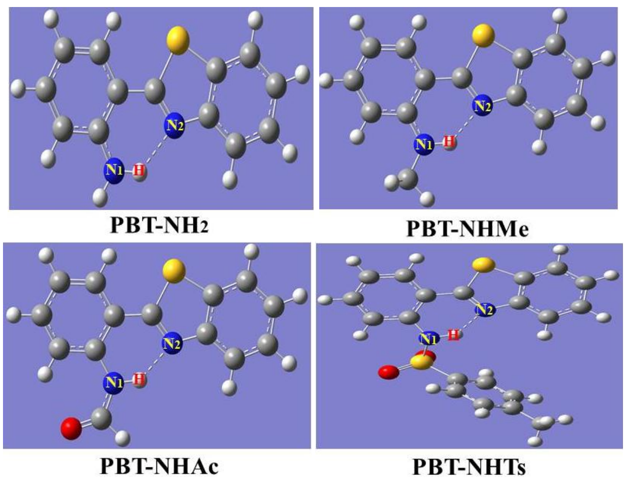

Figure 1: Optimized ground-state geometrical structures of **PBT-NH$_2$**, **PBT-NHMe**, **PBT-NHAc** and **PBT-NHTs** at B3LYP/6-311+G(d, p)/IEFPCM (dichloromethane) theory level.

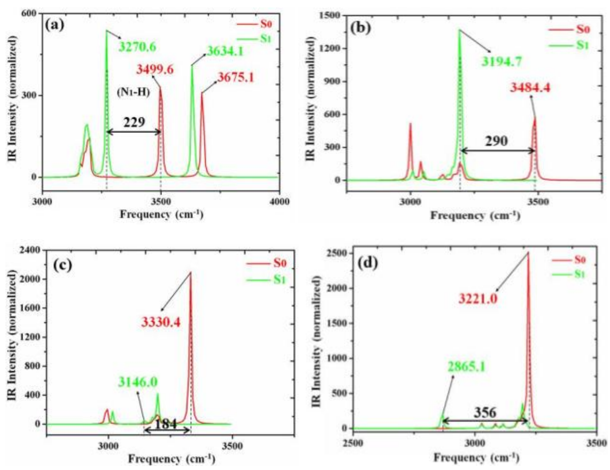

Figure 2: IR spectra of **PBT-NH$_2$** (a), **PBT-NHMe** (b), **PBT-NHAc** (c) and **PBT-NHTs** (d) at the spectral region of N_1-H stretching band in both S_0 and S_1 states at (TD)B3LYP/6-311+G(d, p)/IEFPCM (dichloromethane) theory level.