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

Dapeng Yang1,3,*, Guang Yang1, Min Jia1, Xiaoyan Song1, Qiaoli Zhang1, Tianjie Zhang1

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 ESIIPT) 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-H•••N 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 ESIIPT 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 ESIIPT reaction, while the involvement of an electron-donating methyl group has slight opposite effect on the ESIIPT process of the amino-type hydrogen-bonding system.

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

1. Introduction

Excited state intramolecular proton transfer (ESIIPT) 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 (ESIIPT) reactions of the hydroxyl-type hydrogen-bonding (H-bonding) systems using hydroxyl as a proton donor [1-8]. It is well-known that the ESIIPT 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 ESIIPT 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 ESIIPT [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 ESIIPT 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 ESIIPT 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 ESIIPT process [20]. In the presence of strong electron-withdrawing tosyl group that directly replaces one of

\[ \text{NH}_2 \quad \text{NH} \quad \text{NH} \quad \text{NH} \]

\[ \text{NHMe} \quad \text{NHAc} \quad \text{NHTs} \]

Scheme 1. Geometrical structures of PBT-NH2, PBT-NHMe, PBT-NHAc and PBT-NHTs.
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 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 H-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 S₀ and the first singlet excited state S₁ 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 S₀ and first singlet excited state S₁ are listed in Table 1. For comparisons, we named the intramolecular hydrogen bonds within the four amino-type H-bonding compounds all as N₁-H•••N₂. From Table 1, it can be found that, from ground state S₀ to first singlet excited state S₁, the bond lengths of N₁-H in all the four amino-type H-bonding compounds are all increased, whereas those of hydrogen bond H•••N₂ are all decreased. At the same time, the bond angles...