

Theoretical insights into the excited state hydrogen bond and ESIPT reaction for 2-amino-3-(2'-benzoxazolyl)quinoline and 2-amino-3-(2'-benzothiazolyl)-quinoline

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Abstract. Two N-H type excited state intramolecular proton transfer (ESIPT) systems (i.e., 2-amino-3-(2'-benzoxazolyl)quinoline (ABO) and 2-amino-3-(2'-benzothiazolyl)-quinoline (ABT)) have been investigated. Adopting DFT and TDDFT methods coupling with B3LYP functional and TZVP basis set, our simulations about ABO and ABT molecules have successfully reappraised experimental results, based on which the rationality of our calculations is confirmed. Using Atoms in Molecules (AIM) analytical method, we firstly explore the interactions about chemical bond and verify the formation of hydrogen bond N-H...N for ABO and ABT in the S_0 state. Investigating the primary geometrical parameters involved in N-H...N, we find it should be strengthened in the S_1 state. Upon photoexcitation, charge transfer phenomenon is found via frontier molecular orbitals (MOs), and charge redistribution provides the tendency of ESIPT reaction for ABO and ABT. According to our constructed potential energy curves of both S_0 and S_1 states for ABO and ABT using two kinds of methods (i.e., the elongation of N-H single bond and the weakening of H...N hydrogen bond), we clarify the ESIPT mechanisms and explain the recovery of four-level reaction cycle. Our searching transition state (TS) structures and simulated intrinsic reaction coordinate (IRC) path further confirm the ESIPT reaction.

Keywords: Weak Interaction; Hydrogen Bond; ESIPT; Charge Redistribution.

1. Introduction

It is well known that hydrogen bond should be one of the most primary weak interactions in natural world, which makes our life-cycle to be sustained in the world [1-3]. Hydrogen bonds play significant roles in stabilization of the secondary structures of biomolecules such as proteins, DNA, RNA, and so on. Generally speaking, a double effect can be found in biological systems. On one hand, in the form of strong directional interaction, it can result in the stable supramolecular architectures that are inevitable for the construction of elementary building blocks of our life. On the other hand, it can serve as an active site for the occurrence of a vista of interactions. Thus the investigations about hydrogen bonding interactions would be vital to delve into the critical evaluation of many phenomenon occurring in crystal, in solvent phase, and in living organisms [4-6]. As a fundamental class of photochemistry, proton transfer (PT) is ubiquitous as an elementary reaction throughout nature [7], which occurs along with a pre-existing intra- or inter- molecular hydrogen bond wire. Generally, the photo-induced solvent-solute PT processes could be considered to become a series of fundamental steps, as described by Eigen-Weller mechanism, i.e., the electronic redistribution, ion-pair formation, hydrogen bonding rearrangement processes [8, 9]. Recently, with the

perpetual development of experimental techniques and measure, more and more attention has turned to the excited state dynamical behaviors. By the light of nature, excited state intra- or inter- molecular proton transfer (ESIPT) reactions have attracted much attention [10-19].

To the best of knowledge, the ESIPT represents a complicated photo-tautomerization process and usually involves the transfer of a hydroxyl/imino proton from the pre-existing hydrogen bond wire to the oxygen or nitrogen acceptor in the excited state, which can lead to a new isomer dubbed as the proton-transfer tautomer or the photo-tautomer [20-25]. Basically, upon the photo-excitation process, the normal stable ground-state structure (enol) could be excited to the excited state. After the thermal relaxation, the most stable form (enol*) in the S_1 state should be formed with

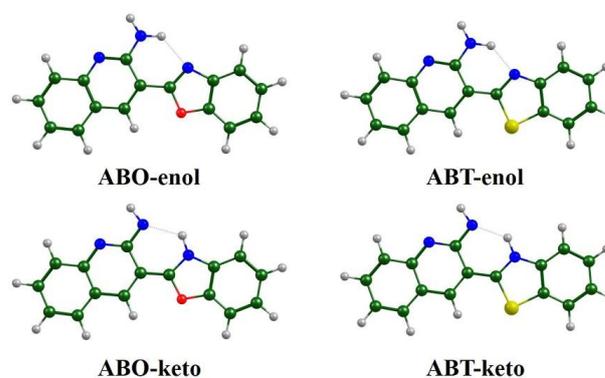


Figure 1: View of the geometrical structures of ABO-enol, ABO-keto, ABT-enol and ABT-keto. Herein, Green: C atoms; Gray: H atoms; Blue: N atoms; Red: O atoms; Greenyellow: S atoms.

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the normal fluorescence. In the process of the ESIPT reaction, enol* can convert into the excited photo-tautomer (keto*). And the keto* structure can be recognized by emission spectrum in experiment due to the longer wavelength fluorescence (the Stokes shift can be as large as $8000 \sim 12000 \text{ cm}^{-1}$) [26-30]. Due to the drastic structural alternations, the photo-tautomers keto* owns different photochemical and photophysical properties from that of the initial enol* species. Just due to the novel characteristics of keto* structure, great versatility could be offered in varieties of applications, such as lasing materials, fluorescent sensors, photostabilizers, solid state emitters, and so on [31-38].

In fact, in the field of ESIPT reactions, most of them refer to the O-H type hydrogen bond. And the investigations indicate that only a few reports have reported the amino-type ESIPT using amine as the proton donors [39-45]. Generally, the amino proton owns much weaker acidity than the hydroxyl proton in the S_0 state [46]. And a similar acidity tendency is expected in the excited states; therefore, the ESIPT rarely occurs in the N-H hydrogen bonding systems unless the acidity of N-H can be enhanced via suitable chemical modifications. Particularly, Chou and coworkers have detailed investigated this aspect in recent years [47-49]. Based on different electron-withdrawing and electron-donor groups, the ESIPT process along with N-H hydrogen bonding wires might be harnessed. Khimich et al. designed and explored the absorption and emission spectra as well as the relative fluorescence quantum yields about two systems (i.e., 2-amino-3-(2'-benzoxazolyl)quinoline (ABO) and 2-amino-3-(2'-benzothiazolyl)-quinoline (ABT)) experimentally [50]. The N-H type ESIPT reactions might exist in ABO and ABT system. And recently, Khimich et al. further investigated the steady-state spectra of ABO and ABT structures under different temperatures and confirmed the different photochemical properties bringing from temperatures [51, 52], while the detailed ESIPT mechanism for both ABT and ABO is absent. To the best of our knowledge, the experimental spectroscopic techniques could just provide the one-sided information about excited state behaviors such as the photophysical and photochemical properties. Further, as a kind of N-H type

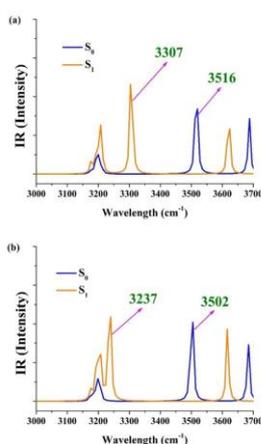


Figure 2: The calculated IR spectra of N-H vibrational mode for ABO-enol (a) and ABT-enol (b) systems in both S_0 and S_1 states under the DFT//TDDFT/B3LYP/TZVP theoretical level.

ESIPT systems, the excited state processes of ABO and ABT might be modified via chemical positions, which may facilitate other applications in future. Thus, as the fundamental aspect, the specific ESIPT mechanism and process for ABO and ABT structure should be principle.

To explore and clarify the explicit excited state dynamical behaviors for both ABO and ABT system, in this present work, a detailed quantum chemical computational calculations have been performed. Adopting density functional theory (DFT) and time-dependent density functional theory (TDDFT) methods, we mainly focus on the fundamental aspects concerning the different electronic states and relative structures involved in the ESIPT reactions. And the remainder of this paper can be organized such that the next section describes the theoretical details. Section 3 presents the discussions and results about ABO and ABT systems including the geometrical analyses, electronic spectra, the charge distributions and potential energy curves. And lastly, a final section provides a summary and conclusion of this present work.

2. Computational Methods

All the calculations have been carried out using DFT and TDDFT methods with the Becke's three-parameter hybrid exchange function with the Lee-Yang-Parr gradient-corrected correlation functional (B3LYP) [53-55] as implemented in the Gaussian 09 program [56]. And after testing basis sets, the triple- ζ valence quality with one set of polarization function (TZVP) has been

Table 1. The calculated bond lengths (\AA) and angles ($^\circ$) involved in intramolecular hydrogen bond N-H...N for ABO-enol, ABO-keto, ABT-enol and ABT-keto forms in S_0 and S_1 states based on the DFT//TDDFT B3LYP/TZVP theoretical level.

| | ABO-enol | | ABO-keto | | ABT-enol | | ABT-keto | |
|------------------------------------|----------|-------|----------|-------|----------|-------|----------|-------|
| | S_0 | S_1 | S_0 | S_1 | S_0 | S_1 | S_0 | S_1 |
| N-H | 1.010 | 1.025 | 1.010 | 2.009 | 1.011 | 1.028 | 1.011 | 1.880 |
| H...N | 2.015 | 1.918 | 2.015 | 1.021 | 1.971 | 1.861 | 1.971 | 1.030 |
| $\delta(\text{N-H}\cdots\text{N})$ | 130.9 | 134.5 | 130.9 | 122.8 | 131.0 | 135.6 | 131.0 | 130.4 |

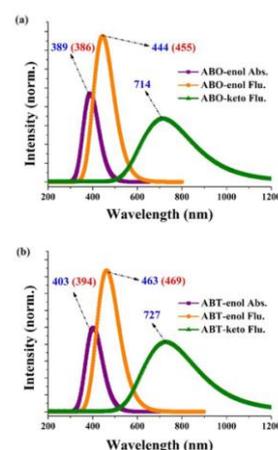


Figure 3: Our calculated absorption and emission spectra of ABO and ABT systems based on the TDDFT/B3LYP/TZVP theoretical level. Herein, the blue values indicate our theoretical results and the red values in brackets stand for the experimental results