



DFT-TDDFT investigation of excited-state intramolecular proton transfer in 2-(2'-hydroxyphenyl)benzimidazole derivatives: Effects of electron acceptor and donor groups



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ABSTRACT

The excited-state intramolecular proton transfer (ESIPT) reactions of 2-(2'-hydroxyphenyl)benzimidazole (HBI) derivatives were investigated using time-dependent density functional theory (TD-DFT) method at B3LYP/TZVP theoretical level. The geometric parameters, infrared (IR) vibrational spectra, frontier molecular orbitals (MOs), Mulliken charge distribution analysis, natural bond orbital (NBO) analysis and potential energy curves were calculated to provide the direct information about the effect of electron acceptor and donor groups on the ESIPT reactions. The intramolecular hydrogen bonds are significantly strengthened and the electronic density is redistributed after a vertical excitation to S_1 state. The proton transfer (PT) reactions are unlikely occur in S_0 state through the analysis of potential energy curves and the Hartree-Fock energy of the stable structures. The presence of the electron acceptor $-\text{NO}_2$ group can facilitate the ESIPT reaction, while the presence of electron donor $-\text{NH}_2$ group can hinder the ESIPT reaction. In general, the electron acceptor $-\text{NO}_2$ group and electron donor $-\text{NH}_2$ group can influence the ESIPT reactions in a completely different way.

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1. Introduction

Excited state intramolecular proton transfer (ESIPT) reaction dynamic was investigated both experimentally and theoretically by many groups since the first experimental observation of the phenomenon by Weller and co-workers in 1965 [1–8]. The researchers studied the fundamental photophysics, proton transfer dynamics, pico-second kinetics, kinetics and thermodynamics at the singlet state, femtosecond and time-resolved ESIPT fluorophores [9–11]. As one of the most important elementary reactions in chemistry and biology [12–14], the ESIPT has been widely applied in molecular probes [15], molecular logic gates [16], luminescent materials [10, 17–19], metal ion sensors [20–22], radiation hard-scintillator counters and organic light emitting devices (OLEDs) [23–25]. The fundamental requirement of the ESIPT reaction occurs is the presence of strong intramolecular hydrogen bond between the acidic proton ($-\text{OH}$, $-\text{NH}_2$) and the basic moiety ($\text{C}=\text{N}$, $\text{C}=\text{O}$) in the molecular system [26], such as 2-(2'-hydroxyphenyl)benzoxazole (HBO) [27, 28], 2-(2'-hydroxyphenyl)benzothiazole (HBT) [29,30], 2-(2'-hydroxyphenyl)benzimidazole (HBI) [31]. The intramolecular hydrogen bond is significantly strengthened in the excited state, which

provides a driving force in facilitating the ESIPT reaction [29,32]. Upon photo-excitation, the electronic density is redistributed to make acceptor atom (usually nitrogen) to be more basic, which can also facilitates the proton transfer from donor (oxygen or nitrogen) atom to the acceptor atom [33]. The ESIPT reaction is extremely fast with a time scale of $k_{\text{ESIPT}} < 10^{12} \text{ s}^{-1}$ and can occur even in rigid glass at very low temperature [34]. To better elucidate the transfer mechanisms, density functional theory (DFT) and time-dependent density functional theory (TD-DFT) methods were adopt to investigate the ESIPT reaction [35].

As a type of proton transfer dye, HBO has emerged to be an interesting material, due to its structural simplicity and facile chemical modification properties [28,36,37]. When an electron-acceptor or -donor substituent is present in the molecular framework, the properties of the ESIPT can be changed [38]. For HBO and HBT derivatives, which contain an electron acceptor substituent ($-\text{NO}_2$, $-\text{COOH}$, $-\text{COOR}$ or $-\text{RCN}$) in the benzazole ring, the proposed mechanism is a proton motion followed by an intramolecular charge transfer process [39–41]. When the substituent is an electron donor group ($-\text{NH}_2$, $-\text{NR}_2$ or $-\text{CH}_3$), such as 2-(2'-hydroxy-4'-diethylaminophenyl)benzothiazole, the intramolecular charge transfer process occurs prior to the ESIPT [42]. Recently, the effect of electron donor and acceptor groups on the excited state intramolecular proton transfer of HBI derivatives in solvents of different polarities has been studied both experimentally and theoretically by Padalkar and co-workers [43]. The absorption and emission wavelengths of HBI derivatives in different solvents were

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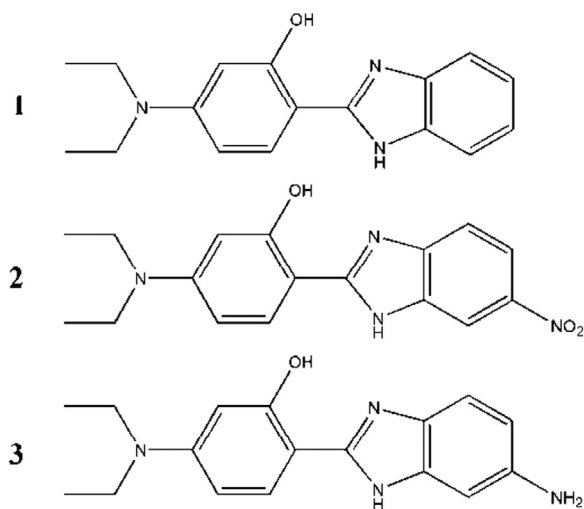


Fig. 1. HBI derivatives 1–3.

computed. The structural properties of HBI derivatives and the effect of solvent polarity on ground and excited state dipole moments have also been discussed. However, there are several deficiencies in the previous work. Firstly, a lack of the discussion about the important role of the intramolecular hydrogen bond plays in the ESIPt reaction. Secondly, the charge redistribution in the electronic excited state was not taken into account. Last but not least, the detailed information about the effect of electron donor and acceptor groups on the ESIPt reaction was absent.

Therefore, in order to provide detailed and unambiguous information about the effect of electron donor and acceptor groups on the ESIPt of HBI derivatives (shown in Fig. 1), a theoretical investigation has been performed based on the DFT and TD-DFT methods. The configurations of the S_0 and S_1 states were optimized, and the geometric parameters were obtained. The IR vibrational spectra, frontier molecular orbitals (MOs), Mulliken charge distribution analysis, natural bond orbital (NBO) analysis and potential energy curves were calculated to provide the direct information about the effect of electron donor and acceptor groups on the ESIPt reaction.

2. Computational details

In the present work, all theoretical calculations were carried out using the Gaussian 09 program suite [44]. The electronic geometric optimizations of HBI derivatives were performed using DFT and TD-DFT methods with Becke's three-parameter hybrid exchange functional with Lee–Yang–Parr gradient-corrected correlation functional (B3LYP) and triple- ζ valence quality with one set of polarization functions (TZVP) [45–47]. Considering that the experiments were conducted in solvent, the dichloromethane (DCM) was selected as the solvent based on the Polarizable Continuum Model (PCM) using the integral equation formalism of the Polarizable Continuum Model (IEFPCM) [48–50]. The vibrational frequencies were calculated using the same method to verify that the optimized structures correspond to the local minima on the energy surface. There were no constraint to all the atoms, bonds, angles and dihedral angles during the geometric optimization. In addition to the unconstrained optimization, constrained calculations on the S_0 and S_1 potential energy curves of the HBI derivatives were scanned keeping the O–H bond lengths fixed at values in the range from 0.99 Å to 2.15 Å in steps of 0.05 Å.

3. Results and discussion

3.1. Optimized geometric structures

The configurations of enol-tautomer and keto-tautomer of the HBI derivatives were optimized at the B3LYP/TZVP basis set level (shown in Fig. 2), with a subsequent vibrational frequency analysis to ensure they are at the minima. The bond lengths and bond angles of these structure parameters were listed in Table 1. The bond lengths of O–H for compound 1 increase by 0.006 Å from S_0 state enol (0.997 Å) to S_1 state enol (1.003 Å) and the H–N hydrogen bonding lengths decrease by 0.022 Å from S_0 state enol (1.711 Å) to S_1 state enol (1.689 Å). For compound 2 and 3, the bond lengths of O–H increase by 0.010 Å (from 0.994 Å to 1.004 Å) and 0.003 Å (from 0.997 Å to 1.000 Å), and the hydrogen bonding lengths of H–N decrease by 0.048 Å (from 1.728 Å to 1.680 Å) and 0.008 Å (from 1.710 Å to 1.702 Å), respectively. In addition to this, the bond angles of O–H–N for compound 1–3 are 148.5°, 147.8° and 148.7°, respectively. While, the bond angles are

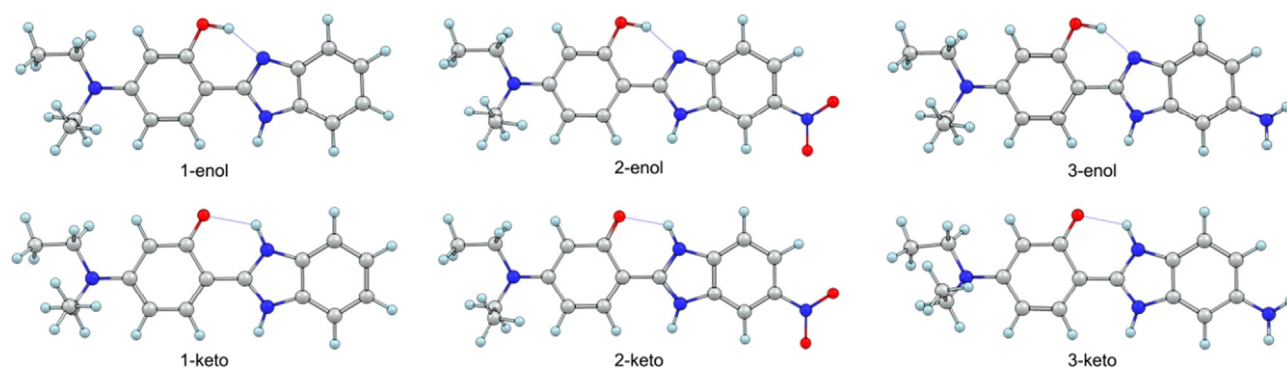


Fig. 2. The optimized enol and keto-tautomer structures of the HBI derivatives 1–3 at the B3LYP/TZVP theoretical level.

Table 1

The calculated geometric parameters (bond lengths in Å and angles in°) for HBI derivatives 1–3 in S_0 and S_1 states based on the DFT and TD-DFT methods, respectively.

	1-enol		1-keto		2-enol		2-keto		3-enol		3-keto	
Electronic state	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1
O–H	0.997	1.003	1.729	1.991	0.994	1.004	1.700	1.943	0.997	1.000	1.736	1.911
H–N	1.711	1.689	1.038	1.016	1.728	1.680	1.043	1.016	1.710	1.702	1.037	1.020
$\delta(\text{O–H–N})$	148.5	150.1	134.4	124.1	147.8	150.5	135.3	125.8	148.7	150.3	134.2	127.2

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