

## APPENDIX A

### Definitions

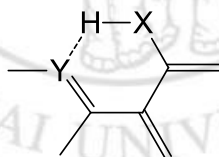
#### 1. Calculation of Reaction Probability

Reaction probability of each system is calculated from all active ESPT trajectories divided by a total number of trajectories.

$$\text{Reaction probability} = \frac{\text{Number of the ESPT reaction trajectories}}{\text{Total number of trajectories}}$$

#### 2. Proton Transfer Time

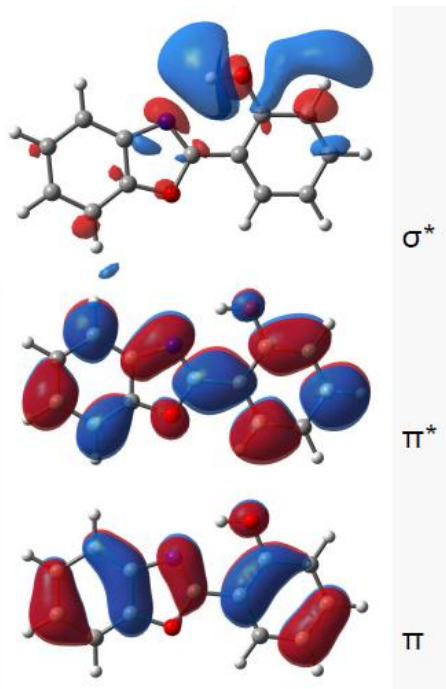
The proton transfer time is an intersection point between the average breaking bond (X–H) and the average forming bond (H–Y) in Å.



Interested part of the molecule used for determining proton transfer time

#### 3. Definition of Proton Transfer and Hydrogen-Atom Transfer

All active excited-state proton transfer trajectories were analyzed. The analysis shows that the first excited state is always characterized by a  $\pi\pi^*$  transition. This implies that the dynamics along the first excited state takes place purely in the  $\pi\pi^*$  state, characterizing a *proton transfer process* and there are rare contributions from  $n\pi^*$  states. However, no  $\pi\sigma^*$  state (a *hydrogen-atom transfer process*) is found in this work.



Molecular orbital of HBO molecule at  $\pi$ ,  $\pi^*$ , and  $\sigma^*$  states

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## **APPENDIX B**

### **Scholarships**

#### **Selected Poster Presentations**

- 1) 14 – 18 January 2013: the ‘The Winter School of Sokendai/Asian CORE Program’  
National Institutes for Natural Sciences, Japan
- 2) 13 – 16 January 2015: the ‘The Winter School of Sokendai/Asian CORE Program’  
National Institutes for Natural Sciences, Japan
- 3) 6 – 10 March 2015: the ‘Asian Academic Seminar and School 2015’, Kolkata,  
India with financial supported by Institute of Molecular Sciences, Japan

#### **Short-Term Visits**

- 1) 21 April – 21 July 2013: Three-month cooperation exchange research in Nagoya  
University, Nagoya, Japan with financial supported by Graduate School of  
Science, Nagoya University, Japan
- 2) 1 September 2014 – 31 August 2015: Cooperation exchange research in Nagoya  
University, Nagoya, Japan with financial supported by Science Achievement  
Scholarship of Thailand (SAST)

## APPENDIX C

### Conferences and Workshops

#### Poster and Oral Presentations

- 1) 14 – 18 January 2013: Poster presentation at ‘The Winter School of Sokendai/ Asian CORE Program’ National Institutes for Natural Sciences, Higashi-Okazaki, Japan
- 2) 23 - 25 January 2013: Poster presentation at ‘Pure and Applied Chemistry International Conference (PACCON2013)’ at The Tide Resort, Burapha University, Chonburi
- 3) 22 February 2013: Poster presentation at ‘RGJ Seminar Series XCIV Materials Science for the Sustainable Society’ at SCB2, Faculty of Science, Chiang Mai University, Chiang Mai
- 4) 9 – 12 December 2013: Poster presentation at ‘International Workshop on Frontiers of Theoretical and Computational Physics and Chemistry (WFTCPC 2013)’ at the Tide Resort, Chonburi
- 5) 21 – 23 August 2014: Poster presentation at ‘The 2<sup>nd</sup> International Conference on Computational Science and Engineering (ICCSE-2014)’ at Rex Hotel, Ho Chi Minh City, Vietnam
- 6) 13 – 16 January 2015: Poster presentation at ‘The Winter School of Sokendai/ Asian CORE Program’ National Institutes for Natural Sciences, Higashi-Okazaki, Japan
- 7) 6 – 10 March 2015: Poster presentation at Asian Academic Seminar and School 2015, Kolkata, India

- 8) 8 – 13 June 2015: Poster presentation at the 15th International Congress of Quantum Chemistry, (15th ICQC), Tsinghua, Beijing, China
- 9) 17 – 19 June 2015: Oral presentation at 19th International Annual Symposium on Computational Science and Engineering (ANSCSE19)' at Ubon Ratchathani University, Ubon Ratchatani
- 10) 9 – 11 February 2016: Poster presentation at 'Pure and Applied Chemistry International Conference (PACCON2016)' at BITEC, Bangkok

### **Workshops**

- 1) 14 – 17 October 2013 : 'The 10<sup>th</sup> Thai Summer School on Computational Chemistry (10-TS<sub>2</sub>C<sub>2</sub>)' at Kasetsart University, Sriracha Campus, Chonburi
- 2) 26 – 27 September 2015 : 'SAST camp for the graduate students' at the Royal River Hotel, Bangkok
- 3) 24 – 27 November 2015 : 'Molecular Designs for Advanced Materials: Workshop and Conference' at Chiang Mai University, Chiang Mai
- 4) 24 – 27 November 2015 : Organizer of 'Molecular Designs for Advanced Materials: Workshop and Conference' at Chiang Mai University, Chiang Mai

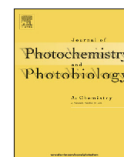
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## APPENDIX D

### Publications and Posters



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## Dynamics simulations of excited-state triple proton transfer in 7-azaindole complexes with water, water–methanol and methanol



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7-Azaindole

ADC(2)

### ABSTRACT

Excited-state triple proton transfer (ESTPT) reactions in 7-azaindole (7AI) complexed with two water, with one water and one methanol, and with two methanol molecules were investigated by dynamics simulations in the first excited state computed with the second order algebraic-diagrammatic construction (ADC (2)) method. The results show that photoexcitation may trigger ultrafast an asynchronous concerted proton transfer via two solvent molecules along an intermolecular hydrogen-bonded network. The probability of occurrence of ESTPT ranges from 32% for 7AI(H<sub>2</sub>O–MeOH) to 64% for 7AI(MeOH)<sub>2</sub>. The average time for completing the ESTPT varies between 58 and 85 fs depending on the complex. The proton transfer (rather than hydrogen transfer) nature of the reaction was suggested by the nonexistence of crossings between the  $\pi\pi^*$  and  $\pi\sigma^*$  states.

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### 1. Introduction

Excited-state proton transfer (ESPT) [1,2] is one important class of reactions in physical, chemical and biological phenomena, with uses in fluorescent probes [3–5], photostabilizers [6] and light-emitting devices [7,8]. Among many molecules undergoing ESPT, 7-azaindole (7AI) has been the most widely investigated by experimental and theoretical techniques [9–36]. All this attention paid to 7AI is owed to its potential as a model system for studying ESPT phenomena in several instances, such as DNA mutagenesis, proton relay in enzymes, and proton transport through membranes [37]. A more complete understanding of the multiple proton transfer processes occurring in 7AI complexed with solvent partners may shed the light on the occurrence of these important phenomena.

7AI is a bicyclic azaaromatic molecule comprising a pyrrole (proton donor) and a pyridine (proton acceptor) rings (Fig. 1). The proton donor and proton acceptor sites can form a hydrogen-bonded network upon dimerization in nonpolar solvents and in complexation with protic solvents such as ammonia, water and alcohol. The excited-state tautomerization of 7AI within water

has been intensively studied in the condensed and gas phases with experimental and theoretical methods [21,23,30,38–41]. The excited-state multiple proton transfers in 7AI complexed with alcohol has been also thoroughly studied [15,21,22,29,32,42]. Most previous theoretical studies related to 7AI, however, were focused only on static calculations either in the ground state or excited state. Therefore, these studies could not provide a time-dependent picture of the proton transfer (PT) or hydrogen transfer (HT) reaction pathways. (The nature of the transfer, whether it is a PT or HT, depends on the energy of the  $\pi\pi^*$  and  $\pi\sigma^*$  states, as PTs occur along the  $\pi\pi^*$  state whereas HTs occur along the  $\pi\sigma^*$  state [43,44]. We will show that for the 7AI complexes investigated here, PT most likely takes place.)

To the best of our knowledge, there has been no theoretical investigation reported on the intermolecular ESPT dynamics in 7AI within mixed solvents such as water–methanol. 7-Hydroxyquinoline (7HQ) with mixed ammonia/water solvent-wire clusters was reported by Tanner et al. [44–46]. Their results showed that replacing NH<sub>3</sub> molecule with one or two water molecules stopped the hydrogen-atom transfer along the solvent wires. For 7AI with water, Kina et al. [40] performed dynamics simulations at the CASSCF level to study complexes with up to two water molecules and simulations at the CASSCF/MM level to investigate water solvation effects. Their results showed that the complete ESPT process was reached around 50 fs in 7AI(H<sub>2</sub>O) and in the range of 40–60 fs

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## Theoretical study on excited-state intermolecular proton transfer reactions of 1*H*-pyrrolo[3,2-*h*]quinoline with water and methanol

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**Abstract** The dynamics of the ultrafast excited-state multiple intermolecular proton transfer (PT) reactions in gas-phase complexes of 1*H*-pyrrolo[3,2-*h*]quinoline with water and methanol (PQ(H<sub>2</sub>O)<sub>*n*</sub> and PQ(MeOH)<sub>*n*</sub>, where *n* = 1, 2) is modeled using quantum-chemical simulations. The minimum energy ground-state structures of the complexes are determined. Molecular dynamics simulations in the first excited state are employed to determine reaction mechanisms and the time evolution of the PT processes. Excited-state dynamics results for all complexes reveal synchronous excited-state multiple proton transfer via solvent-assisted mechanisms along an intermolecular hydrogen-bonded network. In particular, excited-state double proton transfer is the most effective, occurring with the highest probability in the PQ(MeOH) cluster. The PT character of the reactions is suggested by nonexistence of crossings between  $\pi\pi^*$  and  $\pi\sigma^*$  states.

**Keywords** ADC(2) dynamics simulation · Excited-state proton transfer (ESPT) · Excited-state tautomerization · Solvent-assisted proton transfer · 1*H*-Pyrrolo[3,2-*h*]quinoline

### 1 Introduction

The proton transfer (PT) is one of the most important classes of chemical reactions [1, 2]. Because PT processes often take place within hydrogen-bonded systems, and because of the central role played by hydrogen bonds in chemistry and biology, a large number of studies have been performed on PT processes in both the ground and excited states [3, 4]. A special class of compounds exhibiting PT is represented by heteroaromatic molecules [5–7]. In particular, heteroazaaromatic or bifunctional molecules having a hydrogen-bonding donor group (e.g., a pyrrole NH) and a hydrogen-bonding acceptor group (e.g., a quinoline-type N) are of great interests for their dual photochromic properties in a variety of solvents. Examples of molecules exhibiting intramolecular PT are salicylic acid and its derivatives [8]. Naturally, intramolecular PT will occur preferentially when the spatial separation between the donor and the acceptor sites is small [9, 10]. In the case of a larger separation, the PT should proceed through a hydrogen-bond bridge established within a protic solvent. The phenomenon of phototautomerization is driven by a PT process which may occur either in an intramolecular [11–14] or in an intermolecular [5–7, 9, 10, 15–17] manner. Thus, hydrogen-bonding networks of these molecules with the solvent must be formed before molecules undergo excited-state proton transfer (ESPT). The heteroazaaromatic molecule requires a catalytic transfer via a one-molecule hydrogen-bonded proton-donor–acceptor bridge,

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# Effects of the second hydration shell on excited-state multiple proton transfer: dynamics simulations of 7-azaindole: (H<sub>2</sub>O)<sub>1–5</sub> clusters in the gas phase

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**Abstract** Dynamics of the multiple excited-state proton transfer (ESPT) in clusters of 7-azaindole with up to five water molecules was investigated with quantum chemical methods. The ultrafast excited-state dynamics triggered by photoexcitation was simulated with the algebraic diagrammatic construction to the second-order scheme. Multiple ESPT through a hydrogen-bonded network is observed in the 100-fs scale. The probability of tautomerization is anti-correlated with the maximum free energy barrier in the excited state. An increasing number of water molecules tends to reduce the barrier by strengthening the hydrogen-bonded network. Barrierless reactions are found already for clusters with four waters. In structures presenting double hydrogen bond circuits, proton transfer happens mostly through the internal circuit by triple proton transfer. The overall role of the second hydration shell is of

stabilizing the network, facilitating the proton transfer in the internal circuit. Proton transfers involving the second hydration shell were observed, but with small probability of occurrence. The proton-transfer processes tend to be synchronous, with two of them occurring within 10–15 fs apart.

**Keywords** On-the-fly dynamics simulation · Excited-state proton transfer · Excited-state tautomerization · Water-assisted proton transfer · Hydrogen bond rearrangement · 7-Azaindole · ADC(2)

## 1 Introduction

Proton transfer plays crucial roles in a variety of chemical and biological reactions [1–5] such as enol–keto tautomerization [6], proton transport via membrane-spanning proteins [7, 8], and proton relay system in enzymes [8]. The phototropic tautomerism of DNA base pairs, which has attracted much interest due to its relation to UV-induced gene mutation, has the excited-state proton-transfer (ESPT) phenomena as the primary molecular step [9]. Generally, it is specially challenging to monitor ESPT in natural nucleobases and nucleobase pairs due to their conformational and spectroscopic complexity [10, 11]. In this context, 7-azaindole (7AI, Fig. 1), a spectroscopically simpler prototype for purine nucleobases [9], emerges as a good alternative for basic sciences research. It has also been claimed that 7AI can advantageously replace tryptophan, customarily considered as the standard optical probe of protein structure and dynamics [12–14]. As a result, ESPT in 7AI monomer within small molecular clusters and in bulk solvents has been extensively studied by experimentalists and theorists [9, 11, 15–38].

Dedicated to the memory of Professor Isaiah Shavitt and published as part of the special collection of articles celebrating his many contributions.

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## Dynamics simulations of photoinduced proton transfer reactions of 2-(2'-hydroxyphenyl)benzoxazole in the gas phase and its hydrated clusters



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### ABSTRACT

The excited-state dynamics simulations of 2-(2'-hydroxyphenyl)benzoxazole (HBO) and hydrated HBO were performed on their lowest energy structures using RI-ADC(2)/SVP-SV(P). For free HBO, only *syn*-HBO can undergo tautomerization in the excited state. For HBO(H<sub>2</sub>O), two different pathways (A) the excited-state intramolecular proton transfer (PT) and (B) the excited-state intermolecular PT through hydrogen-bonded network occur. PT time of free HBO is ultrafast at 28 fs, whereas, the PT time of HBO(H<sub>2</sub>O) takes longer with time range of 43–193 fs depending on the initial structure. The slow PT process of HBO(H<sub>2</sub>O) is caused by competition between formations of intra- and intermolecular hydrogen bonds.

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### 1. Introduction

The excited-state intramolecular proton transfer (ESIntraPT) is one of the most fundamental and important processes due to its photophysical properties [1,2]. The applications of ESIntraPT are found in many applications such as organic light emitting diodes [3], luminescent materials [4,5], and fluorescent probes [6,7]. Most of the ESIntraPT processes occur in molecules having a strong intramolecular hydrogen bond between the acidic proton (O—H, —NH<sub>2</sub>) and the basic moiety (C=N, C=O), and the suitable geometry such as 2-(2'-hydroxyphenyl)benzoxazole (HBO) [8–15], 2-(2'-hydroxyphenyl)benzothiazole (HBT) [16–21], and 2-(2'-hydroxyphenyl)benzimidazole (HBI) [22,23]. Generally in the ground state, the enol form of these molecules is stable because the phenolic proton is not acidic enough to be deprotonated, implying that tautomerization does not occur in the ground state [14]. Upon photoexcitation, however, the proton transfer (PT) reaction from the excited enol occurs to give the excited keto tautomer in sub-picosecond timescale [8–15] (Scheme 1). Among these molecules exhibiting ESIntraPT as shown in Scheme 1, HBO (in Figure 1) is found to be an interesting system [8–15] because of its high quantum efficiency [21] compared to those of HBT and HBI. HBO comprises the hydroxyl group (O—H acting as a proton donor) and the benzoxazole group (a nitrogen atom acting as a proton acceptor). The O—H group of a proton donor and the N atom of

an acceptor in HBO form an intramolecular hydrogen bond and exhibit a large Stokes shift arising from ESIntraPT [8–15].

To utilize HBO as organic light emitting and fluorescent probing materials, the complete understanding of its photophysical properties of ESIntraPT in the gas phase and in solution is important [8,15,24,25]. Possible conformations of enol HBO have been identified [12,24] as shown in Figure 1a: *syn*-HBO or **I** (intramolecular O—H...N hydrogen bond), *anti*-HBO or **II** (intramolecular O—H...O hydrogen bond), and opened HBO or **III** (no intramolecular hydrogen bond) and only *syn*-HBO (**I**) can give the keto tautomer through the ESIntraPT process [4,8,12,13,24]. This process is known to occur in a femtosecond timescale [25] and the time constant of 60 ± 30 fs (in cyclohexane) of *syn*-HBO (**I**) using time-resolved spectrometry was reported [9]. It has been observed that in the presence of polar solvents, especially polar protic solvents, the formation of strong intermolecular hydrogen bond between HBO and solvents might play a significant role in changing its photophysical characteristics [8,15,24,25]. For solvated enol HBO, the formations of inter- and intramolecular hydrogen bonds between HBO and solvents are shown in Figure 1b: intramolecular hydrogen-bonded structure or **IV** (without an intermolecular hydrogen-bonded network), intermolecular hydrogen-bonded structure or **V** (water forming an intermolecular hydrogen-bonded network between the —OH and —N atom in the benzoxazole moiety), and opened-HBO or **VI** (intermolecular hydrogen bonding with water). Moreover, different PT pathways either ESIntraPT or excited-state intermolecular PT (ESInterPT) can occur depending on the initial structure.

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## Excited-state proton-transfer reactions of 7-azaindole with water, ammonia and mixed water–ammonia: microsolvated dynamics simulation

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Dynamics simulations of excited-state multiple proton transfer (ESMPT) reactions in 7-azaindole (7AI) with ammonia, mixed water–ammonia, and water molecules were investigated by quantum dynamics simulations in the first-excited state using RI-ADC(2)/SVP-SV(P) in the gas phase. 7AI(WW), 7AI(WA), 7AI(AW) and 7AI(AA) clusters (W, water and A, ammonia) show very high probability of the excited-state triple proton transfer (ESTPT) occurrence in ranges from 20% for 7AI(WA) to 60% for 7AI(AW), respectively. Furthermore, 7AI(AW) clusters with ammonia placed near N–H of 7AI has the highest probability among other isomers. In 7AI with three molecules of bridged-planar of water, ammonia and mixed water–ammonia clusters, the excited-state quadruple proton transfer reactions occur ineffectively and rearrangement of hydrogen-bonded network on solvents also takes place prior to either ESTPT or excited-state double proton transfer. The role played by mixed-solvent is revealed with replacing H<sub>2</sub>O with NH<sub>3</sub> in which the ESMPT is found to be more efficient corresponding to lower barrier in the excited state. The preferential number of solvent surrounding 7AI that facilitates the proton transfer process is two for methanol and water but this preferential number for ammonia is one.

Highlights: (i) replacing H<sub>2</sub>O with NH<sub>3</sub> assists ESPT corresponding to lower barrier in the excited state; (ii) the ESMPT time of 7AI with mixed water–ammonia is in the sub-picosecond timescale; (iii) the PT tends to be concerted process with at least one ammonia, but synchronous without ammonia.

**Keywords:** excited-state proton transfer; 7-azaindole; RI-ADC(2); mixed water–ammonia; solvent-assisted molecule

### 1. Introduction

7-Azaindole (7AI) is a bicyclic azaaromatic molecule consisting of a pyrrole (proton donor) ring and a pyridine (proton acceptor) ring. 7AI has proven to be an important model system for the study of excited-state proton transfer (ESPT), which is of key importance to a variety of chemical and biological processes such as proton relay systems in enzymes, ion channels and membrane-spanning proteins ('proton wires'). [1–3] Besides, there are many applications related to ESPT such as fluorescent probes, [4–6] photostabilisers [7] and light-emitting devices. [8–9] The proton donor and proton acceptor sites of 7AI can form a hydrogen-bonded network upon complexation with protic solvents as depicted in Figure 1. Generally, a direct experimental probing of ESPT in 7AI with solvents at the molecular level is difficult due to the short times, microscopic length scales, and the solvent fluctuations involved. [10] Therefore, a theoretical study of ESPT occurring in 7AI with solvents such as water and alcohol in the molecular level has been theoretically studied to shed the light on the occurrence of these important processes. The excited-state tautomerisations of 7AI with pure solvents such as water and methanol have been intensively studied in the condensed and gas phases with experimental and theoretical methods. [10–36] For instance, Kina et al. [37] performed dynamics simulations to study water

solvation effect in clusters of 7AI with water up to two water molecules. Their results showed that the complete excited-state intermolecular proton transfer (PT) process was reached around 50 fs in 7AI(H<sub>2</sub>O) and in the range of 40–60 fs in 7AI(H<sub>2</sub>O)<sub>2</sub> cluster. Another recent investigation using on-the-fly dynamics simulation was done by our group [22,24] on the excited-state multiple proton transfer (ESMPT) reaction in the gas phase clusters of 7AI (MeOH)<sub>n</sub> ( $n = 1–3$ ) and 7AI(H<sub>2</sub>O)<sub>n</sub> ( $n = 1–5$ ) using resolution-of-identity approximations and the second-order algebraic diagrammatic construction method (RI-ADC(2)) level of theory. The results revealed that the PT in all clusters is completed within 78 and 84 fs for water and methanol, respectively. The difference in the ESPT time of 7AI(H<sub>2</sub>O)<sub>n</sub> and 7AI(MeOH)<sub>n</sub> is reasonable because methanol is less polar than water. However, there are only a few studies for 7AI with ammonia. Koizumi et al. [38] reported the electronic spectra of 7AI(NH<sub>3</sub>)<sub>n</sub> ( $n = 1–3$ ) clusters along with their theoretical IR spectra. Their results suggested little reactivity for excited-state proton/hydrogen transfer and the geometries of 7AI(NH<sub>3</sub>)<sub>1–2</sub> clusters were found to be a bridged-planar form.

To this point, theoretical investigation on the intermolecular ESPT dynamics of the mixed solvents with 7AI was only reported by our group [23] on water–methanol, and no report on 7AI with mixed water–

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# Electronic and photophysical properties of 2-(2'-hydroxyphenyl)benzoxazole and its derivatives enhancing in the excited-state intramolecular proton transfer processes: A TD-DFT study on substitution effect



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Substitution effects

## ABSTRACT

The effect of electron donating and withdrawing substituents on the enol absorption and keto emission spectra of 2-(2'-hydroxyphenyl)benzoxazole (**HBO**) and its derivatives has been systematically investigated by means of density functional theory (DFT) and time-dependent DFT (TD-DFT) methods. The enol absorption spectra of **HBO** were simulated by using five different DFTs with various exchange-correlation functions to validate a suitable functional prior to being further used as a method of choice to study the effect of substituents on the spectral characteristics of **HBO** derivatives. The popular B3LYP (Becke, three-parameter, Lee–Yang–Parr) exchange-correlation functional is found to provide the best desirable result in predicting the absorption spectrum close to experimental data. In the ground state, enol forms of **HBO** and its derivatives are more stable than those of keto forms, while in the first lowest excited state, keto forms are found to be more stable than their enol forms. Overall, simulated absorption and emission spectra of **HBO** and its derivatives from TD-B3LYP calculations are in good agreement with the experimental data. For enol, absorption maxima of **HBO** derivatives having electron-withdrawing groups are red-shift corresponding to their lower HOMO–LUMO energy gaps compared to that of **HBO**. For keto emission, **HBO** having electron donating groups (*m*-Me**HBO** and **MHBO**) and withdrawing group (**CNHBO**) at 4'-position on the phenol fragment as well as electron donating groups (**HBOMe** and **HBOM**) at 6-position on the benzoxazole fragment make the position of keto emission peak shift to shorter wavelength (blue-shift). However, **HBO** derivatives with electron withdrawing groups (**HBOF**, **HBOCl**, **HBOA** and **HBOE**) at 6-position give redshifted emission compared to the parent compound (**HBO**). The type of substituent on both 4'- and 6-positions certainly has a pronounced effect on the absorption and emission spectra of **HBO** derivatives.

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## 1. Introduction

Due to its intrinsic photophysical property showing a large Stokes shift driven by the excited state intramolecular proton transfer (ESIPT), 2-(2'-hydroxyphenyl)benzoxazole (**HBO**, shown in Scheme 1) comprising the hydroxyl group (O–H acting as a proton donor) and the benzoxazole group (a nitrogen atom acting as a proton acceptor) has become an interesting compound [1–10]. Typically, molecules exhibiting ESIPT thermodynamically favor enol form ( $S_0$  enol) in the ground state ( $S_0$ ), which is stabilized by the intramolecular hydrogen bonding, however, upon photo-excitation a fast proton transfer (PT) reaction from the excited enol

( $S_1$  enol) triggers to give the excited keto tautomer ( $S_1$  keto) in subpicosecond time scale [1]. After decaying radiatively to the ground keto form ( $S_0$  keto), the reverse PT takes place to give its initial enol form (Scheme 1). Because of their unique optical property given by ESIPT, **HBO** and its derivatives have been employed as luminescent material [11,12], chemical sensors for zinc(II) [13] and anions [14], light-emitting diode devices [15], optical switching [16,17], and fluorescent probe [18,19]. In general, fluorescence spectra of these molecules exhibit both enol and keto emission. However, as ESIPT has emerged as one of the most appealing mechanisms for chemosensing applications [12,20], it is desirable to control their conformers to give only keto emission.

The photophysics of **HBO** as the parent compound in our present work has been widely studied experimentally [1,2,5,7,9,18,21–24] and theoretically [25–35] because of its structural simplicity and easily chemical modification. Thus, its derivatives [14,25,31,36–38] have

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# DYNAMICS SIMULATIONS OF EXCITED-STATE PROTON TRANSFER REACTIONS OF 2-(2'-HYDROXYPHENYL)BENZOXAZOLE AND ITS HYDRATED CLUSTERS IN THE GAS PHASE

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## ABSTRACT

The excited-state dynamics simulations of 2-(2'-hydroxy-phenyl)benzoxazole (HBO) and hydrated HBO were performed on their lowest energy structures using RI-ADC(2)/SVP-SV(P). For free HBO, only *syn*-HBO can undergo tautomerization in the excited state. For HBO(H<sub>2</sub>O), two different pathways (A) the excited-state intramolecular proton transfer (PT) and (B) the excited-state intermolecular PT through hydrogen-bonded network occur. PT time of free HBO is ultrafast at 28 fs, whereas, the PT time of HBO(H<sub>2</sub>O) takes longer with time range of 43-193 fs depending on the initial structure. The slow PT process of HBO(H<sub>2</sub>O) is caused by competition between formations of intra- and intermolecular hydrogen bonds.

## INTRODUCTION

The excited-state intramolecular proton transfer (ESI<sub>intra</sub>PT) is one of the most fundamental and important processes due to its photophysical properties. The applications of ESI<sub>intra</sub>PT are found in many applications such as organic light emitting diodes, luminescent materials, and fluorescent probes. Most of the ESI<sub>intra</sub>PT processes occur in molecules having a strong intramolecular hydrogen bond between the acidic proton (O-H, -NH<sub>2</sub>) and the basic moiety (C=N, C=O), and the suitable geometry such as 2-(2'-hydroxyphenyl)benzoxazole (HBO). To provide more complete pictures of ultrafast PT of HBO, dynamics simulations are required to investigate whether PT occurs through inter- or intramolecular hydrogen bond which is difficult to be obtained from the experiment. Here, we explore ground-state structures of free HBO and its hydrated cluster to find equilibrium conformations undergoing tautomerization. We present both static and dynamics calculations for free HBO and its solvated cluster. Reaction pathways, reaction probabilities and time constants are discussed in details.



Scheme 1. The excited-state intramolecular proton transfer reaction (ESI<sub>intra</sub>PT).

## CALCULATION DETAILS

1. **Ground-state optimizations** computed in Turbomole
  - MP2/SVP-SV(P) level
2. **Excited-state dynamics simulations** performed in Newton-X interfaced with Turbomole
  - RI-ADC(2)/SVP-SV(P) level
  - Fifty trajectories for each complex
  - T<sub>max</sub> = 300 fs and Δt = 1 fs
3. **Analysis**
  - Reaction pathways,
  - Reaction probabilities,
  - Time constants, etc.

## RESULTS AND DISCUSSION

### Ground-state optimization

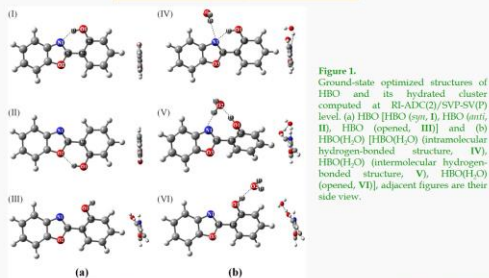


Figure 1. Ground-state optimized structures of HBO and its hydrated cluster computed at RI-ADC(2)/SVP-SV(P) level. (a) HBO [HBO (*syn*, I), HBO (*anti*, II), HBO (*opened*, III)] and (b) HBO(H<sub>2</sub>O) [HBO(H<sub>2</sub>O) (intramolecular hydrogen-bonded structure, IV), HBO(H<sub>2</sub>O) (intermolecular hydrogen-bonded structure, V), HBO(H<sub>2</sub>O) (opened, VI), adjacent figures are their side view].

Table 1. Selected bond distances (Å) and torsional angle (°) and ground-state relative energies of HBO and HBO(H<sub>2</sub>O) computed at RI-ADC(2)/SVP-SV(P) level.

	HBO					HBO(H <sub>2</sub> O)	
	I	II	III	IV	V	VI	
O1-H1	0.986	0.969	0.966	0.981	0.988	-	0.976
Intramolecular hydrogen bond (N1-H1)	1.774	-	-	1.802	-	-	-
Intermolecular hydrogen bond (O2-H1)	-	-	-	-	1.694	1.822	-
Intermolecular hydrogen bond (N1-H2)	-	-	-	-	2.276	1.830	-
O1-N1	2.659	-	2.846	2.686	3.070	2.878	-
O1-O2	-	-	-	3.580	2.682	2.798	-
O2-N1	-	-	-	3.072	2.762	-	-
N1C1C2C3	0.0	180.0	31.6	5.9	38.8	35.3	-
ΔE*	0.00	6.02	12.26	0.00	1.00	8.11	-

\* Relative energies to structure I for HBO and to structure IV for HBO(H<sub>2</sub>O).

### Excited-state dynamic simulations

Table 2. Summary of the excited-state dynamics analysis of HBO systems

Conformer	ESPT (EIP)		No PT (EIP/S <sub>0</sub> )	Probability	Pathway A		Pathway B	
	Intra	Inter			PT1 (fs)	PT1 (fs)	PT2 (fs)	PT2 (fs)
HBO (I)	50	-	-	1.00	28 (10-55)	-	-	-
HBO(H <sub>2</sub> O) (IV)	50	-	-	1.00	43 (30-60)	-	-	-
HBO(H <sub>2</sub> O) (V)	13	52	5	0.90	195 (124-247)	53 (26-95)	70 (37-110)	-

PT time range (fs) from standard deviations given in parentheses.

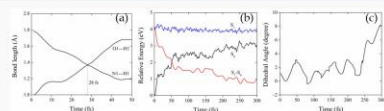


Figure 2. Average values of HBO (I). (a) Time evolution of average breaking and forming bonds. The shaded areas are the standard deviation. (b) Average torsional angle of N1C1C2C3 and (c) Average relative energies of excited state (S<sub>n</sub>), ground state (S<sub>0</sub>), and energy difference of S<sub>n</sub> and S<sub>0</sub> state (S<sub>n</sub>-S<sub>0</sub>).

### Excited-state dynamic simulations

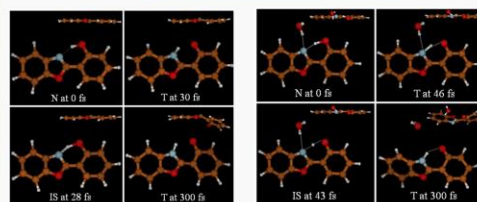


Figure 3. Snapshots of excited-state dynamics simulation of HBO at different time (up: top view, down: front view).

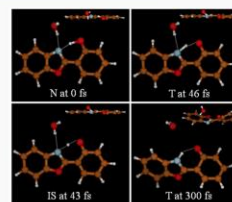


Figure 4. Snapshots of excited-state dynamics simulation of HBO(H<sub>2</sub>O) or IV at different time (up: top view, down: front view).

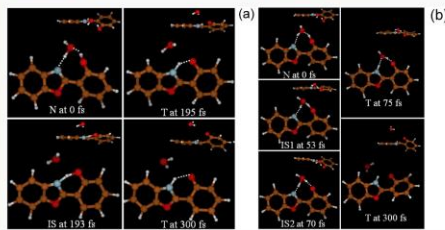


Figure 5. (a) Snapshots for pathway A and (b) for pathway B of the excited-state dynamics simulation of HBO(H<sub>2</sub>O), V at different time (up: top view, down: front view).

## CONCLUSION

- Proton transfers of HBO systems take place in the LLP state.
- Free HBO undergoes ESI<sub>intra</sub>PT at 28 fs which is in good agreement with the experiment.
- There are two possible pathways depending on initial geometries, for hydrated HBO.
- Structure IV of HBO(H<sub>2</sub>O) as an intramolecular hydrogen-bonded structure shows ESI<sub>intra</sub>PT within 43 fs which is about factor two slower than the free HBO.
- Structure V of HBO(H<sub>2</sub>O) as an intermolecular hydrogen-bonded structure, however, shows two pathways:
  - Pathway A) ESI<sub>inter</sub>PT through its starting structure (intermolecular hydrogen-bonded network) within 70 fs.
  - Pathway B) the hydrogen bond rearrangement of water of the starting structure to form the intramolecular hydrogen-bonded conformation of HBO before ESI<sub>intra</sub>PT occurs with longer time at 193 fs.
- This slower process is caused by the competition between the formations of intramolecular hydrogen bond (forming IV) and intermolecular hydrogen bond (remaining original V).
- The twisted skeleton of structure V is found and confirmed by dramatically changes of torsion between two rings of phenol and benzoxazole moieties.
- Overall, PT time of HBO systems is faster than that of the HBT and one water in HBO(H<sub>2</sub>O) can be adequately used to clarify the role of water in competition of inter- and intramolecular hydrogen bonds.

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# Substitution Effect on Absorption and Emission Spectra of 2-(2'-Hydroxyphenyl)benzoxazole: A TD-DFT Study

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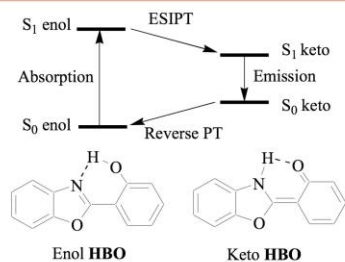
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## Abstract

The effect of substituents on the absorption and fluorescence spectra of 2-(2'-hydroxyphenyl)benzoxazole (HBO) has been systematically investigated by means of density functional theory (DFT) and time-dependent DFT (TD-DFT) methods. The B3LYP exchange-correlation functional is found to provide the best desirable result in predicting the absorption spectrum close to experimental data. Overall, simulated absorption and emission spectra of HBO and its derivatives from TD-B3LYP calculations both in the gas phase and in solution are in good agreement with the experimental data. Moreover, the effects of substitution on the absorption and fluorescence spectra show that most of enol absorptions are redshifted relative to that of HBO. For keto emission, however, substitution on phenol ring gives blueshifted emission while donating and withdrawing substituents on benzoxazole fragment show blueshifted and redshifted emission compared to HBO, respectively.

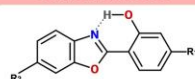
## Introduction



**Scheme 1.** Excited-state intramolecular proton transfer (ESIPT) of 2-(2'-hydroxyphenyl)benzoxazole (HBO).

Due to its intrinsic photophysical property showing large Stokes shift driven by the excited state intramolecular proton transfer (ESIPT), 2-(2'-hydroxyphenyl)benzoxazole (HBO, shown in Scheme 1) comprising the hydroxyl group (O-H acting as a proton donor) and the benzoxazole group (a nitrogen atom acting as a proton acceptor) has become an interesting compound. Typically, ESIPT molecules thermodynamically favor enol form in the ground state ( $S_0$ ), which is stabilized by the intramolecular hydrogen bonding, however, upon photoexcitation a fast proton transfer (PT) reaction from the excited enol triggers to give the excited keto tautomer in subpicosecond time scale.

## Calculations



Name	R <sub>1</sub>	R <sub>2</sub>
HBO	H	H
m-MeHBO	CH <sub>3</sub>	H
MHBO	OCH <sub>3</sub>	H
CNHBO	CN	H
HBOMe	H	CH <sub>3</sub>
HBOM	H	OCH <sub>3</sub>
HBOMF	H	F
HBOfCl	H	Cl
HBOA	H	CHO
HBOE	H	COOC <sub>2</sub> H <sub>5</sub>
m-MeHBON	CH <sub>3</sub>	NO <sub>2</sub>

We systematically compared the effect of substitution on HBO using DFT and TD-DFT calculations.

- HBO derivatives:**
- 2-(2'-hydroxy-4'-methylphenyl)benzoxazole (**m-MeHBO**),  
2-(2'-hydroxy-4'-methoxyphenyl)benzoxazole (**MHBO**),  
2-(2'-hydroxy-4'-cyano phenyl)benzoxazole (**CNHBO**).
  - 2-(2'-hydroxyphenyl)-6-methylbenzoxazole (**HBOMe**),  
2-(2'-hydroxyphenyl)-6-fluorobenzoxazole (**HBOM**),  
2-(2'-hydroxyphenyl)-6-chlorobenzoxazole (**HBOMF**),  
2-(2'-hydroxyphenyl)-6-cabaldethybenzoxazole (**HBOfCl**),  
2-(2'-hydroxyphenyl)benzoxazole-6-carboxylic acid ethyl ester (**HBOA**),  
2-(2'-hydroxy-4'-methylphenyl)-6-nitrobenzoxazole (**m-MeHBON**).

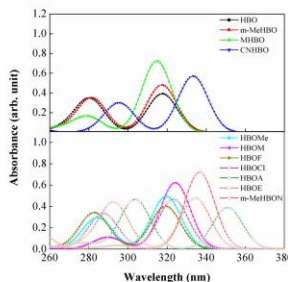
Optimization: B3LYP/6-311+G\*  
Vertical excitation: TD-B3LYP/6-311+G\*

UV-Vis absorption spectra of enol forms and fluorescence emission spectra of keto forms performed by using the Gaussian 09 program.

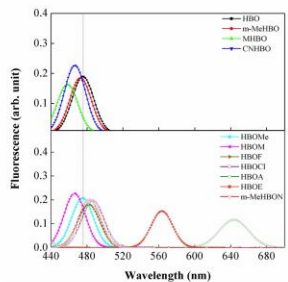
## Results

**Table 1:** Relative energies (kcal mol<sup>-1</sup>) and selected bond distances (Å) from optimized structures of HBO and its derivatives computed at B3LYP/6-311+G\* level (in gas phase). \*intramolecular hydrogen bond.

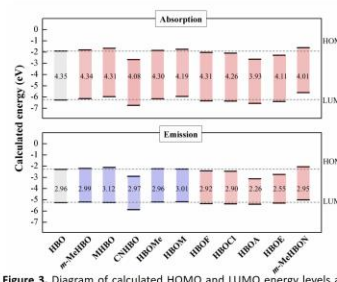
	State	HBO	m-MeHBO	MHBO	CNHBO	HBOMe	HBOM	HBOf	HBOfCl	HBOA	HBOE	m-MeHBON
Relative energy	Enol S <sub>0</sub>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Keto S <sub>0</sub>	85.63	85.96	87.06	81.42	85.13	83.29	85.26	84.30	76.98	81.31	79.63
O-H	Enol S <sub>0</sub>	0.983	0.984	0.985	0.984	0.984	0.983	0.982	0.982	0.983	0.983	0.983
	Enol S <sub>1</sub>	1.019	1.013	1.013	0.999	0.999	1.007	0.992	1.016	1.012	1.036	1.025
O...H*	Keto S <sub>0</sub>	1.732	1.743	1.760	1.747	1.732	1.729	1.722	1.724	1.730	1.726	1.739
	Keto S <sub>1</sub>	1.914	1.925	1.973	1.910	1.923	1.921	1.915	1.908	1.916	1.923	1.942
N...H*	Enol S <sub>0</sub>	1.825	1.828	1.816	1.821	1.825	1.828	1.834	1.834	0.983	1.828	1.829
	Enol S <sub>1</sub>	1.670	1.692	1.749	1.757	1.717	1.788	1.683	1.697	1.612	1.647	1.808
N-H	Keto S <sub>0</sub>	1.040	1.038	1.036	1.038	1.040	1.040	1.040	1.041	1.040	1.042	1.039
	Keto S <sub>1</sub>	1.025	1.024	1.020	1.025	1.024	1.024	1.025	1.026	1.022	1.022	1.023



**Figure 1.** Enol absorption spectra of HBO and its derivatives computed at TD-B3LYP/6-311+G\* in the gas phase.



**Figure 2.** Keto emission spectra of HBO and its derivatives computed at TD-B3LYP/6-311+G\* in the gas phase.



**Figure 3.** Diagram of calculated HOMO and LUMO energy levels and energy gaps (eV) performed at TD-B3LYP/6-311+G\* level of enol absorption and keto emission of HBO and its derivatives.

**Figure 4.** Frontier molecular orbitals of enol and keto for HBO and its derivatives computed at TD-B3LYP/6-311+G\* in the gas phase.

## Conclusions

- B3LYP/6-311+G\* and TD-B3LYP/6-311+G\* showed the best results in predicting the absorption spectrum close to experimental data.
- Most of HBO derivatives show redshifted absorption compared to HBO.
- For keto emission, both electron donating groups (m-MeHBO and MHBO) and withdrawing groups (CNHBO) groups on 4'-position make blueshifted emission.
- Electron donating groups (HBOMe and HBOM) electron on 6-position give blueshifted emission while electron withdrawing groups (HBOf, HBOfCl, HBOA, and HBOE) as well as both substituents (m-MeHBON) give redshifted emission compared to HBO.
- Overall, the effect of electron donor raises the HOMO energy level of the compounds more than its LUMO energy level while electron acceptor stabilizes LUMO energy level more than HOMO level.
- Our theoretical investigation is expected to be helpful for the molecular design for chemosensing applications utilizing molecules having ESIPT to control their desirable photophysical properties.

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