APPENDIX A

Key Word in Route Section for used in This Calculation

Geometry Optimization

For ground state structure:

```
# opt b3lyp/tzvp
```

For excited-state structure:

```
#opt td b3lyp/tzvp
```

Frequency Calculation

For ground state structure:

```
# freq b3lyp/tzvp
```

For excited-state structure:

```
# freq b3lyp/tzvp
```

Potential Energy Curves Calculation

For ground state structure:

```
# opt=modredundant b3lyp/tzvp
```

For excited-state structure:

```
# opt=modredundant td b3lyp/tzvp
```

Vertical Excitation Calculation

For absorption spectra in ground state:

```
# td b3lyp/tzvp
```

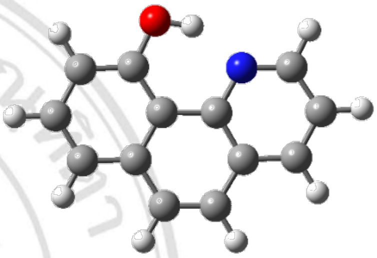
For emission spectra in ground state:

```
# td b3lyp/tzvp
```

APPENDIX B

Cartesian Coordinates of the Optimized Structures Calculation

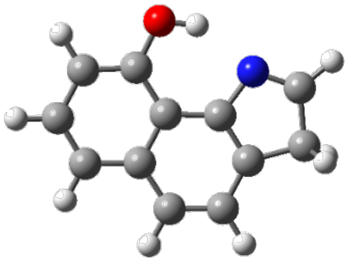
1. HBQ compound



0 1

C	3.49401000	0.11081800	0.00086000
C	2.71454400	1.24947100	0.00183700
C	1.30426400	1.15580000	0.00035300
C	0.68178200	-0.11570200	-0.00009000
C	1.50515000	-1.26562000	-0.00063300
C	2.88194700	-1.15503000	-0.00064200
C	0.50064000	2.34476500	-0.00029700
C	-0.76203900	-0.19586300	-0.00011400
C	-1.52141400	0.99890700	-0.00085000
C	-0.85436400	2.26953300	-0.00138900
C	-2.93345700	0.93601200	-0.00055300
H	-3.50752200	1.87491500	-0.00110000
C	-3.58206200	-0.28190900	0.00067200
C	-2.83363500	-1.47225000	0.00150900
H	1.01797100	3.31645200	-0.00016200
H	4.59127300	0.18425100	0.00116100
H	3.18098700	2.24622800	0.00308000
H	3.50907600	-2.05889100	-0.00168700
H	-1.47579000	3.17817500	-0.00223800
H	-4.68071800	-0.33037900	0.00101900
H	-3.35711500	-2.43983300	0.00253100
O	0.91376600	-2.56760500	-0.00146700
H	0.01115600	-2.89455400	-0.00163000
N	-1.45309300	-1.42987200	0.00097000

2. HBID compound



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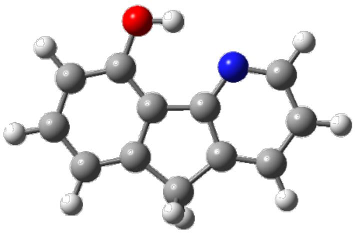
C	3.27697800	0.29758000	-0.03985800
C	2.41747300	1.37947900	-0.04264700
C	1.02868400	1.17230700	-0.00807100
C	0.50500400	-0.15228100	0.02988600
C	1.41746300	-1.24805400	0.03180700
C	2.78563100	-1.00611400	-0.00302300
C	0.12061100	2.28290500	-0.01036800
C	-0.92713500	-0.33238700	0.06484900
C	-1.78945500	0.79877000	0.06113600
C	-1.22299200	2.11170800	0.02249300
H	0.54149700	3.28119700	-0.03954200
H	4.34801500	0.45853700	-0.06655000
H	2.80219200	2.39128300	-0.07130600
H	3.45341600	-1.85767800	-0.00062300
H	-1.89080000	2.96540500	0.02006600
O	1.00195100	-2.52590400	0.06649400
H	0.00757400	-2.51225200	0.08811900
C	-3.22701000	-1.16125700	-0.08463500
C	-3.26971200	0.35511700	0.04079200
N	-1.76666900	-1.58799500	-0.12139800
H	-3.77441000	0.78338900	-0.79990000
H	-4.07441100	-1.81241400	-0.13762100
H	-3.75522700	0.63910000	0.95102800

3. IPDO compound

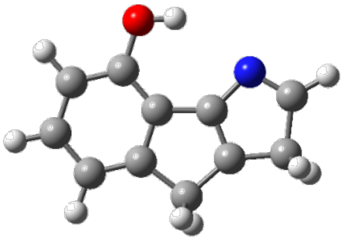


0 1

H	-0.31035800	-2.69377900	-0.90847500
C	-3.00616000	1.22252600	-0.00011900
C	-3.55056800	-0.05826900	-0.00011900
C	-2.72438800	-1.19217700	-0.00011900
C	-1.35414400	-1.01411200	-0.00009800
C	-0.79431400	0.30066700	-0.00016200
H	-3.67071900	2.09914200	-0.00001800
H	-4.64288700	-0.18832400	-0.00014600
H	-3.16530500	-2.19870700	-0.00001300
C	-0.25618500	-2.04201900	0.00005000
H	-0.31051500	-2.69365600	0.90865000
C	0.99659000	-1.20973200	0.00009000
C	2.31854700	-1.61186000	0.00016400
C	3.32077000	-0.63009900	0.00004100
C	2.99556600	0.72306600	0.00026800
C	1.65773600	1.14178300	0.00008300
C	0.66179200	0.17949700	-0.00002700
H	2.58702800	-2.67742100	0.00024000
H	4.37656900	-0.93891900	-0.00013400
H	3.79588000	1.47777800	0.00046200
O	1.33321600	2.53447400	0.00005900
H	0.40576800	2.78234500	-0.00006900
N	-1.61752200	1.41430400	-0.00018200

4. IPRO compound

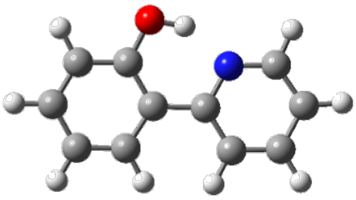
0 1



C	-0.44107600	0.13702500	0.05325500
C	-0.69340800	-1.18857200	0.09605700
C	-2.11531100	-1.72482900	-0.07293300
C	-3.13286400	-0.81561200	-0.16108600
C	-2.84127600	0.71784400	-0.09262200
C	-1.55873900	1.17667400	0.00525600
C	1.08067400	0.30937700	0.03040300
C	0.63594200	-1.97156500	0.32630100
H	-2.30853000	-2.77647100	-0.11312100
H	-4.14018400	-1.15815500	-0.27453300
H	-3.65281300	1.41434900	-0.12712000
H	0.72076500	-2.27023600	1.35026400
C	3.25522100	0.81356000	-0.00048700
N	2.06297800	1.41439000	0.01214500
H	4.18571600	1.30591700	0.19099300
O	-1.27268500	2.57703000	0.05081000
H	-0.47203500	2.72369600	0.55977800
H	0.73977000	-2.84469400	-0.28342400
C	1.64345400	-0.86160300	0.01251100
C	3.10529000	-0.70474300	-0.31416400
H	3.75011100	-1.33635900	0.26043800
H	3.29038700	-0.90036100	-1.34971800

5. PDP compound

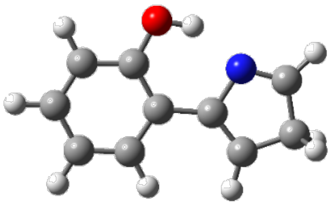
0 1



C	0.69747800	-0.23298200	-0.00346200
C	1.35468000	-1.47069800	0.00466900
C	1.44079300	0.95501900	-0.01117400
C	2.75519800	-1.52041300	0.00508700
H	0.78714300	-2.37776200	0.01055700
C	2.84131100	0.90530300	-0.01075800
C	3.49851300	-0.33241300	-0.00262900
H	3.25698700	-2.46543700	0.01129700
H	3.40884900	1.81236800	-0.01664500
H	4.56784000	-0.37037200	-0.00231300
O	0.77017800	2.21799400	-0.01946800
H	-0.07221800	2.13599300	0.43357100
C	-0.84155300	-0.17834900	-0.00392000
C	-1.58008500	-1.36949500	0.00381700
C	-2.97442700	-1.31066400	0.00334300
C	-3.59532400	-0.06083500	-0.00486400
C	-2.80754100	1.09832800	-0.01238900
N	-1.46679500	1.01087600	-0.01173400
H	-3.55718300	-2.20802700	0.00917000
H	-1.07952500	-2.31517100	0.01003100
H	-4.66285700	0.01178000	-0.00540600
H	-3.27716800	2.05973800	-0.01870000

6. PRP compound

0 1



C	3.16890300	0.66667700	-0.09839400
C	1.09836700	-0.23924000	-0.02834500
N	1.90794300	1.00898800	-0.01774300
C	-0.44064200	-0.29224300	-0.01276300
C	-1.07771100	-1.48817000	-0.03444200
C	-1.25570900	1.01376200	0.02745400
C	-2.61671900	-1.54117200	-0.01885700
H	-0.51139800	-2.39558900	-0.06238400
C	-2.61003600	0.96711900	0.04116800
C	-3.33397800	-0.39188800	0.01653500
H	-3.11971800	-2.48541800	-0.03597400
H	-3.17634900	1.87453800	0.06911300
H	-4.40329000	-0.42871500	0.02736400
O	-0.58347700	2.27569700	0.05032600
H	0.25377300	2.20071700	-0.41334400
C	1.90992500	-1.31903700	-0.07258400
H	3.97088900	1.33525300	-0.33232800
H	1.61005200	-2.32934700	-0.25765300
C	3.32846500	-0.83215900	0.17680600
H	3.60793200	-0.99555800	1.19665900
H	4.05514700	-1.30627300	-0.44933100

APPENDIX C

Definitions

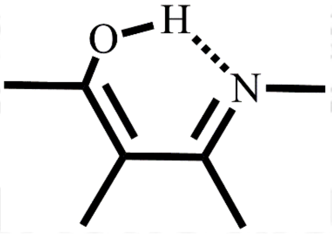
1. Calculation of Reaction Probability

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

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

2. Proton Transfer Time

The intersection between the average value of breaking (O–H) and forming (N···H) bonds are indicated proton transfer time.



APPENDIX D

Conferences and Workshops

Poster presentations

1. Poster presentation: "Influence of the Hydrogen-Bonding Geometries Controlling over the Excited-State Intramolecular Proton Transfer of 10-Hydroxybenzo[*h*]quinoline" in The Pure and Applied Chemistry International Conference 2016 (PACCON 2016), Bangkok, THAILAND, February 9-11, 2016

2. Poster presentation: "Influence of the Hydrogen-Bonding Geometries Controlling over the Excited-State Intramolecular Proton Transfer of 10-Hydroxybenzo[*h*]quinoline" in International Congress for Innovation in Chemistry (Chemistry in ASEAN Economic Community and Beyond) 2016, Pattaya, THAILAND, June 26-29, 2016

3. Poster presentation: "Influence of the Hydrogen-Bonding Geometries Controlling over the Excited-State Intramolecular Proton Transfer of 10-Hydroxybenzo[*h*]quinoline" in the third International Conference on Computational Science and Engineering (ICCSE-3), Ho Chi Minh city, VIETNAM, November 28-30, 2016

4. Poster presentation: "Excited State Intramolecular Proton Transfer in π-Expanded systems of 10-Hydroxybenzo[*h*]quinoline" in The Pure and Applied Chemistry International Conference 2017 (PACCON 2017), Bangkok, THAILAND, February 2-3, 2017

Workshops

1. "Molecular Designs for Advanced Materials: Workshops and Conference" at Chiang Mai University, Chaing Mai, THAILAND, November 24-27, 2015

2. "13th Thai Summer School of Computational Chemistry Workshop" at Chiang Mai University, Chaing Mai, THAILAND, November 16-17, 2016

APPENDIX E

Publications and Poster

Excited State Intramolecular Proton Transfer in π-Expanded systems of 10-Hydroxybenzo[*h*]quinoline

Warinthon Chansen and Nawee Kungwan*

Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Chiang Mai University, 50200, Thailand

*e-mail: naweekung@gmail.com

Abstract: Molecules having excited-state intramolecularproton transfer (ESIPT) have emerged as a new potential fluorescent probes in chemical and biological systems. In this study, the ESIPT reactions of 10-hydroxybenzo[*h*]quinoline (HBQ) and its derivatives with different types of π- expansion were investigated using a hybrid density-functional theory (DFT) and its time-dependent DFT (TD-DFT) at B3LYP with 6-311+G(d) basis set. The π-expansion of the HBQ chromophore was achieved by adding a benzene ring at various positions nearby the pyridine ring, led to compounds possessing diverse photophysical properties. The absorption and emission spectra of these molecules were studied using frontier molecular orbitals. Their hydrogen bonding strengths in the excited-state were revealed by the simulated IR spectra. Moreover, the possibility of ESIPT process was carried out by scanning the potential energy curve of proton transfer coordinate (O–H···N). As a result, both absorption and emission spectra of HBQ derivatives are red-shifted compared to that of HBQ. In addition, the ESIPT occurrence of selected HBQ derivatives is more favorable or comparable to that of HBQ due to the π-expanded substituent.

1. Introduction

Excited state intramolecular proton transfer (ESIPT) is an important process for the understanding of photoreaction in organic system.[1] ESIPT has been appeared as an interesting phenomenon that can be utilized in the design of laser dyes,[2] fluorescent sensor,[3] ultraviolet stabilizers,[4] and organic light emitting devices.[5] Compounds displaying ESIPT must have proton donating and proton accepting moieties in the same molecule such as flavones,[6] imidazoles,[7] 2-(2'-hydroxyphenyl)benzizimidazole,[8] and 10-hydroxybenzo[*h*]quinoline (HBQ).[9]

Among them HBQ, containing both pyridinic nitrogen and phenol groups, possesses the strongest intramolecular hydrogen bond. ESIT process in this molecule is ultrafast proton transfer in sub-picosecond which is independent of solvent perturbation.[9] This ultrafast reaction is triggered by the charge-transfer process occurring between the hydroxyl oxygen (proton donor) and benzoquinolinic nitrogen atom (proton acceptor), acting as the driving force for proton transfer (PT) reaction. HBQ is used as a fluorescent probe to examine the influence of organized media, especially the cyclodextrins in aqueous solution.[10] Its derivatives such as π-expansion systems can be achieved by adding a benzene moiety at various positions adjacent to the pyridine ring which leads to compounds possessing diverse photophysical properties.[11] Generally, it is difficult to experimentally study the ESIPT due to the ultrafast reaction that requires the use of femtosecond spectrometer, which is very,

Influence of the Hydrogen-Bonding Geometries Controlling over the Excited-State Intramolecular Proton Transfer of 10-Hydroxybenzo[*h*]quinoline as Fluorescent Probes

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Abstract

The excited state intramolecular proton transfer (ESIPT) reactions of 10-hydroxybenzo[*h*]quinoline (HBQ) and its derivatives with different hydrogen-bonding geometries have been systematically investigated using a hybrid density-functional theory (DFT) and its time-dependent DFT (TD-DFT) at B3LYP with TZVP basis set. ESIPT can occur easily in the excited state with less required barrier. On-the-fly dynamics simulations in the first-excited state are employed to determine reaction mechanisms and the time evolution of the ESIPT reaction. The ESIPT times in all compounds take place within 100 fs.

Introduction

Excited state intramolecular proton transfer (ESIPT) has received considerable attention both experimentally and theoretically [1]. The ESIPT reaction involves the proton transfer from the hydrogen-donating group to the hydrogen-accepting group in an organic molecule in the excited state. Typical molecules that display ESIPT, such as benzoxazoles, flavones, anthraquinones, pyridyls, or quinolines, possess a large Stokes shift. Hence many important applications have been found for them such as molecular probes, laser dyes, fluorescence recording, luminescent materials, ultraviolet stabilizers, and recently organic light emitting devices [2]. Therefore, it is necessary to study ESIPT mechanism in detail.

HBQ is an organic heterocyclic compound that contains both pyridinic nitrogen as proton-accepting and phenol as proton-donating groups. These functional groups are arranged relatively close to each other so as to form an intrinsic intramolecular hydrogen bonding. As a result, the photophysical properties relevant to the proton-transfer reaction are rather insensitive to solvent perturbation. Therefore, this molecule is considered to be one of the best systems for which we can examine the vibrational coherence in the intrinsic proton-transfer process. In this work, we have studied the effect of hydrogen-bond affected by geometry changes of HBQ and its derivatives on the ESIPT using the on-the-fly dynamics calculations. The main goal is to show the dynamic behavior of different hydrogen-bond strength of HBQ and its derivatives.

Computational details

Ground-state optimizations computed in Turbomole 6.3

- B3LYP/TZVP level

Excited-state dynamics simulations performed in NEWTON-X interfaced with Turbomole 6.3

- TD-B3LYP/TZVP level
- 25 trajectories for each complex, tmax = 300 fs, dt = 1 fs

Analysis

- Ground-state geometries
- Excited-state dynamics geometries at different times
- Proton transfer (PT) time (from forming and breaking bonds)
- Energy difference between S_0 and S_1

Results and Discussion

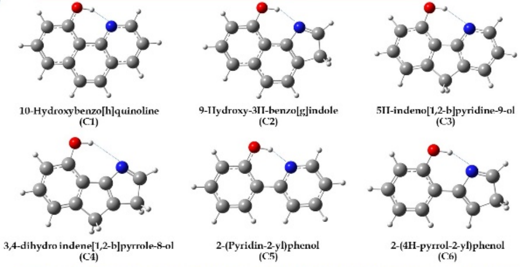
10-Hydroxybenzo[h]quinoline (C1)
9-Hydroxy-3H-benzo[g]indole (C2)
5H-indeno[1,2-b]pyridine-9-ol (C3)
3,4-dihydro indene[1,2-b]pyrrole-8-ol (C4)
2-(Pyridin-2-yl)phenol (C5)
2-(4H-pyrrol-2-yl)phenol (C6)

Figure 1. Ground-state optimized geometries of HBQ and its derivatives computed at B3LYP/TZVP level

Structures	Reaction		Probability (%)	Time (fs)
	ESIPT	No		
C1	25	-	100	15 (13-19)
C2	24	1	96	43 (40-47)
C3	24	1	96	60 (58-63)
C4	5	20	20	71 (69-78)
C5	25	-	100	8 (7-9)
C6	25	-	100	22 (19-22)

Table 1. Summary of the excited-state dynamics analysis of HBQ

	C1	C2	C3	C4	C5	C6
O-H	0.994	0.979	0.978	0.969	0.996	0.985
N---H	1.706	1.877	2.074	2.444	1.677	1.758
O-N	2.604	2.752	2.926	3.262	2.578	2.643
C1C2C3N1	0.00	0.02	0.00	0.00	-4.72	-0.06

Table 2. Selected bond distance (Å) and torsion angle (°) from optimized structures of HBQ and its derivatives computed at B3LYP/TZVP level

Results and Discussion

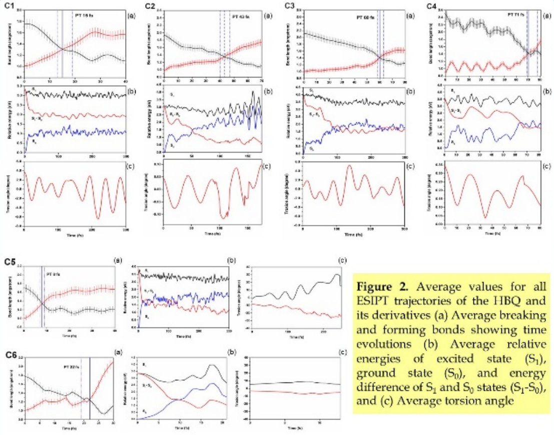

Figure 2. Average values for all ESIPT trajectories of the HBQ and its derivatives (a) Average breaking and forming bonds showing time evolutions (b) Average relative energies of excited state (S_1), ground state (S_0), and energy difference of S_1 and S_0 states (S_1-S_0), and (c) Average torsion angle

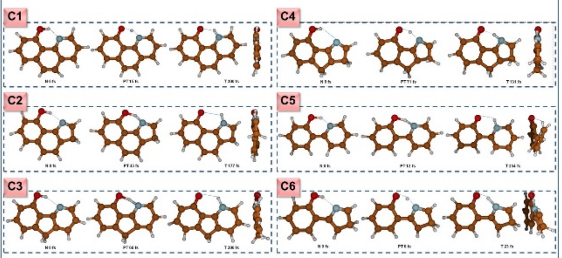

Figure 3. Snapshots of the HBQ dynamics showing the time evolutions of the ESIPT reactions through the hydrogen-bonded network. Normal (N), proton transfer (PT), and tautomer (T). Values correspond to the average over all ESIPT trajectories in femtosecond.

Conclusions

Ground-state geometry optimizations of HBQ and its derivatives are systematically carried out at B3LYP/TZVP level. Intramolecular proton transfer of C5 faster than HBQ (C1). On-the-fly dynamics simulations in the first excited-state have been performed at TD-B3LYP with TZVP basis set. The following conclusions from our results are:

- ESIPT processes through a hydrogen bonded network occur in ultrafast timescale of 15 fs.
- The weaker intramolecular hydrogen-bonded geometries increases the barrier resulting in low probability of the ESIPT.
- The probability of proton transfer occurrence can be as low as 20% (C4) and as high as 100% (C1,C5, and C6).
- After ESIPT is complete, the twisted skeleton in C5 and C6 is found and confirmed by torsion angle changes from -8 to -1 degree for C5 and from -3 to 5 degree for C6.

Acknowledgements

The authors wish to thank the Computational Chemistry Laboratory (CCL) for financial support and the Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai, Thailand.

References

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2. S. Anton J., C. Michal K., G. Daniel T., and S. Miquel, *J. Chem. Theory Comput.* 2015, 11, 1046-1054.
3. P. K. Bijan., and G. Nikhil, *J. of lumin.* 2011, 131, 1918-1926.
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5. T. Satoshi., and T. Tahei, *J. Phys. Chem A.* 2005, 109, 10199-10207.

Influence of the Hydrogen-Bonding Geometries Controlling over the Excited-State Intramolecular Proton Transfer of 10-Hydroxybenzo[*h*]quinoline as Fluorescent Probes

Warinthon Chansen, **Khanittha Kerdpol, Rathawat Daengngern, Nawee Kungwan***
Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand
E-mail: ch.warinthon@gmail.com and naweekung@gmail.com*

Abstract

The excited-state intramolecular proton transfer (ESIPT) reactions of 10-hydroxybenzo[h]-quinolone (HBQ) and its derivatives with different hydrogen-bonding geometries have been systematically investigated using a hybrid density-functional theory (DFT) and its time-dependent DFT (TD-DFT) at B3LYP with TZVP basis set. ESIPT can occur easily in the excited state with less required PT barrier. On-the-fly dynamics simulations in the first-excited state are employed to determine reaction mechanisms and the time evolution of the ESIPT reaction. The ESIPT times in all compounds take place within 100 fs.

Introduction

Excited-state intramolecular proton transfer (ESIPT) has received considerable attention both experimentally and theoretically [1]. The ESIPT reaction involves the proton transfer from the hydrogen-donating group to the hydrogen-accepting group in an organic molecule in the excited state. Typical molecules that display ESIPT, such as benzoxazoles, flavones, anthraquinones, pyridyls, or quinolines, possess a large Stokes shift. Hence many important applications have been found for them such as molecular probes, laser dyes, fluorescence recording, luminescent materials, ultraviolet stabilizers, and recently organic light emitting devices [2]. Therefore, it is necessary to study ESIPT mechanism in detail.

HBQ is an organic heterocyclic compound that contains both pyridinic nitrogen as proton-accepting and phenol as proton-donating groups. These functional groups are arranged relatively close to each other so as to form an intrinsic intramolecular hydrogen bonding. As a result, the photophysical properties relevant to the proton-transfer reaction are rather insensitive to solvent perturbation. Therefore, this molecule is considered to be one of the best systems for which we can examine the vibrational coherence in the intrinsic proton-transfer process. In this work, we have studied the effect of hydrogen-bond affected by geometry changes of HBQ and its derivatives on the ESIPT using the on-the-fly dynamics calculations. The main goal is to show the dynamic behavior of different hydrogen-bond strength of HBQ and its derivatives.

Computational details

Ground-state optimizations computed in Turbomole 6.3

- B3LYP/TZVP level

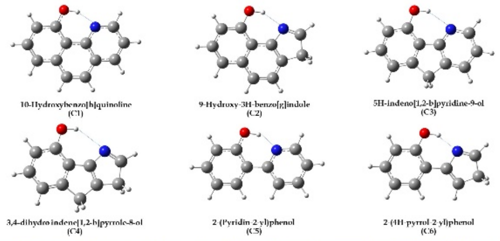
Excited-state dynamics simulations performed in NEWTON-X interfaced with Turbomole 6.3

- TD-B3LYP/TZVP level
- 25 trajectories for each complex, tmax = 300 fs, dt = 1 fs

Analysis

- Ground-state geometries
- Excited-state dynamics geometries at different times
- Proton transfer (PT) time (from forming and breaking bonds)
- Energy difference between S_0 and S_1

Results and Discussion



10-Hydroxybenzo[h]quinoline (C1)
9-Hydroxy-3H-benzo[g]indole (C2)
5H-indeno[1,2-b]pyridine-9-ol (C3)
3,4-dihydro indene[1,2-b]pyrrole-8-ol (C4)
2-(Pyridin-2-yl)phenol (C5)
2-(4H-pyrrol-2-yl)phenol (C6)

Figure 1. Ground-state optimized geometries of HBQ and its derivatives computed at B3LYP/TZVP level.

Structures	Reaction		Probability (%)	Time (fs)
	ESIPT	No		
C1	25	-	100	15 (13-19)
C2	24	1	96	43 (40-47)
C3	24	1	96	60 (58-63)
C4	5	20	20	71 (69-78)
C5	25	-	100	8 (7-9)
C6	25	-	100	22 (19-22)

Table 1. Summary of the excited-state dynamics analysis of HBQ

	C1	C2	C3	C4	C5	C6
O – H	0.994	0.979	0.978	0.969	0.996	0.985
N···H	1.706	1.877	2.074	2.444	1.677	1.758
O – N	2.604	2.752	2.926	3.262	2.578	2.643
C1C2C3N1	0.00	0.02	0.00	0.00	-4.72	-0.06

Table 2. Selected bond distance (Å) and torsion angle (°) from optimized structures of HBQ and its derivatives computed at B3LYP/TZVP level

Results and Discussion

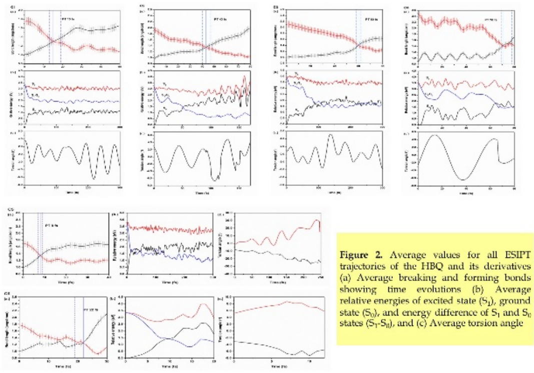


Figure 2. Average values for all ESIPT trajectories of the HBQ and its derivatives (a) Average breaking and forming bonds showing time evolutions (b) Average relative energies of excited state (S_1), ground state (S_0), and energy difference of S_1 and S_0 states (S_1-S_0), and (c) Average torsion angle

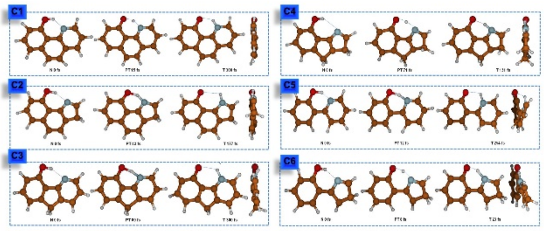


Figure 3. Snapshots of the HBQ dynamics showing the time evolutions of the ESIPT reactions through the hydrogen-bonded network. Normal (N), proton transfer (PT), and tautomer (T). Values correspond to the average values over all ESIPT trajectories in fs.

Conclusions

Ground-state geometry optimizations of HBQ and its derivatives are systematically carried out at B3LYP/TZVP level. On-the-fly dynamics simulations in the first excited-state have been performed at TD-B3LYP with TZVP basis set. The following conclusions from our results are:

- ESIPT processes of all systems occur through a hydrogen bonded network in ultrafast timescale of 15 fs.
- ESIPT of C5 occurs fastest among the others at PT time 8 fs.
- The weaker intramolecular hydrogen-bonded geometries increases the barrier resulting in low probability of ESIPT.
- The probability of proton transfer occurrence can be as low as 20% (C4) and as high as 100% (C1,C5, and C6).
- After ESIPT is complete, the twisted skeleton behavior found in C2, C3, C5 and C6 has initiated the conical intersection between S0 and S1 states, resulting in a low fluorescence intensity in these molecules.

Acknowledgements

The authors wish to thank the Computational Chemistry Laboratory (CCL) for financial support. W. Chansen gratefully thanks the Center of Excellence for Innovation in Chemistry (PERCH-CIC), and the Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai, Thailand.

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Influence of the Hydrogen-Bonding Geometries Controlling over the Excited-State Intramolecular Proton Transfer of 10-Hydroxybenzo[*h*]quinoline as Fluorescent Probes

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Abstract

The excited-state intramolecular proton transfer (ESIPT) reactions of 10-hydroxybenzo[h]-quinolone (HBQ) and its derivatives with different hydrogen-bonding geometries have been systematically investigated using a hybrid density-functional theory (DFT) and its time-dependent DFT (TD-DFT) at B3LYP with TZVP basis set. ESIPT can occur easily in the excited state with less required PT barrier. On-the-fly dynamics simulations in the first-excited state are employed to determine reaction mechanisms and the time evolution of the ESIPT reaction. The ESIPT times in all compounds take place within 100 fs.

Introduction

Excited-state intramolecular proton transfer (ESIPT) has received considerable attention both experimentally and theoretically [1]. The ESIPT reaction involves the proton transfer from the hydrogen-donating group to the hydrogen-accepting group in an organic molecule in the excited state. Typical molecules that display ESIPT, such as benzoxazoles, flavones, anthraquinones, pyridyls, or quinolines, possess a large Stokes shift. Hence many important applications have been found for them such as molecular probes, laser dyes, fluorescence recording, luminescent materials, ultraviolet stabilizers, and recently organic light emitting devices [2]. Therefore, it is necessary to study ESIPT mechanism in detail.

HBQ is an organic heterocyclic compound that contains both pyridinic nitrogen as proton-accepting and phenol as proton-donating groups. These functional groups are arranged relatively close to each other so as to form an intrinsic intramolecular hydrogen bonding. As a result, the photophysical properties relevant to the proton-transfer reaction are rather insensitive to solvent perturbation. Therefore, this molecule is considered to be one of the best systems for which we can examine the vibrational coherence in the intrinsic proton-transfer process. In this work, we have studied the effect of hydrogen-bond affected by geometry changes of HBQ and its derivatives on the ESIPT using the on-the-fly dynamics calculations. The main goal is to show the dynamic behavior of different hydrogen-bond strength of HBQ and its derivatives.

Computational details

1

Ground-state optimizations computed in Turbomole 6.3

- B3LYP/TZVP level

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Excited-state dynamics simulations performed in NEWTON-X interfaced with Turbomole 6.3

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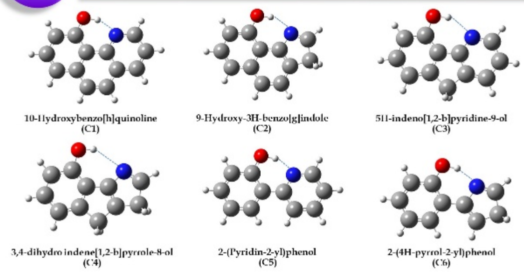
Analysis

- Ground-state geometries
- Excited-state dynamics geometries at different times
- Proton transfer (PT) time (from forming and breaking bonds)
- Energy difference between S_0 and S_1

Results and Discussion



10-Hydroxybenzo[h]quinoline (C1)

9-Hydroxy-3H-benzo[g]indole (C2)

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Figure 1. Ground-state optimized geometries of HBQ and its derivatives computed at B3LYP/TZVP level.

Table 2. Selected bond distance (Å) and torsion angle (°) from optimized structures of HBQ and its derivatives computed at B3LYP/TZVP level .

Distance	State	C1	C2	C3	C4	C5	C6
N···H	S_0	1.706	1.878	2.075	2.445	1.677	1.759
	S_1	1.594	1.712	1.838	2.131	1.526	1.518
O–N	S_0	2.605	2.753	2.926	3.263	2.579	2.643
	S_1	2.513	2.607	2.730	2.989	2.458	2.439
C–N	S_0	2.868	3.020	3.094	3.355	2.840	2.918
	S_1	2.822	2.924	2.999	3.198	2.777	2.809
C1C2C3N1	S_0	0	0	0	0	5	0
	S_1	0	0	0	0	22	0

Table 1. Summary of dynamic analysis and energy barrier of HBQ and its derivatives.

Structures	Reaction		Probability (%)	Time (fs)	Energy barrier (kcal/mol)
	ESIPT	No			
C1	25	-	100	15 (13-19)	0.47
C2	24	1	96	43 (40-47)	0.87
C3	24	1	96	60 (58-63)	2.34
C4	5	20	20	71 (69-78)	21.10
C5	25	-	100	8 (7-9)	0.86
C6	25	-	100	22 (19-22)	0.00

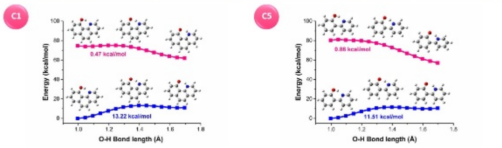
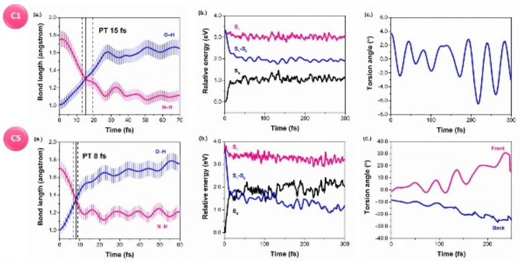


Figure 2. The calculated potential energy curves in the S_0 (black line) and S_1 (red line) states for HBQ and its derivatives. The energies of the S_1 state were calculated using the geometries of the corresponding the S_0 state.



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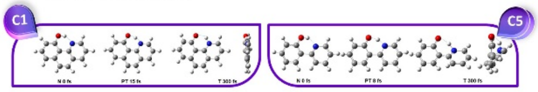

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Results and Discussion

Ground-state geometry optimizations of HBQ and its derivatives are systematically carried out at B3LYP/TZVP level. On-the-fly dynamics simulations in the first excited-state have been performed at TD-B3LYP with TZVP basis set. The following conclusions from our results are:

- Intramolecular hydrogen bond of all compounds is strong in the excited state
- The energy barrier of ESIPT reaction is 0.47 and 0.86 kcal/mol for C1 and C5, respectively
- ESIPT processes of all systems occur through a hydrogen bonded network in ultrafast timescale of 15 fs
- ESIPT of C5 occurs fastest among the others at PT time 8 fs
- The weaker intramolecular hydrogen-bonded geometries increases the barrier resulting in low probability of ESIPT
- The probability of proton transfer occurrence can be as low as 20% (C4) and as high as 100% (C1,C5, and C6)
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Excited State Intramolecular Proton Transfer in π- Expanded systems of 10-Hydroxybenzo[*h*]quinoline

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01 Abstract

Molecules having excited-state intramolecularproton transfer (ESIPT) have emerged as a new potential fluorescent probes in chemical and biological systems. In this study, the ESIPT reactions of 10-hydroxybenzo[*h*]quinoline (HBQ) and its derivatives with different types of π- expansion were investigated using a hybrid density-functional theory (DFT) and its time-dependent DFT (TD-DFT) at B3LYP with 6-311+G(d) basis set. The π-expansion of the HBQ chromophore was achieved by adding a benzene ring at various positions nearby the pyridine ring, led to compounds possessing diverse photophysical properties. The absorption and emission spectra of these molecules were studied using frontier molecular orbitals. Their hydrogen bonding strengths in the excited-state were revealed by the simulated IR spectra. Moreover, the possibility of ESIPT process was carried out by scanning the potential energy curve of proton transfer coordinate (O–H···N). As a result, both absorption and emission spectra of HBQ derivatives are red-shifted compared to that of HBQ. In addition, the ESIPT occurrence of selected HBQ derivatives is more favorable or comparable to that of HBQ due to the π-expanded substituent.

02 Introduction

Excited state intramolecular proton transfer (ESIPT) is an important process for the understanding of tautomerization in organic system. ESIPT has been appeared as an interesting phenomenon that can be utilized in the design of laser dyes, fluorescent sensor, ultraviolet stabilizers, and organic light emitting devices. Compounds displaying ESIPT must have proton donating and proton accepting moieties in the same molecule such as flavones, imidazoles, 2-(2'-hydroxyphenyl)benzizimidazole, and 10-hydroxybenzo[*h*]quinoline (HBQ).

Among them HBQ, containing both pyridinic nitrogen and phenol groups, possesses the strongest intramolecular hydrogen bond. ESIPT process in this molecule is ultrafast in sub-picosecond which is independent of solvent perturbation. This ultrafast reaction is triggered by the charge-transfer process occurring between the hydroxyl oxygen (proton donor) and benzoquinolinic nitrogen atom (proton acceptor), acting as the driving force for proton transfer (PT) reaction. HBQ is used as a fluorescent probe to examine the influence of organized media, especially the cyclodextrins in aqueous solution. Its derivatives such as π-expansion systems can be achieved by adding a benzene moiety at various positions adjacent to the pyridine ring which leads to compounds possessing diverse photophysical properties. Generally, it is difficult to experimentally study the ESIPT due to the ultrafast reaction that requires the use of femtosecond spectrometer, which is very expensive and available only in some institutes in the world. Nowadays theoretical calculations using density functional theory have become an alternative and effective tool to study the ESIPT.

Therefore, in the present work, we theoretically studied photophysical properties and the ESIPT reaction of HBQ and its derivatives depending on the different position of π-expansion.

03 Computational details

Method

Geometries on ground (S_0) and excited (S_1) states of all compounds were optimized using density functional theory (DFT) and time-dependent DFT (TD-DFT) at B3LYP with 6-311+G(d) basis set in the gas phase, respectively.

Analysis

- Structural geometrics
- Simulated infrared (IR) spectra
- Electronic spectra and frontier molecular orbitals (MOs)
- Potential energy curves of ESIPT reactions (PECs)

04 Results and Discussion

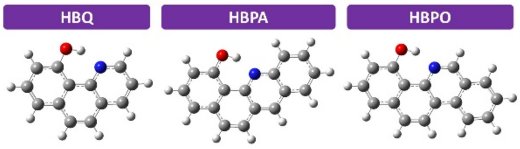

Figure 1. Optimized geometries of HBQ and its derivatives computed at B3LYP/6-311+G(d) level: (a) HBQ, (b) HBPA, (c) HBPO.

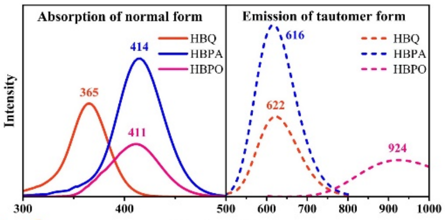

Figure 2. Simulated absorption and emission spectra of HBQ and its derivatives computed at B3LYP/6-311+G(d) level.

Table 1. Intramolecular hydrogen-bonded distances (O–H), important distances between heavy atoms (N···H, O···N, and C1···N) (Å), and a dihedral angle (°) of HBQ and its derivatives (normal form) computed at B3LYP/6-311+G(d) level.

Compound	State	Distance (Å)				Dihedral angle (°)
		O–H	N···H	O···N	C1···N	C1C2C3N
HBQ	S_0	0.990	1.738	2.622	2.877	0
	S_1	0.990	1.625	2.532	2.832	0
HBPA	S_0	0.993	1.722	2.610	2.865	0
	S_1	0.993	1.642	2.549	2.840	0
HBPO	S_0	0.989	1.732	2.614	2.868	0
	S_1	0.989	1.610	2.515	2.813	0

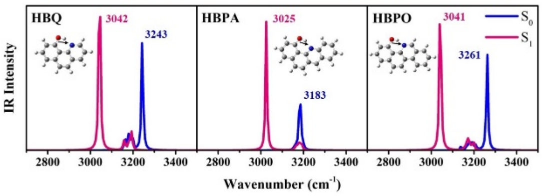

Figure 3. The vibrational frequencies of the O–H stretching vibrational mode of the stimulated IR spectra of HBQ both in the ground (blue line) and the excited-states (pink line).

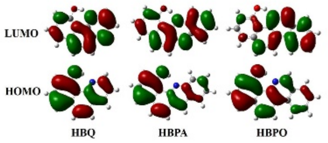

Figure 4. Frontier molecular orbitals (MOs) of normal forms for HBQ and its derivatives computed at B3LYP/6-311+G(d) level.

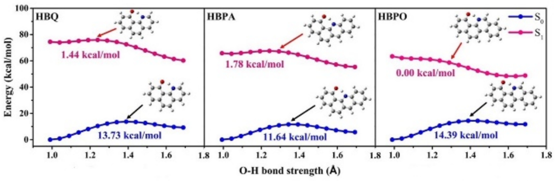

Figure 5. The calculated potential energy curves in the S_0 and S_1 states of HBQ and its derivatives. The energies of the S_1 state were calculated using the geometries of the corresponding the S_0 state.

05 Conclusions

- The electronic and photophysical properties of HBQ, HBPA, and HBPO were theoretically investigated using B3LYP and TD-B3LYP methods.
- The distances of O···N, N···H, and C1···N are found to be shortened in the S_1 state, indicating that intramolecular hydrogen bonds are strengthened in the S_1 state.
- The O–H stretching modes of all compounds are shifted to lower frequencies in S_1 state compared with the S_0 state, confirming that the hydrogen bonding interaction is stronger in the S_1 state.
- The frontier molecular orbitals show that upon photoexcitation ESIPT is triggered by the charge distribution and intramolecular charge transfer between proton donor and proton acceptor.
- The ESIPT can occur via O–H···N intramolecular hydrogen bond because this bond becomes stronger in S_1 state, supported by shorter of N···H, O···N, and C1···N distances and also the red-shifted of O–H vibrational mode.
- The PT barrier is followed this order: HBPA>HBQ>HBPO.

06 Acknowledgements

The authors wish to thank the Center of Excellence for Innovation in Chemistry (PERCH-CIC), Computational Chemistry Laboratory (CCL) for financial support. W. Chansen gratefully thanks the Department of Chemistry, Faculty of Science, and Graduate School, Chiang Mai University, Chiang Mai, Thailand.

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