APPENDICES

APPENDIX A

POTENTIAL ENERGY DIAGRAMS OF SELECTED TRAJECTORIES FOR 2-(IMINOMETHYL)PHENOL DERIVATIVES

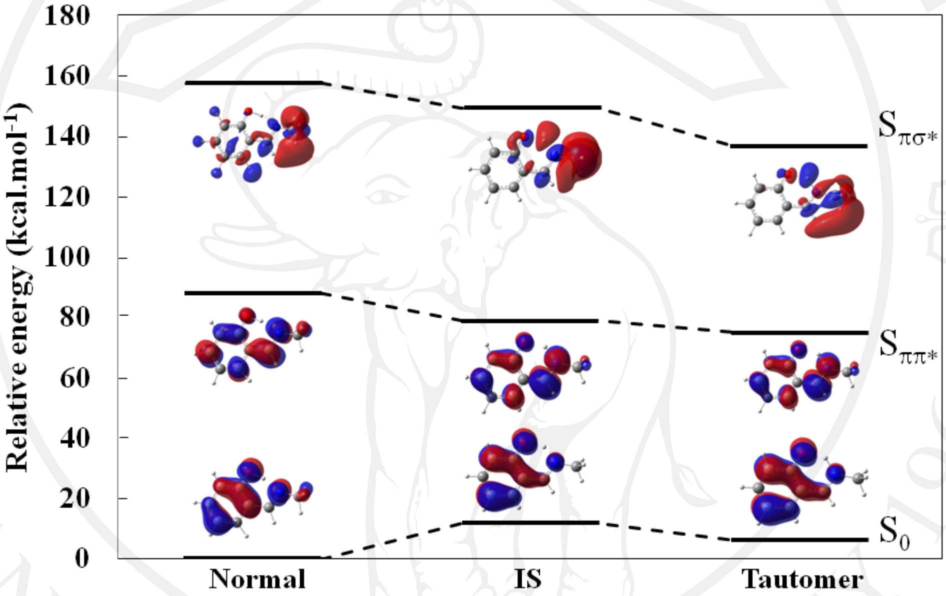

Figure A1 Potential energy diagram of a selected trajectory for 2-(*N*-methyl iminomethyl)phenol (MIMP) at ground state (S_0) and excited states ($S_{\pi\pi^*}$, $S_{\pi\sigma^*}$) performed at B3LYP/SVP level

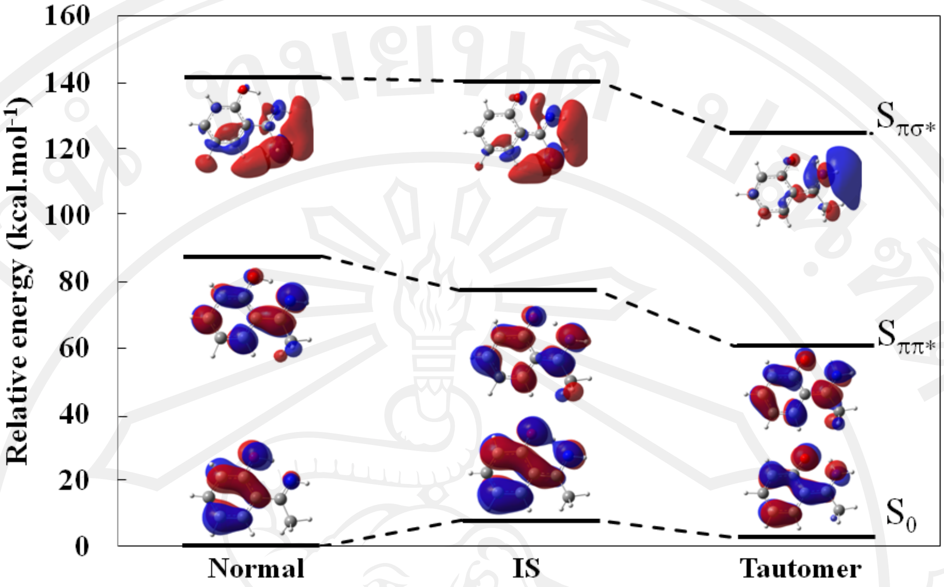

Figure A2 Potential energy diagram of a selected trajectory for 2-(α-imino ethyl)phenol (IEP) at ground state (S_0) and excited states ($S_{\pi\pi*}$, $S_{\pi\sigma*}$) performed at B3LYP/SVP level

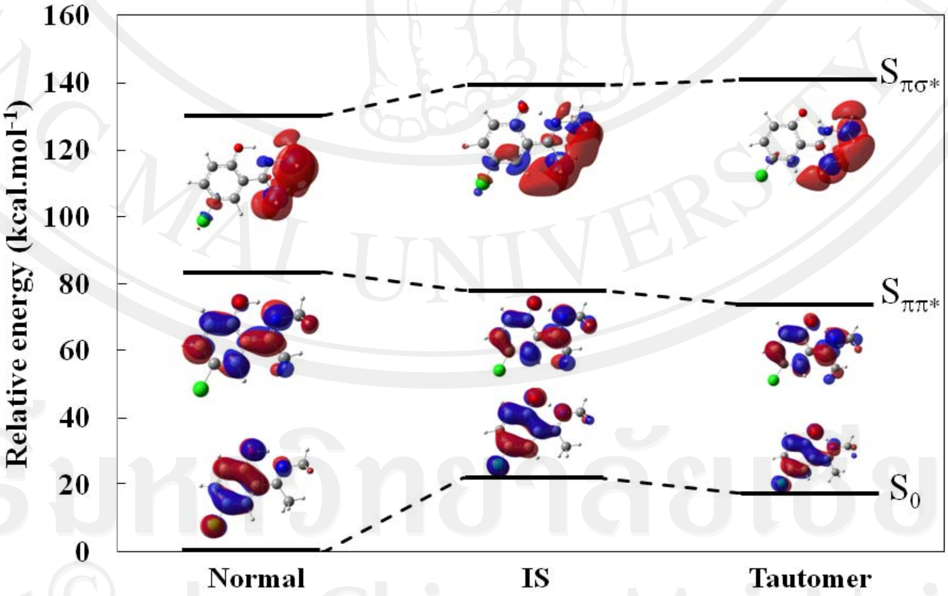

Figure A3 Potential energy diagram of a selected trajectory for 2-(*N*-methyl-α-iminoethyl)-4-chlorophenol (MIECP) at ground state (S_0) and excited states ($S_{\pi\pi*}$, $S_{\pi\sigma*}$) performed at B3LYP/SVP level

APPENDIX B

CALCULATIONS OF REACTION PROBABILITY AND PROTON TRANSFER TIME

Calculation of reaction probability

$$\text{Reaction probability} = \frac{\text{Number of the ESPT reaction trajectories}}{\text{Total trajectories}} \times 100\ \%$$

Proton transfer time

The proton transfer time is the average values of breaking bond (X–H) becomes equal to the average values of forming bond (H–Y) in Å

$$X\text{–}H = H\text{–}Y$$

APPENDIX C

ORAL AND POSTER PRESENTATIONS

1) Excited-State Dynamics simulations of 2-(Iminomethyl)phenol Derivatives, *The Third International Conference on Science and Technology for Sustainable Development of the Greater Mekong Sub-region (3rd STGMS) and the Second International Conference on Applied Science (2nd ICAS)*, Luang Prabang, Lao PDR, 24-25 March 2011. (**Oral presentation**)

2) Quantum Dynamics Simulations of Excited-State Intermolecular Proton Transfer Reactions in 7-Azaindole with Methanol Clusters, *The 6th Congress on Science and Technology for Youths*, Bangkok, Thailand, 18-19 March 2011. (**Poster presentation**)

3) On-the-fly Dynamics Simulations of Excited-State Intermolecular Proton Transfer Reactions in 7-Azaindole with Methanol Clusters, *The Winter School of Sokendai/Asian CORE Program "Frontiers of Molecular Science - Life, Material, Energy, and Space"*, Okazaki, Japan, 19-22 February 2011. (**Poster presentation**)

4) Quantum Mechanics Simulation on Excited-State Proton Transfer Reactions of 1*H*-Pyrrolo[3,2-*h*]quinoline with Methanol and Water Clusters in the Gas Phase: A Density Functional Theory Study, *The 13th Asia Pacific Confederation of Chemical Engineering Congress (APCChE 2010)*, Taipei, Taiwan, 5-8 October 2010. (**Oral presentation**)

5) Quantum Mechanics Simulation on Excited-State Proton Transfer Reactions of 1*H*-Pyrrolo[3,2-*h*]quinoline with Methanol Clusters in the Gas Phase, *The 1st International Conference on Computation for Science and Technology (ICCST-I)*, Chiang Mai, Thailand, 4-6 August 2010. (**Oral presentation**)

6) Quantum Mechanics Simulation on Structure of 7-Azaindole(Methanol)$_2$ Cluster and Excited-State Triple-Proton Transfer Reactions in the Gas Phase, *The 14th International Annual Symposium on Computational Science and Engineering (ANSCSE14)*, Chiang Rai, Thailand, 23-26 March 2010. (**Oral presentation**)

AN EFFECT OF HEAT ABSORBER FROM BLACK RUBBER ON THE EFFICIENCY OF DOUBLE SLOPE SOLAR STILL

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ABSTRACT

This paper presents the effect of size of the heat absorber from black rubber on the efficiency of double slope solar still. Black rubber was chosen to use as heat absorber and was put on the water surface in the second layer of the solar still. The size of black rubber used in the experiment was divided into 9 sizes from 10% to 90% of the surface of the water in the second layer of the solar still. The temperature, condensed water and efficiency of solar still were measured and calculated in the experiment. The result was show that using the size of 10% of black rubber absorber gave the maximum condensed water at 1.17 liters / day and the efficiency of 25.72%.The minimum condensed water was at 0.90 liters / day and the minimum efficiency was 15.76% when the of 90% of black rubber absorber was used. The results were revealed that the efficiency of solar still was decreased according to the increasing of the size of black rubber absorber.

KEYWORDS: Solar still, Efficiency, Absorber, Black rubber

EXCITED-STATE DYNAMICS SIMULATIONS OF 2-(IMINOMETHYL)PHENOL DERIVATIVES

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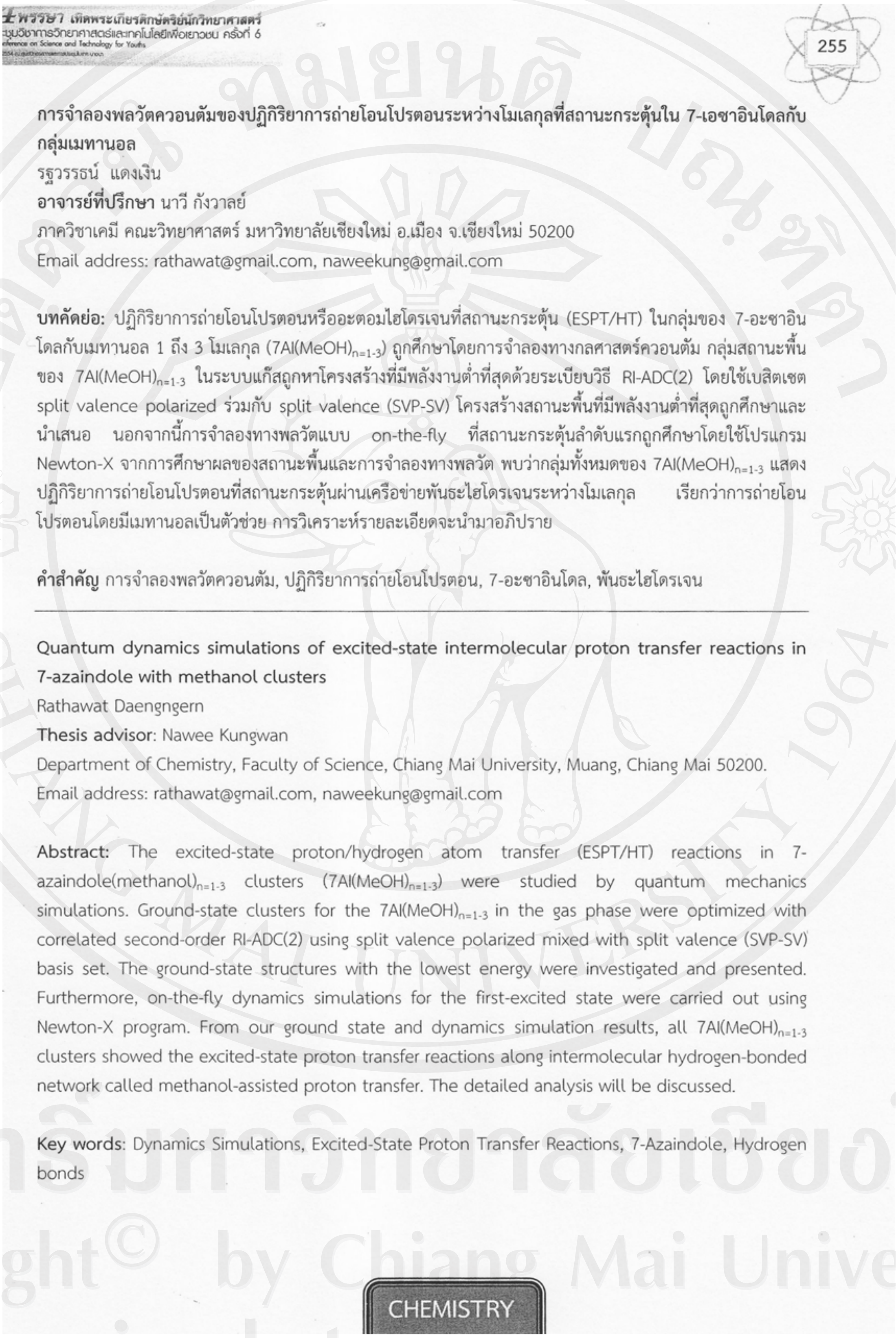
ABSTRACT

o-Hydroxy Schiff base molecules are widely used as model systems to study photophysical processes due to their photochromic behavior and structural variety. The *o*-hydroxy Schiff base having $RR_1C{=}NR_2$ (where R is a phenol ring and $R_1 = R_2 =$ H atom) is called 2-(iminomethyl)phenol. The 2-(iminomethyl)phenol, the hydrogen atom of hydroxy group on a phenol ring forming hydrogen bond to the nitrogen atom on an imine group, is usually investigated for a model system of the intramolecular proton transfer (PT) process which gives enol-keto tautomerization. Ground-state optimizations and excited-state dynamics simulations in the gas phase for the 2-(iminomethyl)phenol and its derivatives were performed. The excited-state dynamics simulations were employed to investigate reaction mechanisms and time evolutions of PT process. From results, substituent that was placed to the phenol ring affected strength of intramolecular hydrogen bond. In addition, steric modification or increased acidity on the phenol ring showed shortening and strengthening of the intramolecular hydrogen bond.

KEYWORDS: *o*-Hydroxy Schiff base, 2-(Iminomethyl)phenol, Ground-state optimization, Excited-state dynamics simulation, Intramolecular hydrogen bond, Substituent effect



การจำลองพลวัตควอนตัมของปฏิกิริยาการถ่ายโอนโปรตอนระหว่างโมเลกุลที่สถานะกระตุ้นใน 7-เอซาอินโดลกับกลุ่มเมทานอล

รฐวรรธน์ แดงเงิน
อาจารย์ที่ปรึกษา นาวี กังวาลย์
ภาควิชาเคมี คณะวิทยาศาสตร์ มหาวิทยาลัยเชียงใหม่ อ.เมือง จ.เชียงใหม่ 50200
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บทคัดย่อ: ปฏิกิริยาการถ่ายโอนโปรตอนหรืออะตอมไฮโดรเจนที่สถานะกระตุ้น (ESPT/HT) ในกลุ่มของ 7-อะซาอินโดลกับเมทานอล 1 ถึง 3 โมเลกุล (7AI(MeOH)$_{n=1-3}$) ถูกศึกษาโดยการจำลองทางกลศาสตร์ควอนตัม กลุ่มสถานะพื้นของ 7AI(MeOH)$_{n=1-3}$ ในระบบแก๊สถูกหาโครงสร้างที่มีพลังงานต่ำที่สุดด้วยระเบียบวิธี RI-ADC(2) โดยใช้เบสิตเซต split valence polarized ร่วมกับ split valence (SVP-SV) โครงสร้างสถานะพื้นที่มีพลังงานต่ำที่สุดถูกศึกษาและนำเสนอ นอกจากนี้การจำลองทางพลวัตแบบ on-the-fly ที่สถานะกระตุ้นลำดับแรกถูกศึกษาโดยใช้โปรแกรม Newton-X จากการศึกษาผลของสถานะพื้นและการจำลองทางพลวัต พบว่ากลุ่มทั้งหมดของ 7AI(MeOH)$_{n=1-3}$ แสดงปฏิกิริยาการถ่ายโอนโปรตอนที่สถานะกระตุ้นผ่านเครือข่ายพันธะไฮโดรเจนระหว่างโมเลกุล เรียกว่าการถ่ายโอนโปรตอนโดยมีเมทานอลเป็นตัวช่วย การวิเคราะห์รายละเอียดจะนำมาอภิปราย

คำสำคัญ การจำลองพลวัตควอนตัม, ปฏิกิริยาการถ่ายโอนโปรตอน, 7-อะซาอินโดล, พันธะไฮโดรเจน

Quantum dynamics simulations of excited-state intermolecular proton transfer reactions in 7-azaindole with methanol clusters

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Abstract: The excited-state proton/hydrogen atom transfer (ESPT/HT) reactions in 7-azaindole(methanol)$_{n=1-3}$ clusters (7AI(MeOH)$_{n=1-3}$) were studied by quantum mechanics simulations. Ground-state clusters for the 7AI(MeOH)$_{n=1-3}$ in the gas phase were optimized with correlated second-order RI-ADC(2) using split valence polarized mixed with split valence (SVP-SV) basis set. The ground-state structures with the lowest energy were investigated and presented. Furthermore, on-the-fly dynamics simulations for the first-excited state were carried out using Newton-X program. From our ground state and dynamics simulation results, all 7AI(MeOH)$_{n=1-3}$ clusters showed the excited-state proton transfer reactions along intermolecular hydrogen-bonded network called methanol-assisted proton transfer. The detailed analysis will be discussed.

Key words: Dynamics Simulations, Excited-State Proton Transfer Reactions, 7-Azaindole, Hydrogen bonds

On-the-fly Dynamics Simulations of Excited-State Intermolecular Proton Transfer Reactions in 7-Azaindole with Methanol Clusters

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7-Azaindole (7AI) has been used as a model compound to reveal a key reaction for chemical mutagenesis of DNA base pairs [1]. Its proton can move easily from pyrrole to pyridine ring upon photoexcitation process [2-4]. Ground-state optimizations and excited-state dynamics simulations in the gas phase were performed [5-6]. The excited-state dynamics simulations were employed to investigate reaction mechanism and time evolution of proton transfer processes. From results, the excited-state proton transfer reactions with no crossing between $^1S_{\pi\pi*}$ and $^1S_{\pi\sigma*}$ states take place along the intermolecular hydrogen-bonded network via methanol molecule called methanol-assisted molecules. Especially, two methanol molecules assist the ESPT reaction well in existence of the lowest reaction barrier.

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The 13th Asia Pacific Confederation of
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APCChE 2010
October 5-8, 2010, Taipei

Quantum Mechanics Simulation on Excited-State Proton Transfer Reactions of 1*H*-Pyrrolo[3,2-*h*]quinoline with Methanol and Water Clusters in the Gas Phase: A Density Functional Theory Study

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Keywords: 1*H*-Pyrrolo[3,2-*h*]quinoline; Excited-State Proton Transfer Reaction; Solvate-Assisted Proton Transfer.

Abstract

A theoretical investigation is performed by quantum mechanics simulation for the excited-state proton transfer reactions (ESPT) of 1*H*-pyrrolo[3,2-*h*]quinoline (PQ) with methanol clusters (PQ-$(CH_3OH)_{n=1-2}$) and water clusters (PQ-$(H_2O)_{n=1-2}$). Ground-state structures of the clusters are optimized using density functional theory (DFT) level with B3LYP. Excited-state on-the-fly dynamic simulations are carried out for the first-excited state using Newton-X program interfaced with Turbomole. Our dynamic simulation results reveal ultrafast reactions occurring in femtosecond. Moreover, the results show that the ESPT reactions take place through solvent bridges of both methanol and water in the clusters; with one molecule of solvent (Figure 1a) called the excited-state double-proton transfer (ESDPT) and with two molecules of solvent (Figure 1b) called the excited-state triple-proton transfer (ESTPT). The detailed analysis will be thoroughly discussed.

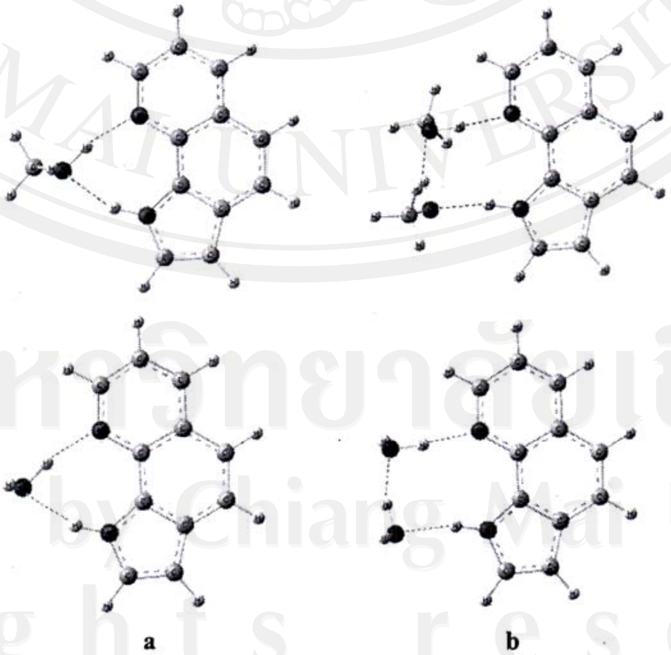

Figure 1: The ground-state structures of the clusters; a) PQ-$(CH_3OH)_1$, PQ-$(H_2O)_1$ and b) PQ-$(CH_3OH)_2$, PQ-$(H_2O)_2$

Acknowledgement: R. Daengngern gratefully thanks to the Science Achievement Scholarship of Thailand (SAST) by Commission on Higher Education for financial support. The authors also thank to the Department of Chemistry, Faculty of Science, Chiang Mai University and the Chang Noi Cluster at Chiang Mai University, Chiang Mai, Thailand for all computational calculations.

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In addition, this paper included the architecture for this simulation method. The architecture shows all hardware system and detail of extended box. This design can reduce hardware and gate delay about 41% compared with basic condition microrotations and thresholding of basic CORDIC.

***Keywords**: rounding threshold, microrotation, punctured radix-8 CORDIC, reduce hardware complexity*

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Quantum Mechanics Simulation on Excited-State Proton Transfer Reactions of 1*H*-Pyrrolo[3,2*h*]quinoline with Methanol Clusters in the Gas Phase

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Excited-state proton transfer reactions (ESPT) of 1*H*-pyrrolo[3,2-*h*]quinoline (PQ) with methanol clusters ($PQ\text{-}(CH_3OH)_{n=1\text{-}2}$) are studied by quantum mechanics simulation. Ground-state structures of the clusters are optimized using density functional theory level with B3LYP. The ground-state structures with the lowest energy are explored and presented. Excited-state on-the-fly dynamic simulations are carried out for the first-excited state using Newton-X program interfaced with Turbomole. Our results show that the ESPT reactions take place along intermolecular hydrogen-bonded network in the clusters. The detailed analysis will be discussed.

***Keywords**: quantum mechanics, excited-state proton, 1H-pyrrolo[3,2-h]quinolin, methanol clusters*

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Theoretical Study of the Ring-Opening Polymerization of ε-Caprolactone Initiated by Novel Tin(II) Alkoxides

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Oral Presentation

The ring-opening polymerization (ROP) mechanisms of ε-Caprolactone (CL) with novel Tin(II) alkoxide, $Sn(OR)_2$ initiators (R = n-C_4H_9, n-C_6H_{13}, n-C_8H_{17}) were investigated using density functional theory (DFT) calculations. The optimized geometries and corresponding energies of stationary along reaction pathway confirmed a four-step coordination-insertion mechanism. The coordination of CL onto Tin(II) metal center led to a nucleophilic addition of the carbonyl group of CL, followed by an intramolecular alkoxide ligand exchange. A monomer insertion was completed by the CL ring opening via acyl-oxygen bond cleavage. The formation of the four-membered ring Tin(II) transition state was found to be the rate-determining step. Furthermore, kinetic rate constants for each reaction of CL with $Sn(OR)_2$ were calculated using the transition state theory. The calculated rate constants were in good agreement with available experimental data. The $Sn(OR)_2$ initiator as R being n-C_4H_9 was found to give the faster rate due to the least steric hindrance effect and the short ligand compared to other R groups. This study could be useful to ROP of CL initiated by Tin(II) alkoxide.

Quantum Mechanics Simulation on Structure of 7-Azaindole(Methanol)$_2$ Cluster and Excited-State Triple-Proton Transfer Reactions in the Gas Phase

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ABSTRACT

The excited-state triple-proton transfer reaction (ESTPT) in 7-azaindole(methanol)$_2$, 7AI(MeOH)$_2$, is studied by quantum mechanics simulation. Ground-state cluster for the 7AI(MeOH)$_2$ in the gas phase is optimized with correlated second-order RI-ADC(2) using split valence polarized mixed with split valence (SVP-SV). The ground-state structure with the lowest energy is explored and presented. Furthermore, on-the-fly dynamic simulations for the first-excited state are carried out using Newton-X program. From our electronic ground state and dynamics simulation results, we found that ESTPT of 7AI(MeOH)$_2$ cluster is observed along intermolecular hydrogen-bonded network called methanol-assisted proton transfer. The detailed analysis will be discussed.

Keywords: 7-Azaindole, Excited-State Proton Transfer/Hydrogen Atom Transfer Reaction, Methanol-Assisted Proton Transfer.

1. INTRODUCTION

The proton/hydrogen atom transfer processes (PT/HT) play an important role in chemistry and biochemistry [1-3]. The excited-state proton/hydrogen atom transfer reaction (ESPT/HT) which is a subclass in PT/HT has been intensively studied due to its application uses in laser dyes, photostabilizers [4], fluorescent probes [5-7] and light-emitting devices [8, 9].

7-Azaindole (7AI) is an important bicyclic aza-aromatic molecule that can form two hydrogen bonds by donating the pyrrole proton and accepting proton on the pyridine nitrogen [10, 11]. The systems of hydrogen-bonded forming with solvent molecules have been shown to form multiple hydrogen-bonded cyclic structures [12-16]. An observation of a PT/HT in 7AI with solvent clusters is intensively studied by many groups [12, 16-20]. Recently, Satoka and co-workers [17, 18, 20-25] investigated the tautomerization of 7AI(MeOH)$_2$ that undergoes an excited-state triple-proton transfer (ESTPT). The tautomeric form of the ESTPT reactions is observed based on dispersed fluorescence and resonance-enhanced multiphoton ionization spectra. However, their experimental results did not give exactly time of ESPT/HT. Therefore, the theoretical investigation used in our study is to support their experiments by showing time evolutions and reaction pathway of ESTPT for 7AI(MeOH)$_2$.

2. COMPUTATIONAL DETAILS

2.1 Ground-State Calculation

The ground-state optimization in gas phase was carried out for 7AI(MeOH)$_2$ using correlated second-order RI-ADC(2) [26] with split valence polarized (SVP) basis [27] for heavy atoms and hydrogen atoms involved in the hydrogen-bonded network of a complex and a split valence (SV) basis for the remaining hydrogen in the cluster. Optimized structure was confirmed by frequency calculations with all positive numbers and it was also further used for dynamic calculations using the Turbomole program package [28, 29].

2.2 Excited-State Dynamic Simulation

Classical dynamic simulations for 7AI(MeOH)$_2$ were carried out on the energy surface of the first-excited singlet state, S$_1$. The initial conditions for each trajectory were generated using a Wigner distribution of the ground-state vibrational quantum harmonic-oscillator and were performed at the RI-ADC(2)/SVP-SV using the Newton-X program [30] interfaced with Turbomole. A hundred trajectories were simulated with a time step of 1 fs and the maximum time up to 300 fs for investigation of the proton transfer which occurs along the hydrogen-bonded network.

3. RESULTS AND DISCUSSION

3.1 Ground-State Structure

Two methanol molecules are added to 7AI, a complex of 7AI(MeOH)$_2$ is formed that illustrated in Figure 1. Hydrogen bond interactions are shown in the dashed lines. The structure of 7AI(MeOH)$_2$ is optimized at the RI-ADC(2)/SVP-SV level. The optimized structure shows that 7AI acts as a proton donor (for H1 atom that forms hydrogen bond to the first methanol) and a proton acceptor for H3 atom of the second methanol. Simultaneously, the first and second methanol molecules also form hydrogen bond through H2---O2. There are three-hydrogen bonds which form between methanol and 7AI molecule with bond lengths of 1.730Å (H1---O1), 1.698 Å (H2---O2) and 1.788 Å (H3---N2), respectively.

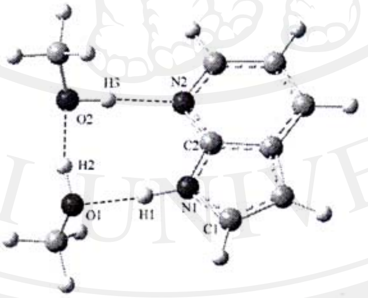
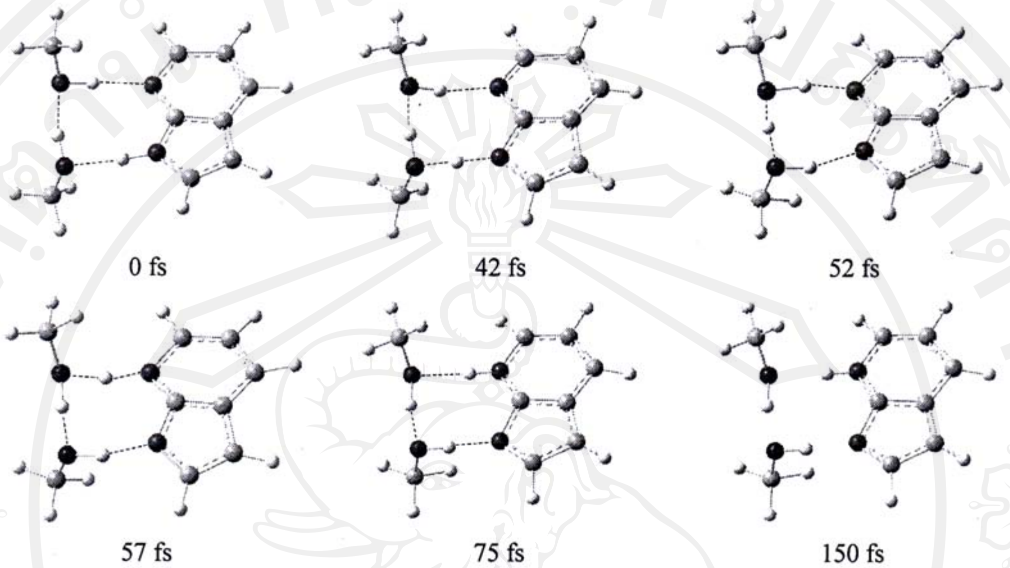


Figure 1. Ground-state optimized structure of 7AI(MeOH)$_2$ at RI-ADC(2)/SVP-SV calculation.

3.2 Dynamic Simulation Results

From Figure 1, the important numbering atoms of 7AI(MeOH)$_2$ are labeled and the proton transfer process is summarized in the following three steps; (1) H1 moves from N1 to O1 (2) H2 moves from O1 to O2, and (3) H3 moves from O2 to N2 (the tautomerization with methanol assistance is achieved). A selected trajectory in the first-excited state during 0 fs to 150 fs reveals that the reaction is the ESTPT through hydrogen-bonded network within 80 fs. The time for proton transfers occur at 42 fs, 52 fs, and 57 fs, for the first, second, and third proton transfer, respectively. The complete proton transfer reaction is obtained after 57 fs as shown in Figure 2.



0 fs 42 fs 52 fs

57 fs 75 fs 150 fs

Figure 2. A selected trajectory along the reaction in the ESTPT pathway through hydrogen-bonded network during the time from 0 fs to 150 fs.

The dynamic simulations are carried out for 7AI(MeOH)$_2$ starting from 100 different initial trajectories. From summarized results of on-the-fly dynamic simulations (Table 1), 67 trajectories of them show the ESTPT reaction with 7 trajectories have the recrossing reaction between 7AI and the second methanol molecules. However, the remaining 33 trajectories have no proton transfer reactions with 6 trajectories of them stop due to errors in the calculations. Therefore, the total of 67 trajectories will be used for analysis.

Table 1. Summarized reaction patterns for dynamic simulations on 7AI(MeOH)$_2$ cluster (trajectories).

Proton transfer reactions		No reactions	
ESTPT	Recrossing	No ESTPT	Error
60	7	27	6

Figure 3A shows the excited-state time evolution of the distances of three-bonded breaking at N1---H1, O1---H2 and O2---H3 and three-bonded forming at H1---O1, H2---O2 and H3---N2 along the proton transfer pathway averaged over 67 trajectories. We adopt a definition for X–H–Y proton transfer for all processes, which is the time for X–H equal to Y–H. According to the dynamics, the three-bonded forming distances (N1---H1, O1---H2 and O2---H3) change rapidly to covalent bond lengths. Simultaneously, the three-bonded breaking interatomic distances (H1---O1, H2---O2 and H3---N2) increase rapidly as the covalent bond is being broken. At 57 fs, the first proton transfer process occurs when average values of N1---H1and H1---O1 bond distances are equal. The second proton is transferred at 70 fs with average values of O1---H2 and H2---O2 distances are equal. And the last proton transfer is achieved at 83 fs as average value of O2---H3 and H3---N2 distances are equal.

After complete proton transfer process, the relative energy difference of S_1-S_0 gradually decreases as shown in Figure 3B. This relative energy difference is always over 2 eV suggesting that the structure is almost planar throughout the process. In addition, the average value of dihedral angle (C1N1C2N2) of $7AI(MeOH)_2$ does not change confirming that its skeleton structure is close to planar.

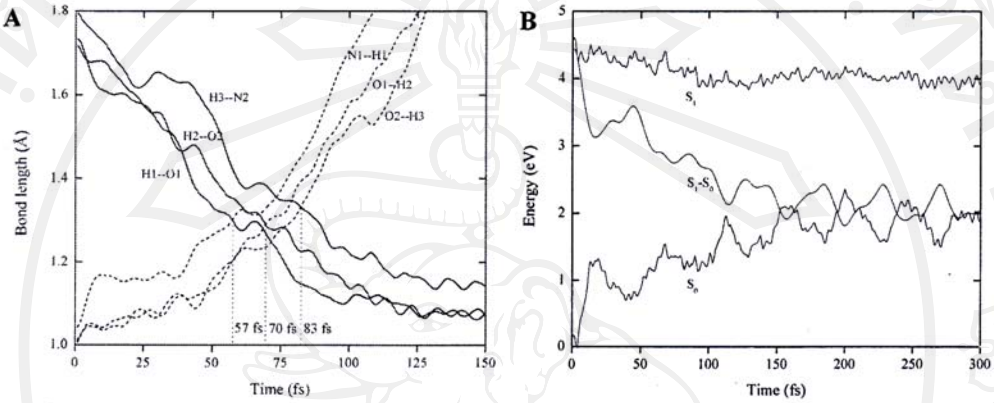


Figure 3. **A)** Time evolution of the distances of three-bonded breaking (N1---H1, O1---H2 and O2---H3) and three-bonded forming (H1---O1, H2---O2 and H3---N2) along the proton transfer pathway averaged over 67 trajectories. **B)** The average energies, S_1, S_0, and relative energy of S_1-S_0 states.

4. CONCLUSION

We presented the $7AI(MeOH)_2$ for electronic ground state which forms hydrogen-bonded network. The ESTPT reactions are achieved and showed that time evolution of bond forming and breaking at 57 fs, 70 fs and 83 fs averaged over 67 trajectories for the first, second and third proton transfer process, respectively. The ESTPT for $7AI(MeOH)_2$ cluster is very fast reaction within 83 fs. This study reveals the importance of dynamic on methanol-assisted proton transfer.

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Publications

1) **R. Daengngern**, N. Kungwan, P. Wolschann, A. J. A. Aquino, H. Lischka, and M. Barbatti, Excited-State Intermolecular Proton Transfer Reactions of 7-Azaindole(MeOH)$_n$ (n=1-3) Clusters in the Gas Phase: On-the-fly Dynamics Simulation, 2011. (*To be submitted*)

2) **R. Daengngern**, M. Barbatti, and N. Kungwan, Quantum Mechanics Simulation on Structure of 7-Azaindole(Methanol)$_2$ Cluster and Excited-State Triple-Proton Transfer Reactions in the Gas Phase, *Proceedings of the 14th International Annual Symposium on Computational Science and Engineering (ANSCSE14)*, 2010, 130.

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