TABLE OF CONTENTS

	Page
Acknowledgements	iii
Abstract in Thai	v
Abstract in English	vi
List of Tables	xi
List of Figures	xii
Abbreviations and Symbols	xviii
Chapter I Introduction	
1.1 Background	1
1.2 Excited-state proton/hydrogen atom transfer (ESPT/HT) reactions	2
1.2.1 Excited-state intermolecular proton/hydrogen atom transfer (ESinterPT/HT) reactions	3
1.2.2 Excited-state intramolecular proton/hydrogen atom transfer (ESIntraPT/HT) reactions	5
1.3 Molecular property	6
1.3.1 Fluorescence	6
1.3.2 Frank-Condon principle	8
1.4 Computational chemistry	9
1.4.1 Schrödinger equation	9
1.4.2 Born-Oppenheimer approximation	9
1.4.3 *Ab initio* method	11

1.4.3.1 Hartree-Fock approximation 11

1.4.3.2 Coupled cluster 13

1.4.4 Density functional theory 15

1.4.4.1 Honnenberg-Kohn theorems 15

1.4.4.2 Kohn-Sham equations 16

1.4.4.3 Hybrid three parameters of Beck and Lee-Yang-Parr correlation functional (B3LYP) 17

1.4.4.4 Time-dependent density functional theory (TD-DFT) 18

1.4.5 Adiabatic dynamics 20

1.4.5.1 Initial conditions 22

1.4.5.2 Wigner distributions 22

1.5 Objectives 24

Chapter II Excited-state intermolecular proton transfer reactions in 7-azaindole with methanol clusters

2.1 Introduction 26

2.2 Methods 28

2.2.1 Ground-state optimizations 28

2.2.2 Excited-state dynamics simulations 29

2.3 Results and discussion 30

2.3.1 Ground-state optimizations 30

2.3.2 Excited-state dynamics simulations 34

2.3.2.1 7AI(MeOH)$_1$ complex 39

2.3.2.2 7AI(MeOH)$_2$ complex 41

2.3.2.3 7AI(MeOH)$_3$ complex 44

2.3.3 Reaction barriers and proton transfer types 47

2.4 Summary 48

Chapter III Excited-state intramolecular proton transfer reactions in 2-(iminomethyl)phenol derivatives

3.1 Introduction 50

3.2 Methods 52

3.2.1 Ground-state optimizations 52

3.2.2 Excited-state dynamics simulations 53

3.3 Results and discussion 53

3.3.1 Ground-state optimizations 53

3.3.2 Excited-state dynamics simulations 57

3.3.2.1 2-(Iminomethyl)phenol (IMP) 61

3.3.2.2 2-(*N*-Methyliminomethyl)phenol (MIMP) 63

3.3.2.3 2-(α-Iminoethyl)phenol (IEP) 65

3.3.2.4 2-(*N*-Methyl-α-iminoethyl)phenol (MIEP) 67

3.3.2.5 2-(*N*-Methyl-α-iminoethyl)-4-fluorophenol (MIEFP) 69

3.3.2.6 2-(*N*-Methyl-α-iminoethyl)-4-chlorophenol (MIECP) 71

3.4 Summary 74

Chapter IV Conclusion 75

References 77

Appendices 83

Appendix A Potential energy diagrams of selected trajectories for 2-(iminomethyl)phenol derivatives 84

Appendix B Calculations of reaction probability and proton transfer time 86

Appendix C Oral and poster presentations 87

Curriculum Vitae 101

LIST OF TABLES

Table		Page
2.1	Summary of intermolecular hydrogen bonds and selected distances (Å) and *ø*N1C1N2C2 dihedral angles (°) of the ground-state structures performed at RI-ADC(2)/SVP-SV(P) level	31
2.2	Summary of excited-state dynamics analysis of $7AI(MeOH)_{n=1-3}$ complexes	34
2.3	Relative ground (S_0) and excited states ($S_{\pi\pi^*}$, $S_{\pi\sigma^*}$) energies (kcal. mol^{-1}) of selected trajectories of each complex for characteristic stationary points of normal (N), intermediary structure (IS), and tautomer (T) along the reaction pathways	35
3.1	Summary of intramolecular hydrogen bonds and selected distances (Å) and *ø*C1C2C3N1 dihedral angles (°) of the ground-state structures performed at B3LYP/TZVP level	55
3.2	Summary of the excited-state dynamics analysis of 2-(iminomethyl) phenol derivatives	57
3.3	Relative ground (S_0) and excited states ($S_{\pi\pi^*}$, $S_{\pi\sigma^*}$) energies (kcal. mol^{-1}) of selected trajectories of each molecule of 2-(iminomethyl) phenol derivatives for characteristic stationary points of normal (N), intermediary structure (IS), and tautomer (T) along reaction pathways	58

LIST OF FIGURES

Figure		Page
1.1	Scheme of the excited-state proton/hydrogen atom transfer (ESPT/HT) reaction	2
1.2	Jablonski diagram	6
1.3	Potential energy diagrams of vertical excitation	8
1.4	Geometries of 7AI(MeOH)$_n$ (n=1-3) and 2-(iminomethyl)phenol derivatives	24
2.1	Scheme of intermolecular PT/HT reaction of 7-azaindole with alcohol	26
2.2	The ground-state optimized structures of 7AI(MeOH)$_n$ (when n=1-3) complexes at RI-ADC(2)/SVP-SV(P) level. Numbering atoms for intermolecular hydrogen bonds to methanol molecules (a) 7AI(MeOH)$_1$ (b) 7AI(MeOH)$_2$ and (c) 7AI(MeOH)$_3$. Intermolecular hydrogen-bonded interactions are shown in dashed lines (Å)	30
2.3	Potential energy diagram of a selected trajectory for 7AI(MeOH)$_1$ complex at ground state (S_0) and excited states ($S_{\pi\pi^*}$, $S_{\pi\sigma^*}$) performed at RI-ADC(2)/SVP-SV(P) level	36
2.4	Potential energy diagram of a selected trajectory for 7AI(MeOH)$_2$ complex at ground state (S_0) and excited states ($S_{\pi\pi^*}$, $S_{\pi\sigma^*}$) performed at RI-ADC(2)/SVP-SV(P) level	37

2.5 Potential energy diagram of a selected trajectory for 7AI(MeOH)$_3$ complex at ground state (S_0) and excited states ($S_{\pi\pi^*}$, $S_{\pi\sigma^*}$) performed at RI-ADC(2)/SVP-SV(P) level 38

2.6 An on-the-fly dynamics simulation of a selected trajectory of a 7AI(MeOH)$_1$ complex showing time evolutions of the ESDPT reaction through hydrogen-bonded network within 78 fs. Normal (N), Proton transfer (PT), and Tautomer (T) 39

2.7 Average values over 54 trajectories of 7AI(MeOH)$_1$ complex (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 state (S_1-S_0) (c) Average dihedral angle of N1C1N2C2 40

2.8 An on-the-fly dynamics simulation of a selected trajectory for a 7AI(MeOH)$_2$ complex showing time evolutions of the ESTPT reaction through hydrogen-bonded network within 75 fs. Normal (N), Proton transfer (PT), and Tautomer (T) 42

2.9 Average values over 67 trajectories of 7AI(MeOH)$_2$ complex (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 state (S_1-S_0) (c) Average dihedral angle of N1C1N2C2 43

2.10 An on-the-fly dynamics simulation of a selected trajectory for a 7AI(MeOH)$_3$ complex showing time evolutions of the ESQPT reaction through hydrogen-bonded network within 112 fs. Normal (N), Proton transfer (PT), and Tautomer (T) 45

2.11 Average values over 26 trajectories of 7AI(MeOH)$_2$ complex (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 state (S_1-S_0) (c) Average dihedral angle of N1C1N2C2 46

3.1 *o*-Hydroxy Schiff base molecule (*R* is phenol ring and R_1 and R_2 are hydrogen atom or methyl substitution) 50

3.2 Scheme of intramolecular PT/HT reaction of *o*-hydroxy Schiff base molecule 51

3.3 The ground-state optimized structures of 2-(iminomethyl)phenol derivatives at B3LYP/TZVP level. Numbering atoms for intramolecular hydrogen-bonded network. Intramolecular hydrogen bond is shown in dashed lines (Å) 54

3.4 Potential energy diagram of a selected trajectory for 2-(iminomethyl) phenol (IMP) at ground state (S_0) and excited states ($S_{\pi\pi^*}$, $S_{\pi\sigma^*}$) performed at B3LYP/SVP level 59

3.5 Potential energy diagram of a selected trajectory for 2-(*N*-methyl-α-iminoethyl)phenol (MIEP) at ground state (S_0) and excited states ($S_{\pi\pi^*}$, $S_{\pi\sigma^*}$) performed at B3LYP/SVP level 60

3.6 Potential energy diagram of a selected trajectory for 2-(*N*-methyl-α-iminoethyl)-4-fluorophenol at ground state (S_0) and excited states ($S_{\pi\pi^*}$, $S_{\pi\sigma^*}$) performed at B3LYP/SVP level 60

3.7 An on-the-fly dynamics simulation of a selected trajectory of a 2-(iminomethyl)phenol (IMP) showing time evolutions along hydrogen-bonded network within 9 fs. Normal (N), Proton transfer (PT), and Tautomer (T) 61

3.8 Average values over 23 trajectories of 2-(iminomethyl)phenol (IMP) (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 state (S_1-S_0) (c) Average dihedral angle of C1C2C3N1 62

3.9 An on-the-fly dynamics simulation of a selected trajectory of a 2-(*N*-methyliminomethyl)phenol (MIMP) showing time evolutions along hydrogen-bonded network within 9 fs. Normal (N), Proton transfer (PT), and Tautomer (T) 63

3.10 Average values over 22 trajectories of 2-(*N*-methylimino methyl)phenol (MIMP) (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 state (S_1-S_0) (c) Average dihedral angle of C1C2C3N1 64

3.11 An on-the-fly dynamics simulation of a selected trajectory of a 2-(α-iminoethyl)phenol (IEP) showing time evolutions along hydrogen-bonded network within 14 fs. Normal (N), Proton transfer (PT), and Tautomer (T) 65

3.12 Average values over 25 trajectories of 2-(α-iminoethyl)phenol (IEP) (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 state (S_1-S_0) (c) Average dihedral angle of C1C2C3N1 66

3.13 An on-the-fly dynamics simulation of a selected trajectory of a 2-(*N*-methyl-α-iminoethyl)phenol (MIEP) showing time evolutions along hydrogen-bonded network within 14 fs. Normal (N), Proton transfer (PT), and Tautomer (T) 67

3.14 Average values over 25 trajectories of 2-(*N*-methyl-α-iminoethyl) phenol (MIEP) (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 state (S_1-S_0) (c) Average dihedral angle of C1C2C3N1 68

3.15 An on-the-fly dynamics simulation of a selected trajectory of a 2-(*N*-methyl-α-iminoethyl)-4-fluorophenol (MIEFP) showing time evolutions along hydrogen-bonded network within 14 fs. Normal (N), Proton transfer (PT), and Tautomer (T) 69

3.16 Average values over 24 trajectories of 2-(*N*-methyl-α-iminoethyl)-4-fluorophenol (MIEFP) (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 state (S_1-S_0) (c) Average dihedral angle of C1C2C3N1 70

3.17 An on-the-fly dynamics simulation of a selected trajectory of a 2-(*N*-methyl-α-iminoethyl)-4-chlorophenol (MIECP) showing time evolutions along hydrogen-bonded network within 14 fs. Normal (N), Proton transfer (PT), and Tautomer (T) 71

3.18 Average values over 24 trajectories of 2-(*N*-methyl-α-iminoethyl)-4-chlorophenol (MIECP) (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 state (S_1-S_0) (c) Average dihedral angle of C1C2C3N1 72

ABBREVIATIONS AND SYMBOLS

o	*ortho*
□	Wavefunction
$\hat{H}$	Hamiltonian
E	Total energy
Z_A, Z_B	Nuclear charges
M_A	Mass of nucleus A
R_{AB}	Distance between nuclei A and B
r_{ij}	Distance between electrons i and j
r_{iA}	Distance between election i and nuclei A
ε_0	Permittivity of free space
$\hbar$	Plank constant
ψ	Wavefunction associated with solving the electron part
χ	Wavefunction associated with nuclear motion
HF	Hartree-Fock
SCF	Self-consistent field
$\hat{h}^F$	Hartree-Fock operator
α , β	Electron spin
ψ_A, ψ_B	Wavefunction of A and B
$\chi_1(x_1)$	Position and spin of the singular electron
CI	Configuration interaction

MCSCF	Multireference configuration self-consistency field
CC	Coupled cluster
RI	Resolution-of-the-identity
CC2	Second-order approximate coupled-cluster model
ADC(2)	Algebraic diagrammatic construction through second order
F	Fock operator
τ_k^c and τ_{kl}^{cd}	Single and double replacement operators
CIS(D_∞)	The doubles correlation to CI singles
DFT	Density functional theory
MP2	Second order Møller–Plesset perturbation
$\rho(r)$	Electron density
B3LYP	Becke's three parameters and Lee-Yang-Parr correlation function
TDDFT	Time-dependent density functional theory
$\rho(r,t)$	Time-dependent potentials and electron densities
Φ_α	Slater determinants of Kohn-Sham orbitals
$c_{i\alpha}$	Coefficients determined form group theory
E_j	Energy of the many-body state
ω	Weight between 0 and 1/2
F_k	Electronic wavefunction
R^c	Single nuclear configuration
TDSE	Time-dependent Schrödinger equation
c_k	electronic state k

V_k	Potential energy surface for state k
v	Nuclear velocity
F_{kj}	Nonadiabatic coupling vector between the states k and j
P_W	Wigner distribution
Q	Normal modes
χ^0_{HO}	Quantum harmonic oscillator wavefunction for the ground vibrational state
P^i	Momentum associated with the normal coordinate Q^i
μ^i	Reduced mass
ω^i_{OH}	Harmonic frequency and the equilibrium
ξ^i_{OH}	Harmonic oscillator wavefunction
$S_{\pi\pi^*}$	Excited-state proton transfer surface
$S_{\pi\sigma^*}$	Excited-state hydrogen atom transfer surface
SVP	Split valence polarized basis set
SV	Split valence basis set
fs	Femtosecond
kcal.mol^{-1}	Kilocalorie per mole
Å	Angstrom
ø	Dihedral angle
º	Degree
eV	Electron volt
TZVP	triple-ζ-valence polarized