CHAPTER III

EXCITED-STATE INTRAMOLECULAR PROTON TRANSFER REACTIONS IN 2-(IMINOMETHYL)PHENOL DERIVATIVES

3.1 Introduction

Intramolecular hydrogen bonds are often applied to model systems in the study of PT/HT reaction [75]. Investigations of hydrogen bonds and related molecular systems are interesting for understanding the various biological and chemical relevant properties at the molecular level [76]. Excited-state intramolecular characters can be investigated under well defined conditions and directly initiated by absorption of photons from a laser pulse allowing time resolved experiments with an extremely high precision. In addition, the ESIntraPT/HT reactions allow studying the basis function of a chemical reaction, i.e. bond fission and formation in a comparative simple situation [19-21,77].

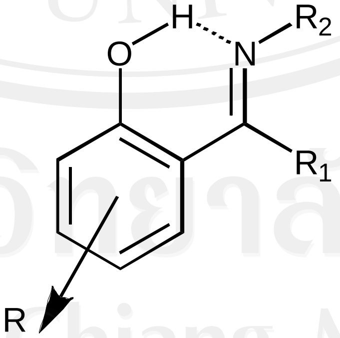


Figure 3.1 *o*-Hydroxy Schiff base molecule (*R* is phenol ring and R_1 and R_2 are hydrogen atom or methyl substitution)

For the intramolecular PT/HT reaction, the development of ultrafast spectroscopic techniques has allowed a direct observation of PT/HT dynamics in several molecular systems. An *o*-hydroxy Schiff base molecule (Figure 3.1) having $RR_1C=NR_2$ (where R is a phenol ring and $R_1 = R_2 =$ hydrogen atom) called 2-(iminomethyl)phenol [19,37] is the most important compound in photochemistry due to its photochromic property and intramolecular hydrogen bonding. 2-(iminomethyl)phenol, the hydrogen atom of hydroxy group of the phenol ring forming hydrogen bond to the nitrogen atom on the imine group which gives enol-keto tautomerization, is investigated for a model system of the ESIntra/HT process in this study (Figure 3.2).

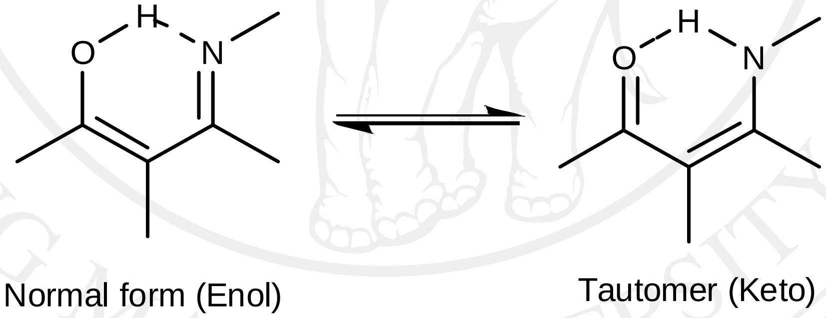


Figure 3.2 Scheme of intramolecular PT/HT reaction of *o*-hydroxy Schiff base molecule

The 2-(iminomethyl)phenol and its derivatives are among the most studied compounds for the intramolecular PT/HT investigation [19,75]. The ESIntraPT/HT reactions taking place in 2-(iminomethyl)phenol and also its derivatives are computationally affordable for theoretical study because of their simple reactions and small molecules for the molecular dynamics on the excited state calculations [18-20].

Scheiner [78] studied the influence of the length and bending of the hydrogen bridge on the barrier height in the ground state and excited state. The stabilization by resonance (Resonance Assisted Hydrogen Bond) permits overpassing of the increase of the interatomic repulsive term when the distance of heavy atoms (O1 and N1) becomes short [77]. His targeted compounds undergo the ESIntraPT/HT reaction after photoexcitation process [18-20]. Moreover, substituent placed or modification to a phenol ring could affect hydrogen-bonding interaction forming between nitrogen atom of imine group and hydroxyl group of *o*-position on the phenol ring.

For this chapter, we will investigate the ESIntraPT/HT reaction on the 2-(iminomethyl)phenol derivatives through intramolecular hydrogen bond. The important molecular properties of the systems in molecular level such as reaction pathway, reaction probability, and time evolution of the ESPT/HT process will be clarified.

3.2 Methods

3.2.1 Ground-state optimizations

As the same criteria used in $7AI(MeOH)_{n=1-3}$ complexes which is presented in chapter II, ground-state optimizations in the gas phase of 2-(iminomethyl) phenol derivatives were performed using density functional theory (DFT) method by Becke's three parameters hybrid functional and the Lee-Yang-Parr correlation function (B3LYP) [79-80]. In this case, triple-ζ-valence polarized (TZVP) [81] basis was assigned to all atoms. This theory and basis sets are small but sufficient enough to describe the structures. All optimized structures of 2-(iminomethyl)phenol derivatives were further used in the excited-state dynamics simulations.

3.2.2 Excited-state dynamics simulations

The ground-state geometries of 2-(iminomethyl)phenol derivatives were prepared before generating the initial condition generation. The initial conditions were generated using a harmonic-oscillator Wigner distribution. Twenty-five trajectories for each molecule were simulated with a time step of 1 fs and the maximum time up to 200 fs of investigating the ESIntraPT/HT reactions. All trajectories of the ESIntraPT/HT reactions were calculated at B3LYP/SVP level and analyzed using the same strategy as used in the ESInterPT/HT investigations of 7AI and methanol.

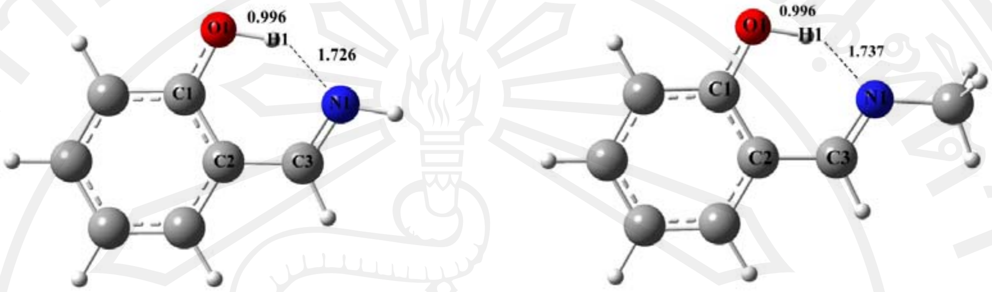
3.3 Results and discussion

3.3.1 Ground-state optimizations

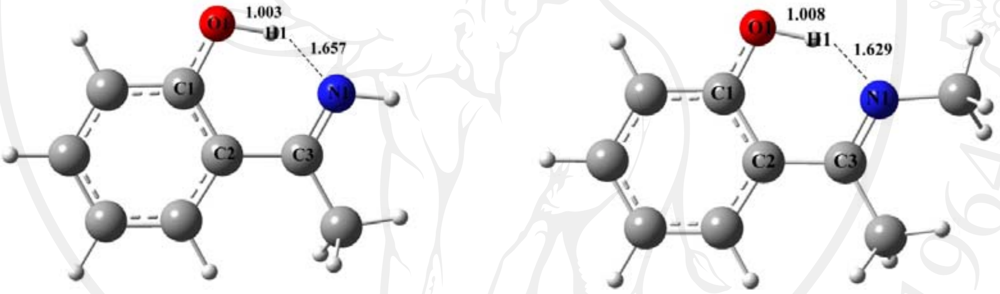
The ground-state structures of the 2-(iminomethyl)phenol derivatives were optimized using B3LYP/TZVP level. The optimized structures of the 2-(iminomethyl)phenol derivatives are depicted in Figure 3.3 with numbering atoms of intramolecular hydrogen bond. There is only one intramolecular hydrogen bond between H1 and N1 on O1–H1···N1 bridge for each molecule in which hydroxy group in the phenol ring forms the hydrogen bond to the nitrogen atom in the imine group presented in dashed line.

For 2-(iminomethyl)phenol (IMP), there is no methyl substitution on imine moiety. If R_1 = hydrogen atom and R_2 = methyl, it is called 2-(*N*-methylimino methyl)phenol (MIMP), In contrast, if R_1 = methyl and R_2 = hydrogen atom, it is called 2-(α-iminoethyl)phenol (IEP). When R_1 = R_2 = methyl substitution, it is call 2-(*N*-methyl-α-iminoethyl)phenol (MIEP). Moreover, the substitution of fluoro and chloro atom on phenol ring at *o*-position called 2-(*N*-methyl-α-iminoethyl)-4-

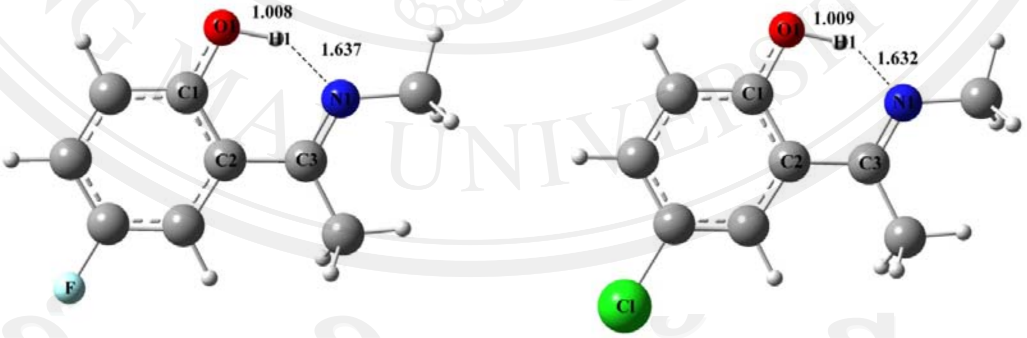
fluorophenol (MIEFP) and 2-(*N*-methyl-α-iminoethyl)-4-chlorophenol (MIECP), respectively. All selected distances and dihedral angles are summarized in Table 3.1.



(a) 2-(Iminomethyl)phenol (b) 2-(*N*-Methyliminomethyl)phenol



(c) 2-(α-Iminoethyl)phenol (d) 2-(*N*-Methyl-α-iminoethyl)phenol



(e) 2-(*N*-Methyl-α-iminoethyl)-4-fluorophenol (d) 2-(*N*-Methyl-α-iminoethyl)-4-chlorophenol

Figure 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)

Table 3.1 Summary of intramolecular hydrogen bonds and selected distances (Å) and øC1C2C3N1 dihedral angles (°) of the ground-state structures performed at B3LYP/TZVP level

	Molecule					
	IMP	**MIMP**	**IEP**	**MIEP**	**MIEFP**	**MIECP**
O1–H1	0.996	0.996	1.003	1.008	1.008	1.009
H1···N1	1.726	1.737	1.657	1.629	1.637	1.632
O1···N1	2.616	2.632	2.560	2.549	2.554	2.551
N1=C3	1.283	1.278	1.288	1.289	1.287	1.287
ø	0.01	0.11	-0.03	-4.03	-0.93	-0.09

Table 3.1 shows selected bonds and distances that we are interested in, for example, O1–H1 of hydroxyl group of phenol, H1···N1 of intramolecular hydrogen bond, O1···N1 of distance between heavy atoms, and N1=C3 of imine group. We can divide these molecules into two sections: first, a substituent on imine group and second, the substituent on phenol ring.

For the first section, a substituent was varied on imine group. For IMP, we found that H1···N1 intramolucular hydrogen bond is 1.726 Å. For MIMP, when *N*-methyl group is added into N1 of imine, H1···N1 is 1.737 Å in which distance is slightly longer than that of IMP molecule. From this point, we can suggest that *N*-methyl affect insignificantly the intramolecular hydrogen bond. For IEP, H1···N1 intramolecular hydrogen bond is 1.657 Å which becomes shorter than that of IMP by 0.07 Å. And, MIEP has intramolecular hydrogen bond of 1.629 Å which is shorter than that of IMP by 0.1 Å. When the substituents are added into the –C(H)=N– group, the intramolecular hydrogen bond becomes shorter. In addition, the bulky of substituents on imine moiety especially in MIEP molecule make the distance between these substituents change due to steric repulsion between them. It leads to shortening of intramolecular hydrogen bond (H1···N1) and distance of O1···N1. Replacement of the methyl group should increase the tendency for the PT/HT process upon the photoexcitation.

However, the MIEP molecule has the shortest intramolecular hydrogen bond, so it has been used to study role of substituent on its phenol ring by adding the substituents such as fluoro and chloro on phenol ring. The fluoro and chloro substituents increase acidity of phenolic part of MIEFP and MIECP in which lone pair electrons possibly delocalize on the phenol ring. So, the H1···N1 intramolecular hydrogen bond of MIEFP and MIECP molecules slightly increases compared to the MIEP molecule. Moreover, O1–H1 for all molecules is slightly change when the substituents are added corresponding to the N1=C3 bond due to the strength of intramolecular hydrogen bond. Such comparisons show the very strong influence of the methyl substitution at the imine moiety. The 2-(iminomethyl)phenol derivatives is slightly planar dihedral angle (øC1C2C3N1) at almost 0°. When the dynamics simulations are performed, the dihedral angle should be slightly twisted because of its rigidity on the imine moiety.

Modification of acid-base properties of the system by changing the substituents on the phenol ring as well as methyl substitution on imine moiety should reduce the barrier height of PT reaction. The molecule that has the shortest intramolecular hydrogen bond or distance between heavy atoms on the O1–H1···N1 bridge should have very low barrier height. Therefore, the MIEP molecule could be the most effective molecule in revealing of the ESIntraPT reaction in the photoexcitation.

These optimized structures at B3LYP/TZVP level for 2-(iminomethyl)phemol derivatives will be used to obtain detailed information about the PT/HT process for excited-state dynamics simulations. In order to reduce computational time for the excited-state dynamics simulation, B3LYP/SVP level was assigned.

3.3.2 Excited-state dynamics simulations

Twenty-five trajectories of on-the-fly dynamics simulations are generated for each molecule to investigate the PT/HT pathway. The analysis using simulation times up to 100 fs should reveal the mechanism including pre- and post-PT/HT processes. By definition, the PT/HT time from the X–H = H–Y distance is used. Furthermore, the trajectories for each molecule are classified and summarized in Table 3.2.

Table 3.2 Summary of the excited-state dynamics analysis of 2-(iminomethyl)phenol derivatives

Molecule	**Reaction[d]**			**Probability[e]**	**PT time (fs)**
	ESPT (200 fs)	**ESPT (<200 fs)**	**No**		
IMP	7	16	2	92	9 (1.320)
MIMP	13	9	3	88	11 (1.382)
IEP	18	7	-	100	7 (1.328)
MIEP	25	-	-	100	8 (1.302)
MIEFP	24	-	1	96	7 (1.298)
MIECP	24	-	1	96	10 (1.353)

[d]Unit in trajectory, [e]The reaction probability (%),

Average distance (Å) of X–H and H–Y intersection for each PT (in parenthesis)

From selected trajectories of excited-state dynamics simulation for each molecule, the energies (kcal.mol^{-1}) of the ground (S_0) and excited states ($S_{\pi\pi^*}$ and $S_{\pi\sigma^*}$) for characteristic stationary points along the reaction pathways (Table 3.3) are computed and compared.

Table 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

State	Form	Molecule					
		IMP	**MIMP**	**IEP**	**MIEP**	**MIEFP**	**MIECP**
S_0	N	0.00	0.00	0.00	0.00	0.00	0.00
	IS	13.50	11.74	7.78	4.41	8.80	21.97
	T	10.49	5.78	2.72	3.06	2.47	17.36
$S_{\pi\pi^*}$	N	96.68	87.78	87.38	92.35	84.80	83.50
	IS	90.98	78.87	77.12	71.75	72.55	77.92
	T	78.12	74.74	60.34	63.62	62.16	73.88
$S_{\pi\sigma^*}$	N	152.95	157.36	141.30	148.96	140.20	130.31
	IS	131.12	149.07	140.12	140.02	140.67	139.01
	T	111.07	136.36	124.42	123.49	129.26	140.56

From Table 3.3, normal or enol forms of all structures show that they are more stable with a lower energy than their tautomers or keto forms in ground state and have low barrier height. However, a deeper minimum for the tautomers is existence for all molecules for the PT in photoexcitation. We used the information in the Table 3.3 to generate potential energy diagrams of selected trajectories for 2-(iminomethyl)phenol derivatives (Figure 3.4-3.6).

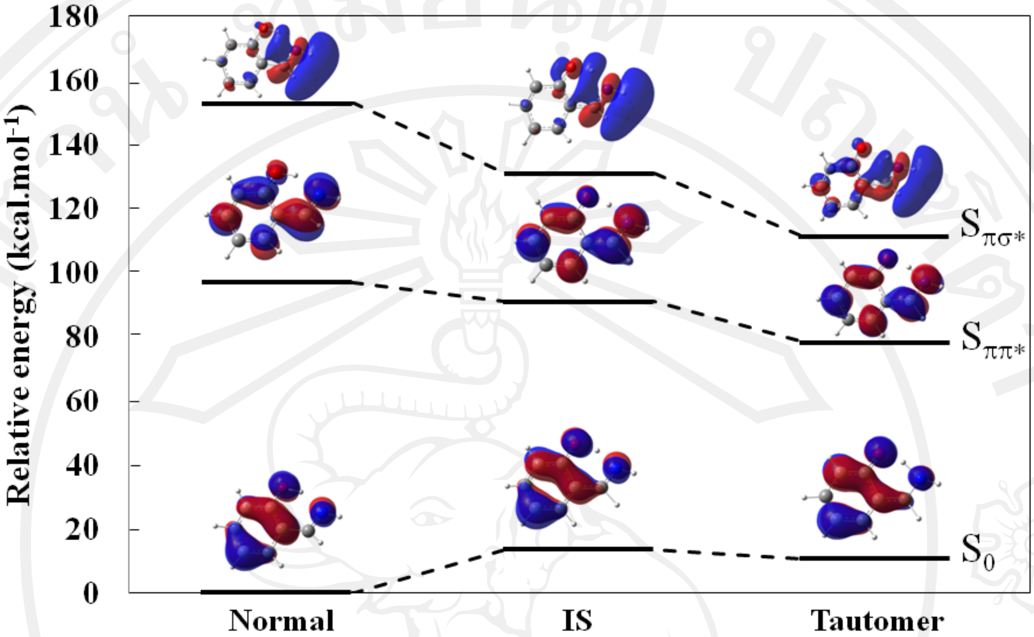


Figure 3.4 Potential energy diagram of a selected trajectory for 2-(iminomethyl) phenol (IMP) at ground state (S_0) and excited states ($S_{\pi\pi*}$, $S_{\pi\sigma*}$) performed at B3LYP/SVP level

These potential energy diagrams show that $S_{\pi\sigma*}$ lies above $S_{\pi\pi*}$ state over 80 kcal.mol^{-1}. These states play a key role in determining the nature of the excited-state reactions since the ESPT occurs on the $S_{\pi\pi*}$ state, whereas the ESHT occurs on the $S_{\pi\sigma*}$ states. Therefore, we can conclude that all 2-(iminomethyl)phenol derivatives exhibit the ESIntraPT reactions confirmed by no crossing between $S_{\pi\pi*}$ and $S_{\pi\sigma*}$ states and all trajectories in this investigation take place only on $S_{\pi\pi*}$ state called PT process.

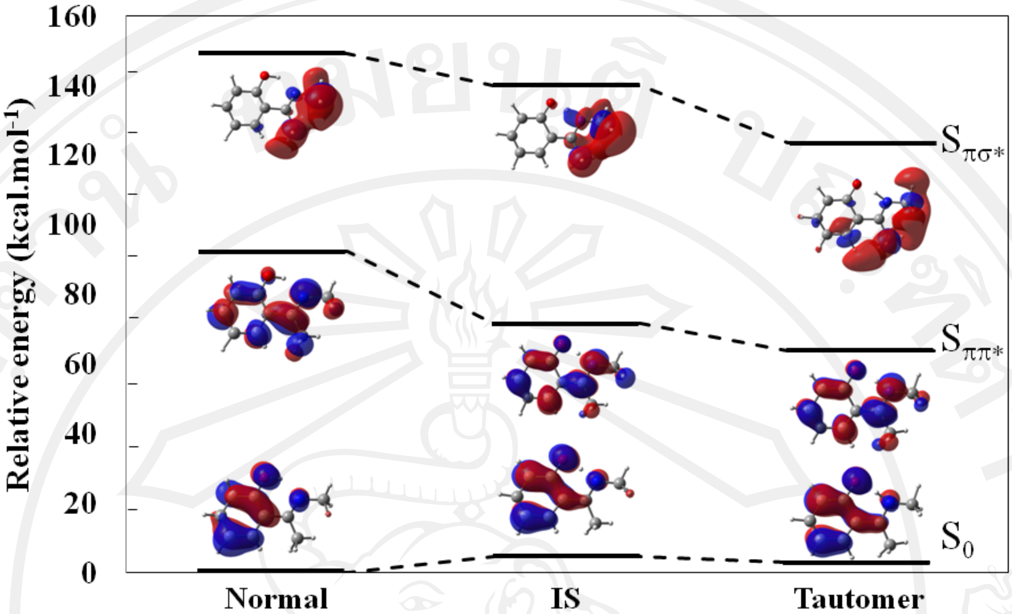


Figure 3.5 Potential energy diagram of a selected trajectory for 2-(*N*-methyl-α-iminoethyl)phenol (MIEP) at ground state (S_0) and excited states ($S_{\pi\pi*}$, $S_{\pi\sigma*}$) performed at B3LYP/SVP level

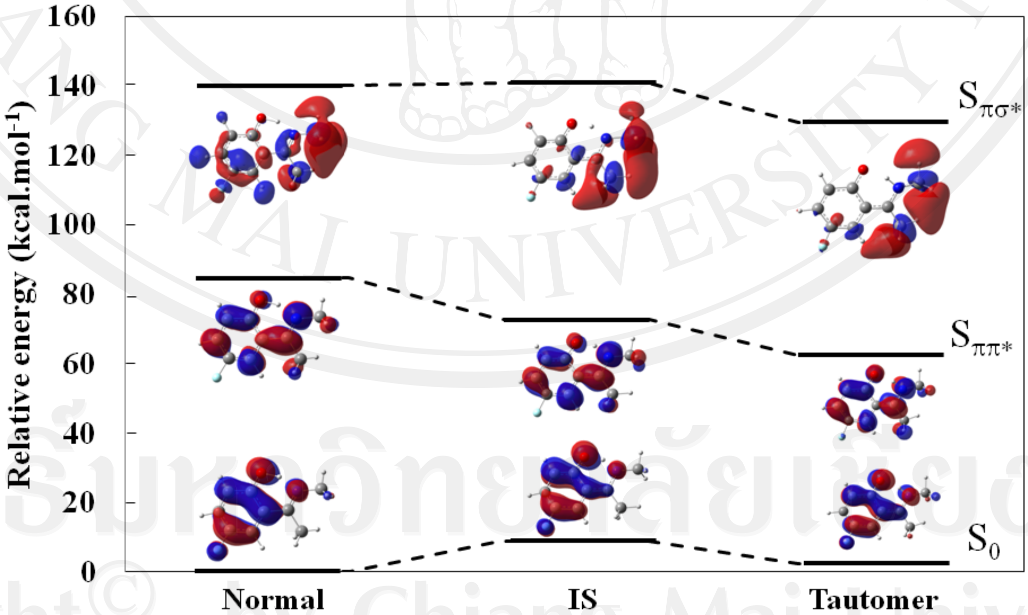


Figure 3.6 Potential energy diagram of a selected trajectory for 2-(*N*-methyl-α-iminoethyl)-4-fluorophenol at ground state (S_0) and excited states ($S_{\pi\pi*}$, $S_{\pi\sigma*}$) performed at B3LYP/SVP level

So, this investigation will focus mainly on the $S_{\pi\pi*}$ state that gives detailed picture of the ESPT mechanism.

3.3.2.1 2-(Iminomethyl)phenol (IMP)

From 25 trajectories, there are only 2 trajectories that have no reaction. From 23 trajectories, we found only 7 trajectories that have the ESIntraPT completing up to 200 fs but the other trajectories show the simulations stopped due to the structural twist in which the conical intersection possibly takes place within the time less than 200 fs. Thus, the reaction probability is 92%.

By a selected trajectory (Figure 3.7), the details of the PT process can be illustrated. The numbering is the same as defined in Figure 3.3a. A normal (N) form is observed at 0 fs. The H1 atom departs from O1 to N1 atom (PT) at 7 fs, and then the tautomer (T) form is formed within 9 fs.

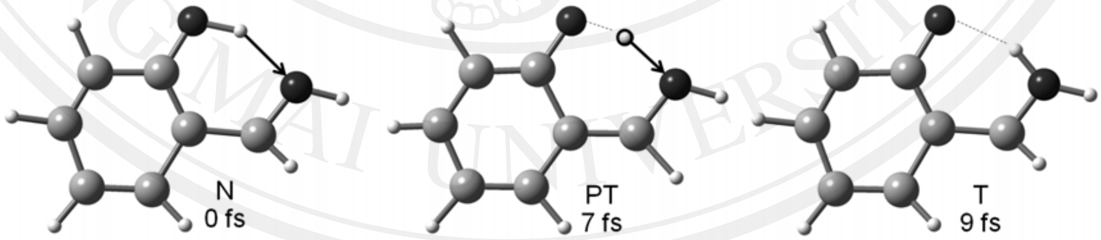


Figure 3.7 An on-the-fly dynamics simulation of a selected trajectory of a 2-(iminomethyl)phenol (IMP) showing time evolution along hydrogen-bonded network within 9 fs. Normal (N), Proton transfer (PT), and Tautomer (T)

Average values for energy and geometric parameters for the 23 trajectories following the ESIntraPT reaction are shown in Figure 3.8. The evolution of the average values of breaking bonds (O1–H1) and forming bonds (H1···N1) is shown in Figure 3.8a. The intersection between the curves indicates that the PT occurs at 9 fs when O1–H1and H1–N1 distances are equal to 1.320 Å. Figure 3.8b shows that the

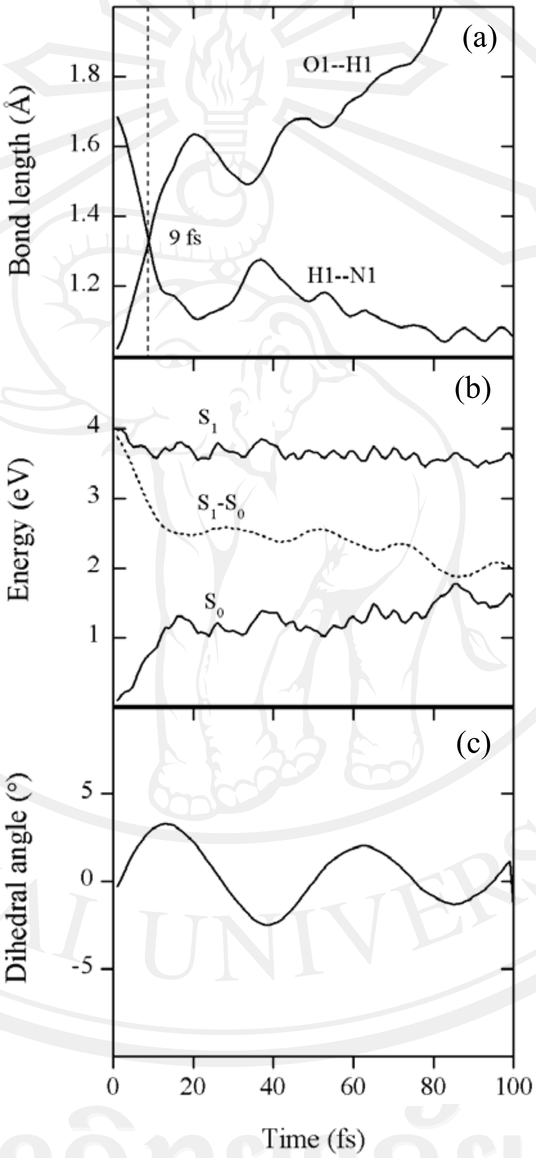


Figure 3.8 Average values over 23 trajectories of 2-(iminomethyl)phenol (IMP) (a) Average breaking and forming bonds showing time evolution (b) Average relative energies of excited state (S_1), ground state (S_0), and energy difference of S_1 and S_0 state (S_1-S_0) (c) Average dihedral angle of C1C2C3N1

average energy difference between S_1 and S_0 decreases but it is still higher than 2 eV suggesting that the structure of IMP during time less than 100 fs be planar. This planarity of IMP is confirmed by average value of the dihedral angle C1C2C3N1 fluctuate less than 4° as shown in Figure 3.8c.

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

From 25 trajectories, there are only 3 trajectories that have no reaction. From 22 trajectories, we found only 13 trajectories that have the ESIntraPT finished to 200 fs but somehow crossing between two excited states possibly take place within the time less than 200 for the other trajectories fs. Thus, the reaction probability is 88% which is slightly lower than that of the IMP molecule.

The details of the PT process can be illustrated by a selected trajectory (Figure 3.9). The numbering is the same as defined in Figure 3.3b. A normal (N) form is observed at 0 fs. The H1 atom departs from O1 to N1 atom (PT) at 8 fs, and then the tautomer (T) form is formed within 9 fs.

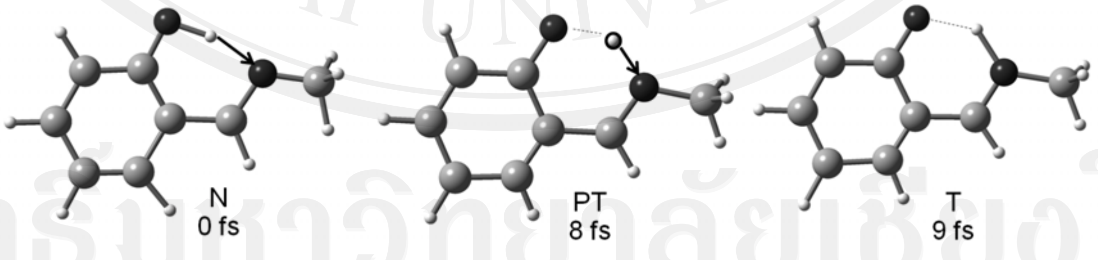


Figure 3.9 An on-the-fly dynamics simulation of a selected trajectory of a 2-(*N*-methyliminomethyl)phenol (MIMP) showing time evolution along hydrogen-bonded network within 9 fs. Normal (N), Proton transfer (PT), and Tautomer (T)

Average values for energy and geometric parameters for the 22 trajectories following the ESIntraPT reaction are shown in Figure 3.10. The evolution of the average values of breaking bonds (O1–H1) and forming bonds (H1···N1) is shown in

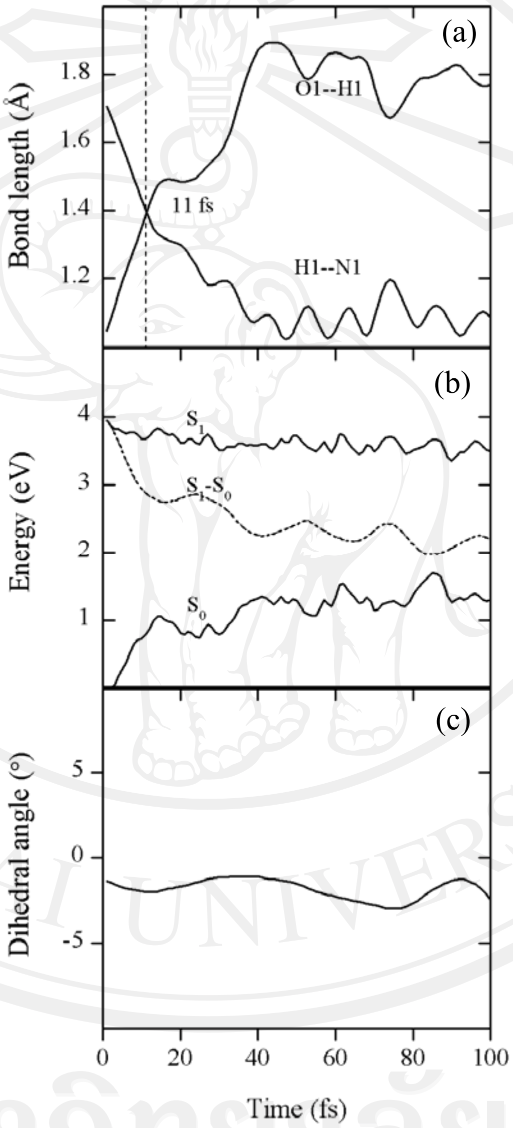


Figure 3.10 Average values over 22 trajectories of 2-(*N*-methyliminomethyl)phenol (MIMP) (a) Average breaking and forming bonds showing time evolution (b) Average relative energies of excited state (S_1), ground state (S_0), and energy difference of S_1 and S_0 state (S_1-S_0) (c) Average dihedral angle of C1C2C3N1

Figure 3.10a. The intersection between the curves indicates that the PT occurs at 11 fs when O1–H1and H1–N1 distances are equal to 1.382 Å. Figure 3.10b shows that the average energy difference between S_1 and S_0 decreases but it is still higher than 2 eV suggesting that the structure of MIMP during time less than 100 fs be planar. This planarity of MIMP is confirmed by average value of the dihedral angle C1C2C3N1 fluctuate less than 3° as shown in Figure 3.10c.

3.3.2.3 2-(α-Iminoethyl)phenol (IEP)

From 25 trajectories, all trajectories show ESIntraPT completely. There are only 18 trajectories that show the time up to 200 fs and 7 trajectories complete the PT process less than 200 fs. Thus, the reaction probability is 100%. It indicates that methyl group added into imine group increases the probability of the PT/HT in the excitation process. Also, steric repulsion between those substituents on imine and phenol ring leads to shortening of O1···N1 distance.

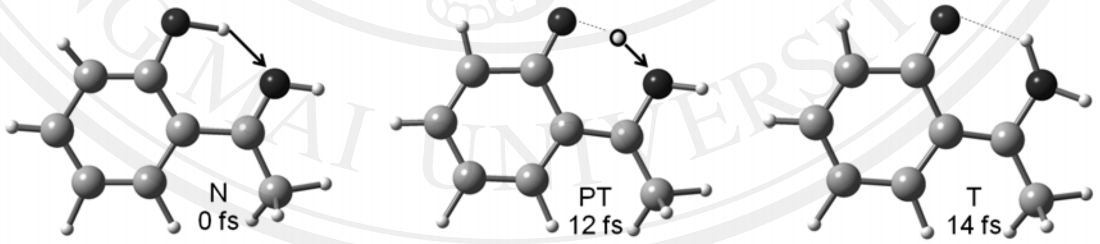


Figure 3.11 An on-the-fly dynamics simulation of a selected trajectory of a 2-(α-iminoethyl)phenol (IEP) showing time evolution along hydrogen-bonded network within 14 fs. Normal (N), Proton transfer (PT), and Tautomer (T)

The details of the PT process can be illustrated by a selected trajectory (Figure 3.11). The numbering is the same as defined in Figure 3.3c. A normal (N) form is observed at 0 fs. The H1 atom departs from O1 to N1 atom (PT) at 12 fs, then the tautomer (T) form is formed within 14 fs.

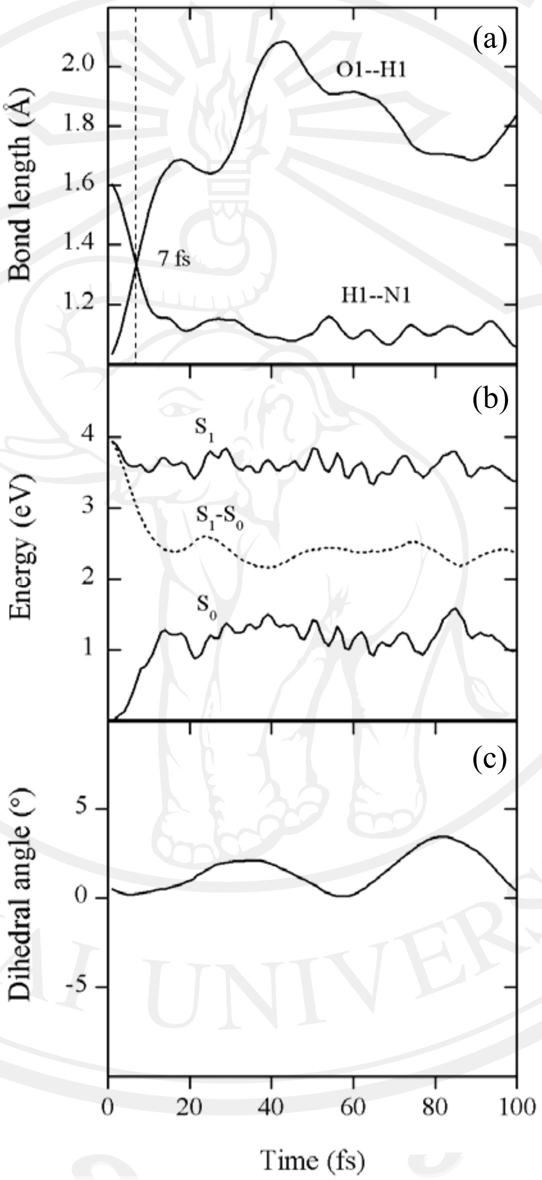


Figure 3.12 Average values over 25 trajectories of 2-(α-iminoethyl)phenol (IEP) (a) Average breaking and forming bonds showing time evolution (b) Average relative energies of excited state (S_1), ground state (S_0), and energy difference of S_1 and S_0 state (S_1-S_0) (c) Average dihedral angle of C1C2C3N1

Average values for energy and geometric parameters for the 25 trajectories following the ESIntraPT reaction are shown in Figure 3.12. The evolution of the average values of breaking bonds (O1–H1) and forming bonds (H1···N1) is shown in Figure 3.12a. The intersection between the curves indicates that the PT occurs at 7 fs when O1–H1and H1–N1 distances are equal to 1.328 Å. Figure 3.12b shows that the average energy difference between S_1 and S_0 decreases but it is still higher than 2 eV suggesting that the structure of IEP during time less than 100 fs be planar. The dihedral angle C1C2C3N1 fluctuates less than 3° as shown in Figure 3.12c.

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

From 25 trajectories, all trajectories show ESIntraPT completely up to time of 200 fs. Thus, the reaction probability is 100%. It suggests that the more methyl groups added into imine group increase the tendency for the PT/HT in the excitation process effectively.

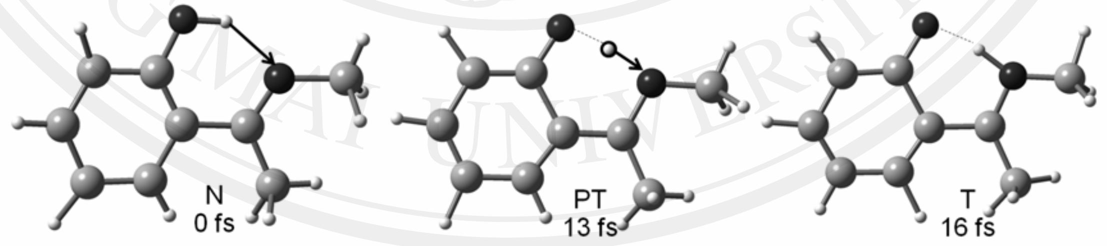


Figure 3.13 An on-the-fly dynamics simulation of a selected trajectory of a 2-(*N*-methyl-α-iminoethyl)phenol (MIEP) showing time evolution along hydrogen-bonded network within 14 fs. Normal (N), Proton transfer (PT), and Tautomer (T)

The details of the PT process can be illustrated by a selected trajectory (Figure 3.13). The numbering is the same as defined in Figure 3.3d. A normal (N) form is observed at 0 fs. The H1 atom departs from O1 to N1 atom (PT) at 13 fs, then the tautomer (T) form is formed within 16 fs.

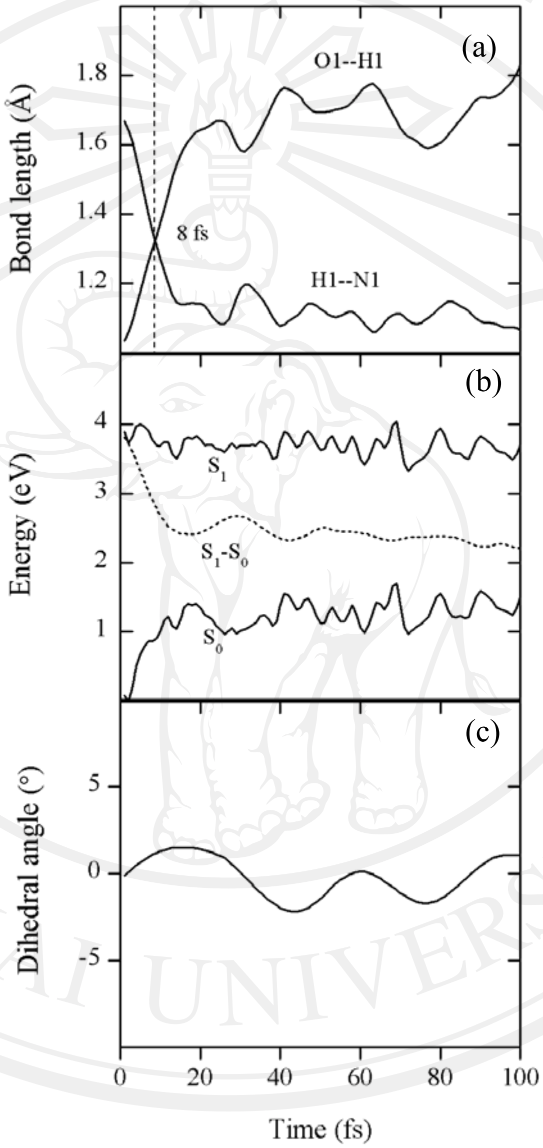


Figure 3.14 Average values over 25 trajectories of 2-(*N*-methyl-α-iminoethyl) phenol (MIEP) (a) Average breaking and forming bonds showing time evolution (b) Average relative energies of excited state (S_1), ground state (S_0), and energy difference of S_1 and S_0 state (S_1-S_0) (c) Average dihedral angle of C1C2C3N1

Average values for energy and geometric parameters for the 25 trajectories following the ESIntraPT reaction are listed in Figure 3.14. The evolution of the average values of breaking bonds (O1–H1) and forming bonds (H1···N1) is plotted Figure 3.14a. The intersection between the curves indicates that the PT occurs at 8 fs when O1–H1and H1–N1 distances are equal to 1.302 Å. Figure 3.14b shows that the average energy difference between S_1 and S_0 decreases but it is still higher than 2 eV suggesting that the structure of MIEP during time less than 100 fs be planar. This planarity of MIEP is confirmed by average value of the dihedral angle C1C2C3N1 which fluctuates less than 3° as shown in Figure 3.14c.

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

From 25 trajectories, almost all trajectories show ESIntraPT complete up to time 200 fs for 24 trajectories. There is only one trajectory that has stopped due to the error of calculations. Thus, the reaction probability is 96%. It should be suggested that increased acidity on phenol ring increase the tendency for the PT/HT in the excitation process effectively.

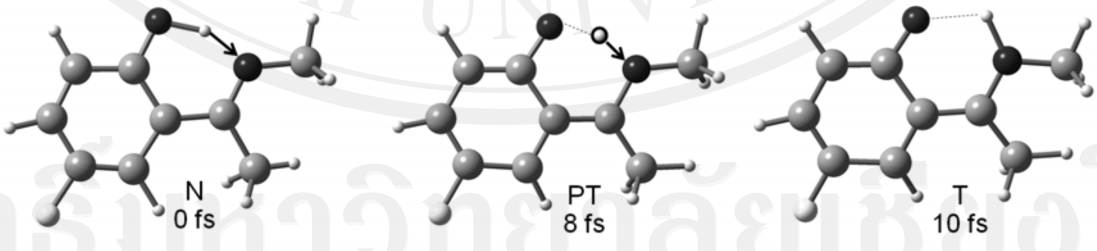


Figure 3.15 An on-the-fly dynamics simulation of a selected trajectory of a 2-(*N*-methyl-α-iminoethyl)-4-fluorophenol (MIEFP) showing time evolution along hydrogen-bonded network within 14 fs. Normal (N), Proton transfer (PT), and Tautomer (T)

The details of the PT process can be illustrated by a selected trajectory (Figure 3.15). The numbering is the same as defined in Figure 3.3d. A normal (N) form is observed at 0 fs. The H1 atom departs from O1 to N1 atom (PT) at 8 fs, then the tautomer (T) form is formed within 10 fs.

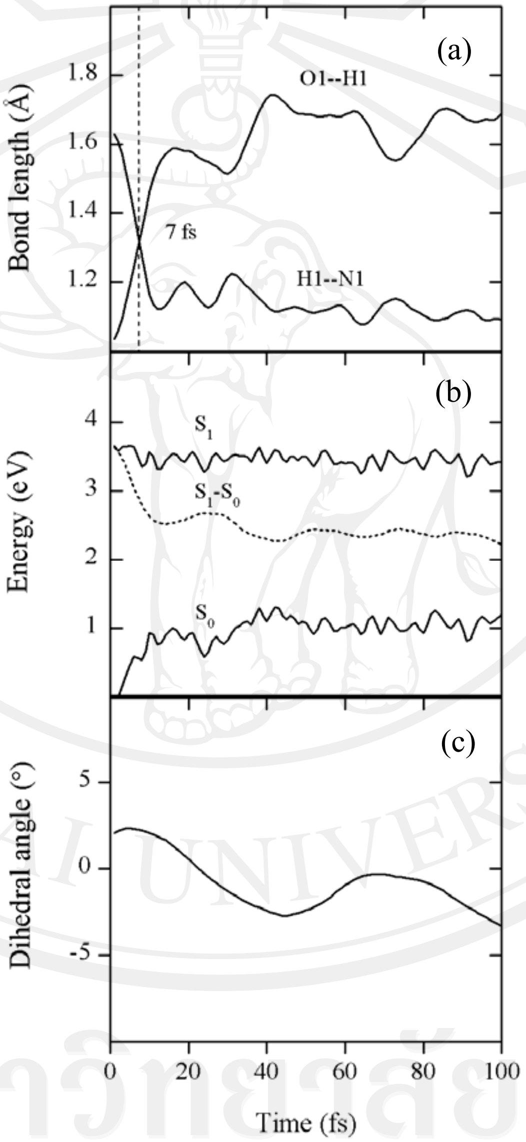


Figure 3.16 Average values over 24 trajectories of 2-(*N*-methyl-α-iminoethyl)-4-fluorophenol (MIEFP) (a) Average breaking and forming bonds showing time evolution (b) Average relative energies of excited state (S_1), ground state (S_0), and energy difference of S_1 and S_0 state (S_1-S_0) (c) Average dihedral angle of C1C2C3N1

Average values for energy and geometric parameters for the 24 trajectories following the ESIntraPT reaction are depicted in Figure 3.16. The evolution of the average values of breaking bonds (O1–H1) and forming bonds (H1···N1) is shown in Figure 3.16a. The intersection between the forming and breaking bond lines indicates that the PT occurs at 7 fs when O1–H1and H1–N1 distances are equal to 1.298 Å. Figure 3.16b shows that the average energy difference between S_1 and S_0 decreases but it is still higher than 2 eV suggesting that the structure of MIEFP during time less than 100 fs be planar. This planarity of MIEFP is confirmed by average value of the dihedral angle C1C2C3N1 which fluctuates and twists within 3° as shown in Figure 3.16c.

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

From 25 trajectories, almost all trajectories show ESIntraPT completely up to time 200 fs for 24 trajectories. There is only one trajectory stopped that could be from any error of the program. Thus, the reaction probability is 96%. It should be indicated that its efficiency is less than that of MIEFP due to lower electron negativity.

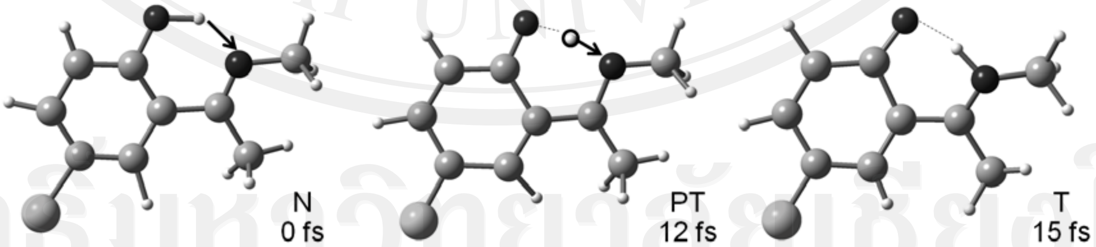


Figure 3.17 An on-the-fly dynamics simulation of a selected trajectory of a 2-(*N*-methyl-α-iminoethyl)-4-chlorophenol (MIECP) showing time evolution along hydrogen-bonded network within 14 fs. Normal (N), Proton transfer (PT), and Tautomer (T)

The details of the PT process can be illustrated by a selected trajectory (Figure 3.17). The numbering is the same as defined in Figure 3.3d. A normal (N) form is observed at 0 fs. The H1 atom departs from O1 to N1 atom (PT) at 12 fs, then the tautomer (T) form is formed within 15 fs.

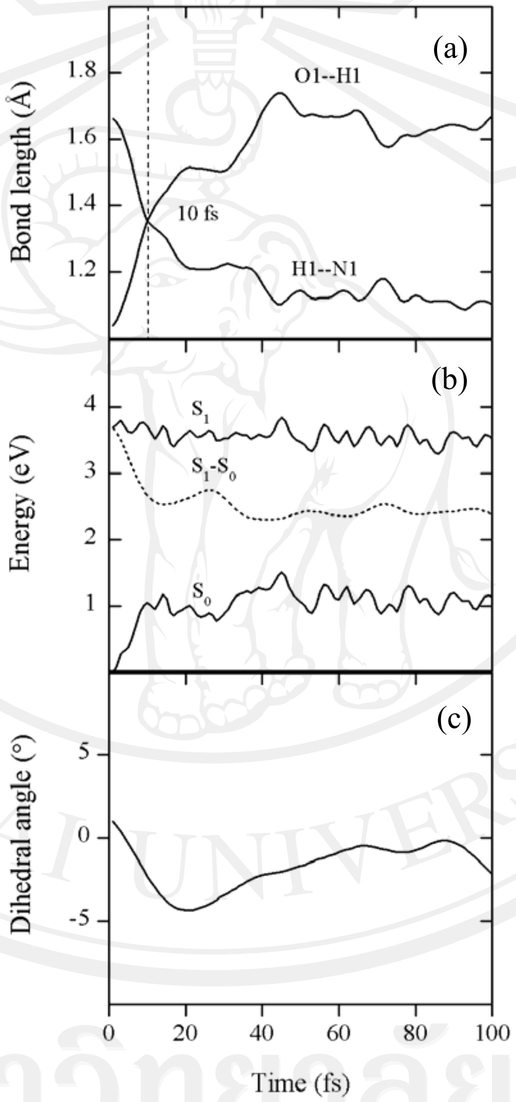


Figure 3.18 Average values over 24 trajectories of 2-(*N*-methyl-α-iminoethyl)-4-chlorophenol (MIECP) (a) Average breaking and forming bonds showing time evolution (b) Average relative energies of excited state (S_1), ground state (S_0), and energy difference of S_1 and S_0 state (S_1-S_0) (c) Average dihedral angle of C1C2C3N1

Average values for energy and geometric parameters for the 24 trajectories following the ESIntraPT reaction are shown in Figure 3.18. The evolution of the average values of breaking bonds (O1–H1) and forming bonds (H1···N1), is shown in Figure 3.18a. The intersection between the curves indicates that the PT occurs at 10 fs when O1–H1and H1–N1 distances are equal to 1.353 Å. Figure 3.18b shows that the average energy difference between S_1 and S_0 decreases but it is still higher than 2 eV suggesting that the structure of MIECP during time less than 100 fs be planar. This planarity of MIECP is confirmed by average value of the dihedral angle C1C2C3N1 that fluctuates and twists within 3° as shown in Figure 3.18c.

From the results, the methyl groups added into imine moiety increase intramolecular hydrogen bond and help the PT reaction in the photoexcitation. It is indicated that the more methyl groups added into imine group, the more increase the effective of the PT reaction for IMP, MIMP, IEP, and MIEP. The MIEP molecule has the shortest intramolecular hydrogen bond, so it has been used to study role of substituent on its phenol ring by adding the substituents such as fluoro and chloro on phenol ring.

However, the fluoro and chloro substituents increase acidity of phenolic part of MIEFP and MIECP in which lone pair electrons possibly delocalize on the phenol ring. The modification of acid-base properties of the system by changing methyl substitution on imine moiety reduces the barrier height of PT reaction more effective than changing the substituent on the phenol ring. In addition, these excited-state barrier heights for all molecules are barrierless. For MIEP molecule, it has the lowest barrierless so the ESIntraPT reaction is the most efficiently confirmed by the 100% probability.

3.4 Summary

We have carried out the ground-state structures of 2-(iminomethyl)phenol derivatives for 6 species using density functional theory at B3LYP/TZVP level. It found that the ESIntraPT at B3LYP/SVP level takes place confirmed by no crossing between $S_{\pi\pi^*}$ and $S_{\pi\sigma^*}$ states. The intramolecular PT is the most important factor in modulating the potential for the PT without any help of solvents. These reactions are ultrafast within 10 fs. In addition, modification of acid-base properties of the systems by changing the substituents in the phenol rings as well as methyl substituent is the way to increase the tendency by promoting the ESIntraPT reactions. Thus, all these complexes can be used as a good prototype for the ESIntraPT process.