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Excited-State Proton Transfer via Hydrogen-Bonded Acetic Acid (AcOH) Wire for 6-Hydroxyquinoline

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Spectroscopic studies on excited-state proton transfer (ESPT) of hydroxyquinoline (6HQ) have been performed in a previous paper. And a hydrogen-bonded network formed between 6HQ and acetic acid (AcOH) in nonpolar solvents has been characterized. In this work, a time-dependent density functional theory (TDDFT) method at the def-TZVP/B3LYP level was employed to investigate the excited-state proton transfer via hydrogen-bonded AcOH wire for 6HQ. A hydrogen-bonded wire containing three AcOH molecules at least for connecting the phenolic and quinolinic $-N-$ group in 6HQ has been confirmed. The excited-state proton transfer via a hydrogen-bonded wire could result in a keto tautomer of 6HQ and lead to a large Stokes shift in the emission spectra. According to the results of calculated potential energy (PE) curves along different coordinates, a stepwise excited-state proton transfer has been proposed with two steps: first, an anionic hydrogen-bonded wire is generated by the protonation of $-N-$ group in 6HQ upon excitation to the S_1 state, which increases the proton-capture ability of the AcOH wire; then, the proton of the phenolic group transfers via the anionic hydrogen-bonded wire, by an overall "concerted" process. Additionally, the formation of the anionic hydrogen-bonded wire as a preliminary step has been confirmed by the hydrogen-bonded parameters analysis of the ESPT process of 6HQ in several protic solvents. Therefore, the formation of anionic hydrogen-bonded wire due to the protonation of the $-N-$ group is essential to strengthen the hydrogen bonding acceptance ability and capture the phenolic proton in the 6HQ chromophore.

1. Introduction

Proton transfer is one of the most important reactions in acid−base chemical and biological dynamics caused by site-specific interaction such as hydrogen bonding.[1–4] As the important role of hydrogen bonds playing in physics, chemistry, and biology has been recognized,[5–18] the proton transfer along hydrogen bonding has been given more and more attention in recent years.[19–25] This is especially true for photoacids, where a well-defined zero-point of time for the proton-transfer reaction due to the acidity of photoacids can be switched by optical excitation.[24,25] Thus, monitoring the hydrogen release of photoacids is the fashionable method to study proton transfer.[20–25] The proton exchange between an acid and a base in aqueous solution is detected to proceed by a sequential, von Grotthuss-type, proton-hopping mechanism through water bridges.[23–25] Furthermore, a mechanism of an excited-state H-atom-transfer reaction along a hydrogen-bonded "wire" has also been proposed and widely studied for the importance in photochemical[26–31] and biological[32–35] processes.

Hydrogen bonding in the ground state has been extensively studied by many different experimental and theoretical methods.[36–38] However, little is known about electronic excited-state hydrogen bonding, due to the extremely short time scales involved. Recently, Zhao et al.[39,40] have successfully simulated the hydrogen-bonded dynamics and theoretically demonstrated that intermolecular hydrogen bonding between solute and alcoholic molecules can be significantly strengthened in the electronic excited state upon photoexcitation, which plays an important role in photochemistry, such as intermolecular charge transfer,[39] fluorescence quenching,[40] excited-state proton transfer,[41] and tuning effects on photochemistry.[42]

A hydrogen-bonded network formed between 6-hydroxy-quinoline (6HQ) and acetic acid (AcOH) has been characterized in the nonpolar solvent benzene by using steady-state spectra and the time-resolved fluorescence technique by Mehata,[28,29] and the interesting triemission (around 357, 419, and 583 nm) has been detected. The presence of an isoemissive point in the emission spectra indicates the existence of more than one emitting species. The normal fluorescence around 357 nm has been assigned to the excited enol form of 6HQ, which undergoes an excited-state proton transfer via AcOH wire, resulting in a keto tautomer (emitting at 583 nm). The intermediate 419 nm emission band of 6HQ appears to originate from the excited-state intermolecular proton transfer. Obviously, the excited-state hydrogen bonding dynamics play an important role in the ESPT process. To provide insight into the proton transfer via hydrogen-bonded wire, a reliable theoretical calculation is necessary.

In the present work, to study the excited-state proton transfer via a hydrogen-bonded AcOH wire, we calculated isolated 6HQ, and the hydrogen-bonded complex between 6HQ and the AcOH wire using DFT/TDDFT methods in the def-TZVP/B3LYP level for the ground state and excited state, respectively. By comparing the optimized structures of 1:2 and 1:3 hydrogen-bonded complexes in the ground state, it was found that the hydrogen-bonded wire should consist of at least three AcOH molecules to connect the donor and acceptor group in 6HQ. Vertical excitation energies in S_0 and S_1 state have been analyzed to

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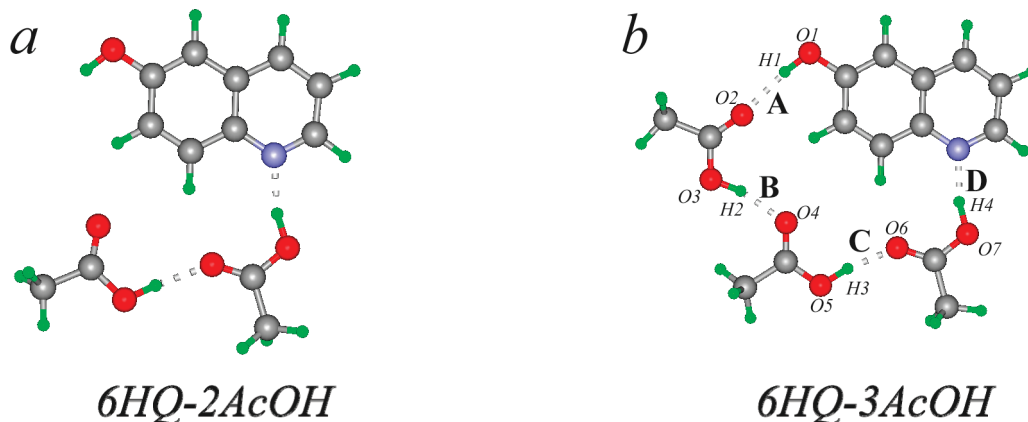‡ Delhi Technological University.

Figure 1. Optimized geometric structures of 6HQ-2AcOH (a) and 6HQ-3AcOH (b) complexes in the electronic ground state.

assign the absorption and emission spectra in the experiments.[28,29] The large Stokes shift of 583 nm emission is due to the keto-tautomer generated by excited-state proton transfer via the AcOH wire. Moreover, the excited-state structure optimization suggests that a fast excited-state proton transfer from the last AcOH to quinolinic $-N-$ site in 6HQ occurs and results in an anionic hydrogen-bonded AcOH wire in the hydrogen-bonded complex. Hence, a stepwise excited-state proton transfer of 6HQ-3AcOH complex via hydrogen-bonded wire has been proposed, which is also supported by the analysis of the property parameters of solvents used in expriments.[20,28,50,51]

2. Theoretical Methods

All the electronic structure calculations were carried out using the TURBOMOLE program suite.[43–49] The geometry optimizations of the isolated monomers and the hydrogen-bonded solute−solvent complexes considered here for the ground state were performed, using density functional theory (DFT) with Becke's three-parameter hybrid exchange function with the Lee−Yang−Parr gradient-corrected correlation functional (B3-LYP functional).[44] The triple-ζ valence quality with one set of polarization functions (TZVP) was chosen as the basis sets throughout.[45] The excited-state electronic structures were calculated using time-dependent density functional theory (TD-DFT) with the B3-LYP hybrid functional and the TZVP basis set. Fine quadrature grids 4 were employed.[46] In addition, considering the solvent effects, the conductor-like screening model (COSMO)[48] was also used to calculated the single-point energies for the optimized structure in a vacuum. Notice that the energetic change is less than 0.1 kcal/mol between the single-point energy and the result of global optimization in solution.[49]

3. Results and Discussion

In the preceding articles by Mehata[28,29] a hydrogen-bonded molecular wire consisting of two AcOH molecules was used, through which an excited-state intermolecular proton transfer proceeds and results in a keto-tautomer and emits with a large Stokes shift. However, two AcOH would not be enough for the long distance between the donor and acceptor groups in 6HQ. Therefore, the DFT calculation has been performed for 6HQ-2AcOH and 6HQ-3AcOH, and the optimized structures of these in the electronic ground state are shown in Figure 1a,b. In the optimized structures, all the hydrogen bonds are located in the molecular plane of the 6HQ chromophore. As shown in Figure 1b, three AcOH molecules are obviously requested at least to form the hydrogen-bonded bridge which would connect the donor phenolic group and the acceptor group ($-N-$) of

6HQ. Recently, a hydrogen-bonded ammonia wire consisting of three NH_3 has been reported to connect the donor and acceptor groups of 7-hydroxyquinoline (7HQ),[25] and a hydrogen-bonded wire consisting of two AcOH also works, whereas, for the 6HQ molecule, two AcOH molecules are not long enough according to the conformation of the 6HQ-2AcOH complex shown in Figure 1a. The length of hydrogen-bonded wire should be dependent on both the distance between the donor and acceptor groups of the chromophore and the volume of molecule which builds up the hydrogen-bonded wire. Hence, we focus our attention on 6HQ-3AcOH complex to investigating the hydrogen-bonded wire.

Interestingly, a triemission (located at 357, 419, and 583 nm) has been found in the steady-state and time-resolved emission spectra of 6HQ in benzene in the presence of AcOH, after an excitation at 310 nm.[28,29] To assign these complicated spectra, TDDFT calculation has been performed for several species in different electronic states. The COSMO ($\varepsilon = 3.0$) package has been used for considering the bulk effect of the binary solvent, which consists of benzene ($\varepsilon = 2.27$) and a small quantity of acetic acid ($\varepsilon = 6.15$). The calculated vertical excitation energies and oscillator strengths for the ground state are listed in Table 1, as well as the corresponding orbital transfer. The results of calculated absorption spectra within and without COSMO are almost identical, which suggests the ground-state 6HQ and its hydrogen-bonded complex are independent of the polarity of the solvent. As shown in Table 1, the very strong absorption for both 6HQ-enol and 6HQ-3AcOH are located at higher electronic energy levels. In the long wave range, the calculated maximum absorption energies of 6HQ-enol and 6HQ-3AcOH due to the S_1 state are located at 4.05 and 3.80 eV, respectively. All of the calculated maximum absorption energies are around 330 nm, which is in good agreement with the maximum absorption peak in the experiments.[28,29] Moreover, the formation of hydrogen-bonded wire around the chromophore could lead to a red shift in the absorption spectra. This is accordant with the shoulder in the experimental absorption spectra,[28] which has a long tail extending up to 380 nm. Hence, a small quantity of the hydrogen-bonded complex should be formed in the ground state. From the calculated electronic excitation energies, we can expect that the 6HQ chromophore can be electronically excited to the S_1 state upon photoexcitation by 310 nm laser pulse used in the experiments,[28,29] while the AcOH wire in 6HQ-3AcOH will remain in its electronic ground state. Thus, we consider the S_1 state only in the present work.

We have performed the excited-state structure optimization and listed their calculated emission energies within COSMO

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TABLE 1: Calculated Electronic Excitation Energy (EEE) without and within COSMO (CEEE), and Corresponding Oscillator Strength (OS) for Low-Lying Electronically Excited States for 6HQ-enol and 6HQ-3AcOH, as Well as Orbital Transition (OT) Contributions to the Electronic States
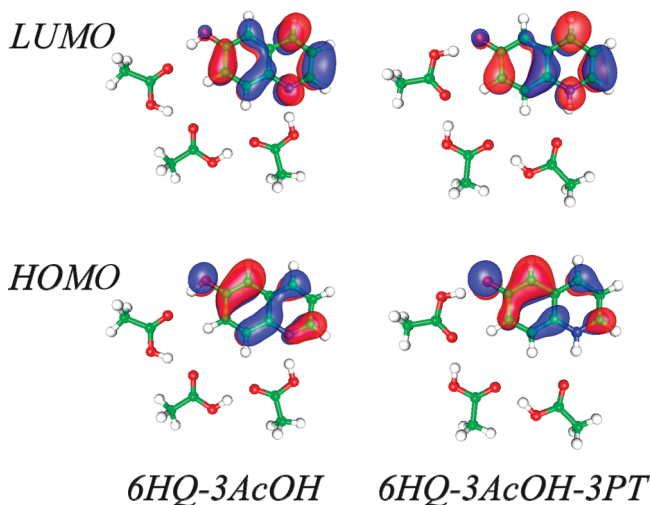
state	6HQ-enol				6HQ-3AcOH			
	EEE (eV)	CEEE (eV)	OS	OT	EEE (eV)	CEEE(eV)	OS	OT
S_1	4.05	4.05	0.063	H→L	3.72	3.80	0.067	H → L
S_2	4.26	4.38	0.004	H−2 → L	4.33	4.38	0.015	H−1 → L
S_3	4.55	4.54	0.011	H−1 → L	4.87	4.85	0.002	H−2 → L
S_4	5.31	5.44	0.000	H−2 → L+1	5.16	5.32	0.090	H → L+2
S_5	5.61	5.61	0.254	H → L+2	5.24	5.37	0.086	H → L+3
S_6	5.76	5.75	0.345	H → L+1	5.38	5.49	0.355	H → L+1

TABLE 2: Calculated Electronic Emission Energy (EEE) without and within COSMO (CEEE) of $S_1 \rightarrow S_0$, and the Corresponding Orbital Transition (OT) Contributions to the Electronic States for 6HQ-enol, 6HQ-3AcOH, and 6HQ-3AcOH-PT, as Well as the Experimental Emission Energy for Comparing

	6HQ-enol	6HQ-3AcOH-PT	6HQ-3AcOH-3PT
$EEE_{S1 \rightarrow S0}$ (eV)	3.60	2.64	1.76
$CEEE_{S1 \rightarrow S0}$ (eV)	3.60	2.78	1.99
expt (eV)	3.47	2.96	2.13
OT	H → L	H → L	H → L

($\varepsilon = 3.0$) in Table 2. It is interesting that the excited-state structure optimization of 6HQ-3AcOH in the S_1 state leads to 6HQ-3AcOH-PT conformation (see below in Figure 5b). This maybe suggests that there is no barrier in the process of hydrogen release from the last AcOH. The protonation of the −N− group in 6HQ-3AcOH-PT reveals a strong donation ability of the hydrogen-bonded wire consisting of three AcOH in the lowest singlet excited state. The emission energies of 6HQ-enol, 6HQ-3AcOH-PT, and 6HQ-3AcOH-3PT calculated using the COSMO model are localized at 3.60, 2.78, and 1.99 eV, respectively. As shown in Table 2, the emission of 6HQ-enol is not sensitive with the polarity of solvent. However, the bulk effect could influence the emission of ESPT products notably due to the variety of dipole moment in the proton transfer. To simulate the experimental emission spectra of 6HQ in benzene at several concentrations of AcOH, we expand these three emissions by Lorentzian shape and increase them with weight coefficients. The results of this simulation are shown in Figure 2, which is in good agreement with the experimental results.[28] By combining theoretically calculated results and the experimental spectra,[28,29] we can confirm that the intermediated fluorescence band localized at 419 nm in the experimental results should be attributed to the fast protonation of the −N− group (<10 ps). Moreover, the H transfer through the AcOH wire subsequently proceeds in 200 ps and shifts the fluorescence at around 583 nm.

Before discussing the excited-state hydrogen bonding dynamics in ESPT reaction, it is useful to understand the nature of the excited states of the reactant and product. Herein, the MOs of 6HQ-3AcOH and 6HQ-3AcOH-3PT (shown in Figure 5c), which contribute dominantly to the wave function of the lowest excited singlet state, are shown in Figure 3. By comparing the HOMO and LUMO of 6HQ-3AcOH and 6HQ-3AcOH-3PT, the character of $\pi\pi^*$ transfer can be clearly found. It is interesting that the σ character of N···H bond involved in the LUMO of both hydrogen-bonded complexes suggests a strong electron pair donation ability of the −N− group to form a covalent bond with the H atom of the adjacent AcOH after photoexcitation to the S_1 state. And there is more electronic density distribution located around the phenolic oxygen atom of 6HQ, and less located around nitrogen in the HOMO than that in the LUMO.
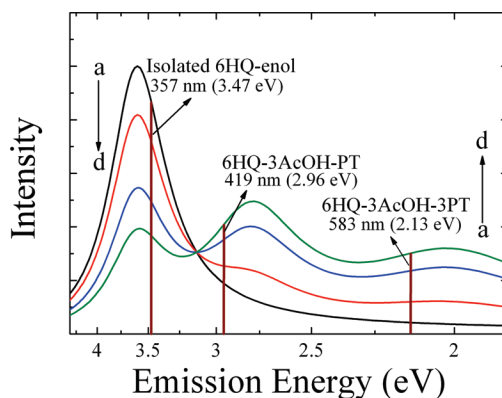
Figure 2. Simulated emission spectra of 6HQ in benzene at several concentrations of AcOH by expanding the calculated emission energies by Lorentzian shape and plus them with weight coefficients as (a) 1, 0, 0 for the fluorescence of 6HQ-enol, 6HQ-3AcOH-PT, and 6HQ-3AcOH-3PT, respectively; (b) 0.8, 0.125, and 0.075; (c) 0.5, 0.3125, and 0.1875; (d) 0.33, 0.42, and 0.25. Wine-red lines denote the corresponding peaks in experiments.[28]

Figure 3. Frontier molecular orbitals (MOs) of the hydrogen-bonded 6HQ-3AcOH and 6HQ-3AcOH-3PT complexes.

Therefore, the excited-state 6HQ should favor the keto tautomer by protonation of the −N− group and deprotonation of phenolic group. Additionally, it should be noted that the electron densities of all the MOs are strictly localized on the 6HQ moiety. So it has been confirmed that the hydrogen-bonded wire stays in its electronic ground state in the whole excited-state proton-transfer process.

As proposed by vertical excitation results and experimental spectra,[28,29] the protonation of the −N− group should occur first. However, the results of ab initio calculations and the two-color resonant two-photon ionization (2C-R2PI) spectrum of 7HQ-$(NH_3)_3$ suggest that a preliminary step of fast hydroxyl depro-
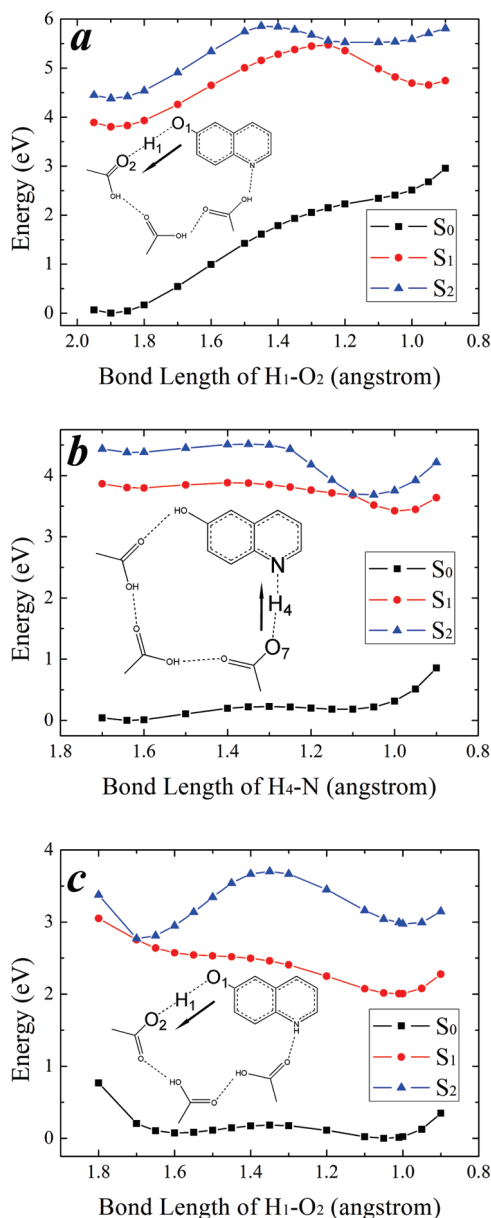
Figure 4. Calculated potential energy curves of single proton transfer along different coordinates: (a) PE curves of H_1 transfer from O_1 to O_2 in excited 6HQ-3AcOH; (b) H_4 transfer from O_7 to N in excited 6HQ-3AcOH; (c) H_1 transfer from O_1 to O_2 when the other proton transfers are all completed. The insets depict the coordinates of the single proton transfers.

tonation in excited 7HQ producing the 7HQ anion species occurs before imine protonation to generate the excited 7HQ-keto tautomer. Notice that the order of proton transfer is sensitive to the environment pH for hydroxyquinoline.[19] Herein, calculated potential energy (PE) curves are necessary to ensure the proton-transfer mechanism of the 6HQ-3AcOH complex. The PE curves of single proton transfer along different coordinates have been calculated. The PE curves of H_1 transfer from O_1 to O_2 and H_4 transfer from O_7 to N in excited 6HQ-3AcOH as the first step are shown in Figure 4a,b, respectively, and Figure 4c depicts the H_1 transfer as the last step when the other proton transfers are all completed. Obviously, a quite large barrier has been found in single proton transfer H_1 of the 6HQ-3AcOH complex in Figure 4a, where the curve of the S_1 state goes across the S_2 state at around 1.25 Å of the bond length. Moreover, the energy of the single PT product is much higher than that of the localized

excited (LE) state 6HQ-3AcOH. On the other hand, there is almost no barrier to the PE curve of H_4 transfer as the first step of ESPT in Figure 4b. Hence, the ultrafast reaction rate of protonation of the −N− group in the 6HQ moiety after photoexcitation has been revealed, which is accordant with the absent rise time of intermediate emission in time-resolved emission spectra.[29] Additionally, a more stable species can be formed in the excited state after the H_4 transfer to N. Herein, protonation of the −N− group has been confirmed to be the first step in the ESPT process through the hydrogen-bonded AcOH wire, meanwhile, an anion hydrogen-bonded wire would be formed. As shown in Figure 4c, the potential barrier of H_1 transfer in the S_1 state has been decreased and even vanished after other H transfers are complete. This suggests that the transfer of H_1 would follow the transfers of H_3 and H_2, and the proton transfers of H_1, H_2, and H_3 should be correlated. Therefore, an overall "concert" process after the fast protonation of the −N− group as the second step can be revealed according to experimental results.[28,29]

Obviously, hydrogen bonding plays an important role in the ESPT process. Thus, the study of hydrogen bonding dynamics in the excited state is the key to understand the H transfer via hydrogen-bonded wire. The excited-state geometry optimized structure of the accepted 6HQ:AcOH complexes with the hydrogen-bond length of the mentioned complexes are shown in Figure 5. As discussed above, the AcOH moiety remains in its electronic ground state even after excitation. Herein, all the differences of the AcOH−AcOH hydrogen bonds involved between the 6HQ-3AcOH-PT complex in the S_1 state (Figure 5b) and 6HQ-3AcOH in the S_0 state (Figure 5a) are caused by the hydrogen release of the AcOH molecule adjacent the −N− group in the chromophore. The hydrogen bond C (cf. Figures 1 and 5) in the wire is strongly shortened (for 0.304 Å) to 1.380 Å due to the powerful acceptance ability of AcO⁻. Since the acceptance ability of AcOH is much weaker than that of AcO⁻, the length of the hydrogen bond B has only shortened for 0.157 Å (from 1.737 to 1.580 Å). These indicate that the influence caused by protonation of the −N− group should become weaker and weaker along the hydrogen-bonded wire. However, the hydrogen bond of the phenolic group in the 6HQ molecule is significantly shortened to 0.233 Å (from 1.899 to 1.666 Å), which should be caused not only by the formation of the anionic AcO⁻ but also by the excited-state hydrogen bond strengthening due to the excitation of chromophore, which has been studied for many systems in Zhao's works.[39,40] The lengths of these hydrogen bonds in excited-state 6HQ-3AcOH-PT can reveal that the second "concert" step would be ended by deprotonation of the phenol group in 6HQ. Additionally, after the ESPT via the hydrogen-bonded wire, the 6HQ-3AcOH-3PT complex can be formed in the S_1 state shown in Figure 4c. By the protonation of AcO⁻, hydrogen bond D has been strongly weakened to 1.971 Å, while, thhydrogen bond A has been shortened to 1.603 Å due to the static electronic effect of O⁻ in the 6HQ moiety. Moreover, syn−anti isomerization of AcOH is also involved in the ESPT process.

As for the discussion above, the formation of an anionic hydrogen-bonded wire due to the protonation of the −N− group would play an important role in ESPT process. In earlier experiments,[20,50,51] 6HQ shows no excited-state proton transfer in methanol solvent whose hydrogen bonding acceptance (HBA) ability ($\beta = 0.66$[52]) is much higher than that of AcOH, because the hydrogen bonding donation (HBD) ability ($\alpha = 0.98$[52]) is too weak to supply a proton to 6HQ to form an anionic hydrogen-bonded wire. However, the excited-state tautomer
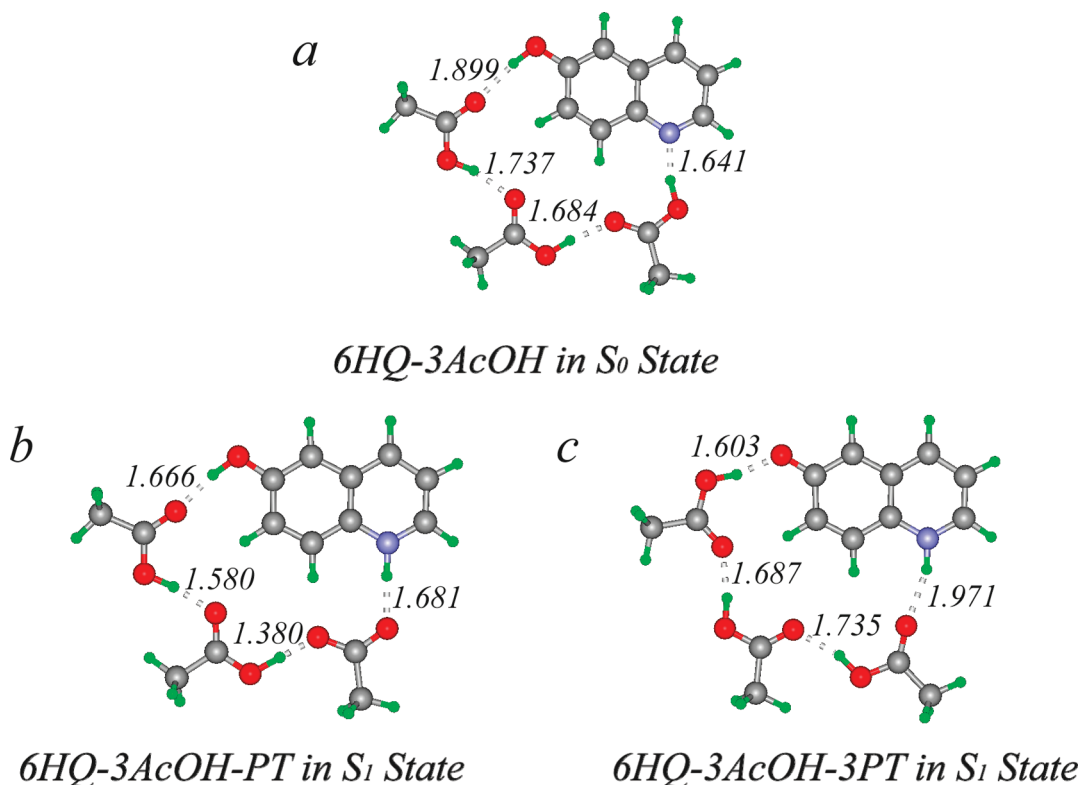
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Figure 5. Optimized geometric structures of 6HQ-3AcOH in the ground state (a), 6HQ-3AcOH-PT (b) and 6HQ-3AcOH-3PT (c) complexes in the S_1 state, and the bond lengths (Å) of the hydrogen bonds in these complexes.

species appears in the emission spectra due to the presence of water ($\alpha = 1.17$, $\beta = 0.47^{52}$) in the solution. With the low HBA ability ($\beta = 0.45$) and a strong HBD ability ($\alpha = 1.12$),[52] the AcOH wire should capture the proton of the phenolic group in the 6HQ molecule, unless the anionic hydrogen-bonded wire has been formed by the protonation of the chromophore. Hence, the conformation of an anionic hydrogen-bonded wire should happen first in the process of excited-state proton transfer via the AcOH wire, which would increase the HBA ability of the hydrogen-bonded wire to capture the phenolic proton in 6HQ. Base on these discussions, a stepwise excited-state proton transfer of 6HQ-3AcOH complex should be proposed. The H transfer through the hydrogen-bonded wire is triggered by the H releasing of the AcOH molecule adjacent the −N− group in the chromophore, which would lead to an anionic proton chain conformation. Subsequently, the 6HQ moiety releases the proton to the anionic hydrogen-bonded AcOH wire and forms 6HQ-3AcOH-3PT. The second step should be an overall "concerted" process involving sequential movement of the protons, just as how the ESPT does in GFP[35] with the anionic proton chain transfer.[32,33] This mechanism has a good agreement with the experimental emission spectra.[28,29]

4. Conclusion

The dynamics of excited-state proton transfer via the hydrogen-bonded AcOH wire for the 6HQ chromophore has been studied using the time-dependent density functional theory (TDDFT) method. The geometric structures of 1:2 and 1:3 hydrogen-bonded complexes have been optimized in the ground state. It is demonstrated that at least three AcOH molecules are required to form a hydrogen-bonded wire to reach both donor and acceptor groups in the 6HQ molecule. The calculated vertical excitation energies suggest that the hydrogen-bonded wire should be formed already in the ground state in a small quantity.

Moreover, the excited-state proton transfer via the hydrogen-bonded wire gives the keto tautomer of 6HQ and leads to a large Stokes shift in the emission spectra. To investigate the detailed aspects of the tautomerization induced by the hydrogen-bonded wire, the structures of hydrogen-bonded complexes are also optimized and analyzed in the S_1 state. The protonation of the −N− group with a negligible potential barrier is accordant with the absent rise time of the 419 nm emission in the time-resolved emission spectra.[29] Hence, a stepwise excited-state proton transfer beginning with the protonation of the −N− group in the 6HQ moiety via the hydrogen-bonded wire has been proposed. These are also supported by the analysis of solvent property parameters. In the process of excited-state proton transfer, AcOH molecules always remain in the electronic ground state. Therefore, the anionic hydrogen-bonded wire with strong proton acceptance ability should be formed first, to capture the phenolic proton in 6HQ molecule.

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