Theoretical Characterization of the Structures and Reactivity of 7-Hydroxyquinoline−(H$_2$O)$_n$ (n = 1−3) Complexes

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The minimum-energy structure of the 7HQ−(H$_2$O)$_n$ (n = 1−3) complexes (where 7HQ is 7-hydroxyquinoline) and the potential energy surfaces governing triple proton transfer in 7HQ−(H$_2$O)$_2$ and quadruple proton transfer in 7HQ−(H$_2$O)$_3$ have been characterized by means of different ab initio quantum mechanical methods. The solvent effects on the structures and reactivity of the complexes have been studied through the use of Onsager self-consistent reaction field models. A comparison was made between the calculated results and experimental data where available. The role of electron correlation in describing geometric features and the proton-transfer reactions was discussed in detail.

Introduction

Structures and properties of complexes between aromatic molecules (benzene, phenol, aniline, etc.) and small polar molecules (H$_2$O, NH$_3$, CH$_3$OH, etc.) have received a great deal of attention in recent years both from experimental and theoretical points of view.[1−24] For example, benzene−(H$_2$O)$_n$ (n = 1, 3) clusters have been investigated with a wide range of spectroscopic techniques[4−9] and theoretical calculations at different levels.[10,11] The aniline−NH$_3$ cluster structures and the cluster binding energies in both the ground and first excited electronic states have been determined employing two-color mass-resolved excitation spectroscopy, hole-burning spectroscopy, and model potential energy calculations.[12] Intermolecular vibrations of the clusters of phenol with water have been characterized with UV double resonance spectroscopy and ab initio calculations.[13−17] A number of experimental studies have been initiated whose aim has been to determine proton transfer in the H-bonded complexes.[18−23] Meanwhile, several theoretical calculations have been devoted to this subject in order to elucidate the mechanistic chemistry.[24−28]

When no H-bond exists because of a too large distance between donor and acceptor groups of bifunctional molecules, solvent molecules such as H$_2$O and CH$_3$OH may assist proton transfer in the ground or excited state by acting as a proton relay. Perhaps the most frequently studied system of the solvent-assisted proton-transfer reaction is methanol and aqueous solutions of 7-hydroxyquinoline (7HQ). The methanol solution photochemistry of 7HQ has been the subject of numerous experimental investigations and has been reviewed in my previous work.[28] In comparison, the aqueous photochemistry of 7HQ has received less attention. In 1968, Mason, Philp, and Smith[29] had investigated photochemical properties of 7HQ and pointed out that four protropic equilibrium species probably exist in its aqueous solution. It had been found that the OH group and ring nitrogen atom become more acidic and basic, respectively, in the first excited singlet state than in the ground state.[29,30] The stability of the ground-state keto tautomer of 7HQ has been observed by Bohra et al. in room-temperature aqueous solution.[31] They suggested that it is easier to form the cyclic 7HQ−(H$_2$O)$_2$ complex, which undergoes ground-state proton transfer, leading to the ground-state keto tautomer (NH form),

than to form noncyclic water hydrogen-bonded 7HQ, which stay in the normal form (OH form) until excitation. Recently, Lahmnai et al.[32] have reported fluorescence studies of solvent effects of jet-cooled 7HQ. The 1:1 and 1:3 complexes of 7HQ with water were observed, but no significant excited-state proton transfer was found in the water cluster of 7HQ in the jet-cooled condition. Triplet state proton transfers in aqueous solution of 7HQ were observed by measuring the kinetic profiles and spectra of absorption and emission,[33] and tunneling was suggested to be significant in the proton-transfer reactions.[34]

The complex of 7HQ with H$_2$O is of particular interest because there are many distinct types of bonding interactions. The ring nitrogen atom and OH group of 7HQ can behave as hydrogen acceptor and donor, respectively. The complex of 7HQ with H$_2$O can also be formed by the interaction between hydrogen atoms of H$_2$O and the aromatic π-electron density of 7HQ. In addition, the cyclic and noncyclic complexes probably coexist in aqueous solution. One can anticipate that it is more difficult to characterize the structures and proton-transfer reaction of the 7HQ−(H$_2$O)$_n$ in comparison with the other clusters mentioned above, which stimulates my interest in performing an ab initio study of the complex. In this paper, we have carried out calculations on the potential energy profiles governing multiproton transfers in the ground state. The structures of 7HQ−(H$_2$O)$_n$ (n = 1−3) and the mechanisms of proton-transfer reactions in solution of the complexes have been characterized employing advanced techniques. The influence of the environment on the reactivity and structures of the complexes was taken into account via a continuum model in which the complex is included in a spherical cavity and surrounded by a dielectric continuum. Theoretical study of excited-state multiproton transfers in the complex of 7HQ with H$_2$O is still in progress.

Computational Methods

The stationary structures on the potential energy surface of the ground state are fully optimized at HF, SCRF, CASSCF, and MP2 (FC) levels with the energy gradient technique, where FC denotes the frozen 1s core of oxygen, nitrogen, and carbon atoms. To carry out CASSCF calculation, the crucial step is the selection of the proper active space. The obvious choice

for describing the low-lying electronic states of 7HQ would be 10 electrons in the five π and five π^* orbitals as well as four electrons in the two nonbonding orbitals located at O and N atoms, respectively, referred to as CAS(14,12). However, it is very difficult to fully optimize all stationary structures at the CAS(14,12) level under the present condition. Two π^* orbitals are excluded from the active space. An agreement between theory and experiment would provide justification for the overall accuracy of the CASSCF calculations with the active space of (14,10). Two different basis sets were used in this work. The first is a standard 3-21G basis set, used for all the levels of theory considered here. The second is a nonstandard basis set that is composed of 6-31++G** for N, O, and H atoms of the H-bonded structures and 6-31G for the other atoms in the complex. The optimization was terminated when the maximum force and its rms were less than 0.000 45 and 0.0003 hartree/bohr, respectively. Once convergence was reached, the harmonic frequencies were examined at this point to verify that the geometry obtained was a true minimum or saddle point. The solvent effects have been considered employing the self-consistent reaction field (SCRF) method.[35,36] In the reaction field model, the solvent is considered to be a uniform dielectric characterized by a given dielectric constant (80.0 for water). The solute is assumed to occupy a spherical cavity (the radius of the cavity is 5.4 Å, obtained from the calculated complex volume) in the medium. The permanent dipole of the solute will induce a dipole in the surrounding medium, which in turn will interact with the molecular dipole. The solute–solvent interaction is added as a perturbation to the Hamiltonian of the free solute, and the wave function is determined by appropriate iterative methods. The scale factor of 0.85 for HF or SCRF zero-point energy is used in calculation of the relative energies.[37] All the calculations have been performed using the Gaussian 94 package of programs.[38]

Results and Discussion

1:1 Complexes of 7HQ with H_2O. 7HQ monomer has trans and cis conformers of the 7-OH group with respect to the ring N atom. Since the cis conformer is more stable, its complexes are mainly considered in the present work. 7HQ may act as a donor via the 7-OH group, as an acceptor via the ring N atom, or as a donor via the π system of the aromatic ring. The corresponding energy minimum structures, 7HQ(O)–H_2O, 7HQ(N)–H_2O, and 7HQ(π)–H_2O, have been identified on the ground-state potential energy surface. The geometry of the bare 7HQ molecule, shown in Figure 1 of ref 28, is almost unaffected by complex formation. Therefore, only the parameters describing H-bonded structures are given in Figure 1. Upon inspection of geometries in Figure 1, one can note that complex–water interaction does not lead to a significant change in the intermolecular H-bond lengths of 7HQ(O)–H_2O and 7HQ(N)–H_2O. The reason is that the interaction between the lone pair of the oxygen or nitrogen atom and the H–O σ^* orbital plays an important role in the formation of the H-bonded complexes. The striking change occurs in 7HQ(π)–H_2O. The distance between the center of the 7HQ ring (X in Figure 1) and the H_2O hydrogen atom is lengthened by 0.069 Å with solvent effects considered. The 7HQ(π)–H_2O complex is formed mainly by electrostatic interaction between the two monomers, as found previously in weakly bonded systems.[39] It is easy to understand that solvent effects increase significantly the distance between the bare 7HQ molecule and H_2O because of the large dielectric constant of water. Since the potential energy surface is very flat with respect to the H-bond angles, we do not attribute much significance to the change in the H-bond angles.
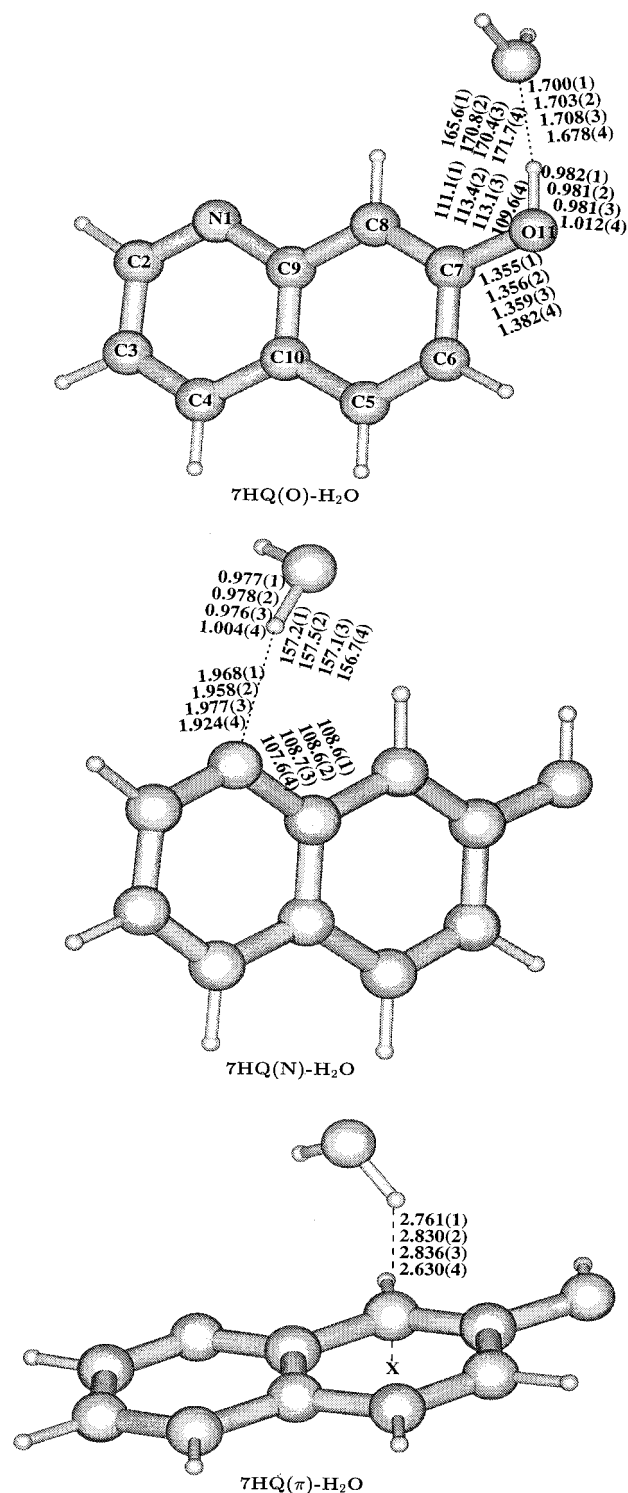

Figure 1. Schematic structures (bond length in Å and bond angle in deg) of 7HQ–H_2O. (1), (2), (3), and (4) represent the parameters obtained at the HF, SCRF, CAS, and MP2 levels, respectively.

Significant effects appear to be associated with the incorporation of electron correlation. Intermolecular H-bond distance is reduced by about 0.022 Å in 7HQ(O)–H_2O, 0.044 Å in 7HQ-(N)–H_2O, and 0.13 Å in 7HQ(π)–H_2O in going from HF to MP2, whereas intramolecular H-bond length is elongated about 0.03 Å at the MP2 level, in comparison with that from the HF optimizations. The analogous situation occurs for the 7HQ–$(H_2O)_2$ and 7HQ–$(H_2O)_3$ complexes, as given below. Since electron correlation is not taken into account by the HF method, the HF calculations underestimate H-bond interaction, thus

TABLE 1: Relative Energies (kcal/mol) of the 7HQ−H₂O Complexes

	7HQ(O)−H₂O[a]	7HQ(N)−H₂O[b]	7HQ(π)−H₂O[b]
HF/3-21G	0.0 (−547.167 20)	2.2 [2.8]	13.6 [12.2]
SCRF/3-21G	0.0 (−547.167 76)	1.8 [2.5]	13.5 [12.2]
CAS/3-21G	0.0 (−567.239 96)	2.2 [2.8]	13.8 [12.4]
MP2/3-21G	0.0 (−568.294 97)	1.3 [1.9]	15.9 [14.6]

[a] Energies in parentheses are in atomic units. [b] Relative energies with zero-point energy correction are given in brackets.

predicting larger intermolecular H-bond distance and smaller intramolecular H-bond length with respect to MP2 calculations. The CAS(14,10) and HF optimized geometric parameters of 7HQ(O)−H₂O or 7HQ(N)−H₂O are close to each other, which shows that nondynamical correlation does not play an important role in describing the structures of the 7HQ(O)−H₂O and 7HQ-(N)−H₂O complexes.

Here, we pay attention to the relative stability of the complexes. With respect to 7HQ(O)−H₂O, the relative energies of 7HQ(N)−H₂O and 7HQ(π)−H₂O are, respectively, 2.8 and 12.2 kcal/mol at the HF level with zero-point energy correction, as given in Table 1. Again, the CAS(14,10) calculated relative energies are very close to those from HF calculations. The relative energies become 2.5 and 12.2 kcal/mol, respectively, with the solvent effect considered by the self-consistent reaction field method. The MP2 calculations place 7HQ(N)−H₂O and 7HQ(π)−H₂O above 7HQ(O)−H₂O in energy by 1.9 and 14.6 kcal/mol, respectively. The different ab initio calculations give nearly the same relative energies and agree in predicting 7HQ-(O)−H₂O to be the global minimum. Since the energy difference between 7HQ(N)−H₂O and 7HQ(O)−H₂O is very small, they probably coexist in an aqueous solution of 7HQ. In comparison, 7HQ(π)−H₂O has less stability. It should be noted that there is little possibility that the solvent-assisted proton-transfer reaction occurs in 1:1 complexes because of a too large distance between the H₂O hydrogen atom and the ring N atom. Konijnenberg and co-workers have pointed out that photoexcitation of 1:1 7HQ−alcohol complexes or bare 7HQ molecules does not lead to phototautomerization.[40]

1:2 Complexes of 7HQ with H₂O. The interaction between the H atom of H₂O and the aromatic π electron of bare 7HQ can lead to formation of the 7HQ(π)−(H₂O)₂ complex. This complex is a high-energy conformer of 7HQ−(H₂O)₂ and is not discussed here. All attempts to search for a minimum-energy structure of noncyclic cis-7HQ−(H₂O)₂−OH complex lead to formation of the cyclic complex. Figure 2 shows the optimized noncyclic OH form of the 7HQ−(H₂O)₂ complex in which bare 7HQ has the trans conformation. As described below, tautomerization from the OH to the NH form can take place in the complexes. The noncyclic NH forms of the complexes are also depicted in Figure 2, where the SCRF and CAS(14,10) optimized key parameters are given. The relative energies calculated at the different levels are listed in Table 2. Upon inspection of the SCRF computed relative energies in Table 2, one can see that the noncyclic complex lies 6.0 kcal/mol above the cyclic complex for the 7HQ−(H₂O)₂−OH form, while the noncyclic 7HQ−(H₂O)₂−NH form is only 2.1 kcal/mol higher than the corresponding cyclic form. As pointed out by Bohra and co-workers,[31] there is not much energy difference between the NH forms involving cyclic and noncyclic water hydrogen-bonded. In the 7HQ−(H₂O)₂−OH cyclic complex, 7HQ monomer has the cis conformation, which is about 4 kcal/mol lower than its trans conformation. The energy difference between the cis and trans conformers of the 7HQ monomer is responsible for the larger difference in energy of noncyclic and cyclic OH
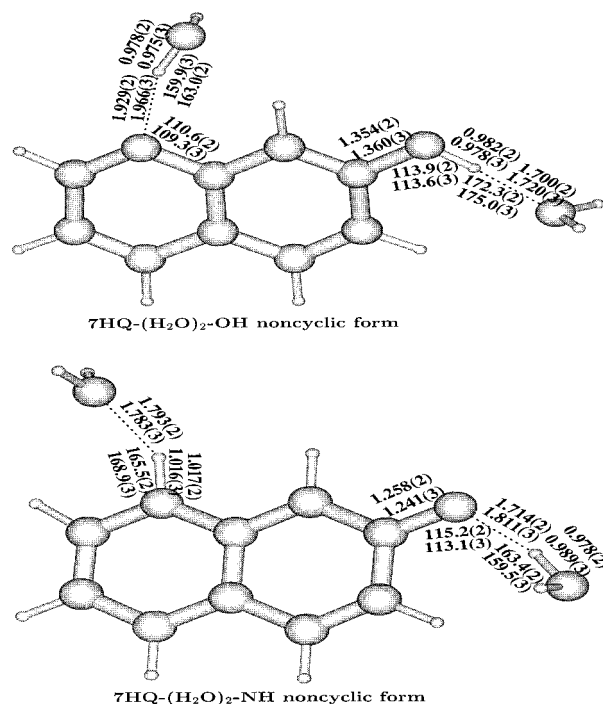

Figure 2. Schematic structures (bond length in Å and bond angle in deg) of the noncyclic 7HQ−(H₂O)₂. (2) and (3) represent the parameters obtained at the SCRF and CAS levels, respectively.

forms, compared with the NH form. The above discussion predicts that the cyclic complexes are more stable than the corresponding noncyclic complexes, especially for the OH form. The cyclic complexes is further stabilized by the CAS(14,10) calculations, as seen in Table 2. The previous experiments have indicated cyclic complexes in aqueous solutions of 7HQ.

Formation of the cyclic 7HQ−(H₂O)₂−OH complex makes the tautomerization from OH to NH form feasible. The understanding at the molecular level of the reaction mechanism for proton transfer in the 7HQ−(H₂O)₂ complex requires a detailed knowledge of reactant (7HQ−(H₂O)₂−OH form), transition state (7HQ−(H₂O)₂−TS), and product (7HQ−(H₂O)₂−NH form). Their structures with C_1 symmetry are fully optimized at the HF, SCRF, CAS(14,10), and MP2 levels and are confirmed to be minimum or saddle point on the ground-state potential energy surface by the HF and SCRF calculated frequencies. The results are summarized in Table 2 and Figure 3. Similar to the 1:1 complex of 7HQ with H₂O, intermolecular H-bond distances are strongly reduced and intramolecular H-bond lengths are significantly increased by the MP2 calculations, in comparison with the HF optimized structure of the 7HQ−(H₂O)₂−OH cyclic complex. From the viewpoint of valence bond theory, the interaction between the lone pair of the acceptor oxygen or nitrogen atom and the σ* orbital of the O−H bond is mainly responsible for the proton transfer to the acceptor. The barrier height of the tautomerization reaction is dependent on the distance between two neighboring heavy atoms, such as O13−O11, O15−O13, and O15−N1. The shorter the O−O or N−O distance is, the stronger the interaction is and the more easily the proton transfer takes place. The optimized O13−O11, O15−O13, and O15−N1 distances in the 7HQ−(H₂O)₂−OH cyclic complex are 2.725, 2.794, and 3.000 Å at the HF level and 2.708, 2.762, and 2.928 Å at the MP2 level, respectively. As a consequence, the barrier height

TABLE 2: Relative Energies (kcal/mol) of the 7HQ−(H₂O)₂ Complexes

	OH-form			NH-form	
	cycle[a]	noncycle[b]	TS[b]	cycle[b]	noncycle[b]
HF/3-21G	0.0 (−622.788 69)		25.8 [21.8]	11.6 [12.0]	
SCRF/3-21G	0.0 (−622.788 31)	7.2 [6.0]	23.6 [19.5]	9.5 [10.0]	12.7 [12.1]
CAS/3-21G	0.0 (−622.861 18)	11.6 [10.4]	26.8 [22.8]	13.8 [14.2]	19.7 [19.1]
MP2/3-21G	0.0 (−624.048 32)		16.6 [12.6]	9.9 [10.3]	
MP2/NSBS	0.0 (−627.690 18)		29.0 [25.0]	14.0 [14.4]	

[a] Energies in parentheses are in atomic units. [b] Relative energies with zero-point energy correction are given in brackets.
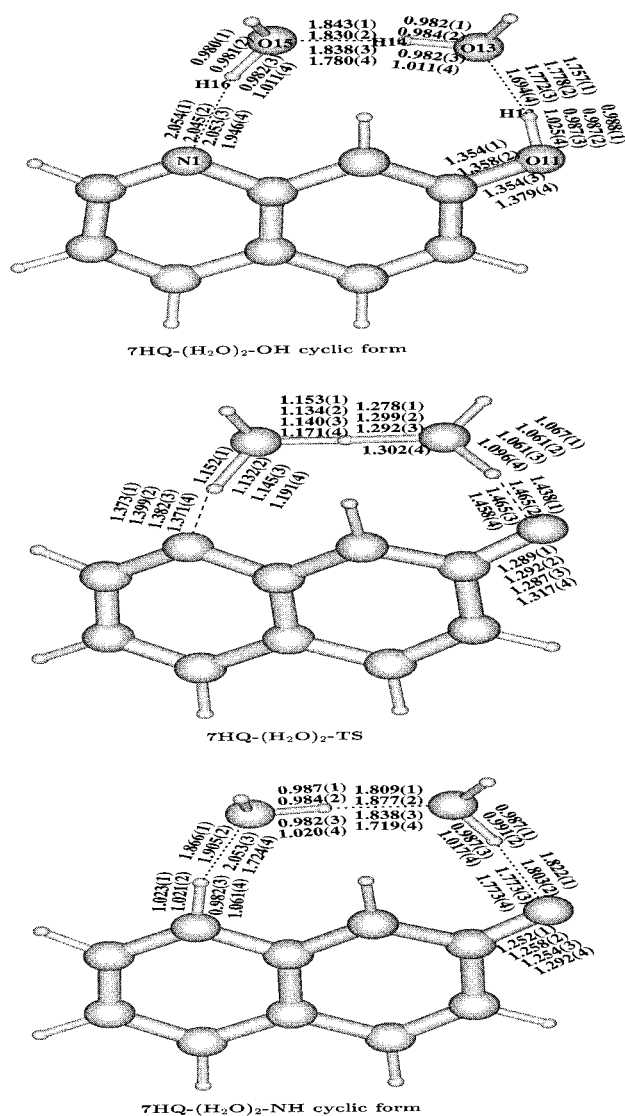

Figure 3. Schematic structures (bond length in Å and bond angle in deg) of 7HQ−(H₂O)₂−TS. Atomic numbers of atoms in the H-bond ring are given in the 7HQ−(H₂O)₂−OH form. For atomic numbers of the 7HQ rings and key to notation, see Figure 1.

predicted by MP2 should be lower than that predicted by HF. This will be confirmed by the following quantitative calculations.

In the optimized 7HQ−(H₂O)₂−TS, the proton H12 is nearly transferred to the H₂O molecule, while the H16 atom is still bonded to the O15 atom. In fact, the 7HQ monomer in 7HQ−(H₂O)₂−TS is of negative ion character, which is supported by the calculated atomic charges with hydrogen summed into heavy atoms. Overall, there is about 0.7 atomic charge on the H₅O₂ moiety of the transition state at the SCRF level. When the H12 proton moves toward the H₂O molecule from the 7-OH group, charge transfers takes place via the π-conjugation system. As a

result, the O and N atoms of bare 7HQ in 7HQ−(H₂O)₂−TS possess, respectively, −0.5 and −0.2 atomic charge more than the corresponding values in the 7HQ−(H₂O)₂−OH cyclic complex. The HF and SCRF calculated imaginary frequency of the transition state is about 1000 cm⁻¹. The internal coordinate reaction vector corresponding to this imaginary frequency is mainly composed of the O−H and N−H bonds and has been identified as $-0.34R_{O11-H12} + 0.17R_{H12-O13} - 0.42R_{O13-H14} + 0.33R_{H14-O15} - 0.41R_{O15-H16} + 0.57R_{N1-H16}$. This clearly shows that 7HQ−(H₂O)₂−TS is a transition state governing proton transfer from 7HQ−(H₂O)₂−OH to the 7HQ−(H₂O)₂−NH cyclic complex and that a concerted mechanism is involved in the tautomerization reaction. Bardez et al.[41] have distinguished three types of bifunctional molecules that can undergo a tautomerization reaction. In the second category, including the alcohol solution of 7HQ, tautomerization results from a concerted proton transfer from one function to the other.

The tautomerization reaction from the OH to the NH form is endothermic by 12.0, 10.0, 14.2, and 10.3 kcal/mol at the HF, SCRF, CAS(14,10), and MP2 levels, respectively. In comparison with the enthalpy difference between the NH and the OH forms of the 1:2 complex of 7HQ with CH₃OH, which was measured to be 9.7 kcal/mol at room temperature,[42] it can be expected that our calculations give a good estimate of the endothermic character of the reaction. However, on the basis of the fact that the stabilized NH-form band intensity at 398 nm in the excitation spectrum is greater than that of OH-form, Bohra et al. had suggested that the 7HQ−(H₂O)₂−NH cyclic or noncyclic complex is more stable than 7HQ−(H₂O)₂−OH cyclic complex in aqueous solution.[31] The potential barrier of the tautomerization reaction from the OH to the NH form is calculated to be 21.8, 19.5, 22.8, and 12.6 kcal/mol at the HF, SCRF, CAS-(14,10), and MP2 levels, respectively. The barrier of the reverse reaction from the NH to the OH form is 9.8, 9.5, 8.6, and 2.3 kcal/mol, respectively, at the corresponding levels. The MP2 calculated energy difference between OH and NH forms is close to that from HF, SCRF, and CAS(14,10) calculations; however, the barrier height is significantly reduced by the MP2 calculations. The reason is that the position of the barrier is more sensitive to electron correlation than the equilibrium structure. The activation energy of the reverse proton-transfer reaction in a methanol solution of 7HQ was estimated to be in the range 4.0−5.0 kcal/mol by transient absorption and two-step laser-induced fluorescence spectroscopies.[30,40] An unusually large tunneling effect on the proton-transfer rate was observed at room temperature by measuring transient absorption kinetic profiles of aqueous 7HQ solution. The Arrhenius activation energy of the water-catalyzed reverse proton-transfer reaction was deduced to be 3.9 kcal/mol.[33,34] It is evident that the MP2 calculations provide a good estimate of the barrier height. Since the barrier of the reverse reaction is much smaller than the forward reaction, the 7HQ−(H₂O)₂−NH cyclic complex is kinetically unstable.

All results reported above are obtained with the 3-21G basis set. To check the influence of basis set on the structures and

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reactivity of the complexes, a nonstandard basis set, referred to as NSBS, which is composed of 6-31++G** for N, O, and H atoms in the H-bond ring and 6-31G for the other atoms in the complexes, is also used to investigate the tautomerization of the 7HQ−(H₂O)₂ cyclic complex. The first observation is that the MP2/NSBS intermolecular H-bond distance is, on average, 0.122 Å longer than the MP2/3-21G values, while the intramolecular H-bond length is reduced by about 0.04 Å from MP2/-21G to MP2/NSBS. The transition state optimized with the MP2/3-21G method is a more compact structure than that from the MP2/NSBS optimization. It seems that the MP2/NSBS calculations underestimate the interaction of the 7HQ with H₂O in the complex. The tautomerization reaction from the OH to the NH form is endothermic by 14.4 kcal/mol at the level of MP2/NSBS, which is 4.1 kcal/mol higher than the MP2/3-21G values of 10.3 kcal/mol. The MP2/NSBS barrier heights of the forward and reverse reactions are, respectively, 12.4 and 8.3 kcal/mol larger than the corresponding MP2/3-21G values. Compared with the experimental data where available, the MP2/NSBS calculations do not provide a better prediction of the structure and reactivity of the complexes than the MP2/3-21G calculations. In 1990, Johnson and co-workers[43] have investigated the structures and properties of the 1- and 2-hydroxynaphthalenes. They found that the results obtained with the 3-21G basis set are in good agreement with experimental findings in all their cases. A good consistency between the MP2/3-21G calculated results and the experimental findings was found in my previous study on the triple-proton-transfer reaction of 7HQ in methanol solution.[28] Corrections for basis set superposition error (BSSE) is expected to be important in a description of the formation and dissociation of a complex. However, only the relative stability of different forms of complexes and tautomerization reactions between them are discussed in the present work. The BSSE corrections, although sizable with the 3-21G basis set, are similar for the different forms of the complexes, and the errors cancel each other in the calculation of the relative energies and barrier heights. All of these give us a reason to expect that the structures and reactivity of the 7HQ complexes with H₂O can be well described with the 3-21G basis set, which will be used in the following subsections.

1:3 Complexes of 7HQ with H₂O. Only the cyclic forms were found to be the energy minimum for the 1:3 complex of 7HQ with H₂O, as shown in Figure 4 where the structural parameters, obtained with the different methods, are also given. There is only a little change of intramolecular O−H (N−H) bond lengths in the 7HQ−(H₂O)₃ complex in comparison with the 7HQ−(H₂O)₂ complex. But intermolecular H-bond distances are reduced by about 0.25 Å in 7HQ−(H₂O)₃. As a consequence, the distances between the neighboring heavy atoms, such as in O13−O11 and O15−O13, are shortened by more than 0.2 Å. As discussed before, the potential barrier for proton transfer decreases with decreasing O−O or O−N distance. It can be expected that the tautomerization reaction takes place more easily in 7HQ−(H₂O)₃ than in 7HQ−(H₂O)₂.

It should be noted that there are drastic changes in the optimized 7HQ−(H₂O)₃−TS structures when electron correlation is taken into account at the MP2 level. In the HF optimized transition state, the proton H12 is still bonded to the O11 atom, while the proton H18 has already transferred to the ring N atom of 7HQ, that is, 7HQ monomer is of positive ion character. But in the MP2 optimized transition state, the proton H12 has moved to the O13 from the O11 atom, whereas the proton H18 is mainly bonded at the O17 atom. This predicts that 7HQ monomer in the MP2 transition state is of negative ion character.
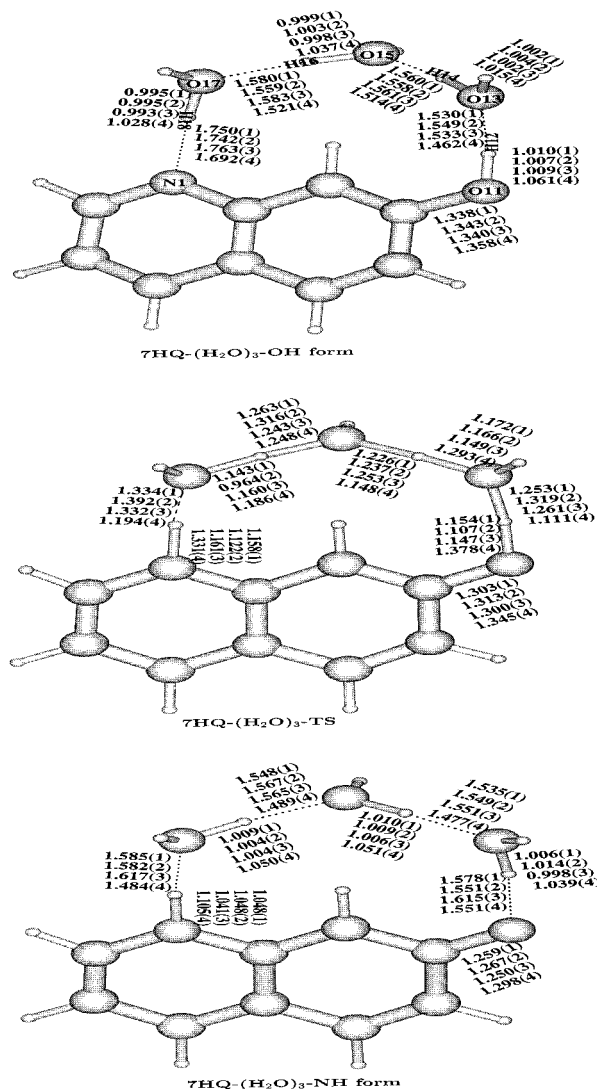

Figure 4. Schematic structures (bond length in Å and bond angle in deg) of 7HQ−(H₂O)₃−OH, 7HQ−(H₂O)₃−TS, and 7HQ−(H₂O)₃−NH. Atomic numbers of atoms in the H-bond ring are given in the 7HQ−(H₂O)₃−OH form. For atomic numbers of the 7HQ rings and key to notation, see Figure 1.

It is known that the proton transfer between two oxygen atoms of H₅O₂⁺ is barrierless when the O−O separation is smaller than 2.3 Å. We suppose that a similar situation holds here. Since the O−O and O−N separation in 7HQ−(H₂O)₃−TS is about 2.4 Å, it is estimated that proton transfer in each step is nearly barrierless. Therefore, a large change in the position of the proton shared between two oxygen atoms only leads to a small change in the energy of the system. The experimental study of proton transfer in an aqueous 7HQ solution by Lee and Jang[33] has predicted the energy difference between the deprotonated anion and protonated cation of 7HQ to be small. It is also possible that quadruple proton transfer may proceed via a stepwise mechanism. If an unconcerted mechanism is involved, one or more intermediates should exist. However, all attempts to find an intermediate on the reaction pathway was unsuccessful. We can exclude the possibility of a stepwise proton transfer from the 7HQ−(H₂O)₃−OH to 7HQ−(H₂O)₃−NH cyclic complex.

The relative energies of the different forms of 7HQ−(H₂O)₃ are listed in Table 3. The tautomerization reaction is endothermic by 7.8 and 7.0 kcal/mol with a potential barrier of 10.9 and 10.9 kcal/mol, respectively, at the HF and SCRF level with zero-

TABLE 3: Relative Energies (kcal/mol) of the 7HQ−H₃O Complexes

	7HQ−(H₂O)₃−OH[a]	7HQ−(H₂O)₃−TS[b]	7HQ−(H₂O)₃−NH[b]
HF/3-21G	0.0 (−698.41871)	15.9 [10.9]	7.4 [7.8]
SCRF/3-21G	0.0 (−698.42046)	15.0 [10.9]	6.6 [7.0]
CAS/3-21G	0.0 (−698.49047)	21.8 [14.9]	11.7 [12.1]
MP2/3-21G	0.0 (−699.80536)	8.5	5.8

[a] Energies in parentheses are in atomic units. [b] Relative energies with zero-point energy correction are given in brackets.

point energy correction. As predicted from the above analysis of the structural parameters, the barrier of the tautomerization is smaller for 7HQ−(H₂O)₃ than for 7HQ−(H₂O)₂. The CAS-(14,10) calculations overestimate slightly the endothermic character and barrier height of the reaction, as seen in Table 3. The enthalpy difference and barrier height are, respectively, reduced to 5.8 and 8.5 kcal/mol with electron correlation included at the MP2 level. It is estimated that the barrier of the reverse proton-transfer reaction is nearly zero at the MP2 level with zero-point energy correction, indicating that the 7HQ−(H₂O)₃−OH complex is predominant in the ground state. Lahmani et al.[32] had pointed out that the large red shift and the narrow-banded spectrum of the 1:3 complex predicted a rigid bridge structure of 7HQ−(H₂O)₃−OH to be stable. However, no excited state tautomerization was found in that study. The initial CIS/3-21G calculations give a barrier of 3.9 kcal/mol for proton transfer from OH to NH on the first excited state. With CIS zero-point energy correction, it becomes 0.2 kcal/mol. This shows that the excited-state tautomeization occurs very easily. Although CIS is not a good method for studying excited-state reaction because of limiting inclusion of electron correlation, the results from the CIS calculations are at least semiquantitatively or qualitatively reliable. The excited-state reverse proton transfer takes place very difficultly because of a large barrier on the pathway. As pointed out before, the ground-state reverse proton transfer takes place very easily. The 7HQ−(H₂O)₃−OH cyclic complexes populated in the excited state by photoexcitation undergo three very fast process: the excited-state isomerization to the 7HQ−(H₂O)₃−NH form, decay of the 7HQ−(H₂O)₃−NH to its ground state, and the ground-state reverse reaction, returning to the initial 7HQ−(H₂O)₃−OH complex. This may be the reason no tautomerization was observed in the experiment of Lahmani and co-workers.

Summary

In this paper, the HF, SCRF, CAS(14,10), and MP2 calculations were carried out in characterizing the structure and proton-transfer reactions of the 7HQ−(H₂O)ₙ (n = 1−3) complexes. Ab initio calculations predicted the existence of three stable isomers of 7HQ−(H₂O), the global minimum being 7HQ(O)−H₂O. Four different conformers have been characterized for 1:2 complexes of 7HQ with H₂O. The energy difference between the cyclic and noncyclic forms is about 2.0 kcal/mol for the NH form and 6.0 kcal/mol for the OH form with the cyclic forms more stable. The global minimum is the cyclic 7HQ−(H₂O)₂−OH form, which is 10.3 kcal/mol in energy below the 7HQ−(H₂O)₂−NH cyclic form. The potential barrier of the tautomerization from the OH form to the NH form is about 12.6 kcal/mol for the 1:2 complexes, while the barrier height of the reverse reaction is only 2.3 kcal/mol. This shows that the NH form is kinetically unstable. With respect to *cis*-7HQ, only the cyclic structure was obtained for the 7HQ−(H₂O)₃ complexes. The tautomerization from the OH to the NH form

is endothermic by 5.8 kcal/mol with a barrier of 8.5 kcal/mol at the MP2/3-21G level. The barrier of the reverse reaction is nearly equal to zero with zero-point energy correction. So, tunneling must be efficient in the conversion from the NH to the OH form in the 7HQ−(H₂O)₃ complex. The complex−water interaction does not have a large influence on the structures and reactivity of the complexes, but the striking changes are associated with electron correlation.

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