# Ab Initio Study of the Triple-Proton-Transfer Reactions of Ground and Excited States of 7-Hydroxyquinoline in Methanol Solution

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**Abstract:** The triple-proton-transfer reactions in the ground and first excited states of 7-hydroxyquinoline (7HQ) in methanol solution have been investigated by employing different ab initio quantum mechanical methods. The solvent effects on the structures and potential energy profiles of the reactions were included with the use of the Onsager self-consistent reaction field model. The potential energy profiles governing multiproton transfers were optimized at the HF and MP2 levels for the ground state and at the CIS and CASSCF levels for the first excited state. A conclusive description of the photoinduced proton-transfer cycle is given on the basis of the calculated potential energy profiles and transition energies, together with the experimental findings. The main features of the absorption and emission spectra concerning the ground and the first excited states of 7HQ were elucidated by analyzing the CIS and CASSCF calculated results. Electron correlation plays an important role in the description of the geometric features of 7HQ and the proton-transfer reactions in the complex, and this has been discussed in detail.

## 1. Introduction

Transfer of a proton from one atom to another in electronic ground and excited states of molecules is a fundamentally important reaction playing a crucial role in a large variety of biological and photochemical processes.[1−4] As a consequence, the proton transfer is attracting great attention, both from experimental and theoretical viewpoints.[5−20] In the past 10 years, a number of experimental studies have been initiated whose aim has been to determine proton transfer in van der Waals complexes between heteroaromatic molecules and small polar molecules.[21−26] Molecular complexes involving small polar molecules together with an aromatic chromophore are quite attractive systems for the study of H-bond for several reasons: (1) simple aromatic ring compounds with a substituent such as an hydroxy group can serve as prototypes for structurally related subunits in biomolecules. Thus, knowledge of structure and reactivity for a series of such solute−solvent complexes or clusters with different aromatic molecules is of value for a better understanding of the nature of biomolecules. (2) A manifold of different H-bond conditions can be studied simply by choosing a proper solute molecule together with an appropriate solvent, ranging from relatively weak to strong interactions including proton-transfer reactions. (3) Molecular clusters containing an aromatic chromophore allow the convenient use of selective laser-spectroscopic methods in molecular beam experiments.

In solutions of some bifunctional heteroaromatic molecules possessing both proton donor and acceptor groups, solvent molecules, such as $H_2O$ and $CH_3OH$, may assist proton transfer in the ground and excited states by acting as a proton relay because of a too large distance between donor and acceptor groups of the molecules. Perhaps the most frequently studied

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(1) Levy, D. H. *Annu. Rev. Phys. Chem.* **1980**, *39*, 197−232.

(2) Cantor, C. R.; Schimmel, P. R. *Biophysical Chemistry I*; Freemann: San Francisco, 1980; pp 1−25.

(3) Arnaut, L. G.; Formosinho, S. J. *J. Photochem. Photobiol. A: Chem.* **1993**, *75*, 1−20.

(4) Formosinho, S. J.; Arnaut, L. G. *J. Photochem. Photobiol. A: Chem.* **1993**, *75*, 21−48.

(5) Kim, Y. *J. Am. Chem. Soc.* **1996**, *118*, 1522−1528.

(6) Stoeckli, A.; Meier, B. H.; Kreis, R.; Meyer, R.; Ernst, R. R. *J. Chem. Phys.* **1990**, *93*, 1502−1520.

(7) Meyer, R.; Ernst, R. R. *J. Chem. Phys.* **1990**, *93*, 5518−5532.

(8) Schwartz, B. J.; Peteanu, L. A.; Harris, C. B. *J. Phys. Chem.* **1992**, *96*, 3591−3598.

(9) Moog, R. S.; Maroncelli, M. *J. Phys. Chem.* **1991**, *95*, 10359−10369.

(10) Chen, Y.; Rich, R. L.; Petrich, J. W. *J. Phys. Chem.* **1993**, *97*, 1770−1780.

(11) Gerritzen, D.; Limbach, H. H. *J. Am. Chem. Soc.* **1984**, *106*, 869−879.

(12) Rumpel, H.; Limbach, H. H. *J. Am. Chem. Soc.* **1989**, *111*, 5429−5441.

(13) Scherer, G.; Limbach, H. H. *J. Am. Chem. Soc.* **1989**, *111*, 5946−5947.

(14) Schlabach, M.; Scherer, G.; Limbach, H. H. *J. Am. Chem. Soc.* **1991**, *113*, 3550−3558.

(15) Meschede, L.; Limbach, H. H. *J. Phys. Chem.* **1991**, *95*, 10267−10280.

(16) Schlabach, M.; Limbach, H. H.; Bunnenberg, E.; Shu, A. Y. L.; Tolf, B. R.; Djerassi, C. *J. Am. Chem. Soc.* **1993**, *115*, 4554−4565.

(17) Scherer, G.; Limbach, H. H. *J. Am. Chem. Soc.* **1994**, *116*, 1230−1239.

(18) Braun, J.; Limbach, H. H.; Williams, P. G.; Morimoto, H.; Wemmer, D. *J. Am. Chem. Soc.* **1996**, *118*, 7231−7232.

(19) Bardez, E.; Chatelain, A.; Larrey, B.; Valeur, B. *J. Phys. Chem.* **1994**, *98*, 2357−2366.

(20) Bardez, E.; Devol, I.; Larrey, B.; Valeur, B. *J. Phys. Chem. B* **1997**, *101*, 7786−7793.

(21) Kim, S. K.; Bernstein, E. R. *J. Phys. Chem.* **1990**, *94*, 3531−3539.

(22) Chapman, C. F.; Maroncelli, M. *J. Phys. Chem.* **1992**, *96*, 8430−8441.

(23) Douhal, A.; Sastre, R. *Chem. Phys. Lett.* **1994**, *219*, 91−94. Douhal, A.; Dabrio, J.; Sastre, R. *J. Phys. Chem.* **1996**, *100*, 149−154.

(24) Lavin, A.; Collins, S. *Chem. Phys. Lett.* **1993**, *204*, 96−100; *207*, 513−516.

(25) Lee, S.-I.; Jang, D.-J. *J. Phys. Chem.* **1995**, *99*, 7537−7541.

(26) Fernandez, J. A.; Bernstein, E. R. *J. Chem. Phys.* **1997**, *106*, 3029−3037.

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system of the solvent-assisted proton transfer reaction is methanol solution of 7-hydroxyquinoline (7HQ). Early in 1968, Mason, Philp, and Smith[27] had investigated photochemical properties of 7HQ and pointed out that the OH group is more acidic and the ring nitrogen atom more basic in the excited state than in the ground state. The two-stage prototropic change in the excited state from the neutral molecule to zwitterion was proposed to take place. After this earlier study, Thistlethwaite et al.[28] reported the picosecond fluorescence of 7HQ in methanol solution. They observed the excitation wavelength dependence of the fluorescence intensity ratio of normal (N) and tautomer (T) of this compound and suggested an important participation of the solvent methanol. Photoinduced proton transfer in methanol solution of 7HQ has been investigated by Itoh et al..[29] The activation energy for proton-transfer reaction on the excited state, N* → T*, was estimated to be 0.54 kcal/mol in methanol solution from temperature dependence of the fluorescence rise time of T*. They observed the electronically deactivated phototautomer (T) and found that it yields the original form of 7HQ in a thermal reaction, T → N, by transient absorption and two-step laser induced fluorescence (TS-LIF) spectroscopies, whose activation energy is 4.2 kcal/mol. These were about five years before transient absorption spectra by Konijnenberg et al.,[30] in which the reverse proton-transfer reaction, T → N, was further studied. The obtained activation energy of 21.3 kJ/mol (5.1 kcal/mol) is close to Itoh et al.'s experimental value of 4.2 kcal/mol. The enthalpy difference between the tautomer and normal is 3400 $cm^{-1}$ (9.7 kcal/mol) in the ground state and $-4200$ $cm^{-1}$ ($-12.0$ kcal/mol) in the excited state, indicating the predominant normal form in the ground and the tautomer form in the excited state.[31]

Recently there has been renewed interest in the stability of the ground-state tautomer and in the spectroscopy of 7HQ in methanol solution. The T form of 7HQ has been observed in the mixture of methanol and argon at 10 K[24] and in methanol solution at room temperature,[32] which predicts that the potential barrier for the reverse proton-transfer reaction on the ground state is probably larger than that previously reported. The stabilized ground-state tautomer has been further identified as the isolated 1:2 bridged complex between 7HQ and two molecules of methanol, 7HQ$-$(MeOH)$_2$. The dual fluorescence of 7HQ in methanol from N* and T* forms has been observed at room temperature as well as at 10 K.[23-25,28-30] The excitation and emission bands of N form appear at 320 and 378 nm, respectively, while the tautomer excitation band appears at 420 nm and emission band at 520 nm. The methanol H-bonded complex formations of 7HQ and methyl-substituted 7HQ were investigated by methanol concentration dependence of absorption spectra in methanol/hexane mixed systems.[33] The effective 1:2 methanol H-bonded complex formation was observed in 6-Me-7HQ/methanol solution, while the mostly 1:1 H-bonded complex was observed in 8-Me-7HQ/methanol. Taking account of the steric factor of 6- and 8-methyl groups, the cis conformer of the 7-OH group with respect to the ring N atom was suggested to be required for the 1:2 complex formation of 7HQ with methanol molecules. This work further demonstrated that the excited-state proton transfer takes place from the 1:2 H-bonded complexes of 7HQ and 6-Me-7HQ with methanol molecules and that no significant excited-state proton transfer occurs in the 1:1 H-bonded complex of 8-Me-7HQ with methanol. On the basis of the experimental observation, the mechanism of the solvent-assisted proton-transfer reactions of 7HQ in methanol solution has been proposed: Excitation of a ground-state normal complex at 320 nm leads to excited-state proton transfer to form the excited-state tautomer. Subsequently, relaxation takes place, giving rise to the ground-state tautomer followed by regeneration of the normal form.

7HQ dissolved in the different solid polymeric matrixes shows a similar dual fluorescence at room temperature,[23] a blue one (375$-$400 nm) from the normal form and a green one (500$-$520 nm) from the tautomer. The bridged normal form, similar to the 7HQ$-$(MeOH)$_2$ complex in methanol solution, can undergo an excited-state proton-transfer reaction, leading to the tautomer through an energy barrier. The reverse process, however, does not occur upon excitation of the tautomer due to the greater stabilization (about 79 kJ/mol) of this tautomer relative to the normal form in the excited state. The ground-state tautomer is stable in these media. Room-temperature spectra of 7HQ in these media show the coexistence of free monomers and complexes.

Though numerous experiments have been devoted to the investigation of the spectroscopy and tautomerization of 7HQ in methanol solution and solid polymeric matrixes, as we know, very little theoretical information is available for 7HQ. The theoretical treatment of photochemical processes within the framework of the Born$-$Oppenheimer approximation requires knowledge of the potential energy surfaces of the ground state and of one or more excited states. In the present paper, we have performed calculations on the ground- and excited-state ($S_1$) potential energy profiles in order to obtain details for the mechanism of photoinduced proton-transfer reactions of 7HQ in methanol solution as well as information on the main features of the absorption and emission spectra of the system of interest.

Over the past few years, numerous quantum mechanics calculations have been undertaken in order to predict structures, properties, and several hydrogen bonding arrangements of van der Waals complexes between aromatic molecules (phenol, aniline, and naphthol) and small polar molecules ($H_2O$, $NH_3$, and $CH_3$ OH).[34-37] These studies, however, have been done for a single proton transfer in the ground state. In comparison, multiproton ($\geq 3$) transfers in excited states, in which more than two protons are transferred, either synchronously or asynchronously, have received less attention. Double proton transfers in some hydrogen-bonded complexes between the smaller aromatic molecules (2-pyrimidinone, cytosine, and 2-hydroxypyridine) and water molecules have been investigated by Sobolewski and Adamowicz.[38-40] In their studies the molecular

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(27) Mason, S. F.; Philp, J.; Smith, B. E. *J. Chem. Soc. A* **1968**, 3051$-$3067.

(28) Thistlethwaite, P. J.; Corkill, P. J. *Chem. Phys. Lett.* **1982**, *85*, 317$-$321. Thistlethwaite, P. J. *Chem. Phys. Lett.* **1983**, *96*, 509$-$512.

(29) Itoh, M.; Adachi, T.; Tokumura, K. *J. Am. Chem. Soc.* **1983**, *105*, 4828$-$4829; **1984**, *106*, 850$-$855.

(30) Konijnenberg, J.; Ekelmans, G. B.; Huizer, A. H.; Varma, C. A. G. O. *J. Chem. Soc., Faraday Trans II* **1989**, *85*, 39$-$51.

(31) Terazima, M.; Azumi, T. *J. Am. Chem. Soc.* **1989**, *111*, 3824$-$3826.

(32) Bohra, A.; Lavin, A.; Collins, S. *J. Phys. Chem.* **1994**, *98*, 11424$-$11427. Lavin, A.; Collins, S. *J. Phys. Chem.* **1993**, *97*, 13615$-$13619.

(33) Nakagawa, T.; Kohtani, S.; Itoh, M. *J. Am. Chem. Soc.* **1995**, *117*, 7952$-$7957.

(34) Schutz, M.; Burgi, T.; Leutwyler, S. *J. Chem. Phys.* **1993**, *99*, 1469$-$1481.

(35) Hobza, P.; Burcl, R.; Spirko, V.; Dopfer, O.; Muller-Dethlefs, K.; Schlag, E. W. *J. Chem. Phys.* **1994**, *101*, 990$-$997. Vener, M. V.; Scheiner, S.; Sokolov, N. D. *J. Chem. Phys.* **1994**, *101*, 9755$-$9765.

(36) Schmitt, M.; Muller, H.; Henrichs, U.; Gerhards, M.; Perl, W.; Deusen, Ch.; Kleinermanns, K. *J. Chem. Phys.* **1995**, *103*, 584$-$594; Gerhards, M.; Kleinermanns, K. *J. Chem. Phys.* **1995**, *103*, 7392$-$7400.

(37) Watanabe, H.; Iwata, S. *J. Chem. Phys.* **1996**, *105*, 420$-$431.

(38) Sobolewski. A. L.; Adamowicz, L. *J. Chem. Phys.* **1995**, *102*, 5708$-$5718.

(39) Sobolewski. A. L.; Adamowicz, L. *J. Phys. Chem.* **1995**, *99*, 14277$-$14284.

geometries were optimized at the Hartree−Fock level for the ground state and at the single-excitation configuration interaction (CIS) level for the excited states. The effect of electron correlation on geometries is not taken into account, which has an important influence on the H-bond configurations in H-bonded intermolecular complexes. In addition, their studies did not incorporate the influence of the environment on the stabilization of the tautomers and on the shift of tautomeric equilibrium of complexes. In this paper, we have investigated the proton-transfer reactions of 7HQ in methanol solution. On one hand, two molecules of methanol act as a "bridge" which assists the transfer of protons between the oxygen and nitrogen atoms of bare 7HQ. On the other hand, the interaction between the 7HQ−$(MeOH)_2$ complex and solvent is taken into account via a continuum model in which the 7HQ−$(MeOH)_2$ complex is included in a spherical cavity and surrounded by a dielectric continuum.

## 2. Computational Methods

The geometries of the stationary points on the ground-state ($S_0$) potential energy profile are fully optimized with energy gradient technique. After a preliminary search with a 3-21G basis set at the Hartree−Fock level (HF/3-21G), the structures are optimized further at the level of HF/6-31+G, HF/6-31G*, and MP2(FC)/3-21G, where FC denotes the frozen 1s core of nitrogen, oxygen, and carbon atoms. In the optimization of the geometries for the excited-state PES, the configuration interaction with single excitations (CIS) method[41] is first used with the 3-21G basis set, and then the complete active space self-consistent-field (CASSCF)[42] optimization is performed with the CIS optimized structures as the initial guess. To carry out CASSCF calculation, the crucial step is the selection of the proper active space. The obvious choice for describing the first excited singlet state ($S_1$) of 7HQ would be 10 electrons in the 5 $\pi$ molecular orbitals and 4 electrons in the 2 nonbonding orbitals located at O and N atoms, respectively. The initial test CASSCF calculations with 14 electrons in 12 active orbitals [CASSCF(14,12)] show only three antibonding $\pi$ orbitals with occupation numbers larger than 0.05. Therefore, the active space with 14 electrons in 10 orbitals is used in the CASSCF optimization of the geometries for the $S_1$ PES. Due to the size of system of interest, a 3-21G basis set is employed for the CASSCF(14,10) calculations. The similar basis set has been successfully used for the investigation of the first excited electronic state with valence character.[38−40,43] We have used the scale factor of 0.85 for zero-point vibrational energy corrections[44] in calculations of the barrier heights and reaction energies.

For a chemical reaction where changes in polarity among the reactant, transition state, and product take place, solvent effects can have an influence on the potential barrier of the reaction and enthalpy difference between the reactant and product. The solvent effects have been considered employing the self-consistent reaction field (SCRF) method.[45,46] In the reaction field model, the solvent is considered to be uniform dielectric, characterized by a given dielectric constant (31.2 for methanol). The solute is assumed to occupy a spherical cavity (the radius of the cavity is 5.4 Å based on the calculated complex volume) in the medium. The permanent dipole of 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 ground-state geometries have been reoptimized with the SCRF method with 3-21G, 6-31+G, and 6-31G* basis sets. At the MP2/3-21G optimized geometries of the ground state and CASSCF(14,10)/3-21G optimized geometries of the excited state, energies are recalculated with the CASSCF(14,10)/3-21G method but including solvent effects. All the calculations are performed by using the Gaussian 94 package of programs.[47]

## 3. Results and Discussion

**3.1. 7HQ Monomer.** Let us start the discussion with an analysis of structures and properties of 7HQ monomer. The molecule formally described as 7-hydroxyquinoline (N) potentially exists in a second tautomeric form, 7-quinolone (T). They have $C_s$ planar structures, which are confirmed to be energy minimum points by the vibrational frequency calculations which gave all real frequencies. The optimized geometrical parameters and calculated energies of N and T forms in the ground state as well as in the excited state are supplied as Supporting Information. It is interesting to make a comparison among the SCF, SCRF, and MP2 optimized ground-state structures as well as the CIS and CASSCF optimized excited-state geometries. It has to be pointed out first that solute−solvent interaction does not lead to a significant change of geometry in solution with respect to the geometry in the gas phase, especially for the normal form. The analogous situation occurs for the 7HQ−$(MeOH)_2$ complex, as pointed out below. Wong et al.[46] had noticed that the introduction of a solvent reaction field has little effect on the calculated geometry of 2-hydroxypyridine. This provides justification for the calculation of solute−solvent interaction energy on the basis of the gas-phase geometry. One might have expected that the intermolecular interaction in solution would have a larger influence on the dihedral angles of the solute molecule. However, the planar structures of N and T forms in methanol solution are confirmed to be minima by the SCRF calculated frequencies.

The HF/3-21G and HF/6-31G* optimized geometrical parameters are close to each other, except for the C−O and H−O bond lengths. The optimized geometries are slightly affected by the inclusion of s- and p-diffuse functions on C, N, and O atoms. This gives us a reason to expect that the properties of the investigated system can be better described with the use of the 3-21G basis set. The electronic rearrangements induced by excitation from the ground state to the $S_1$ state significantly influence the structures of 7HQ. Compared with the MP2 optimized geometries of the ground state, the single-bond lengths

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(40) Sobolewski. A. L.; Adamowicz, L. *J. Phys. Chem.* **1996**, *100*, 3933−3941.

(41) Foresman, J. B.; Head-Gordon, M.; Pople, J. A.; Frisch, M. J. *J. Phys. Chem.* **1992**, *96*, 135−149.

(42) Mcdouall, J. J. W.; Pleasley, K.; Robb, M. A. *Chem. Phys. Lett.* **1988**, *148*, 183−189.

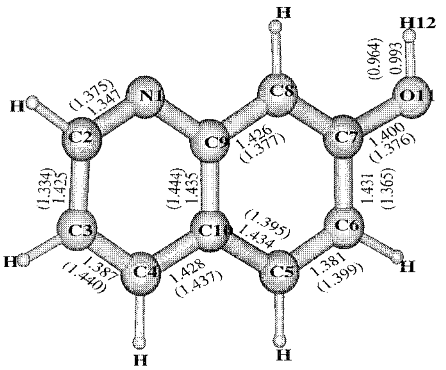
(43) Bearpark, M. J.; Bernardi, F.; Clifford, S.; Olivucci, M.; Robb, M. A.; Smith, B. R.; Vreven, T. *J. Am. Chem. Soc.* **1996**, *118*, 169−175.

(44) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502−16513.

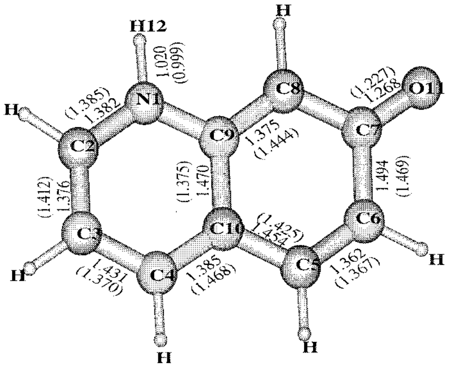
(45) Wong, M. W.; Frisch, M. J.; Wiberg, K. B. *J. Am. Chem. Soc.* **1991**, *113*, 4776−4782.

(46) Wong, M. W.; Wiberg, K. B.; Frisch, M. J. *J. Am. Chem. Soc.* **1992**, *114*, 1645−1652.

(47) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; J. A. Montgomery, J. A.; K. Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94, Revision D.4*; Gaussian, Inc.: Pittsburgh, PA, 1995.



N (N*) form



T (T*) form

**Figure 1.** Normal (N or N*: ground or excited state) and tautomer (T or T*: ground or excited state) forms of 7HQ monomer, along with the atomic numbers in N and T forms. The key bond lengths (Å), optimized at the MP2 level for the ground state and at the CASSCF level for the excited state (in parentheses), are given.

are shortened and the double-bond lengths are elongated in the CASSCF optimized geometries of the excited state, as given in Figure 1. The ground-state structures are of alternate single- and double-bond character, while this character becomes unclear in the excited state. Significant effects appear to be associated with the incorporation of electron correlation. For the ground state, the change is systematic such that the MP2 calculated bond lengths are uniformly longer than the corresponding HF calculated values. However, the average difference of 0.056 Å obtained at the HF/3-21G level between the lengths of single and double bonds is reduced to 0.035 Å at the MP2/3-21G level. A method which underestimates electron correlation will predict very different lengths of single and double bonds of the molecule, whereas an overestimate of these effects will lead to nearly equal distances. The HF calculations in which electron correlation is not taken into account thus predict a large difference between lengths of single and double bonds. The same trend is not found for the $S_1$ state in going from the CIS to CASSCF method, since an electron excitation from bonding to antibonding orbital can be partially responsible for the excited-state structural variation which is superimposed on those due to the increase of electron correlation. Generally speaking, geometries optimized at the MP2 level for ground state and at the CASSCF level for excited state provide good agreement with experimental findings. So the MP2/3-21G and CASSCF-(14,10)/3-21G optimized structures will be our reference points for further calculations.

The energy difference between T and N forms, calculated with the zero-point energy corrections, is 15.6, 16.0, 14.6, and 13.2 kcal/mol at the HF/3-21G, HF/6-31G*, HF/6-31+G, and MP2/3-21G levels, respectively, for the ground state and −16.5, −12.0, and −16.1 kcal/mol at the CIS/3-21G, CIS/6-31G*, and CASSCF(14,10)/3-21G levels, respectively, for the excited state. With the solvent effects considered, the energy differences become 8.2 and 8.8 kcal/mol at the HF/6-31+G and MP2/3-21G levels, respectively, for the ground state and −18.1 kcal/mol at the CASSCF level for the excited state. The calculated energy differences are close to the experimental values for the methanol solution of 7HQ, as mentioned in the first section. The adiabatic transition energies with the vibrational zero-point energy correction (0−0 energy gap) for N and T forms are calculated to be 88.6 and 55.8 kcal/mol, respectively, at the CASSCF level. The solvent−solute interaction decreases the 0−0 energy gap of the N form to 84.7 kcal/mol and of the T form to 53.1 kcal/mol. The 0−0 energy gap of 82.0−85.4 kcal/mol for the N form was reported by Lavin and Collins.[24] They also estimated the 0−0 energy gap for the T form in the range of 59.6−62.6 kcal/mol on the basis of the measurements of transient absorption and TS-LIF room-temperature methanol-solution spectra.[29,31] A good consistency was found between the computed and measured 0−0 energy gaps for the N form; however, the calculated 0−0 energy gap for the T form is about 7 kcal/mol lower than the experimental estimate. The CASSCF-(14,10)/3-21G calculated vertical transition and emission energies are 4.78 and 3.10 eV for the N form and 3.42 and 1.92 eV for the T form, respectively. Compared with the absorption and emission wavelengths at the peaks which were given in the first section, there is a deviation of about 0.5 eV in the CASSCF calculated values. A further comparison with the complex will be made in the following.

**3.2. 7HQ−(MeOH)$_2$ Complex. Ground and Excited-State Geometries.** The equilibrium geometries of the ground-state 7HQ−(MeOH)$_2$ complex in the gas phase and in methanol solution are first optimized with the 3-21G basis set under the $C_s$ symmetry constraint. The calculated frequencies show that the optimized planar structures are not minimum points on the potential energy surfaces. The nonplanar geometries, optimized at the HF/3-21G, HF/6-31G* with and without the inclusion of solvent effects, are confirmed to be minima or saddle points by the SCF and SCRF calculated frequencies. As mentioned before, the interaction between the 7HQ−(MeOH)$_2$ complex and $CH_3$ OH does not have a significant influence on the bond lengths and angles of the 7HQ−(MeOH)$_2$ complex. In comparison, the dihedral angles C7−O11−H12−O13 and O11−H12−O13−H14 are 4.5 and 12.5 degrees, respectively, in the gas phase, while in solution they are close to zero degree. Even so, the SCF and SCRF calculated energy differences among the reactant, transition state, and product are almost equal. This is consistent with a typical theoretical conclusion that a dihedral angle changes by a large number of degrees but that it is not very important for the energy. The equilibrium geometries characterized the ground-state 7HQ−(MeOH)$_2$ complex at the MP2/3-21G level are shown in Figure 2 where only parameters which describe geometry of the "reaction center" (close to the hydrogen bonds) are given, since the rest of them are very close to those given in Figure 1 for the monomers. As pointed out before, the MP2 optimized bond lengths of bare 7HQ are longer than those optimized at the Hartree−Fock level; in contrast, the MP2/3-21G optimized intermolecular H-bond distances are about 0.15 Å shorter than the corresponding HF/3-21G optimized distances. Since electron correlation is not taken into

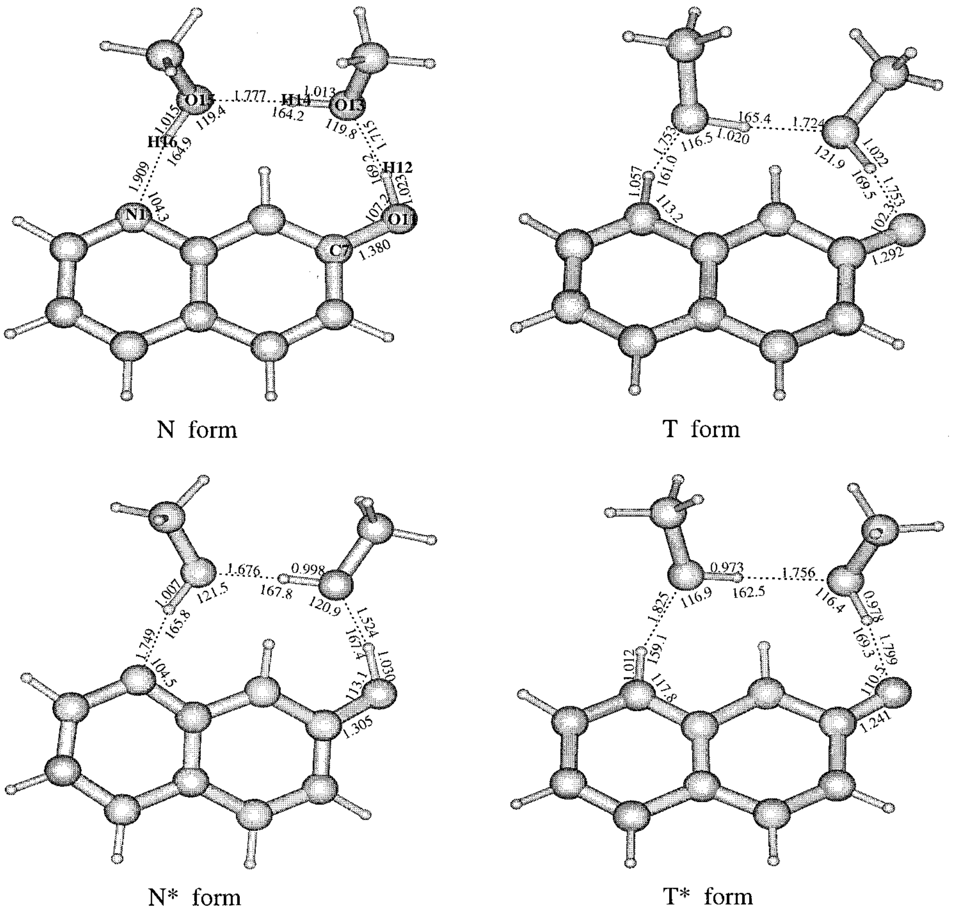


**Figure 2.** Normal (N: ground state, N*: excited state) and tautomer (T: ground state, T*: excited state) forms of 7HQ$-$(MeOH)$_2$. The atomic numbers of the H-bonded structures were shown in N form (for the atoms of the aromatic rings and their numbers see N or T form of Figure 1). The parameters in N and T forms come from the MP2 calculations and the parameters in N* and T* forms from the CASSCF calculations.

account by the Hartree$-$Fock calculations, the HF method underestimates H-bond interactions, thus predicting H-bond distances that are too long.

The equilibrium geometries of the excited-state complex in the gas phase are first optimized at the CIS/3-21G level of theory without any symmetry constraint. The obtained structures are further confirmed by the CIS/3-21G calculated frequencies. It has been well established that the CASSCF with appropriate active space is a more reliable approach than the CIS for the study of excited electronic states, since the CIS approach is related to the limited inclusion of electron correlation. With the CIS optimized structures as an initial guess, the CASSCF optimized geometries are shown in Figure 2. The most striking change is the strengths of intermolecular H-bonds. The H-bond lengths of H16$-$N1, H14$-$O15, and H12$-$O13 in N* form are 1.900, 1.768, and 1.633 Å, respectively, at the CIS/3-21G level; however, they become 1.749, 1.676, and 1.524 Å, respectively, at the CASSCF/3-21G level. Similar to the HF method for the ground state, the CIS treatment underestimates electron correlation and H-bond interactions, predicting too long H-bond distances in the excited-state complex. A further consequence of electron correlation is a significant distortion of the geometrical parameters in the neighborhood of the intermolecular H-bond. In particular, the O11$-$C7 and C9$-$N1 distances decrease by about 0.03 Å in going from CIS to CASSCF, while the C2$-$N1 bond length increases by 0.058 Å. The effect of electron correlation shifts the geometrical structure of N* form toward that of the transition state (TS*) governing excited-state proton transfer, thus reducing the potential barrier of the proton-transfer reaction, which is consistent with the CASSCF and CIS calculated results.

Upon inspection of the parameters in Figure 2, one can notice a significant variation of the O$-$H and C$-$O bond lengths of normal (N) form upon electron excitation. Compared with the ground state, in the excited electronic state the C7$-$O11 bond length is strongly reduced, while the bond length of O11$-$H12 is slightly elongated. On the average, the intermolecular H-bond distances (N1$\cdots$H16, H15$\cdots$O14 and O13$\cdots$H12) are decreased by 0.15 Å in the excited state with respect to those in the ground state. For the T-form complex, on the contrary, the intermolecular H-bond distances (H16$\cdots$O15, H14$\cdots$O13, and H12$\cdots$O11) in the excited state are longer than those in the ground state, whereas the N1$-$H16 and C7$-$O11 bond lengths become shorter upon excitation. All of these are in agreement with the fact that the OH group of 7HQ is more acidic and the ring nitrogen more basic in the excited state than in the ground state.[27] In addition, the significant increase of H-bond strength in the N-form complex is responsible for the decrease of activation energy in the excited state with respect to the ground state. The opposite behavior of H-bond strength and activation energy is further demonstrated by the following calculated energies. Another feature is the O$-$H$\cdots$O and N$\cdots$H$-$O H-bond structures in the 7HQ$-$(MeOH)$_2$ complex. They are all significantly bent, which is unchanged with an electron excitation, electron correlation, and proton transfers. The previous experiments and theoretical calculations,[35,48,49] how-

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(48) Lim, J.-H.; Lee, E.-K.; Kim, Y. *J. Phys. Chem. A* **1997**, *101*, 2233$-$2309.

ever, show that the O−H···O and N···H−O hydrogen-bond structures in the intermolecular complexes are of linear character. For example, on the assumption that the O−H···N bonds in the complex between 1-hydroxynaphthalene and ammonia is linear, Humphrey and Pratt deduced the potential energy profiles of proton transfer reactions. The formation of the cyclic structure is probably responsible for the significantly bent hydrogen-bond structure in the 7HQ−$(MeOH)_2$ complex.

Here we pay attention to the O−O and N−O distances in the N- and N*-form complexes on which the heights of the reaction barriers are dependent. From the viewpoint of valence bond, an interaction between the lone pair of the acceptor oxygen or nitrogen atom and the $\sigma$ * orbital of the O−H bond is mainly responsible for the proton transfer to the acceptor. 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 N1−O15 diatances in N-form complex are 2.732, 2.794, and 3.038 Å at the HF/3-21G level and 2.726, 2.766 and 2.901 Å at the MP2/3-21G level, respectively. In N*-form complex, they become 2.624, 2.731, and 2.865 Å at the CIS/3-21G level and 2.539, 2.660, and 2.736 Å at CASSCF(14,10)/3-21G level, respectively. On the basis of the data and analysis above, the barrier height of the process N → T predicted by the MP2/3-21G is lower than that predicted by the HF/3-21G. There exists an analogous relation between the CASSCF(14,10)/3-21G and CIS/3-21G predicted barrier height of the process N* → T*. It should be emphasized that the O−O or N−O distance is much shorter in N* form than in N form. This predicts that the barrier height of the process N* → T* is much lower than that of the process N → T. All the results predicted above are consistent with the quantitative calculations below.

**Main Features of the Absorption and Emission Spectra.** Three highest occupied and two lowest unoccupied molecular orbitals are n, $\pi$, $\pi$, $\pi^*$, and $\pi^*$ orbitals, referred to as HOMO-2, HOMO-1, HOMO, LUMO, and LUMO+1 in the increasing order of energy. These orbitals have valence character. The simple molecular orbital model shows that a few configurations related to excitations between the HOMO, HOMO-1, HOMO-2 and LUMO, LUMO+1 are responsible for the $S_1$ states of N and T forms. So the $S_1$ states of N and T forms are the valence excited states. For the $S_1$ state of N form of bare 7HQ, the singly excited configuration, HOMO-2 → LUMO contributes up to 96% to the final CASSCF wave function of this state, which predicts that the $S_1$ state of N form of bare 7HQ is of n$\pi^*$ character. However, the double excitations from the HOMO to LUMO play an important role (contribution larger than 40%) in the final CASSCF wave functions of the excited-state N form of the complex. This state is better described by the asymmetric combination of the ground-state configuration and its doubly excited configuration. This shows that the $S_1$ state of N form of the 7HQ−$(MeOH)_2$ complex is of $\pi\pi^*$ character. The energy difference between n$\pi^*$ and $\pi\pi^*$ states is usually small for most of the heteroaromatic molecules, the intermolecular interaction can change the energy order of n$\pi^*$ and $\pi\pi^*$ states. This is the reason why the feature of the $S_1$ state is varied from bare 7HQ to its complex with methanol. It is interesting to examine CIS calculated configurations of the $S_1$ state. Because of only single excitations included in this method, the doubly excited feature cannot be reflected in the CIS calculations. However, the two singly excited configurations, HOMO → LUMO and HOMO-1 → LUMO+1, make a main contribution to the first excited-state wave function of the complex. Because of a small energy difference between HOMO and HOMO-1 and between LUMO and LUMO+1, as a matter of fact, the CIS calculated $S_1$ state wave function of the complex is consistent with that obtained by the CASSCF method. The CIS calculated transition moment and oscillator strength are 1.32 au and 0.20, respectively. Unlike the N* form, the double excitations from HOMO to LUMO make a great contribution (larger than 50%) to the T* form wave functions of both bare 7HQ and its complex. The CASSCF wave function is well characterized by the asymmetric combination of the ground-state and its doubly excited configurations. The CIS calculations show that the first excited-state wave functions of both bare 7HQ and its complex with methanol are composed of the two singly excited configurations, HOMO → LUMO and HOMO-1 → LUMO. Again due to a small energy difference between HOMO and HOMO-1, the CIS calculated wave functions of the T* forms are consistent with the CASSCF calculated results. The transition moment and oscillator strength for the T-form complex are 1.34 au and 0.3, respectively, close to the corresponding values of the N form.

Employing the MP2 optimized ground-state geometries and the CASSCF(14,10) optimized excited-state structures, the adiabatic excitation energies (0−0 energy gap between the ground state and first excited state) and the vertical excitation and emission energies are calculated at the CASSCF(14,10)/3-21G level of theory. The calculated adiabatic excitation energy in solution of 98.6 kcal/mol for the N form is an overestimate of about 15 kcal/mol compared with the corresponding experimental value. For the T form, the adiabatic excitation energy is 62.1 kcal/mol, agreement with the experimental estimate. The calculated values of the vertical excitation and emission energies of the complex, 4.68 and 3.08 eV for the N form, 3.41 and 1.88 eV for the T form, are in accord with the respective values of the monomers. This is not surprising, because the complex formation has little influence on the geometry of the 7HQ bare molecule. It should be noted that the calculated 0−0 energy gaps of the N form for the monomer and of the T form for the complex are in good agreement with the experimental findings, but there exists a large deviation for the T-form monomer and N-form complex. This suggests that the blue fluorescence of 7HQ in methanol solution mainly originates from the N forms of the free monomer and noncyclic complex and the green fluorescence from the T-form complex. Room-temperature absorption and fluorescence spectra have shown the coexistence of the free monomer and cyclic complex in hydroxylic matrice of 7HQ.[23] The stabilized ground-state tautomer has been experimentally identified as the bridge complex.[32] Because of a too large separation (about 5 Å) between the OH group and the ring N atom in bare 7HQ, the proton-transfer reactions in the ground and excited states take place only in the complex.

**The Ground-State Triple-Proton-Transfer Processes.** The understanding at the molecular level of reaction mechanism for a given chemical reaction requires a detailed knowledge of stationary points: reactants, transition states (TS), and products on the potential energy surface (PES). The geometries of the reactant and product of the ground-state proton-transfer reaction in the 7HQ−$(MeOH)_2$ complex have been discussed above. Here we pay particular attention to the transition state of this reaction. Normally finding the transition state can still be quite challenging, especially for larger molecules. Sobolewski and Adamowicz[38−40] had investigated the intramolecular single proton-transfer and intermolecular double proton-transfer reac-

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(49) Humphrey, S. J.; Pratt, D. W. *J. Chem. Phys.* **1996**, *104*, 8332−8340.

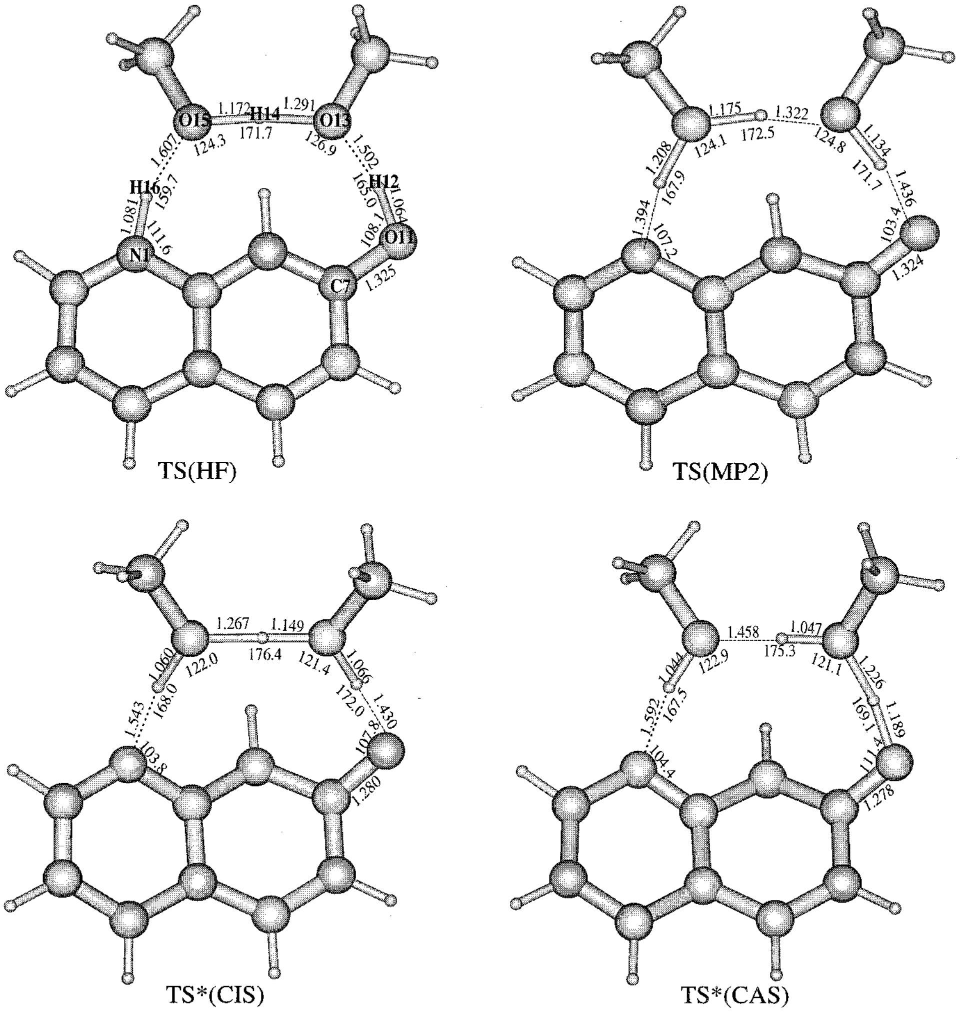

**Figure 3.** Structures of the transition states optimized at the HF [TS(HF)] and MP2 [TS(MP2) levels for the ground state and at the CIS [TS*(CIS)] and CASSCF [TS*(CAS)] levels for the excited state. The atomic numbers of the H-bonded structures were shown in TS(HF) and for the atoms of the aromatic rings and their numbers see N or T form of Figure 1.

tions with the use of the concept of the minimum potential energy reaction coordinate. They chose one of the H−O or H−N distances as reaction coordinate, and the remaining coordinates were optimized at each step of the reaction. As pointed out by Sobolewski and Adamowicz, for the multiproton ($\geq 3$) transfer reaction in larger molecules without any symmetry, an effective single-coordinate model cannot be applied, due to very complicated reaction paths. The geometry of the transition state (TS) with $C_1$ symmetry was fully optimized at the HF/3-21G level with the use of redundant internal coordinates. The HF/3-21G calculated imaginary frequency is 1346i 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 $-0.07\ R_{C7-O11} + 0.38\ R_{O11-H12} - 0.48\ R_{H12-O13} + 0.44\ R_{O13-H14} - 0.41\ R_{O15-H14} + 0.38\ R_{H16-O15} - 0.24\ R_{N1-H16}$. Upon inspection of the HF/3-21G optimized transition state [TS(HF)] structure shown in Figure 3, we can see that the proton H16 already migrated from the methanol molecule to the ring N atom, while the O−H bond of 7HQ is only slightly elongated with respect to the N form. This predicts that bare 7HQ in the TS(HF) is of positive ion character. The HF/6-31G* optimization gives the same conclusion. The introduction of a solvent reaction field leads to a significant change in the structure of the "reaction center". These changes, lengthening of C7−O11, H12−O13, H14−O15, and O15−H16 bonds and shortening of O11−H12, O13−H14, and H16−N1 bonds, correspond to a small increase in positive ion character of bare 7HQ. However, in the MP2/3-21G optimized structure of the transition state [TS(MP2)], the O11−H12 bond is almost broken, while the N1−H16 bond is nearly unformed, as depicted in Figure 3. This shows that bare 7HQ is of partially negative ion character, which is supported by the calculated atomic charges given in the Table 1.

Comparing with the equilibrium geometries, we see that the H bonded to C8 participates in weak hydrogen bonding in the transition state, both at the HF and MP2 levels.

Although in the TS(HF) the proton H16 has transferred to the nitrogen, the proton H12 bonded to the O13 atom in the TS(MP2) is still bonded to the O11 atom. With respect to the TS(HF), the geometric parameters of the aromatic rings in the TS(MP2) are closer to those in the T-form product. It is clear that the TS(MP2) structure is more product-like.

The increase of electron correlation from the HF to MP2 shifts the TS geometry toward the T-form product. This structural feature, which has been noticed in the previous calculations,[50] agrees with Hammond's postulate:[51] the endothermic reaction has a transition state geometry close to the product.

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[50] Richards, Jr. C. A.; Vacek, G.; DeLeeuw, B. J.; Yamaguchi, Y.; Schaefer, H. F. III *J. Chem. Phys.* **1995**, *102*, 1280−1287. Yamaguchi, Y.; Richards, C. A., Jr.; Schaefer, H. F. III *J. Chem. Phys.* **1994**, *101*, 8945−8954.

[51] Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334−338.

**Table 1.** Selected Mulliken Charges of the Complex

| | N | T | N* | T* | TS(HF) | TS(MP2) | TS(CIS) | TS(CAS) |
|---|---|---|---|---|---|---|---|---|
| N1 | −0.76 | −0.59 | −0.82 | −0.67 | −0.58 | −0.92 | −0.93 | −0.95 |
| C2 | 0.39 | 0.52 | 0.35 | 0.38 | 0.59 | 0.44 | 0.44 | 0.28 |
| C3 | −0.08 | −0.12 | −0.08 | −0.06 | −0.13 | −0.10 | −0.15 | −0.10 |
| C4 | 0.12 | 0.13 | 0.11 | 0.09 | 0.20 | 0.13 | 0.15 | 0.02 |
| C5 | 0.03 | 0.04 | 0.03 | 0.08 | 0.06 | 0.01 | 0.04 | 0.09 |
| C6 | 0.04 | 0.02 | 0.01 | −0.08 | 0.04 | 0.01 | −0.03 | −0.05 |
| C7 | 0.38 | 0.48 | 0.47 | 0.50 | 0.46 | 0.45 | 0.50 | 0.54 |
| C8 | −0.03 | −0.08 | −0.06 | 0.20 | 0.04 | −0.08 | −0.15 | 0.05 |
| C9 | 0.30 | 0.44 | 0.37 | 0.49 | 0.46 | 0.37 | 0.40 | 0.40 |
| C10 | −0.11 | −0.13 | −0.09 | −0.28 | −0.16 | −0.12 | −0.15 | −0.15 |
| O11 | −0.35 | −0.73 | −0.36 | −0.68 | −0.34 | −0.80 | −0.81 | −0.22 |

Energies of the normal, tautomer, and transition state, calculated at the different levels, are supplied as Supporting Information. The tautomeric reaction N → T is endothermic by 12.0, 10.8, and 9.2 kcal/mol at the HF/3-21G, HF/6-31G*, and MP2/3-21G levels of theory with the HF/3-21G zero-point energy corrections, respectively. As pointed out before, solvent−solution interaction has little influence on the geometric features of the stationary points, but this interaction leads to a noticeable change in the enthalpy difference of the reaction. The endothermic character in solution of the reaction, N → T, becomes 11.2, 7.0, and 10.1 kcal/mol at the HF/3-21G, HF/6-31G*, and MP2/3-21G levels, respectively. In comparison with the enthalpy difference of 9.7 kcal/mol measured at room temperature. The MP2/3-21G and HF/3-21G calculations give an excellent result, while the HF/6-31G* method underestimates the endothermic character of the reaction. The potential barrier of the reverse proton-transfer reaction, T → N, is computed to be 14.1, 12.9, and 10.3 kcal/mol at the HF/3-21G, HF/6-31G*, and MP2/3-21G levels with the HF/3-21G zero-point energy corrections, respectively. With the solvent effects included, the barrier of the reaction T → N becomes 9.1, 12.9, and 9.9 kcal/mol at the respective levels. It is obvious that the MP2/3-21G and HF/3-21G calculated barriers are close to the experimental estimate of 5.4 kcal/mol, while the HF/6-31G* calculations overestimate the height of the barrier. The potential energy profiles of the triple-proton-transfer reactions in the ground and in the excited states are shown in Figure 4 where the CASSCF calculated transition and emission energies are also given. From electrostatics arguments, the molecule with strong polarity is stabilized when solvent effects are included. So the MP2 calculated dipole moments in solution, 4.4, 6.5, and 5.5 D for N, TS, and T, respectively, can give some hints how effects of solvent affect the relative energies.

**The Excited-State Triple-Proton-Transfer Process.** As pointed out by Sobolewski and Adamowicz, forcing the system into a planar symmetry makes sense only if the distortions from the $C_s$ symmetry have a negligible influence on the energy. This point was carefully checked for the system considered in this work. We attempt to optimize stationary points on the excited-state PES with $C_s$ symmetry constraint. The obtained results are qualitatively not consistent with the experimental conclusion. The optimized nonplanar structure associated with the transition state (TS*) of the excited-state reaction, N* → T*, is illustrated in Figure 3, along with the most relevant geometrical parameters. In the CIS optimized transition state [TS*(CIS)], the 7HQ monomer lost one proton and becomes 7HQ$^-$ ion. With the CIS structure as an initial guess, the transition state is reoptimized with the CASSCF approach. In the CASSCF optimized transition state [TS*(CAS)], the O11−H12 bond is partially broken, H12−O13 bond partially formed, while the H14−O15 and H16−N1 bonds are shortened with respect to the N* form. An increase of the correlation effect from CIS to CASSCF shifts the TS* significantly toward the N*-form reactant. This is consistent with Hammond's postulate:[51] the exothermic reaction has a transition state geometry close to the reactant. Unlike the ground-state TS, the H bonded to C8 does not participate in hydrogen bonding in the TS*.

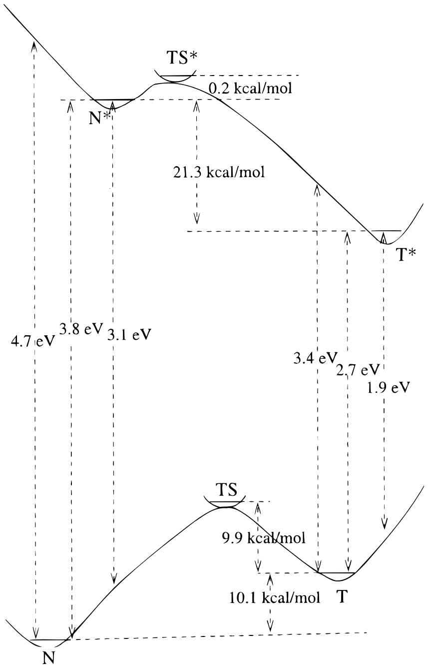

**Figure 4.** Schematic potential energy profiles of the reactions, along with the calculated transition and emission energies.

It should be noted that there are the drastic changes in the optimized TS and TS* structures when electron correlation is increased from the HF to MP2 and from the CIS to CASSCF, respectively, which shows that the tautomerization of the 7HQ−(MeOH)$_2$ may occur through a stepwise proton transfer. If an unconcerned mechanism is involved in the tautomerization reaction, one or more intermediates should exist. However, all attempts to find intermediate on the ground- or excited-state reaction pathway was unsuccessful. It can be expected that there is little possibility of a stepwise proton transfer in the tautomerization. Recently, Bardez et al.[20] have distinguished three types of bifunctional molecules which can undergo photoinduced tautomerization. In the second category, including the 7HQ complex with solvent alcohol, photoinduced tautomerization results from a concerned proton transfer from one function to the other in the hydrogen-bonded complexes.

The triple-proton-transfer reaction in the excited state is exothermic by 13.9 and 20.4 kcal/mol at the CIS and CASSCF levels, respectively. With the solvent effects incorporated, the energy difference between N* and T* forms becomes 21.3 kcal/

mol at the CASSCF level with the T* form being more stable. The barrier height on the excited-state pathway is 1.4 kcal/mol obtained by the CASSCF calculations. Solute−solvent reduces the CASSCF calculated barrier height to 0.2 kcal/mol. The CIS calculations give a higher estimate of the barrier, 5.8 kcal/mol. The activation energy of the proton-transfer reaction, N* → T*, was estimated to be 0.54 kcal/mol from the temperature dependence of the fluorescence rise time of T* form.[29] The excited-state reaction is so rapid that the solvent molecules do not have sufficient time to reorient themselves. It cannot be assumed that an equilibrium between the electronic state of the solute and the reaction field occurs in the reaction process. The calculated change in the barrier from gas phase to solution only provides a qualitative estimate of solvent effects on the barrier. Despite this inaccuracy, from the CASSCF and CIS calculations together with the experimental estimates, we can draw a conclusion that a very small barrier exists on the $S_1$ PES for the proton-transfer reaction of 7HQ in methanol solution. As noted earlier, typical models of the PES for proton-transfer reaction in the condensed phase[52] include tunneling along the reaction coordinate. A small barrier on the $S_1$ PES is consistent with this idea. Konijnenberg et al.[30] have suggested a two-step process for the proton-transfer reactions in the $S_1$ state: the first step involves thermally activated solvent reorganization to achieve a proper conformation of a solute−alcohol complex; the second step is considered to be a thermally unassisted proton-tunneling process in the complex with the proper conformation.

From a chemical viewpoint, there are two main effects which govern the proton-transfer reactions. The first one is an intrinsic effect due to the motion of the proton across the H-bond, which is strongly dependent on the H-bridge structures. This effect has been discussed in detail above. Here we pay attention to the second effect, the charge distribution of the $\pi$ electron system, and its change induced by the proton transfer, which is determined by the structure and its rearrangement of the backbone. From the calculated atomic charges given in Table 1, it can be seen that there is a coupling between the proton and the electrons in the tautomerization of the complex. The proton transfer from the OH group of the 7HQ to the ring N atom via the H-bridge induces charge transfer from the ring N atom to the OH group through the $\pi$-conjugation system. An alternate positive and negative charge distribution exists on the rings of 7HQ.

It is a little surprising that the MP2/3-21G and CASSCF/3-21G calculated enthalpy differences and barrier heights for the proton-transfer reactions in the 7HQ−$(MeOH)_2$ complex are in excellent agreement with the experimental findings. The MP2 and CASSCF are appropriate methods for the study of ground- and excited-state reactions; however, the 3-21G seems to be a too small basis set for the description of the nature of van der Waals complex. Johnson et al.[53] have investigated the structures and properties of the 1- and 2-hydroxynaphthalenes (1HN and 2HN), both from experiment and theory. They found that the results obtained with the 3-21G basis set are in a good agreement with experimental findings in all their cases. Dispersion force makes a great contribution to the weak binding in van der Waals complexes. To describe accurately formation or decomposition of the complexes, larger basis sets with diffuse functions are necessary. In addition, formation or dissociation energy of a complex is affected by the basis set superposition error (BSSE). However, these systematic errors in the N and T forms probably cancel each other in our calculations, since only the tautomerization reactions between the N and T forms are considered in the present study.

## 4. Summary

This paper is devoted to a study of the triple-proton-transfer reactions in the ground and excited states of 7HQ in methanol solution as well as the main features of the spectra of the investigated system. A conclusive description for the mechanisms of photoinduced proton-transfer reactions was obtained. Since the forward reaction from normal to tautomer in the ground state has a barrier height of 20.0 kcal/mol, the overall proton-transfer cycle originates from the excitation of the ground-state normal form. In the resulting $S_1$ state complex, the protons tunnel through a very small barrier on the way to the product, the $S_1$ state tautomer. The reverse process from $S_1$ tautomer to $S_1$ normal form, however, does not occur, due to the greater stabilization of the tautomer relative to the normal in the excited state. Subsequently, relaxation takes place, giving rise to the ground-state tautomer. Because of a barrier of 9.9 kcal/mol on the pathway, the reverse proton transfer reaction may occur but not very easily. The calculated transition and emission energies together with the experimental values show that the absorption and emission bands in methanol solution of 7HQ originate mainly from the normal forms of the 7HQ monomer and noncyclic complex and the tautomer of the 7HQ−$(MeOH)_2$ complex, respectively. The important role played by electron correlation in the description of the geometric features and the proton-transfer reactions is well evidenced by the significant differences between HF and MP2 and between CIS and CASSCF calculated results.

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**Supporting Information Available:** Vibrational zero-point energies and the geometrical parameters of 7HQ monomer and energies with and without solvent effect of 7HQ monomer and its complex with methanol (4 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(52) Staib, A.; Borgis, D.; Hynes, J. T. *J. Chem. Phys.* **1995**, *102*, 2487−2505.

(53) Johnson, J. R.; Jordan, K. D.; Plusquellic, D. F.; Pratt, D. W. *J. Chem. Phys.* **1990**, *93*, 2258−2273.