Proton-Transfer Reaction in Isolated and Water-Complexed 8-Hydroxyimidazo[1,2-*a*]Pyridine in the S_0 and S_1 Electronic States. A Theoretical Study

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The intramolecular proton-transfer reaction of 8-hydroxyimidazo[1,2-*a*]pyridine (HIP) is studied in both the ground (S_0) and first singlet excited (S_1) electronic states. Ab initio calculations at the HF/MP2 and CIS/MP2 levels, respectively for S_0 and S_1, reveal the existence of two tautomers. In gas phase the enol (E) form is the more stable one in S_0, whereas in S_1 the zwitterionic (Z) tautomer becomes the lowest in energy. The energy barrier for the proton-transfer process is quite high in both electronic states. Introduction of one water molecule in the system greatly changes the picture of the whole process. A 1:1 complex involving two hydrogen bonds between HIP and water is formed. The H-bond bridge greatly facilitates the proton transfer in both S_0 and S_1 states. Additionally, for the two considered electronic states the Z structure is more stabilized than the E one. The trends of lowering the energy barrier and stabilizing the Z structure with respect to E are more prominent when the bulk effect of the solvent is introduced through a continuum (i.e. cavity) model. The energy profiles obtained for both S_0 and S_1 allow prediction of the electronic spectra of HIP in different media.

1. Introduction

Proton (or hydrogen atom) transfer reactions play a central role in a large number of chemical and biological phenomena.[1,2] Among the huge diversity of these reactions, the photoinduced intramolecular proton transfer is a topic of current interest.[3] Part of this interest comes from the recent development of very fast and precise spectroscopic techniques (femtochemistry)[4] and possible potential applications.[3−5]

Due to the electronic excitation, the proton-transfer process in an excited molecule differs significantly from that of the ground state. In many cases the rate of the transfer is increased in the excited state due to the modification of the acid−base properties of the system under study.[3,5−8] Depending on the properties of the medium, these reactions can also be influenced by the solvent.[7,8] The emission of a strongly Stokes-shifted fluorescence band is a common feature of the excited-state intramolecular proton-transfer (ESIPT) process.[2,3]

From a theoretical point of view, the ESIPT has not yet received the attention it deserves. This comes in part from the inherent difficulty in dealing with the electronic excited states when using the customary electronic quantum chemical techniques. However, considerable effort has been devoted in the past few years to overcome this problem, and an increasing number of theoretical studies of ESIPT reactions can be found in the recent literature.[9−11]

In this paper we present a theoretical study based on ab initio calculations of a simple molecular system, 8-hydroxyimidazo-[1,2-*a*]pyridine (HIP) (Scheme 1). This molecule can undergo an intramolecular proton-transfer reaction in the enol (E) structure leading to a zwitterionic (Z) form. One point of interest in this particular system lies in the fact that the proton-transfer reaction induces also a (formal) charge separation. This suggests that polar solvents can alter significantly the reaction by stabilizing the Z structure.

We have selected HIP as a simple model system to understand intramolecular charge separation processes produced by proton-transfer reactions that may play a significant role in biological phenomena such as enzymatic reactions and mutagenesis.[12] Moreover, an intramolecular rotational process which may control the whole dynamics and related spectroscopy as occurring in 2-(2′-hydroxyphenyl)azole and 2-(2′-hydroxyphenyl)-benzazole derivatives (the most studied molecules showing ESIPT reaction) is prevented in HIP due to the rigidity of the molecular framework of the system.[5,9b]

Recently we have carried out a detailed absorption and emission study of HIP in different (polar and apolar) media. A complete report of the results will be given elsewhere.[13a] Here we outline the points directly related to the present work. In apolar media HIP shows a single absorption band centered at ∼280 nm. The fluorescence spectrum presents also a single band ($\lambda_{max} = 350$ nm) independently of the excitation wavelength. In aqueous solution the situation is different. The absorption spectrum shows a broader band centered at 280−300 nm. The fluorescence spectrum recorded upon excitation at 280 nm exhibits a single broad band. Upon increasing the excitation wavelength up to 320 nm the maximum of the fluorescence spectrum shifts to the red side. Earlier Cazé and co-workers reported the absorption spectra of HIP in water at different pH values and our results agree with their findings.[13b]

In the present study we will analyze the theoretical results considering the two tautomeric structures (E and Z) of HIP and the proton-transfer reaction linking them in both the ground (S_0) and first singlet excited (S_1) electronic states. As the experiment

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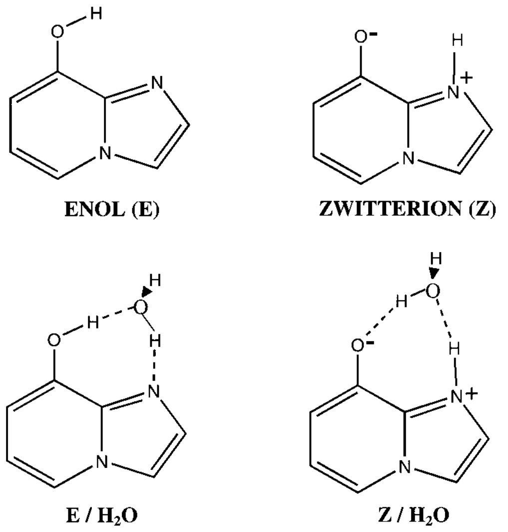
SCHEME 1



has been done in the condensed phase, we will also consider the solvent effect by explicitly including in the calculations one molecule of water (see Scheme 1). Finally, the bulk effect of the solvent will also be introduced through a continuum (i.e. cavity) theoretical model.

2. Methodological Details

Ab initio calculations have been performed within the Gaussian 94 series of programs.[14] The S_0 state has been studied through the restricted Hartree−Fock method (RHF), whereas a CI all-single-excitations with a spin-restricted Hartree−Fock reference ground state (CIS) has been used for the S_1 state.[15]

All calculations have been done with the 6-31+G* basis set[16] which includes a set of d polarization functions and a set of diffuse functions on heavy atoms. This allows a better description of the expected charge separation in the Z structure. Full geometry optimization and direct location of stationary points (minima and transition states) have been calculated with the Schlegel gradient optimization algorithm[17] at the RHF and CIS levels for S_0 and S_1 states, respectively. Diagonalization of the energy second-derivative matrix has been carried out to disclose the nature of each stationary point: no negative eigenvalues indicate a minimum, whereas one negative eigenvalue identifies a transition state. Correlation energy has been evaluated with the Møller−Plesset perturbation theory up to second order (MP2).[15,18] Due to the size of the system, geometries have been kept frozen when introducing MP2.

The bulk effect of the solvent has been introduced through the isodensity surface-polarized continuum model (IPCM).[14] We have used an electronic density of 0.001 a.v. to define the cavity in this model. The IPCM calculations have been carried out both in S_0 and S_1 without reoptimization of the geometries. The energies in the IPCM calculations were obtained at the MP2 level in the ground electronic state. In the excited electronic state only the CIS energies are compatible with IPCM. In this case we have added up the MP2 corrections to the CIS/IPCM result.

3. Results and Discussion

We will first analyze the proton-transfer reaction in the isolated HIP molecule. Later on, the effect of water will be explicitly included in our calculations.

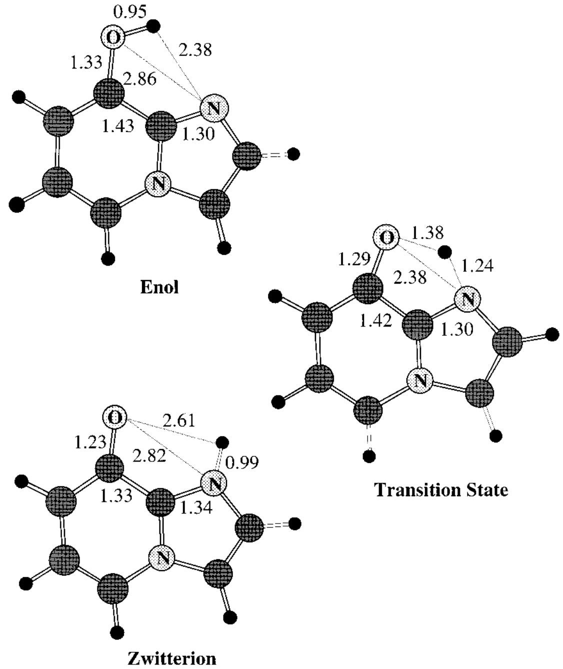


Figure 1. Geometries of the stationary points for the studied enol (E), zwitterion (Z), and transition state (TS) of the proton-transfer process of HIP in the electronic ground-state S_0. Interatomic distances are given in Å.

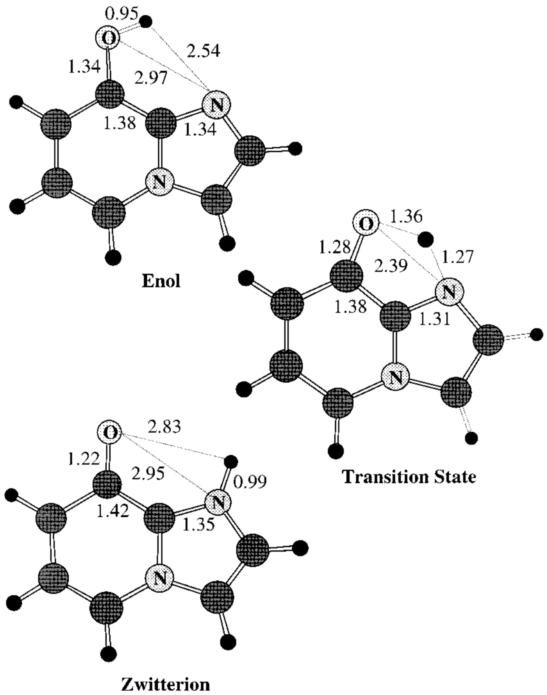


Figure 2. Geometries of the stationary points for E, Z, and TS of the proton-transfer process of HIP in the first singlet excited electronic state S_1. Interatomic distances are given in Å.

3.1. Tautomerization Process of HIP in the Gas Phase and in Apolar and Non-Hydrogen-Bonding Solvents. Figures 1 and 2 show respectively for S_0 and S_1 the geometries of the two minimum energy structures of E and Z as well as those of the transition states (TS) corresponding to the proton-tranfer reaction. A schematic energy profile of the intramolecular proton-transfer process is given in Figure 3. Note that from now on, and as explained in the previous methodological section, geometries are optimized at the RHF and CIS levels of calculation for S_0 and S_1, respectively. However, the energies we will use, unless explicitly stated, will come from the MP2 calculations.

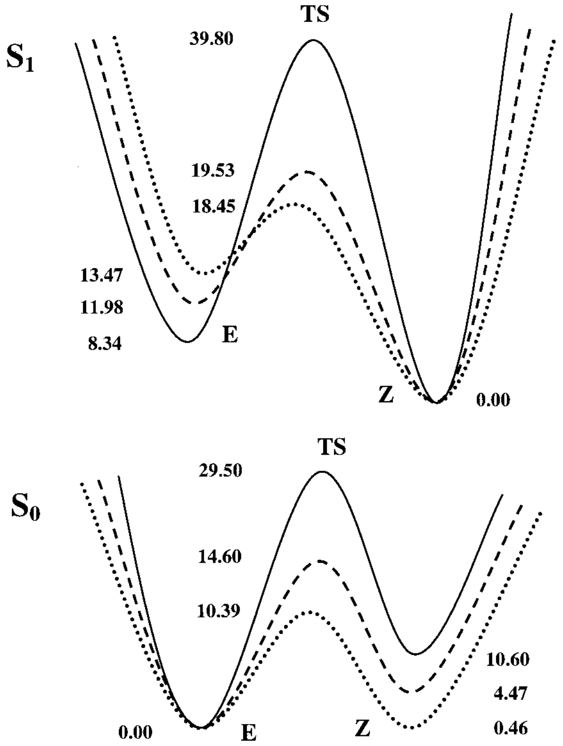


Figure 3. Schematic energy profiles for the proton-transfer process involving E, TS, and Z in S_0 and S_1 states. Relative energies are given in kcal/mol: solid line, gas-phase results; dashed line, HIP:H_2O; dotted line, HIP:H_2O and including the rest of the solvent through the IPCM model (see the text).

As Figure 3 shows, the already high energy barrier in S_0 increases upon electronic excitation to S_1. Opposite results have been found for a number of intramolecular proton-transfer processes.[3,9−11] Interestingly, the increase of the energy barrier takes place even if the zwitterionic structure becomes the most stable form in S_1 state. We note that the change in the stability pattern of both tautomers upon electronic excitation has been found in the majority of systems studied insofar.[2,3,9−11]

An explanation of this abnormal behavior of the energy barriers can be envisaged when looking at the geometries of the three stationary points in S_0 and S_1 (Figures 1 and 2). The geometries of the E and Z tautomers reveal that in the S_1 state the (O−H···N) intramolecular H-bond always presents a longer distance. For E this distance is 2.54 Å in S_1 and 2.38 Å in S_0. For the Z structure it is 2.83 Å in S_1 and 2.61 Å in S_0. In addition to this, the N−O distance, the two atoms between which the H atom is transferring, is clearly longer in the S_1 state of E and Z structures. It is interesting to note that the geometries of the transition states (TS) show that the triangle formed by the three atoms directly implied in the transfer are quite similar in both states. Thus, the TS in S_1 state involves a more severe distortion from both the reactants and products sides with a correspondingly higher energy barrier. This distortion of HIP in the TS takes place in order to approach the H-donor and H-acceptor atoms for the occurrence of the proton-transfer reaction. This phenomenon has also been noted in virtually all the intramolecular proton-transfer reactions studied up to now.[2,3,9−11,19,20] Given the fact that the two rings between which the proton moves are held together by two common atoms, there is also less flexibility to the internal deformations needed to ease the proton transfer.

At this point it should be mentioned that, recently, the CIS-MP2 method has been seriously questioned.[21] In particular it has been shown that CIS-MP2 electronic excitation energies are, in some cases, poorer than the CIS ones. This failure has been attributted to the fact that CIS-MP2 is non-size-consistent. Given that in this work we are not discussing electronic excitation energies but we are dealing with energy differences within a given excited electronic state, CIS-MP2 results are quite reasonable. Anyway, for the sake of comparison we will also provide the CIS energies for S_1. In particular, the energy barrier and the energy of the E tautomer relative to the Z tautomer are, respectively, 43.31 and −3.03 kcal/mol. We note that CIS results, in accordance with CIS-MP2, predict a stabilization of the Z tautomer with respect to the E one in the excited electronic state S_1, though not enough to reverse the stability pattern as found at the CIS-MP2 level. As said above we are not directly interested in excitation energies. However, it may be interesting for the reader to know these data for future use. In particular, the energy difference between the optimized enol structures in both S_0 and S_1 electronic states (that is, the so-called adiabatic transition) is 115.63 kcal/mol when using CIS and HF levels for S_1 and S_0, respectively. At the MP2 level the same calculation gives an energy difference of 154.75 kcal/mol.

TABLE 1: Net Mulliken Atomic Charges, in Atomic Units, at the Ground and First Electronically Excited States of Pyridine and Imidazole Rings of (a) Isolated HIP, (b) HIP:H_2O Complex, and (c) HIP:H_2O Complex in the Bulk Solvent (Water) Using the IPCM Model

	S_0				S_1			
	enol		zwitterion		enol		zwitterion	
	pyridine ring	imidazole ring	pyridine ring	imidazole ring	pyridine ring	imidazole ring	pyridine ring	imidazole ring
a	0.164	−0.016	−0.326	0.634	0.041	0.017	−0.250	0.473
b	0.165	−0.300	−0.415	0.531	−0.015	0.163	−0.352	0.196
c	0.246	−0.248	−0.451	0.607	−0.076	0.302	−0.460	0.330

TABLE 2: Dipole Moment, in Debyes, at the Ground and First Electronically Excited States of (a) Isolated HIP, (b) HIP:H_2O Complex, and (c) HIP:H_2O Complex in the Bulk Solvent (Water) Using the IPCM Model

	S_0		S_1	
	enol	zwitterion	enol	zwitterion
a	3.39	7.42	2.15	5.58
b	4.18	6.18	2.69	3.88
c	4.25	10.16	3.21	7.75

A way to analyze the theoretical results is to compare the evolution of the charges separation along the reaction. Table 1 shows the global Mulliken charges in the pyridinic and imidazole rings of both tautomers in the two electronic states S_0 and S_1. As CIS/MP2 charges are not yet available, we present in Table 1 the charges at the RHF and CIS levels of calculation for S_0 and S_1, respectively. We note that in S_0 the tautomerization from E to Z involves an important positive charge transfer from the pyridine moiety to the imidazole one. Whereas in S_1 this charge transfer is slightly lower. The Z structure shows more charge separation than the E one, in accordance with its zwitterionic character. The charge separation, considerably lower in S_1, correlates with the greater stabilization of Z upon electronic excitation. In gas phase the processes of charge separation are usually costly in energy terms. Supporting conclusions can be obtained from the analysis of the dipole moment of both tautomers given in Table 2. The zwitterionic form has always a dipole moment higher than that of the E structure. However, this dipole moment is remarkably lower in the excited electronic state.

An easy way to interpret the difference in geometries and charge distribution between S_0 and S_1 is to look at the molecular orbitals mainly involved in the electronic transition. Figure 4

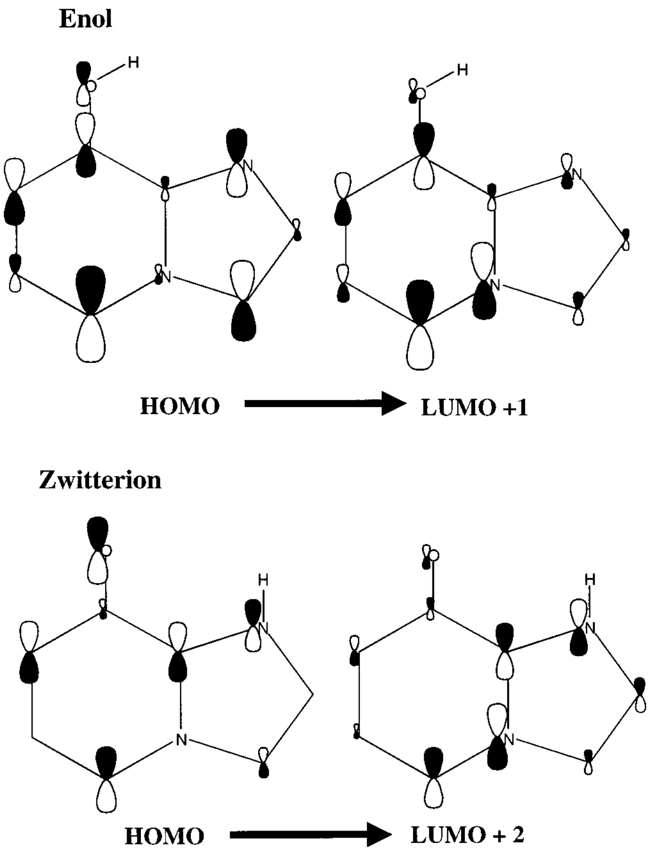


Figure 4. Shape of the orbitals implied in the electronic excitation $S_0 \rightarrow S_1$ for the E and Z structures.

shows these orbitals for both E and Z structures. In going from excited E to excited Z the destination orbital switches from the LUMO + 1 to the LUMO + 2. It can be verified that both orbitals are of π type and almost identical. Therefore, the electronic excitation can be termed as $\pi\pi^*$. The observed changes in bond distances between the heavy atoms of the two rings upon electronic excitation can be easily correlated with the bonding/antibonding character of the two orbitals. In addition to this, the changes in the relative contribution of each atomic orbital in both origin and destination molecular orbitals of Z point to a flow of electronic charge from the pyridone ring to the imidazole one. This alleviates the charge separation caused by the proton-transfer reaction.

To study the effect of an apolar media in the gas-phase behavior, we have included the solvent through the continuum IPCM model. The dielectric constant of the cyclohexane ($\epsilon = 2.02$) has been used. Results (not shown) for the ground electronic state suggest a very minor effect in the energy profile. Relative to the E structure the energy barrier is slightly reduced from 29.50 to 28.50 kcal/mol. The Z structure is also stabilized by 3.80 kcal/mol. These small modifications do not affect the picture of the whole process as we have just described above.

The very high energy barrier for the E−Z tautomerization process and the fact that the Z structure is higher in energy than the E one in S_0 indicate that only E will be appreciably populated in the ground electronic state. Upon irradiation of the enol to the S_1 state the tautomerization process becomes energetically favored, but the higher energy barrier makes the proton-transfer process very unlikely. As a consequence, deactivation of the excited state through intersystem crossing and/or internal conversion are the most likely processes. Therefore only one absorption band and a mirror-image fluorescence one (corresponding to the enol tautomer) are expected to be observed when irradiating HIP in gas phase or in apolar and non-hydrogen-bonding media.

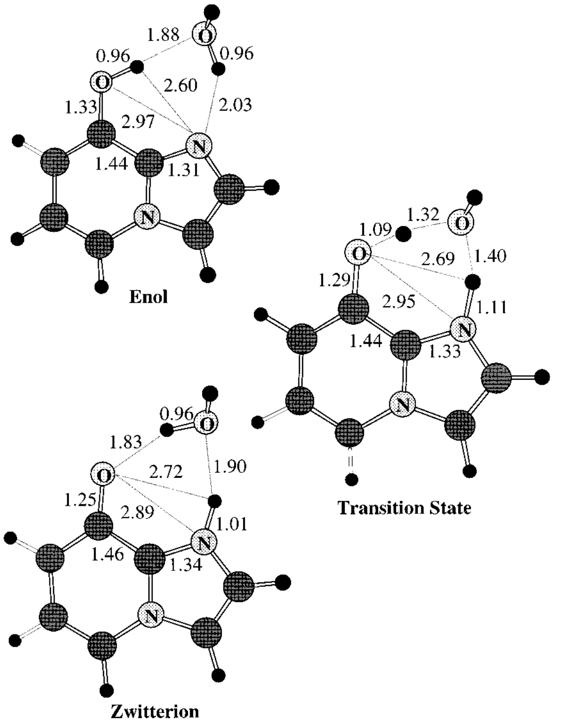


Figure 5. Geometries of the stationary points for the proton-transfer process in the S_0 state of the HIP:H_2O complex. Interatomic distances are given in Å.

3.2. Tautomerization Process of the Isolated HIP:H_2O Complex. We will now analyze the effect of the water solvent in the proton-transfer reaction in the gas phase. Therefore, we have first considered the effect of one discrete water molecule. Studies of comparable systems, where geometry restrictions impede the proton transfer, have shown that one molecule of water can act as a bifunctional catalyst. The molecule of water transfers one proton and accepts another one from the adduct.[22] Examples of these systems are the extensively studied hydroxypyridine/pyridone, 7-azaindole, and related systems.[23,24] Scheme 1 depicts the expected geometry of HIP under both E and Z structures complexed to one molecule of water.

Figures 5 and 6 display the geometries of the stationary points for both S_0 and S_1 states, and Figure 3 exhibits the relative energy profiles in both states (dashed line). As previously noted, the water molecule plays the role of a bifunctional catalyst by connecting the two H-donor and H-acceptor groups of HIP through two intermolecular H-bonds. This interaction breaks the intramolecular hydrogen bond formed in the isolated HIP molecule. Formation of intermolecular H-bonds between HIP and water has been experimentally observed.[13a] In addition to this, the preference of HIP to establish intermolecular H-bonds accords with the crystal structure of HIP, where the OH group of the six-membered ring of the enol tautomer is engaged in an intermolecular H-bond with the N atom of another HIP molecule.[25]

Figure 3 displays a remarkable lowering in the energy barrier for the proton transfer in both the ground and excited electronic states when the water molecule is introduced. This result is explained by the simultaneous proton donor and acceptor role of water, which allows the tautomerization of HIP without extensive deformation of the solute. A similar situation has been found in complexes of 7-azaindole with water and methanol.[24]

As for the relative stability of both tautomers, the Z structure becomes more stable, an unsurprising result on the grounds of

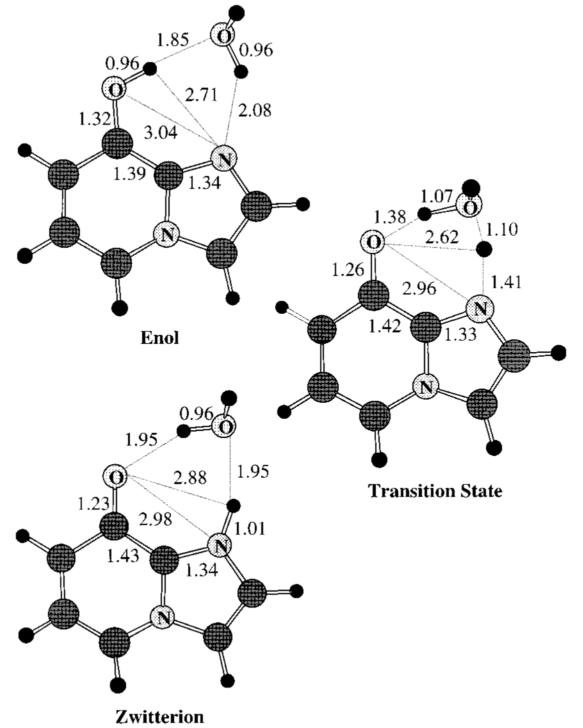


Figure 6. Geometries of the stationary points for the proton-transfer process in the S_1 state of the HIP:H_2O complex. Interatomic distances are given in Å.

the stabilizing interaction of a polar structure by the (polar) water molecule. In the S_0 state, where Z is energetically above E, the energy gap between both minima is reduced. In the S_1 state, the less stable E tautomer increases its energy with respect to the lower energy Z structure (Figure 3). As done in section 3.1 we also present the CIS results for the excited electronic state which are not changing the qualitative picture just outlined with the CIS-MP2 results. At the CIS level the energy barrier and the energy of the E tautomer with respect to the Z form are 25.44 and 1.88 kcal/mol, respectively. As for the adiabatic excitation energy of the enol form (that is, the energy difference between the optimized enol structures in both S_0 and S_1 electronic states), it has a value of 114.71 kcal/mol at the HF/CIS level and a value of 153.85 kcal/mol at the MP2 level of calculation. Note that the addition of a single water molecule has a very minor effect (less than 1 kcal/mol) in this excitation energy.

A charge analysis similar to that done for the gas phase has also been performed for the HIP:H_2O system. The second row of Tables 1 and 2 respectively gives the charge separation and the dipole moments of both tautomers in the two electronic states. Changes in the charges and dipole moments upon proton transfer and/or electronic excitation exactly follow the trends observed in the gas phase situation. On the other hand, electronic excitation weakens somewhat the difference between both tautomers. A less foreseable result appears when comparing the charges and dipole moments with and without water. The total dipole moments for the E structure are now larger, but for Z they decrease. The reason of this different behavior can be found in the clearly larger dipole moment of the isolated Z that impels the water to orient in such a way that the dipole moments of the two fragments (Z + water) cancel out somewhat. In this sense the Mulliken charges listed in Table 1 are more useful. They indicate a higher charge separation in the Z tautomer in both the S_0 and S_1 states.

Let us now focus on the proton-transfer process from a geometrical point of view. As previously noted, the water molecule leads to a double proton transfer. Only one TS is found for each electronic state, however. The geometry of the TS indicates that the two migrating protons of the complex are not jumping at the same time. In fact, in going from the E tautomer to the transition state, one of the protons has been almost transferred, whereas the other one is still at the beginning of its "flight". A difference appears at this point between the two electronic states. In S_0, the first proton jumps from the water molecule to the E adduct. However, in S_1 the situation is reversed. The water molecule first receives a proton from the E unit. In other words, HIP in front of water acts as a base molecule in S_0 and as an acid in S_1. Thus, in the transition state for S_0, the water molecule almost becomes a negative hydroxyl OH^- unit, whereas it becomes a hydronium H_3O^+ in the TS of S_1 state. An explanation of this difference can be obtained by analyzing the Mulliken charges. Charges of the hydrogen atoms to be transferred in complexed E reveal that the atom with the highest positive charge (the more "proton-like") is the first to be transferred. The charge separations shown in the second row of Table 1 also shed some light on this difference. The most important changes in charges between the S_0 and S_1 enol tautomers are found in the imidazole ring. They switch from a high negative value (−0.300) to a clearly positive one (0.163). This allows the imidazole ring to accept a proton in S_0. In a parallel but contrary way the pyridine ring, which switches from 0.165 to −0.015, shows the reverse behavior.

3.3. Tautomerization Process in Water Solution. In the previous section, we have seen that one water molecule produces a dramatic effect on the HIP tautomerization process. However, it is also evident that a water molecule alone does not play the role of the bulk solvent. To progressively include the effect of the rest of the solvent we first considered the introduction of a second water molecule in the system. Attempts to introduce the additional water molecule in a cyclic way (forming H-bond cycle) were unsuccessful. The second water molecule showed a tendency to disjoin from the 1:1 adduct and to form a H-bond with the "free" hydrogen atom of the first water molecule. This result is in good agreement with the experimental observation.[13a] Note that the situation is different from the one found in the pyridone/hydroxypyridine system, where complexes with one and two water molecules have been suggested.[23]

This 1:1 complex between HIP and water is the most stabilized complex in aqueous solution. To introduce the effect of the rest of the solvent without H-bonding interaction we have opted for a continuum self-consistent model, the isodensity polarized continuum model (IPCM).[14] As the IPCM method does not possess analytic first derivatives, geometries have not been reoptimized. The new energy profiles thus obtained for both S_0 and S_1 states are shown in Figure 3 (dotted lines). The differences between gas phase results are remarkable and quite easy to describe. Upon addition of solvent the energy barrier decreases (specially in S_0) and the zwitterionic complex is also more stabilized. Now in S_0 the two structures are almost degenerate (the difference of 0.46 kcal/mol in favor of the enol form is well below the expected accuracy of the calculations). In S_1 the stability of the Z adduct with respect to the E one increases only slightly. As before, CIS results are not qualitatively different from the CIS-MP2 ones shown in Figure 3. With respect to the Z tautomer, the energy barrier and the energy of the E tautomer are, respectively, 24.36 and 3.37 kcal/mol.

Charge distribution and dipole moments of both tautomers in the two electronic states are given in the last row of Tables 1 and 2. It is clear that the effect of the bulk solvent is to favor more polarized structures so that the charge separation and, accordingly, the dipole moments are clearly higher now. Compared to the isolated 1:1 complex an important increase of the dipole moment is observed for the more polarized Z structures. In contrast, the increment of dipole moment for E is quite modest in both electronic states.

Our theoretical results indicate that in S_0 both complexed tautomers are very close in energy and separated by a moderate energy barrier. Then the proton transfer can occur at normal temperatures and an equilibrium between both E and Z will be established. This expectation agrees with the experimental observation.[13] The UV absorption spectrum ($S_0 \rightarrow S_1$) of HIP in aqueous solution will show two bands corresponding to the photexcitation of both E and Z structures. Moreover, the band at longer wavelengths will correspond to absorption of the Z structure. In turn, the fluorescence spectrum of HIP in water solution will also have two bands corresponding to the photoemission of both excited E and Z structures. However, given that E and Z will absorb at different regions, one can tune the excitation wavelength to control the fluorescence behavior. According to the energy profiles shown in Figure 3 (dotted lines), we can predict that when selectively exciting E to S_1, two fluorescence bands might be observed. This is because an intramolecular proton-transfer reaction in this structure might occur, leading to excited Z tautomer, in competition with the vibrational relaxation and emission of E. Thus a dual fluorescence, from E and Z, might be observed and the relative intensity will depend on the relative probability of the above process and nonradiative relaxation pathways of E and Z. On the other hand, when selectively exciting Z, one or two fluorescence bands might be observed. This depends on whether the energy of the initially accessed Z structure in S_1 is below or above the zero-point energy of excited E. In the first situation, a single emission band (from Z) is expected, while in the second situation, where the vibrationally excited Z structure is energetically above the zero-point energy level of E, a dual emission from E and Z might be observed. As noted above, this will depend on the rates of the proton transfer, intramolecular vibrational relaxation, and fluorescence quantum yields of E and Z.

By selectively exciting E or Z and studying the temperature dependence and the H/D isotope exchange effects on the absorption and steady-state and time-resolved emission spectra of HIP in H-bonding solvents, one can get detailed information on the energy gap and energy barriers in both ground and excited electronic states. Similar experiments have been done in 7-hydroxyquinoline, a system showing excited-state intermolecular proton-transfer reaction with H-bonding solvents.[8] Such studies of HIP are underway and form part of our project on exploring proton-transfer spectroscopy and dynamics.

In conclusion, the present study provides a theoretical ground that will be very helpful for understanding the absorption and emission spectra of HIP and related derivatives in different media.

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