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Ab Initio Based Exploration of the Potential Energy Surface for the Double Proton Transfer in the First Excited Singlet Electronic State of the 7-Azaindole Dimer

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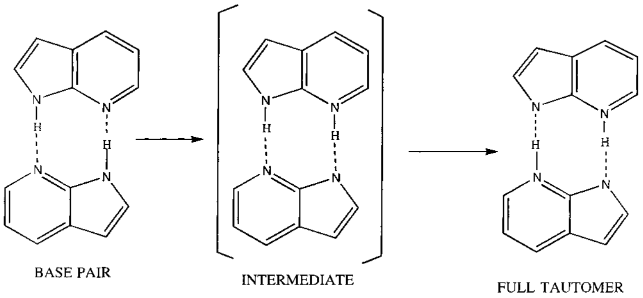
In this paper ab initio full geometry optimizations are carried out for the ground and first excited singlet electronic states of the 7-azaindole dimer, a well-known prototype of the DNA base pairs. Results indicate that the C_{2h} symmetry of the ground-state minimum energy is not maintained in the excited state that has to be described as a dimer between an excited base unit and another one in the ground state. Given this asymmetry, the double proton transfer in the excited state is found to be stepwise in nature, passing through a very shallow zwitterionic intermediate. Inclusion of the zero point energy and the rest of the thermodynamic corrections points to the nonexistence of bound states for the intermediate well. Our theoretical calculations have also confirmed the presence of another intermediate where the transfer of a single proton is compensated by a charge-transfer electronic excitation. This *neutral* intermediate is found lower in energy than the zwitterionic one and could be responsible for the stepwise reaction observed in several recent experiments done at the femtosecond time scale. A nonadiabatic transition should occur between the initially accessed electronic state (involving an excitation localized in one base unit) and the one possessing the neutral intermediate that involves a charge-transfer transition. When including the bulk effect of a polar solvent it is observed that the energies of the intermediates are lowered so that the zwitterionic intermediate may exist in solution. The transition state energies are also lower, a result that points to an increase in the rate constant of the process in condensed phase.

1. Introduction

Proton-transfer reactions have received a great deal of attention in recent years due to the ubiquity of these processes in molecular science.[1] Among them the double proton transfer in the 7-azaindole dimer (7-AI)$_2$ ranks one of the most intensely studied systems, as it has been claimed that it can be used as a prototype system to mimic the elementary reactions involved in the photomutagenesis phenomenon in the DNA base pairs (BP).[2−18] In particular, the phototautomerization process involving a double proton-transfer reaction has been thoroughly studied in order to understand whether this process can be of significance in mutagenesis.[19]

Femtosecond dynamic studies in the gas phase indicate the involvement of two steps that take place in different time scales.[9,12,14] The first process (taking place in ca. 650 fs near the zero-point energy) is attributed to the jump of one proton producing a quite stable intermediate. This structure has then the two protons within the two H-bonds in one side of the dimer. Following this mechanism, the second proton-transfer reaction takes place more slowly (ca. 3.3 ps at vibrational energy near zero in the dimer), leading to the final full tautomer (see Scheme 1).[9] The N···N and N−H stretches directly involved in the reaction have times of 280 and 12 fs, respectively. Thus, on the time scale of 0.2−1 ps (typical reaction times) the "asymmetric reaction coordinate" for the two protons is established.[9] In solution, the mechanism might be affected by solvation dynamics and thermalization as has been pointed out by solution femtosecond studies.[15,18] In both gas and bulk solution works, the quantum nature of the double proton-transfer reaction was observed.[2,6,7,9,18]

SCHEME 1



From a theoretical point of view, the first ab initio results, done with a modest basis set (4-31G) and using the single configuration interaction method (CIS) to deal with the excited state, pointed to a stepwise process.[10] A shallow zwitterionic intermediate, the product of a single proton transfer from one moiety to the other, was located in the potential energy surface of S$_1$. Further works, using the CIS but with the 6-31G basis set, have confirmed these findings.[17] Additionally, the existence of another intermediate without charge separation (which will be called "covalent") has been found. This intermediate lies lower in energy than the zwitterionic one, so it may play a

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fundamental role in the ultrafast dynamics of the double proton-transfer reaction. On the other hand, Catalan and collaborators have questioned the stepwise mechanism, by using what they call a hybrid density functional theory (HDF).[20] They claim that the double proton transfer in S_1 takes place in a synchronic way with the two hydrogen atoms transferring in a symmetric manner.

In recent contributions to the field, we have addressed the inadequacy of the calculations using HDF model for the S_1 state and the inconsistencies of the conclusion of the works of Catalan and co-workers.[21] The most serious drawback in their results arise from the fact that their HDF methodology does not allow for geometry optimizations in the excited electronic states. To settle this controversy from a theoretical point of view we undertake in this work a thorough analysis of the potential energy surface (PES) corresponding to the double proton transfer in the excited electronic state S_1. To this aim ab initio full geometry optimization has been undertaken by using the CIS level with a large basis set. The effect of a polar solvent has also been analyzed through a continuum (i.e., cavity) model.

2. Calculational Details

All calculations were performed with the double-ζ quality 6-31G(d) basis set which includes d polarization functions on heavy atoms.[22] The larger 6-31G(d,p) basis set, which adds p polarization functions on hydrogen atoms, was also used in some selected cases (see next section).[23]

The ground electronic state geometries and energies were obtained with the B3LYP hybrid density functional[24] in conjunction with the 6-31G(d) basis set. The CI all-single excitations with a spin-restricted Hartree−Fock reference ground state (CIS)[25] was used to optimize the geometries and calculate the energies of the excited S_1 state. Stationary points were located by using the minimization procedure of Schlegel by using redundant internal coordinates.[26] The nature of the located stationary points was ascertained through diagonalization of the energy second-derivatives matrix. Intrinsic reaction coordinate calculations (IRC)[27] were performed to ascertain which minima are connected through each located transition state. The use of a higher level of calculation for the complete PES analysis such as the complete active space CAS SCF was not possible due to our present computer capabilities. Introduction of correlation energy with the second-order Møller−Plesset perturbative theory up to second order[25] was also not considered, as within this method optimization of geometries is not possible. Besides, this method has been proven very unreliable,[28] given too low an energy barrier for H-atom transfer reactions.[29]

Diagonalization of the second derivative matrix also provides the vibrational harmonic frequencies which were used to evaluate the thermodynamic corrections at 1 atm and 298.15 K to the initially obtained electronic energy by using the standard statistical formulas assuming that the system behaves as an ideal gas and that the rotational and vibrational degrees of freedom are well described through the rigid rotor and harmonic approximations, respectively.[30] As customarily done, for the transition states the imaginary frequency was withdrawn from the calculation of the thermodynamic corrections.

The bulk effect of the solvent was introduced through the isodensity surface-polarized continuum model (IPCM).[31] We used an electronic density of 0.0001 au to define the cavity. The value provided for the dielectric constant was that of acetonitrile (36.2). The IPCM calculations were carried out both in the ground and the excited electronic states without reoptimization of the geometries.

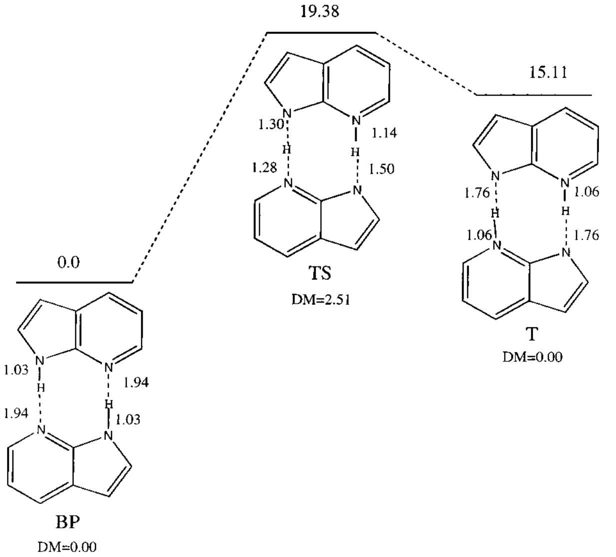

Figure 1. Geometries and relative potential energies (in kilocalories per mole) for the stationary points corresponding to the double proton-transfer process in the ground electronic state. Distances between the transferring hydrogens and the acceptor/donor nitrogens are given in angstroms. Dipole moments (DM) are also posted (in debye).

All the calculations presented here were done with the Gaussian 98 series of programs.[32]

3. Results and Discussion

3.1. Double Proton Transfer in the Ground Electronic State S_0. First we will briefly consider the double proton transfer in the ground electronic state S_0. Calculations performed using the B3LYP hybrid density functional lead to the schematic energy profile depicted in Figure 1. As seen in the figure there is only one transition state that connects the base pair (BP) with the full tautomer (T), where both hydrogen atoms have been transferred from the pyrrol to the pyridine nitrogen atoms. The energy barrier for the process is quite high (19.38 kcal/mol) and the whole process is highly endothermic (15.11 kcal/mol). In this sense, the theoretical results indicate that the double proton transfer is quite a disfavored process in the ground electronic state, a result which agrees with the experiments carried out so far that have not found evidence of this process taking place without photoexcitation. Previous theoretical works have also found a large endothermicity for the double proton transfer in the ground state.[10,33]

The optimized geometries of the stationary points, depicted also in Figure 1, indicate that even if the process is concerted (that is, it takes place in a single chemical step), the two hydrogen atoms do not transfer synchronously. This result is similar to that found using a smaller basis set.[10] In the two minima (BP and T) the two hydrogen atoms to be transferred are equivalent (C_{2h} symmetry) as seen in Figure 1. However, the transition state (TS) does not belong to the C_{2h} symmetry group but to the lower C_S one as the two in-flight hydrogen atoms are at quite different stages of their trip. In the TS, one of the hydrogen atoms has been already transferred from the pyrrol ring to the pyridine, whereas the second one is almost equidistant between the acceptor and donor nitrogen atoms (Figure 1). This indicates that the reaction path corresponding to the double proton transfer in S_0 is highly asynchronic, with one hydrogen transferring first and the second one beginning its flight when the first one has almost reached its final destination. As the reaction is highly endothermic, the transition state is located near the product of the reaction (that is, the tautomer).

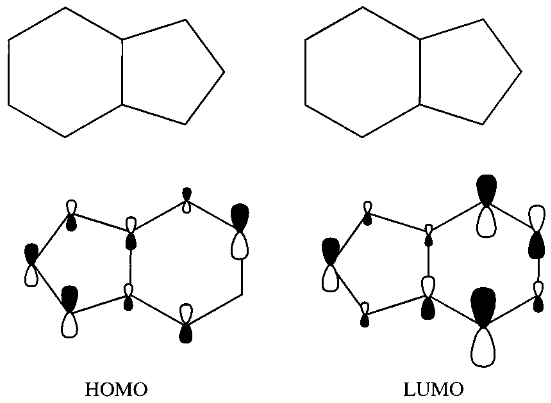

Figure 2. Shape of the HOMO and LUMO for the 7-azaindole dimer in the minimum energy structure of the first excited singlet state.

Introduction of the solvent through the continuum IPCM method does not appreciably affect the gas-phase results depicted in Figure 1. The transition state and the tautomer are stabilized by less than 1 kcal/mol with respect to the base pair. This very small effect was to be expected given the null dipole moments of both tautomers and the very small (2.51 D) value for the (less symmetric) transition state.

3.2. Double-Proton Transfer in the First Excited Singlet Electronic State S$_1$. *3.2.1. Localization of the Electronic Excitation and Its Relevance to the Stepwise Mechanism.* Let us first briefly consider the nature of the electronic excitation despite that this point was already discussed in our previous theoretical works.[10,21,34] The use of a larger basis set does not modify the former results. As stated in the previous subsection, the ground-state minima belongs to the C_{2h} symmetry so that orbitals are symmetrically distributed between both 7-AI units. However, upon electronic excitation the geometry corresponding to the minimum energy of the dimer is no longer maintaining its symmetry. This one lowers to the C$_s$ point group (that is, the molecular plane is the only symmetry element retained). At this point the two base units have different geometries and the orbitals are totally localized in one of the 7-AI moieties. The first excited singlet electronic state corresponds to the HOMO−LUMO excitation. As depicted in Figure 2 both orbitals belong to the same base unit so that the excitation is *localized* in one moiety. In a sense, one could imagine the excited state of (7-AI)$_2$ at S$_1$ as a dimer formed by one electronically excited 7-AI molecule and another molecule still having the ground electronic state character. This is clearly seen in Figure 2. The HOMO−LUMO excitation induces an electronic flow from the pyrrol part to the pyridine one of the excited 7-AI unit that drives the excited moiety to act as a proton-donor partner in the reaction. As discussed earlier the photoinduced rupture in the molecular symmetry of the pair is the driving force behind the stepwise nature of the proton-transfer process in the pair.[9,10]

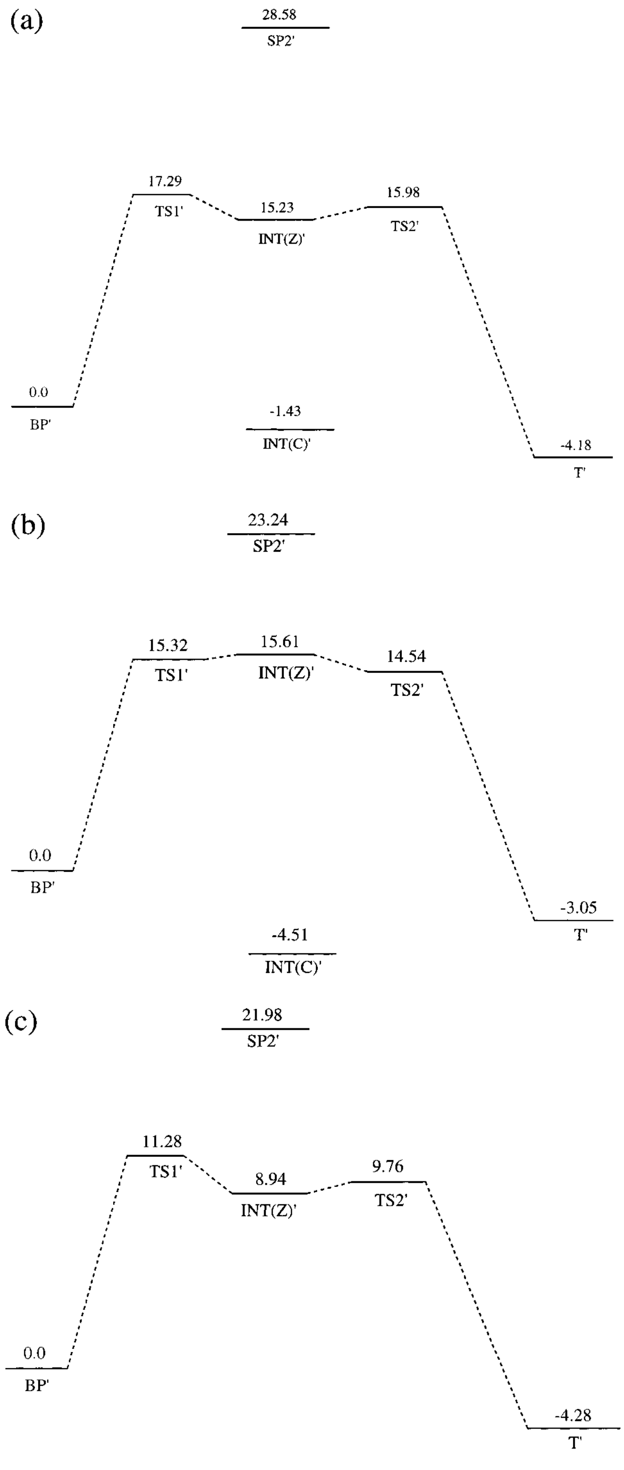

Figure 3. Schematic energy profiles (relative energies are given in kilocalories per mole) for the stationary points located for the double proton transfer in the excited electronic state. (a) Potential energy in the gas phase. (b) Gibbs free energy in the gas phase. (c) Gibbs free energy in the condensed phase.

The analysis of the PES in the first excited singlet electronic state S$_1$ is the main point of the present paper. Figure 3 gives a scheme of the energy profiles. The distances of the H-bonds for all the stationary points located in the potential energy surface (PES) are given in Figure 4. A schematic diagram of the potential energy of all the stationary points is given in Figure 3a. Two transition states (TS1′ and TS2′) have been found and characterized. The dashed lines indicate the connections between the two transition states and the corresponding minima ascertained through IRC calculations. In this way TS1′ links the reactant (BP′) with INT(Z)′, an intermediate with zwitterionic character as it corresponds to the transfer of one proton (not a H-atom) from one moiety to the other. The second transition state connects this intermediate to the final product, the full tautomer (T′).

We are aware that the CIS calculations performed for the excited state are not precise enough to allow for definitive conclusions on the magnitude of the energy profiles. In recent

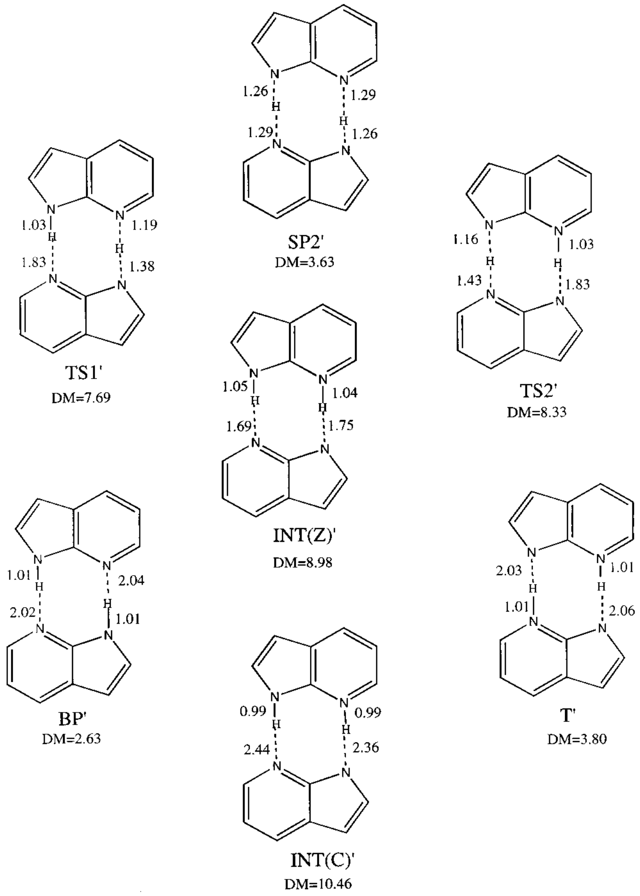

Figure 4. Geometries of the stationary points located for the double proton-transfer process in the excited electronic state. Distances between the transferring hydrogens and the acceptor/donor nitrogens are given in angstroms. Dipole moments (DM) are also posted (in debye).

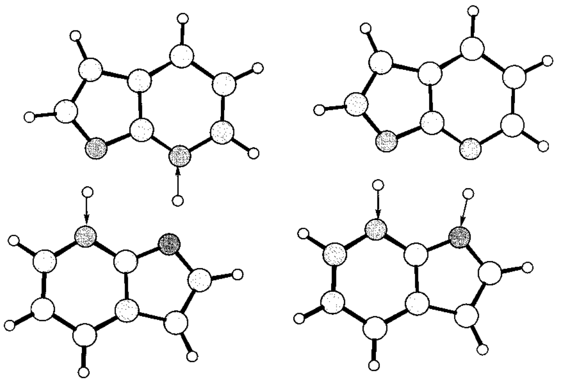

Figure 5. Eigenvector corresponding to the second imaginary frequency for the symmetric double proton-transfer SP2′ structure.

studies on systems quite similar to the 7-AI dimer, the obtained barriers for the intramolecular H-atom transfer reaction at the CIS level tend to dissappear when correlation is taken into account or a very large active space is considered.[35] In any case, it is not possible to carry out geometry optimizations at these levels of calculation for the large system studied here and it is customarily accepted that geometries obtained at the CIS level are correct in a first approach.[28,29a]

3.2.2. The Synchronic Mechanism. We have also considered the synchronic mechanism where both protons move at the same time. By imposing that the distances between each of the two transferring hydrogen atoms and their corresponding acceptor and donor nitrogen atoms remain identical along the reaction coordinate, we have located a stationary point corresponding to the maximum of this mechanism. Its potential energy is indicated in Figure 3a as SP2′. Diagonalization of its second derivative matrix reveals that it is not a true transition state as it has two imaginary frequencies. The larger frequency corresponds to the double proton transfer and the other leads to the break of the synchronic motion of the two hydrogen motions, as indicated by arrows in Figure 5. According to the Murrell-Laidler theorem,[36] when a saddle point of second order is obtained, there must be an alternative reaction path passing through a true transition state (a saddle point of first order) and involving a lower energy barrier. This transition state must be located in the direction of the eigenvector corresponding to the smallest imaginary frequency. Figure 5 shows that the second frequency corresponds to the breaking of the symmetry in the double proton transfer. Therefore, the true reaction path is the one passing through the two transition states and the zwitterionic intermediate. It involves the stepwise mechanism previously discussed. Our results seem to rule out the synchronic mechanism defended by Catalan et al. using fixed geometries at S_1.[20]

3.2.3. Nature of the Intermediate. Once the synchronous mechanism is disregarded, one may ask about the nature of the intermediate in the stepwise reaction. To get more insight we have considered other structures besides that of the previously reported zwitterionc intermediate. In addition to SP2′ (Figure 3a), we have located another stationary point which does not belong to the "direct" mechanism from BP′ to T′ through TS1′, INT(Z)′ and TS2′. The related structure located at an energy intermediate between BP′ and T′ corresponds to a neutral intermediate. In this structure one hydrogen atom has been transferred from one moiety to the other one, but the positive charge transfer involved in this process has been compensated by a previous electronic excitation that involves a negative charge transfer between the two 7-AI units. This neutral (or covalent) intermediate is labeled accordingly as INT(C)′. It is worth to noting that this intermediate does not belong to the same PES as do all the other stationary points shown in Figure 3. INT(C)′ is a minimum coming from a *different* electronic state, due to an electronic excitation between one orbital located in one moiety of the base pair and another orbital located in the other moiety, that is, an electron transfer between both monomers. Because the involved two orbitals are localized in different parts of the dimer, the overlap between both is almost null, so that the electronic excitation that leads to such charge-transfer excited states has a very small Franck−Condon factor.

This charge-transfer excited state seems the lowest one in the region of the PES corresponding to a single proton-transfer. However, it does not correlate with the lowest excited singlet state in the reactant or product zone of the PES. In fact the CIS calculation of the base pair reveals that such a charge-transfer state does not appear among the first 20 excited singlet states calculated with the Gaussian 98 program. This does not mean that such a state is not present, but it puts a lower limit to the energy where it is to be found: more than 98.63 kcal/mol above the lowest excited state (BP′ in Figure 3a). Therefore, at some point along the proton-transfer coordinate the potential of this charge-transfer state must cross with the S_1 state potential corresponding to the double proton-transfer reaction. As the energy of this charge-transfer state raises quickly when we move away from the intermediate zone, the crossing zone is probably not far away from the zone where the intermediate is found. Given the different nature of both excited states, this is a nonadiabatic transition, so that the probability to jump from the initial excited state to this charge-transfer one (or vice-versa) is expected to be small, even if the crossing point is not, as it seems here, high in energy. As a final point with respect to this neutral intermediate we note that its geometry is very different from that of the zwitterionic one (Figure 4). This neutral intermediate has significantly longer H-bond distances, so that both monomer units are more separated in the INT(C)′ minimum than in the INT(Z)′ structure, as in the former one there are no direct electric charge attraction between both base units.

The two tautomeric structures and the neutral intermediate were also calculated with a slightly larger basis set (6-31G(d,p)). Results were not qualitatively different from the ones presented here. Within this basis set the CIS energies of T′ and INT(C)′ relative to BP′ are, respectively, −4.05 and −1.29 kcal/mol. Those using the 6-31G(d) basis set are −4.18 and −1.43 kcal/mol, respectively (Figure 3a). Then the similarity of these values validates the use of the slightly smaller basis set for the full study. Finally we also note that a basis set without polarization functions, such as the 4-31G, gives a quite different relative energy of T′ (−2.69 kcal/mol).[10] However, the main difference from the previous 4-31G results is found in the energetics of the zwitterionic mechanism as the intermediate INT(Z)′ was only 0.11 kcal/mol below the second transition state TS2′ in the 4-31G results,[10] whereas with the larger 6-31G(d) basis set INT(Z)′ is 0.75 kcal/mol below TS2′ (see Figure 3a).

As a final part of the analysis of the energy profile for the double proton-transfer process, we have also calculated the zero point energy, thermic and entropic contributions to the Gibbs free energy. To study the contribution of these terms, some severe approximations have been made (ideal gas, rigid rotor, harmonic vibrations), and the results must be taken just as a qualitative indication. Figure 3b shows the energy scheme of the stationary points in terms of Gibbs free energy (G). As a most notorious qualitative difference with the pure potential energy profile shown in Figure 3a, we note the disappearance of the zwitterionic intermediate as a true minimum given that, in terms of Gibbs free energy, it lies higher than both transition states. Of the different terms that are added up to obtain the final value of G, the only one that can be held responsible for this fact is the zero point energy. This indicates that the intermediate is probably present, but it is not deep enough to support any bound vibrational state. Curiously enough, if the zwitterionic intermediate increases its energy when the thermodynamic corrections are included, the neutral intermediate clearly stabilizes. The main factor of the lowering in energy of INT(C)′ is not the zero point energy but the entropy, which is clearly higher for INT(C)′. This result was expected given the less tightly bonded structure (therefore more disordered) of both base units in INT(C)′ as already noted above.

As for the rest of the G values shown in Figure 3b, the zero point energy is the factor that leads to the more significant differences with the relative potential energies of Figure 3a. The false synchronic transition state SP2′ is clearly lowered, but this is mostly due to the fact that in that case two imaginary frequencies are withdrawn prior to the calculation of G. The removal of one (imaginary) vibrational frequency in the two transition states TS1′ and TS2′ also accounts for the slight lowering of the relative free energy of these two structures as compared with their potential energy.

3.2.4. Effect of Solvent Polarity. Finally the bulk effect of the solvent has also been considered by the use of the IPCM continuum model as explained in the methodological section. The dielectric constant of acetonitirile ($\epsilon = 36.2$) was introduced to study the polarity effect on the energetics of the pair. Figure 3c depicts the relative free energy of all the stationary points previously found. When comparing parts b and c of Figure 3, we note that the solvent polarity effect mainly stabilizes both intermediate minima, and mostly the neutral intermediate. The stabilization of INT(Z)′ was expected, given the charge separation present in that zwitterionic structure. However, the tremendous lowering in energy of the neutral intermediate comes, at first sight, as a surprise. To explain this fact the dipole moments of these structures have to be taken into account. Dipole moments (in Debye) are posted in Figure 4 for each stationary point. We see that a clear correlation can be made between higher dipole moments and higher energy stabilization, not a surprising result given that the continuum model is based in a multipolar series decomposition of the solvent energy interaction. At first sight one could wonder why the SP2′ symmetrical double proton-transfer structure has a nonzero dipolar moment. This is because only the distances between the transferring hydrogen atoms have been restricted to remain equal so that the stationary point precisely located does not possess an inversion center and the dipole moment is not strictly zero. In any case the dipole moment of SP2′ is clearly smaller than the corresponding value for the two asynchronic transition states.

Another result that strikes as "counter-intuitive" is the larger stabilization of the neutral intermediate as compared with the zwitterionic one. This result, however, agrees with the higher dipole moment calculated for the neutral case as depicted in Figure 4. In short, it has to be taken into account that the dipole moment comes from the global electronic distribution, so that it cannot be quantitatively predicted using one single Lewis structure.

INT(Z)′ surrounded by a polar solvent appears again as a true minimum. The second transition state is higher by less than 1 kcal/mol though now zero point energies are already included, so that the minimum is predicted to actually exist at our level of calculation. Note that the energy values given in Figure 3c are for the isolated gas-phase optimized structures as the IPCM method is not able to optimize the geometry in condensed phases. In any case, optimization of such a large system found in a solvent cavity is a task out of reach with our present computer capabilities.

3.2.5. Mechanism of the Double Proton Transfer. After this discussion about the energies of the different stationary points of the BP during its photochemical transformation in the excited state, the reader will probably be confused about what the actual mechanism we propose for the double proton transfer in S_1 is. To "univocally" answer that question from the point of view of theory, a molecular dynamics study using quantum mechanics (as the reaction involves motion of light hydrogen atoms) should be performed on the full 3N-6 PES. As this study will probably be out of reach for years to come, here we can just use the facts we have come to know about the shape of the PES in the first excited singlet electronic state along with the existence of the low-energy neutral intermediate. We propose the following picture on the basis of the localization of the excitation in one part of the pair and on the stepwise mechanism.

The starting point is BP, the base pair in its ground electronic state formed at a high concentration of the monomer. After UV irradiation, BP is brought to the first excited singlet electronic state, but not to the minimum of S_1 BP′. It is found in a vibrational state of S_1 with a structure that results from a *vertical* excitation. This structure has an energy 8.95 kcal/mol above the base pair minimum BP′, so it can proceed to the photoreaction through a tunneling mechanism. Even if the initially accessed geometry has C_{2h} symmetry so that the excitation is delocalized within the dimer, the minimum energy has the electronic excitation located in only one side of the pair.

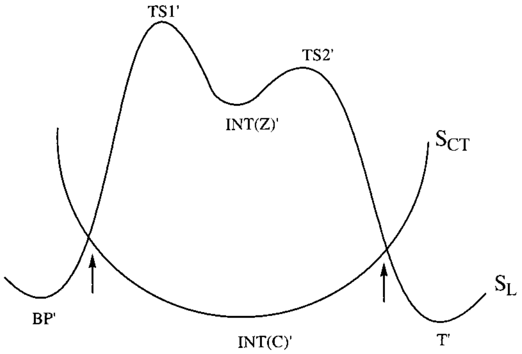

Figure 6. Schematic energy profile showing the presence of two nonadiabatic crossings between the two excited electronic states S_L and S_{CT}. The positions of the stationary points and the crossings have to be considered only qualitatively (see text for details).

Therefore, a fast electronic redistribution induced by light and a vibrational coherence of the elementary modes for the photoreaction drive a deformation in the initially symmetric architecture of the pair. This will quickly lead to the double proton-transfer process, not between two identical monomers but between two formally different molecules, one excited and the other yet in the ground electronic state. This explains the asymmerty of the reaction taking place by successively passing through the TS1′, INT(Z)′, and TS2′ structures. This mechanism is formally stepwise, though there is some doubt about whether the zwitterionic intermediate INT(Z)′ is a deep enough minimum to support bound states. Note that the lifetime of the intermediate in the gas phase is very short (3.3 ps).[9] In any case the two hydrogen atoms are being transferred at very different stages of the reaction path. In this sense the synchronic double proton-transfer process, proposed by Catalan et al.,[20] can be disregarded as it involves geometries without optimization and a maximum (SP2′) which is not a true transition state. It clearly implies a notoriously higher energy barrier than the asynchronic mechanism, in disagreement with the experimental result (barrier energy ∼1.3−1.5 kcal/mol).[2c,9,18]

However, there exists another mechanism for the double proton transfer, a mechanism that involves the neutral intermediate INT(C)′. This intermediate has a geometry very different from that of the zwitterionic intermediate and it belongs to a very different excited state, a state that results from a charge transfer between one 7-AI unit and the other. This state will be called S_{CT} from now on. In the region corresponding to the initial excitation of the base pair, this state lies very high in energy so that it can only be accessed through a nonadiabatic crossing with the initially obtained state (which will be called *localized* excited-state S_L). Our results seem to point out that such a crossing is not very high in energy, so that the probability of the system to cross to INT(C)′ can be important. Once INT(C)′ has been obtained, there must be another nonadiabatic crossing between the two excited states as in the final product T′_; the first electronic excited state is again the one corresponding to S_L. The whole situation is schematically depicted in Figure 6. Note that in this figure the position of the (obtained) stationary points and the (up to now not calculated) crossing points is merely qualitative. Recently, Miller and co-workers performed quantum dynamic calculations on a reduced 2-D PES and concluded that the most likely mechanism for the whole double proton-transfer process involves passing through the neutral intermediate.[17] Direct experimental studies are needed to clarify the nature of the intermediate. As a final point in this regard we note that INT(C)′ is the only intermediate that can be accessed from the vertical excitation of the base pair as INT(Z)′ lies higher in energy at our level of calculation.

Our purely quantum chemical calculations do not allow for a quantitative measure of the probability that such an intermediate is to be accessed from the initially excited state as it implies a prohibited crossing (a conical intersection). However, its role in the mechanism can be important and account for the experimental evidence of two steps for the full double proton-transfer process. Given that 7-$(AI)_2$ is usually considered a model for the DNA base pairs, it is interesting to note that such neutral intermediates have also been theoretically predicted in the DNA adenine-thymine and cytosine-guanine normal base pairs.[37]

4. Concluding Remarks

In this paper we have analyzed the PES of the first excited singlet electronic state of 7-azaindole dimer. In this state, the electronic excitation is localized in one base unit so that the excited dimer is formed by two formally different species where only one base unit is excited. Our PES analysis has clearly shown that the mechanism for the double proton transfer in this state is stepwise in nature. It involves a zwitterionic intermediate where only one hydrogen atom has been transferred. Some years ago, analyzing different types of organic chemical reaction (mostly cycloaddition reactions), Dewar concluded that multibond reactions, which are reactions where more than one chemical bond are formed and/or broken, cannot normally be synchronous.[38] Dewar clearly emphasized that such a nonsynchrony does not mean that multibond reactions have to be stepwise. They can still be concerted but the two (or more) forming/breaking bonds are not progressing at the same pace. The double proton-transfer reaction in the 7-(AI) dimer is a clear model of this behavior. At our level of calculation the formally stepwise double proton-transfer found in analyzing the PES evolves into a concerted, though very asynchronic, process when the zero point energy and the rest of thermodynamic corrections are accounted for. As the energy differences are very small, higher level calculations would be necessary to ascertain if the shallow intermediate well possess any bound state.

In addition to that "direct" mechanism, our results indicate the presence of a very different electronic excited state that results from an excitation between one base unit and the other one of the dimer. Such a charge-transfer state is very high in energy in the region of reactants (the base pair) and products (the full tautomer), but it is very stable in the intermediate region as the transfer of one negative charge is compensated by the transfer of one proton. This intermediate can only be accessed through a nonadiabatic transition from the initially obtained excited state. This neutral intermediate was already considered in a previous theoretical work by Guallar et al.,[17] where it is predicted that it has a very prominent role in the dynamics of the double proton transfer. If this is the only available mechanism, the total reaction rate will not then depend on energy barriers but on probabilities of surface hoping. To ascertain the probability of crossing these conical intersections is the most interesting task remaining from a theoretical point of view for this system.

We have also studied the bulk effect of a polar solvent. Results are not very different from the ones in the gas phase, though the intermediates and transition states are lower in energy with respect to the BP and the zwitterionic intermediate is predicted to really exist in the condensed phase. Therefore, solvation will affect the rate constants of the elementary processes taking place in the full dynamics, a result that agrees with the recent experimental observations.[15,18]

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