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ARTICLES

Role of Electron-Driven Proton-Transfer Processes in the Excited-State Deactivation of the Adenine−Thymine Base Pair

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Exploratory electronic structure calculations have been performed with the CC2 (simplified singles and doubles coupled-cluster) method for two conformers of the adenine (A)−thymine (T) base pair, with emphasis on excited-state proton-transfer reactions. The Watson−Crick conformer and the most stable (in the gas-phase) conformer of the A−T base pair have been considered. The equilibrium geometries of the ground state and of the lowest excited electronic states have been determined with the MP2 (second-order Møller−Plesset) and CC2 methods, respectively. Vertical and adiabatic excitation energies, oscillator strengths, and dipole moments of the excited states are reported. Of particular relevance for the photochemistry of the A−T base pair are optically dark $^1\pi\pi^*$ states of charge-transfer character. Although rather high in energy at the ground-state equilibrium geometry, these states are substantially lowered in energy by the transfer of a proton, which thus neutralizes the charge separation. A remarkable difference of the energetics of the proton-transfer reaction is predicted for the two tautomers of A−T: in the Watson−Crick conformer, but not in the most stable conformer, a sequence of conical intersections connects the UV-absorbing $^1\pi\pi^*$ state in a barrierless manner with the electronic ground state. These conical intersections allow a very fast deactivation of the potentially reactive excited states in the Watson−Crick conformer. The results provide evidence that the specific hydrogen-bonding pattern of the Watson−Crick conformer endows this structure with a greatly enhanced photostability. This property of the Watson−Crick conformer of A−T may have been essential for the selection of this species as carrier of genetic information in early stages of the biological evolution.

1. Introduction

Organic molecules generally are not stable under persistent irradiation with UV light. UV photons break covalent bonds and thus can induce a multitude of isomerization and fragmentation reactions. Photostability, that is, minimization of the quantum yields of destructive photochemical reactions, clearly is of utmost importance for the molecular encoding of the genetic information of life in DNA. Although the DNA bases absorb strongly in the UV range around 300 nm, the yields of photoproducts are astonishingly low.[1] It seems that the evolution in the early stages of life has selected molecular structures for the encoding of the genetic information which are particularly robust with respect to destruction by UV radiation. It is generally believed that ultrafast (femtosecond) excited-state deactivation (via internal conversion to the electronic ground state) is the key for the photostability of DNA.[2]

The origin of the photostability of DNA can be traced back to some extent to the bare nucleic acid bases. They are the main chromophores of DNA and seem to be able to convert electronic energy nonradiatively into heat on a subpicosecond time scale.[2] In recent years, significant progress has been made in the understanding of the mechanisms of radiationless relaxation of the isolated nucleobases. Recent experimental[3−6] and theoretical investigations[7−17] of single DNA bases have led to the conclusion that internal conversion via energetically low-lying conical intersections[18] is responsible for the efficient nonradiative decay dynamics of these systems. On the basis of theoretically identified decay pathways,[7−17] it has become possible to develop a relatively simple mechanistic picture of the photophysics of isolated nucleic acid bases. For example, it has been found that conical intersections related to specific out-of-plane deformations of the six-membered aromatic ring dominate the radiationless deactivation of the lowest excited states of cytosine (C),[7,9] uracil (U),[10,14] adenine (A),[11−13,15,16] guanine (G), and thymine (T).[17] It has furthermore been shown for the example of adenine that conical intersections related to hydrogen atom abstraction[8,12,13] and the opening of the five-membered ring[12] become operative at higher excitation energies (∼5.5 eV). Taken together, these decay channels seem to provide the isolated DNA bases with a high degree of photostability over a wide range of the UV spectrum.

In DNA or RNA oligomers, the individual nucleic acid bases interact with each other via hydrogen bonding (base pairing),

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noncovalent $\pi-\pi$ interactions (stacking), as well as via covalent bonding to the sugar–phosphate backbone. These interactions can considerably modify the photophysics of the whole system, not only by changing the energetic ordering and spacing of the excited states, but also by providing additional decay channels.

The influence of base pairing on the excited-state dynamics has been investigated by Schultz et al. for the model system 2-aminopyridine.[19] Femtosecond time-resolved mass spectroscopy of 2-aminopyridine clusters in the gas phase has revealed a significant shortening of the excited-state lifetime of the near-planar hydrogen-bonded dimer in comparison with the lifetime of either the monomer or the three- and four-membered nonplanar clusters. The A–T[20] and G–C[21] base pairs were studied with resonant two-photon ionization (R2PI) spectroscopy in a supersonic jet. The first experiments have indicated the absence of R2PI spectra originating from the Watson–Crick (WC) structure of G–C.[22] Further investigations[23] revealed that the WC conformer of the G–C base pair exhibits a dramatically broadened UV absorption spectrum, in sharp contrast to the other (non-WC) G–C structures, for which well-resolved vibronic progressions were observed.[21,22] These findings indicate the existence of an additional excited-state deactivation channel in hydrogen-bonded dimers, which is especially efficient in the case of the WC structure of G–C.

Crespo-Hernandez et al. have studied the influence of base stacking on photophysics of A–T DNA oligomers and have observed the formation of intrastrand excimer states with lifetimes of 50–150 ps when A is stacked with itself or with T.[24] They argued that vertical base stacking rather than base pairing determines the fate of excited singlet states in single- and double-stranded oligonucleotides composed of A and T.

A model of the enhancement of excited-state decay upon base pairing has been proposed by Sobolewski, Domcke, and collaborators.[19,25–27] It is based on the properties of dark $^1\pi\pi^*$ excited states of charge-transfer (CT) character,[28,29] which drive the transfer of a proton between the monomers (electron-driven proton transfer). The energies of these CT states have been found to be stabilized enormously by the transfer of a (single) proton in both the 2-aminopyridine dimer and in the G–C base pair, leading in both cases to a crossing (more precisely, a conical intersection) of the S_1 and S_0 energy surfaces.[19,25–27] These conical intersections provide an efficient pathway for the depopulation of the lowest excited singlet states[18] and thus endow the dimer with additional photostability in comparison with that of the monomers. The considerable differences in the energetics of the lowest $^1\pi\pi^*$(CT) excited state relative to those of the locally excited (LE) states in different conformers of G–C provide a qualitative explanation of the dramatically different R2PI spectra[23] and the uniquely efficient excited-state deactivation of the WC conformer of G–C.[27]

Herein, we extend the proposed model[19,25–27] to the A–T base pair. We have investigated the energetics of the excited-state (single) proton-transfer reaction for the two most relevant conformers of A–T, the WC structure and the energetically most stable (in the gas phase) conformer of A–T.[30]

2. Computational Methods

The initial guesses of the geometries of the two A–T conformers were taken from the molecular dynamics simulations reported in ref 31. The ground-state geometry optimization of both structures was performed with the second-order Møller–Plesset (MP2) method, employing Dunning's correlation-consistent polarized valence double-ζ (cc-pVDZ) basis set.[32] The resolution-of-the-identity (RI) approximation[33] has been employed to speed up the evaluation of the electron repulsion integrals.

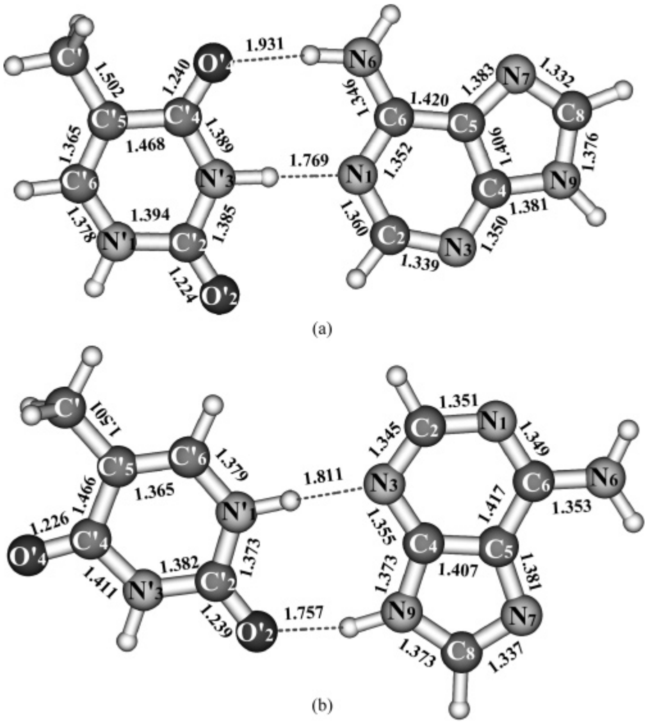

Figure 1. Ground-state equilibrium geometries of the WC (a) and MS (b) conformers of the A–T base pair, determined at the MP2/cc-pVDZ level. Bond lengths are given in angstroms.

The vertical excitation energies and excited-state properties were calculated with the second-order approximate coupled-cluster method, CC2,[34] employing again the RI approximation.[35] The same level of theory was employed for the determination of the excited-state analytic energy gradients.[36] The minimum-energy path for proton transfer in the lowest CT excited state has been determined by CC2 geometry optimization, choosing the NH bond length of the donor group as the driving coordinate, as demonstrated previously.[25–27] To reduce the considerable cost of these calculations, the economical def-SV(P) split-valence double-ζ Gaussian basis set with polarization and diffuse functions[37] was used in the excited-state geometry optimization. All calculations were performed with the TURBOMOLE-5.7 program package.[38]

3. Results and Discussion

3.1. Ground-State Structures and Vertical Excitation Energies. The ground-state equilibrium structures of the WC conformer and the most stable (MS) conformer of the A–T base pair are shown in Figure 1, parts a and b, respectively. Since the ground-state geometries of isolated A and T are known to be slightly nonplanar,[11,17] the structures of A–T are expected to reflect these features, in particular the WC structure, because in this form the amino group of A, which is pyramidized in isolated A, is involved in the intermolecular hydrogen bonding. Indeed, previous calculations of the structure of the WC form of A–T have revealed that this structure is slightly buckled and propeller-twisted.[39,40] However, the lowering of the ground-state energy due to out-of-plane deformation is merely 0.3 kcal/mol[41] and is thus rather small in comparison to the vertical excitation energies, excited-state stabilization energies due to relaxation of the geometry, and the precision of the computational method.

TABLE 1: Vertical Excitation Energy (ΔE), Dipole Moment (μ), and Oscillator Strength (f) of the Lowest Excited Singlet States of the WC and the MS Conformers of the A−T Base Pair, Calculated at the MP2/cc-pVDZ Optimized Equilibrium Geometries of the Ground State with the CC2/cc-pVDZ Method

	conformer							
	WC				MS			
state	transition[a]	ΔE, eV	μ, D	f	transition[a]	ΔE, eV	μ, D	f
S_1	$^1n\pi^*$ (A−T → T*)	5.13	4.14	0.0001	$^1n\pi^*$ (T → T*)	5.09	1.34	0.0001
S_2	$^1\pi\pi^*$ (A → A*)	5.25	2.66	0.0782	$^1\pi\pi^*$ (A → A*)	5.28	4.87	0.1731
S_3	$^1\pi\pi^*$ (T → T*)	5.37	2.17	0.1620	$^1\pi\pi^*$ (A → A*)[b]	5.40	3.41	0.3611
S_4	$^1\pi\pi^*$ (A → A*)	5.45	1.18	0.2495	$^1\pi\pi^*$ (T → T*)[c]	5.44	4.39	0.1003
S_5	$^1n\pi^*$ (A → A*)	5.51	2.50	0.0003	$^1n\pi^*$ (A → A*)	5.47	3.74	0.0000
S_6	$^1n\pi^*$ (A → A*)	6.03	2.30	0.0001	$^1n\pi^*$ (A → A*)	6.23	3.08	0.0007
S_7	$^1\pi\pi^*$ (A → T*)	6.26	10.74	0.0249	$^1n\pi^*$ (A → A*)	6.36	3.81	0.0008
S_8	$^1n\pi^*$ (A−T → T*)	6.31	7.03	0.0000	$^1\pi\pi^*$ (A → A*)	6.51	2.93	0.2457
S_9	$^1\pi\pi^*$ (A → T*)	6.42	16.97	0.0202	$^1\pi\pi^*$ (T → T*)[c]	6.71	5.86	0.1051
S_{10}	$^1\pi\pi^*$ (T → T*)	6.64	0.88	0.4166	$^1\pi\pi^*$ (T → T*)[c]	6.71	7.69	0.2225
S_{11}	$^1\pi\pi^*$ (A → A*)	6.82	3.11	0.0002	$^1\pi\pi^*$ (A → A*)	6.80	4.76	0.0191
S_{12}	$^1\pi\pi^*$ (T → T*)	6.91	4.10	0.2863	$^1\pi\pi^*$ (A → T*)	6.83	29.61	0.0001

[a] The transitions are classified according to the localization of orbitals, which are involved in the excitation, on A or T. [b] Minor contribution of T → T* excitation. [c] Minor contribution of A → A* excitation.

We have therefore performed the geometry optimization of the WC and MS structures of A−T with C_s symmetry constraint.

The ground-state energy of the MS conformer was found to be lower than the energy of the WC form by 0.14 eV (3.2. kcal/mol), in good agreement with results of Hobza and collaborators, who obtained an energy difference of 0.19 eV (4.4 kcal/mol).[42] The calculated dipole moments are 2.98 D for the MS structure and 0.97 D for the WC conformer, respectively. The calculated lengths of covalent bonds of both conformers are generally very similar to those determined for the isolated bases[11,17] with the same methodology, with exception of the bonds between atoms which are involved in the intermolecular hydrogen bonding. The length of the $O'_4\cdots HN_6$ hydrogen bond of the WC conformer is longer (by 0.15 Å), and the $N_1\cdots H'N_{3'}$ hydrogen bond is shorter (by 0.05 Å), than the corresponding hydrogen bonds of the MS conformer. The lengths of $O'_4\cdots HN_6$ and $N_1\cdots H'N_{3'}$ hydrogen bonds of the WC form of A−T are in reasonable agreement with their values obtained with density functional theory,[43] while they are about 0.2 Å shorter than those obtained with the Hartree−Fock method.[44]

The CC2 vertical excitation energies, dipole moments, and oscillator strengths of the lowest 12 transitions of the WC and the MS conformers of A−T were calculated with the def-SV(P) and cc-pVDZ basis sets. The two basis sets give the same ordering of the excited states and yield dipole moments and oscillator strengths of similar magnitude for both conformers. The CC2/cc-pVDZ values of the vertical excitation energies of the lowest six excited states of the WC and MS conformers of A−T are, on the average, 0.05 eV lower than those determined with the def-SV(P) basis, while the CC2/cc-pVDZ and CC2/def-SV(P) energies of the next six transitions differ by about 0.1 eV. The calculated CC2/cc-pVDZ values are given in Table 1.

As can be seen from Table 1, the lowest-energy transition in the vertical absorption spectrum of the WC form of A−T is of $^1n\pi^*$ character. The n orbital in this case is partly delocalized over A and T, while the π^* orbital is completely localized on T. The calculated dipole moment of this state (4.14 D) is almost 4 times larger than the dipole moment of the ground state. Previous single-excitation configuration−interaction (CIS) calculations[41] have predicted the lowest $^1n\pi^*$ transition to be the sixth state (!) in the vertical absorption spectrum of the WC conformer of A−T, most likely due to the neglect of electron correlation in the CIS method.

The lowest excited state of $^1\pi\pi^*$ type is the second state in the vertical absorption spectrum of the WC form of A−T (Table 1). This state is of locally excited (LE) character, both π and π^* orbitals being localized on A. It is interesting to compare the energy of this state with the energy of the first $^1\pi\pi^*$ transition of isolated adenine computed at the same level. It turns out that the complexation with T lowers the energy of the lowest $^1\pi\pi^*$ state of A by 0.13 eV (from 5.38 to 5.25 eV). A similar red-shift in energy is observed for the higher $^1\pi\pi^*$ transitions of LE character localized either on A or T. The higher transitions of $^1n\pi^*$ type, on the other hand, are blue-shifted in comparison with those of isolated A (see Table 1).

The character and ordering of the lowest $^1\pi\pi^*$ transitions of LE character determined here resemble those reported previously at the CIS level:[28,41] the lowest state of A → A* type is followed by a T → T* state and another one of A → A* character. However, the CIS energies[41] are about 1.0 eV higher than the corresponding CC2/cc-pVDZ values.

The seventh transition in the vertical absorption spectrum of the WC form of A−T is the lowest $^1\pi\pi^*$ transition of CT character. The electronic structure of this state is similar to that determined previously at the CIS level:[28,41] the π and π^* orbitals are completely localized on A and T, respectively. The charge separation results in a very large dipole moment of 10.74 D. Another characteristic feature of this transition is its very low oscillator strength. The vertical energy (6.26 eV) of this lowest $^1\pi\pi^*$(CT) excited state is about 1 eV higher than the energy of the lowest $^1\pi\pi^*$ transition. A previous CIS calculation[41] has predicted a similar gap between these two states, but the energy of the CT state was reported to be 7.22 eV at the CIS level. It is interesting that there exists another $^1\pi\pi^*$ excited state of CT character in the WC conformer of A−T. This transition is the ninth one, with an excitation energy of 6.42 eV and a dipole moment of 16.97 D, which is the largest value among the dipole moments of all calculated excited states of the WC conformer.

The lowest transition in the vertical absorption spectrum of the MS conformer of A−T is of $^1n\pi^*$ character, as for the WC conformer (Table 1). In this case, both orbitals are localized on T. The dipole moment of this lowest excited state (1.34 D) is even smaller than that of the ground state (2.98 D). The energy of this state is blue-shifted by about 0.1 eV in comparison with the first $^1n\pi^*$ transition of isolated T.[17] A blue-shift of similar magnitude is also observed for the next three $^1n\pi^*$ transitions of LE character relative to the $^1n\pi^*$ excited states of isolated A.

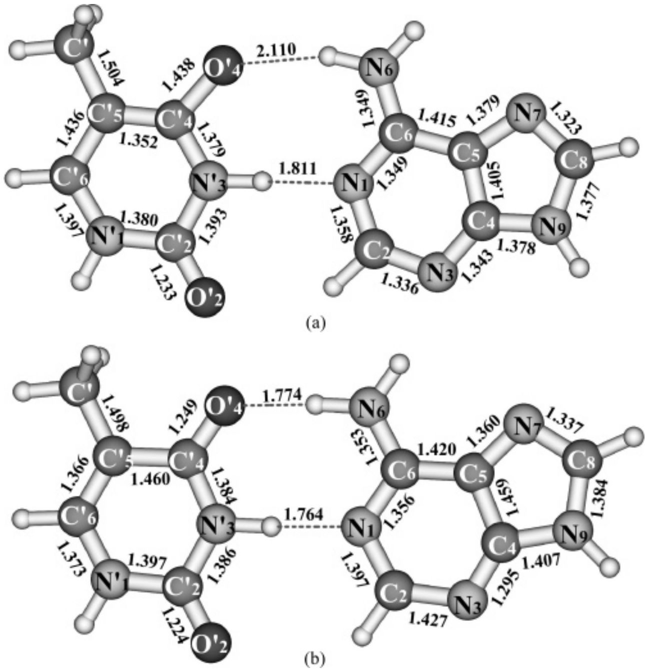

Figure 2. Equilibrium geometries of the lowest $^1n\pi^*$ (a) and $^1\pi\pi^*$ (b) excited states of the WC conformer of A−T, determined at the CC2/def-SV(P) level. Bond lengths are given in angstroms.

The first $^1\pi\pi^*$ excited state of the MS conformer of A−T is localized on A, as in the case of the WC conformer. Its energy is very close to that determined for the WC conformer. The energies of the lowest transitions calculated for the MS form generally resemble those obtained for the WC conformer, although the character of these transitions is not always the same. The S_3, S_4, S_9, and S_{10} states of the MS conformer are characterized by a minor contribution from electronic configurations which are localized on the complementary moiety (see Table 1).

Only one excited state of CT character has been found among the first 12 transitions in the vertical absorption spectrum of the MS conformer of A−T (see Table 1). The singly occupied orbitals of this state are localized on A and T, respectively, like in the case of the WC form. This CT state with vertical excitation energy of 6.83 eV is located about 0.6 eV higher than the lowest transition of CT type in the vertical absorption spectrum of the MS form. It possesses a very large dipole moment (29.61 D).

3.2. Excited-State Minimum-Energy Structures and Energetics. It is well-known by now that the equilibrium geometries of the $n\pi^*$ or $\pi\pi^*$ excited singlet states of DNA bases can be significantly nonplanar.[7,9−17] It is expected that the hydrogen bonding in DNA base pairs has the tendency to quench out-of-plane deformations. Preliminary investigations of the interplay of excited-state out-of-plane deformation of the aromatic rings and hydrogen bonding have been performed for the GC base pair.[26] These results indicate that out-of-plane deformations of the purine base G are suppressed in the GC base pair, whereas a low-barrier out-of-plane reaction path exists when the pyrimidine base C is excited to its $^1\pi\pi^*$ state. In the present work, we have restricted ourselves to the investigation of in-plane hydrogen-transfer reaction paths in the lowest excited states of the A−T dimer. The study of potentially competing reaction mechanisms involving out-of-plane deformation of A or T is deferred to future work.

The C_s-optimized equilibrium geometries of the lowest $^1n\pi^*$ and $^1\pi\pi^*$ excited states of the WC conformer of A−T are shown in Figure 2. The bond distances of T in the $^1n\pi^*$ state are close to the bond lengths determined for the equilibrium geometry of the $^1n\pi^*$ state of isolated T,[17] as expected due to the localization of the π^* orbital on T. The significantly elongated $C'_4O'_4$ bond of about 1.440 Å is noteworthy. The changes of the bond lengths of A, on the other hand, are moderate and mostly confined to the $C_6C_5N_7C_8$ fragment (see Figure 2).

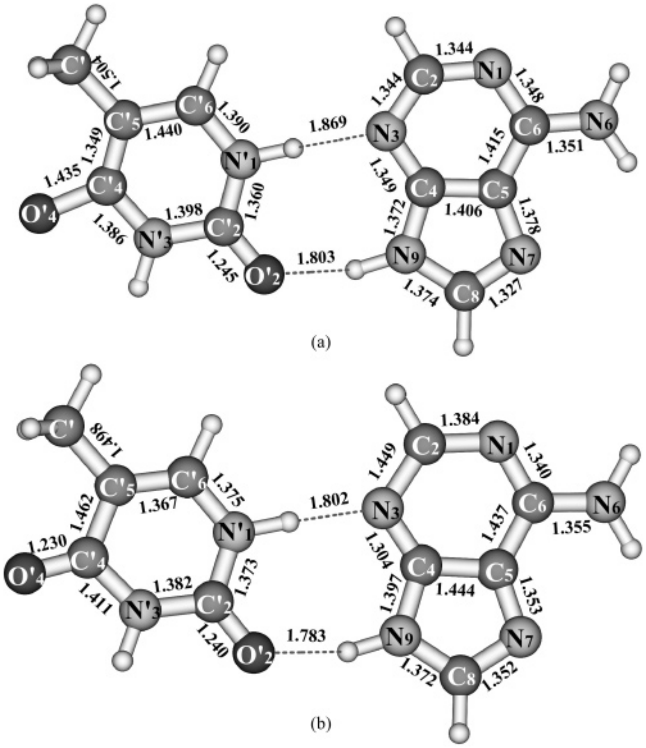

Figure 3. Equilibrium geometries of the lowest $^1n\pi^*$ (a) and $^1\pi\pi^*$ (b) excited states of the MS conformer of A−T, determined at the CC2/def-SV(P) level. Bond lengths are given in angstroms.

The opposite behavior is observed for the minimum-energy structure of the lowest $^1\pi\pi^*$ excited state of the WC conformer. In this case, the bond lengths of T are changed only little in comparison to those of the ground-state structure, while the covalent bond distances of adenine are altered significantly. This reflects the localization of the lowest $^1\pi\pi^*$ transition of the WC conformer on A.

It follows from the comparison of Figure 2, parts a and b, with Figure 1 that the relaxation of the geometries of the $^1n\pi^*$ and $^1\pi\pi^*$ states of the WC form toward equilibrium involves a change of the lengths of the $O'_4\cdots HN_6$ and $N_1\cdots H'N'_3$ hydrogen bonds. The length of the former bond increases by about 0.2 Å and that of the latter by 0.05 Å in the $^1n\pi^*$ state. In the $^1\pi\pi^*$ state, on the other hand, the corresponding bonds are shortened by about 0.2 and 0.005 Å, respectively. Qualitatively similar changes of hydrogen-bond distances were predicted at the CIS level.[41] In this case, the predicted increases of the bond distances in the $^1n\pi^*$ state were more pronounced.

The equilibrium geometries of the $^1n\pi^*$ and the $^1\pi\pi^*$ excited states of the MS conformer of A−T are shown in Figure 3. The general trends of the geometry changes are the same as for the WC conformer, i.e., they reflect the localization of the orbitals involved in the electronic excitation. The bond lengths of T are primarily affected in the lowest $^1n\pi^*$ excited state, while the bond distances of A are mainly changed in the $^1\pi\pi^*$ state. Similar as in the WC form, the lengths of both intermolecular hydrogen bonds are enlarged (by about 0.05 Å) in the $^1n\pi^*$ state in comparison with those of the ground-state

TABLE 2: Adiabatic Excitation Energies (ΔE), Dipole Moments (μ), and Oscillator Strengths (f) of the Lowest $^1n\pi^*$ and $^1\pi\pi^*$ Excited States of the WC and MS Conformers of the A−T Base Pair, Calculated with the CC2/cc-pVDZ Method at the Corresponding CC2/def-SV(P) Optimized Excited-State Geometries

	WC conformer			MS conformer		
state	ΔE, eV	μ, D	f	ΔE, eV	μ, D	f
$^1n\pi^*$	4.08	4.68	0.00002	4.00	1.84	0.00002
$^1\pi\pi^*$	4.86	3.61	0.17640	4.92	5.64	0.20114

geometry. In the $^1\pi\pi^*$ state, on the other hand, the $N_3\cdots H'N'_1$ hydrogen-bond length is decreased by 0.009 Å, while the $O'_2\cdots HN_9$ distance is larger by nearly 0.03 Å than in the ground state.

The adiabatic excitation energies, dipole moments, and oscillator strengths of the lowest $^1n\pi^*$ and $^1\pi\pi^*$ excited states of the WC and MS conformers of A−T, calculated with the CC2/cc-pVDZ method at the corresponding CC2/def-SV(P) optimized excited-state geometries, are given in Table 2. As can be seen, the relaxation of the geometry in the excited state leads to a stabilization of the energy of the $^1n\pi^*$ state by 1.05 and 1.09 eV in the case of the WC and MS conformer, respectively. This stabilization is of the same order of magnitude as in the case of isolated T, where it was about 1.0 eV.[17] The adiabatic excitation energies of the lowest $^1n\pi^*$ excited state of the WC and MS conformers are blue-shifted by about 0.1 eV in comparison with those calculated for isolated T. The dipole moments of the $^1n\pi^*$ excited states increase by about 0.5 D upon geometry optimization, while the oscillator strengths slightly decrease.

The calculated adiabatic excitation energies of the lowest $^1\pi\pi^*$ excited states of both conformers are stabilized by about 0.4 eV relative to the corresponding vertical excitation energies. The corresponding dipole moments and oscillator strengths increase in both cases. The adiabatic excitation energy of the $^1\pi\pi^*$ excited state of the WC form is lower by 0.06 eV than the corresponding excitation energy of the MS form. The $^1\pi\pi^*$ adiabatic energies of both conformers are red-shifted in comparison to the energy of the lowest $^1\pi\pi^*$ transition of isolated A determined on the same computational level. The calculated magnitude of the shift is 0.13 eV for the WC conformer and 0.07 eV for the MS conformer, respectively. Considering the expected precision of the present calculations (which is limited, for example, by the C_s symmetry constraint), this result is in reasonable agreement with the measured value of the red-shift of 1045 cm^{-1} (0.13 eV), determined in the R2PI experiments for the MS conformer.[20]

The calculated adiabatic excitation energies of the $^1\pi\pi^*$(LE) states of the WC and MS conformers indicate that the R2PI spectrum of the WC conformer should be located 700−800 cm^{-1} to the red of the observed R2PI spectrum[20] of the MS conformer. This energy range has partly been covered in the one-color R2PI spectrum of ref 20, and no sharp lines were detected. However, this energy region may be below the two-photon ionization threshold of A−T, which would explain the absence of a signal. Clearly, additional UV−UV and UV−IR double-resonance measurements are necessary.

The $^1\pi\pi^*$ adiabatic excitation energy of the MS conformer predicted at the CC2/cc-pVDZ level is higher by about 0.5 eV than the 0−0 line observed in the R2PI spectrum of this conformer (4.35 eV).[20] Since it is expected that CC2 with a double-ζ basis set overestimates the excitation energies by a few tenths of an eV,[35] this agreement is satisfactory and confirms the assignment of this line as the lowest $^1\pi\pi^*$ origin. So far, no evidence of the low-lying $^1n\pi^*$ transitions has been found experimentally.[20,22]

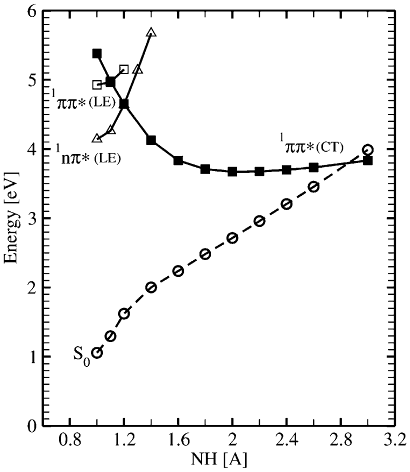

Figure 4. Minimum-energy profiles of the lowest $^1n\pi^*$ (triangles), $^1\pi\pi^*$(LE) (open squares), and $^1\pi\pi^*$(CT) (full squares) excited states of the WC conformer of A−T, calculated at the CC2/def-SV(P) level as functions of the proton-transfer coordinate with C_s symmetry constraint. The energy of the ground state (circles) has been calculated at the optimized geometries of the CT state. The CC2/cc-pVDZ ground-state energy computed at the corresponding MP2/cc-pVDZ optimized geometry is used as the reference.

3.3. Excited-State Proton-Transfer Reaction in the A−T Base Pair. Two possible reaction paths for the transfer of a single proton exist in the WC and MS conformers of the A−T base pair. One of them involves the transfer of a proton from A to T along the $O'_4\cdots HN_6$ or $O'_2\cdots HN_9$ hydrogen bonds in the WC or MS forms, respectively. The alternative single-proton-transfer reaction involves the transfer of a proton from T to A along the $N_1\cdots H'N'_3$ or $N_3\cdots H'N_{1'}$ hydrogen bonds, respectively. The only CT states among the lowest 12 transitions in the vertical absorption spectra of both conformers are of the A → T* type, corresponding to the formation of A^+-T^- ion pair structures. Thus, the transfer of a proton from A to T along the $O'_4\cdots HN_6$ or $O'_2\cdots HN_9$ hydrogen bonds can compensate the charge separation, or, in other words, the electronic charge separation drives the proton from A to T. Therefore, this process is energetically highly preferred compared to the proton-transfer reaction along the $N_1\cdots H'N'_3$ or $N_3\cdots H'N_{1'}$ hydrogen bonds. The opposite applies for CT states of T → A* character. However, these states are predicted to lie higher in energy, probably because the ionization potential of T is higher than that of A.[28,45] Thus, we will consider here only the transfer of a proton from A to T along the $O'_4\cdots HN_6$ or $O'_2\cdots HN_9$ hydrogen bonds.

The potential-energy profiles of the lowest excited states of $^1n\pi^*$, $^1\pi\pi^*$(LE), and $^1\pi\pi^*$(CT) character of the WC conformer of A−T as a function of the N_6H distance are shown in Figure 4. The energies of the excited states have been optimized for a given N_6H distance, while the energy of the electronic ground state (circles) has been calculated for the optimized geometries of the CT state. The energy of the lowest excited states of $^1n\pi^*$ and $^1\pi\pi^*$ (LE) character increases along the N_6H reaction coordinate, as does the energy of the ground state. The energy profile of the $^1\pi\pi^*$(CT) excited state, on the other hand, is essentially repulsive along this reaction path. This remarkable phenomenon has previously been discovered in investigations of the WC conformer of the G−C base pair.[26,27] The strongly repulsive potential-energy function of the $^1\pi\pi^*$(CT) state crosses the energy profiles of the $^1\pi\pi^*$(LE) and $^1n\pi^*$ excited states at N_6H distances of 1.12 and 1.20 Å, respectively. These crossing

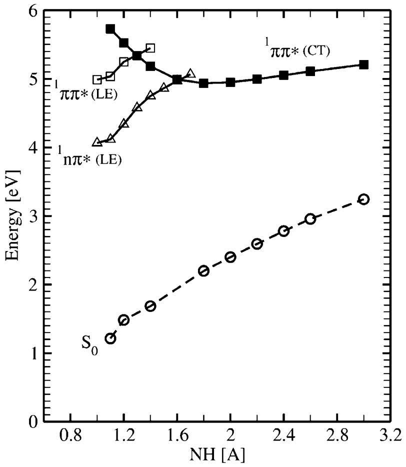

Figure 5. Minimum-energy profiles of the lowest ^{1}nπ* (triangles), $^1\pi\pi$*(LE) (open squares), and $^1\pi\pi$*(CT) (full squares) excited states of the MS conformer of A−T, calculated at the CC2/def-SV(P) level as functions of the proton-transfer coordinate with C_s symmetry constraint. The energy of the ground state (circles) was calculated at the optimized geometries of the CT state. The CC2/cc-pVDZ ground-state energy computed at the corresponding MP2/cc-pVDZ optimized geometry is used as the reference.

points are about 0.1 and 0.5 eV higher in energy than the minima of the $^1\pi\pi$*(LE) and ^{1}nπ* excited states, respectively. The energy profile of the $^1\pi\pi$*(CT) state exhibits a shallow minimum at an N_6H distance of about 2.0 Å, which corresponds to a structure in which the proton has been transferred to T. This minimum, with an energy of about 3.7 eV above the ground-state minimum, is lower than the minima of the ^{1}nπ* and $^1\pi\pi$*(LE) excited states by about 0.3 and 1.2 eV, respectively. Note, in particular, that the energy function of the $^1\pi\pi$*(CT) state crosses the energy of the ground state at an N_6H distance of about 2.8 Å. The energy of this crossing point is only about 0.1 eV higher than the energy of the minimum of the $^1\pi\pi$*(CT) state.

The proton transfer from A to T in the MS conformer of A−T has been studied by constructing the energy profiles of the four states of interest as a function of the N_9H distance (cf., Figure 1b). The resulting potential-energy profiles are shown in Figure 5. The energies of the ^{1}nπ* and $^1\pi\pi$* (LE) excited states as well as the energy of the ground state increase with increasing N_9H distance, while the energy of the $^1\pi\pi$*(CT) state decreases along this reaction path. The crossing of the $^1\pi\pi$*(LE) and $^1\pi\pi$*(CT) profiles occurs at an N_9H distance of about 1.3 Å. The crossing point is about 0.4 eV higher than the minimum of the $^1\pi\pi$*(LE) excited state. The $^1\pi\pi$*(CT) energy crosses the ^{1}nπ* energy at an N_9H distance of approximately 1.6 Å. It is seen that the energy function of the $^1\pi\pi$*(CT) excited state exhibits a shallow minimum at about 1.8 Å. In remarkable contrast to the WC conformer, the energy of this minimum is about 5.0 eV, which is nearly 0.9 eV higher than the minimum of the ^{1}nπ* excited state and only 0.1 eV lower than the minimum of the $^1\pi\pi$*(LE) state. The difference between the energy of the minima of the $^1\pi\pi$*(CT) excited state of the WC and MS conformers is about 1.2 eV. The most important difference between the $^1\pi\pi$*(CT) energy profiles of the WC and MS conformers is, however, the fact that the $^1\pi\pi$*(CT) energy of the MS form does not cross the ground-state energy along the minimum-energy path for proton transfer (cf., Figures 4 and 5). The energy gap between these states remains as large as 2.0 eV at an N_9H distance of 2.8 Å in the MS conformer, while a potential-energy crossing (conical intersection) exists at the same NH bond length in the WC conformer. This finding has important implications for the photophysical behavior of the two conformers of A−T, as will be discussed below.

3.4. Discussion of the Photophysics of A−T Base Pairs. It has previously been shown that the lowest optically allowed excited states of A and T are characterized by the existence of low-lying conical intersections with the ground state which are accessible via essentially barrierless minimum-energy reaction paths.[11−13,15−17] The existence of these conical intersections determines to a large extent the excited-state lifetimes of A and T. Some of these radiationless decay mechanisms may be quenched in hydrogen-bonded base pairs, while others may remain active.[26] As has been pointed out previously,[19,25,27] the photochemistry of hydrogen bonds may introduce additional excited-state deactivation mechanisms which are specific for hydrogen-bonded dimers. Specific for the dimers is, first of all, the existence of excited states of CT character. Although the lowest CT states are located relatively high in energy at the ground-state equilibrium geometry (6.26 and 6.83 eV for the WC and MS conformers of A−T, respectively) in comparison to the lowest transitions of LE character, their energy is lowered dramatically upon the transfer of a proton from A to T.

The very low oscillator strengths of the CT states prevent the direct optical excitation of these states. The CT states can be populated, however, via nonadiabatic coupling after the excitation of the optically allowed LE states. The height of the barrier which arises as a consequence of the LE−CT crossing as a function of the proton-transfer coordinate is a decisive factor for this process. As can be seen by inspection of Figure 4, the $^1\pi\pi$*(LE) state of the WC conformer of A−T is crossed very close to its minimum by the repulsive potential-energy function of the $^1\pi\pi$*(CT) state. Although this crossing of the energy profiles is an apparent crossing (since the minimum-energy reaction paths have been determined for the individual electronic states), this finding indicates that a conical intersection of the $^1\pi\pi$*(LE) and $^1\pi\pi$*(CT) energy surfaces is likely to exist close to the minimum of the $^1\pi\pi$*(LE) surface. As a result, we expect a fast electronic population flow from the optically excited $^1\pi\pi$*(LE) state to the dark $^1\pi\pi$*(CT) state. Long-lived vibronic levels may exist, on the other hand, near the minimum of the lowest ^{1}nπ* surface, since this local minimum is separated by a sizable barrier (of the order of a few tenths of an eV, see Figure 4) from the minimum of the $^1\pi\pi$*(CT) surface. Because of the very low oscillator strength of the ^{1}nπ* state, these potentially long-lived vibronic levels play no role for the optical absorption of the A−T dimer. They may become populated, on the other hand, via internal conversion from the $^1\pi\pi$*(LE) state, in competition with the quenching of the latter state by the $^1\pi\pi$*(CT) state. Further spectroscopic and computational investigations are necessary for the clarification of this issue. Of course, alternative decay channels (presumably those prevailing in isolated T) can lead to the depopulation of the ^{1}nπ* local minimum. In any case, a biexponential excited-state decay is expected, the fast and slow components arising from the quenching of the $^1\pi\pi$*(LE) state by the CT state and the decay of the low vibronic levels of the ^{1}nπ* state, respectively. This conclusion is in agreement with the first (not yet conformer-specific) time-resolved measurements for the A−T dimer.[46]

In the MS conformer of A−T, the $^1\pi\pi$*(CT) state is located higher in energy and its energy profile as a function of the proton-transfer coordinate is less repulsive. As a result, the crossing of the $^1\pi\pi$*(LE) and $^1\pi\pi$*(CT) energy profiles occurs about 0.4 eV above the minimum of the $^1\pi\pi$*(LE) state, see Figure 5. The lowest vibronic levels of the $^1\pi\pi$*(LE) state are thus expected to be long-lived, in agreement with the observation of sharp vibronic structure in the R2PI spectrum of the MS conformer of A−T.[20]

The minimum of the $^1\pi\pi^*$(CT) surface, which corresponds to a bond length of the NH donor group of 1.8−2.0 Å in both conformers (see Figures 4 and 5), corresponds to a biradical electronic structure: one electron and one proton have been transferred from A to T. In contrast to the LE singlet states, for which singet−triplet splittings typically amount to several eV, the singlet and triplet states are essentially degenerate for the biradical. Therefore, intersystem crossing does not endow the triplet state with a large amount of vibrational excess energy in this case, which renders intersystem crossing relatively harmless in the biradical. Nevertheless, the open-shell biradical structure is potentially reactive and therefore a threat for the chemical stability of the base pair. In the WC conformer, the $^1\pi\pi^*$(CT) surface exhibits a crossing (conical intersection) with the S_0 surface only slightly above the minimum of the former (see Figure 4). Thus, ultrafast decay of the biradical is expected via this S_1−S_0 photochemical funnel. In the MS conformer, on the other hand, no evidence of a $^1\pi\pi^*$(CT)−S_0 conical intersection has been found (see Figure 5). The biradical structure of the MS conformer is thus expected to be a metastable and potentially reactive species. Relaxation to the ground state with or without the transfer of an additional proton could lead to rare tautomers of A or T and thus mutations.[47,48] The present results, together with the results of ref 27 for the G−C base pair, support the hypothesis that the WC conformers of the A−T and G−C base pairs are distinguished by uniquely efficient excited-state deactivation mechanisms which minimize deleterious effects of photochemical reactions after the absorption of UV photons.

It should finally be mentioned that the model of the photochemistry of the A−T base pair proposed here, which focuses on the electron-driven proton-transfer mechanism, does not exclude the existence of the competing decay pathways, for example, those which are associated with specific out-of-plane deformations of the six-membered rings.[11−13,15−17] The calculations of the present investigation have been performed with C_s symmetry constraint, which excludes reaction mechanisms which involve out-of-plane deformations of the bases. Considering that out-of-plane deformations are likely to be constrained by intermolecular stacking interactions in real DNA, this should be a useful approximation to start with. However, the development of a complete picture of the photophysics of the A−T base pair may require the consideration of the competition of out-of-plane with in-plane dynamics.

4. Conclusions

Calculations of the excited-state potential-energy surfaces of two conformers of the A−T base pair have been performed with the CC2 method. The Watson−Crick form of A−T and the most stable (MS) tautomer (in the gas phase) of this base pair have been considered. The equilibrium geometries and the excitation energies of the low-lying spectroscopic states ($^1n\pi^*$ and $^1\pi\pi^*$ of LE character) have been calculated. For both conformers, the lowest $^1\pi\pi^*$ state is located on A and complexation with T leads to a red-shift of about 0.1 eV (800 cm^{-1}) relative to the lowest $^1\pi\pi^*$ transition of A. The lowest $^1n\pi^*$ state, on the other hand, is localized on T in both conformers and is blue-shifted by about 0.1 eV (800 cm^{-1}) relative to the lowest $^1n\pi^*$ state of T. Of particular interest for the excited-state dynamics of the A−T base pair are $^1\pi\pi^*$ states of CT character. The π and π^* orbitals involved in these CT transitions are completely localized either on A or on T. The electronic charge separation results in very large dipole moments of these states. Another characteristic feature of these CT states is their vanishingly small transition dipole moments with the electronic ground state.

Although the energy of the lowest $^1\pi\pi^*$(CT) state of the WC and MS conformers of A−T is about 1.5 eV higher than the energy of the lowest optically allowed transition, these states are essentially involved in the photochemistry of the A−T base pair. It has been shown that the transfer of a proton, which thus neutralizes the electronic charge separation, leads to a dramatic lowering of the energy of these states. Interestingly, significant differences have been found in the energetics of the CT states for the WC and MS conformers of A−T. The potential energy of the CT state as a function of the proton-transfer coordinate is higher in the MS conformer and less repulsive than in the WC conformer. As a result, the energy surface of the UV-absorbing $^1\pi\pi^*$(LE) state of the WC form is intersected near its minimum by the energy surface of the CT state, while this curve crossing occurs about 0.4 eV above the $^1\pi\pi^*$(LE) minimum in the MS conformer. Moreover, the CT surface exhibits a crossing (conical intersection) with the electronic ground state in the WC form, while the CT−S_0 energy gap has been found to remain larger than 2 eV in the MS conformer.

The sequence of conical intersections which exist in the WC conformer allows a barrierless and thus very fast deactivation of the UV-absorbing states to the electronic ground state. The dangerous energy of the UV photon is thus very efficiently dissipated as heat. We have obtained evidence that the specific hydrogen-bonding pattern of the WC conformer endows this structure with a greatly enhanced photostability. These findings have important implications for the spectroscopy of the different conformers of the A−T base pair and, more importantly, for the rationalization of the decisive factors which have governed the selection of molecular structures for the encoding of the genetic information in early stages of biological evolution.

The present results pertain to the isolated A−T base pair. The binding of A−T to the sugar−phosphate backbone as well as stacking interactions with neighboring bases pairs may modify the excited-state dynamics and may induce additional photochemical reactions pathways. These issues need to be investigated in the future.

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