

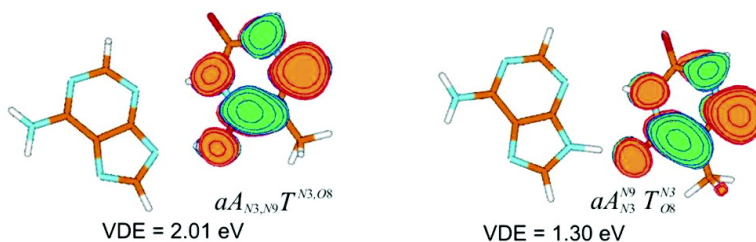
Article

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## AT Base Pair Anions versus (9-Methyl-A)(1-Methyl-T) Base Pair Anions

Dunja Radisic,<sup>†</sup> Kit H. Bowen, Jr.,<sup>\*,†</sup> Iwona Dąbkowska,<sup>‡,§</sup> Piotr Storonik,<sup>‡</sup> Janusz Rak,<sup>‡</sup> and Maciej Gutowski<sup>\*,‡,||</sup>

Contribution from the Department of Chemistry, Johns Hopkins University, Baltimore, Maryland 21218, Department of Chemistry, University of Gdańsk, Sobieskiego 18, 80-952 Gdańsk, Poland, Institute of Organic Chemistry and Biochemistry, The Academy of Sciences of the Czech Republic (ASCR), Flemingovo nám.2, 166 10 Prague 6, Czech Republic, and Chemical Sciences Division, Pacific Northwest National Laboratory, Richland, Washington 99352

Received February 3, 2005; E-mail: kbowen@jhu.edu; maciej.gutowski@pnl.gov

**Abstract:** The anionic base pairs of adenine and thymine, (AT)<sup>-</sup>, and 9-methyladenine and 1-methylthymine, (MAMT)<sup>-</sup>, have been investigated both theoretically and experimentally in a complementary, synergistic study. Calculations on (AT)<sup>-</sup> found that it had undergone a barrier-free proton transfer (BFPT) similar to that seen in other dimer anion systems and that its structural configuration was neither Watson–Crick (WC) nor Hoogsteen (HS). The vertical detachment energy (VDE) of (AT)<sup>-</sup> was determined by anion photoelectron spectroscopy and found to be in agreement with the VDE value predicted by theory for the BFPT mechanism. An AT pair in DNA is structurally immobilized into the WC configuration, in part, by being bonded to the sugars of the double helix. This circumstance was mimicked by methylating the sites on both A and T where these sugars would have been tied, viz., 9-methyladenine and 1-methylthymine. Calculations found no BFPT in (MAMT)<sup>-</sup> and a resulting (MAMT)<sup>-</sup> configuration that was either HS or WC, with the configurations differing in stability by ca. 2 kcal/mol. The photoelectron spectrum of (MAMT)<sup>-</sup> occurred at a completely different electron binding energy than had (AT)<sup>-</sup>. Moreover, the VDE value of (MAMT)<sup>-</sup> was in agreement with that predicted by theory. The configuration of (MAMT)<sup>-</sup> and its lack of electron-induced proton transfer are inter-related. While there may be other pathways for electron-induced DNA alterations, BFPT in the WC/HS configurations of (AT)<sup>-</sup> is not feasible.

## Introduction

The nucleic acid bases, adenine (A) and thymine (T) as well as guanine (G) and cytosine (C), exist as the well-known Watson–Crick (WC) pairs, AT and GC, in DNA. Hydrogen bonding between the complementary bases is very specific, and it is the basis for the high informational fidelity of DNA. Reverse Watson–Crick, Hoogsteen, and reverse Hoogsteen are also possible pairing configurations, and they are found in RNA and other biological structures.

Gas-phase studies of base pairs afford the opportunity to examine the inherent hydrogen-bonding interactions of nucleic acid bases without local environmental effects. For neutral pairs, calculations find the most stable structure of the gas-phase, guanine–cytosine dimer to correspond to the Watson–Crick structure, while the most stable gas-phase adenine–thymine pair does not correspond to a biologically relevant structure.<sup>1,2</sup> Methylation of the N1 position of thymine and the N9 position

of adenine (the sites that are connected to sugars in DNA) is predicted by theory to yield Hoogsteen, reversed Hoogsteen, and two stacked structures as similarly stable geometries.<sup>2</sup> Experimental studies of the gas-phase, neutral base pairs, GC, GG, and CC, found that the most stable pairing configuration in GC is similar to that of WC, but with the tautomer of cytosine in the enol form.<sup>3</sup> Other experimental work has mimicked WC pairing in AT by studying gas-phase, neutral complexes of 2-aminopyridine•2-pyridone.<sup>4,5</sup>

Electron binding to the gas-phase, nucleic acid bases and base pairs has been studied both experimentally<sup>6–14</sup> and theo-

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retically<sup>14–24</sup> to determine the energetics and mechanisms involved in electron transfer and radiation-induced damage in DNA. When biological tissue is irradiated with ionizing radiation, free radicals and low energy electrons are produced, and both are involved in processes that ultimately lead to biological damage. While historically radicals have received more attention, the role of electrons is becoming more appreciated. Recently, for example, it has been found that low energy electrons initiate complex reactions leading to strand breaks in DNA.<sup>13,25,26</sup>

Molecular nucleic acid bases typically have large dipole moments. Gas-phase, experimental studies of electron-nucleobase interactions found that they often formed dipole bound anions.<sup>9–11,16–19</sup> Isolated conventional (valence) anions were found to be unbound (or weakly bound), but in any case, all could be stabilized with a sufficient number of solvent molecules.<sup>6–8</sup> Vertical electron affinities were measured by electron transmission spectroscopy of transient (temporary) anions.<sup>27</sup> Adiabatic electron affinities (EA<sub>a</sub>) of nucleobases valence states have been predicted by theory to decrease in the following order: uracil (U)  $\approx$  thymine (T) > cytosine (C) > adenine (A) > guanine (G).<sup>15,28</sup>

Rydberg electron transfer<sup>12</sup> studies of the gas-phase base pair anions: U<sub>2</sub><sup>-</sup>, A<sub>2</sub><sup>-</sup>, (AT)<sup>-</sup>, T<sub>2</sub><sup>-</sup>, as well as negative ion photoelectron spectroscopic studies<sup>29,30</sup> of the pairs: U<sub>2</sub><sup>-</sup>, T<sub>2</sub><sup>-</sup>, [1-(CH<sub>3</sub>)T]<sub>2</sub><sup>-</sup>, and [1,3-(CH<sub>3</sub>)<sub>2</sub>U]<sub>2</sub><sup>-</sup>, found that most are valence anions. The only exception was T<sub>2</sub><sup>-</sup>, for which both dipole bound and valence anions were observed.<sup>12</sup> Computational studies<sup>20–23,31–34</sup> of gas-phase, base pair anions have mainly focused on (GC)<sup>-</sup> and (AT)<sup>-</sup> in WC configurations, owing to the presence and function of the neutral WC configuration in DNA. Their results on (AT)<sup>-</sup> will be compared with ours below.

Proton-transfer processes are important in mutagenesis, and several theoretical studies have investigated proton transfer in base pairs.<sup>34–37</sup> Proton-transfer reactions are also important in the initial stabilization of radical ions formed during DNA

irradiation.<sup>38</sup> It has been suggested that the radical ion distribution is dependent on proton-transfer reactions between the base pairs. Base pair anions are also susceptible to proton transfer.<sup>32,34</sup> In related work, our joint theoretical/experimental studies found proton transfer to play a pivotal role in the mechanism by which dimer anions composed of a nucleic acid base (NAB) and a weak acid (HX) internally rearrange themselves.<sup>39–44</sup> Our computational results have implied that the excess electron is localized on the nucleic acid base and that the electron attachment might be accompanied by a barrier-free proton transfer (BFPT) from the weak acid to the anionic base, resulting in an anionic complex composed of a hydrogenated base radical and a deprotonated acid as shown below.



The computations also predicted the vertical detachment energies of the resulting complexes. Our measured vertical detachment energies, which could not be explained by a simple solvation model, were in agreement with those calculated in the theoretical portion of the project, thereby supporting the reliability of the calculated results.

In the present study, we report our joint experimental/theoretical study of anionic complexes of adenine–thymine and 9-methyladenine–1-methylthymine base pairs. In the latter case, we have chosen to methylate the positions of adenine and thymine that are bonded to deoxyribose and ribose molecules in DNA and RNA, respectively. Our goal is to study the effect of electron attachment on the AT and dimethyl–AT complexes and to determine if the most stable neutral and anionic configurations of these dimers correspond to biologically significant ones. We do this by taking advantage of the following synergy between experiment and theory. Theory can calculate both structure and vertical detachment energies for these dimer anions, while experiment can measure their vertical detachment energies. When measured and computed vertical detachment energies for a given system are in agreement, our confidence in the computed geometrical configuration grows stronger.

## Methods

**Experimental Details.** Anion photoelectron spectroscopy (PES) is conducted by crossing beams of mass-selected negative ions and fixed frequency photons and energy-analyzing the resultant photodetached electrons. This technique is governed by the following energy-conserving relationship:

$$h\nu = \text{EBE} + \text{EKE} \quad (2)$$

where  $h\nu$  is the photon energy, EBE is the electron-binding energy, and EKE is the measured electron kinetic energy.

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The apparatus has been described previously.<sup>45</sup> Anions were produced in our supersonic expansion, nozzle-ion source, where a mixture of the two individual nucleic acid bases of interest was heated to approximately 180–200 °C and co-expanded with 1–2 atm of argon through a 25- $\mu$ m nozzle. A negatively biased hot filament, placed very close to expansion, injected low-energy electrons into the jet, which in the presence of an axial magnetic field, formed a microplasma. Anions were then extracted and mass-selected with a 90° magnetic sector mass selector, having a resolution of  $\sim$ 400. The mass-selected ion beam was then crossed with an intracavity laser beam, and the photodetached electrons were energy-analyzed with a hemispherical electron energy analyzer. Typical resolution of our electron energy analyzer is 25 meV, and photodetachment was accomplished with  $\sim$ 200 circulating Watts of 2.54 eV photons. The photoelectron spectra of (adenine–thymine)<sup>−</sup> and (9-methyladenine–1-methylthymine)<sup>−</sup> were both calibrated against the well-known photoelectron spectrum of O<sup>−</sup>.<sup>46</sup>

**Computational Details.** We have applied primarily the density functional theory method with Becke's three-parameter hybrid functional (B3LYP)<sup>47–49</sup> and the 6-31+G\*\* (6d) basis set.<sup>50</sup> The ability of the B3LYP method to predict excess electron-binding energies has recently been reviewed, and the results were found to be satisfactory for valence-type molecular anions.<sup>51</sup> The values of electron vertical detachment energy for valence anions of pyrimidine nucleic acid bases are typically overestimated by 0.15–0.20 eV at the B3LYP level of theory.<sup>39,40</sup> The concepts of electron vertical detachment energy (VDE) and adiabatic electron affinity (AEA) are derived within the Born–Oppenheimer approximations and are related to characteristic features of potential energy surfaces of the neutral and the anion; see Figure 1 in ref 51.

All geometries presented here have been fully optimized without any geometrical constraints, and the analysis of harmonic frequencies proved that all of them are also geometrically stable (all force constants were positive). The relative energies of neutral complexes are defined with respect to the energy of the Watson–Crick neutral complex, whereas in the case of anions they are defined with respect to the anionic Watson–Crick pair.

The stabilization energies  $E_{\text{stab}}$  of neutral complexes are calculated as a difference between the energy of the complex and the sum of the energies of fully optimized isolated monomers. Therefore,  $E_{\text{stab}}$  obtained in this way includes deformation energies of the monomers. Basis set superposition error has not been corrected for, as it was predicted in the earlier studies<sup>20</sup> that it shall not exceed 2 kcal/mol and is of a similar value for each base pair arrangement. Therefore, it does not alter the relative order of different configurations. The value of  $E_{\text{stab}}$  for an anionic complex is obtained by subtracting from the energy of the (AT)<sup>−</sup> dimer the energy of fully relaxed neutral adenine (A) and the energy of fully relaxed anion of thymine (T<sup>−</sup>). This approach is justified by the fact that in every anionic complex investigated by us in this study an excess electron is always localized on the thymine moiety. In addition to the stabilization energies,  $E_{\text{stab}}$ , we calculated stabilization free energies,  $G_{\text{stab}}$ . The latter result from correcting the values of  $E_{\text{stab}}$  for zero-point vibration terms, thermal contributions to energy, the pV terms, and the entropy terms. These terms were calculated in the rigid rotor-harmonic oscillator approximation for  $T = 298$  K and  $p = 1$  atm.

On the basis of our previous results,<sup>39–44</sup> we assumed that the attachment of an electron to the AT dimer may result in two stable but distinct structures: (i) a structure with the same set of hydrogen bonds

as the neutral AT dimer and (ii) a structure that results from intermolecular proton transfer (PT) from adenine to thymine. In both cases, the stabilization energies were evaluated with respect to the energy of neutral adenine and the anion of thymine.

Electron vertical detachment energies, direct observables in our PES experiments, were evaluated as a difference between the energy of the neutral and anionic complex at the geometry of the fully relaxed anion. A difference in Gibbs free energy between the neutral and the anion at their corresponding fully relaxed structures is denoted  $\text{EBE}_G$ .

Throughout our computational study we used a notation in which the symbols of nucleic acid bases were followed by superscripts and subscripts. These indices tell us, respectively, which atoms are proton donors and proton acceptors in a hydrogen-bonded network for a given base pair; see Figures 1 and 2. For example,  $\text{A}_{\text{N}_3}^{\text{N}_9}\text{T}_{\text{O}_8}^{\text{N}_3}$  stands for the adenine–thymine base pair bound via two hydrogen bonds: N9–H of adenine interacting with O8 of thymine and N3–H from thymine interacting with N3 of adenine. The Watson–Crick is labeled as  $\text{A}_{\text{N}_1}^{\text{N}_9}\text{T}_{\text{O}_8}^{\text{N}_3}$ . For the numbering of the atoms, see Figure 1. The anionic structures are preceded by a prefix “a”.

## Results

**Photoelectron Results.** The photoelectron spectra of (AT)<sup>−</sup> and (MAMT)<sup>−</sup> recorded with 2.54 eV photons are shown in Figure 3. The vertical detachment energies of these two spectra are very different, their values being separated by about 1 eV. The photoelectron spectrum of (AT)<sup>−</sup> consists of a broad peak with maximum at  $\sim$ 1.7 eV, while the photoelectron spectrum of (MAMT)<sup>−</sup> consists of a broad peak with a maximum at  $\sim$ 0.7 eV.

Let us consider the (AT)<sup>−</sup> spectrum. Both thymine<sup>7,10,52</sup> and adenine<sup>10,14</sup> form dipole bound anions, and photoelectron spectra of dipole bound anions are characterized by single narrow peaks at low electron-binding energies.<sup>9</sup> Also, while solvent stabilization results in spectral shifts to higher electron binding energies, they are quite small for dipole bound anions. Thus, since the actual spectrum of (AT)<sup>−</sup> is broad and sits at a relatively high electron-binding energy, it is clear that (AT)<sup>−</sup> is not dipole bound T<sup>−</sup> solvated by A or dipole bound A<sup>−</sup> solvated by T.

It is also clear that (AT)<sup>−</sup> is not the valence anion of one of its components solvated by the neutral molecule of the other. If it were, it would be T<sup>−</sup>(A), because as mentioned above, the electron affinity of thymine is larger than that of adenine.<sup>15,28</sup> One can get a reasonable idea of what the photoelectron spectrum of T<sup>−</sup>(A) should look like by examining the measured photoelectron spectrum of T<sup>−</sup>(H<sub>2</sub>O).<sup>7</sup> The VDE of T<sup>−</sup>(H<sub>2</sub>O) is 0.8 eV, while its threshold energy is 0.4 eV. The VDE of (AT)<sup>−</sup>, on the other hand, is 1.7 eV, while its threshold energy is 1.1 eV. They are very dissimilar. The comparison between T<sup>−</sup>(H<sub>2</sub>O) and T<sup>−</sup>(A) is valid because the dipole moments of adenine<sup>53</sup> and water<sup>54</sup> are similar (2.5 and 1.86 D, respectively), and in any case, water is a powerful solvating agent that produces maximal spectral shifts. Thus, (AT)<sup>−</sup> should not be characterized as the T<sup>−</sup>(A) anion molecule complex. Our calculations, in fact, clearly predict that (AT)<sup>−</sup> undergoes BFPT. Moreover, our measured VDE value for (AT)<sup>−</sup> is in agreement with our calculated VDE value for a (AT)<sup>−</sup> dimer anion that has undergone BFPT. Also note that the spectrum of (AT)<sup>−</sup> is

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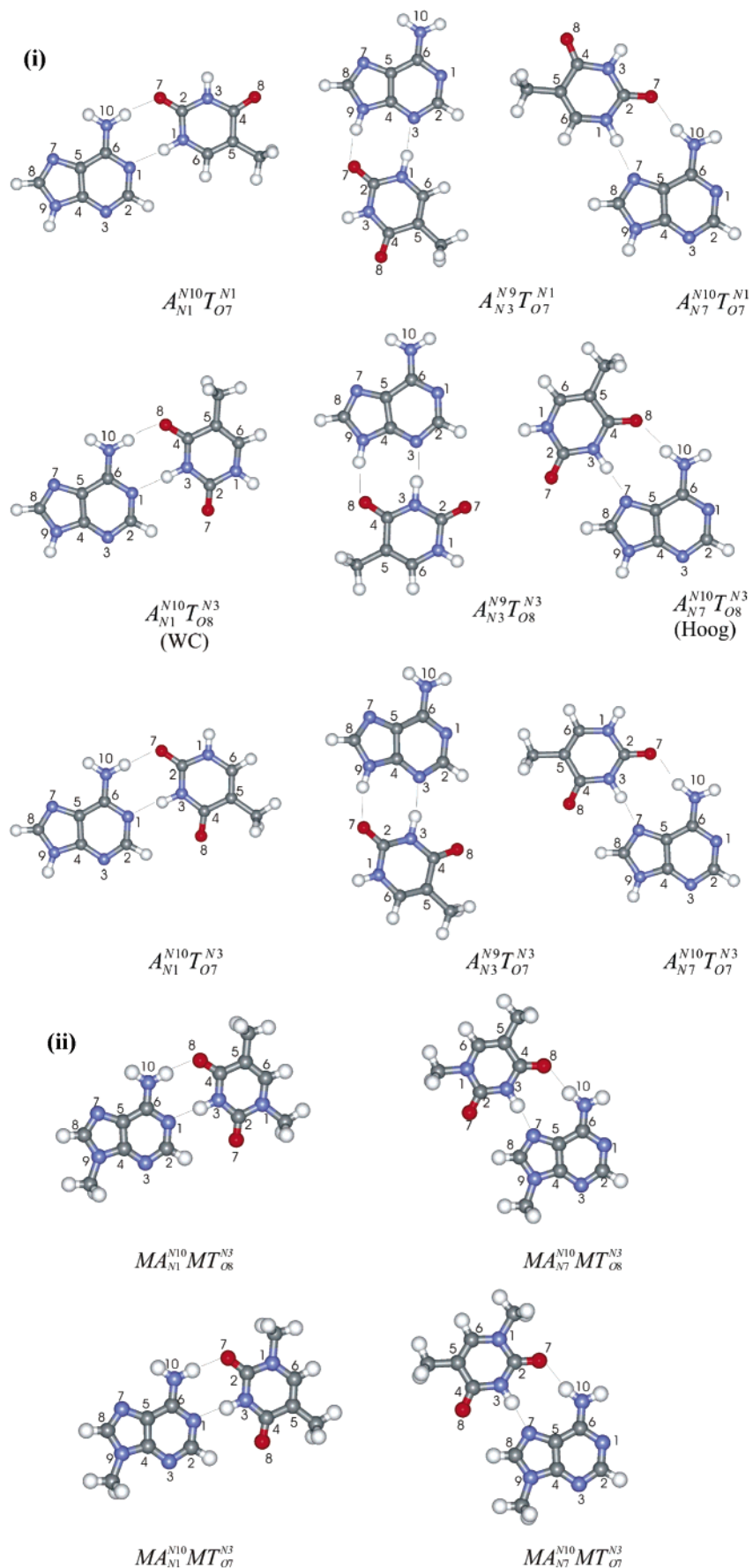
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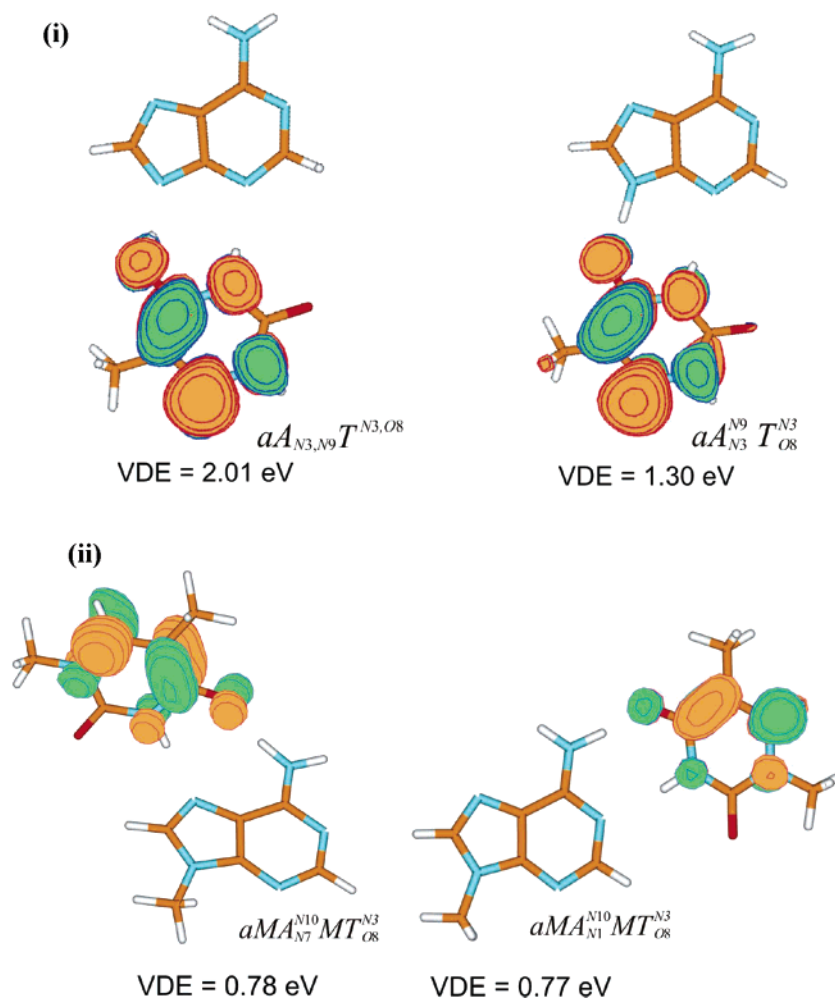
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**Figure 1.** Optimized structures of neutral complexes of (i) adenine with thymine and (ii) 9-methyladenine with 1-methylthymine.



**Figure 2.** Unpaired electron orbital plotted with a contour line spacing of  $0.03 \text{ bohr}^{-3/2}$  for the two most stable anions of (i) AT pair and (ii) MAMT pair.

similar to that of the thymine–glycine dimer anion,<sup>40</sup> which is an analogous system that has undergone BFPT.

Let us now turn to the spectrum of  $(\text{MAMT})^-$ . In contrast to the spectrum of  $(\text{AT})^-$ , the spectrum of  $(\text{MAMT})^-$  is similar to the spectrum of  $\text{T}^-(\text{H}_2\text{O})$ , suggesting that  $(\text{MAMT})^-$  can be described as  $(\text{MT})^-(\text{MA})$ . While the photoelectron spectrum of  $(\text{MT})^-(\text{H}_2\text{O})$  is not available for comparison, it is no doubt similar to that of  $\text{T}^-(\text{H}_2\text{O})$ , because methylation only tends to change electron binding energies slightly, for example,  $\text{EA}_a(\text{uracil}) \approx \text{EA}_a(\text{thymine})$ .<sup>15,28</sup> Thus, in  $(\text{MAMT})^-$ , the excess electron is probably associated with MT, implying that this dimer anion should be characterized as an  $(\text{MT})^-$  anion interacting with a neutral MA molecule, that is, the anion molecule complex,  $(\text{MT})^-(\text{MA})$ . Certainly, there is no experimental signature of BFPT in the photoelectron spectrum of this system. In agreement with this assessment, our calculations also characterize  $(\text{MAMT})^-$  as  $(\text{MT})^-(\text{MA})$ , and our measured VDE value is consistent with our calculated VDE value for this system.

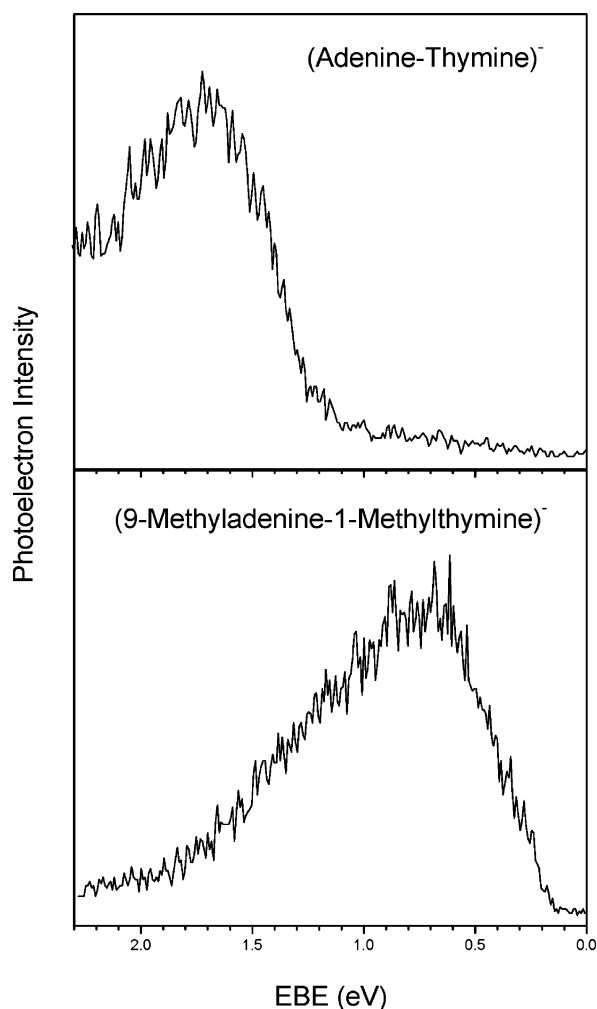
### Computational Results

**Neutral Complexes.** In the case of the adenine–thymine pair, a combination of three proton donor and acceptor pairs of adenine with three proton donor and acceptor pairs of thymine leads to nine possible, planar, cyclic H-bonded complexes. The neutral AT complexes are displayed in Figure 1, and their

stabilization energies and free energies are presented in Table 1. The stabilization energies vary from  $-12.4$  to  $-16.8$  kcal/mol. This range closely resembles the one obtained from the MD-quenching and  $\text{MP2}/6\text{-}31\text{G}^*(0.25)$  calculations:<sup>1,55</sup>  $-11.7$  to  $-16.6$  kcal/mol. Moreover, the relative stability of hydrogen-bonded structures determined at the B3LYP level matches almost exactly the one obtained previously.<sup>1,55</sup> Thus the B3LYP method provides a qualitatively correct description of stationary points on the potential energy surface of the AT complex. Both the MP2 and B3LYP theoretical approaches place the Watson–Crick arrangement as the second *least* stable among the adenine–thymine complexes in the gas phase. Perusal of Table 1 also reveals that the most favorable proton acceptor and donor pairs for hydrogen bonding in neutral clusters are O7 and N1H of thymine and N3 and N9H of adenine.

$\text{A}_{\text{N}3}^{\text{N}9}\text{T}_{\text{O}7}^{\text{N}1}$  is the most stable neutral complex, which involves N9H of A and N1H of T in hydrogen bonding. These sites, however, are bound to sugar units in DNA and cannot participate in hydrogen bonding in biological conditions. The dominance of  $\text{A}_{\text{N}3}^{\text{N}9}\text{T}_{\text{O}7}^{\text{N}1}$  demonstrates that the gas phase AT pair cannot serve as a model of biologically relevant interactions. A methylation at N9 of A and N1 of T is desirable to exclude these sites from hydrogen bonding.

Indeed, for the MAMT family only four structures are possible, with the Hoogsteen structure  $\text{MA}_{\text{N}7}^{\text{N}10}\text{MT}_{\text{O}8}^{\text{N}3}$  being the (55) Šponer, J.; Leszczyński, J.; Hobza, P. *J. Phys. Chem.* **1996**, *100*, 1965.



**Figure 3.** Photoelectron spectra of (adenine-thymine)<sup>−</sup> and (9-methyladenine-1-methylthymine)<sup>−</sup> recorded with 2.54 eV photons.

most stable. The B3LYP stabilization energies span a range from  $-12.2$  to  $-13.6$  kcal/mol, again in good agreement with the MP2 results ( $-11.2$  to  $-12.6$  kcal/mol).<sup>56</sup> The differences in  $E_{\text{stab}}$  for complexes with methylated and unmethylated bases do not exceed 0.24 kcal/mol. Thus, methylations have only minor effects on the energies of hydrogen bonds.

It is worth noticing that the relative stability of AT complexes may be incorrectly predicted when based on the values of proton affinity (PA) and deprotonation enthalpy (DPE) of the centers involved in hydrogen bonding (see Table S-1 for the reference data). For example, the Watson-Crick pair ( $A_{N1}^{N10}T_{O8}^{N3}$ ) differs from the Hoogsteen pair ( $A_{N7}^{N10}T_{O8}^{N3}$ ) only by the proton acceptor site on adenine. However, the PA values for the N1 and N7 sites (224.3 and 216.2 kcal/mol, respectively) would suggest that the WC pair is more stable than the Hoogsteen pair, whereas the theoretical results suggest otherwise.

**Anionic Complexes.** The results of B3LYP/6-31+G\*\* calculations for anions of various hydrogen-bonded AT and MAMT complexes are summarized in Table 2, and representative structures are displayed in Figure 2. A common feature of anionic wave functions identified by us for the AT and MAMT complexes is that the excess electron is localized on a  $\pi^*$  orbital of thymine, in close resemblance to the valence anionic state

**Table 1.** Values of Stabilization Energy ( $E_{\text{stab}}$ ) and Stabilization Free Energy ( $G_{\text{stab}}$ ) as Well as Their Relative Values ( $\Delta E$  and  $\Delta G$ ) with Respect to the Watson-Crick Pair for the Neutral Adenine-Thymine and 9-Methyladenine-1-Methylthymine Complexes Calculated at the B3LYP/6-31+G\*\* Level<sup>a</sup>

structure <sup>b</sup>	$E_{\text{stab}}$	$\Delta E$	$G_{\text{stab}}$	$\Delta G$
T <sub>O7</sub> <sup>N1</sup> Family				
$A_{N3}^{N9}T_{O7}^{N1}$	-16.81	-4.03	-3.28	-4.36
$A_{N1}^{N10}T_{O7}^{N1}$	-14.13	-1.35	-0.39	-1.47
$A_{N7}^{N10}T_{O7}^{N1}$	-13.05	-0.27	0.48	-0.60
T <sub>O8</sub> <sup>N3</sup> Family				
$A_{N3}^{N9}T_{O8}^{N3}$	-14.50	-1.72	-1.35	-2.43
$A_{N7}^{N10}T_{O8}^{N3}$ (Hoog)	-13.57	-0.79	0.42	-0.66
$A_{N1}^{N10}T_{O8}^{N3}$ (WC)	-12.78	0.0	1.08	0.0
T <sub>O7</sub> <sup>N3</sup> Family				
$A_{N3}^{N9}T_{O7}^{N3}$	-14.06	-1.28	-1.12	-2.20
$A_{N7}^{N10}T_{O7}^{N3}$	-13.34	-0.56	0.57	-0.51
$A_{N1}^{N10}T_{O7}^{N3}$	-12.45	0.33	1.26	0.18
9-Methyladenine-1-Methylthymine				
MT <sub>O8</sub> <sup>N3</sup> Family				
$MA_{N7}^{N10}MT_{O8}^{N3}$ (Hoog)	-13.62	-0.88	0.08	-0.70
$MA_{N1}^{N10}MT_{O8}^{N3}$ (WC)	-12.74	0.0	0.78	0.0
MT <sub>O7</sub> <sup>N3</sup> Family				
$MA_{N7}^{N10}MT_{O7}^{N3}$	-13.34	-0.61	0.26	-0.52
$MA_{N1}^{N10}MT_{O7}^{N3}$	-12.21	0.53	1.13	0.35

<sup>a</sup> All quantities in kilocalories per mole. <sup>b</sup>  $A_{A1}^{D1}T_{A2}^{D2}$  stands for an adenine-thymine dimer stabilized by two hydrogen bonds (for the sites numbers and structures, see Figure 2; D1/A1 = proton donor/acceptor site of adenine, D2/A2 = proton donor/acceptor site of thymine); M stands for "methylated".

of isolated thymine.<sup>40</sup> A neutral molecule of isolated thymine has a symmetry plane. However, occupation of the antibonding  $\pi$  orbital by an excess electron induces buckling of the ring because nonplanar structures are characterized by a less severe antibonding interaction. The same kind of ring distortion takes place in all aAT and aMAMT complexes upon an excess electron attachment.

As a consequence of the excess charge, the stabilization energies in anionic complexes can be as large as  $-23.9$  kcal/mol, compared with the largest stabilization energy of  $-16.8$  kcal/mol in neutral complexes. One may also notice that in anionic complexes the most favorable proton acceptor and donor pair involves O8 and N3H, whereas in neutral complexes the O7 and N1H sites led to the most stable hydrogen-bonded structures. This change in the most favorable binding sites is related to the characteristic charge distribution of the unpaired electron, which is primarily localized in the O8-C4-C5-C6 region of thymine.<sup>39-44</sup> The most favorable binding sites of adenine are the same in the neutral and anionic complexes: N3 and N9H.

The valence anionic state of isolated thymine is adiabatically unbound with respect to the neutral, though vertically bound by 0.46 eV.<sup>40</sup> The solvation of T<sup>−</sup> with adenine leads to not only vertically but also adiabatically bound anionic states at the B3LYP/6-31+G\*\* level of theory; see the values of  $EBE_G$  and VDE in Table 2. The two anionic structures  $aA_{N3}^{N9}T_{O8}^{N3}$  and  $aA_{N3,N9}T_{O8}^{N3}$ , which are the most stable in terms of  $E_{\text{stab}}$  and  $G_{\text{stab}}$ , are also characterized by the largest values of VDE and  $EBE_G$ .

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**Table 2.** Values of Stabilization Energy ( $E_{\text{stab}}$ ), Stabilization Free Energy ( $G_{\text{stab}}$ ), Their Relative Values ( $\Delta E$  and  $\Delta G$ ) with Respect to the Watson–Crick Pair, Electron Vertical Detachment Energy (VDE), and Adiabatic Electron Binding Energy ( $\text{EBE}_G$ ) for the Anionic Adenine–Thymine and 9-Methyladenine–1-Methylthymine Complexes Calculated at the B3LYP/6-31+G\*\* Level<sup>a</sup>

structure	$E_{\text{stab}}$	$\Delta E$	$G_{\text{stab}}$	$\Delta G$	$\text{EBE}_G$	VDE
T <sub>O8</sub> <sup>N3</sup> Family						
aA <sub>N3</sub> <sup>N9</sup> T <sub>O8</sub> <sup>N3</sup>	-22.85	-7.39	-11.11	-8.42	14.65	1.30
aA <sub>N3,N9</sub> T <sup>N3,O8</sup>	-23.89	-8.43	-11.07	-8.39	14.62	2.01
aA <sub>N7</sub> <sup>N10</sup> T <sub>O8</sub> <sup>N3</sup>	-17.52	-2.06	-3.86	-1.18	9.18	0.91
aA <sub>N1</sub> <sup>N10</sup> T <sub>O8</sub> <sup>N3</sup>	-15.46	0	-2.68	0	8.66	0.89
T <sub>O7</sub> <sup>N1</sup> Family						
aA <sub>N3</sub> <sup>N9</sup> T <sub>O7</sub> <sup>N1</sup>	-20.24	-4.78	-8.52	-5.84	10.14	0.52
aA <sub>N7</sub> <sup>N10</sup> T <sub>O7</sub> <sup>N1</sup>	-16.11	-0.65	-4.17	-1.49	9.55	0.33
aA <sub>N1</sub> <sup>N10</sup> T <sub>O7</sub> <sup>N1</sup>	-15.53	-0.07	-3.46	-0.78	7.96	0.26
T <sub>O7</sub> <sup>N3</sup> Family						
aA <sub>N3</sub> <sup>N9</sup> T <sub>O7</sub> <sup>N3</sup>	-17.46	-2.0	-4.90	-2.22	8.68	1.03
aA <sub>N7</sub> <sup>N10</sup> T <sub>O7</sub> <sup>N3</sup>	-14.80	0.66	-0.93	1.75	6.40	0.80
aA <sub>N1</sub> <sup>N10</sup> T <sub>O7</sub> <sup>N3</sup>	-11.95	3.52	0.48	3.16	5.68	0.61
9-Methyladenine–1-Methylthymine						
MT <sub>O8</sub> <sup>N3</sup> Family						
aMA <sub>N7</sub> <sup>N10</sup> MT <sub>O8</sub> <sup>N3</sup>	-16.72	-1.97	-3.66	-1.18	8.17	0.78
aMA <sub>N1</sub> <sup>N10</sup> MT <sub>O8</sub> <sup>N3</sup>	-14.76	0	-2.48	0	7.69	0.77
MT <sub>O7</sub> <sup>N3</sup> Family						
aMA <sub>N7</sub> <sup>N10</sup> MT <sub>O7</sub> <sup>N3</sup>	-14.00	0.75	-0.90	1.58	5.58	0.69
aMA <sub>N1</sub> <sup>N10</sup> MT <sub>O7</sub> <sup>N3</sup>	-11.20	3.55	-0.37	2.11	5.93	0.41

<sup>a</sup>  $E_{\text{stab}}$ ,  $G_{\text{stab}}$ ,  $\Delta E$ ,  $\Delta G$ , and  $\text{EBE}_G$  are in kilocalories per mole; VDE is in electronvolts.

In our previous studies on anionic complexes of thymine with various proton donors, we reported PT from some proton donors to the O8 atom of T.<sup>40,41</sup> Here, we tested the stability of anionic complexes with respect to PT from A to T<sup>-</sup>. Indeed, the global minimum on the anionic potential energy surface results from proton transfer from N9H of A to O8 of T, and the resulting structure is labeled aA<sub>N3,N9</sub>T<sup>N3,O8</sup>; see Figure 2. A barrier that separates the global minimum from the aA<sub>N3</sub><sup>N9</sup>T<sub>O8</sub><sup>N3</sup> structure is only 0.25 kcal/mol at the B3LYP/6-31+G\*\* level of theory. This barrier is encountered on the surface of electronic energy, but it disappears on the surface of free energy, after inclusion of zero-point energies, thermal energies, and the entropy terms.

The PES spectrum will be dominated by contributions from the most stable AT<sup>-</sup> structures (i.e., aA<sub>N3</sub><sup>N9</sup>T<sub>O8</sub><sup>N3</sup> and aA<sub>N3,N9</sub>T<sup>N3,O8</sup>), with the corresponding VDE values of 1.3 and 2.0 eV; see Table 2. The latter structure is more stable in terms of  $E_{\text{stab}}$  by 1.0 and 2.3 kcal/mol at the B3LYP and MP2 levels of theory, respectively. In terms of Gibbs free energy, the difference in stability is smaller by 1 kcal/mol. Thus, both structures might contribute to the PES spectrum. Indeed, the maximum of the PES spectrum is at 1.7 eV, in agreement with the calculated values of VDE.

The most stable anionic complexes for methylated bases correspond to the Hoogsteen aMA<sub>N7</sub><sup>N10</sup>MT<sub>O8</sub><sup>N3</sup> and Watson–Crick aMA<sub>N1</sub><sup>N10</sup>MT<sub>O8</sub><sup>N3</sup> structures, with the former being more stable by 2.0 and 1.2 kcal/mol in terms of  $\Delta E$  and  $\Delta G$ , respectively; see Table 2 and Figure 2. Both structures are characterized by a VDE of 0.8 eV at the B3LYP/6-31+G\*\* level. The results are

consistent with the maximum of the PES peak for MAMT<sup>-</sup> at 0.7 eV; see Figure 3.

## Discussion

There have been four theoretical studies of the AT base pair anion, (AT)<sup>-</sup>, and in each of these, the WC structural configuration was assumed.<sup>20–23</sup> All of these found only valence anions, and in three of the four studies, adiabatic electron affinity values in the range of 0.3–0.36 eV were found. Noting that the adiabatic electron affinity ( $\text{EA}_a$ ) value can probably be estimated by going a few tenths of an electronvolt up in energy beyond the threshold electron-binding energy in our photoelectron spectra, it is clear that their predicted values are in disagreement with any reasonable  $\text{EA}_a$  estimate that could be extracted from our (AT)<sup>-</sup> spectrum.

On the other hand, these three theoretically predicted  $\text{EA}_a$  values do much better at predicting the  $\text{EA}_a$  value of MAMT. From our photoelectron spectrum of (MAMT)<sup>-</sup>, one can estimate that the  $\text{EA}_a$  of MAMT is probably between 0.2 and 0.4 eV, and this range of values is consistent with their predictions. One of the theoretical studies also calculates the VDE value to be 0.6 eV, which is reasonably close to the measured VDE of (MAMT)<sup>-</sup> (i.e., 0.7 eV). As described above, our study shows that (MAMT)<sup>-</sup> is in the quasi-degenerate HS or the WC configuration. With this in mind and recalling that methylation tends to change electron-binding energies only slightly, one can see that (MAMT)<sup>-</sup> is a better structural and an energetic mimic of the WC (AT)<sup>-</sup> base pair anion that was studied by those four theoretical investigations.

Favorable deprotonation enthalpy is an important prerequisite for BFPT to take place.<sup>39–44</sup> The deprotonation enthalpy of the N9H site of adenine in the gas phase is only 335.6 kcal/mol; see Table S-1. Occurrence of BFPT from this position in (AT)<sup>-</sup> further supports our previous results and is expected based on them. The N10H position that is involved in hydrogen bonding in (MAMT)<sup>-</sup> has an acidity lower than the N9H position in adenine by approximately 20 kcal/mol. Our calculated acidities in adenine for N10(N7) and N10(N1) sites are 354.7 and 354.0 kcal/mol, respectively. Theoretical results found these to be 355.0 and 354.4 kcal/mol for the same sites in 9-ethyladenine.<sup>57</sup> Electron attachment to the MT is not followed by the proton transfer from MA because of the higher deprotonation enthalpy of the N10H site in MA. Instead, the electron mainly occupies the MT molecule, and thus we interpret the methylated pair as the anion molecule system, (MT)<sup>-</sup>(MA).

Before closing, we should point out that thus far we have characterized the aA<sub>N3,N9</sub>T<sup>N3,O8</sup> and aA<sub>N3</sub><sup>N9</sup>T<sub>O8</sub><sup>N3</sup> minima on the potential energy surface of the (AT)<sup>-</sup> complex. In the case of quasi-degenerate minima, the description limited to the coexisting classical structures might not be sufficient. In view of the small proton mass both electrons and the proton should be treated quantum mechanically to include nuclear quantum effects such as zero-point vibration energy and proton tunneling. The multiconfigurational nuclear-electronic orbital method<sup>58</sup> provides the proper framework to include these effects.

The resonance structure of the damage quantum yield versus incident electron energy was reported by Sanche et al.<sup>26</sup> They

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suggested that the process proceeds via metastable, that is, resonance, anionic states, probably localized on the nucleic base (NB) molecules. The interpretation was strengthened by the results of electron transmission spectroscopy experiments, in which only temporary, that is, resonance, anionic states NBs were detected.<sup>27</sup> In our opinion, it is premature to focus attention exclusively on anionic resonance states as critical intermediates leading to DNA strand breaks. The agreement between the PES spectra and computational results obtained for bound anionic states of the AT or MAMT complexes implies that bound anionic states might be operational in DNA, despite the fact that the valence anionic state of isolated T is adiabatically unbound. Clearly, the environment of  $T^-$ , even as simple as the complementary base A, is sufficient to render the valence anionic state bound; see Table 2.

The field of computational studies of DNA radiation damage has been rapidly growing over the past few years, and our contribution to the study of the anionic AT and MAMT complexes should be viewed from a broader perspective. The group of Schaefer has recently studied DNA nucleosides and their radical anions.<sup>59</sup> They found that the values of adiabatic electron affinity are uniformly greater than those of the corresponding isolated bases. The group of Simons developed a computational model for indirect dissociative electron attachment that simplifies calculations on electronically metastable anions.<sup>60</sup> The groups of Sevilla and Sanche studied the energetics of hydrogen atom loss in pyrimidine DNA bases.<sup>61</sup> The hydrogen loss is the dominant channel of dissociative electron attachment to pyrimidine bases. We are convinced that future computational studies will provide critical insight into molecular mechanisms of DNA damage by low-energy electrons.

### Summary

The photoelectron spectra of the anionic adenine–thymine and 9-methyladenine–1-methyladenine, recorded with 2.54 eV photons, are both characterized with broad features, but differ significantly in measured VDEs. The maxima of measured spectra for  $(AT)^-$  and  $(MAMT)^-$  are at approximately 1.7 and 0.7 eV, respectively. This indicates that two different ionic configurations are observed in the nonmethylated and methylated dimers.

The theoretical results, acquired at the density functional theory and second-order Møller–Plesset levels, indicate that the

electron attachment to AT is able to induce proton transfer from adenine to thymine with no kinetic barrier. This process can be described as following. The electron is primarily located on the O8–C4–C5–C6 portion of thymine, the molecule with the higher electron affinity. Proton transfers from the H9N position of adenine to the O8 position of thymine to stabilize this extra charge, resulting in a complex that consists of hydrogenated neutral thymine and deprotonated adenine. The anionic dimers of AT that match this description are found to be the most stable, and their calculated VDEs fall within the range observed in the photoelectron spectrum of  $(AT)^-$ . On the other hand, intermolecular proton transfer does not develop in  $(MAMT)^-$ , which is an anion molecule complex, with electron localized on MT molecule, and MA acting as a solvent. Calculated VDEs for these most stable configurations of  $(MAMT)^-$  are in agreement with the measured PES VDEs. The methylation of the N9H site in MA is responsible for lack of BFPT in  $(MAMT)^-$ . The deprotonation enthalpy of this site is approximately 20 kcal/mol lower than deprotonation enthalpy of the N10H, the site involved in hydrogen bonding with the O8 position of MT.

The global minimum of  $(AT)^-$  does not correspond to any biologically relevant structure. The most stable structures of  $(MAMT)^-$  correspond to Hoogsteen and Watson–Crick. Calculations found Hoogsteen to be 2 kcal/mol lower in energy than Watson–Crick.

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**Supporting Information Available:** Proton affinities and deprotonation enthalpies obtained at the B3LYP/6-31+G\*\* level for selected sites of the canonical form of adenine and thymine. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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