

Intermolecular proton transfer induced by excess electron attachment to adenine(formic acid)_n ($n = 2, 3$) hydrogen-bonded complexes

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Abstract

The propensity of the neutral complexes between both adenine and 9-methyladenine (A/MA) with formic acid (FA) in 1:2 and 1:3 stoichiometries to bind an excess electron was studied using photoelectron spectroscopy and quantum chemistry computational methods. Although an isolated canonical adenine does not support bound valence anions, solvation by one formic acid molecule stabilizes the excess electron on adenine. The adiabatic electron affinities of the A/MA(FA)_{2,3} complexes span a range of 0.8–1.23 eV indicating that the anions of 1:2 and 1:3 stoichiometries are substantially more stable than the anionic A–FA dimer (EA = 0.67 eV), which we studied previously and an attachment of electron triggers double-BFPT, confirmed at the MPW1K level of theory, in all the considered systems. Hence, the simultaneous involvement of several molecules capable of forming cyclic hydrogen bonds with adenine remarkably increases its ability to bind an excess electron. The calculated vertical detachment energies for the most stable anions correspond well with those obtained using photoelectron spectroscopy. The possible biological significance of our findings is briefly discussed.

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1. Introduction

It is now well established that under ultra high vacuum conditions interactions between low energy electrons (LEEs) and dry DNA lead to the biopolymer cleavage [1,2]. On the other hand, it has been long known that in aqueous solutions solvated electrons attachment to DNA shows little to no effect [3] even though the pyrimidine anion radicals are formed [4]. In fact it is found that by scavenging electrons with N₂O in water and thus converting them to hydroxyl radicals, an approximate doubling

of DNA strand breaks occurs from the conversion of ineffective hydrated electrons to reactive hydroxyl radicals [5,6].

Many experimental and theoretical reports emphasize the crucial role of anionic states in dry DNA damage induced by low energy electrons (LEEs) [1,2]. The through-bond electron transfer (TBET) from an initially formed resonance localized on a pyrimidine base to the σ^* orbital associated with the C3'–O bond in a pyrimidine nucleotide was postulated to be responsible for the LEE-induced single-strand breaks (SSBs) formation in DNA [7]. On the other hand, it is well known that the valence anions of canonical nucleobases, unstable in the gas phase [8], become adiabatically stable due to even marginal solvation. For instance, employing photoelectron spectroscopy (PES) Bowen and co-workers [9] demonstrated that

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isolated uracil forms a stable dipole bound anion (DB). However, when it interacts with xenon both DB and valence anions are seen, and for uracil complexed with a single water molecule only the valence anion signal appears in the PES spectrum. Moreover, a series of studies concerning the complexes of nucleobases with organic or inorganic proton donors indicate that electron attachment to those species in the gas phase induces proton transfer which leads to the strong stabilization of the resulting valence anions [10–19]. Thus, the formation of stable anions in the DNA environment, where proton donors, polar and conjugated species are present rather than resonant states, seems to be quite probable. Indeed, EPR signals that originated from the stable T^- and C^- anions, were measured in the past by Sevilla and co-workers [4]. Hence, alternatives to TBET models of electron transfer leading to SSBs in DNA assume stable valence anions of nucleobases (NBs) rather than resonances to be involved in its electron-induced degradation process. As a matter of fact two cleavage mechanisms based on adiabatically stable anions have been put forward recently [20–22]. The mechanism deduced by Leszczynski's group [20,21] assumes that one excess electron is necessary for SSB to be generated, consistent with high vacuum experiments on dry DNA which are usually carried out in a single-electron regime. In the second model, published by Dąbkowska et al. [22], the attachment of the first electron to a pyrimidine nucleotide is accompanied by proton transfer that, in turn, is followed by the attachment of a second electron (alternatively one can see this process as an attack of hydrogen atom followed by the attachment of electron). Therefore, only in the presence of sufficient numbers of low energy electrons such two-electron processes might be feasible.

In all the above-mentioned mechanistic proposals, DNA damage begins with the formation of a pyrimidine anion, i.e., an excess electron initially localizes on thymine or cytosine. Recently, we have pointed out that stable anionic species based on the purine rather than pyrimidine bases might be also involved in a reaction sequence leading to the splitting of $CX'-O$ bonds in nucleotides [18,19]. This anti-intuitive process (solution electron affinities of pyrimidine bases are larger than those of purines [23], thus, pyrimidines rather than purines should be primary sites for electron attachment) could take place while DNA is involved in interactions with external proton donors (e.g., side chains of amino acids from an interacting protein). Then an excess electron might be better stabilized on purines than pyrimidines since the former are the major sites of amino acid–nucleobase interactions [24]. Although studies on hydrated DNA show that electrons are mainly trapped on pyrimidines [4], Barnes and Bernhard [25] reported that in some cases adenine bound in DNA oligomers plays a role of the competitive electron trap.

The current work extends our previous studies concerning the anionic, binary complexes (1:1) of adenine/9-methyladenine (A/9MA) with formic acid (AFA/9MAFA) [18] to systems with more complex stoichiometries. In the fol-

lowing we will discuss the effect of electron attachment to the complexes of adenine (A) and 9-methyladenine (MA) with formic acid (FA) in 1:2 or 1:3 stoichiometries. Since the analysis of anionic complexes requires basic knowledge of the corresponding neutral species, our description of the anions is preceded by the analysis of neutral complexes. Therefore, the structure and energetics of the possible $A(FA)_n/MA(FA)_n$ hydrogen-bonded complexes in 1:2 or 1:3 stoichiometries stabilized by cyclic hydrogen bonds are first considered. Next, the propensity of those neutral complexes to attach an excess electron is analyzed in terms of adiabatic electron affinity. Finally, the most stable anions are identified and their calculated vertical detachment energy (VDE) values are compared to those in the measured PES spectra.

2. Methods

2.1. Experimental

Negative ion photoelectron spectroscopy is conducted by crossing a mass-selected beam of negative ions with a fixed-frequency laser beam and energy-analyzing the resultant photodetached electrons [26]. Our apparatus has been described elsewhere [27]. To prepare the species of interest, a mixture of adenine and formic acid was placed in the stagnation chamber of a nozzle source and heated to $\sim 180^\circ\text{C}$. Argon gas at a pressure of 1–2 atm was used as the expansion gas, and the nozzle diameter was 25 μm . Electrons were injected into the emerging jet expansion from a negatively biased ThO_2/Ir filament in the presence of an axial magnetic field. The resulting anions were extracted and mass-selected with a magnetic sector mass spectrometer. Electrons were then photodetached from the selected anions with ~ 200 circulating Watts of 2.54 eV photons and energy-analyzed with a hemispherical electron energy analyzer.

2.2. Computational

The structures of neutral complexes characterized in the current study will be labeled as $A(FA)_n$ or $MA(FA)_n$, where A, MA, and FA stands for adenine, 9-methyladenine and formic acid, respectively, while n assumes a value of 2 or 3. In order to indicate the regions of adenine where formic acid molecules are coordinated to, the region symbols (I, II or III – see Fig. 1) will appear as superscripts. For example a symbol $A(FA)_2^{\text{I/II}}$ denotes the adenine–formic acid complex in 1:2 stoichiometry where formic acid molecules are coordinated to the regions I and II (see Fig. 1), whereas a symbol $A(FA)_3^{\text{I/II/III}}$ stands for fully saturated adenine/formic acid tetramer where all three adenine regions are involved in cyclic hydrogen bond interactions with FA. The symbols of anions are preceded with an a indicating the *parent* neutral structure the anionic structure is related to. More precisely, an anionic structure $aA(FA)_2^{x/y}$ ($aMA(FA)_2^{\text{I/II}}$) or $aA(FA)_3^{\text{I/II/III}}$ is determined

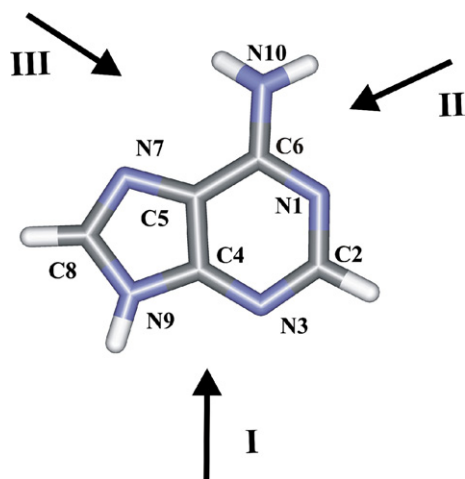


Fig. 1. Regions of adenine capable of forming two hydrogen bonds with a molecule of formic acid.

in the course of geometry optimization initialized from the optimal geometry for the neutral structure $A(FA)_2^{x/y}$, $MA(FA)_2^{I/II}$ or $A(FA)_3^{I/II/III}$. Electron attachment to particular complexes might induce proton transfer(s) (PT(s)) in some or all regions of adenine–formic acid cluster. These anionic structures are additionally labeled with a PT symbol appearing as a subscript to the region symbol where proton transfer takes place. For instance the fact that electron attachment to $A(FA)_2^{I/II}$ triggers proton transfer in both regions will be denoted with a $aA(FA)_2^{I_{PT}/II_{PT}}$ symbol.

The stabilization energies, E_{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. E_{stab} obtained in this way includes, thus, deformation energies of the monomers. These stabilization energies were corrected for basis set superposition error using the counterpoise correction [28,29]. In addition to the stabilization energies we calculated stabilization free energies, G_{stab} . The latter result from correcting the values of E_{stab} for zero-point vibration terms, thermal contributions to energy, the pV (expansion work) term, and the entropy terms. These terms were calculated in the rigid rotor-harmonic oscillator approximation for $T = 298$ K and $p = 1$ atm.

Electron vertical detachment energies 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 energies of the neutral and the anion at their corresponding fully relaxed structures is denoted AEA_G .

As our primary research method we applied density functional theory (DFT) with a Becke's three parameter hybrid functional (B3LYP) [30–32]. In the DFT approach, we employed the 6-31++G** basis set [33,34]. The usefulness of the B3LYP/6-31++G** method to describe intra- and intermolecular hydrogen bonds has been demonstrated through comparison with the second order Møller–Plesset (MP2) predictions [35]. 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 [36]. Moreover, in a series of studies concerning the binary complexes of nucleic acid bases with various proton donors we demonstrated that this level of theory seems to be reasonable for the description of electron attachment phenomenon in that type of systems [10–18].

Recently, we have demonstrated that the inaccuracies in VDEs calculated at the B3LYP level are related to the deficiencies of the B3LYP model to predict correct geometries for valence anions [18]. Therefore, besides the B3LYP estimated VDEs, the VDEs calculated at the MP2 level and using a correlation equation [18] that corrects for those deficiencies were compared.

It is known that the B3LYP method underestimates barriers for proton transfer [37] and thus lack of a barrier for the proton transfer reaction may be an artifact of the B3LYP method. For this reason, we performed additional geometry optimizations using the MP2 method and the MPW1K exchange–correlation functional, which was parameterized to reproduce barrier heights for chemical reactions [37]. In the MP2 calculations, we used aug-cc-pVDZ basis sets [38], while we settled for the 6-31++G** basis set in the MPW1K approach. Finally, to strengthen our conclusion, the CCSD/aug-cc-pVDZ (coupled-cluster theory with single and double excitations) calculations [39] were performed for the most stable structures of anions and neutrals of $A(FA)_2$. These single-point calculations were carried out at the optimal MP2/aug-cc-pVDZ geometries. The 1s orbitals of carbon, nitrogen, and oxygen were excluded from the MP2 and coupled-cluster treatments.

All MP2 and DFT calculations were carried out with the GAUSSIAN 03 [40] code. The single-point CCSD calculations were performed with the NWChem 4.7 software package [41] while the pictures of molecules and orbital were plotted with the Molden program [42].

3. Results and discussion

In the following we shall demonstrate that even though an isolated canonical adenine does not support bound valence anions [8], interaction with molecules having proton-donor properties makes the adenine anion adiabatically stable in the gas phase. Recently, we have shown such a profound increase in the stability of valence anion of adenine in its binary, i.e., 1:1 complexes with formic acid [18]. Here, we will show how the electron affinity evolves with increasing numbers of solvating formic acid molecules.

3.1. PES spectrum of the anionic complexes of adenine with formic acid

Two types of anions are commonly registered with the PES spectroscopy – valence and dipole bound anions. Due to large differences between the neutral and anionic geome-

tries as well as high electron binding energies (EBEs) the photoelectron spectra of the former represent broad bands appearing at relatively large EBEs. On the other hand, the PES spectra of dipole bound anions are dominated by narrow and sharp peaks at low electron binding energies. Hence, the spectra depicted in Fig. 2 are indicative of valence anions. These spectra cover a broad range of binding energies, 1.4–2.3 eV, with a plateau between 1.9 and 2.3 eV. Furthermore, one can conclude that a proton transfer (PT) process induced by electron attachment is probably coupled to the formation of the $A(FA)_2^-$ and $MA(FA)_2^-$ π^* -valence anions. Indeed, the PES spectra of anionic complexes, in which a NB interacts with a proton-donor molecule, an excess electron resides on a π^* orbital localized on the NB molecule and a PT triggered by an excess electron takes place, typically spread over a broad range of 1 eV, with the maximum intensity at EBE larger than 1.5 eV [10–18].

Mass signals corresponding to the anionic adenine:formic acid complexes with stoichiometry of 1:3 was also observed in our experiment. However, we were not able to record the PES spectrum for the $A(FA)_3^-$ tetramer due to the EBE's of this system being greater than 2.54 eV.

3.2. Structures and energetics of the neutral $A(FA)_n$ and $MA(FA)_2$ complexes

In order to explain the properties of $A(FA)_2^-$ and $A(FA)_3^-$ anions described in the previous section one should

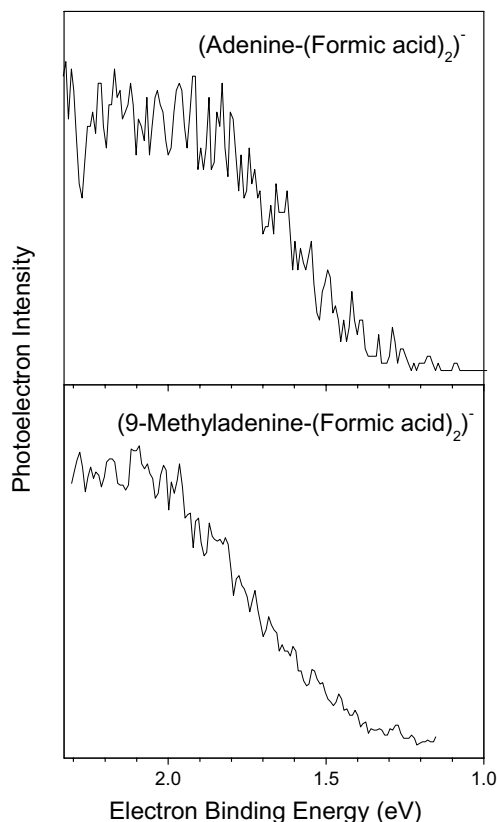


Fig. 2. Photoelectron spectra of adenine-(formic acid) $_2^-$ and 9-methyladenine-(formic acid) $_2^-$ measured with 2.54 eV photons.

first describe the neutral complexes since these species actually bind electrons (recall that isolated canonical adenine forms only unstable resonances in the gas phase [8]). In this section we, therefore, analyze the structure and energetics of the possible $A(FA)_n$ hydrogen-bonded complexes of 1:2 or 1:3 stoichiometries stabilized by cyclic hydrogen bonds (CHBs; see Fig. 3). We limited our discussion to CHBs since this type of hydrogen bonding assures the formation of the maximum number (two) of hydrogen bonds between A and a single FA molecule leading, thus, to the most stable structures which should dominate in the gas phase. Here, we also characterize the hydrogen-bonded complex between 9-methyladenine and formic acid – $MA(FA)_2$. MA is a better model of adenine occurring in DNA (in the nucleotide adenine is bound to the sugar residue by the C–N bond) and it represents a simpler system than adenine itself since region I (see Fig. 1) is blocked against the formation of a CHB.

The optimized geometries of systems considered in the current work are displayed in Fig. 3 and their energetic characteristics are gathered in Table 1. Out of three possible complexes, involving adenine, of 1:2 stoichiometry $A(FA)_2^{I/II}$ is the most stable trimer (see Table 1 and Fig. 3). It is worth noticing, that region I of adenine, comprising the most acidic N9 atom, is engaged in the formation of one of the CHB's in this system. As demonstrated by the E_{stab} and G_{stab} values (see Table 1), all complexes are quite stable with the stabilization energies and free energies spanning the range between –29.7 and –33.5 kcal/mol and between 3.4 and –7.1 kcal/mol, respectively. As expected, these values are ca. twice as much as the average stabilization effects calculated for the respective pair of the $A \cdots FA$ dimers that formally appear in a given trimer.

In contrast to the 1:2 complexes involving adenine, only one trimer stabilized by CHBs exists for 9-methyladenine. E_{stab} and G_{stab} estimated for $MA(FA)_2^{II/III}$ (see Fig. 3), –30.2 and –4.3 kcal/mol, respectively, are only slightly lar-

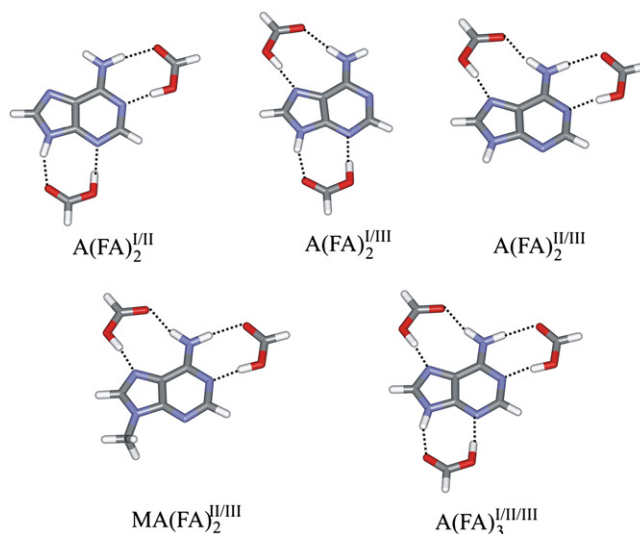


Fig. 3. The neutral $A(FA)_2$, $A(FA)_3$ and $MA(FA)_2$ complexes.

Table 1

Values of stabilization energy (E_{stab}) and stabilization free energy (G_{stab}) as well as their relative values (ΔE and ΔG) with respect to the most stable system for the neutral complexes of adenine with two molecules of formic acid calculated at the B3LYP/6-31++G** level

Complex	E_{stab}^a	ΔE	G_{stab}	ΔG
<i>Adenine-(formic acid)₂</i>				
A(FA) ₂ ^{II/III}	−29.7 (−28.2)	3.9	−3.4	3.7
A(FA) ₂ ^{I/III}	−32.7 (−31.2)	0.8	−6.5	0.6
A(FA) ₂ ^{I/II}	−33.5 (−31.9)	0.0	−7.1	0.0
<i>9-Methyladenine-(formic acid)₂</i>				
MA(FA) ₂ ^{II/III}	−30.2 (−28.7)	0.0	−4.3	0.0

All values given in kcal/mol.

^a Values corrected for BSSE given in parentheses.

ger than those calculated for the corresponding A(FA)₂^{II/III} complex (cf. Table 1). This small effect is probably related to the increase in the basicity of the respective N atoms in the regions II and III due to the presence of the methyl group in 9-methyladenine.

Since the isolated adenine possesses three regions capable of forming cyclic hydrogen bonds (see Fig. 1), three molecules of formic acid are sufficient to completely saturate adenine's capacity to form CHBs. The molecular structure of the A(FA)₃^{I/II/III} complex is depicted in Fig. 3. Its B3LYP/6-31++G** stabilization energy of −47.2 kcal/mol (of −45.0 kcal/mol while BSSE corrected) and free stabilization energy of −8.4 kcal/mol are ca. three times larger than the average value calculated for the three A···FA dimers [18] formally present in the A(FA)₃^{I/II/III} structure.

3.3. Thermodynamic stabilities, vertical detachment energies and proton transfer within the anionic A(FA)_n and MA(FA)_n complexes

Electron attachment to the A(FA)₂ or MA(FA)₂ complexes leads to the formation of adiabatically stable valence anions. Indeed, the adiabatic electron affinity is substantial and spans a range of 0.80–1.07 eV (see Table 2). A common feature of the anionic wave function is that the excess electron is localized on a π^* orbital of adenine (see Fig. 4) which is consistent with the shape of the PES spectra (see Fig. 2) and characteristic of valence bound anions. Moreover, electron attachment leads to the spontaneous proton transfer from the OH groups of the FA molecules to the proton-acceptor sites of A(MA) (see Fig. 4). Because both FA molecules coordinated to adenine undergo barrier-free PT it is rational to dub this process as a double barrier-free proton transfer (double-BFPT). Since the B3LYP method predicts kinetic barriers which are too low [37], we checked the occurrence of proton transfer using more reliable computational models. It turned out that the double-BFPT reactions are predicted to be barrier-free at the MPW1K level. Double-BFPT was also confirmed at the MP2 level for the anionic aA(FA)₂ and aMA(FA)₂ dimers.

Table 2

Values of relative electronic energy and free energy (ΔE and ΔG) with respect to the most stable anion and adiabatic electron affinity (AEA_G) and electron vertical detachment energy (VDE) for the anionic complexes of adenine with two formic acid molecules

Anion	ΔE	ΔG	AEA_G	VDE		
				B3LYP	MP2	Corr
<i>Adenine-(formic acid)₂</i>						
aA(FA) ₂ ^{II_{PT}/III_{PT}}	9.6	8.9	0.84	2.43	2.08	2.34
aA(FA) ₂ ^{I_{PT}/III_{PT}}	2.4	0.8	1.06	1.86 (2.05) ^a	1.93	1.94
aA(FA) ₂ ^{I_{PT}/II_{PT}}	0.0	0.0	1.07	2.72 (2.74) ^a	2.43	2.68
<i>9-Methyladenine-(formic acid)₂</i>						
aMA(FA) ₂ ^{II_{PT}/III_{PT}}	0.0	0.0	0.80	2.27	1.89	2.17

The values of ΔE , ΔG and VDE(B3LYP) were calculated at the B3LYP/6-31++G** level, values of VDE(MP2) were obtained at the MP2 level, whereas values of VDE(corr) were estimated using the correlation model [18]. ΔE and ΔG given in kcal/mol, AEA_G and VDE given in eV.

^a CCSD estimates for the MP2 geometries given in parentheses.

A driving force for the PT process is the stabilization of the excess electron on a π^* orbital of the anionic adenine. Contrary to the anionic complexes of pyrimidine bases with FA [13] all anionic A(FA)₂ and MA(FA)₂ complexes identified in the current work undergo double-BFPT. The excess electron is distributed evenly over the proton-acceptor centers in adenine (see Fig. 4). In pyrimidines, on the other hand, the excess electron distribution is highly asymmetric, which explains why only certain complexes of pyrimidines are susceptible to intermolecular PT.

Similarly, to relate the average stability of the neutral A···FA dimer moiety, formally present in a given trimer, and the stability of trimer itself, described in the previous section for the neutral complexes, AEA_G values were examined. The AEA_G values calculated for the 1:2 anionic complexes are approximately two times larger than the predicted for the respective pair of 1:1 anions. For the most stable anion, aA(FA)₂^{I_{PT}/II_{PT}}, its AEA_G is almost additive in terms of the AEA_G 's specific for the particular A···FA anionic dimers. In fact, the sum of the adiabatic electron affinities of the aA_{N3}^{N9}FA and aA_{N1}^{N10}FA dimers (atom symbols displayed in indices indicate the adenine nitrogen atoms involved in hydrogen bonding – proton-donor in superscript, proton-acceptor in subscript), formally present in the trimeric anion (see Fig. 4), is equal to 1.03 eV [18], whereas the AEA_G for aA(FA)₂^{I_{PT}/II_{PT}} assumes 1.07 eV (see Table 2). For the remaining cases the sum of AEA_G 's calculated for the individual dimers [18] is larger than the actual trimeric AEA_G by 0.20, 0.11, and 0.08 eV for aA(FA)₂^{I_{PT}/III_{PT}}, aA(FA)₂^{II_{PT}/III_{PT}}, and aMA(FA)₂^{II_{PT}/III_{PT}}, respectively.

This situation is different for the anionic tetramer – aA(FA)₃. Here we located two structures, aA(FA)₃^{I_{PT}/II/III} and aA(FA)₃^{I_{PT}/II_{PT}/III}, characterized by the AEA_G of 1.22 and 1.23 eV, respectively (see Table 3). The first one – a BFPT type anion – aA(FA)₃^{I_{PT}/II/III} is 3.1 kcal/mol less stable, in terms of electronic energy, than the second geometry, aA(FA)₃^{I_{PT}/II_{PT}/III}, where two protons

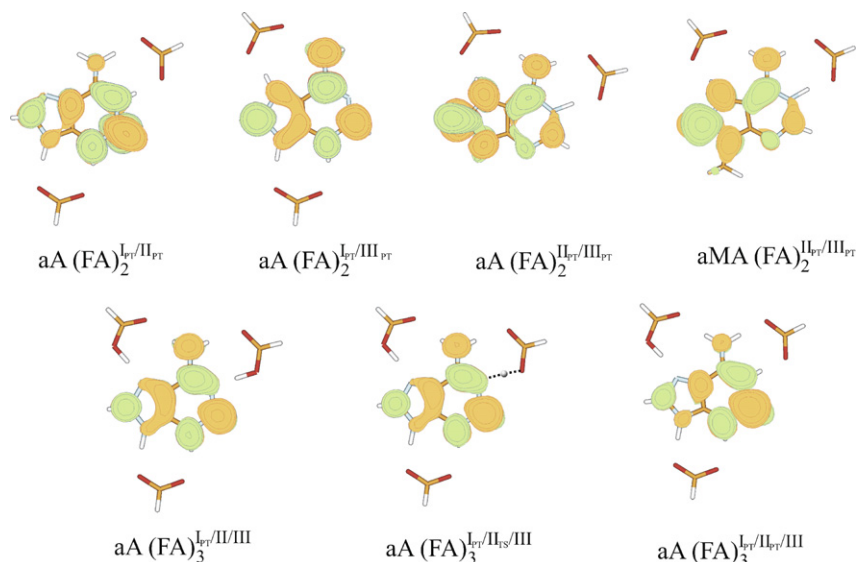


Fig. 4. The anionic AFA and MAFA complexes and their singly occupied molecular orbital plotted with a spacing $0.03 \text{ bohr}^{-3/2}$.

Table 3

Values of relative electronic energy and free energy (ΔE and ΔG) with respect to the most stable anion and adiabatic electron affinity (AEA_G) and electron vertical detachment energy (VDE) for the anionic complexes of adenine with three molecules of formic acid calculated at the B3LYP/6-31++G** level

Anion	ΔE	ΔG	AEA_G	VDE
$aA(FA)_3^{I_{PT}/II/III}$	3.1	0.3	1.22	1.85
$aA(FA)_3^{I_{PT}/II_{PT}/III}$	0.0	0.0	1.23	2.86

ΔE and ΔG in kcal/mol, AEA_G and VDE in eV.

are transferred to nitrogen atoms on adenine (see Table 3). Contrary to the 1:2 complexes the $aA(FA)_3^{I_{PT}/II_{PT}/III}$ structure is formed in the PT process accompanied by an activation barrier. However, the barrier separating the single- and double-PT anion amounts to only 0.05 kcal/mol in terms of electronic energy and disappears when the respective electronic stabilities are converted to the free energy scale. By geometry optimization we checked that a structure where three protons reside on adenine moiety is not a minimum on the potential energy surface of the tetrameric anion. In the double-PT anion, $aA(FA)_3^{I_{PT}/II_{PT}/III}$, the adenine moiety carries a positive charge. Therefore, transferring of a proton from the third FA molecule, leading to a hypothetical $aA(FA)_3^{I_{PT}/II_{PT}/III_{PT}}$, would require overcoming a significant barrier resulting from the electrostatic repulsion between protonated adenine and that proton. Moreover, the energetic effect related to the formation of the third N–H bond and further stabilization of the unpaired electron would have to counterbalance the repulsive potential together with the energy of O–H bond that has to be partially broken during the proton transfer, if the $aA(FA)_3^{I_{PT}/II_{PT}/III_{PT}}$ geometry was a minimum on the potential energy surface of the tetrameric anion. Apparently this is not the case since geometry optimizations starting from the $aA(FA)_3^{I_{PT}/II_{PT}/III_{PT}}$ structure always lead to the

$aA(FA)_3^{I_{PT}/II_{PT}/III}$ anion. All the above-mentioned facts suggest that in the gas phase the tetrameric anion exists as the $aA(FA)_3^{I_{PT}/II_{PT}/III}$ complex.

Finally, we compare the calculated vertical detachment energies with the experimental findings. The B3LYP estimated VDEs, the VDEs calculated at the MP2 level and using a correlation equation [18] that corrects for those deficiencies are displayed in Tables 2 for the $aA(FA)_2$ and $aMA(FA)_2$ anions. VDEs were also calculated at the CCSD level for the two lowest energy structures of the $aA(FA)_2$ complex (see Table 2). Comparing VDEs predicted by the DFT method and correlation equation (see Table 2) one may conclude that B3LYP fails to reproduce the MP2 geometry for $aA(FA)_2^{I_{PT}/III_{PT}}$. Indeed, the difference between VDE resulting from the B3LYP (incremented with -0.2 eV [2]) and the correlation model assumes ca. -0.3 eV . On the other hand, the MP2 method works better than B3LYP since the VDE(MP2) values incremented with $+0.1$ [2] deviate from those obtained at the CCSD level by -0.19 eV at most (see Table 2). Finally, VDEs predicted by the correlation model and the CCSD method agree to 0.1 eV.

Taking into account the VDEs values and thermodynamic stabilities gathered in Table 1 one can predict that the PES spectrum for the $A(FA)_2$ system should appear as a broad feature covering EBEs from the 2–3 eV region. Indeed, two anionic conformers that differ in the thermodynamic stability by 0.75 kcal/mol, $aA(FA)_2^{I_{PT}/III_{PT}}$ and $aA(FA)_2^{I_{PT}/II_{PT}}$ (see Table 2), should contribute to the spectrum. These two low energy conformers possess the VDE of 2.74 and 2.05 eV, respectively, at the CCSD level (see Table 2). Our computational results also explain the experimental finding concerning the $aA(FA)_3$ anion. Since in the gas phase only the $aA(FA)_3^{I_{PT}/II_{PT}/III}$ isomer characterized by the VDE of 2.86 eV exists (cf. the above discussion on the thermodynamic stabilities of the $aA(FA)_3^{I_{PT}/II/III}$ and

aA(FA)₃^{I_{PT}/II_{PT}/III} anions), we were not able to observe a PES signal of that anion using 2.54 eV photons. Lastly, we predict that the PES spectrum of the MA(FA)₂ anion will represent a broad feature with a maximum intensity localized around 2.17 eV (see VDE(corr) in Table 2). Indeed, the spectrum recorded for aMA(FA)₂ anions corresponds well to our computational result (see the lower part of Fig. 2). Thus, our computational findings justify the fact that the maximum intensity of the PES signal is reached earlier for the aA(FA)₂ than for aMA(FA)₂ anions (cf. the spectra depicted in Fig. 2). In fact, the main contribution to the PES signal displayed in the upper part of Fig. 2 (aA(FA)₂) comes from the less stable of two isomers present in the gas phase, aA(FA)₂^{I_{PT}/III_{PT}}, characterized by the VDE of ca. 2.0 eV (the second, more stable anion, aA(FA)₂^{I_{PT}/II_{PT}}, with the VDE of 2.74 eV (see Table 2) is out of the 2.54 eV range), whereas the signal showed in the lower part (aMA(FA)₂) of Fig. 2 is due to aMA(FA)₂^{II_{PT}/III_{PT}} having the VDE of ca. 2.2 eV.

4. Conclusions

The propensity of the neutral complexes between adenine and 9-methyladenine with formic acid in 1:2 and 1:3 stoichiometry to bind an excess electron was studied using photoelectron spectroscopy and quantum chemistry computational methods. This work extends our combined PES/computational studies carried out recently for the A/MA(FA) dimers [18] to the systems of more complex stoichiometry. In particular, we demonstrate how the simultaneous interactions of adenine regions comprising proton-donor/proton-acceptor sites with multiple FA molecules influence electron binding energy. The results of our studies can be summarized as follows:

1. Due to topological reasons adenine may bind up to three molecules of formic acid by cyclic hydrogen bonds whereas two FA molecules saturate MA capability to form CHBs. Hence, in the gaseous mixture of A(MA) and FA the clusters of 1:2 and 1:3 stoichiometry are possible. Indeed, as our calculations demonstrate the 1:2 complexes should be stable and the stabilization energies and free energies span, in the gas phase, a range of −28.2 to −31.9 kcal/mol and −3.4 to −7.1 kcal/mol, respectively. As expected, the 1:3 cluster is even more stable than the 1:2 complexes with E_{stab} and G_{stab} equal to −47.2 (to −45.0 kcal/mol while BSSE corrected) and −8.4 kcal/mol, respectively.
2. Even though an isolated canonical adenine does not support bound valence anions [8] interactions with the FA molecules makes its 1:2 and 1:3 anionic complexes adiabatically stable. An attachment of electron triggers double-BFPT, confirmed at the MPW1K level, in all the considered systems, which role is to stabilize an excess electron localized on the π^* orbital of A(MA). These anions are quite stable and their AEA_G fall in a range of 0.80–1.23 eV. It is worth noticing that AEA_G 's
3. The VDEs of the most stable 1:2 anions that dominate in the gaseous mixture of both A and MA with FA correspond very well to our PES spectra. Moreover, the fact that we were not able to detect photoelectrons coming out of the aA(FA)₃ anions is well explained by the calculated VDE of aA(FA)₃^{I_{PT}/II_{PT}/III} being 2.86 eV, which is larger than the energy of our photon source used in the PES experiment.
4. Purine molecules possess more proton-donor and -acceptor centers than pyrimidines and may therefore be involved in more hydrogen bonding interactions. Moreover, the findings of the current work show unequivocally that the more species which are involved in hydrogen bonding with a nucleobase, the more stable is its valence anion. Therefore, we suggest that the interaction between purines bound in DNA and various species from the physiological environment (water, histones, repair or replication enzymes, etc.) might counterbalance the larger electron affinities of free pyrimidines and as a consequence both types of nucleic bases could play a crucial role in DNA damage induced by low energy electrons.

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