Uracil−Adenine Dimer Connected by an Excess Electron

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In this work we consider a new form of the uracil−adenine dimer anion (AU⁻) where the two monomers are connected by an excess electron suspended between them. An equilibrium structures of the anion was predicted using uncorrelated and correlated ab initio quantum-mechanical calculations. An AU⁻ anion of this kind can be formed in the gas phase by an attachment of an adenine molecule to a dipole-bound electron of uracil. Removal of the excess electron from the anion and optimization of the geometry of the neutral cluster starting from the geometry of the anion initially leads to a significant increase of the separation between the bases, but eventually the optimization converges to an H-bonded structure very dissimilar from the anion structure.

1. Introduction

The existence of the dipole-bound (DB) anion of uracil was first predicted theoretically in our group[1] and subsequently detected in the gas-phase experiments by the groups of Schermann[2] and Bowen.[3] The calculations performed to search for stable anions of adenine[4] rendered a near zero, but positive, electron affinity of the major N(9)H tautomer of this system. The predicted electron affinity of the N(7)H tautomer that has not been detected in the gas phase, but coexists with the N(9)H tautomer in polar solutions, was 0.12 eV. In both cases the excess electron was bonded to the dipole field of the adenine molecule. No stable "valence" anionic states of adenine were found in the calculations.

Though the DB anion seems to be the only anionic form possible for an isolated uracil molecule, dimers and hydrates of this and other nucleic acid bases may also form covalent anions. For example, the study of the adenine−thymine (A−T) canonical base pair anion with the use of ab initio calculations[5] resulted in the prediction that the A−T covalent anion has a positive vertical electron detachment energy (VDE), indicating its vertical stability. However, as the calculations also showed, the A−T base pair is not an effective trap of excess electrons because its adiabatic electron affinity is negative.

Recently a somewhat different behavior in attaching an excess electron by cytosine and uracil has been described in a photodetachment−photoelectron (PDPE) study by Schiedt et al.[6] They found two peaks in the PDPE spectrum of cytosine anions, a sharp one at 85 ± 8 meV and a wider, significantly less intense one at 230 meV. These peaks were assigned to amino−oxy and amino−oxo DB anions, respectively. Following this finding, we performed correlated, ab initio calculations of three tautomers of cytosine and the corresponding anions.[7] In addition to three DB anions of the amino−oxo and amino−oxy tautomers (two rotamers) with the adiabatic electron affinities of 58, 22, and 6 meV, respectively, the calculations described a metastable

valence-bound (VB) anion of the amino−oxo tautomer with the vertical electron detachment energy (VDE) of 102 meV. Following our study, the cytosine anions were also investigated with ab initio calculations by Dolgounitcheva et al.[8] and their results were similar to ours with one exception. For the VB amino−oxo anion due to employing a larger basis set (i.e., 6-311++G(2df,2p) vs 6-31++G** used in our calculations) they obtained the VDE value of 271 meV. Clearly, to adequately describe the electron correlation contributions to the binding of a VB excess electron one needs to use a much larger basis set than needed to describe a DB electron whose binding is dominated by electrostatic interactions. Both Dolgounitcheva et al. and our works were concluded with tentatively assigning the 85 and 230 meV experimental peaks to the DB and VD anions of the amino−oxo tautomer, respectively. It is worth noticing that the amino−oxy and not the amino−oxo is the most thermodynamically stable form of cytosine in the gas phase. What the calculations did not explain was how the metastable VB cytosine anion was formed in the gas phase.

In the calculations of DB anions of adenine−water clusters, [adenine−(water)$_N$], $N = 1-3$,[9] an interesting configuration landscape has been predicted for these systems. Because the DB electron affinity of the main tautomer of adenine and the DB electron affinity of water are practically zero, only if the water dipole(s) align(s) with the adenine dipole can the adenine ability to dipole-attach an excess electron be sufficiently amplified to enable formation of a DB anion.

Finally in the more recent calculations,[10] we considered a new form of the uracil dimer anion (U$_2$⁻) with an excess electron suspended between the two uracil molecules and providing sufficient bonding between them to stabilize the dimer in a local minimum on its potential energy surface (PES) (we called the bonding an "e-bond" due to its similarity to the H-bond). A possible formation mechanism of such an anion could involve an attachment of a neutral uracil molecule to the DB electron of the uracil anion. In the resulting system, the two uracil molecules are positioned at opposite sides of the very diffuse DB electron with their dipoles antiparallel.

In the present work we have performed ab initio calculations

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to determine whether a purine−pyrimidine base pair can form an e-bonded anion. Because purine−pyrimidine base pairs are building blocks of the RNA and DNA double helices, electron trapping by the purine−pyrimidine pairs is certainly more biologically relevant than the trapping by the uracil−uracil pair. Also the formation of e-links between the purine−pyrimidine bases may add new structural elements to the DNA and RNA helices penetrated by excess electrons.

As a model system for the study we used the adenine−uracil (AU) dimer, because, as mentioned before, the electron attachment capabilities of the two individual bases have been elucidated in our previous calculations. In the formation of the e-bonded AU dimer, the uracil molecule is the species that would first bind an excess electron and form a DB anion. Than the adenine molecule would approach the electron confined into a diffuse DB orbital of uracil and form an e-bonded cluster. A mechanism starting with formation of a DB adenine anion followed by an attachment of a uracil molecule to the adenine DB excess electron is also possible. However, because, as the previous calculations showed, the DB anion of the primary adenine tautomer is only marginally stable, such a mechanism is less likely.

There are two questions that we have attempted to answer in this work. The first concerns the structure and the vertical and the adiabatic stability of the e-bonded AU dimer, and the second concerns the structural rearrangement that occurs in the dimer when the excess electron is removed from the system. The ab initio calculations that we have performed provided answers to the questions.

2. Calculations and Discussion

All the calculations in this work have been done using the Gaussian98 program package.[11] The purpose of the first series of calculations was to search for equilibrium structures of e-bonded AU dimers. We initiated the searches with a configurations consisting of a uracil DB anion and an adenine molecule placed several ångstroms away from the uracil at the opposite side of the diffuse uracil DB excess electron. In these starting configurations the positive pole of the adenine molecule was directed at the excess electron. Three different orientations were considered, two almost planer differing by a 180° rotation of the adenine molecule around the uracil dipole, and a configuration where the uracil ring was perpendicular to the adenine ring.

First, the geometry optimizations were performed with the UHF (spin-unrestricted Hartree−Fock) method and with the basis set consisting of the standard 6-31++G**(5d) basis augmented with six diffuse Gaussian sp-shells with the exponents equal to 0.01, 0.002, 0.0004, 0.00008, 0.000016, and 0.0000032, and a p-shell with the exponent 0.036. These additional orbitals were placed at the hydrogen atom located closest to the positive direction of the molecular dipole of uracil. The purpose of using very diffuse orbitals in the basis was not only to describe the expected very diffuse state of the excess electron trapped between the two base molecules but also to allow the electron to escape from the system, if this would lower the system's total energy. The augmented basis set will be called 6-31++G**X in the discussion that follows.

The use of the UHF method in geometry optimizations of the e-bonded AU anions is justified by a significant electrostatic component in the interaction of both A and U with the excess electron (charge−dipole interaction). However, the dispersion forces may also play a significant role. Thus, a series of
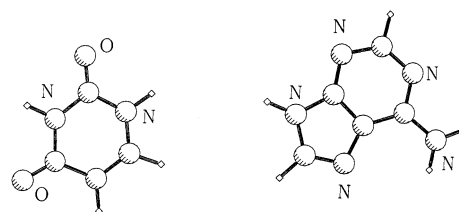

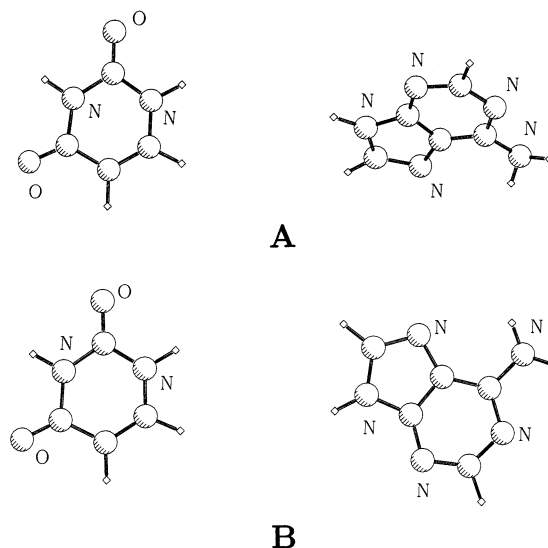**Figure 1.** UHF/6-31++G**X structure of the e-bonded adenine−uracil anion.

A

B

Figure 2. UMP2/6-31++G**X structures of the e-bonded adenine−uracil anion.
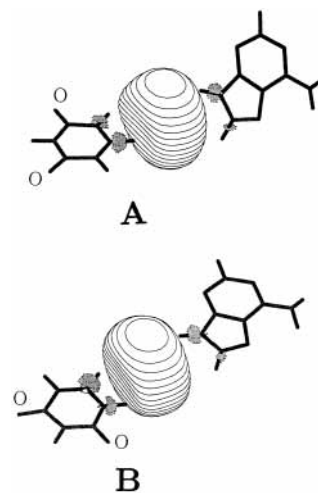

A

B

Figure 3. The orbitals occupied by the excess electrons in the e-bonded A and B adenine−uracil anions. The orbitals are drawn with the contour value of 0.025.

calculations was also performed to locate equilibrium geometries of the e-bonded AU anion at the UMP2/6-31++G**X level of theory.

All UHF/6-31++G**X searches for an equilibrium structure of the AU e-bonded anion converged to a single geometry shown in Figure 1. The structure is nearly planar with the uracil and adenine dipoles pointing at each other and at the excess electron suspended between them. This type of configuration is very different from any equilibrium H-bonded configuration of the neutral AU dimer. The UMP2/6-31++G** geometry optimizations converged to two structures shown in Figure 2 and denoted as A and B. The structures differ from the UHF structure in two respects. The first difference is the relative angular

Uracil−Adenine Dimer

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TABLE 1: Total Energies (hartrees) of the e-Bonded Adenine−Uracil Anion and the Corresponding Neutral System, and the Vertical and Adiabatic Electron Detachment Energies (VDE and ADE) (meV s)[a]

method	anion//anion	neutral//anion	VDE	neutral//neutral	ADE
HF//HF	−877.047023	−877.040905	166	−877.060340	−362
MP2//HF	−879.680726	−879.672071	236	−879.697717	−462
ZPE(HF)	0.215484			0.217395	
MP2 + ZPE	−879.465242			−879.480322	−410
HOMO/LUMO	−0.00901	−0.00377		−0.00022	

[a] The structure of the anion was determined at the UHF/6-31++G**X level of theory. "Neutral//anion" notation indicates that the energy of the neutral dimer was calculated at the equilibrium geometry of the anion. The 6-31++G**X basis was used in all calculations. Only the valence electron correlation was included.

TABLE 2: MP2/6-31++GX VDE Calculations of the e-Bonded Adenine−Uracil Anions Whose Structures Were Determined at the UMP2/6-31++G**X Level of Theory[a]**

| system	anion//anion	neutral//anion	VDE
A	−877.047023	−877.040905	362
B	−879.680726	−879.672071	360

[a] Total energies in hartrees, VDE's in meV s. "Neutral//anion" denotes that the energy of the neutral dimer was calculated at the equilibrium geometry of the anion. Only the valence electron correlation was included.

orientation of the A and U molecules with respect to each other. Although in the UHF structure the two monomers are coplanar, there is significant deviation from the planarity in the A structure. Second, the monomers in the UMP2 structures are much closer to each other than in the UHF structure. Although in the UHF structure the two closest atoms of the two monomers are located 6.78 Å apart, the distance decreases to 4.67 and 4.48 Å in A and B, respectively. This clearly shows the imortance of the dispersion interaction between A and U and the excess electron in the e-bonded AU anion. It also indicates that the UHF geometry optimization is unreliable for the class of anions studied in this work.

In Figure 3 we present the UHF orbitals occupied by the excess electrons in the A and B anions (the HOMOs) taken from the UMP2 calculations performed at their respective UMP2 equilibrium geometries. They clearly show that in both systems the excess electron is located between the two monomers and both systems can be described as e-bonded anions.

The aim of the next series of calculations was to determine the vertical detachment energies (VDE) of the anions. The MP2/6-31++G**X level of the theory was used and the calculations for the anion and the neutral system were first done for the anion located at the UHF/6-31++G**X level of theory. For this anion we also calculated the harmonic UHF/6-31++G**X IR frequencies to confirm that the structure found corresponds to a stationary point on the anion PES. The frequencies were also used to calculate the zero-point vibrational energy (ZPE) of the anion. All the calculated energies for the anion and the neutral system and the values of the vertical electron detachment energy are shown in Table 1. Next, VDE calculations were also done for the A and B anions whose equilibrium structures were located at the UMP2/6-31++G**X level of theory, and the results are shown in Table 2.

When the energy results are examined, it becomes clear that it takes considerable energy to remove the excess electron from the anion without relaxing its structure. The VDE values of 236 meV for the anion, whose structure was determined at the UHF level of theory, and 362 and 360 meV for the anions with UMP2-determined structures indicate that the interaction of the two monomers with the excess electron in the anion is relatively strong. To further examine this interaction, we performed calculations to determine the dissociation energy of splitting
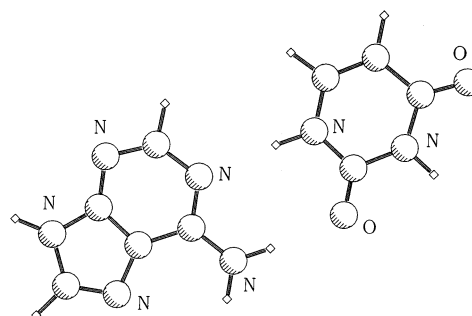
Figure 4. RHF/6-31++G**X structure of the neutral adenine−uracil dimer obtained in the geometry optimization initiated with the UHF geometry of the e-bonded anion.

the anion into a neutral adenine molecule and a uracil DB anion. The analysis was performed for the MP2 equilibrium structure of the AU dimer anion B (similar calculations for anion A should yield a very close result). In these calculations we first computed MP2 energies of the dissociation products at their respective MP2/6-31++G**X and MP2/6-31++G** geometries for the adenine neutral molecule and the uracil dipole-bound anion, respectively, using the basis set of the dimer. Next these energies were subtracted from the MP2/6-31++G**X energy of the AU anion. The calculations rendered the interaction energy of 5.3 kcal/mol, showing that it would take a considerable amount of energy, similar to the energy of an average hydrogen bond, to dissociate the AU e-bonded dimer into the lowest energy products.

There is one feature that should be noted in the results presented in Table 2. It is that the total MP2 energies of the A and B anions are very similar despite a noticeable difference in the degree of nonplanarity in their structures. Clearly, the rotation of the monomers around the e-bond is almost free and there seems to be no tendency for delocalization of the π-electrons between A and U, which would favor the planar anion structure. Such delocalization is disabled by the σ excess electron of the e-bond.

The aim of the last series of calculations was to determine what happens when the excess electron is removed from the anion. To determine that, we performed a RHF/6-31++G**X geometry optimization of the neutral dimer, initiating it from the anion UHF equilibrium geometry. In the initial stage of the calculation the uracil−adenine distance increased considerably, leading almost to dissociation of the complex. This was clearly a result of the adenine and uracil dipoles pointing at each other in the initial structure of the e-bonded dimer used as the starting point for the optimization. However, after several additional steps, the geometry optimization converged to an equilibrium structure of the neutral dimer with a much shorter uracil−adrenine distance and with the two monomers connected via H-bonds. The equilibrium geometry of the neutral AU dimer obtained in the calculation is shown in Figure 4. At that geometry we calculated the MP2/6-31++G**X and ZPE

energies of the dimer to determine whether it is more or less stable than the e-bonded anion. The results showed that the anion MP2 + ZPE energy is by 0.410 eV higher than the energy of the neutral dimer (the value of the adiabatic electron detachment energy (ADE) in Table 1). Thus, though vertically stable, the e-bonded AU dimer anion is an adiabatically unstable system. However, the strong interaction of the two monomers with the excess electron in the anion indicates that the local minimum on the PES corresponding to the anion should have a considerable depth and, thus, the e-bonded anion may be a long-lived species. Eventually, however, the anion will dissociate to a neutral H-bonded dimer and a free electron or undergo a transformation to a dimer anion with either a covalently attached or a DB excess electron. It is also apparent that, only if an excess electron is suspended between adenine and uracil, the local minimum (minima) appears on the anion PES. The minimum corresponding to the e-bonded anion structure(s) is absent in the PES of the neutral dimer.

3. Conclusions

The theoretical calculations performed in this work revealed an interesting metastable form of the adenine−uracil dimer anion. In the anion the excess electron is solvated from opposite sides by the two base molecules. The dipoles of the two bases point at the excess electron and are antiparallel. For the neutral adenine−uracil dimer such an orientation would be very unfavorable. The formation mechanism of the anion could proceed with a DB attachment of an excess electron to a uracil monomer first, and with subsequent attachment of an adenine molecule at the opposite side of the DB excess electron with respect to the position of the uracil. The electrostatic and dispersion forces primarily contribute to the interaction of the adenine and uracil molecules with the excess electron suspended between them. Including the electron correlation effects in the calculations of the equilibrium structure of the anion, and, thus, accounting for the dispersion interactions, result in a considerable shortening of the e-bond in the AU anion.

The e-bonded adenine−uracil dimer anion corresponds to a local minimum on the PES of the dimer anion. The calculations showed that it would take a considerable amount of energy to dissociate the anion into a neutral adenine molecule and a DB uracil anion, i.e., into the lowest energy products. Although we have not explored the PES around the minimum, the strength of the interaction of the adenine and uracil molecules with the excess electron and the structure of the e-bond anion, which is significantly different from any local minimum on the PES of the neutral dimer, suggest that the minimum has probably a

considerable depth and the e-bonded anion is a long-lived species. The calculations also showed that the rotation of the monomers around the e-bond in the anion is almost free.

In our recent work[12] we showed evidence of existence of an e-bonded anion the hydrogen fluoride trimer in the gas phase. Thus, it is possible that e-bonded adenine−uracil anions can also be observed.

Trapping electrons in e-bonded anions of pyrimidine−purine base dimers can potentially be a biologically significant event. Such trapping may not only affect the DNA electron conductivity but also produce additional binding links between purine−pyrimidine base pairs in DNA and RNA when excess electrons penetrate these systems.

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