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Two Uracil Molecules Connected by an Excess Electron

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In this work we considered a new form of the uracil dimer anion (U_2^-). In this system the excess electron is suspended between two uracil molecules and provides sufficient bonding between them to stabilize the dimer in a local minimum on its potential energy surface. Ab initio calculations are employed to describe the system. Anions of the nucleic acid bases of this kind can be formed in two steps. First a dipole-bound anion is formed by a molecule of one of the bases. Then a molecule of the second base attaches to the diffuse dipole-bound electron at the opposite side with respect to the first base. Removal of the excess electron leads to a significant change of the structure of the complex. Its geometry optimization initiated with the anion geometry converges to a conventional hydrogen-bonded dimer with a total energy lower than the energy of the anion. Thus the two uracils connected by a suspended excess electron in the middle are a metastable system.

1. Introduction

The existence of the dipole-bound anion of uracil was first predicted theoretically in our group[1] and subsequently detected in gas phase experiments by the groups of Schermann[2] and Bowen.[3] While the dipole-bound electron attachment seems to be the only anionic form possible for isolated nucleic acid bases, dimers of the bases may also form covalent anions. In our recent theoretical ab initio calculations we investigated the ability of the hydrogen-bonded uracil dimer to form stable anions and we described both dipole-bound and covalent anions of this system.[4] We determined that (i) at least three of the hydrogen-bonded conformers of the uracil dimer can form stable dipole-bound anions with excess electrons, (ii) the uracil dimer can form a covalent anion that has a structure dissimilar to the structures of the neutral dimer, (iii) in the covalent uracil dimer anion the excess electron is localized on one of the uracil molecules and this molecule shows an out-of-plane distortion, and (iv) the covalent uracil dimer anion is stable with respect to a vertical electron detachment, but at the level of theory (MP2) used in the calculations is marginally unstable with respect to an adiabatic electron detachment.

While the realization that isolated molecules of nucleic acid bases form dipole-bound anions answered some questions, some more recent experiments concerning anion formation of hydrated molecules of nucleic acid bases[5] have raised some new intriguing ones. Those experiments showed that hydration dramatically changes the nature of the uracil anion. It takes only one water molecule to transform the very weak dipole-bound uracil anion to a more stable conventional covalent anion. Although, as the calculations showed,[6,7] the excess electron does not delocalize into the water molecule, the presence of this molecule is crucial in stabilizing the electron in the valence region of the uracil molecule. The role of the second uracil molecule in the uracil dimer covalent anion is similar to the role of water in the covalent uracil•water anion. Here also, the spectator uracil molecule stabilizes the excess electron without accepting it into its valence region.

Besides dipole-bound and covalent anions of the uracil dimer, there is still another way an excess electron can be captured by two uracils. In our recent work concerning anions of complexes consisting of three hydrogen fluoride molecules, we described an interesting new type of anions where the diffuse electron have not one, as in the dipole-bound anions, but two or more contact points with the molecular subunits of the complex.[8] The subunits are connected only by their attraction to the excess electron. The formation of such anions can proceed in two steps. First a dipole-bound anion is formed by one of the subunits of the complex. Next the second subunit (or the remaining subunits if there is more than one of them) attaches to the dipole-bound electron on its opposite side from the site where the first unit is connected. In the resulting system the excess electron is suspended between two or more closed-shell molecular fragments. In our previous work, where we considered such anions formed by uracil with the H_2O and HF molecules,[10] we called these systems “anions with internally suspended electrons”, or AISE for short. The presence of the electron facilitates a weak bonding between the fragments. For this reason and due to some similarity of this bonding to the H-bonding, we called the interaction in AISEs an e-bond.

AISEs belong to a broader category of anions called “solvated electrons”, since in these systems the excess electron exists inside the cluster and not on its surface, as in the dipole-bound anions. Our calculations of AISEs of HF clusters[8] and uracil•H_2O and uracil•HF clusters[10] showed that these anions have higher energy than the dipole-bound anions of the clusters. Thus their stability, if they are formed in the gas phase, will be probably due to kinetic factors. In our recent work on hydrogen fluoride trimer anions,[8] which combined photoelectron spectroscopy (PES) experiments of Bowen and co-workers with the theoretical calculations performed by Gutowski and our group, we presented evidence that the dipole-bound anion of this system can coexist with the AISE in the gas phase despite its total internal energy being significantly higher than the energy of the dipole-bound anion. We presented arguments showing that this can happen at elevated temperatures due to the entropy factors. Another reason may be related to the experimental

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conditions of the anion formation process. If the dipole-bound anions of the monomers (or, in general, subunits of the cluster) are formed first, there is a possibility that the AISEs are formed next in the reaction of the anions with the monomers that still remain neutral.

AISEs are systems similar to the HF dimer anion called "solvated electron" and described by Gutowski and Skurski.[9] However, while in the AISEs one of the monomers is a polar system that forms a dipole-bound anion with the excess electron in the first phase of the AISE formation process, the mechanism of trapping an excess electron in systems such as the "solvated electron" HF dimer involves surrounding a localized excess electron by polar molecules that may not have large enough dipoles for each of them to form a dipole-bound anion.

Since most nucleic acid bases form dipole-bound anions and those that do not still have rather significant dipole moments, a possibility of AISE formation exists for these systems. In the present work we have tested this possibility in the model system consisting of two uracil molecules. The study complements our previous work where we calculated the dipole-bound and covalent anions of this system. In the first part of the paper we describe the approach used in the calculations. In the second part we discuss the results and their relation to the previous calculations.

2. Calculations and Discussion

The questions which we attempt to answer in this work are the following:

(i) Is there a local minimum on the potential energy surface of the uracil·uracil (U_2) anion that corresponds to AISE?

(ii) What is the vertical electron detachment energy (VDE) of the AISE of U_2? Since this quantity can be measured using the PES experiment, its theoretical prediction could provide useful information to those who would attempt the experiment.

To provide answers to the above questions, a series of calculations were performed with the use of the Gaussian 98 quantum-chemical program package.[11] The results are described below.

The purpose of the first series of calculations was to search for the equilibrium AISE structure of the U_2 dimer. We initiated the search with a configuration consisting of a uracil dipole-bound anion and a second uracil molecule placed several angstroms from the first uracil on the opposite side of the diffuse dipole-bound excess electron. In this starting configuration the positive pole of the second molecule was directed at the excess electron. The geometry optimizations were performed with the MP2 method and with the basis set consisting of the standard 6-31++G** basis augmented with six diffuse Gaussian sp-shells with exponents equal to 0.01, 0.002, 0.0004, 0.000 08, 0.000 016, and 0.000 003 2, and a p-shell with exponent 0.036. These additional orbitals were placed at the hydrogen atom located closest to the positive direction of the molecular dipole. By including Gaussians with very small exponents in the basis, we allowed the excess electron to escape from the system if such a process would lower the system's total energy. Thus we eliminated the possibility that the excess electron stayed confined to the system due to a too-confining orbital basis, and not due to the anion energy being lower than the energy of the neutral. The augmented set will be denoted 6-31++G**X in the discussion that follows.

Although the electrostatic interaction (charge−dipole) should primarily be responsible for the stability of AISE, the dispersion forces should also play a significant role. Thus the use of a method that adequately describes these interactions was essential to obtain a reliable AISE structure of U_2. The need for describing the dispersion interactions in optimizations of AISE structures became apparent in our studies of the HF-trimer AISEs[8] and of the uracil·HF and uracil·H_2O AISEs.[10] The converged equilibrium structure of U_2 AISE is shown in Figure 1 along with a picture showing the orbital occupied by the excess electron in this system. One notices that the two uracils are coplanar, they are separated by a distance of nearly 4.5 Å, and the diffuse excess electron is localized in the gap between them forming an e-bond. The intermolecular distance in U_2 AISE is more than 2 times larger than the intermolecular distance in the neutral uracil dimer (for example, in the configuration shown in Figure 2 and discussed later in the text the distance between the two uracil molecules is about 2 Å).

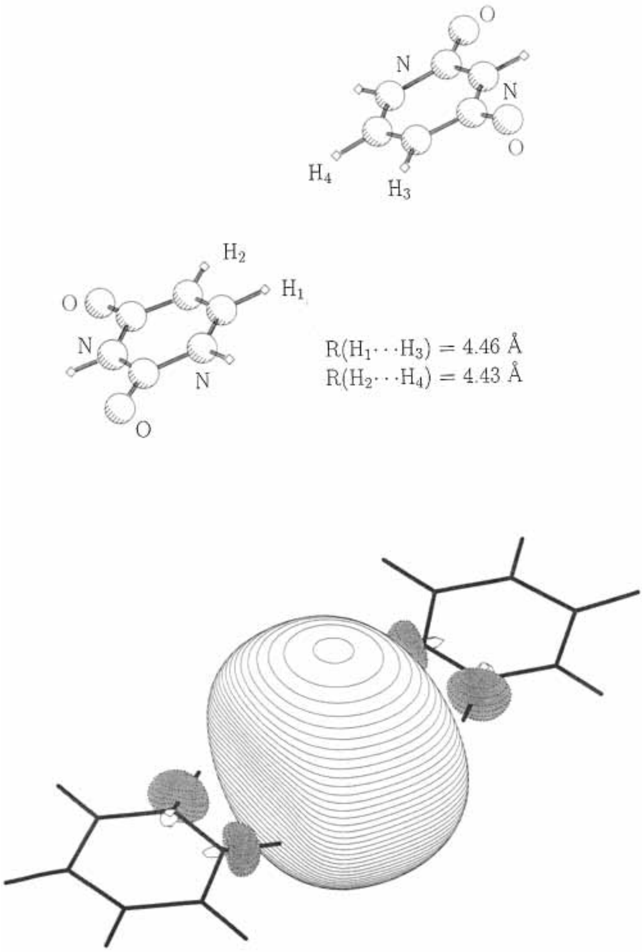

Figure 1. MP2/6-31++G**X structure of the U_2 AISE and the orbital occupied by the excess electron in this system.

The purpose of the next calculation was to determine the vertical detachment energy (VDE) of the U_2 AISE. In the calculation we used the MP2 anion geometry obtained in the previous step, and at that geometry we determined the MP2/6-31++G**X energy of the neutral system. The results of the anion/neutral calculations are shown in Table 1. The VDE value of 0.47 eV shown there indicates that the interaction of the two uracils with the excess electron is relatively strong. To further examine this interaction, we performed calculations to determine the dissociation energy of the U_2 AISE corresponding to splitting the system into a neutral uracil molecule and a uracil dipole-bound anion. In these calculations we first computed MP2 energies of the dissociation products at their respective MP2/6-31++G**X geometries using the 6-31++G**X basis set of

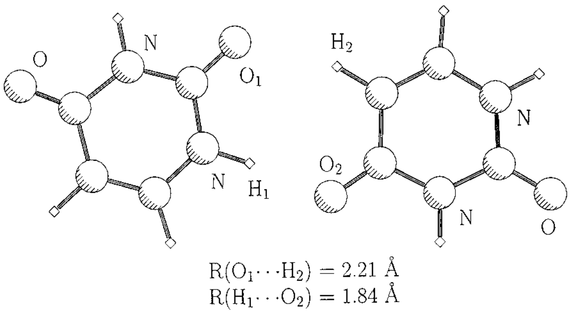

Figure 2. MP2/6-31++G**X equilibrium structure of the U_2 complex obtained in the geometry optimization initiated with the AISE equilibrium geometry.

TABLE 1: Calculations of the Vertical Electron Detachment Energy (VDE) of the AISE of the Uracil·Uracil Complex[a]

method	anion	neutral//anion[b]	VDE
HF//MP2[c]	−824.980 578	−824.966 241	0.39
HOMO/LUMO	−0.021 85	−0.008 31	
MP2/MP2	−827.372 896	−827.355 596	0.47

method	neutral//neutral[d]
MP2//MP2	−827.380 575

[a] Calculations performed with the 6-31++G**X basis set. Total and HOMO/LUMO energies in hartrees; VDE in EV. Only the valence electron correlation has been included in the calculations. [b] Calculations performed at the equilibrium anion geometry. [c] The notation denotes the level of theory used in the calculation//the level of theory used in calculating the structure. [d] Calculations performed at the equilibrium geometry of the neutral complex obtained in the geometry optimization initiated with the equilibrium geometry of the anion.

U_2 AISE. We obtained the energies of −413.679 282 and −413.681 526 hartrees for the neutral uracil molecule and the uracil dipole-bound anion, respectively. Next, these energies were subtracted from the MP2/6-31++G**X energy of the U_2 AISE of −827.372 896 hartrees to determine the dissociation energy and the value of 0.33 eV was obtained. Since we used the same basis set (i.e., the basis of the dimer) to calculate all three energies, the basis set superposition error (BSSE) in the determined dissociation energy should significantly reduced. The obtained dissociation energy value indicates that it would take a considerable amount of energy, almost equal to the energy of two average hydrogen bonds, to dissociate the U_2 AISE. This shows that the intermolecular interaction is strong in this system.

The following calculation showed us what happens when the excess electron is removed from the anion. To determine that, we performed an MP2/6-31++G**X geometry optimization of the neutral dimer, initiating it from the equilibrium geometry of the AISE. The calculation converged to the structure shown in Figure 2. Clearly the structure, though also planar, is very different from the AISE structure, showing again the significant role that the presence of the excess electron has on the structure of the dimer. It is apparent that, only if an excess electron is suspended between the two uracil monomers, the AISE local minimum appears on the potential energy surface. The MP2 energy of the neutral U_2 complex corresponding to the energy minima found in the calculation is shown in Table 1. This energy is noticeably lower than the energies of the AISE. Thus it is clear that the U_2 AISE is a metastable system that has finite lifetime, and upon interconversion, it should transform to either the neutral complex and a free electron or to another type of dimer anion (e.g., dipole-bound anion or covalent anion).

3. Conclusions

The theoretical calculations performed in this work have revealed an interesting metastable form of the uracil dimer anion. In the anion the excess electron is solvated by two uracil molecules that are not attached to each other and whose dipoles are antiparallel. The uracil dimer would not favor such an orientation as a neutral system. Similar systems can be formed by pairs of other nucleic acid molecules provided that at least one of the bases in the pair forms a stable dipole-bound anion and the other has a nonzero dipole allowing it to attach to the dipole-bound excess electron of the first base. The electrostatic and dispersion forces primarily contribute to the interaction of the two uracils with the excess electron suspended between them. It is perhaps appropriate to call this interaction an e-bond due to its similarity to the H-bond.

e-Bonded uracil dimer corresponds to a local minimum on the potential energy surface of the anion of the complex. The calculation showed that it would take a considerable amount of energy to dissociate the system into products, i.e., a neutral uracil molecule and a dipole-bound uracil anion. Although we have not explored the potential energy surface around the minimum, the strength of the interaction of the two uracil molecules with the excess electron and their orientation, which is significantly different from any local minimum on the potential energy surface of the neutral uracil dimer, suggest that the minimum probably has a considerable depth. However, as the calculation also showed, the adduct has a higher energy than the neutral complex at its geometry obtained from the optimization initiated with the anion geometry as the initial guess. This makes the U_2 AISE a metastable system. As we showed before, AISE of hydrogen fluoride trimer, which according to the calculations is also a metastable system, forms under certain conditions in the PSE experiment.[8] Thus, observation of the AISE of U_2 is also a possibility.

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