Anions of the Hydrogen-Bonded Uracil Dimer. *Ab Initio* Theoretical Study

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Theoretical ab initio calculations have been performed to determine the ability of the hydrogen-bonded uracil dimer to form stable anions. The major conclusions of this work are (i) three of the hydrogen-bonded conformers of the uracil dimer can form stable dipole-bound anions with excess electrons; (ii) uracil dimer can form a covalent anion that has a structure dissimilar from 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; (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 the anion is marginally unstable with respect to an adiabatic electron detachment.

1. Introduction

The theoretical and experimental determination of the electron affinities (EA) of nucleic acid bases (NAB) has proven to be a difficult problem. The experimental work on this subject has proceeded along two different directions. Chen and co-workers[1] used measurements of reversible reduction potentials by cyclic reduction voltommetry in DMSO solutions to study NAB anions. Bowen and co-workers[2] used photoelectron spectroscopy (PES) to study electron affinities of NABs in the gas phase. Photodetachment−photolelectron spectroscopy was also recently used by Schiedt et al.[3] to study electron affinities of the pyrimidine NAB's and their complexes with water. A gas-phase study of NAB anions was also carried out by Schermann and co-workers[8,9] using Rydberg electron transfer (RET) and field-detachment spectroscopy. The gas-phase studies have been directly related to the theoretically calculated electron affinities including the values obtained by our group[4−7] using various quantum-mechanical ab initio methods, because both the theoretical calculations and the experimental measurements concerned NAB molecules in isolation.

On the basis of the calculations, which we and others[10] have done, and on the basis of the recent experiments in the gas phase of Schermann et al.,[8,9] Bowen et al.,[2] and Schiedt et al.,[3] we can conclude that while the dipole-bound (DB) anions of NAB's are quite well understood, the existence of isolated covalent anions of NAB's is still an open problem. (DB anions are systems in which the excess electron is attached by virtue of its interation with the dipole moment of the molecule.[11]) For example, there are two recent experimental findings related to electron attachment to uracil (U) in the gas phase which provided somewhat different pictures of the outcome of the electron attachment process.[2,9] In the PES experiment of Bowen et al., only the DB uracil anion was observed. Since the PES source usually leads to the production of the most energetically stable species, one has to assume that, if the covalent anion of uracil existed in the gas phase, it would have higher energy than the DB anion. In the most recent RET studies of Schermann et al. they identified what they claim to be the covalent uracil anion. The anion was not produced via a direct electron attachment to uracil, but by detachment of Ar atoms from the [U•Ar]$^-$ anions. The two experiments seem to suggest that both DB and covalent uracil anions can be generated in the gas phase and, depending on the procedure of anion production, one or the other can be detected.

2. Anion of Uracil-Water Complex

In our recent work,[13] we investigated the anion of the U•(H_2O)$_3$ complex and studied the ability of water to stabilize the excess electron in a covalent state of the uracil anion. While the covalent attachment to uracil in the gas-phase still remains an open question, in our view, there seems to be no doubt that [U•(H_2O)$_3$]$^-$ can appear as a stable covalent anion. Our calculations showed that a rearrangement of the H-bonds in the [U•(H_2O)$_3$]$^-$ complex occurs when an excess electron attaches and that this provides an additional stabilization to the anion. We have recently examined in more detail the differences in the geometrical and electronic structures of the neutral and anionic U•(H_2O)$_3$, and we would like to add some comments to the discussion we presented before.[12] First, an analysis of the shape of the orbital occupied by the excess electron in the [U•(H_2O)$_3$]$^-$ cluster (see Figure 1) shows that it is clearly a π orbital with the highest amplitudes located away from the plane of the uracil molecule. As we noticed previously, the electron attachment causes the water molecules to release their weaker H bonds and move their free OH bonds perpendicularly to the plane of the molecule (we show this effect in Figure 2). It is now clear that the hydrogens of these OH bonds, which usually have some residual positive charge, move out of plane and become submerged in the π density of the excess electron and provide additional stabilization to it. This may explain why it is easier to form a covalent anion of a U•water complex than a covalent anion of uracil.

Finally, by examining the structure of the uracil molecule in [U•(H_2O)$_3$]$^-$ we noticed that the uracil ring deviates noticeably from planarity. A similar effect was noticed before in DFT calculations of U$^-$ by Schermann et al.[9] The out-of-plane distortion of the ring seems to provide additional stabilization to the U•(H_2O)$_3$ anion in addition to the stabilization of the anion by waters.

3. Uracil Anion

The study of the uracil−water anion has raised the question of whether the covalent uracil anion can be made stable by only the ring distortion without extra stabilization provided by

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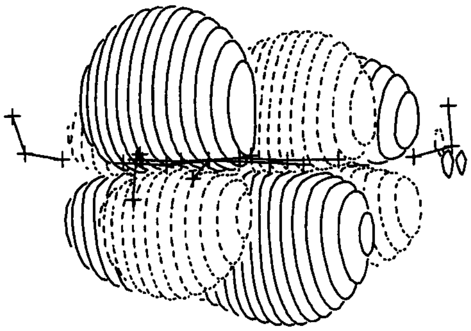


Figure 1. The orbital occupied by the excess electron in the covalent $[U{\cdot}(H_2O)_3]^-$ anion.

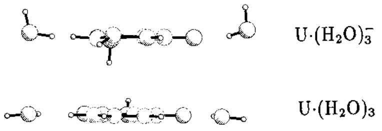


Figure 2. Structures of $U{\cdot}(H_2O)_3$ and $[U{\cdot}(H_2O)_3]^-$.

hydration. To test this possibility, we performed geometry optimization of U^- at the UMP2/6-31++G**(6d) level of theory (the second-order Møller−Plesset perturbation theory with the spin-unrestricted Hartree-Fock, UHF, reference wave function using the standard 6-31++G** Gaussian basis set with six−component d−orbitals) starting with the geometry of the uracil molecule taken from the equilibrium structure of the $U{\cdot}(H_2O)_3$ anion. At the converged geometry of the anion, its UMP2, UMP3, and UMP4 (the second, third, and fourth orders of the Møller−Plesset perturbation theory with the UHF reference wave function) energies, as well as the RHF (spin-restricted Hartree−Fock method), MP2, MP3, and MP4 (the second, third, and fourth orders of the Møller−Plesset perturbation theory with the RHF reference wave function) energies of the neutral uracil molecule were calculated using the 6-31++G**(6d) basis set to estimate the vertical electron detachment energy (VDE). The VDE values resulted from the calculations are the following: 0.53 eV (RHF−UHF), 0.27 eV (MP2−UMP2), 0.44 eV (MP3−UMP3), and 0.25 eV (MP4−UMP4), where in the paretheses the levels of theory used in the calculations for the neutral and anion systems, respectively, are indicated. The above results indicate the valence uracil anion, which was calculated, is a stable system with respect to a vertical electron detachment.

To determine the adiabatic electron affinity of uracil the geometry of the neutral uracil molecule was reoptimized at the MP2/6-31++G**(6d) level of theory starting with the anion geometry. At the equilibrium point the converged geometry obtained in the calculation was virually planar unlike the anion geometry which was noticably puckered. During the optimization the MP2 energy of the neutral uracil dropped 0.46 eV below the energy of the anion indicating that the anion which we obtained before is an unstable system with respect to an adiabatic electron detachment. We also calculated the (MP3-UMP3) and (MP4-UMP4) EA values which were −0.39 and −0.42 eV, respectively, and confirmed the anion metastability. The ring geometries of uracil and uracil anion are compared in Figure 3. One notices the dissimilarities in the two structures.

This last observation brings an interesting point in relation to Schermann's RET experiment where, as he claims, he detected the covalent anion of uracil. Since the anion could not be formed by a direct electron attachment to uracil, but indirectly by fragmentation of $[U{\cdot}Ar]^-$, it is possible that the system which was observed was not U^- in its lowest vibrational state but U^- in a vibrationally excited state. The vibrational excitation may have been generated in the fragmentation process. Furthermore, since the lowest vibrational frequencies in uracil correspond to ring-puckering modes, it is possible that the mode which was excited involved a ring distortion similar to the distortion which, according to our calculations, accompanies formation of the covalent anion of uracil. If the vibration of this mode was indeed excited in Schermann's experiment by at least one vibrational quanta, the structure of the uracil molecule would effectively become nonplanar since the vibrational wave function of the first excited state has zero amplitude for the planar geometry. It is possible that the most probable structure of uracil in the first excited vibrational state resembles the puckered structure of the covalent anion. As our calculation showed, at this structure the anion is more stable than the neutral system. Thus, such a vibrational excitation would increase the propensity of uracil to form a covalent anion.

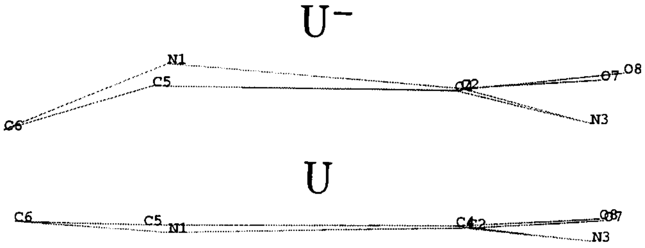


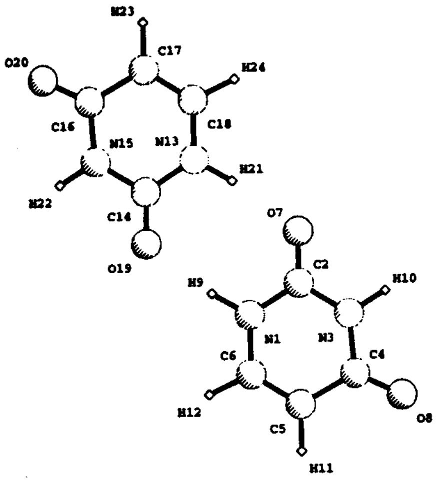
Figure 3. Comparison of the ring planarity in uracil and uracil anion.

4. Calculations and Discussion

In the biological environment equally important as the anions of hydrated NAB's are anions of NAB clusters and particularly the anions of NAB dimers. The NAB pairs play an essential role in conveying genetic information, and this justifies the interest in how electron attachment may affect the structures of these systems. One source of free electrons (or hydrated electrons) in biological environments are secondary reactions which follow the UV-induced radiolysis of water. The damaging effect of free electrons on the DNA and RNA structures are directly related to the outcome of the electron attachment to the NAB pairs. In the present work we study this problem on a model system which is the uracil dimer. We selected this system because of the insight on its electron bonding properties, which we gained in our previous theoretical studies of DB and covalent anions of uracil and its hydrated complexes.

As mentioned before we have determined that two factors may contribute to the stability of the excess electron in uracil anion. The first factor is the interaction with solvating molecules, in the case of the uracil dimer this being the second uracil molecule, and the second factor is a puckering deformation of the uracil ring. The questions which we attempt to answer in this work are (i) Can hydrogen-bonded uracil dimers form DB anions with excess electrons and, if they do, what are the electron binding energies in these systems? (ii) Can uracil dimer form a covalent anion and, if it does, what is the structure of this system? Is the electron localized on one of the uracil molecules or delocalized over the whole dimer? Is the covalent uracil dimer anion a stable system with respect to the electron detachment? If it is stable, what are the factors that facilitate the stability? Are these factors similar as in the case of the hydrated uracil anion?

To provide answers to the above questions a series of calculations were performed with the use of the GAUSSIAN94 quantum-chemical program package,[13] and the results are described in the following sections.



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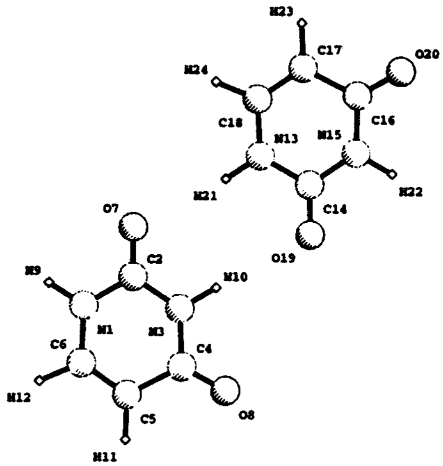

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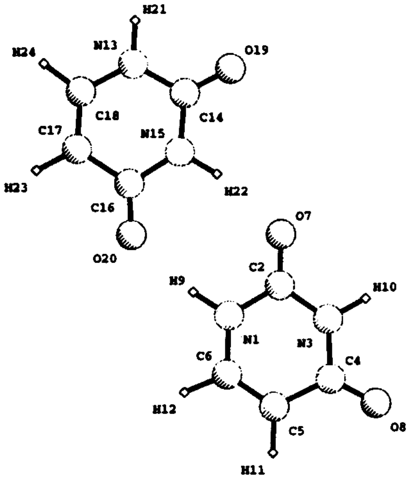

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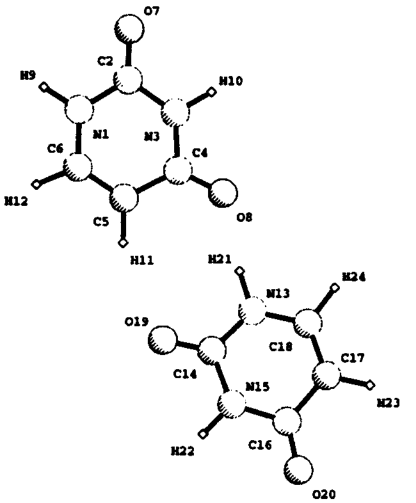

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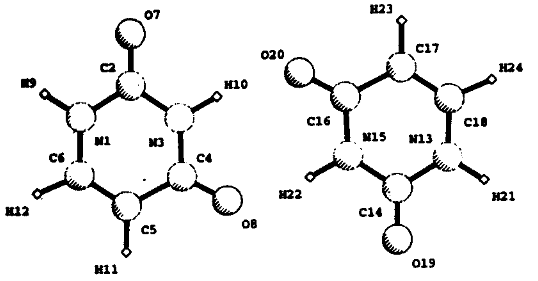

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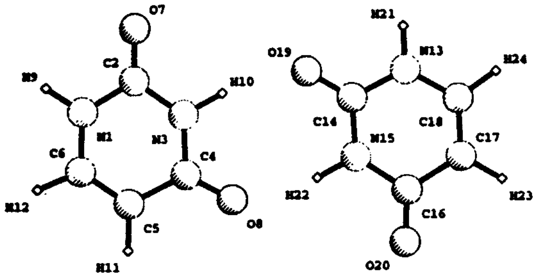

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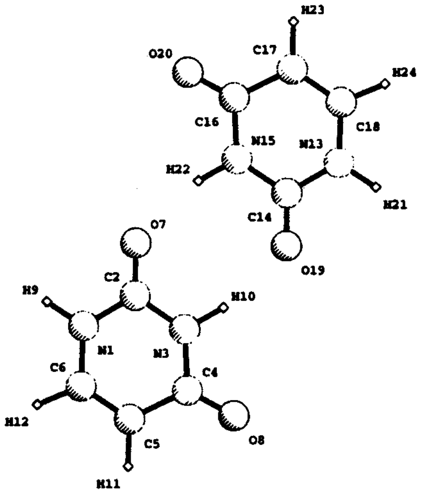

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Figure 4. The optimal hydrogen-bonded conformers of the uracil dimers found in the RHF/6-31++G**(6d) calculations.

TABLE 1: MP2/6-31++G(6d) Total and Relative Energies of Uracil Dimers Calculated with the RHF/6-31++G**(6d) Geometries[a]**

structure	RHF	MP2	MP2 relative energy	RHF dipole moment
1	−835.012 947	−827.408 901	0.0	0.0
2	−825.006 840	−827.402 720	3.9	9.4
3	−825.006 814	−827.400 852	5.1	8.8
4	−825.004 983	−827.399 874	5.7	4.7
5	−825.002 968	−827.398 951	6.2	0.0
6	−825.002 729	−827.398 564	6.5	2.5
7	−825.002 594	−827.398 243	6.7	0.0

[a] Total energies in hartrees, relative energy in kcal/mol molecular dipoles in debyes.

TABLE 2: Dipole-Bound Anions of the Uracil Dimer. Calculations Performed with the 6-31++G(5d)X[a] Basis Sets[b]**

	anion		neutral		
structure	UHF	UMP2	RHF	MP2	AEA
2	−825.008 493	−827.375 190	−825.005 003	−827.370 324	132
3	−825.008 162	−827.374 615	−825.006 089	−827.371 585	82
4	−825.003 810	−827.369 247	−825.003 148	−827.367 459	49

[a] The X set of diffuse orbitals consists of the sp-shells with the following exponents: 0.01, 0.02, 0.0004, 0.000 08, 0.000 016, 0.000 003 2, located at the atom nearest to the positive pole of the dipole of the dimer. [b] Dimer anion and neutral structures optimized at the UHF and RHF levels of theory, respectively. Total energies in hartrees, adiabatic electron affinities (AEA) calculated at the MP2 level in meV.

4.1. Uracil Dimer. The purpose of the first series of calculations was to determine possible equilibrium configurations of the hydrogen-bonded neutral dimer of uracil. This problem was studied before by Piskorz and Wojcik[14] using the HF/3-21G method with the purpose of identifying the dimer structure which corresponds to the hydrogen bonded crystals. The determination of the structure was based on a comparison of the low frequency IR and Raman experimental spectra with the theoretically predicted frequencies and intensities. Also, recently Kratochv'il *et al.*[15] performed an exhaustive search for equilibrium structures of the uracil dimer. In this search they used the HF/6-31G** level of theory for the H-bonded configurations and at the MP2/6-31G* level for the stacked configurations. They also calculated the basis-set-superposition-error-corrected interaction energies at the MP2/6-31G*(0.25) level of theory for all the equilibrium structures found in the calculations and performed a thermodynamic conformation analysis of the uracil dimer in the gas phase. Since in the present studies we have been concerned with the ability of the uracil dimers to form DB anions, we searched particularly for those configurations with dipole moments exceeding the value of 2.5 D. This dipole value is the experimentally determined threshold for a molecular system to form a stable DB anion with an excess electron. In the present calculations, the optimizations of the dimer structures have been performed at the RHF/6-31++G**(6d) level of theory and the final energy of each of the seven dimer structures found was determined at the MP2/6-31++G**(6d) level. The energy and dipole moment results are presented in Table 1 and the dimer structures are shown in Figure 4. The structures are ordered according to the increasing value of their total MP2 energies and numbered **1**−**7**. In the search for the equilibrium structures of the dimers we first examined all distinct ways in which two uracil molecules can connect via two N−H···O hydrogen bonds. This resulted in structures **1**−**3** and **5**−**7**. Structure **4**, which has one H-bond involving C−H···O linkage, resulted from optimization which was initiated with the optimal geometry of the covalent uracil dimer anion (see section 4.3).

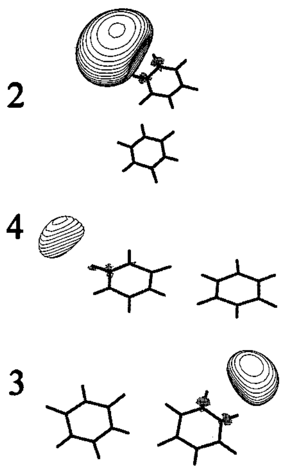

Figure 5. The orbitals occupied by the excess electrons in the dipole-bound uracil dimer anions of conformers **2**−**4**.

TABLE 3: Covalent Anion of Uracil Dimer[a]

anions	
UHF/6-31+G*(6d)//UHF/6-31+G*(6d)	−824.979 883
UMP2/6-31+G*(6d)//UHF/6-31+G*(6d)	−827.337 268
UHF/6-31++G**//UHF/6-31++G**(6d)	−825.003 025
UMP2/6-31++G**//UHF/6-31++G**(6d)	−827.406 325
Neutral (at the Anion Geometry)	
RHF/6-31++G**(6d)	−824.958 166
MP2/6-31++G**(6d)	−827.373 627
Neutral (at the Equilibrium Geometry)	
RHF/6-31++G**(6d)//RHF/6-31++G**(6d)	−825.004 983
MP2/6-31++G**(6d)//RHF/6-31++G**(6d)	−827.399 874

[a] SCF and MP2 energies in hartrees.

The results compiled in Table 1 indicate that in the most stable form of the dimer the dipoles of the monomers are antiparallel and the overall dipole of the dimer is zero. However, the next three structures on the energy scale (structures **2**−**4**) have significant dipole moments and can be expected to form stable DB anions with excess electrons.

4.2 Dipole-Bound Uracil Dimer Anions. In the next series of calculations we considered DB electron attachment to uracil dimers **2**−**4**. As it was the case in our previous calculations on DB anions of molecular clusters, a standard basis set was augmented with a set of diffuse functions centered on the atom in the cluster which is positioned closest to the positive direction of the cluster dipole and is most distant from the center of the cluster. The basis set used in the present calculations consisted of the standard 6-31++G**(5d) basis set augmented with six sp shells with exponents 0.01, 0.002, 0.0004, 0.000 08, 0.000 016, and 0.000 003 2. This additional diffused set will be denoted as "X" in further discussion. At the equilibrium geometries of the **2**−**4** neutral clusters, UHF/6-31++G**(5d)X calculations converged to stable DB anion states. For these states the anion geometries were optimized at the UHF/6-31++G**(5d)X level of theory and the total energy was calculated at the UMP2/6-31++G**(5d)X level. The results are presented in Table 2. In the following step, starting from the equilibrium structures of the DB anions, the geometries of neutral clusters were optimized at the RHF/6-31++G**(5d)X level of theory to obtain the reference energies of the neutral clusters for determination of their adiabatic electron affinities. For all the neutral dimers considered the RHF/6-31++G**(5d)X geometries are virtually identical to the RHF/6-31++G**(5d) geometries described in the previous section. Also there are very small differences

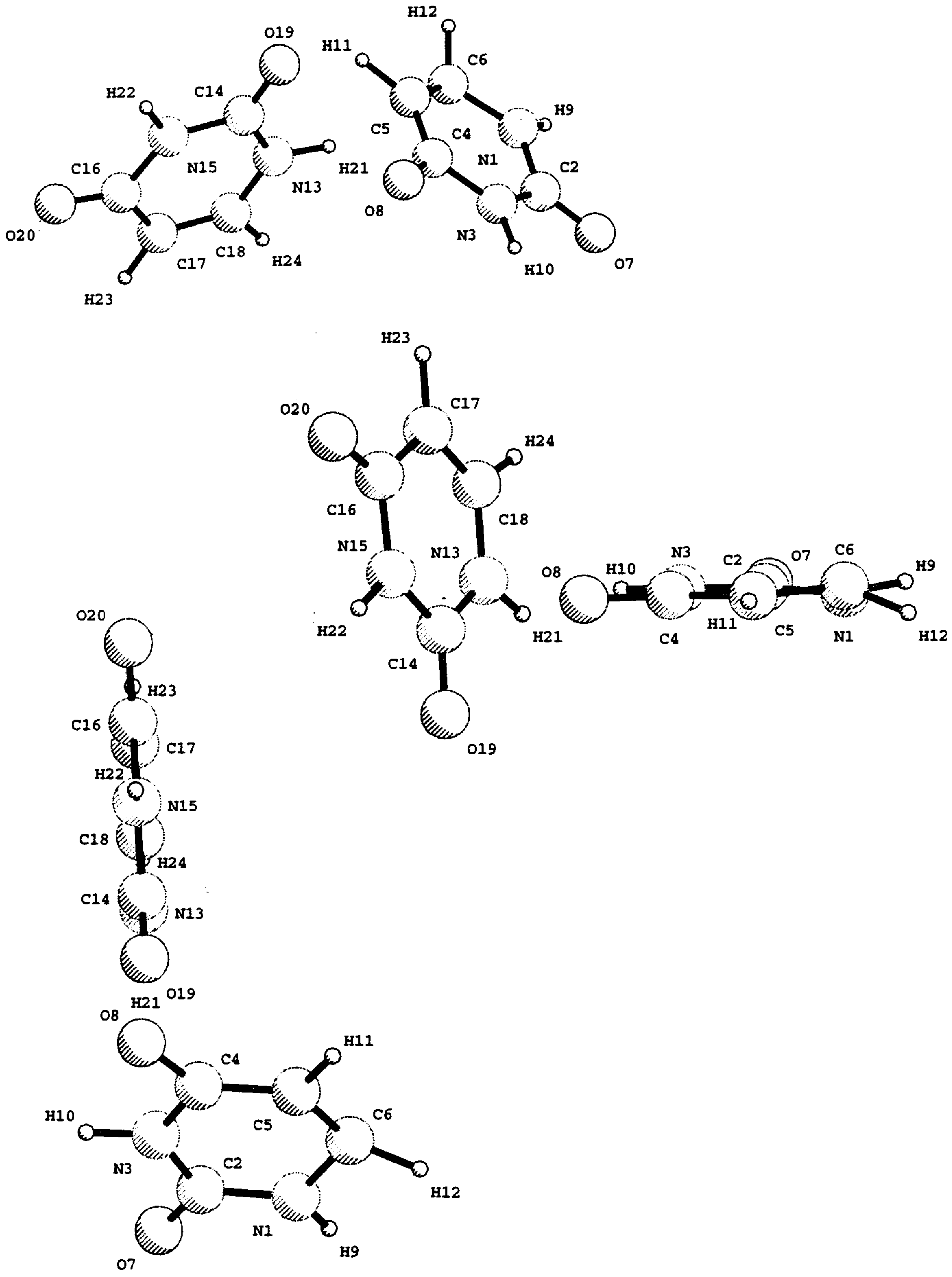

Figure 6. Different views of the structure of the covalent anion of the uracil dimer.

between the anion geometries and the geometries of the corresponding neutral dimers. We only observed a small decrease in the H bond distances upon the DB electron attachment.

The results for the neutral and anion dimers of uracil presented in Table 2 allowed determination of the adiabatic electron affinities (AEA) of these systems. The most stable anion is formed by dimer **2**, and the corresponding AEA is 132 meV as calculated at the MP2/6-31++G**(5d)X level of theory (UMP2 for the anions and MP2 for the neutral). Adding this value to the dimer **2** MP2/6-31++G**(6d) energy in Table 1 reduces the energy difference between dimer **1** and dimer **2** from 3.9 kcal/mol to 0.8 kcal/mol. Dimer **1** cannot form a DB anion due to its zero dipole moment. Therefore, if we consider a theormodynamically equilibrated mixture of uracil dimers, we should notice a significant increase in the population of dimer **2** with respect to dimer **1** when free electrons are introduced to the sample.

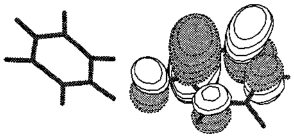

Figure 7. Orbital occupied by the excess electron in the covalent uracil dimer anion.

A characteristic feature of the DB anions are very diffuse states of the excess electrons and their localization outside the molecular frame of the system. In Figure 5 we demonstrate these features for the three DB anions of the uracil dimer.

4.3. Covalent Uracil Dimer Anion. To determine whether a uracil dimer can form a stable covalent anion one needs to first determine the structure of such a system. The study of the water−uracil cluster anion has shown that the anionic cluster with the excess electron occupying a valence orbital may have a dissimilar structure from the neutral cluster. Thus, a search for the equilibrium geometry of the cluster anion cannot be initiated with the geometry of the neutral cluster because at that geometry the anion may be unstable. In the present calculations we started the geometry optimization of the covalent uracil dimer anion from a stacked π-bonded configuration. The optimization was first performed at the UHF/6-31+G*(6d) level of theory and was followed by an optimization at the UHF/6-31++G**(6d) level. At both levels the UMP2 energy was calculated with the respective basis set. Also, we calculated the MP2/6-31++G**(6d) energy of the neutral cluster at the UHF/6-31++G**(6d) equilibrium geometry found for the anion. Following this calculation the geometry of the neutral dimer was optimized at the RHF/6-31++G**(6d) level starting with the UHF/6-31++G**(6d) anion geometry. For the converged structures, which appear to be the same as structure **4** found before, the energy was calculated at the MP2/6-31++G**(6d) level of theory. The results are presented in Table 3.

The first observation which one makes upon examining the results is that at the MP2 level of theory the uracil anion found in the calculations is stable both in terms of the vertical and adiabatic electron detachments (the latter determined with respect to dimer **4**). Before we move to discussion of the electron affinity values, let us first examine the geometry and the wave function of the anion which was found in the calculations. In Figure 6 we present an analysis of the structure of the anion and in Figure 7 we present the picture of the orbital (HOMO) occupied by the excess electron. The most interesting feature of the HOMO is that it has π symmetry, and it is exclusively localized on one of the uracil molecules. Structure analysis indicates that this molecule is out-of-plane distorted in a similar way as in the uracil−water cluster anion. The two uracil molecules in the dimer anion are neither coplanar nor have parallel stacked configuration, but they appear to form an almost perpendicular conformation. Again, as in the case of the uracil−water anion, where the water molecules stabilized the covalent uracil anion, in the uracil dimer anion the stabilizing role in played by the “spectator” uracil molecule.

Finally, based on the energy results presented in Table 3 we calculated the vertical electron detachment energy (VDE) of the uracil dimer anion and the adiabatic electron affinity (AEA) of the uracil dimer, and the results are presented in Table 4. The results indicate the vertical electron detachment energy is positive at both the HF and MP2 levels of theory and its values are 1.2−0.9 eV, respectively. The AEA values in Table 4 were calculated with respect to the neutral dimer (dimer **4**) which was obtained when the geometry optimization was initiated with the optimal structure of the dimer anion. With respect to this dimer, the MP2 AEA value is positive and equal to 176 meV indicating that the anion is adiabatically stable with respect to the neutral dimer **4**. According to the results presented before, dimer **4** has by 5.7 kcal/mol or 246 meV higher energy than the most stable dimer **1**. Comparing the 246 meV energy difference with the AEA value of 176 meV suggests that the dimer anion is marginally adiabatically unstable (by about 70 meV). However, calculations at a higher level of theory are needed to make a more definite determination of this effect.

TABLE 4: Covalent Uracil Dimer Anion[a]

Vertical Electron Detachment Energy			
Method			
Anion	Neutral	Basis	VDE
UHF	RHF	6-31++G**(6d)	1221
UMP2	MP2	6-31++G**(6d)	890
Adiabatic Electron Affinity			
method			
anion	neutral	basis	AEA
UHF	RHF	6-31++G**(6d)	−53
UMP2	MP2	6-31++G**(6d)	176

[a] Adiabatic vertical electron detachment energy (VDE) and adiabatic electron affinity (AEA) in meV.

5. Conclusions

Dipole-bound and covalent anions of uracil dimer have been studied using ab initio theoretical calculations. On the basis of the calculated results, we have made the following predictions: (i) At its most stable structure the hydrogen-bonded uracil dimer forms neither a stable DB nor a covalent anion with an excess electron. (ii) As results from the present calculations and from the previous theoretical analysis of Kratochv’il et al.[15] indicate, two uracil molecules may form several complexes, which are thermodynamically accessible at room temperature and which possess sufficient dipole moments to form stable DB anions with excess electrons. For one such complex (structure 2 in the present work or the equivalent structure HB1 in the work of Kratochv’il et al.[15] the energy decrease due to the dipole-bound electron attachment makes this complex nearly as stable as the most stable complex (i.e., structure 1 in the present work or the equivalent structure HB4 in the work of Kratochv’il et al.[15] This opens a possibility of a significant shift in the thermodynamic equilibrium of different dimers in an electron-rich environment by stablizing the dimers with larger dipole moments. (iii) Two uracil molecules can form a covalent dimer anion with an excess electron. In this dimer the electron is localized on one of the uracil molecules which, as a result, undergoes a ring−puckering distortion. Similar electron localization at one of the uracil units was predicted by Voityuk and Rösch in their recent theoretical study of the anion of the uracil dimer $C_5-C_{5'}$, $C_6-C_{6'}$ adduct.[16] In the uracil dimer anion, which we obtained in the calculations, the uracil molecules are oriented nearly perpendicularly to each other. At the theoretical level used in the calculations in the present work, the covalent anion is stable with respect to the vertical electron detachment, but marginally unstable with respect to the most stable neutral dimer. However, it is possible that higher order calculations may reverse this instability. (iv) Due to the ring-puckering distortion of one of the uracils in the covalent uracil dimer anion, the formation rate of this anion may be enhanced by an IR excitation of the ring-puckering vibration. It would be interesting to test this possibility by irradiating the beam of uracil molecules before it is crossed with a beam of electrons with IR radiation which covers the range where the ring-puckering mode appears in the spectrum.

The above predictions open an interesting challenge for an experimental verification.

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