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Isomerism of the Covalent Anion of the Uracil−Thymine Dimer. Ab Initio Study

Dayle M. A. Smith, Johan Smets, and Ludwik Adamowicz*

Department of Chemistry, University of Arizona, Tucson, Arizona 85721

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Theoretical ab initio calculations have been performed to determine the ability of the uracil−thymine (U•T) dimer to form stable covalent anions. The are two major conclusions of this work (i) Two isomeric structures of the covalent U•T dimer have been found in the calculations. The anion, where the excess electron is located at the uracil molecule, is 1.4 kcal/mol more stable than the form where the excess electron is located at the thymine molecule. (ii) The ring of the molecule where the excess electron is localized in noticeably nonplanar.

1. Introduction

The theoretical and experimental determination of the electron affinities (EA) of nucleic acid bases (NAB) in the gas phase has proven to be a difficult problem. Bowen and co-workers[1] used photoelectron spectroscopy (PES), and Schermann and co-workers[2,3] used Rydberg electron transfer (RET) and field-detachment spectroscopy to determine the electron affinities of NABs. These two studies have been directly related to the theoretically calculated electron affinities including the values obtained by our group.[4−7] On the basis of the calculations, which we and others[8] have done, and on the basis of the recent experiments in the gas phase of Schermann et al. and Bowen et al., one can conclude that while the dipole-bound (DB) anions of NABs are quite well understood, the existence of covalent anions of isolated NABs is still uncertain.

In recent works, we addressed the question of the covalent electron attachment to uracil assisted by interactions with "spectator" molecules (water molecules and the second uracil molecule).[9,10] In the work on the hydrated uracil anion[9] we considered the $[U{\bullet}(H_2O)_3]^-$ complex and studied the ability of water to stabilize the excess electron in a covalent state at the uracil anion. Our calculations showed that a rearrangement of the H-bonds in the $[U{\bullet}(H_2O)_3]^-$ complex occurs when an excess electron attaches, and this provides an additional stabilization to the anion. We also noticed that 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. 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, providing additional stabilization to the anion. 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 $[U{\bullet}(H_2O)_3]^-$ we noticed that the uracil ring shows an out-of-plane distortion. This distortion also appears to contribute to the stabilization of the excess electron in the valence state. Our calculations on the covalent uracil dimer anion revealed similar features as in the hydrated uracil anion. We predicted that the uracil dimer, apart from formation of stable dipole-bound anions, will also attach an excess electron in a covalent state and form an anion with a structure dissimilar from any hydrogen-bonded equilibrium structures of the neutral dimer. The calculations also revealed that the excess electron in the covalent uracil dimer is exclusively localized at one of the uracil molecules and this molecule shows an out-of-plane distortion similar to that in the hydrated uracil anion. According to the calculations, 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, it is marginally unstable with respect to electron detachment and simultaneous transformation to the most stable H-bonded conformation of the neutral dimer.

The purpose of the present work is to determine whether covalent anions can be formed by dimers of two different pyrimidine nucleic acid bases. In the study we have considered the uracil−thymine (U•T) dimer model system. This system was selected due to its structural similarity to the previously studied uracil dimer, where we have developed a considerable theoretical insight into the structural and electronic properties of the covalent anion. Our interest in the electron attachment to the U•T dimer has also been related to the question whether the methylation at C5, which differentiates thymine from uracil, results in a smaller electron affinity of the former and in a localization of an excess electron in the dimer anion at the uracil molecule rather than at the thymine molecule. This type of localization can be expected to occur due to an electron-donating effect of the methyl group, which should result in a higher electron density at the thymine ring than at the uracil ring and in a reduced ability of thymine to form a stable covalent anion.

The questions we will attempt to answer in the present work are the following: (i) Can the uracil−thymine dimer form a stable covalent anion (or anions)? (ii) Is the excess electron localized in the anion at one of the monomers in a manner similar to that in the uracil dimer anion? (iii) Are the intramolecular and intermolecular structural features of the covalent uracil−thymine anion similar to those in the covalent uracil dimer anion? (iv) If more than one covalent U•T anion is predicted, what are the relative energies of these systems? Is, as expected, the anion with the excess electron localized at the uracil molecule more stable than the anion where the excess electron is localized at the thymine molecule? What can be said about the possibility of interconversion between the two ions?

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* Corresponding author. E-mail: ludwik@u.arizona.edu. Fax: (520) 621-8407.

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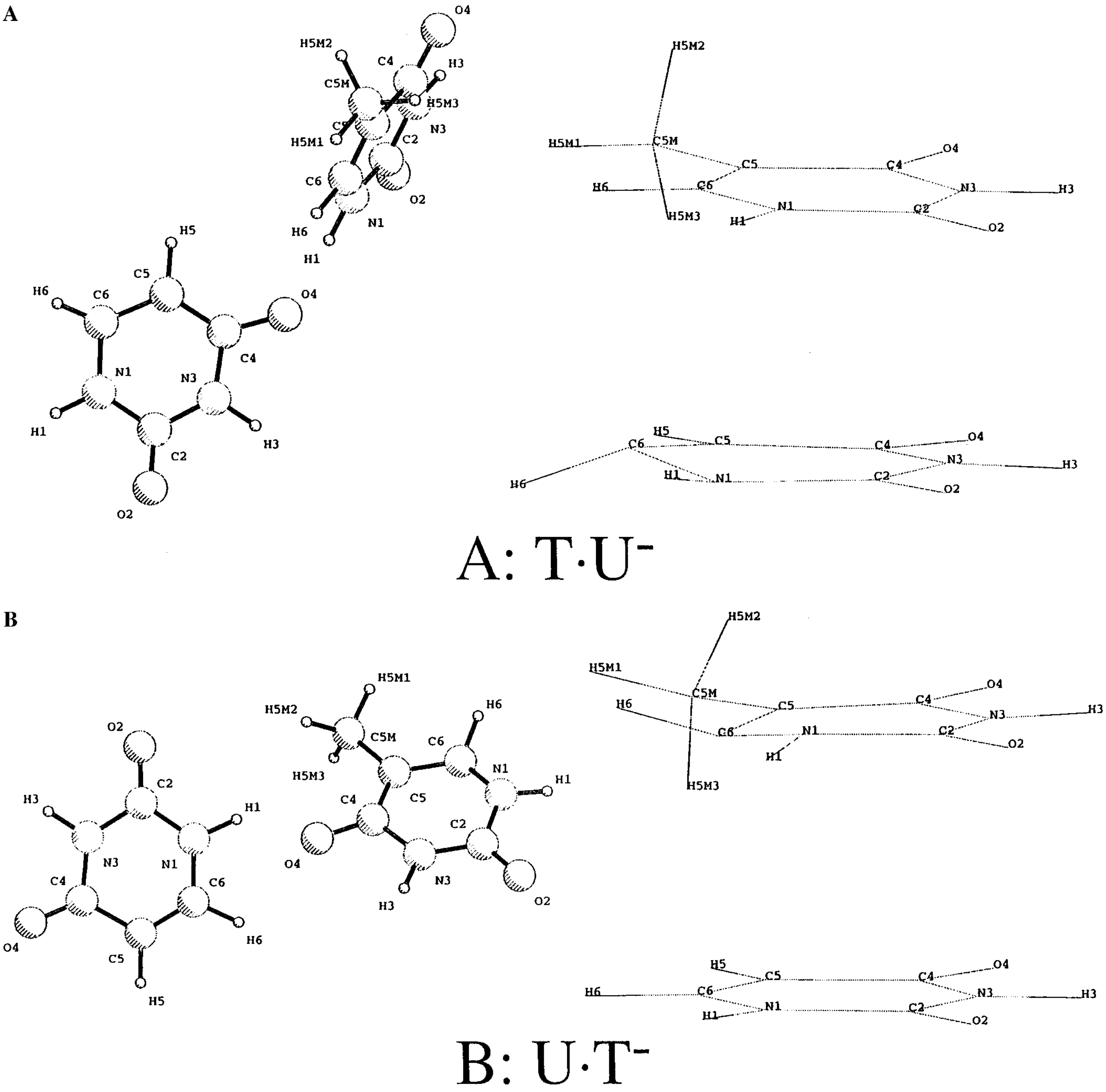

Figure 1. Structures of the covalent uracil–thymine dimer anions: (A) T·U⁻ anion; (B) UT⁻ anion. The dimer structures are shown on the left, and the structures of their uracil and thymine monomers on the right. In dimer anion A, uracil, where the excess electron is localized, is distorted from planarity at C6. A similar distortion is present in thymine in dimer anion B. Geometrical parameters of the anion and neutral structures are available from the corresponding author.

The recent study of the conformational flexibility by Shishkin[11] demonstrated that the molecules of uracil and thymine are not conformationally rigid due to nonaromatic and antiaromatic characters of the cyclic π-systems in these molecules. This feature is relevant to the formation of covalent anions of these molecules since, as mentioned, the out-of-plane distortion occurs when an excess electron attaches to their valence shells. Since the vibrational modes of uracil and thymine are quite well characterized both theoretically and experimentally,[12,13] knowing the geometrical structures of their anions and the puckering deformations of their rings will make it possible to determine which vibrational mode (or modes) needs to be excited in the neutral system to assist a covalent electron attachment.

2. Calculations and Discussion

As mentioned before, we determined that two factors may contribute to the stabilization of an excess electron in the uracil covalent anion: the first being the intermolecular interaction with the accompanying molecule (or molecules) and the second being a puckering deformation of the ring. Since in the T·U dimer anion the excess electron can attach to either the thymine or uracil molecule or simultaneously to both, deformations of the rings in both systems need to be considered. The following calculations have been performed with the use of the GAUSSIAN94 quantum-chemical program package[14] to elucidate the questions raised in this work:

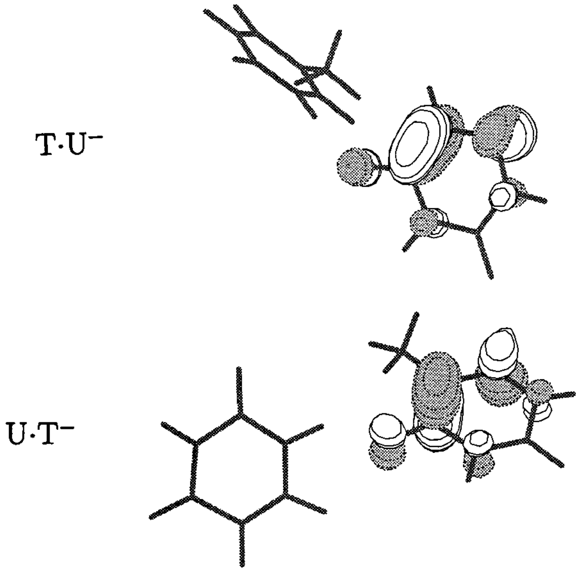

Figure 2. HOMO's of the T·U$^-$ and U·T$^-$ anions.

1. The first series of calculations were aimed at determining the equilibrium structures of stable covalent anions of the uracil—thymine dimer. On the basis of the previously found structure of the covalent uracil dimer anion, there are two possible choices of the T·U anion geometry with which the structural determination search can be initiated. Both choices can be generated on the basis of the optimal geometry of the covalent uracil dimer anion by replacing one or the other uracil molecule in this system by the thymine molecule. As mentioned before, the two uracil molecules in the covalent uracil dimer anion are structrally dissimilar, because the one where the excess electron is located shows a noticeable nonplanar deformation and the second is virtually planar. Therefore, in the two starting geometries of the uracil-thymine anion, either the uracil molecule or the thymine molecule was out-of-plane distorted (the former system will be called T·U$^-$ and the latter U·T$^-$). The anion structure optimizations were performed at the UHF/6-31++G** level of theory and converged to two geometries, which are presented in Figure 1A,B. As can be seen, in both structures the uracil and thymine molecules are not coplanar. The figures also show an analysis of the planarity of the thymine and uracil rings in the two anions. As one notices, while the thymine ring is virtually planar and the uracil ring in noticeably nonplanar in the optimal T·U$^-$ structure, the opposite is the case in the U·T$^-$ anion. The plots of the orbitals occupied by the excess electrons in T·U$^-$ and U·T$^-$, which are shown in Figure 2, indicate that the excess electron in located exclusively on the monomer with the out-of-plane-distorted ring. This is a behavior similar to that observed before in the covalent uracil dimer anion.

2. In the next series of calculations we considered the neutral uracil−thymine dimer. Optimizations of its structures were performed at the RHF/6-31++G** level by starting with the equilibrium anion geometries. This approach may not lead to the lowest energy configurations, but the obtained structures probably provide a good representation of the dimer configurations, which are populated when excess electrons are removed from the anions and the dimer structures are allowed to relax toward the nearest local minima (in this process the excess vibrational energy has to be removed to prevent tunneling toward lower-lying energy minima and more significant configurational rearangements). The two optimal structures of the T·U dimer obtained in the calculations are shown in Figure 3.

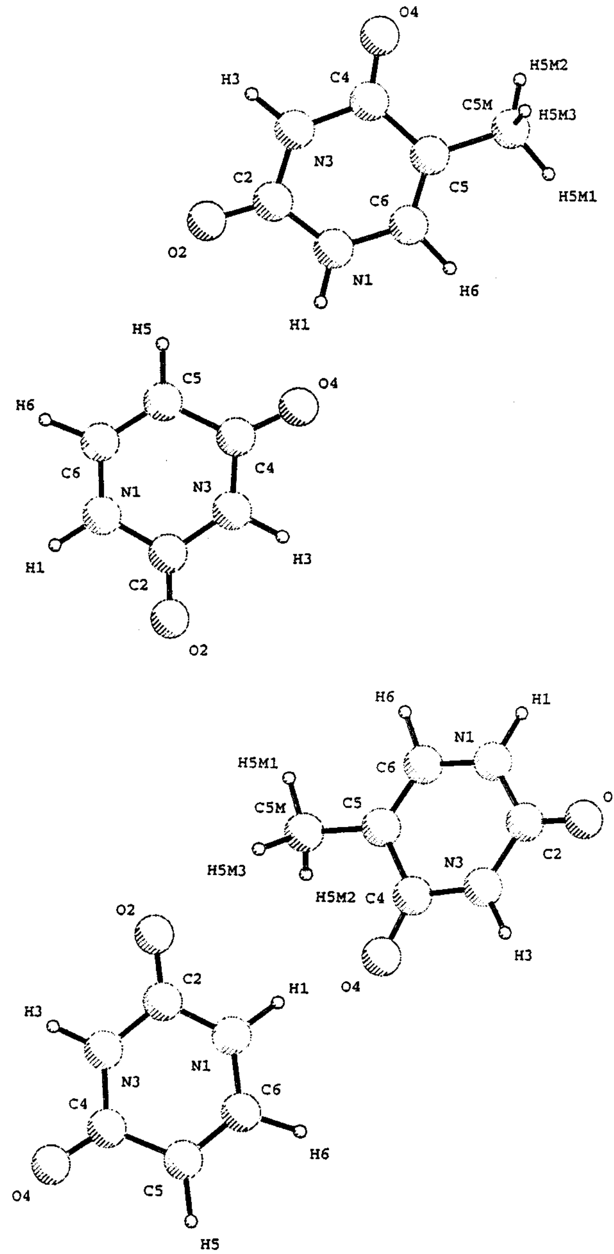

Figure 3. Uracil−thymine neutral dimer structures obtained in geometry optimizations started with the equilibrium structures of the covalent dimer anions.

3. In the next step calculations were performed at the MP2/6-31++G** level of theory for the two different anion structures and the two corresponding neutral dimer structures. MP2 calculations were also done for the neutral dimers at the equilibrium geometries of the anions. The energy results are presented in Table 1. As one notices, both T·U$^-$ and U·T$^-$ anions are stable systems with respect to the vertical electron detachment. The vertical detachment energies (VDE) calculated using the MP2 total energies from Table 1 are 0.87 and 0.71 eV for T·U$^-$ and U·T$^-$, respectively (see Table 2). Also, both anions appear to be "adiabatically" stable with respect to electron detachment and a simultaneous transformation to the nearest local minimum of the neutral dimer. The calculated adiabatic detachment energies (ADE) are 0.15 and 0.16 eV for the T·U$^-$ and U·T$^-$ anions, respectively. The comparison of the total MP2 energies of the two anions shows that the T·U$^-$ system is by 1.4 kcal/mol more stable than the U·T$^-$ system. This indicates that the electron localization at the uracil molecule in the U·T

TABLE 1: Uracil−Thymine Dimer Anions[a]

system	T·U$^-$//T·U$^-$	T·U//T·U$^-$	T·U$^-$//T·U
SCF	−864.042976	−863.997824	−864.046466
MP2	−866.595466	−866.563396	−866.589837
HOMO	−0.08666		
system	**U·T$^-$//U·T$^-$**	**U·T//U·T$^-$**	**U·T//U·T**
SCF	−864.040794	−864.002564	−864.044007
MP2	−866.593296	−866.567122	−866.587471
HOMO	−0.08242		

[a] Calculations were performed with the 6-31++G** basis set. The spin-unrestricted and spin-restricted methods were used for the anions and neutrals, respectively. [b] Notation (A·B//(A·B)′ denotes that the calculation on the A·B system was performed at the equilibrium geometry of the (A·B)′ system. Anions were optimized at the UHF/6-31++G** level, and neutrals, at the RHF/6-31++G** level of theory.

TABLE 2: Vertical Detachment Energy (VDE) and Adiabatic Detachment Energy (ADE) of the Uracil−Thymine Dimer Anions (in eV) Calculated at the MP2/6-31++G Level of Theory**

system	VDE	ADE
U·T$^-$	0.87	0.15
U·T$^-$	0.71	0.16

dimer anion is thermodynamically more favorable than its localization at the thymine molecule.

3. Conclusions

Ab initio theoretical calculations performed in this work revealed an interesting isomerism of the thymine−uracil covalent dimer anion. Two configurations of the anion have been found that differ in the location of the excess electron. In the more stable configuration, the excess electron is exclusively localized at the uracil molecule and the ring of this molecule is noticeably distorted out of the molecular plane. In the second anion configuration, whose energy is 1.4 kcal/mol higher than that of the first configuration, the electron is localized at the thymine molecule and the ring of this molecule is distorted from planarity. The puckering distortions of the ring in the anions at the sites where the excess electrons are located indicates that it may be possible to induce transfer of the excess electron in the U·T dimer by a selective vibrational excitation. Since the electron and the ring-puckering distortion appear to follow each other in the uracil−thymine dimer anion, or, as one can also say, the vibrational energy transfer and the transfer of the excess electron occur in the same direction, it may be possible by selective excitations of the puckering vibrations in the uracil or thymine ring to change the location of the excess electron in the dimer. This interesting coupling between the vibrational deformation and the position of the excess electron may be a phenomenon, that can be investigated experimentally.

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