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An excess electron connects uracil to glycine

Ab–initio study

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Abstract. In recent work Gutowski *et al.* [Eur. Phys. J. D **20**, 431 (2002)] reported photoelectron–spectroscopy and theoretical study of covalent anion of the uracil–glycine complex. In present work we use *ab initio* calculations to describe an anionic complex of uracil and glycine where the excess electron is localized in a diffuse state between the two monomers. In this system the uracil and glycine molecules are separated by about 4.5 Å and the dipoles of the two monomers point at the excess electron located in the middle of the complex. The calculated fragmentation energy of the anion into a dipole–bound uracil anion and a neutral glycine molecule is 1.7 kcal/mol.

PACS. 31.15.Ar Ab initio calculations – 32.10.Hq Ionization potentials, electron affinities – 36.40.Wa Charged clusters

1 introduction

Interaction between proteins and nucleic acids occurs at all stages of replication and expression of DNA and in many processes of bioregulation. However, the knowledge and understanding of the mechanisms of the DNA-protein interactions is limited. This lack of information is mainly due to the large size of the systems involved and the complexity of the interactions. In recent series of papers [1–4] we have investigated the formation of complexes between nucleic acid bases and systems modeling the amino–acid side chains that contain structural features characteristic to the protein–DNA complexes. The purpose of the study has been to determine how specific are the interactions between the protein polar groups and the nucleic acid sites. The studies allowed determination of local thermodynamic and structural parameters of the interacting sites. This information provided and continues to provide useful background for consideration of more complex models and eventually of real biological systems.

The interactions between nucleic acid bases and amide group involving intermolecular H-bonds were described in many works. The "base–amino" acid point contacts were found in the X-ray study of the structure of a specific "repressor–operator" complex of bacteriophage 434 [5]. Smolyaninova *et al.* studied the DNA–protein interactions and demonstrated that amino acids asparagine and glutamine destabilize the DNA by forming H-bonds between their amide groups and nucleic acid bases in single stranded DNA [6]. The H–bonding interaction between the amino–acid amide group and nucleic acid bases was also characterized in the chloroform solvent by the NMR spectroscopy [7]. Due to the H–bonding interaction, the amide group plays an important role as a part of the protein structure and its ability to untwist the DNA double helix. Direct interactions between nucleic acid bases and the Asparagine and Glutamine amide groups were observed experimentally for adenine [8–10], cytosine [5,7,11], uracil [12,13] and guanine [14].

There has been also significant interest both experimental and theoretical in determining the ability of nucleic basis to form stable aducts with excess electrons [15–25]. There has been some theoretical work concerning electron affinities of DNA base pairs [26–31]. Recently, Gutowski *et al.* [32] reported photoelectron spectra (PES) and theoretical calculations of the uracil–glycine anion. The PES revealed a broad feature with a maximum at 1.8 eV. They concluded that the vertical detachment energy value was too large to associate the anionic complex with an anion of intact uracil solvated by the amino acid, or *vice versa*. Their calculations revealed that the excess electron in the uracil–glycine anion is described by a π^* orbital localized on the uracil ring. Furthermore, they determined that the excess electron can induce a barrier–free proton transfer in the anion from the carboxylic group of glycine to the O8 atom of uracil and this transfer stabilizes the negative excess charge localized at the O8–C4–C5–C6 fragment of uracil. The anionic complex with O8 protonated resulting from the transfer is the most stable anion of the uracil–glycine complex.

The aim of this work is to describe another type of anion that uracil and glycine can form with an excess electron. In this anion the electron is located between the two

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monomers and the configuration of the dimer is very dissimilar from any configuration of the neutral dimer. The provided results complement those presented before [32] and reveal an additional complexity of the uracil–glycine–anion configurational topology. They also show that the point–contacts between amino acids and nucleic acid bases and their recognition properties can be altered by excess electrons.

The only anions that uracil forms in the gas phase is the dipole–bound anion as predicted by theoretical calculations performed by our group [25] and subsequently detected in the gas phase experiments by the groups of Schermann [33] and Bowen [34,35]. In our recent study on hydrogen–fluoride trimer anions [36], where photoelectron experiments of Bowen and his coworkers were combined with theoretical calculations performed by Gutowski and our group, we presented evidence that the dipole–bound (DB) anion for this system coexists under certain conditions in the gas phase with an anion where there are two H–bonded HFs on one side of the excess electron and one HF on the other side. The two anions produced two sharp peaks in the photoelectron spectrum. In our work on $[\text{uracil}\cdot\text{HF}]^-$ and $[\text{uracil}\cdot\text{H}_2\text{O}]^-$ [37] we called the latter anion an anion with an internally suspended electron, or AISE for short. The formation of an AISE can proceed in two steps. First a DB anion is formed by one of the subunits of the complex. Next the second subunit (or the remaining subunits in the case there are more than one of them) attaches to the DB 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 and 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 used the term "*e*–bond" to describe the intermolecular interaction in AISEs. Here we investigate whether an *e*–bond can be formed between uracil and glycine and we determine the strength of the interaction.

The *e*–bond can be viewed as a special form of a quadrupole–bound electron [38] that occupies an orbital located between two polar units of a complex. When the dipole moments of the two units point at each other, a strong quadrupole field is generated in the middle of the complex that can bind an excess electron. There have been some calculations of such internally suspended quadrupole–bound electrons in small clusters of water molecules [39].

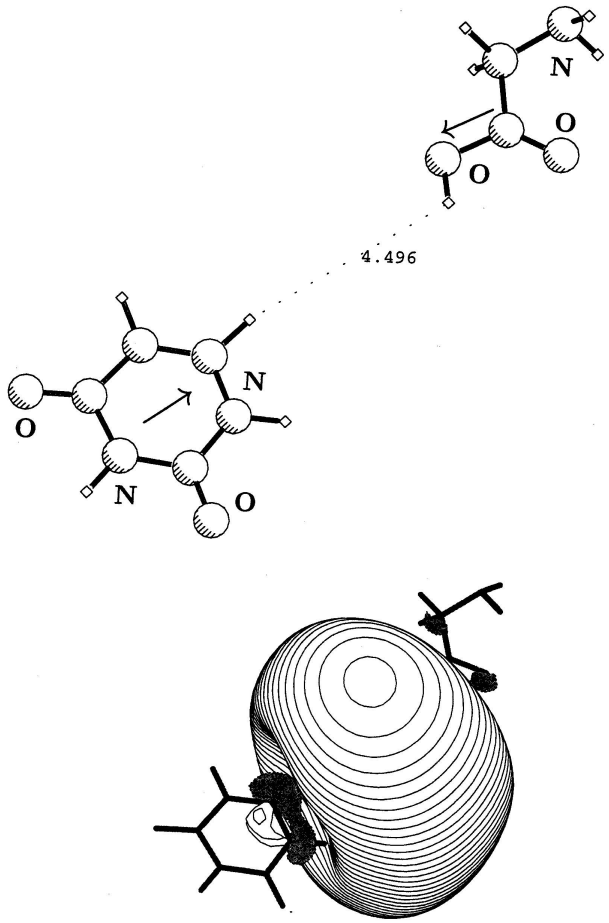

Fig. 1. The UMP2/6-31++G**X equilibrium structure of the uracil–glycine AISE and the orbital occupied by the excess electron in this system. The distances shown are in Å. The arrows indicate the directions of the dipole moment vectors for the monomers.

2 Calculations and discussion

All the calculations in this work have been done using the Gaussian98 program package [40]. The aim of the first series of calculations was to search for the equilibrium structure of uracil–glycine (UG) AISE. This search was first conducted using the UHF (spin–unrestricted Hartree–Fock method) and the geometry optimizations was initiated with an glycine molecule placed at the opposite side of the excess electron from the uracil molecule in the uracil dipole–bound anion. The calculations were performed with the 6-31++G**(5d) basis set augmented with a *p*–subshell with exponent 0.036 and with six additional diffuse *sp*–shells with the exponents: 0.1×10^{-1}, 0.2×10^{-2}, 0.4×10^{-3}, 0.8×10^{-4}, 0.16×10^{-4}, and 0.32×10^{-5}. The additional shells were placed at the hydrogen atom of uracil located the closest to the positive pole of its dipole. The 6-31++G** set augmented with the diffuse shells will be called 6-31++G**X in the further discussion. After the UHF/6-31++G**X equilibrium structure was determine, the search continued with the use of the UMP2/6-31++G**X method (second–order Møller–Plesset perturbation theory). The converged UMP2/6-31++G**X UG AISE is shown in Figure 1. 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 its energy. Thus we eliminated the possibility that the excess electron stayed in the anion due to too confining orbital basis, and not due to the anion energy being lower than the energy of the neutral system.

Table 1. Vertical and adiabatic electron detachment energies (VDE and ADE) of the uracil–glycine AISE. Calculations performed with the 6-31++G**X basis set. Equilibrium geometries calculated at the MP2/6-31++G**X level of theory. Total energies and the HOMO/LUMO energies in Hartrees and the VDE and ADE in meV. Only the valence electron correlation included. The diagonal elements of the RHF quadrupole moment tensor of the uracil–glycine dimer at the AISE geometry are [in Debye-Ang]: $XX = -125$, $YY = -97$, $ZZ = -75$ in the center–of–mass coordinate system. The notation "Anion//Anion" (and similar ones) indicates that the anion energy was calculated at the equilibrium molecular geometry for the anion.

Method	Anion//Anion	Neutral//Anion	Neutral//Neutral	VDE	ADE
MP2//MP2	–697.343402	–697.337413	–697.353270	163	–269
HOMO/LUMO	–0.00480	–0.00125	–0.00125		

In Figure 1 we also present the orbital occupied by the excess electron in the UG anion. The most characteristic feature of an AISE is that the dipole moments of the two monomers point at the excess diffuse electron which is located between them. This is clearly the case for the UG AISE (the orientations of the dipole moments of glycine and uracil are shown in Fig. 1 with arrows). In the anion the monomers are separated by about 4.5 Å. This creates a sufficient gap for the excess electron to localize in a diffuse bound state between the two monomers.

To estimate the vertical electron detachment energies (VDE) of the two AISEs, the energy of the neutral UG complex was calculated at the MP2/6-31++G**X level of theory at the equilibrium geometry of the AISE and subtracted. The results are presented in Table 1. The VDE value of 163 meV obtained in the calculation indicates that the interactions of the excess electron with the uracil and glycine molecules in the AISE is fairly strong. We also calculated the fragmentation energy of the AISE to the most stable dissociation products, *i.e.*, the uracil dipole–bound anion and the neutral glycine molecule. The calculations for the two systems have been done at their respective equilibrium geometries (MP2/6-31++G**X for uracil anion and MP2/6-31++G** for glycine) using the basis set of the AISE to reduce the basis set superposition error (BSSE). The results showed that the AISE is by 1.7 kcal/mol more stable than the dissociation products.

We also carried out a geometry optimization of the neutral UG complex at the MP2/6-31++G**X level initiating it with the AISE equilibrium structure. The calculations converged to an equilibrium geometry shown in Figure 2 which is very dissimilar from the AISE geometry. The neutral dimer is a conventional H–bonded complex. The distance between the monomers is reduced from about 4.5 Å in AISE to about 2 Å in the neutral complex. This results indicates that when the excess electron is removed, the geometry of the AISE rearranges to a conventional H–bonded structure. The MP2 energy of the UG neutral dimer is by −269 meV lower that the AISE energy indicating that the AISE is a metastable system with finite lifetime. Although we have not explored the AISE potential energy surface (PES) around the minimum, the strength of the interaction between the uracil and glycine molecules with the excess electron and the AISE configuration, which is significantly different from any local minimum on the PES of the neutral complex, suggest that the minimum probably has a considerable depth. Thus the AISE, if formed, is a long–lived species. In our work [36] on the hydrogen fluoride trimer an experimental evidence was presented of the existence of an AISE of this system in the gas phase. Thus, it is possible that the UG AISE can also be observed.

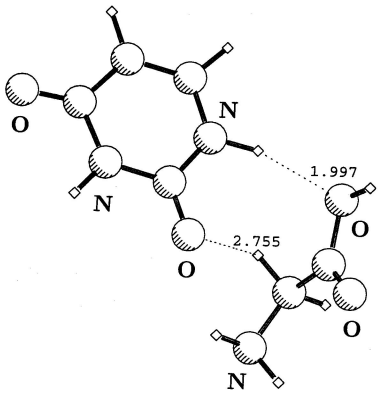

Fig. 2. The MP2/6-31++G**X equilibrium structure of the neutral uracil–glycine dimer obtained by initiating the geometry optimization from the two AISE equilibrium geometry. The distances shown are in Å.

3 Summary

As the calculations presented here showed, uracil and glycine can form an interesting aduct with an excess diffuse electron between them. This configuration corresponds to a local minimum on the potential energy surface of the UG anion and the excess electron is bound in this system. Upon electron detachment from the anion the structure of the complex changes considerably since the relative orientation of the two monomers in the anion with their dipole moments pointing at each other becomes very unfavorable when the electron is removed.

However, this unfavorable orientation of the dipoles of the monomers in the *e*–bond UG anion gives rise to a strong quadrupole moment in the middle of the complex that can support the excess electron in a bound state (see the caption of Tab. 1 for the quadrupole moment values). Naturally, the *e*–bond anion is not the only minimum of the UG anion potential energy surface. Another minimum with a lower total energy corresponds to the previously described proton–transferred anion species [31]. The others include dipole–bound anions that can be formed by

the UG complex where the dipoles of the two monomers are aligned and point in the same direction. There is also a possibility of excess–electron trapping in a quadrupole–bound state between a uracil molecule and a glycine *zwitter* ion.

The UG anion described in this work can be formed in a gas–phase collision between an uracil dipole–bound anion and a glycine molecule (provided that the excess inter–molecular vibrational energy is removed from the system allowing the *e*–bonded anion to settle in its local minimum). Once stabilized, the conversion of the *e*–bonded anion to the more stable proton–transferred anion is unlikely (or very slow) because the structures of the two are very dissimilar and separated by, what is likely to be, a considerable barrier. This gives rise to a possibility of an experimental detection of the UG *e*–bonded anion in the gas phase.

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