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Theoretical Study of Neutral, Anionic, and Cationic Uracil−Ag and Uracil−Au Systems: Nonconventional Hydrogen Bonds

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The interaction of Ag and Au with uracil has been studied using the B3LYP density-functional approach. Neutral, cationic, and anionic systems were analyzed in order to study the influence of the atomic charge on bond formation. This interaction becomes stronger as the charge increases. In the case of neutral systems, a weak association is present. In the case of cations, the interaction is mainly electrostatic. The extra electron of the anions is localized on the metal atom. Consequently, nonconventional hydrogen bonds are formed. The ionization energy of uracil−Ag and uracil−Au is lower than the corresponding values for the metal atoms and uracil molecule, while the electron affinity is higher for uracil−Ag and uracil−Au than the analogous values for the isolated Ag, Au, and uracil. This might have significance for further experiments and possibly for applications, where the movement of the electrons is important. In the case of uracil−Ag and uracil−Au (anions), it may be possible to induce the detachment of one electron from the anion and also to remove a single hydrogen atom. It is possible that tight competition exists between the H dissociation and electron aloofness.

Introduction

DNA is a fundamental molecule, which is very important due to its role in biology and its possible use for the development of miniature electronic devices.[1−4] Metal atoms and ions, attached to conjugated molecular systems such as DNA, may function as electron donors or acceptors, increasing the electron donor capacity of the system. For the study of electron transport along strands of DNA, a detailed understanding of the interaction between metal atoms and ions with a nitrogen basis is of fundamental importance. Concerning biological processes involving DNA, metal effects are also crucial[5−17] as these may change the orientation of hydrogen bonds, which are essential for the formation of the double helix structure. The interaction of metal ions with the nitrogen basis is able to stabilize various tautomers, modifying the structure and biological function of DNA. Recent experiments suggest that electrons are able to cause DNA damage, and some authors have reported that excess electrons trapped in temporary anionic states are able to induce chemical reactions, leading to single- and double-strand breaks.[18,19] Metal atoms and ions, interacting with DNA, are able to provide extra electrons with important consequences on the biological function of this molecule.

Studies of metal−DNA and metal−RNA systems provide valuable thermodynamic and structural information. The interaction of DNA and DNA nitrogen bases with transition, alkali, and alkaline earth metal atoms and clusters has been reported previously.[20−41] Experimental results are focused on the analysis of the toxicity of some metals and also the reactivity and conductivity of various atoms, interacting with DNA and DNA bases. Photoelectron spectroscopy (PES)[37−39] represents a very effective tool for the study of small anionic systems in the gas phase. In these experiments, an extra electron is photo-detached from the system and the anion spectroscopically accesses the ground electronic states of the neutral form. This is important because many electronic states of the neutral species are undetectable, using other spectroscopic techniques. These results can be analyzed theoretically, since the electron vertical detachment energies can be calculated, using a variety of methods. Taking these values, it is possible to interpret the spectra and to define the structures that are present in the experiment. Thus, both theory and experiment are necessary for the interpretation of these interactions in the gas phase. To analyze whether it is possible to use PES in the study of the interaction of DNA bases with copper atoms, an analysis of the interaction of copper atoms with guanine and uracil was undertaken.[20] It was concluded that it must be possible to detach an electron from the anion and also to remove a single hydrogen atom from the system, owing to the fact that the vertical ionization energy of the anion is similar to the dissociation energy of a single hydrogen atom. In another work,[40] we analyzed the interaction between cytosine and metals which have a closed-shell electronic configuration, such as Ca, Zn, and Cd (in their neutral and ionic forms). In these systems, the most stable isomer is derived from the canonical isomer of cytosine. The interaction between metal and cytosine is predominantly electrostatic, and it becomes stronger as the global charge of the metal increases. In general, metal cations bind more strongly to neutral cytosine than they do to neutral metals.

Most of the theoretical studies dealing with the interaction of metal−DNA bases and metal−RNA are focused on binding sites and the electron-transfer process. Recently, Kryachko and Remacle[35] reported a theoretical study of gold neutral clusters interacting with DNA bases, such as adenine, guanine, and cytosine. They used small gold clusters as simple models for Au particles, and reported that, “in the most stable planar base

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complexes, the Au−N or Au−O anchor bonds are reinforced by N−H−Au bonds”. They discussed the formation of these nonconventional hydrogen bonds and concluded that “one of the unanchored gold atoms served as a nonconventional proton acceptor”. This is possible due to the charge redistribution on the gold neutral clusters. An important question which is addressed in the present work refers to whether nonconventional hydrogen bonds are also present when metal anions interact with DNA bases. Some metal atoms (such as Cu, Ag. and Au) with an extra electron have a stable closed-shell electronic configuration. It is to be expected that these anionic metal atoms interacting with DNA bases will form stable complexes and have an extra electron localized on the metal atom. In this situation, metal atoms may serve as nonconventional proton acceptors, and nonconventional hydrogen bonds may be formed and will play an important role in stabilizing, as well as destabilizing, DNA base pairs. Following this idea, in a previous work we reported a theoretical study of cytosine−Cu and cytosine−Ag (neutral and ions) and discovered nonconventional hydrogen bonds.[41] Here we continue with the analysis of uracil−Ag and uracil−Au (neutral and ions) in order to establish the influence of the metal atomic charge on bond formation, and in order to examine the presence of nonconventional hydrogen bonds. Optimized geometries, Mulliken atomic charges, and binding energies are used to provide insight into the binding mechanism of these nucleobases with Au and Ag atoms. In order to analyze whether it is possible to cause the detachment of one electron from the anion and also the dissociation of one hydrogen atom, the dissociation energy of a single hydrogen atom from (uracil−M)$^-$ is also described. This information may turn out to be useful for further experimental studies.

Computational Details

Density functional theory[42−44] as implemented in *Gaussian 03*[45] was used for all the calculations. The hybrid, three-parameter B3LYP[46−48] functional was used for the calculation of complete optimizations, without symmetry constraints. Two base sets were employed: LANL2DZ[49−51] for Ag and Au, and 6-311G(d,p)[52] for C, H, O, and N. Harmonic frequency analyses permitted us to verify optimized minima.

Previous studies show that DFT reproduces equilibrium geometries and relative stabilities with hybrid functionals, which partially include the Hartree−Fock exchange energy. These results are largely consistent with those obtained using the Møller-Plesset perturbational theory at second order and basis sets of medium quality, such as 6-31G(d,p) and cc-pVDZ.[53−55]

Owing to the fact that an adequate number of isomers were used during the initial stage of the study, we were able to extensively explore the potential surface energy in search of the global minimum. The number of initial geometries examined here is great enough to reliably identify the global minima. In order to compute the vertical electron detachment energies (VEDE) of anionic species, further single-point calculations were required. Formation energies for neutral and cationic species were calculated using zero-point corrected energies. The M−uracil compounds were considered to be at their lowest electronic state (singlets and doublets).

Although there is no universally accepted method for assigning electrostatic charges to atoms, and no experimental technique is currently available, in a previous study de Oliveira et al.[56] made a comparison of the charges obtained using the Mulliken and Bader population analysis methods. The qualitative description of the atomic charges was the same, using either of these methods. For this reason, in this paper Mulliken atomic charges are used in the discussion of the qualitative behavior involved in the charge-transfer process. Results were analyzed using the Molekel[57,58] and the Ball&Stick[59] packages.

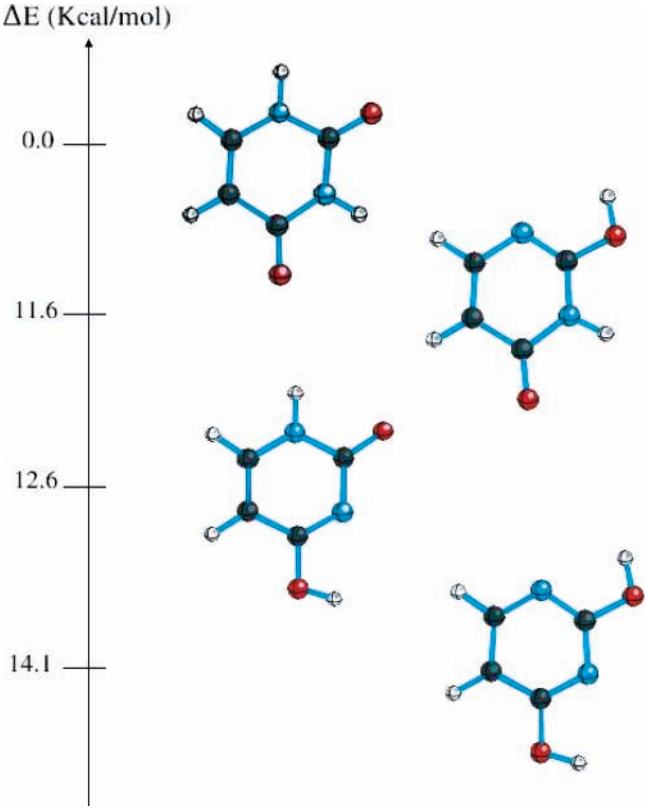

Figure 1. Most stable tautomers of uracil. Energy differences (in kcal/mol) with respect to the ground state are reported.

Results and Discussion

1. Isolation of Uracil, Ag, and Au. Optimized structures for different tautomers of uracil are presented in Figure 1. Energy differences with respect to the most stable structure are also shown. As may be observed, the ground state has two carbonyls and the amino groups are protonated. Other tautomers are less stable by more than 10 kcal/mol. In the second and third structures, there is a proton transfer from the nitrogen to the oxygen atom. The structure at 14.1 shows two hydroxyl groups.

The interaction of metal atoms with nitrogen bases may stabilize different tautomers of the nitrogen bases. This means that the stability order of different isomers of uracil may change with the presence of the metal. For this reason, all the tautomers shown in Figure 1 were used to construct initial geometries for the optimization of uracil−Ag and uracil−Au. In order to provide necessary information for the analysis of possible charge-transfer processes between uracil and the metal atoms, electron affinity (EA) and ionization energy (IE) of uracil, Au, and Ag were obtained and are reported in Table 1, together with the available experimental results. Theoretical and experimental IE values largely coincide (error is less than 3%). For Au and Ag, the theoretical EA value coincides with that of the experiment (error is less than 18%). However, for uracil the error in the EA calculation is quite large. Note that EA for uracil is very small; for this reason, it is more difficult to obtain reliable theoretical and experimental values (as may be inferred from the varying values reported in the literature). A general trend emerges from observing both experimental values and theoretical calculations; that is, the value of EA of uracil is less than the

TABLE 1: Theoretical Results of the Ionization Energy (IE) and the Electron Affinity (EA) of Uracil, Ag, Au, Uracil−Ag, and Uracil−Au (Available experimental results are also shown.)

	theoretical results (B3LYP)		experimental results	
	IE (eV)	EA (eV)	IE (eV)	EA (eV)
uracil	9.1	−0.2	9.35 ± 0.01[a]	0.054 ± 0.035[b] 0.085 ± 0.015[b] 0.093 ± 0.007[b] 0.030 ± 0.060[b] 0.086 ± 0.008[b]
Ag	7.8	1.1	7.57	1.30
Au	9.4	2.2	9.23	2.31
uracil−Ag	5.9	1.9		
uracil−Au	6.9	3.0		

[a] Reference 61. [b] Reference 62.

corresponding value for Ag and Au, whereas the value of IE for uracil is similar to the value for Au and greater than that of Ag. Hence, our calculations provide a correct general description for the IE and EA of the reactants—a prerequisite for explaining the charge-transfer process, which may be occurring in the reactions studied.

2. Uracil−Ag and Uracil−Au Systems. Silver and gold are both iso-electronic with regard to their valence shells and hence they are expected to manifest similar chemical behavior. In order to analyze the influence of the global charge in the interaction of these metals with uracil, we studied neutral, anionic, and cationic systems. In the following, we report the results for neutral, cationic, and anionic systems separately, emphasizing the most important effects of the charge in the bonding of the metal atom to the uracil molecule.

*Neutral Systems***.** The most stable structures of uracil−Ag and uracil−Au (both neutrals) are shown in Figures 2 and 3. The ground state for each group is planar and related to the most stable tautomer of uracil. In the case of the most stable structures, the metal atom is interacting with one oxygen atom. In each system, up to 5 or 6 isomers were found within 10 kcal/mol from the respective ground state. Among these isomers, only two uracil tautomers of the uracil are implicated. For uracil−Ag and uracil−Au, the ground state is almost degenerated, along with other similar structures. All of them contain the most stable tautomer of uracil. The metal atom is bonded to different atoms of uracil with diverse spatial orientations, but their stability is almost the same. Only the isomer that in both cases is less stable involves a different tautomer from the uracil molecule. The structure that is at 10.0 and 7.1 kcal/mol from the ground state (for uracil−Ag and uracil−Au, respectively) has another tautomer of uracil, which is less stable by 12.6 kcal/mol (see Figure 1). In these systems, as in others,[40,41] the stability order does not depend on the atom of uracil which is bonded to the metal, but rather on the tautomer of the uracil, which is in the compound.

In order to determine the nature of the bond, we analyzed the molecular orbital diagram. There is no evidence from these molecular orbitals, upholding the possibility that these interactions are covalent in character. In the case of the Mulliken atomic charges, we can say that an electrostatic interaction between the metal (which has a small negative charge) and the hydrogen atoms of the uracil (which have a small positive charge) may exist. The formation energy of uracil−Ag and uracil−Au (neutrals) is −2.9 and −4.9 kcal/mol, respectively. These values are very small, and we can thus conclude that neutral uracil is not greatly attracted to the neutral metal atoms.

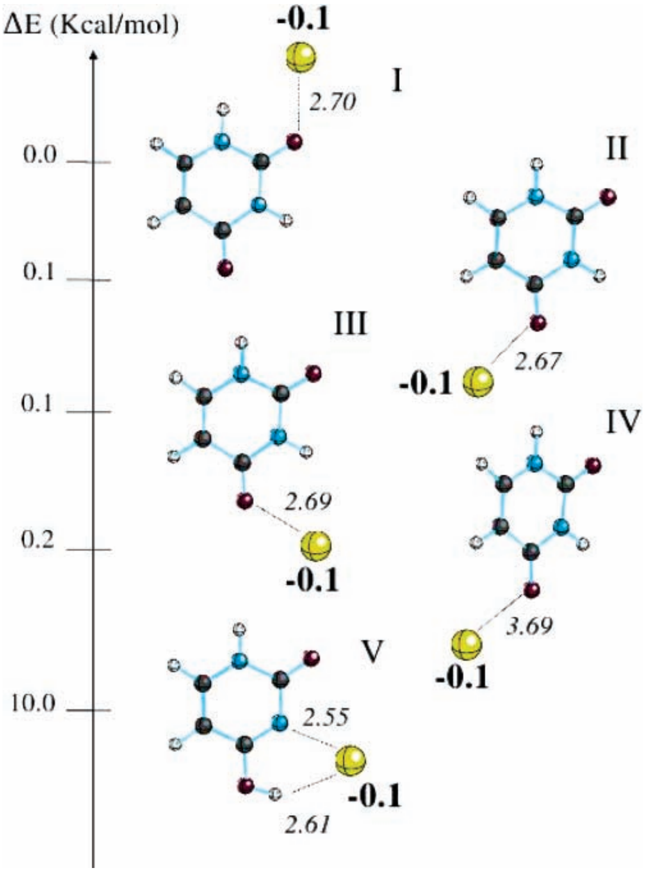

Figure 2. Optimized structures of uracil−Ag (neutral). Bond distances (in Å and italics) and Mulliken atomic charges (in bold letters) are reported. Energy differences with respect to the ground state are also shown.

Cationic Systems. We optimized the cationic systems, with the aim of investigating the influence of the global charge. In Figures 4 and 5, optimized geometries of the most stable isomers of (uracil−Ag)$^+$ and (uracil−Au)$^+$ are presented. In each group, up to 8 isomers were found within 15 kcal/mol from the respective ground state. Metal atoms (Ag and Au) have a charge, which is partially positive, in all cases. The IE values of uracil are similar to those of Au. This explains why the positive charge of (uracil−Au)$^+$ is partially localized on the metal atom. However, the IE for Ag is smaller than that for uracil. This gives a good reason for explaining why the positive charge of Ag in (uracil−Ag)$^+$ is greater than the positive charge of Au in (uracil−Au)$^+$.

The interactions between metal atoms and nitrogen bases stabilize different tautomers of uracil in the cationic systems. The most stable structures are those where the metal positive atoms are bonded to the N or O atoms (negatively charged) of uracil. The interaction is mainly electrostatic and stronger than that of neutral systems. Metal−uracil bond distances are shorter for the cations than for the neutrals. In the case of the molecular orbitals (not shown), we can say that no covalent bond exists. Consider the following reaction scheme:

$$\text{uracil}^+ + \text{M} \rightarrow \text{uracil}{-}\text{M}^+$$

in which the formation energies are −77.2 and −56.1 kcal/mol, for (uracil−Ag)$^+$ and (uracil−Au)$^+$, respectively. Comparing these formation energies with those of neutral systems, they are greater in the case of the cations than in the case of the neutral form, indicating that the cationic uracil is more reactive with the neutral metal atoms than it is with the neutral uracil.

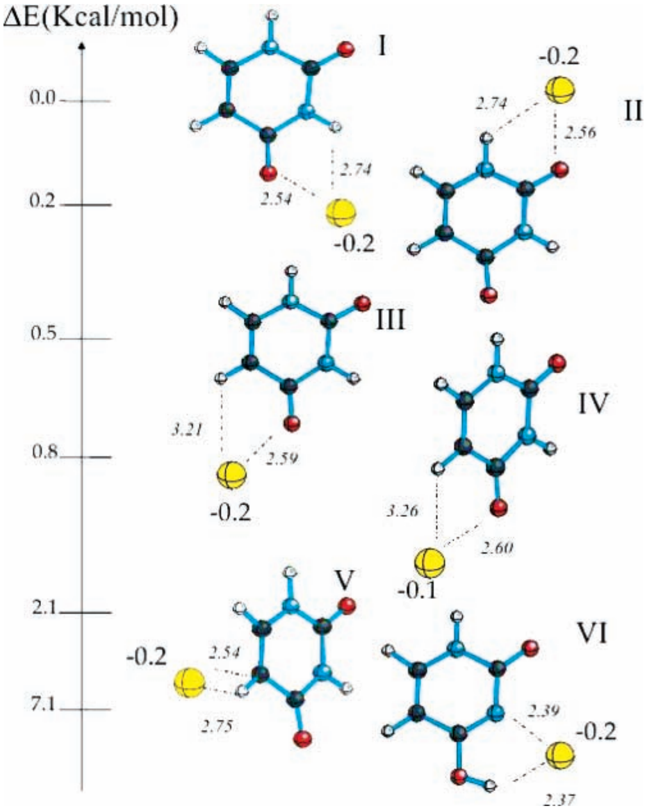

Figure 3. Optimized structures of uracil−Au (neutral). Bond distances (in Å and italics) and Mulliken atomic charges (in bold letters) are reported. Energy differences with respect to the ground state are also shown.

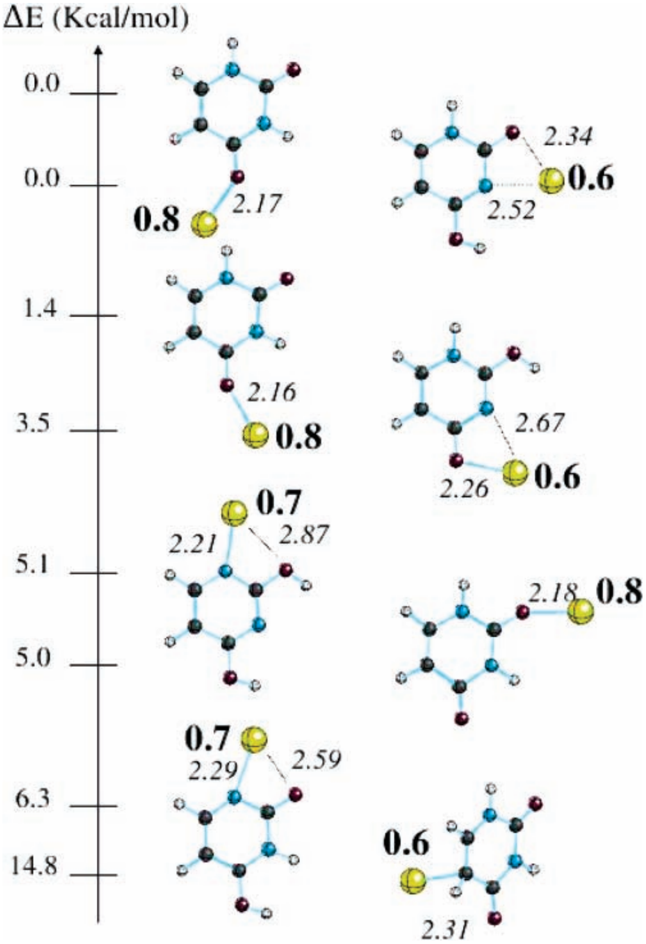

Figure 4. Optimized structures of (uracil−Ag)$^+$. Bond distances (in Å and italics) and Mulliken atomic charges (in bold letters) are reported. Energy differences with respect to the ground state are also shown.

Another approach for the analysis of these results is to consider neutral uracil and metal cations. Consider the following reaction scheme:

$$\text{uracil} + \text{M}^+ \rightarrow \text{uracil}-\text{M}^+$$

in which the formation energies are −43.9 and −62.0 kcal/mol, for Ag and Au, respectively. In these circumstances, cationic metals are more reactive than neutral atoms toward neutral uracil. In view of the fact that these values are negative, it is possible to say that these reactions favor the formation of compounds over the separated atoms and molecules. These values indicate a strong interaction in the cationic system.

Ionization energies of uracil−Ag and uracil−Au are presented in Table 1. IE values for uracil−M are smaller than those for the isolated uracil molecule. The uracil ionization energy changes from 9.1 to 5.9 or 6.9 eV for uracil−Ag or uracil−Au, respectively. In the case of Ag and Au, the IE are also greater than the values of uracil−Ag and uracil−Au. Among the uracil−M ionization energies, uracil−Au is greater than that of uracil−Ag. This means that the ionization of the uracil−M system is easier than the ionization of the isolated molecule or the ionization of the metal atoms. As observed in other systems,[40,41] the bond between the metal atoms and the uracil molecule diminishes the energy which is necessary for an electron to be removed from the system, a fact which may be important for further applications where electron movement is crucial.

Anionic Systems. Figures 6 and 7 report the optimized structures for (uracil−Ag)$^-$ and (uracil−Au)$^-$. As can be seen, ground states are similar for both metals. The ground state for each group is planar and related to the canonic tautomer of uracil. In the case of the most stable structures, the metal atom is interacting with two hydrogen atoms. In each system, only 2 isomers fall within a range of 10 kcal/mol. Other isomers exist which are less stable by 9.4 and 8.5 kcal/mol in the case of Ag and Au, respectively. These include an alternative tautomer for uracil. In all the isomers shown in Figures 6 and 7, four different tautomers of uracil are implicated. In any isomer, the negatively charged metal atom is found close to the positive hydrogen atoms of the uracil. The charge distribution of the systems closely coincides with the EA values. Values in Table 1 indicate that the EA of the metals is greater than the EA of the uracil molecule; for this reason, in the uracil−M compound, the extra electron is localized on the metal atom. In Table 1, it is possible to see that the EA values are greater for uracil−Ag (anion) than for the isolated uracil or Ag atom. A similar result was found for uracil−Au (anion). In the case of an extra electron, Ag and Au have a closed-shell electronic configuration which is stable. This fact is reflected in the vertical electron detachment energies (VEDEs) of the anions. The values are 2.1 and 3.8 eV, for (uracil−Ag)$^-$ and (uracil−Au)$^-$, respectively. These results may be useful for further experiments and may have other possible applications.

Concerning the interaction of the metal atom with uracil, the charge distribution on the system has resulting consequences which are important. As previously mentioned, all the interactions are through two hydrogen atoms, which are positively charged. The orientation of the bonds is similar to the nonconventional hydrogen bonds reported by Kryachko and Remacle.[35] They studied the reaction between gold clusters and DNA bases,

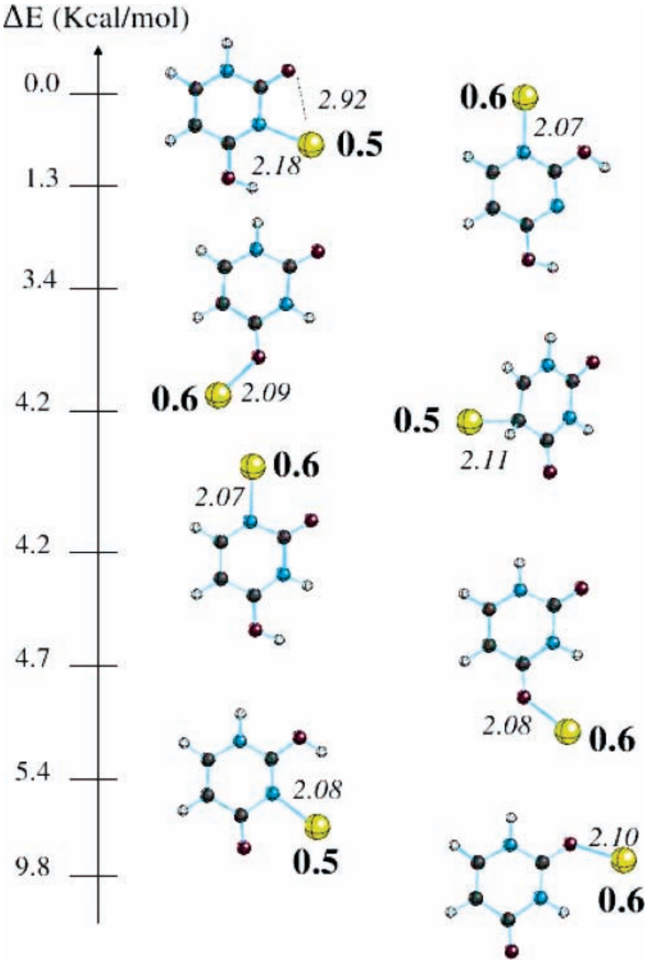

Figure 5. Optimized structures of (uracil−Au)$^+$. Bond distances (in Å and italics) and Mulliken atomic charges (in bold letters) are reported. Energy differences with respect to the ground state are also shown.

discovering stable structures with clusters orientated toward the hydrogen atoms, which have a positive charge. The most negative metal atom of the cluster was closer to the hydrogen atom than the other metal atoms. They call this bond a "nonconventional hydrogen bond", since it fulfills all the prerequisites that are necessary for this type of interaction. In uracil−Ag and uracil−Au (anions), at least four prerequisites of the nonconventional hydrogen bonds are satisfied, namely: (i) there is evidence of bond formation (one M−H stretching mode is found around 80 cm^{-1}); (ii) this bond involves a hydrogen atom which is bonded to Au along the N−H bond direction; (iii) the N−H bond elongates in the compound, relative to the isolate uracil; and (iv) the sum of the van der Waals radii (2.92 Å for H−Ag, and 2.86 Å for H−Au) is larger than the hydrogen bond distances (2.52 Å for H−Ag and 2.33 Å for H−Au). In these nonconventional hydrogen bonds, the negative metal atom (Ag and Au) represents a proton acceptor. In the case of uracil, the bond is formed between a proton donor group (N−H) and a proton acceptor (Ag$^-$ and Au$^-$). Hydrogen bonds are geometrically described in terms of bond lengths and angles. In the case of (uracil−Ag)$^-$, the N−H−Ag bond angle measures 144°. We compare this bond angle with those previously reported[60] (the N−H−O hydrogen bond measured 177° and 127° for strong and weak hydrogen bonds, respectively); these can be classified as intermediate. However, binding energies fall within a range of −22.4 to −52.2 kcal/mol (depending on the scheme of the reaction, in the case of either Ag or Ag$^-$ interacting with uracil$^-$ or uracil, respectively; therefore these can be classified as strong (>10 kcal/mol) hydrogen bonds. In order to explain this elevated value for the binding energy, we must consider the possibility that another

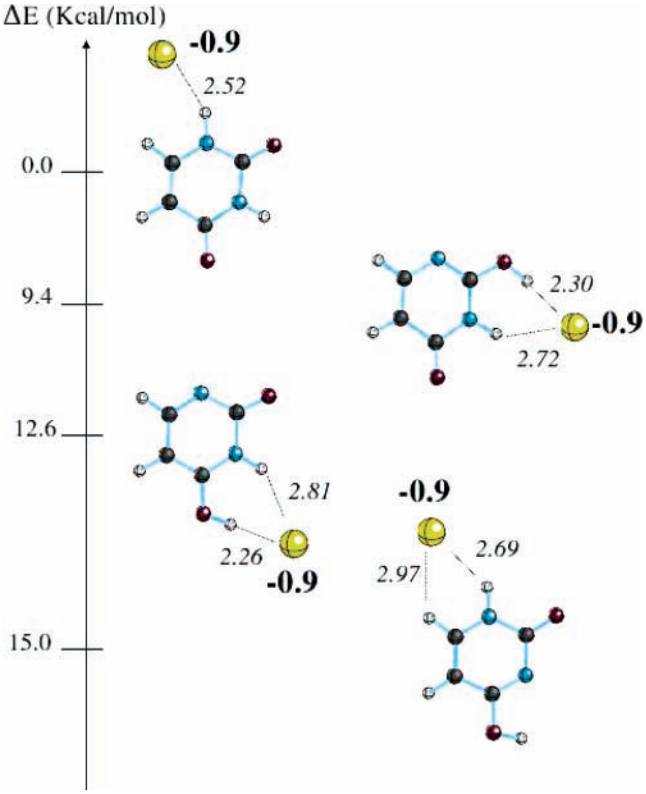

Figure 6. Optimized structures of (uracil−Ag)$^-$. Bond distances (in Å and italics) and Mulliken atomic charges (in bold letters) are reported. Energy differences with respect to the ground state are also shown.

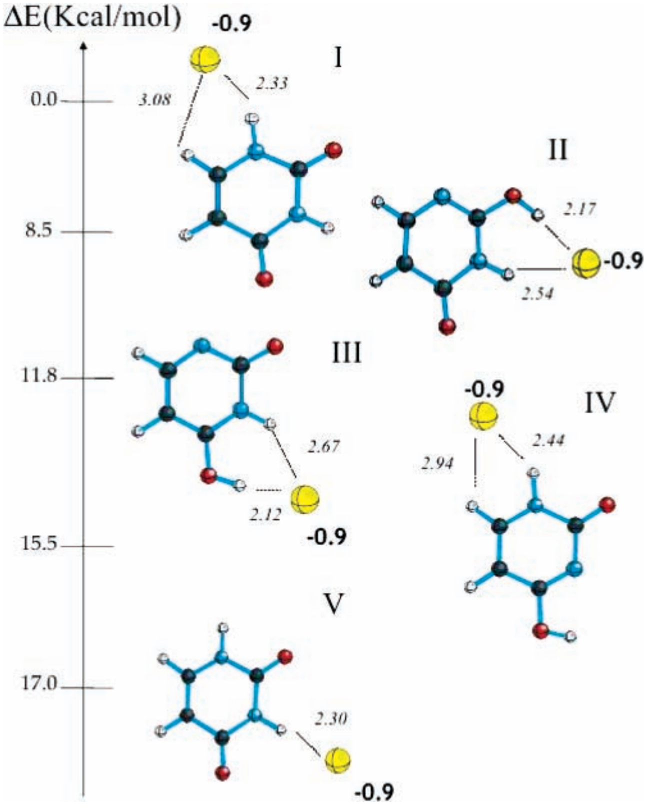

Figure 7. Optimized structures of (uracil−Au)$^-$. Bond distances (in Å and italics) and Mulliken atomic charges (in bold letters) are reported. Energy differences with respect to the ground state are also shown.

hydrogen bond is formed (in the case of the C−H groups, which is close to the metal atom). The individual hydrogen bond is intermediate, if one refers to the bond angle, but the two hydrogen bonds strengthen the interaction between uracil and the metal anion and thus the binding energy is elevated. We found similar results for (uracil−Au)$^-$. The N−H−Au bond angle is 148° and hence, the interaction may also be considered as representing an intermediate hydrogen bond. The fact that the binding energies fall within a range of −24.8 to −79.6 kcal/mol (depending on the scheme of the reaction, with Au or Au$^-$), points to the same conclusions. In summary, in the case of Ag and Au, the anions show nonconventional hydrogen bonds, similar to those previously reported for other systems.[35,41]

3. Electron Detachment versus Dehydrogenation. The formation of covalent bonds between copper anions and guanine or uracil when one hydrogen atom from the DNA bases is exchanged with Cu has been reported previously.[20] In the case of these systems, tight competition may exist between the H dissociation and the electron detachment. In order to study whether this is the situation in the case of Ag and Au with uracil, a calculation of the anionic dehydrogenated products was undertaken. The dehydrogenation energies are

$$[\mathrm{Ag-uracil}]^- \rightarrow [\mathrm{Ag-uracil-H}]^- + \mathrm{H} \qquad 2.7\ \mathrm{eV}$$

$$[\mathrm{Au-uracil}]^- \rightarrow [\mathrm{Au-uracil-H}]^- + \mathrm{H} \qquad 3.6\ \mathrm{eV}$$

These systems need this energy in order to remove H from (uracil−M)$^-$. For the dehydrogenated compounds, the atomic charges of Ag and Au are less negative. When a single hydrogen atom is removed, the metal binds covalently to uracil. The vertical electron detachment energies are 2.1 and 3.8 eV for (uracil−Ag)$^-$ and (uracil−Au)$^-$, respectively. These values are close to the detachment energy of a single hydrogen atom and indicate that tight competition may exist between the detachment of an electron and the dissociation of H from uracil.

Conclusions

There is no stabilizing effect on the tautomerization of the uracil isomers, due to interaction with Ag or Au. The stabilization order of uracil tautomers with Ag or Au remains the same as it is for the isolated molecule, that is, the most stable isomers include the most stable tautomer of the uracil. The global charge strengthens the bond between the metal atom and the uracil molecule. The interaction becomes stronger as the charge increases. For the neutral system, almost no interaction was found. For the cations, the nature of the bonding is mainly electrostatic. The interaction is between the metal cation and N or O atoms of uracil, which are negatively charged. As a consequence of the electronic configuration of the metal atom, both Ag and Au are negatively charged on M−uracil anions. In these cases, the interaction is between the nonconventional hydrogen bonds and the negatively charged metal atoms.

The presence of Ag and Au bonded to the uracil molecule decreases the amount of energy which is necessary for ionization. Besides this, the electron affinity of uracil−Ag and uracil−Au is higher than the corresponding value of the metal atoms and the uracil molecule. This may be important for future applications, where the movement of the electrons is important. In these cases, as with copper, it may be possible to remove an electron from the anion and also to dissociate H from (uracil−M)$^-$, because the vertical ionization energy of the anions is similar to the dissociation energy of a single hydrogen atom from (uracil−M)$^-$.

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