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Dipole-Bound Anions to Adenine−Imidazole Complex. Ab Initio Study

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An interesting configurational change has been predicted for the adenine−imidazole complex upon dipole-bound attachment of an excess electron to this system. The presence of the electron reverses the stability order of the two lowest energy configurations of the complex. One should be able to detect this effect experimentally using Rydberg electron-transfer spectroscopy.

1. Introduction

The hydrogen bonding interaction of two heterocyclic systems occurs in various biological complexes and is one of the most important factors determining the biological functions of these complexes. Most interactions in dimers of nucleic acid bases (NABs) and interactions between NABs and amino acids (AAs) are hydrogen bond interactions and are similar to those that appear in the adenine−imidazole complex. This complex is used as a model in the present work to allow us to study the effect of its interaction with an excess electron on the configurational topology of the hydrogen bonds in dimers of polar heterocyclic biomolecules.

The interaction of NAB and NAB−AA complexes with excess electrons is an effect which may have important biological consequences.[1] Excess electrons or hydrated electrons may appear in the cell environment due to secondary reactions which follow the interaction of high-frequency radiation with the cell. This may cause damage to the cell material, through attachment and the chemical reactions involving the electron that follow. The free electron is an extremely potent and reactive chemical agent. When it covalently binds to a molecule, it can considerably alter the molecular structure. However, the dipole-bound attachment, which places the excess electron outside the molecular frame, usually affects the intramolecular structural parameters less than the covalent attachment. This type of attachment can, however, lead to more significant changes in intermolecular structural parameters in complexes with hydrogen bond interactions. For example, our recent theoretical−experimental studies on the indole−water clusters have revealed that some of these clusters change their geometric-thermodynamic topology after a dipole-bound electron attachment.[2]

In the present work, we use ab initio calculations to examine the configurational topology of the dipole-bound anions of adenine−imidazole clusters. The goal of this study is to determine whether the interaction of the clusters with an excess electron can result in a change of their thermodynamic stability and their geometric configurations.

The major N_9H tautomeric form of adenine has three proton acceptor sites at N_1, N_3, and N_7, and three hydrogens connected to nitrogen atoms (one at N_9 and two at the amino group), which can be donated to hydrogen bonds. Due to this diversity, adenine can form several different cluster structures with imidazole. Protonation studies of adenine in the solid state showed evidence for having the largest protonation strength at the N_1 site.[3] This result is consistent with recent DFT calculations of Russo and co-workers,[4] who estimated the proton affinity at this site to be 945.3 kJ/mol. The calculations by Smets et al. MP2/6-311G** (Møller−Plesset second-order perturbation theory) on 9-methyladenine yielded the proton affinities at the N_1, N_3, and N_7 sites of 961.3, 951.6, and 933.7 kJ/mol, respectively.

Since both adenine and imidazole are polar systems with nonzero dipoles, some of their complexes may have sufficient dipole moments to form dipole-bound anions. This effect is investigated in the present work. It was shown[6] that binding a low-energy electron to the dipole field of a polar system is strongly dependent upon the value of its dipole moment, but the system size, its polarizability, etc. are also important contributing factors. The binding energy of the dipole-bound electron is a rapidly varying function of the magnitude of the dipole moment, and it is greater than zero only if the dipole moment exceeds the threshold value of about 2−2.5 D.[7] For larger systems, like the adenine−imidazole dimer, this threshold is probably larger and approachs 3 D.

One of the experimental techniques that allows the study of dipole-bound anions of molecular complexes is Rydberg electron transfer (RET) spectroscopy,[8] which is based on transferring electrons from highly excited atoms into diffuse orbitals of polar systems. Since the method allows discrimination between different geometric configurations of the system, if their dipole moments differ, it can be used to verify the results for the adenine−imidazole dipole-bound anions that are calculated in the present work.

2. Computational Method and the Results

First, the configurational landscape of the adenine−imidazole neutral clusters was explored using both the Hartree−Fock method (HF) and the standard 6-31++G**(6d) basis set. Nine different dimer configurations where found in these calculations. They are denoted by letters, from **A** to **I**, and are shown in Figure 1. The energy (HF and MP2 with the electron correlation accounting for only for the valence electrons) and dipole moment results corresponding to the nine structures are presented in Table 1. For each configuration we also calculated the IR frequencies to verify whether the calculated structures correspond to true minima on the potential energy surface of the complex. From the IR frequencies, the zero-point vibration energies (ZPE) were calculated, and they are also shown in Table 1. Based on the sum of the MP2 and ZPE energies, the

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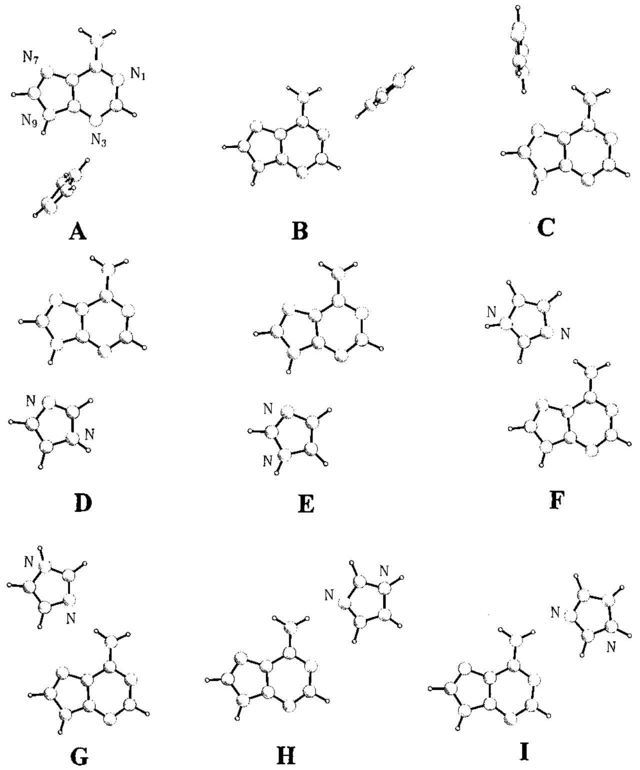

Figure 1. HF/6-31++G** equilibrium structures of the adenine−imidazole complex.

TABLE 1: Complexes of Adenine with Imidazole[a]

com-plex	HF	MP2	ZPE[b]	dipole	Δ*E* [MP2+ZPE]
A	−689.393907	−691.602153	0.199046	3.98	3.08
B	−689.392956	−691.600239	0.199106	7.30	4.32
C	−689.392738	−691.600882	0.199130	5.11	3.93
D	−689.398645	−691.607111	0.199077	4.21	0.00
E	−689.396324	−691.604880	0.198890	6.31	1.27
F	−689.392761	−691.599807	0.199461	6.66	4.82
G	−689.390994	−691.598006	0.199261	6.39	5.82
H	−689.393388	−691.600253	0.199508	1.82	4.57
I	−689.391341	−691.598125	0.199253	3.00	5.74

[a] Total energies and zero-point vibrational energies (ZPE) in hartrees, dipoles in debyes, relative energies in kilocalories per mole. Calculations performed with the 6-31++G**(6d) basis set. [b] Unscaled Hartree−Fock zero-point vibrational energy.

relative thermodynamic stability of the calculated configurations was determined. In the two lowest energy structures, the imidazole molecule is connected via two hydrogen bonds to the adenine molecule. The stronger of the two bonds is between the imidazole nitrogen and H− N_9 of adenine. The weaker bond is formed by one of the C−H's of imidazole with N_3 of adenine. The energy difference between the two configurations of 1.27 kcal/mol (MP2 + ZPE result) is low enough to allow the two systems to coexist in the low-temperature (estimated at about 150 K) jet conditions of the RET experiment. The other dimer configurations are higher in energy and can be expected to appear only at higher temperatures. It is worth noticing that almost all of the dimers (except for **H** and **I**) have sufficient dipole moments to form stable dipole-bound anions with an excess electron. This includes the two lowest-energy configurations (**D** and **E**), whose predicted HF/6-31++G** dipole moments are 4.21 and 6.31 D, respectively.

In the next step, for the complexes with dipole moments exceeding 3 D the dipole-bound anions were calculated. The anion geometries were first optimized using the spin-unrestricted HF method (UHF) and the standard 6-31++G**(5d) basis, which was augmented with six very diffuse Gaussian sp shells, with the exponents equal to 0.01, 0.002, 0.0004, 0.00008, 0.000016, and 0.0000032, and a p orbital with the exponent 0.036. The additional diffuse Gaussians were centered at the most peripheral hydrogen atom of either the adenine or the imidazole in the complex, whichever was located closest to the positive direction of its dipole moment vector. The 6-31++G**(5d) basis, augmented with the additional diffuse shells, will be denoted as 6-31++G**(5d)X in further discussion. In our previous studies, we determined that this set of additional orbitals should be sufficient to describe the ground states of the dipole-bound excess electron in systems with dipole moments similar to the dipole moments of the complexes considered in the present work.[9] The use of the UHF method for the anionic complexes did not introduce any noticeable spin contamination because the dipole-bound electron was located outside the molecular frame in these systems. The exchange interaction of the excess electron with the core electrons, which would induce the contamination, was very small due to negligible overlap.

Following the anion geometry optimizations, the obtained equilibrium structures of the anions were used as the starting geometries in the optimizations of the neutral complexes. These optimizations were performed with the spin-restricted HF method (RHF) and the 6-31++G**(5d)X basis set to generate the reference geometries and energies of the neutral complexes for calculation of the adiabatic electron affinities (AEA). For both the anions and the neutral systems at their respective equilibrium HF/6-31++G**(5d)X geometries, we calculated the HF harmonic-vibrational frequencies and the zero-point vibrational energies (ZPE). We also performed MP2/6-31++G**(5d)X energy calculations for all of the systems. This level of theory is the minimum that one should use in calculations of dipole-bound anions, since the electron correlation effects are important for these types of systems. We have not been able to perform more sophisticated calculatations in the present work due to the limitations of our computational resources. Among the works where selection of the basis set and the theoretical level for AEA calculations of NABs is discussed, one should mention the recent papers by Wetmore et al.[10] and by Russo et al.[11]

Based on the ZPE and MP2 results, the AEAs were calculated as the difference of the energies of the anions and the corresponding neutrals. All of the calculations presented in this work have been performed with the GAUSSIAN94 program package.[12] The results of the AEA calculations are presented in Table 2.

As one sees upon reviewing the results in Table 2, seven different dipole-bound anions are predicted for the adenine−imidazole complex. The electron affinities of the corresponding neutral complexes vary over a wide range of values. The most interesting result is the fact that upon electron attachment, the two lowest-energy configurations change their order. Configuration **D**, which was the most stable form for the neutral complex, is less stable with the excess electron than configuration **E**, which has a higher dipole moment and a stronger interaction with the electron. As a result, the anion's configuration **E** has slightly lower energy than configuration **D**, by 0.20 kcal/mol. This stability reversal is a phenomenon which can be experimentally investigated using RET. The present results suggest that the RET spectrum of the adenine−imidazole dipole-bound anion should show two peaks, which appear at considerably different positions, in the mass spectrum; these are

TABLE 2: Dipole-Bound Anions of Adenine−Imidazole Complexes[a]

complex		HF	MP2	ZPE[b]	Δ [MP2+ZPE]	AEA [MP2+ZPE]
A	neutral	−689.392608	−691.573548	0.199151	3.11	0.5
	anion	−689.392633	−691.573553	0.199138	3.83	
B	neutral	−689.391661	−691.571638	0.199200	4.34	61.4
	anion	−689.392694	−691.573746	0.199053	3.66	
C	neutral	−689.391469	−691.572295	0.199235	3.95	71.5
	anion	−689.392381	−691.574741	0.199053	3.03	
D	neutral	−689.397378	−691.578552	0.199193	0.00	22.9
	anion	−689.397612	−691.579580	0.199379	0.20	
E	neutral	−689.395033	−691.576309	0.199077	1.33	89.6
	anion	−689.396730	−691.579953	0.199429	0.00	
F	neutral	−689.391480	−691.571196	0.199569	4.85	49.7
	anion	−689.392404	−691.573053	0.199601	4.44	
G	neutral	−689.389752	−691.569453	0.199390	5.83	33.7
	anion	−689.390343	−691.570723	0.199421	5.79	

[a] Total energies in hartrees, relative energies with respect to the lowest energy configuration (Δ) in kilocalories per mole, adiabatic electron affinities (AEA) in millielectronvolts. Calculations performed with the 6-31++G**(6d)X basis set. The X-set consists of six diffused sp shells, with the exponents 0.01, 0.002, 0.0004, 0.00008, 0.000016, and 0.0000032, and a p orbital, with the exponent 0.036. X-set is centered at the hydrogen atom closest to the positive pole of the dipole moment of the complex. [b] Unscaled Hartree−Fock zero-point vibrational energy.

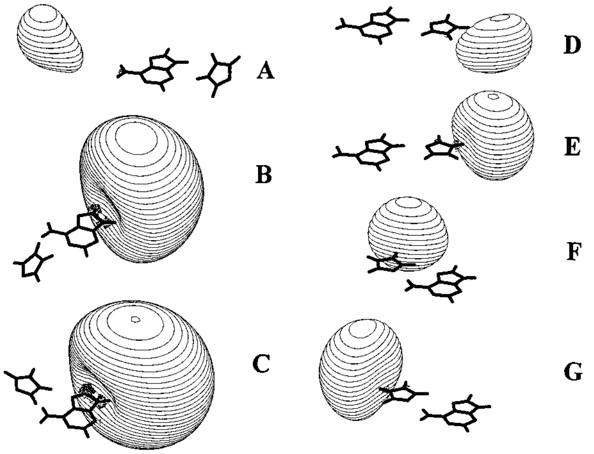

Figure 2. Orbitals occupied by excess electrons in dipole-bound anions of adenine−imidazole complexes.

determined as a function of the Rydberg quantum number of the Xe atoms, which are used in the experiment as electron carriers. Although the present calculations predict that the peaks should appear at 71.5 and 22.9 meV, their positions may shift somewhat if a more accurate level of theory is used in the calculations.

The dipole-bound character of the excess electrons in the dipole-bound adenine−imidazole anions is demonstrated in Figure 2, where the orbitals occupied by the electrons are shown. As is typical of the dipole-bound anions, the orbitals have σ-character and they are located outside the molecular frames of the complexes. The diffuse orbital characters and shapes confirm that the calculations describe dipole-bound anions. It is interesting that in some of the anions the excess electron is located by the adenine molecule, and in others it is located by the imidazole molecule. However, in the two most stable configurations (**D** and **E**), the electron is located by the imidazole and away from the adenine.

3. Conclusions

The formation of stable dipole-bound anions by the adenine−imidazole dimer is investigated with the use of ab initio calculations. Since both adenine and imidazole are polar systems and have several hydrogen bonding sites, the number of possible dimer configurations whose dipole exceeds the threshold for the dipole-bound electron attachment is significant. Among these configurations, the two most stable ones have comparable energies and should appear in the low-temperature jet in the RET experiment. Since the adiabatic electron affinities of the two configurations are predicted to be considerably different, the RET spectrum should show two distinct peaks. An interesting phenomenon, which is predicted in the present calculations and which can carry some biological significance, is the reversal of the low-temperature thermodynamic equilibrium of the two lowest energy dimer configurations upon dipole-bound electron attachment. The reversal is due to higher stabilization of the configuration with the larger dipole moment by interaction with the excess electron.

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