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Interaction of the uracil dipole-bound electron with closed-shell systems (Ar and N_2)

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Abstract. A very diffuse, but spatially confined, electron trapped in a dipole–bound state of a polar molecule provides an excellent target for testing the interaction of a localized electron positioned outside the molecular frame of its host molecule with other atomic or molecular systems. In this work we use *ab initio* calculations to investigate systems where a dipole–bound electron attached to a uracil molecule is interacting with an N_2 molecule and an Ar atom. Neither of the two systems forms a stable anion and in the aducts they form with the dipole–bound electron the electron becomes suspended between the uracil molecule and Ar or N_2. Calculations are performed to determine the vertical electron detachment energies of these anions and to determine the molecular rearrangements occurring when the excess electron is removed from them.

Keywords: Cluster anions – Uracil anion – Dipole–bound electron – Solvated electron – *Ab initio* calculations

1 Introduction

From the insightful works of Tomasi and his coworkers [1] we have learned the importance of solvation in chemical processes. Solvation has a particularly profound effect if the solvated species are charged, polar or very polarizable. In this context the solvation of an electron is particularly interesting. In this work we investigate microsolvation of an "almost" free electron, which forms a dipole–bound (DB) state with a polar molecule, by nonpolar closed–shell systems.

Closed–shell atoms and nonpolar molecules rarely form stable anions with excess electrons. This is related to a usually significant gap between the HOMO and LUMO levels in these systems. However, if an excess electron can be shared between two or more molecules a closed–shell system may be able to accommodate a fraction of the electron. Sharing of an excess electron between two closed–shell molecules is the phenomenon studied in this work with the use of *ab initio* quantum mechanical calculations. We consider two model systems consisting of a uracil molecule and an argon atom (uracil·Ar) in the first model and of a uracil molecule and a nitrogen molecule (uracil·N_2) in the second model. This study follows our previous study on the uracil·He and uracil·Ne anions [2].

An isolated uracil molecular is sufficiently polar to form a DB anion with an excess electron in the gas phase as predicted by theoretical calculations performed by our group [3] and subsequently detected in gas-phase experiments by the groups of Schermann [4] and Bowen [5]. This is the only type of anion formed by uracil molecules in isolation. This and previous studies of uracil performed by our group have been motivated by the biological importance of this system. The DB electron of uracil is very diffuse, but is still localized, and it is almost entirely located outside the uracil molecular frame. Only from one side the access to it is blocked by the uracil molecule. In such a state the electron is accessible to a direct electron–atom or electron–molecule interaction. The diffuse orbital that describes the state of the uracil DB electron decays exponentially to zero at larger distances. If a neutral molecule or an atom that approaches the electron has a higher electron affinity than uracil, the uracil DB excess electron should transfer to the approaching molecule. If, however, the atom or the molecule has a lower electron affinity than uracil and does not form a stable anion, we may see either some concentration of the density of the uracil excess electron or some local reduction of the density around the approaching system. These changes will be indicative of the electrophilic or electrophobic character of the system.

Both Ar and N_2, whose interaction with the uracil DB electron we test in this work, will remove the excess electron from uracil, but they will form a complex with it.

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The stability of such a complex is investigated here with the use of the calculations. One should note that at large distances between the uracil DB anion and either Ar or N_2 the interaction between the two systems should be attractive because it is dominated by charge – induced–dipole effects. Apart from the electrostatic interaction, particularly at intermediate distances, the dispersion interaction should also play a role. This interaction depends on the polarizabilities of the two interacting systems, and, since the DB excess electron is very polarizable, one should see a sizable dispersion contribution to the interaction energy.

Since neither Ar nor N_2 forms a stable anion and one may expect that it would take some energy to force an electron to enter the valence region of each of these systems, it is unlikely that these systems, when placed on the other side of the DB electron from the uracil molecule, would tunnel through the excess electron and approach the uracil molecule more closely. However, if the electron is taken away, the distance between the uracil and Ar or N_2 should decrease and each of the two systems should position itself at a distance where its attractive interaction with uracil is maximized. In this case the dominant contribution to the interaction energy will come from either dipole – induced–dipole or dispersion interaction. Thus in the uracil·e·Ar or the uracil·e·N_2 system the DB uracil electron forms a barrier between the uracil molecule and Ar or N_2. This barrier separates the two systems, i.e. uracil and Ar or uracil and N_2, but it still holds them bound at a more extended distance. When the barrier is removed the two systems should approach each other more closely to form a van der Waals complex.

The experimental evidence [6] indicates that the uracil·Ar complex forms an anion that shows a DB–electron signature in the photoelectron spectrum. It is a sharp peak almost identical to the spectrum of the DB anion of the uracil monomer. There are probably a number of local minima for the complex of a DB uracil anion and an Ar atom. One of them could be a structure where the Ar atom is attached to the excess electron at the opposite side from the uracil molecule. Another structure, which is also described in this work, has a DB electron attached to a uracil·Ar complex. A similar structure is also possible for the anion of the uracil·N_2 complex.

In our recent study on hydrogen fluoride trimer anions [7], where photoelectron experiments of Bowen and coworkers were combined with the theoretical calculations performed by Gutowski and our group, we presented evidence that a DB anion for this system coexists under certain conditions in the gas phase with an anion where there are two hydrogen–bonded hydrogen fluorides on one side of the excess electron and one hydrogen fluoride on the other side. The two anions produced two sharp peaks in the photoelectron spectrum. The latter anion is similar to the uracil·Ar or uracil·N_2 anions considered in the present work.

In our previous work on uracil·e·HF and uracil·e·H_2O [8] we called these systems anions with internally suspended electrons, or AISEs 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 attaches to the DB electron on the side opposite from the site where the first unit is connected. In the resulting system the excess electron is suspended between the two units and it facilitates weak bonding between them.

AISEs belong to a broader category of anions called "solvated electrons", since in these systems the excess electron exists inside the cluster and not on its surface as in the DB anions. In uracil·e·H_2O and uracil·e·HF [8] the electron is solvated by two polar molecules. In uracil·e·Ar and uracil·e·N_2 there is only one polar unit. Actually, in an AISE with more than two units only one needs to be polar to bind an electron in a localized bound state.

In the first part of the paper we describe the approach used in the calculations. In the second part we present and discuss the results.

2 Calculations and discussion

The questions which we attempt to answer in this work are

- Is there a local minimum on the potential-energy surfaces of the complex of a DB uracil anion with Ar or N_2 that corresponds to AISE? Are there any other minima?
- What are the vertical and adiabatic electron detachment energies (VDE and ADE) of the uracil·e·Ar and uracil·e·N_2 AISEs and other isomers of these anions?

In order to provide answers to these questions, a series of calculations were performed with the use of the GAUSSIAN98 quantum chemical program package [9], and the results are described in the following.

The purpose of the first series of calculations was to search for equilibrium AISE structures of uracil·e·Ar and uracil·e·N_2. We initiated each search with a configuration consisting of a uracil DB anion and Ar or N_2 placed several angstroms from the uracil molecule on the opposite side of the diffuse DB excess electron. The geometry optimizations were performed with the MP2 method and with the basis set consisting of the standard 6-31++G**(5d) basis augmented with six diffuse Gaussian *sp* shells with exponents of 0.01, 0.002, 0.0004, 0.00008, 0.000016, and 0.0000032, and a *p* shell with exponent 0.036. These additional orbitals were placed at the hydrogen atom located closest to the positive end of the uracil dipole. 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 the total energy of the system. Thus we eliminated the possibility that the excess electron stays confined to the system owing to the use of a too spatially restricted orbital basis, and not owing to the higher stability of the anion than the neutral system at the geometry of the anion. The augmented set is called 6-31++G**X in the discussion that follows.

The electrostatic interaction (charge – induced dipole) can be expected to contribute primarily to the stability of AISEs including the uracil·e·Ar and uracil·e·N_2 AISEs; however, the dispersion forces should also play a significant role in these systems. Thus the use of a method that includes electron correlation effects and adequately describes these interactions was essential to obtain reliable AISE structures. All the geometry optimizations reported here were carried out using the MP2/6-31++G**X level of theory. Owing to the weak magnitude of the interaction, the tightest thresholds for the integral evaluation and for the convergence of the self-consistent-field procedure were used. The uracil·e·N_2 and uracil·e·Ar AISE structures obtained in the calculations are shown in Fig. 1. In this figure we also show the orbitals occupied by the excess electrons in these systems. In both systems the monomers are separated by a considerable distance (about 20 Å) and both dimers are almost planar. A slightly larger distance for Ar than for N_2 can be explained by a higher HOMO/LUMO gap in the former system that leads to a stronger repulsion between the excess electron and the Ar atom than between the electron and the N_2 molecule. Thus, even though both Ar and N_2 at large distances from uracil are attracted by the DB uracil electron, any overlap of the Ar wave function with the orbital occupied by the uracil excess electron is energetically more unfavorable than for the N_2 molecule. Another factor that can contribute to the effect is the difference in the dispersion interaction between Ar and N_2 and the uracil excess electron.

The orbitals representing the states of the excess electrons in uracil·e·N_2 and uracil·e·Ar presented in Fig. 2 show that the excess electron indeed forms a barrier between Ar or N_2 and the uracil molecule and we can describe the electron as being suspended between the uracil and Ar or N_2. As expected, Ar and N_2 "avoid" the excess electrons owing to their valence regions being highly repulsive towards them. Once the excess electron is taken out from uracil·e·N_2 or uracil·e·Ar and the barrier is removed, the two monomers approach each other much more closely than in AISEs and form typical van der Waals complexes. The closest distance between the Ar atom and the atoms of uracil reduces to only 2.87 Å. For the AISE with N_2 the distance reduces to 2.33 Å. This was determined in the MP2/6-31++G**X geometry optimizations of the neutral dimers initiated with the equilibrium geometries of the respective AISEs. The equilibrium geometries of the neutral dimers are shown in Fig. 3. It is apparent that only if an excess electron is suspended between uracil and Ar of N_2 the AISE local minimum appears on the potential-energy surface.

The total MP2/6-31++G**X and MP4/6-31++G**X energies of the two AISEs corresponding to the equilibrium structures are presented in Table 1 along with the energies of the neutral systems calculated at the equilibrium geometries of the anions. These latter values were used to determine the VDE also shown in Table 1. In the table we also present the ADE determined for each system as the difference between the anion energy and the energy of the respective neutral dimer calculated at its equilibrium geometry. The VDE and ADE calculations show a notable difference between uracil·e·N_2 and uracil·e·Ar. While the MP4 VDE values are identical for the two systems (59 meV), the ADE values are different (−66 meV for uracil·e·N_2 and −3 meV for uracil·e·Ar). The difference results from stronger attractive interaction between uracil and N_2 than between uracil and Ar, leading to higher stability of the neutral ura-

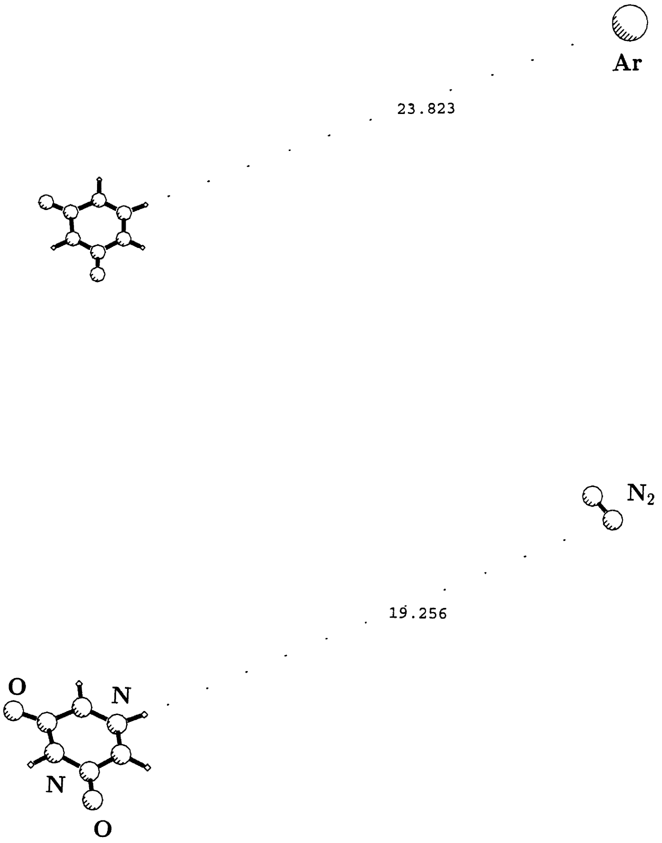

Fig. 1. The MP2/6-31++G**X equilibrium structure of uracil·e·Ar and uracil·e·N_2

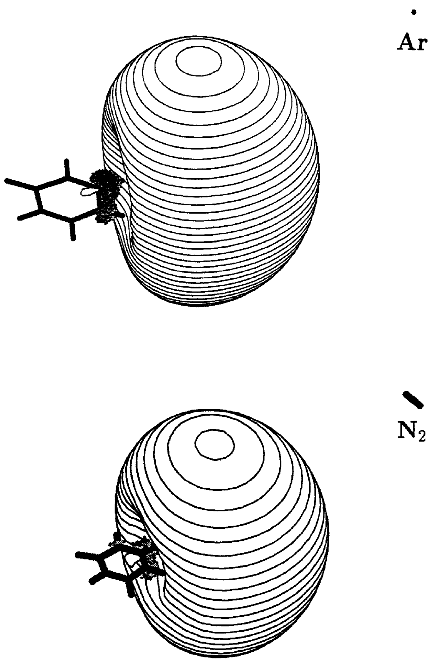

Fig. 2. Orbitals occupied by the excess electron in uracil·e·Ar and uracil·e·N_2

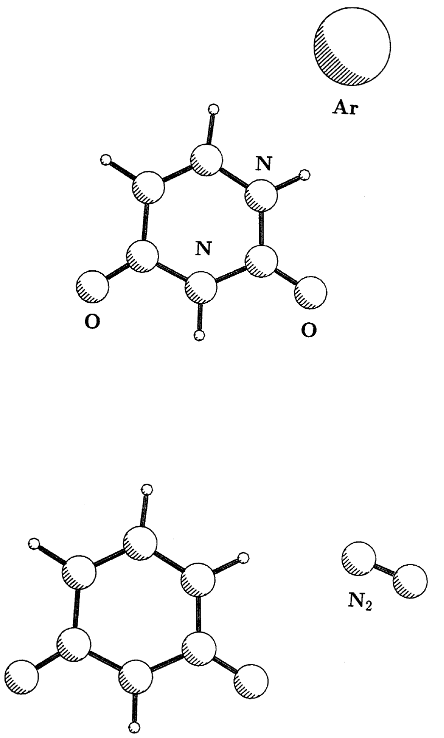

Fig. 3. The MP2/6-31 + + G**X equilibrium structures of the neutral uracil·Ar and uracil·N_2 complexes

cil·N_2 complex than the uracil·Ar complex and higher energy yield upon adiabatic electron detachment from uracil·e·N_2 than from uracil·e·Ar. One notices that while the uracil·e·N_2 anion is adiabatically unstable (metastable), uracil·e·Ar is almost as stable as uracil·Ar.

Finally, the dipole moments of the neutral uracil·Ar and uracil·N_2 complexes at their equilibrium MP2/6-31 + + G**X geometries of 5.44 and 5.30 D, respectively, indicate that both system should form DB anions with excess electrons. These anions will be structural isomers to AISEs. In both types of ions the excess electron is very diffuse, but while in AISEs the monomers are located at opposite sides of the electron, in the DB anions both of them are located at the same side of the electron. In the calculations on uracil·Ar·e and uracil·N_2·e DB anions we first optimized the geometries of these systems at the MP2/6-31 + + G**X level of theory. This was followed by calculations of VDEs and ADEs and the results are presented in Table 2. The structures of the two DB anions and the orbitals occupied by the excess electrons in these systems are presented in Fig. 4. The orbitals show all the characteristics of DB electrons and the anion structures are very similar to the respective structures of the neutral complexes. The VDEs and ADEs for both uracil·Ar·e (both equal to 19 meV) and uracil·N_2·e (26 and 25 meV, respectively) are all positive, indicating that these anions, unlike AISEs, are vertically and adiabatically stable. Furthermore the total energies of both DB anions are lower than the energies of the corresponding AISEs, indicating higher stability of the former systems.

3 Conclusions

The theoretical calculations performed in this work have revealed interesting forms of complexes formed by the uracil DB anion with closed–shell atomic and molecular systems, Ar and N_2, which do not form stable anions in the gas phase. In these complexes the excess electron is solvated from one side by a uracil molecule and from the other side by Ar or N_2. The uracil and Ar or N_2 are separated from each other by a considerable distance (about 20 Å). The excess electron in both systems is suspended between the two monomers and the electron prevents the monomers from approaching each other more closely. When this barrier is removed by ejecting the excess electron from the anions the monomers in both systems move much closer to each other (about 2.5 Å) and form conventional van der Waals complexes. The calculations of VDEs and ADEs showed that the aducts of Ar and N_2 with the uracil DB electron are stable with respect to vertical removal of the excess electron, but they have different adiabatic stability. While uracil·e·N_2 is noticeably unstable uracil·e·Ar is only marginally unstable. Calculations were also performed for DB uracil·Ar·e and uracil·N_2·e anions and it

Table 1. Calculations of the vertical and adiabatic electron detachment energies (*VDE* and *ADE*) of the anions with internally suspended electrons of the uracil·N_2 and uracil·Ar complexes. Calculations performed with the 6-31 + + G**X(5d) basis set. Total HOMO (for anions) and LUMO (for neutral systems) energies in hartrees; VDE and ADE in millielectonvolts

Method	Anion//anion	Neutral//anion[a]	Neutral//neutral[c]	VDE	ADE
Uracil·N_2					
MP2//MP2[b]	−522.937921	−522.936031	−522.940609	51	−73
MP4//MP2	−523.041254	−523.039075	−523.043688	59	−66
HOMO/LUMO	−0.00187	−0.00120	−0.00060		
Uracil·Ar					
MP2//MP2[b]	−940.590606	−940.588732	−940.590950	51	−9
MP4//MP2	−940.689806	−940.687644	−940.689908	59	−3
HOMO/LUMO	−0.00186	−0.00121	−0.00049		

[a] Calculations performed at the equilibrium anion geometry

[b] The notation denotes *the level of theory used in the calculation//the level of theory used in calculating the structure*

[c] Calculations performed at the equilibrium geometry of the neutral complex obtained in the geometry optimization initiated with the equilibrium geometry of the anion

Table 2. Calculations of the VDE and ADE of the dipole–bound anions of the uracil·N_2 and uracil·Ar complexes. Calculations performed with the 6-31 + + G**X(5d) basis set. Total HOMO (for anions) and LUMO (for neutral systems) energies in hartrees; VDE and ADE in millielectronvolts

Method	Anion//anion	Neutral//anion[a]	VDE	ADE[c]
Uracil·N_2				
MP2//MP2[b]	−522.941514	−522.940565	26	25
HOMO	−0.00092	−0.00065		
Uracil·Ar				
MP2//MP2[b]	−940.591632	−940.590921	19	19
HOMO	−0.00066	−0.00053		

[a] Calculations performed at the equilibrium anion geometry

[b] The notation denotes *the level of theory used in the calculation//the level of theory used in calculating the structure*

[c] The energy for the neutral complex used in the calculation is provided in Table 1

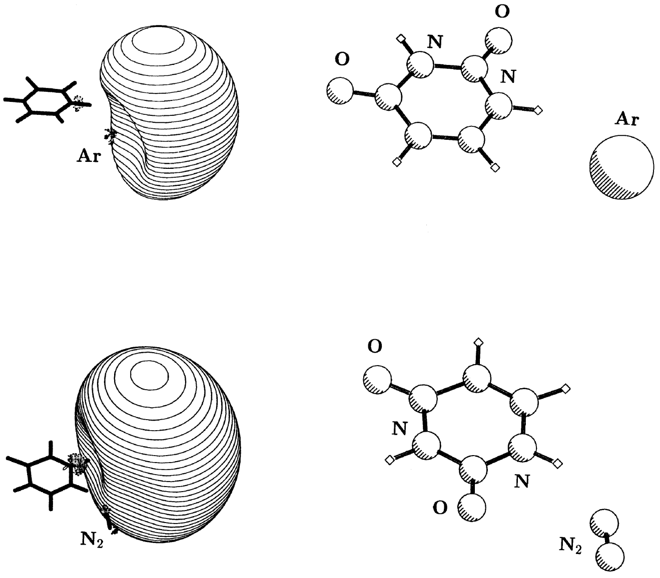

Fig. 4. The MP2/6-31 + + G**X equilibrium structures and orbitals occupied by the excess electrons in the uracil·Ar·e and uracil·N_2·e dipole–bound anions

was shown that these systems are both vertically and adiabatically stabled and stables than uracil·e·Ar and uracil·e·N_2.

The existence of two minima on the potential-energy surface of uracil·Ar and uracil·N_2 corresponding to the two different locations of the closed–shell system, Ar or N_2, with respect to the diffuse DB electron of uracil is an interesting phenomenon. We showed before that the AISE formed by a DB anion of the hydrogen fluoride dimer and a hydrogen fluoride monomer can be produced under certain conditions in a photoelectron spectroscopy experiment [7]. It would be interesting to determine whether the AISE/DB–anion isomerism can be observed for the uracil·Ar and uracil·N_2 anions.

Acknowledgements. We dedicate this work to Prof. Jacopo Tomasi. Through his numerous important contributions to the field of quantum chemistry he has inspired many works of others, including ours. He has been one of the pioneers of quantum chemistry and owing to his dedication and intellectual input to the field it has grown to become one of the leading research branches of chemistry.

References

1. Tomasi J, Cammi R, Mennucci B, Cappelli C, Corni S (2002) Phys Chem Chem Phys 4: 5697
2. Hall CS, Adamowicz L (2002) Mol Phys 100: 3469
3. (a) Oyler NA, Adamowicz L (1993) J Phys Chem 97: 11122; (b) Oyler NA, Adamowicz L (1994) Chem Phys Lett 219: 223
4. Desfrançois C, Abdul–Carime H, Schermann JP (1996) J Chem Phys 104: 7792
5. Hendricks JH, Lyapustina SA, de Clercq HL, Snodgrass JT, Bowen KH (1996) J Chem Phys 104: 7788
6. Hendricks JH, Lyapustina SA, de Clercq HL, Bowen KH (1998) J Chem Phys 108: 8
7. Gutowski M, Hall CS, Adamowicz L, Hendricks JH, de Clercq HL, Lyapustina SA, Nilles JM, Xu S-J, Bowen KH (2002) Phys Rev Lett 88: 143003
8. Jalbout AF, Hall CS, Adamowicz L (2002) Chem Phys Lett 354: 128
9. Frisch MJ *et al.* (1998) Gaussian 98, revision A.7. Gaussian, Pittsburgh, PA