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# Anions of the hydrogen-bonded guanine–cytosine dimer – theoretical study

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## Abstract

The quantum mechanical calculations performed in this work revealed an interesting nature of the stationary states of an excess electron in the guanine–cytosine (G–C) anion. The electron can form either a dipole-bound (DB) state or a covalent state. The coexistence of the two states may enhance the ability of the G–C dimer to capture an excess electron. © 2001 Elsevier Science B.V. All rights reserved.

## 1. Introduction

The theoretical and experimental determination of the electron affinities (EAs) of nucleic acid bases (NABs) has proven to be a challenging problem [1–14]. The gas-phase experimental work on this subject has proceeded along two different directions. Bowen and coworkers [1] used photoelectron spectroscopy (PES) to study EAs of NABs in the gas phase. Photodetachment-PES was also recently used by Schiedt et al. [2] to study EAs of the pyrimidine NABs and their complexes with water. A gas-phase study of NAB anions has been also carried out by Schermann and coworkers [3,4] using Rydberg electron transfer (RET) and field-detachment spectroscopy. This technique was used in detection of anions of NAB dimers including, for example, the anion of the thymine dimer (T–T) [5]. An interesting feature of the RET spectroscopy

is its ability to detect coexisting dipole-bound (DB) and covalent anions of the same system if the states describing the excess electrons in these two anions are sufficiently long lived. The theoretical calculations performed in the present work indicate that the guanine–cytosine (G–C) dimer anion may be a good model for observation of such a phenomenon.

The NAB pairs play an essential role in conveying genetic information, justifying the interest in the electron attachment mechanism and in showing how electron attachment affects the structures of these systems. These transformations may cause lesions in the genetic material since free radicals, among them free electrons or hydrated electrons, are very potent damaging factors in the cell environment. One source of free electrons (or hydrated electrons) in biological environments are secondary reactions which follow the UV-induced radiolysis of water. The damaging effect on free electrons on the DNA and RNA structures are directly related to the outcome of the electron attachment to the NAB pairs. The present work on electron adducts of the hydrogen-bonded G–C

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dimer is motivated by the biological relevance of this system.

## 2. Calculations and discussion

Our work on the uracil dimer anion [12] showed that the excess electron can either be DB or can covalently attached. In the covalent uracil dimer anion, the excess electron is exclusively located at one of the uracil molecules and the second uracil molecule only plays the role of ‘spectator’. However, due to the almost perpendicular relative orientation of the two uraciles, the anion acquires considerable stability due to the solvation effect which the spectator uracil molecule has on the molecule carrying the excess electron. Another notable structural feature of the covalent uracil dimer anion was a puckering deformation of the ring of the uracil molecule where the excess electron is located.

In a subsequent study we investigated the adenine–thymine (A–T) canonical base pair anion with the use of *ab initio* calculations [13]. The calculated results allowed us to conclude that the A–T base pair is not an effective trap of excess electrons since the adiabatic electron affinity (AEA) was predicted to be negative. However, the calculations performed for the A–T covalent anion converged to a structure whose vertical electron detachment energy (VDE) was positive, indicating its vertical stability.

The present study on the G–C dimer anion allowed us to contrast the  $[A-T]^-$  and  $[G-C]^-$  systems. The questions which we attempt to answer in this work are:

- Is the G–C dimer a more effective electron trap than the A–T dimer?
- If the G–C dimer anion is an adiabatically stable system with respect to the electron detachment, what are its geometrical structure and its electronic structure (or structures in case it can form more than anion)?
- Can DB and covalent adiabatically stable anions coexist for G–C anion?

In order to provide answers to the above questions, a series of calculations were performed with the use of the GAUSSIAN 94 quantum chemical

program package [15]. The results are described below.

The purpose of the first set of calculations, performed at the UHF/6-31++G\*\*(6d) level of theory, was to determine equilibrium configurations of covalent anion of the hydrogen-bonded G–C dimer. The two structures corresponding to the Watson–Crick and reversed Watson–Crick configurations were found (see Fig. 1). In both configurations the excess electron is localized at cytosine as is shown in the depictions of the highest occupied molecular orbitals (HOMOs) presented in Fig. 1. This is not unexpected since pyridine bases are known to have higher covalent electron affinities than purine bases. The analysis of the geometrical structures of the two dimer anions shows that in both systems the cytosine ring is noticeably puckered. This puckering effect resulting from electron attachment has been observed in other NAB dimer anions [12,13] and has been attributed to the stabilizing effect the deformation has on the excess electron.

In the next set of calculations, structures of the neutral G–C dimer were determined at the RHF/6-31++G\*\*(6d) level of theory. The geometry optimizations were initiated with the previously obtained structures of the dimer anions. Following the optimizations, MP2/6-31++G\*\*(6d) calculations were performed at the equilibrium geometries of the anions and the neutral dimers. Energies of the neutral dimers were also calculated at the anion equilibrium geometries. The results are shown in Table 1. Based on the MP2 energies, the VDEs and the AEAs were determined for both anions; the results are also shown in Table 1. Both anions have positive VDEs, indicating stability of the two systems with respect to the vertical electron detachment. However, the AEA values for both systems are negative, indicating that at the MP2/6-31++G\*\*(6d) level of theory the anions are not adiabatically stable. One notices that for the Watson–Crick configurations the AEA is only marginally negative and equal to  $-56$  meV. A comparison of this value with the HF AEA of  $-355$  meV indicates a significant positive electron correlation contribution that may further increase if higher order correlation effects are included. It is quite possible that these higher order effects can

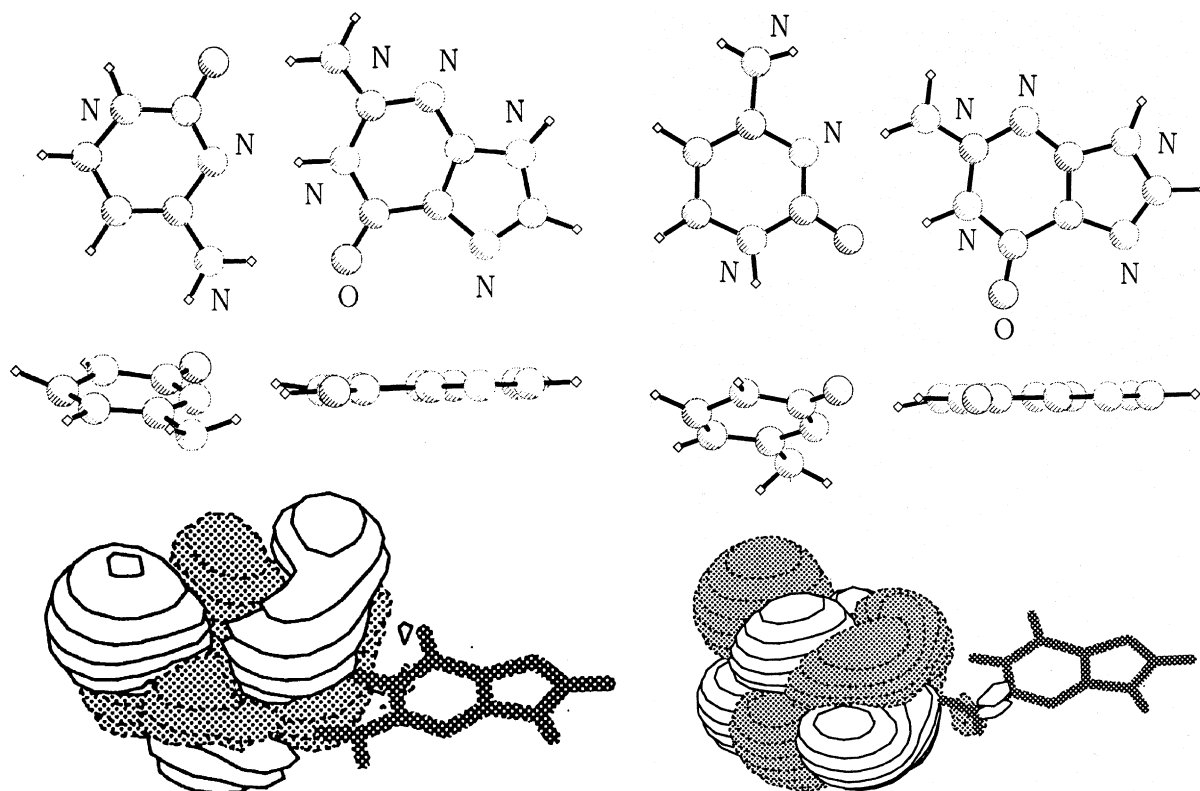


Fig. 1. Structures of the covalent anions of the regular and reversed Watson–Crick G–C dimers, and the orbital occupied by excess electron in the anion of the regular dimer.

Table 1

G–C dimer total MP2/6-31++G\*\*(6d)//HF/6-31++G\*\*(6d) energies (in hartree), and anion VDEs and AEAs (in meV) of the neutral dimer

Base pair	Anion	Neutral at anion geometry	Neutral	VDE	AEA
Watson–Crick G–C	–934.948495	–934.927746	–934.950539	565	–56
Reversed Watson–Crick G–C	–934.939249	–934.911678	–934.945759	750	–177

make the anion adiabatically stable. Since our computational resources have not permitted us to run ab initio calculations beyond the second-order, we used the density functional theory (DFT) with the B3LYP correlation-exchange functional to estimate the total correlation effects. It should be pointed out that the parametrization of the DFT/B3LYP method was not developed to provide accurate EA values and thus our result should be considered as an approximation with a rather uncertain trust bracket. Using the HF/

6-31++G\*\*(6d) optimal structures of the Watson–Crick G–C dimer anion and the neutral in the DFT/B3LYP/6-31++G\*\*(6d) calculations, we obtained a positive AEA value equal to 391 meV. Considering this value and the argument above, it is likely that including higher order correlation effects will lead to positive AEA, and thus we have a reason to believe that the G–C dimer in the regular Watson–Crick configuration forms an adiabatically stable covalent anion. That may not be true for the reversed Watson–Crick dimer since

its MP2 AEA is also negative but three times larger than for the regular dimer.

Another form of electron attachment to the G–C dimer may be caused by the interaction of the dimer dipole moment with the excess electron. This would require that the dipole moment of the dimer exceeds the value of 2.5 D. This dipole value is the experimentally determined threshold for a molecular system to form a stable DB anion with an excess electron [16]. Since the calculated HF/6-31++G\*\*(6d) dipole moments are 6.4 and 2.9 D for the Watson–Crick and reversed Watson–Crick G–C dimers, respectively, the former should form a stable DB anion. To test this possibility, we performed a series of calculations with a basis set that consisted of the standard 6-31++G\*\*(5d) set and an additional set containing six very diffuse sp gaussian shells with the exponents 0.01, 0.002, 0.0004, 0.00008, 0.000016, 0.0000032, and a p-orbital with the exponent 0.036. The additional diffuse set was positioned at the most peripheral hydrogen atom of the dimer located closest to the dipole vector direction at its positive side. The 6-31++G\*\*(5d) basis augmented with the diffuse orbitals will be called 6-31++G\*\*(5d)X in the further discussion.

In considering the G–C DB anion, we first optimized its structure at the UHF/6-31++G\*\*(5d)X level of theory initiating the optimization with the neutral G–C Watson–Crick dimer obtained earlier. This was followed by a single-point energy calculation at the UMP2/6-31++G\*\*(5d)X level. The geometry optimization of the DB anion did not significantly change the structural parameters in relation to the neutral dimer. We observed only a small decrease in the H-bond distances. In the next step, starting from the equilibrium structure of the DB anion, the geometry of neutral dimer was reoptimized at the RHF/6-31++G\*\*(5d)X level of theory. At the equilibrium geometry, the MP2/6-31++G\*\*(5d)X energy was calculated. The HF and MP2 AEA values obtained by subtracting the respective total energies of the neutral and the anion, and the total energy values are shown in Table 2. As shown, both HF and MP2 AEAs are positive, indicating that the DB anion is an adiabatically stable system. The MP2 result, equal to 95 meV, is our best estimate of the G–C DB AEA.

Table 2

Total energies and LUMO/HOMO orbital energy (in hartree), dipole moment (in D), and AEA (in meV) of Watson–Crick G–C dimer<sup>a</sup>

	Neutral	Anion
HF	–932.108677	–932.110940
MP2	–934.912745	–934.916219
LUMO/ HOMO	–0.00166	–0.00303
Dipole	6.4	
AEA		
HF		62
MP2		95

<sup>a</sup> Calculations performed with the 6-31++G\*\*(5d)X basis set. X set consists of the following Gaussian orbitals: p (0.036), sp (0.01), sp (0.002), sp (0.0004), sp (0.00008), sp (0.000016), sp (0.0000032); gaussian exponents in parentheses.

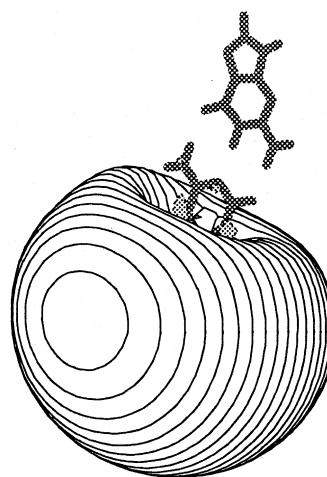


Fig. 2. The orbital occupied by the excess electron in the DB anion of the regular Watson–Crick G–C dimer.

A characteristic feature of the DB anion is a very diffuse state of the excess electrons and its localization outside the molecular frame of the system. In Fig. 2 we demonstrate these features for the G–C DB anion. The plot clearly shows the DB character of the excess electron in this system.

### 3. Conclusions

Stationary states of an excess electron in the regular Watson–Crick and reversed Watson–Crick

hydrogen-bonded G–C dimers have been studied using quantum chemical calculations. Based on the calculated results we concluded the following:

- A DB anion and a covalent anion should coexist in the gas phase for the regular Watson–Crick G–C dimer. Thus we predict that this dimer is a trap for excess electrons. The reversed Watson–Crick dimer is expected to form neither an adiabatically stable DB anion nor a covalent anion.
- In both anions of the regular G–C dimer the excess electron is near the cytosine moiety. In the DB anion its state is described by a very diffuse  $\sigma$ -orbital located by cytosine, and in the covalent anion the electron occupies a  $\pi$ -orbital located at cytosine. In the covalent anion the cytosine ring is noticeably puckered.
- One can speculate that an attachment of a free electron to the G–C dimer should first lead to formation of the DB anion since a distant free electron would first be attracted and captured by the interaction with the dipole field of the dimer. The DB anion can then interconvert to the covalent anion. Since the transition moment between the two anionic states is probably small due to the diffuse character of the DB state and the localized character of the covalent state, but not zero, the interconversion, although not frequent, should occur.

The above predictions open an interesting challenge for an experimental verification. Particularly interesting is the predicted coexistence of the covalent and DB anions of the G–C dimer in the gas phase which can be verified, for example, using the RET spectroscopy used by Schermann and coworkers [5].

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