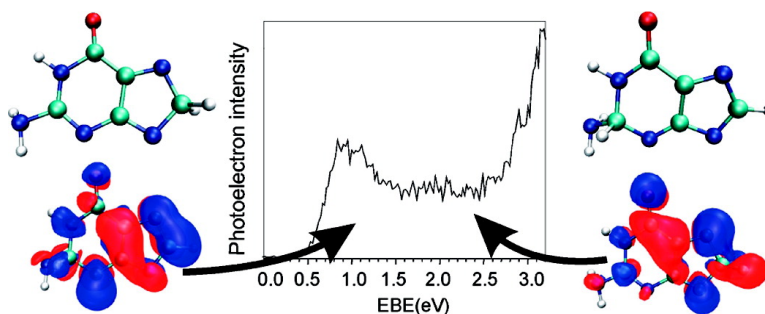


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J. Phys. Chem. B, **2007**, 111 (51), 14073-14076 • DOI: 10.1021/jp077439z • Publication Date (Web): 04 December 2007

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Adiabatically Bound Valence Anions of Guanine

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Received: September 15, 2007; In Final Form: November 18, 2007

It is believed that guanine, a basic component of DNA and RNA, has the smallest affinity to an excess electron among all nucleic acid bases. Our experimental and computational findings indicate, however, that many so far neglected tautomers of guanine support adiabatically bound anionic states in the gas phase. The computed values of electron vertical detachment energy for the most stable anionic tautomers are within a broad range of the dominant feature of the photoelectron spectrum. We suggest that guanine might be the strongest excess electron acceptor among nucleic acid bases. Thus it might be critical to radiobiological damage of DNA and it might contribute to those chemical transformations of DNA that proceed through bound anionic states.

Introduction

Nucleic acid bases (NBs) govern the storage and processing of genetic information. When ionizing radiation interacts with a living cell, electrons and hydroxyl radicals are among the most abundant reactive species formed. The resultant radicals then participate in a chain of chemical reactions that can lead to permanent alteration of DNA.¹ Low-energy electrons have not been considered to be important actors in radiation damage to DNA until relatively recently. That began to change with the seminal work of Sanche and co-workers who demonstrated in electron impact experiments on thin films of plasmid DNA that single strand breaks occur in DNA due to electrons with energies below ~ 4 eV, and that double strand breaks occur at electron energies as low as ~ 10 eV.^{2,3} This is astonishing given that much of this damage occurs at energies significantly below the ionization threshold of DNA. The resonant character of the experimental evidence points to these processes occurring through the formation of transient anions on the subunits of DNA, quite likely on the NBs themselves, because they have the largest electron affinities among DNA constituents. NB anions thus play an important role in radiation-induced mutagenesis. Furthermore, charged NBs play a critical role in electron and hole transfer in DNA.^{4,5}

Purine bases, i.e., adenine (A) and guanine (G), are believed to have a much smaller affinity to an excess electron than pyrimidine bases, as deduced from experimental^{6–8} and computational studies.^{9–12} As a consequence, pyrimidine rather than purine bases have been considered as trapping sites for excess electrons in DNA.^{13–15} The most recent results suggest, however, that purines might play an important role in excess

electron binding.^{16–21} Ray et al.¹⁶ demonstrated that the probability of capturing of an excess electron increases with the number of guanines in short single and double strands of DNA. Mazurkiewicz et al.²⁰ predicted that adenine might become a favorable site for localization of an excess electron in the Watson–Crick AT pair providing that a weak acid coordinates to the Hoogsteen sites of adenine.

Our recent results provide new insights into the stability of valence anions of NBs.^{17,21–24} We recognized that the most stable tautomers of anionic NBs are obtained from canonical tautomers through unconventional N-to-C proton transfers, i.e., a proton is transferred from a NH group to a carbon atom, whereas in conventional tautomers the proton is transferred to another electronegative atom, such as N or O. In a preliminary computational study¹⁷ we reported new N-to-C tautomers of anionic guanine, with the adiabatic electron affinity (AEA) values as large as 8.5 kcal/mol, thus even larger than those of the pyrimidine bases.^{22–24} This surprising and potentially important theoretical prediction demands experimental verifications. Noncanonical tautomers of NBs might be critical for the stability of genetic information. They have been suggested for a long time as triggers of point mutations in DNA.^{25,26}

In this contribution we present photoelectron spectroscopy (PES) data for G^- , which confirm existence of very stable valence anionic states. Moreover, we extend the past study¹⁷ with computational results for nine new adiabatically bound tautomers of anionic guanine. The calculated values of electron vertical detachment energy (VDE) are consistent with the PES spectrum. The valence state species observed here, unlike dipole-bound states, could potentially exist in solutions and biological cells, and therefore might be relevant to radiobiological damage of DNA.

Methods

Negative ion PES is conducted by crossing a mass-selected beam of negative ions with a fixed frequency photon source

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and energy analyzing the resultant photodetached electrons. This technique is governed by the energy-conserving relationship $h\nu = \text{EKE} + \text{EBE}$, where $h\nu$ is the photon energy, EKE is the measured electron kinetic energy, and EBE is the electron binding energy. Briefly, both mass spectra and photoelectron spectra were collected on an apparatus consisting of a laser vaporization source employing a Nd:YAG laser, a linear time-of-flight mass spectrometer for mass analysis and selection, a second Nd:YAG laser used for photodetachment, and a magnetic bottle used for electron energy analysis. The details of our apparatus have been described in ref 27. The ion source consisted of a rotating, translating guanine-coated metal rod (Cu or Ag), a laser beam entrance port, a pulsed gas valve to feed helium into the laser-sample interaction region, and a gas expansion exit nozzle. Typically, helium gas at 4 bar was expanded in synchronization with laser ablation pulses. The guanine-coated rods were prepared by pressing guanine powder directly onto the metal rod to form a thin layer on its surface. The guanine coating was then ablated at very low laser power with the second harmonic (532 nm) of a Nd:YAG laser.

The new ion source arrangement produces anion states that differ dramatically from those generated in our previous studies. In our earlier work, nucleic acid bases were thermally evaporated in an argon filled stagnation chamber before being expanded through a small nozzle. At that point, low-energy electrons from a filament were injected into the jet in the presence of a weak axial magnetic field, and the resultant nucleic acid base anions were then extracted into the photoelectron spectrometer. Photoelectron spectra of parent NB anions formed in this way revealed them to be dipole-bound,^{28–30} whereas photoelectron spectra of G^- generated by the laser irradiation method described above showed them to be exclusively valence-bound.

The computational search for the most stable valence anions of G was performed according to a combinatorial/quantum chemical procedure.³¹ It consists of three steps: (i) combinatorial generation of an extended library of tautomers, (ii) prescreening at the B3LYP/6-31++G** level of theory, and (iii) the final geometry, zero-point vibrational energy, and electronic energy refinements for the top hits from step (ii). The geometries and harmonic frequencies were determined at the second-order Møller–Plesset level of theory and electronic energies were calculated at the coupled cluster level of theory with single, double, and perturbative triple excitations (CCSD(T)).³² The augmented, polarized, correlation-consistent basis set of double- ζ quality (AVDZ) has been used at this stage.³³ The effects of hydration were included within the IEF-PCM method with the cavity built up using the United Atom (UA0) model.³⁴ The calculations were performed with the Gaussian03³⁵ and Molpro³⁶ codes. The molecular structures and orbitals were drawn with the VMD³⁷ program.

Results

The photoelectron spectrum of G^- was measured with 3.493 eV photons and the result is presented in Figure 1. A broad band (or a combination of bands) begins from ~ 0.5 eV and reaches a local maximum at 0.8–1.1 eV. In a broad region of 1.2–2.3 eV the intensity is reduced to half the local maximum intensity. Finally, the intensity steeply increases from 2.4 until 3.2 eV, which is an end of meaningful EBEs obtained with 3.493 eV photons. Because a dipole-bound anion state has a distinctive signature, wherein its spectrum is dominated by a single narrow peak at very low EBE,^{28–30} the spectrum of G^- presented here is clearly not that of a dipole-bound state and in fact is due to a valence-bound state or states. The observed broad band

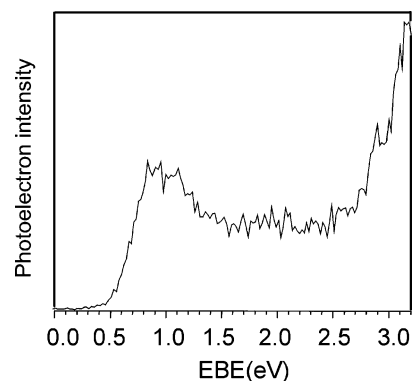


Figure 1. Photoelectron spectrum of G^- measured with 3.493 eV photons.

TABLE 1: AEA and VDEs (in eV) for 16 Most Stable Anionic Tautomers of Guanine

tautomer	structure DEA (G/GN) ^a	energetics			
		gas phase ^b		water ^c	
		AEA	VDE	AEA ^d	VDE ^e
G	−/1	−0.459	0.585	1.329	3.381
GN	1/−	−0.503	0.212	1.496	2.643
G1	1/1	0.369	2.426	1.861	5.350
G2	1/2	0.365	1.604	2.026	4.424
G3	1/2	0.304	1.699	2.211	4.625
G4	2/1	0.278	2.205	2.157	5.094
G5	2/2	0.201	1.316	1.861	4.243
G6	2/2	0.174	1.484	1.671	4.343
G7	2/2	0.173	1.289	1.855	4.237
G8	1/2	0.165	1.617	1.953	4.566
G9	2/1	0.116	2.427	1.884	5.234
G10	1/1	0.104	1.137	2.018	4.295
G11	2/2	0.094	1.414	1.702	4.334
G12	2/2	0.078	2.542	1.462	5.434
G13	3/3	0.002	1.450	1.388	4.238
G14	3/2	−0.019	2.318	1.831	5.183

^a Number of elementary DEA steps required to form the anionic tautomer from G and GN. ^b Calculated at the CCSD(T)/AVDZ//MP2/AVDZ level. ^c Calculated at the B3LYP/6-31++G** level. ^d $\epsilon = 78$. ^e $\epsilon = 78$ and 2 for the initial and final state, respectively.

spectral congestion is probably due to the simultaneous presence of several tautomers of G^- .

On the computational side, a library of 499 considered tautomers has been described in ref 31. At the prescreening stage and using the B3LYP/6-31++G** approach, we identified 14 adiabatically bound anionic tautomers. These tautomers are labeled G_x ($x = 1–14$) and their adiabatic stability decreases as x increases. In addition, we studied valence anions of the canonical tautomer (G) and of the most stable neutral tautomer (GN). All 16 anionic tautomers are presented in the Supporting Information (Figure S-1). In Table 1 we present their energetic characteristics determined at the CCSD(T) level: AEAs (defined with respect to the neutral G) and VDEs.³⁸ Selected tautomers are illustrated in Figure 2. Singly occupied molecular orbitals for G^- , GN^- , G1^- , and G2^- are illustrated in Figure 3. The excess electron occupies a π^* antibonding orbital that is delocalized over both rings. The bonding/antibonding characteristics of the orbitals will be characterized in detail elsewhere using cheminformatics methods.³⁹

Thirteen anionic tautomers remain bound at the CCSD(T) level. The anions of G1–G7 are adiabatically more strongly bound than any pyrimidine base studied so far.^{22–24} G2^- , G3^- , and G8^- are biologically meaningful; i.e., they have a hydrogen atom at the N9 position, where a sugar unit is attached to guanine in DNA. The more stable G2^- and G3^- cannot form

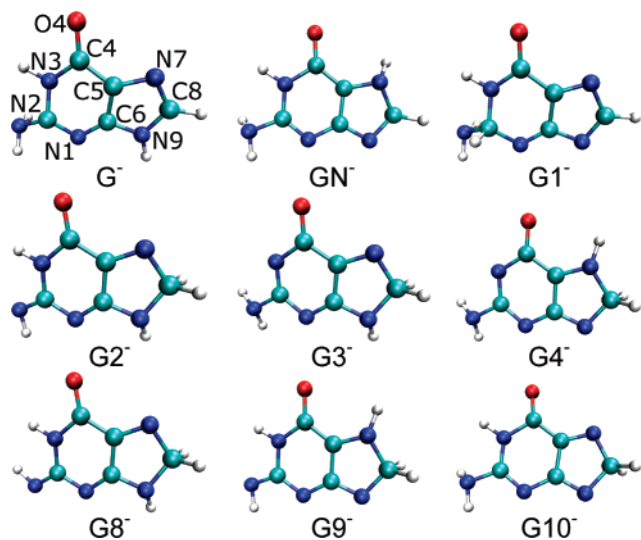


Figure 2. Tautomers of G^- important for interpretation of the PES spectrum.

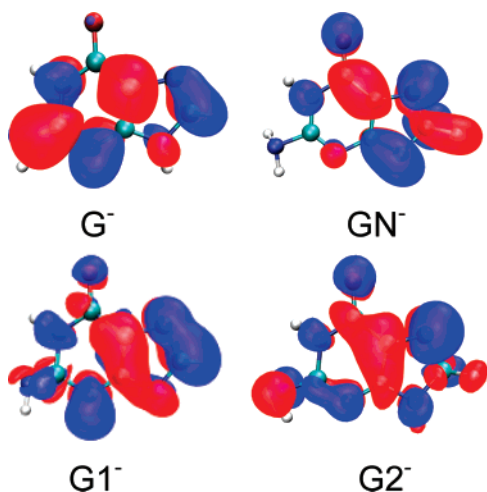


Figure 3. Singly occupied molecular orbitals in selected tautomers of valence anions of guanine.

Watson–Crick-type hydrogen bonds with cytosine; thus they may contribute to the instability of DNA. The stability of $G8^-$ can be further enhanced in DNA because its hydrogen binding sites are complementary with those of cytosine. The valence anions based on the most stable neutral tautomers (G and GN) are adiabatically unbound by ca. 0.5 eV.

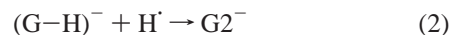
The VDE values for adiabatically bound anions of guanine span a range 1.1–2.5 eV (Table 1), which overlaps with this range of EBEs, where the PES spectrum has a significant intensity (Figure 1). The intensity is negligible for EBEs smaller than 0.6 eV, thus in the region where the VDEs of G^- and GN^- are. This is consistent with adiabatic instability of the latter anions. Our computational results do not provide an interpretation of a feature in the PES spectrum that develops for EBEs exceeding 2.7 eV. Our library of molecular structures was limited to various tautomers of five-plus-six-member ring structures. The high EBE feature might be related to products with partially or completely broken double-ring structures. Indeed, it is known that guanine undergoes decomposition into molecular fragments in dissociative electron attachment experiments.¹⁸ Further analysis of the high EBE feature would require PES experiments with photon energies larger than 3.493 eV.

What might be formation pathways for the new anionic tautomers? For analogous tautomers of pyrimidine bases the

barriers for intramolecular proton transfer are prohibitively large at standard conditions.^{22–24} We suggest two formation pathways of the new anionic tautomers. First, they might be formed through intermolecular proton transfer. Second, dissociative electron attachment (DEA) might facilitate their formation.^{18,19} The population of neutral guanine in the gas phase is dominated by two tautomers: GN (70%) and G (30%).¹² Let us consider formation of $G2^-$, which is the most stable among biologically relevant species. Scattering of an excess electron on the neutral target G might lead to



where $(G)^{* -}$ denotes a scattering state for an excess electron and $(G-H)^-$ denotes a deprotonated guanine (deprotonation at N2 amino group) in the ground electronic state. The attachment of a hydrogen atom to C8



is found barrierless. The hydrogen atom attachment reaction is also barrierless for five other tautomers discussed in the following paragraph, whereas the barrier is only 0.03 kcal/mol for $(G10-H)^-$.

We calculated the overall thermodynamic barrier for the DEA step given by eq 1 for all hydrogen sites in G and GN at $T = 0$ K. Thus only electronic energies and zero-point vibrational corrections were considered. The results obtained at the B3LYP/AVDZ level of theory are 20.0, 21.5, 22.3, and 60.8 kcal/mol for N9, N2, N3 and C8 of G , respectively, and 20.1, 20.7, 25.0, and 57.0 for N3, N7, N2, and C8 of GN , respectively. Thus the thermodynamic limit for (1) to proceed through the NH sites is approximately 0.87 eV and this is the minimum kinetic energy of electrons required to trigger the above process. Higher kinetic energies, preferably those that match positions of electronic resonances in G and GN , would also be appropriate, and the excess energy will be distributed among translational, rotational, and vibrational energy levels of the products. The thermodynamic limit for DEA to proceed through the C8H site is much higher and amounts to ca. 2.47 eV.

The DEA formation pathway would favor formation of these anionic tautomers that are separated from G or GN by one DEA elementary step. The numbers of DEA elementary steps required to form an anionic tautomer from G and GN are presented in Table 1. For the dominating neutral tautomer, GN , only four adiabatically bound anions can be formed by a single DEA step followed by a H atom attachment, namely $G1^-$, $G4^-$, $G9^-$, and $G10^-$. From the second most populated neutral tautomer, G , only five adiabatically bound anions might be formed by a single DEA step: $G1^-$ – $G3^-$, $G8^-$, and $G10^-$. Notice that $G10^-$ and $G1^-$ can be formed from both G and GN . There is indeed a local maximum in the PES spectrum at ~ 1.0 eV, whereas the calculated VDE of $G10^-$ is 1.14 eV. A fingerprint of $G1^-$ is expected at 2.43 eV, but it would be masked by the unidentified feature that develops for EBEs larger than 2.7 eV. The only anionic tautomers that have VDEs in the 1.2–2.3 eV range and can be associated with a single DEA step are $G2^-$, $G3^-$, and $G8^-$. They all can be formed from the less populated G but not from the more populated GN . This might explain why the intensity in the PES spectrum is less intense in the 1.2–2.3 eV range.

How relevant are our findings about new anionic tautomers for solvated species?^{40,41} We considered the effect of electrostatic stabilization by water using the polarizable continuum model,³⁴ and the results are presented in Table 1. The new anionic

tautomers are again more stable than G^- and GN^- , both adiabatically and vertically. Moreover, the ordering of Gx^- according to their stability is different from that in the gas phase. The biologically relevant tautomers are the first, third, and fifth most stable ($G3^-$, $G2^-$, and $G8^-$); see Table 1. Hence the biologically relevant $G3^-$ and $G2^-$ might dominate in water solutions. The newly identified anionic tautomers have much larger VDEs than G^- or GN^- , a feature that is amenable to experimental verification. We believe that the new anionic tautomers will dominate not only in the gas phase but also in solvents and we suggest experimental studies in aprotic solvents to verify our predictions.

Summary

There are more than ten tautomers of guanine that support adiabatically bound anions in the gas phase. The computed values of VDE for the new tautomers are within the broad range of the dominant PES feature. These tautomers are obtained from conventional tautomers through N-to-C proton transfers, i.e., a proton is transferred from a nitrogen atom to a carbon atom. Seven of these tautomers are adiabatically more strongly bound than any pyrimidine base studied so far. The results suggest that guanine might be the strongest excess electron acceptor among nucleic acid bases. This property might explain why the probability of capturing of an excess electron increases with the number of guanines in short single and double strands of DNA.¹⁶ We conclude that, ignored so far, guanine might be critical to radiobiological damage of DNA and it might contribute to those chemical transformations of DNA that proceed through bound anionic states. In future studies we will study the effect of the DNA backbone and surrounding DNA bases on the stability of new anionic tautomers. Our first experimental results on the nucleoside parent anions have already been reported.⁴²

Acknowledgment. The calculations were performed at the Academic Computer Centre in Gdańsk, the National Energy Research Scientific Computing Centre, and the Molecular Science Computing Facility of the William R. Wiley Environmental Molecular Sciences Laboratory through a Computational Grand Challenge Application grant. The computational portion of this work was supported by Polish State Committee for Scientific Research Grants DS/8221-4-0140-7 (to M.G.) and N204 127 31/2963 (to M.H.). M.H. holds the Foundation for Polish Science award for young scientists. The experimental material in this paper (that of K.H.B.) is based on work supported by National Science Foundation Grant CHE-0517337.

Supporting Information Available: Sixteen of the most stable tautomers of anionic guanine identified at the B3LYP/6-31++G** level of theory. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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