Theoretical Determination of Electron Affinity and Ionization Potential of DNA and RNA Bases

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ABSTRACT: The ionization potentials and electron affinities of thymine, cytosine, adenine, guanine, and uracil were determined at density functional level using different exchange-correlation functionals and basis sets. Results showed that the computed ionization potentials are very close to the experimental counterparts. The sign of adiabatic electron affinities of adenine, thymine, and uracil is unaffected by the used level of theory while that for guanine and cytosine depends on both the used potential and basis set. Vertical electron affinities are always negative in agreement with the experimental indications. © 2000 John Wiley & Sons, Inc. J Comput Chem 21: 1243–1250, 2000

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Introduction

The electronic properties of nucleic acid bases are of fundamental importance for the knowledge of the storage and transfer mechanisms of the genetic information. For this reason the investigation of nucleotides and nucleosides, at a molecular level, was carried out to better understand nucleic acid reactivity,[1–3] base tautomerism,[4,5] hydrogen bonding and solvation,[6] proton transfer,[7] and radiation-induced damage.[8] When ionizing radiation interacts with living organisms, the genetic damage can involve the attachment of electrons to nucleic acid bases. The effect of radiation on DNA produces thymine and cytosine anions and guanine and adenine cations.[9–14] These charged species are known to undergo protonation and deprotonation reactions that in turn can lead to a permanent alteration of the original bases and to an uncorrected transfer of genetic information.[15,16] In this context the determination of ionization potential (IP) and electron affinities (EA) of DNA and RNA bases can assume a great significance, and theoretical and experimental studies were devoted to this subject. Experimentally, molecular beams,

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electron spin resonance (ESR), photoelectron spectroscopy (PE), electron nuclear double resonance (ENDOR), Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR), and low-energy electron transmission (ETS) spectroscopy provide means to determine ionization potentials and electron affinities. Although the situation is rather defined for ionization energies,[17–22] there are only few recent direct experimental determinations on electron affinities.[23–29] Recently, the ETS technique has been used to measure the vertical electron affinities of the nucleic acid bases,[26] and Rydberg electron transfer spectroscopy (RET) has been applied to obtain adiabatic electron affinities of thymine, adenine, and uracil.[23, 25] The electron affinities of thymine and uracil[24, 28] have also been determined by using negative ion photoelectron spectroscopy.

Theoretical IPs[30–34] and EAs[25, 30–35, 37] have been computed in a series of articles with different methods.

The anions of nucleic acid bases with large polarity (higher than 2.5 D) can exist as covalent or dipole binding of electrons types.[26, 38]

Computations of electron affinities present a complicate task, because the electron correlation contribution is mandatory to obtain reliable results. The description of the spatial expansion of electron density for the anions needs diffuse basis functions. At a density functional level it was recently found[39, 40] that the hybrid potentials (i.e., B3LYP) predicts well the anion properties, although the description of dipole-bound states is difficult, because the use of very diffuse electron distributions creates problems of numerical integration in the computation of matrix elements of the exchange-correlation potentials. This means that in our work the discussion will be restricted essentially to the conventional valence electron affinities that are the only biological relevant quantities.

Notwithstanding the presence in the literature of *ab initio* and density functional studies, we have considered it interesting to establish the influence of the exchange-correlation potentials and orbital basis set in the reproduction of these properties in DNA and RNA bases.

Theoretical Details

The computations were performed with the Gaussian 94[41] and the AllChem[42] codes.

Becke's three parameter exchange functional (B3)[43] in combination with Lee, Yang, and Parr's (LYP)[44] and Perdew and Wang (PW91)[45] correlation counterparts and Becke's exchange (B)[46] and Perdew's correlation (P)[47] potentials were used in connection with TZVP[48] and 6-311++G**[49] basis sets. B3LYP calculations were redone also using the D95++** set.[50] The 6-311++G** standard basis set was successfully employed in the EA determination of a series of small molecules.[40, 51] The other sets were chosen to explore their performance in this field considering that the treatment of large systems requires a compromise between reliability and computational cost.

Full geometry optimization and vibrational analysis for neutral, cation, and anion species were performed at all levels of theory.

Adiabatic IPs and EAs were obtained from the energy differences between the optimized structures of neutral and charged systems. The optimized geometry of neutral forms was used to compute the energy of the corresponding anions to obtain the vertical EA values.

Results and Discussion

Following the indications coming from previous studies,[25, 31–36] the tautomers of nucleic acid bases were chosen on the basis of their stability or biological importance.

Although the geometry optimization was performed at all the theoretical levels mentioned above, the obtained results are very similar between them. For this reason the discussion about the main structural features can be limited only to the B3LYP/6-311++G** case, however retaining a general validity.

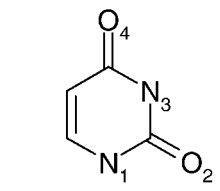
Neutral and cation forms are almost planar, while rather large deviations from planarity can be observed in the anions. The negative purine systems are more distorted than the pyrimidine ones.

The main torsional angles of uracil, thymine, and cytosine anions, obtained at the B3LYP/6-311++G** level, are reported in Figure 1. The same dihedrals in the corresponding neutral systems are equal to 180 or 0 degrees.

The attachment of an electron to the planar neutral adenine induces the —NH_2 group to go out of the molecular plane. The geometry optimization of guanine anion leads to a structure in which the amino group is twisted with respect to the neutral form.

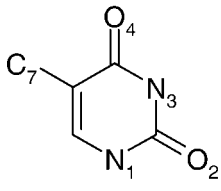
The planar pyrimidine ring of neutral cytosine, thymine, and uracil is strongly distorted in the corresponding anions (see Fig. 1).

The adiabatic ionization potentials of DNA and RNA bases are reported in Table I. All the employed



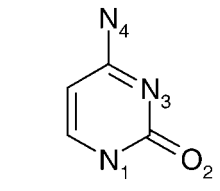
U -

$N_1C_2N_3C_4 = 3.6$
$C_2N_3C_4O_4 = 174.2$
$O_4C_4C_5C_6 = 177.1$
$C_4C_5C_6N_1 = 12.4$
$C_5C_6N_1C_2 = -16.2$
$C_6N_1C_2N_3 = 8.4$
$O_2C_2N_3C_4 = -176.7$



T -

$N_1C_2N_3C_4 = -4.3$
$C_2N_3C_4O_4 = -178.3$
$O_4C_4C_5C_6 = 176.3$
$C_4C_5C_6N_1 = 8.2$
$C_5C_6N_1C_2 = -11.9$
$C_6N_1C_2N_3 = 9.6$
$O_2C_2N_3C_4 = -175.9$
$N_1C_6C_5C_7 = 174.8$



C -

$N_1C_2N_3C_4 = -3.9$
$C_2N_3C_4N_4 = 176.8$
$N_4C_4C_5C_6 = 179.9$
$C_4C_5C_6N_1 = 9.8$
$C_5C_6N_1C_2 = -18.4$
$C_6N_1C_2N_3 = 15.6$
$O_2C_2N_3C_4 = 177.3$
$N_3C_4N_4H = 20.2$

FIGURE 1. Torsinal angle values (in degrees) for uracil, thymine, and cytosine anions.

levels of theory predict IP values very similar between them with differences that fall in a range of 0–0.1 eV. Comparison with the experimental available PE data[17,20] is excellent, and the maximum deviations are of about 0.1 eV. In the case of adenine, the most recent value, proposed by the FT-IRC experiment,[21] is 8.55 ± 0.1 eV. This result has been obtained using as reagent the ethyl methyl sulfide, but, in the same article, are reported ionization energies determined using other reagents, ranging from 8.10 to 8.88 eV. Furthermore, we can note that the value of 8.55 ± 0.1 eV is closer to the vertical IPs reported in the literature.[30] Our results also compare well with the previous MP2/6-31+G* values of Sevilla et al.[30] This means that any used combination, of exchange-correlation functional and basis set quite extended, is able to correctly reproduce this quantity, especially if diffuse functions are included. Differences slightly higher than 0.2 eV occur between our B3LYP data and those reported previously[31–34] obtained using the same functional. These discrepancies can be ascribed to the smaller basis set used in the optimization and to the lack of diffuse functions.

Much more complex is the determination of electron affinities for which, only after 1995, some experimental result has been published.[23–26] In most of the previous theoretical studies especially regarding thymine and uracil, the central problem was to establish the nature of the anion species that originate from neutral DNA and RNA bases. In particular, two interpretations, that postulate the existence of valence or dipole binding of electron to bases, have been proposed. Recently, Desfrancois et al.,[25] on the basis of a RET experiment and a DFT computation on uracil, have underlined that "both the interpretations lead to results that are only apparently different and represent two complementary aspects of the reality."

The calculated adiabatic electron affinities with and without zero-point energy corrections are reported in Table II. As is evident, the results depend on both the exchange-correlation potential and basis set quality. First of all, we can note that vibrational corrections play a decisive role in determining absolute value and, in some case, the sign of EA.

Adenine has the most negative EA at all levels of theory because its anion is the most destabilized with respect to the neutral specie. This means that the extra electron interacts only weakly with the LUMO of the neutral molecule, as confirmed by the small geometrical distortion in going from the neutral to the anionic structure. On the other hand, adenine has a dipole moment of only a 2.46 D at B3LYP/6-311++G** level (dipole moments values obtained by the other methods are similar), and should not form a dipole bound anion that stabilizes the negative structure.

Comparison between our results provide evidence that the smallest values for adenine arise from the TZVP basis set used in conjunction with the hybrid B3LYP and B3PW91 functionals. This situation occurs for all other bases (see Table II), and is probably due to the fact that the TZVP set was optimized at the local VWN[52] level and to the lack of diffuse functions that are mandatory in the description of anions. The remaining hybrid data are quite similar. The TZVP basis set destabilizes the anion more than the 6-311++G** one also in the case of BP gradient-corrected computations. In this latter case we obtain the EA value closer to the experimental data that has, however, an opposite sign. Instead, we are in agreement with the predicted *ab initio* value of Sevilla et al.[30] obtained scaling of the MP2 result. As in the case of the IP evaluation, the previous B3LYP computations of Wetmore et al.[31]

TABLE I.
Adiabatic Ionization Potentials (in eV) of DNA and RNA Bases by Different Theoretical and Experimental Methods.

Method	Adenine	Guanine	Thymine	Cytosine	Uracil
B3LYP/TZVP	8.09	7.66	8.76	8.57	9.25
B3LYP/6-311++G**	8.12	7.68	8.76	8.59	9.25
B3PW91/6-311++G**	8.14	7.69	8.85	8.66	9.33
B3PW91/TZVP	8.10	7.64	8.85	8.63	9.32
B3LYP/D95++**	8.08	7.65	8.84	8.59	9.28
BP/6-311++G**	8.10	7.68	8.79	8.61	9.27
BP/TZVP	8.00	7.61	8.63	8.48	9.17
B3LYP/6-311G(2df,p)//6-31G(d,p)	7.90[a]	7.45[b]	8.50[c]	8.42[d]	9.10[c]
MP2/6-31+G*[e]	8.18	7.66	8.85	8.74	/
Exp[f]	8.26	7.77	8.87	8.68	/
Exp[g]	/	/	/	/	9.35 ± 0.01
Exp[h]	8.55 ± 0.10	/	/	/	/

[a] Ref. 31.
[b] Ref. 34.
[c] Ref. 33.
[d] Ref. 32.
[e] Ref. 30.
[f] Ref. 17.
[g] Ref. 20.
[h] Ref. 21.

give EAs of a completely different order of magnitude for all bases.

Guanine electron affinities, obtained coupling the hybrid B3LYP and the gradient-corrected BP potentials with D95++** and 6-311++G** basis sets, respectively, are positive, while all other combinations give negative values. The dipole moment of this base is sufficiently high (6.71 D at B3LYP/6-311++G** level) to hypothesize the formation of a dipole bound anion that could stabilize, more than in adenine, the negatively charged species. Other previous computations give negative EAs that are, in any case, quite more negative with respect to our values. The reasons for the discrepancy could be searched again in the poor description of anion orbitals in terms of diffuse functions and in the fact that the MP2 results[30] arise from single-point computations on geometries optimized at the HF level.

Comparisons between B3LYP and B3PW91 data obtained with the same basis set (6-311++G**) show that the latter potential tends to destabilize the anion not only in guanine but also in the other studied bases. On the contrary, the influence of the basis set change, with the same number of diffuse functions, is less significant when the same exchange-correlation functional is used (see B3LYP/6-311++G** and B3LYP/D95++** data in Table II).

All the employed computational levels give for thymine positive adiabatic electron affinities. The stabilization of its anion is accompanied by a distortion of the geometry, suggesting the entrance of the extra electron in the LUMO of the neutral molecule. The dipole moment of thymine is 4.53 D (B3LYP/6-311++G** value), and a further stabilizing contribution can arise from the dipole–electron interaction. Except for the concordance in the sign, our results are quite different than the previous theoretical[30, 33, 35] and experimental[23, 24, 28] data. The agreement between B3LYP/TZVP and B3PW91/TZVP results with the experiment is casual, because the tendency of these combinations of potentials and basis set, in the other cases, is that to destabilize the anions.

An intricate situation emerges from our results for cytosine. At 0 K four computations propose negative EAs. The values without vibrational corrections are, instead, more homogeneous (only one positive value). These results indicate clearly that the influence of zero-point corrections is, in this case, relevant because they are of the same order of the values obtained at SCF level. Although the negative sign of EA predominates in our computations at 0 K and also in the previous theoretical determinations, the discrepancy with the experimental information available in the literature[28, 29] prevents,

TABLE II.

Adiabatic Electron Affinities at 0 K (in eV) of DNA and RNA Bases by Different Theoretical and Experimental Methods. In Parentheses Are Given the Values without Vibrational Corrections.

Method	Adenine	Guanine	Thymine	Cytosine	Uracil
B3LYP/TZVP	−0.481 (−0.605)	−0.381 (−0.505)	0.084 (−0.047)	−0.115 (−0.222)	0.136 (0.016)
B3LYP/6-311++G**	−0.264 (−0.314)	−0.004 (−0.059)	0.179 (0.049)	0.006 (−0.118)	0.215 (0.095)
B3PW91/6-311++G**	−0.310 (−0.360)	−0.064 (−0.119)	0.148 (0.018)	−0.024 (−0.148)	0.184 (0.065)
B3PW91/TZVP	−0.569 (−0.619)	−0.469 (−0.519)	0.063 (−0.067)	−0.118 (−0.238)	0.112 (−0.007)
B3LYP/D95++**	−0.257 (−0.307)	0.001 (−0.050)	0.185 (0.055)	0.020 (−0.100)	0.229 (0.110)
BP/6-311++G**	−0.120 (−0.125)	0.124 (0.074)	0.272 (0.142)	0.164 (0.044)	0.294 (0.175)
BP/TZVP	−0.290 (−0.417)	−0.295 (−0.422)	0.158 (0.026)	−0.050 (−0.167)	0.175 (0.073)
MP2/6-31+G*	~0.0006[a]	/	0.088[b]	/	0.086[c]
B3LYP/6-311G(2df,p)//6-31G(d,p)	−0.902[d]	−0.685[e]	0.642[f]	−0.570[g]	0.399[f]
B3LYP/6-31++G[h]	/	/	/	/	0.070
MP2/6-31+G(d)//6-31G*[i]	−1.47	−1.79	−0.54	−0.83	−0.51
Predicted ab-initio[i]	−0.3	−0.7	0.3	0.2	0.4
Exp[l]	(0.012 ± 0.005)	/	0.068 ± 0.020	/	0.054 ± 0.035
Exp[m]	/	/	/	/	0.085 ± 0.015
Exp[n]	/	/	0.069 ± 0.007	/	0.093 ± 0.007
Exp[h]	/	/	/	/	0.030–0.060
Exp[o]	/	/	0.062 ± 0.008	0.085 ± 0.008	0.086 ± 0.008

[a] Ref. 23.
[b] Ref. 35.
[c] Ref. 36.
[d] Ref. 31.
[e] Ref. 34.
[f] Ref. 33.
[g] Ref. 32.
[h] Ref. 25.
[i] Ref. 30.
[l] Ref. 23.
[m] Ref. 25.
[n] Ref. 24.
[o] Ref. 28.

however, a definitive conclusion. In fact, it is work noting that the EA of cytosine in these works was obtained by extrapolation to zero water molecules from the data referred to as a cytosine–water cluster.

Because of the large dipole moment of this molecule (6.75 D at B3LYP/6-311++G** level) it is probable that the contributions deriving by the dipole-bound states must be considered, but it is impossible to quantify the weight that the various levels of theory attribute to the dipole–electron interaction.[40]

Four experimental studies[23–25, 28] are available for the adiabatic EA of uracil. The values range from 0.030 to 0.093 eV, but they are all positive. Our computations give also only positive EAs, in agreement with experimental and most[25, 30, 33, 36] of theoretical data previously reported. In particular, they are closer (but, however, higher) to the experimental data of Hendricks et al.[24] The authors of this work state that the anions of uracil and thymine have essentially the same structure as the corresponding neutral forms underlying that, under these circumstances, the vertical detachment energy (VDE) corresponds to the adiabatic electron affinity. Because in our calculations we found significant geometry distortions of the anions with respect to the neutral uracil and thymine, it is probable that the disagreement with our values can be attributed to this fact.

Also, in uracil as in cytosine, the contributions of the zero-point corrections are significant. The positive sign suggests a covalent electron attachment that can be confirmed by the rather large rearrangement of the geometry in the anion, but the dipole-bound states can be possibly due to the dipole moment value that is 4.58 D (B3LYP/6-311++G**). The B3LYP/6-311++G** value of EA without ZPE corrections is very similar to that obtained by Desfrancois et al.[25] with the same functional and similar basis set. The authors underline the agreement with their RET experimental value, but do not specify if the theoretical value is referred to a temperature of 0 K.

As is evident from our and previous theoretical and experimental studies, the problem of adiabatic EA evaluation is still now a matter of controversy, essentially because of the very small values but also for the lack of a sure determination of the sign.

Because the optimization of geometry allows a relaxation of the structure, and consequently a lowering of the total energy, it is reasonable to hypothesize that a calculation performed on a charged species in the same geometry as the corresponding neutral must give electron affinity values much more negative. On the other hand, a very recent work of Aflatooni et al.[26] demonstrates that, on the basis of ETS measurement, all the vertical EAs of nucleic acid bases have negative signs.

In Table III we report our vertical electron affinities obtained using only somewhat the levels of theory employed for the adiabatic EA determination. Previous theoretical and experimental data are also reported for the purpose of comparisons. All methods give negative EAs, in agreement with the ETS results.[26] As in the case of adiabatic computations, the vertical EAs obtained by B3LYP and BP functionals coupled with TZVP basis set, are twice as large as than those deriving from the experimental measurement. B3LYP/6-311++G** data are closer to the experimental counterparts, but the concordance in the trend is not completely reproduced.

Conclusions

The aim of the present work was essentially to explore the influence of exchange-correlation potentials and basis sets on the ionization potentials and

TABLE III.
Vertical Electron Affinities (in eV) of DNA and RNA Bases by Different Theoretical and Experimental Methods.

Method	Adenine	Guanine	Thymine	Cytosine	Uracil
B3LYP/TZVP	−0.94	−1.40	−0.48	−0.73	−0.42
B3LYP/6-311++G**	−0.34	−0.08	−0.34	−0.31	−0.11
BP/TZVP	−0.77	1.27	−0.41	−0.75	−0.40
MP2/6-31+G*[a]	/	/	−1.08	−1.34	−1.12
Exp[a]	/	/	/	/	−0.19
Exp[b]	−0.54	/	−0.29	−0.32	−0.22

[a] Ref. 27.
[b] Ref. 26.

electron affinities computations of the nucleic acid bases. On the basis of our results, some conclusions can be drawn.

First of all, we underline that the employed levels of theory give ionization potentials in excellent agreement with the experimental evidences.

The vertical electron affinities were found to be negative in all cases and by all methods.

Only few considerations can be made about the adiabatic values of electron affinities. The choice of a basis set that describe sufficiently well the diffusion of anion orbitals is crucial in order to have comparable data irrespective of the used exchange-correlation potential.

All the computations confirm the positive value of adiabatic electron affinities of thymine and uracil in agreement with the experiment. For adenine, we found always a negative value in agreement with other theoretical data, but not with the available measurement. For guanine and cytosine, the situation is more confused, and the sign of the electron affinity depends on the employed level of theory. The lack of experimental information for guanine and the uncertainty of the measurements for cytosine does not allow any kind of conclusions, although we think that further study considering different tautomers can be useful to solve the problem.

Acknowledgments

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