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Radicals Derived from Adenine: Prediction of Large Electron Affinities with a Considerable Spread

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The electron affinities of five radicals of adenine minus a hydrogen atom are predicted using carefully calibrated (*Chem. Rev.* **2002**, *102*, 231) computational methods. Density functional theory (DFT) and hybrid DFT/Hartree−Fock functionals were used with double-ζ quality basis sets augmented with polarization and diffuse functions, DZP++. Vibrational frequency analyses were performed to compute zero-point energy corrections and to determine the nature of the stationary points. The energetic spacing of the five adenine-related radicals and five anions is predicted and found to be quite different between the radicals and anions. The electron affinities are found to be large, ranging from 0.9 to 3.2 eV. In all anions, the "last" electron displays little diffuse character. Breaking a N−H bond leads (experimentally corresponding to deprotonating the electron-oxidized adenine radical) to the most stable radical, which in turn has the highest electron affinity. Radicals and anions which are created at carbon centers are less stable with respect to those generated at nitrogen centers in the adenine framework.

Introduction

Adenine radicals and the analogous anions are interesting both theoretically and experimentally. Nucleic acid base radicals are potentially very important in mechanisms of DNA cleavage.[1,2] Experimental work has shown that radicals play a key role in DNA damage.[3,4] In particular, there is evidence that X-ray irradiation of adenine and its derivatives may result in homolytic cleavage of bonds to hydrogen in the adenine framework.[5−11] In addition, the major species formed in the negative ion chemical ionization mass spectrometry of adenine is the dehydrogenated anion.[12,13] Currently, there are no experimental values for the electron affinities of the adenine radicals investigated in this paper. One recent attempt to produce the radicals involved the reaction of adenine with positively charged phenyl radicals.[14] It was observed that the major product of this reaction is addition of the phenyl radicals to the adenine molecule. The relative yield for the abstraction reaction is low (a maximum of 14%). In this research, we investigate the electron affinities of the radicals derived from adenine by removing a hydrogen atom.

Many experimental and theoretical studies have been carried out on the nucleic acid bases, for example.[14−21] Photoelectron spectroscopy of microsolvated nucleic acid bases[17] has shown that uracil has a dipole-bound anion which becomes a covalent bound anion when one water molecule is attached to it. In the case of adenine, there is some debate as to whether it forms a dipole or covalently bound anion. Half-wave reduction potential experiments[18] suggest a *substantial positive* electron affinity for adenine (0.95 ± 0.05 eV) and thus a valence-bound character for the open-shell anion. However, photoelectron spectroscopy experiments[19] give for adenine a *negative* electron affinity (−0.45 eV). This finding is in agreement with the theoretical results of Wesolowski et al.[20] that estimate a slightly negative adiabatic electron affinity (AEA), −0.17 eV. Richardson and co-workers conclude that the adenine anion has dipole-bound character.[22] The adenine−thymine base pair was investigated by means of both semiempirical and DFT methods[22,23] and found to have a positive electron affinity, with a valence-bound anion.

There are few theoretical studies of adenine radicals, their anions, and the electron affinities of the radicals. The results of Sevilla et al.[24] on one of the five radicals refer to the Hartree−Fock 6-31G*//3-21G level of theory. The electron affinity of one of the radicals computed by means of semiempirical methods was reported by Chen, Chen, and Sane.[25] Wetmore, Boyd, and Eriksson[26] have calculated the relative stability of a variety of adenine radicals and their isotropic and anisotropic hyperfine coupling constants. Thus some experimental and theoretical data are available for the anions.[27,28] In this research, we complement these contributions with a comprehensive study of the radicals and anions derived from adenine. Because of reasons associated with both stability and incorporation into nucleic acids, we have focused on the 9H-adenine tautomer.

This research contributes to the growing field of research on biomolecules in the gas phase. The 2003 Gordon Conference on this theme confirms that a more detailed understanding of the structure and energetics of these systems should ultimately contribute to biochemistry.

Theoretical Methods

Energies, optimized structures, vibrational frequencies, and spin densities were determined using three generalized gradient approximation (GGA) exchange-correlation functionals: B3LYP, BLYP, and BP86. These are a combination of Becke's exchange functionals: the 3-parameter HF/DFT hybrid exchange functional (B3)[29] or the pure exchange functional (B)[30] with the dynamical correlation functional of Lee, Yang, and Parr (LYP)[31] or that of Perdew (P86).[32,33] All computations were performed

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using double-ζ-quality basis sets with polarization and diffuse functions, DZP++.

The DZP++ basis sets were constructed by augmenting the Huzinage–Dunning[34,35] sets of contracted double-ζ Gaussian functions with one set of p-type polarization functions for each H atom and one set of five d-type polarization functions for each C and N atom ($\alpha_p(H) = 0.75$, $\alpha_d(C) = 0.75$, $\alpha_d(N) = 0.80$). To complete the DZP++ basis, one even-tempered s diffuse function was added to each H atom, while even-tempered s and p diffuse functions were centered on each heavy atom. The even-tempered orbital exponents were determined according to the prescription of Lee and Schaefer[36]

$$\alpha_{\text{diffuse}} = \frac{1}{2}\left(\frac{\alpha_1}{\alpha_2} + \frac{\alpha_2}{\alpha_3}\right)\alpha_1$$

where α_1, α_2, and α_3 are the three smallest Gaussian orbital exponents of the s- or p-type primitive functions for a given atom ($\alpha_1 < \alpha_2 < \alpha_3$). The final DZP++ set contains 6 functions per H atom (5s1p/3s1p) and 19 functions per C or N atom (10s6p1d/5s3p1d), yielding a total of 220 contracted functions for the adenine molecule. This basis set has been used in systematic calibrative EA studies[37] on a wide range of molecules. This combination of functionals and basis sets has shown to predict electron affinities with average errors less than 0.12 eV in the case of a closed-shell anion and the corresponding open-shell neutral. An unrestricted version of DFT was used for the radicals and the restricted form for the anions. All structures were optimized using analytic gradients with tight convergence criteria. Vibrational frequency evaluations were done on all structures, and no scaling factor was applied. Numerical integration was performed using the Gaussian 94[38] default grid consisting of 75 radial shells with 302 angular points per shell. Adiabatic electron affinities were computed as the difference between the absolute energies of the appropriate neutral and anion species at their respective optimized geometries

$$\text{AEA} = E_{\text{neut}} - E_{\text{anion}}$$

The vertical detachment energies (VDEs) were computed as the energy difference between the neutral and the anion, both at the optimized anion geometry

$$\text{VDE} = E_{\text{neut(anion-opt)}} - E_{\text{anion(anion-opt)}}$$

The gas-phase acidities (GPAs) were computed as

$$\text{GPA} = \text{IP(H)} - \text{AEA(X)} + \text{D(XH)}$$

where AEA(X) is the AEA of radical X, and D(XH) is the bond dissociation energy for the X–H link.

For all the radicals, plots of the total spin density were computed. This quantity is given in standard DFT methods by the difference between the density of α and β electrons

$$\rho^s(\mathbf{r}) - \rho^\alpha(\mathbf{r}) - \rho^\beta(\mathbf{r}).$$

The total spin density allows us to examine out the extent of delocalization of the unpaired electron within the molecular framework.

Results

3.1. Radicals. The orders of stability and the optimized bond lengths at the B3LYP/DZP++ level of theory for the five radicals investigated in this research are shown in Table 1. In Table 2 are reported the total and relative energies of the radicals, computed with the B3LYP, BLYP, and BP86 functionals with and without zero-point vibrational energy corrections. The structure and numbering scheme for adenine is shown in Figure 1.

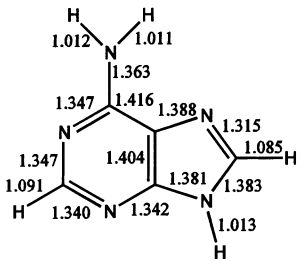
From the adenine molecule, by removing (pedagogically) one hydrogen atom, we can generate four radicals, with one of these having two rotational conformers, namely, **4** and **6** (Table 1). Radicals such as **4** are actually one-electron-oxidized adenine radicals that deprotonate reversibly at the exocyclic nitrogen. In adenosine, the adenine molecule is bound to a sugar through nitrogen N_9, and thus radical **2** and anion **3** could not be formed. In DNA, one of the two hydrogens that belong to the amino group forms a hydrogen bond with thymine, and this must be kept in mind when extending the results to the base pairs. All three functionals predict the same energetic order for the radicals. For the three nitrogen radicals **2**, **4**, and **6**, all three DFT functionals predict that these are close in energy and that they are more stable than the carbon radicals **8** and **10** by more than 6 kcal/mol.

Some evidence of the energetic ordering of these radicals can be found in the experimental results available for adenine and adenosine. The results of electron spin resonance and electron nuclear double resonance experiments on various irradiated adenine derivatives show that radicals could form both from H abstraction and addition.[6] Irradiating the adenosine–5-bromouracil cocrystal at 12 K[7] leads to radical **6**. The same radical was generated from adenosine crystals.[8] In irradiated adenosine hydrochloride, either the rotational conformer **4** or its N_3 protonated version is likely to be formed.[9] Hydrogen abstraction from adenine and its derivatives can also be observed using radicals such as hydroxyl ($OH^\bullet$) or the sulfate radical anion ($SO_4^{\bullet-}$).[10,11] Both the $OH^\bullet$ and the $SO_4^{\bullet-}$ radicals can give rise to reactions with hydrogen at the N_9 and N_6 centers, leading to the radicals **2**, **4**, and **6**. In the case of the hydroxyl radical, the reaction with adenine and its derivatives proceeds with an addition of $OH^\bullet$ and consequent elimination of a water molecule. With the sulfate radical anion, the radicals are produced by one-electron oxidation and deprotonation. Thus, all these experimental studies confirm that radicals produced by hydrogen abstraction at nitrogen centers are more stable than the radicals generated at carbon centers.

However, it must be noted that the actual stability of a radical depends on the separation of charge and spin through protonation and deprotonation reactions. For example, reduction products tend to protonate. This creates a neutral radical that is relatively stable. However, if there is no protonation pathway available, the original charged radical will be subject to recombination with the positive oxidation products. Also, one should remember that deprotonation at nitrogen is reversible, whereas carbon deprotonation is irreversible. This explains why the thymine-derived allyl radical is so stable.

The three nitrogen radicals were found to have C_s symmetry. A spin-density plot of four of the five radicals (at the contour value of 0.001 au) is presented in Figure 2. Investigation of the spin density shows that the unpaired electron is delocalized over the molecular frame and has the typical shape of a π system. The energy difference between the two conformers **4** and **6** is very small, less than 1.5 kcal/mol. The geometries of the three radicals differ substantially from adenine. The optimized bond lengths for adenine computed at the B3LYP level are shown in Table 1. As found for the spin density, the change in bond lengths is not localized around the radical center. Thus in radical **2**, the bond length C_6–N_6 is decreased (1.363 → 1.346 Å,

TABLE 1: B3LYP DZP++ Bond Lengths of Adenine, the Radicals, and Respective Anions and Absolute and ZPVE-Corrected Relative Energies of the Radicals and Anions[a]



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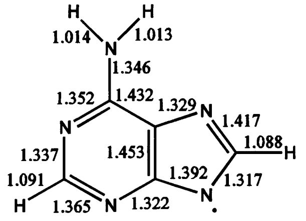
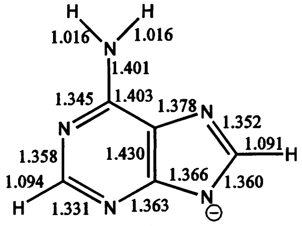
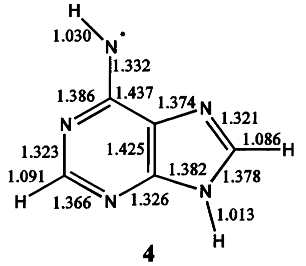
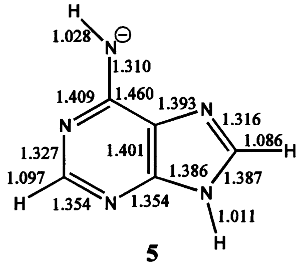
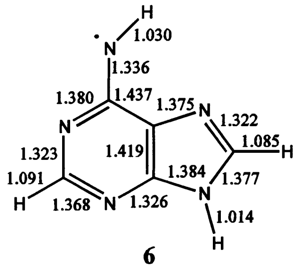
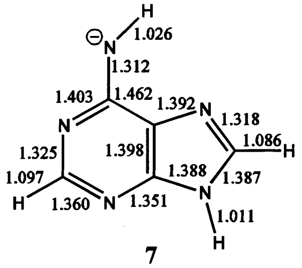
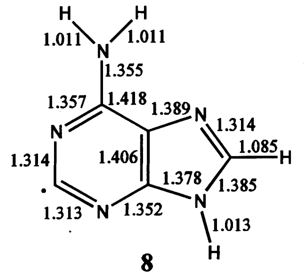
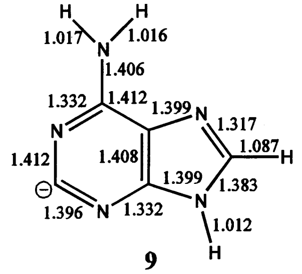
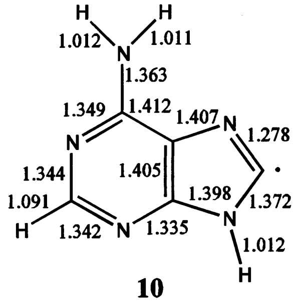
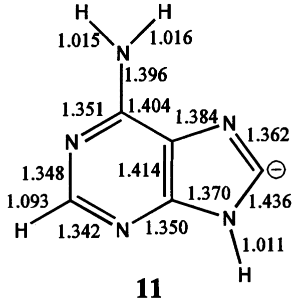
Structure	Energy	Structure	Energy
 **2**	-466.73827 **0.00**	 **3**	-466.85796 **0.00**
 **4**	-466.73409 **2.61**	 **5**	-466.82778 **18.42**
 **6**	-466.73238 **3.68**	 **7**	-466.82706 **18.89**
 **8**	-466.72310 **9.79**	 **9**	-466.75625 **62.18**
 **10**	-466.71107 **17.45**	 **11**	-466.79846 **36.71**

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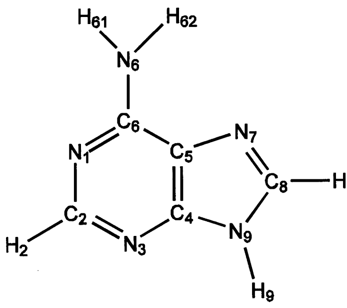
[a] Total energies are in Hartree; relative energies are in kcal/mol.

TABLE 2: Total and Relative Energies of Radicals Derived from Adenine[a]

	B3LYP		BLYP		BP86	
structure	relative energy (kcal/mol)	total energy (Hartree)	relative energy (kcal/mol)	total energy (Hartree)	relative energy (kcal/mol)	total energy (Hartree)
2	0.00 (0.00)	−466.73827	0.00 (0.00)	−466.60969	0.00 (0.00)	−466.75796
4	2.62 (2.61)	−466.73409	3.16 (3.27)	−466.60466	3.28 (3.42)	−466.75273
6	3.70 (3.68)	−466.73238	4.29 (4.39)	−466.60286	4.35 (4.47)	−466.75102
8	9.52 (9.79)	−466.72310	11.50 (11.97)	−466.59137	9.93 10.50	−466.74213
10	17.07 (17.45)	−466.71107	18.37 (18.76)	−466.58042	17.28 (17.78)	−466.73042

[a] ZPVE-corrected energies are in parentheses.



1

Figure 1. IUPAC numbering of atoms for adenine.

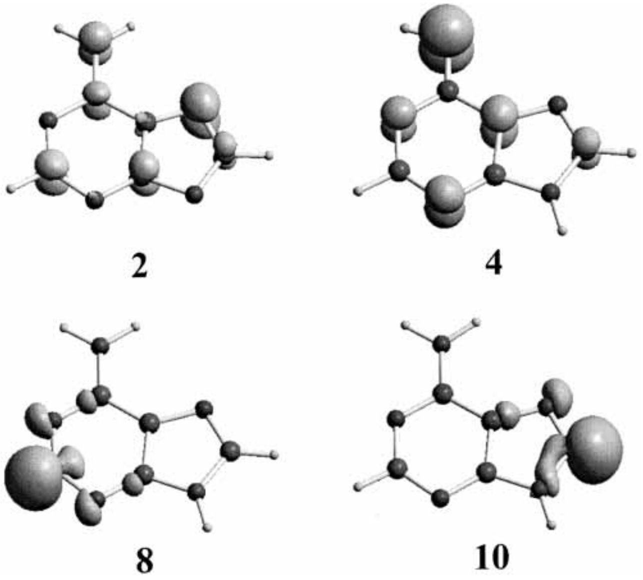


Figure 2. B3LYP DZP++ total spin densities for adenine radicals.

DZP++ B3LYP) compared to adenine, showing one effect of the delocalization of the unpaired electron. In radicals **4** and **6**, we find that delocalization causes large geometry changes only in the six-membered ring.

The carbon atom radicals **8** and **10** are both nonplanar, having the amino group hydrogens protruding out of the molecular plane. Imposing C_s symmetry on the molecules resulted in a higher energy optimized geometry with respect to the one where the symmetry constraint is absent. The spin density of the carbon radicals is localized on the atom where the hydrogen atom was abstracted, and in both cases the shape is that of a σ lobe. Radical **10** shows a hyperconjugation effect, but this does not require that it be more stable than radical **8**. Comparison of the delocalization of the carbon radical, based on Mulliken spin densities and the relative stability of the two radicals, shows that those two quantities are not related in a trivial way. In fact, radical **8** has a Mulliken spin density computed with the B3LYP functional at the carbon atom equal to 0.97, while in the case of radical **10**, the value drops to 0.93.

Wetmore, Boyd, and Eriksson[26] have computed the relative stability of four of the five radicals, optimizing geometries using the B3LYP functional with Pople's 6-31G(d,p) basis set and then performing single-point computations using the 6-311G-(2df,p) basis set. In their work, they take into consideration only one of the two conformational isomers **4** and **6**. There is good agreement with the present results in the relative energies of the radicals. Wetmore found the following relative energies: 0.00 (**2**), 2.7 (**4** or **6**), 9.2 (**8**), and 16.9 (**10**) (kcal/mol).

If we compare the dissociation energies for the reactions RH → R + H of NH_3 (104.8 kcal/mol) and CH_4 (108.6 kcal/mol), we see that the difference, 3.8 kcal/mol, is in agreement with the simple hypothesis that the nitrogen radicals are more stable than those for which a hydrogen atom is removed from one of the carbon atoms. However, when compared to the energy difference between the adenine carbon radical **10** and the nitrogen radical **2**, 17.4 kcal/mol, the values for methane and ammonia show that a more sophisticated model must be adopted to explain the larger ΔE values.

While trying to understand the relationship between the energetics and the delocalization of the radicals, we investigated the radicals generated from two model compounds: ^{1}H-imidazole (**12**) and 4,5-dihydro-1*H*-imidazole (**15**). From those two molecules, one can generate two nitrogen radicals, **13** and **16**, which mimic radical **2**, and two carbon radicals, **14** and **17**, which mimic radical **10** (Figure 3). A spin-density plot of the four radicals generated from 1*H*-imidazole and 4,5-dihydro-1*H*-imidazole is presented in Figure 4. In this case, since the molecule is smaller, the unpaired electron can delocalize in a smaller region of space. The spin density is found to be very different with respect to radical **2**. In radical **13**, the spin density is mostly found on the carbon atoms. In radical **16**, the spin density is localized on the two nitrogen atoms, this being typical of an allyl system. For the carbon radicals **14** and **17**, the spin density is found to be similiar to that for radical **10**. The relative energy of the carbon radical **14** compared to the nitrogen radical **13** is 20.6 kcal/mol. Between radicals **16** and **17**, the energy difference is 23.9 kcal/mol. Comparing those values to the energy difference of adenine radicals **2** and **10**, 17.4 kcal/mol, we conclude that the delocalization of the unpaired electron is not the only factor dictating the energetics of the radicals.

3.2. Anions. The total and relative energies of the anions computed with the B3LYP, BLYP, and BP86 functionals using the DZP++ basis set are reported in Table 3. For the anion

TABLE 3: Total and Relative Energies of Anions Derived from Adenine[a]

	B3LYP		BLYP		BP86	
structure	relative energy (kcal/mol)	total energy (Hartree)	relative energy (kcal/mol)	total energy (Hartree)	relative energy (kcal/mol)	total energy (Hartree)
3	0.00	−466.85796	0.00	−466.72185	0.00	−466.87843
	(0.00)		(0.00)		(0.00)	
5	18.94	−466.82778	17.57	−466.69384	17.85	−466.84998
	(18.42)		(16.94)		(17.24)	
7	19.39	−466.82706	18.01	−466.69315	18.22	−466.84940
	(18.89)		(17.39)		(17.62)	
9	63.82	−466.75625	61.91	−466.62319	62.93	−466.77814
	(62.18)		(60.08)		(61.17)	
11	37.33	−466.79846	36.47	−466.66372	37.03	−466.81942
	(36.71)		(35.80)		(36.42)	

[a] ZPVE-corrected energies are in parentheses.

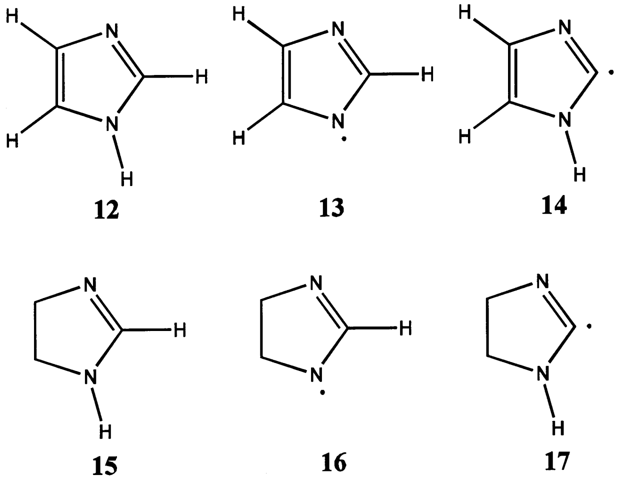


Figure 3. 1*H*-imidazole, 4,5-dihydro-1*H*-imidazole, and related radicals.

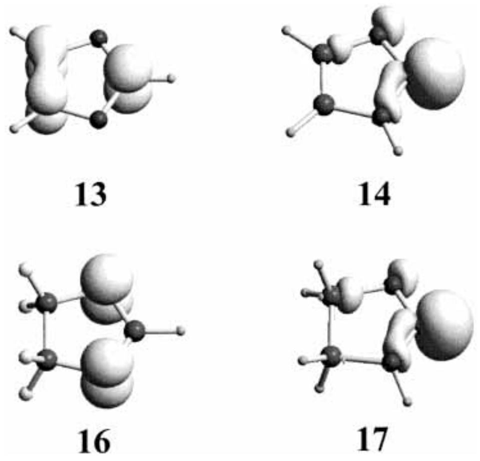


Figure 4. B3LYP DZP++ total spin densities for the 1*H*-imidazole and the 4,5-dihydro-1*H*-imidazole radicals.

only, the singlet states are taken into consideration. The triplets were found to be higher in energy by more than 25 kcal/mol (1.1 eV). The order of stability of the anions is in agreement with a simple prediction based on the electronegativity and the s and p character of the atoms from which the proton is abstracted. By inspecting the HOMO DFT orbital of each anion, we readily conclude that all five are of covalent-type character. This is typical of a system where the extra electron is strongly bound. Moreover, the significant alteration of bond lengths observed for the five radicals when one electron is added to the radicals, provides further confirmation that the anions are quite different from the neutral radicals.

TABLE 4: GPAs (Adenine → Anion X + H^+) of Adenine in eV[a]

structure	B3LYP	BLYP	BP86
3	14.85	14.85	14.81
	(14.50)	(14.51)	(14.47)
5	15.67	15.61	15.58
	(15.30)	(15.24)	(15.21)
7	15.69	15.63	15.60
	(15.32)	(15.26)	(15.23)
9	17.61	17.54	17.54
	(17.19)	(17.11)	(17.12)
11	16.46	16.43	16.42
	(16.09)	(16.06)	(16.05)

[a] ZPVE-corrected energies are in parentheses.

The anions produced by loss of a proton from the nitrogen atoms are energetically favored with respect to the carbanions. This has been confirmed both by experiments and theoretical studies.[27,28] The three nitrogen anions have the same energetic order as the three radicals. The anions are planar with the amino group hydrogens in the molecular plane. Again this was checked imposing C_s symmetry. Adding an electron to radicals **2**, **4**, and **6** produces significant change in all bond lengths. If we compare the C_4-N_9 and the N_9-C_8 bond lengths in radical **2** and anion **3**, we see that the former is increasing while the latter is decreasing (C_4-N_9, 1.392 → 1.366 Å; N_9-C_8, 1.317 → 1.360 Å).

The carbanions **9** and **11** are both nonplanar. The energetic order is inverted with respect to the radicals, for which **9** lies above **11**. The higher energy of anion **9** may be explained on the basis of the s and p character of the carbon atom. The bond angle of anion **9** at C_2 is 133°, while in anion **11**, the bond angle at C_8 is 115°. From this, we conclude that the HOMO in anion **9** has less s character than that for anion **11**. It is well appreciated that for localized carbanions the more s character in the HOMO, the more stable is the carbanion. In the case of radicals at carbon centers, going to the anion species involves major changes in the bond lengths only around the radical center. For example, when one electron is added to radical **10** to form anion **11**, we observe the following bond changes: N_7-C_8, 1.278 → 1.362 Å; N_9-C_8, 1.372 → 1.436 Å.

The GPAs are reported in Table 4. The values are found in the range 14.5−17.6 eV (334−396 kcal/mol). The GPAs follow the trend found for the anions, with the hydrogens linked to nitrogen atoms being the most acidic ones. Our results agree with the relative order obtained by semiempirical computations[25,39] and the MP2 computations of Freitas and co-workers.[40] Sharma and Lee experimentally bracketed the GPAs for the two most acidic sites and found the values 333 ± 2 kcal/mol (**3**) and 352 ± 2 kcal/mol (**5** and **7**).[27] These experiments compare

TABLE 5: Adiabatic Electron Affinities of Radicals Related to Adenine in eV[a]

structure	B3LYP	BLYP	BP86
2	3.26	3.05	3.28
	(3.23)	(3.03)	(3.25)
4	2.55	2.43	2.65
	(2.55)	(2.44)	(2.65)
6	2.58	2.46	2.68
	(2.57)	(2.46)	(2.68)
8	0.90	0.87	0.98
	(0.96)	(0.94)	(1.06)
10	2.38	2.27	2.42
	(2.40)	(2.29)	(2.44)

[a] ZPVE-corrected EAs are in parentheses.

TABLE 6: VDEs of Anions Related to Adenine in eV

structure	B3LYP	BLYP	BP86
3	3.61	3.35	3.58
5	2.64	2.50	2.72
7	2.67	2.53	2.75
9	1.73	1.66	1.78
11	2.89	2.73	2.90

remarkably well with our theoretical predictions, 334 kcal/mol (**3**) and 353 kcal/mol (**5** and **7**).

3.3. Electron Affinities. The electron affinities and the VDEs of the five adenine radicals are reported in Tables 5 and 6, respectively. All functionals predict positive substantial electron affinities (nearly 1 eV or higher) for each radical. The order is the same for the three functionals. For each radical, the maximum deviation of the AEA between methods is less than 0.25 eV. BP86 predicts larger values while the BLYP EAs are the smallest. The nitrogen radicals have higher AEAs with respect to the carbon radicals. Of the two carbon radicals, the isomer created in the five-membered ring (**10**) has a higher AEA than the one created at the six-membered ring (**8**). This is caused by the high stability of anion **11** with respect to anion **9**. To elucidate this point, we compared the AEAs of the following radicals: HN═CH (cis), HN═C−NH$_2$ (cis), and radical **14** of 1*H*-imidazole. The results obtained were AEA(HN═CH) = 0.45 eV, AEA(HN═C−NH$_2$) = 0.95 eV, and AEA(**14**) = 1.70 eV. Here the AEA increases for two main reasons. First, going from HN═CH to HN═C−NH$_2$, the anion is stabilized by a second highly electronegative atom, nitrogen. Second, by comparison of the anion NCN angle for the bent radical HN═C−NH$_2$ (118°) with the cyclic radical **14** (105°), from the analysis of the last section, we conclude that the HOMO of the carbon atom increases its s character and the AEA rises. Thus when comparing the AEA of radicals **8** and **10**, we notice that the "chemical environment" is similar. This means that the first effect (described earlier) must not be taken into account and we have to consider only that the bond angle at the carbon center of the anion **11** compared to anion **9** is smaller. We conclude that the AEA found for radicals **8** and **10** follows the trend found for the HN═CH, HN═C−NH$_2$, and **14** radicals. Chen, Chen, and Sane reported (using the semiempirical AM1-MCCI CURES EC method) that the adenine radical **2** has an AEA of 3.50 eV,[25] compared to our 3.23 eV. Sevilla and co-workers[24] reported the EA of adenine radical **6** at the 6-31G*//3-21G level, predicting a VDE of 2.47 eV using Koopmans theorem and an AEA of 1.07 eV by computing the energy difference between the neutral radical and the closed-shell anion. The latter result may be compared to the AEA predicted here, namely, 2.57 eV (Table 5).

Conclusions

We computed the electron affinities of five radicals generated from adenine by hydrogen atom abstraction. All computations were carried out using carefully calibrated DFT methods employing the B3LYP, BLYP, and BP86 functionals with a double-ζ plus polarization and diffuse functions basis set, DZP++. Previous investigations have shown that these methods lead to reasonable electron affinities.[37] Radicals generated at the nitrogen centers are shown to have a delocalized unpaired electron. The carbon radicals are localized on the center where the hydrogen is abstracted. Analogous studies carried out on two molecules similiar to adenine, 1*H*-imidazole and 4,5-dihydro-1*H*-imidazole, provide evidence that the higher stability of the nitrogen radicals is not simply related to electron delocalization. At present, there are no experimental data available with which to compare these theoretical predictions.

The theoretical electron affinities are large and range from 0.9 to 3.2 eV. The radical created at the pyrrole nitrogen (**2**) has the highest electron affinity. It is also the most stable radical, and the corresponding anion is likewise the most stable. However, it should be noted that the analogous radical is not possible for adenosine, as nitrogen N$_9$ is linked to the sugar moiety.

Our results for radical **2** agree with the previous Hartree−Fock calculations by Sevilla et al.[24] and the semiempirical calculations by Chen et al.[25] The AEA for **6** is significantly higher than the values reported by Sevilla. The calculations for the five radicals greatly extend existing theoretical predictions for adenine.

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