DFT Calculations of the Electron Affinities of Nucleic Acid Bases: Dealing with Negative Electron Affinities

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To better understand the cause of the diversity in reported values of the electron affinities (EAs) for DNA bases, we performed a series of DFT (B3LYP functional) calculations at different basis set sizes. Through investigation of (1) trends in the values of EAs, (2) the excess electron spin distribution of the anion radical dependence on basis set size, (3) effect of the excess electron on ZPEs, we are able to identify the features of a basis set that allows for dipole-bound and continuum states to compete with molecular states for the electron. Smaller basis sets that confine the excess electron to the molecule allow for reasonable estimates of relative valence electron affinities excluding dipole-bound states and suggest the order of adiabatic valence electron affinities to be U ≈ T > C ≈ I (hypoxanthine) > A > G with G nearly 1 eV less electron affinic than U. Combining the best estimates from theory and experiment we place the adiabatic valence electron affinities of the pyrimidines as zero to +0.2 eV, whereas the purines A and G are predicted to be clearly negative with electron affinities of ca. −0.35 and −0.75 eV, respectively. The virtual states (i.e., negative electron affinities) for A and G in the gas-phase become relevant to biology when their energies are lowered to bound states in solvated systems. Indeed, our calculations performed including the effect of solvation (PCM model) show that all EAs for the DNA bases are positive and have the same relative order as found with the compact basis sets in the gas-phase calculations.

Introduction

The electron affinities of the DNA bases are of interest owing to their significance to the understanding of DNA radiation damage as well as excess electron transfer through DNA.[1−5] There have been a series of reports,[6−18] both experimental and theoretical, concerning the electron affinities (EAs) and ionization potentials (IPs) of the DNA/RNA bases. We[19] and others[9,10,16] have noticed that the values of EAs lack the self-consistency of those reported for the IPs (see Table 1).

As shown in Table 1 vertical electron affinities of the DNA/RNA bases have been reported experimentally and are all negative. Theory suggests the adiabatic electron affinities of the pyrimidine bases thymine and uracil to be slightly positive, with purine bases predicted to be negative, whereas experiments are inconclusive with one report of a positive EA for uracil,[12] another[17] suggesting no positive EA (except for the dipole-bound state), and extrapolated results suggesting slightly positive values for pyrimidines.[18] The greatest disagreement in values is for guanine, which has experimental and theoretical values of adiabatic EA reported from −0.7[11] to +1.5 eV.[15] Recent theoretical efforts by Wesolowski et al.[10] suggest the higher value is not reasonable, while values from −0.7 to 0 eV are still in contention.

What are the reasons for these wide discrepancies? While some problems with DFT theory and negative ions have been suggested, it is now clear that for bound systems reasonable estimates of EAs can be obtained with DFT theory. The major difficulty in obtaining precise electron affinities theoretically is not limited to DNA bases but includes all molecules with negative electron affinities.[20−22] All theoretical calculations for negative electron affinities are problematic. Only stable bound states are readily accessible to DFT or HF theories, and for molecules with negative valence electron affinities, no stable bound state exists, other than possible dipole-bound or continuum states. For this reason excess electrons are energetically driven to leave the molecular structure to either become trapped nearby in a dipole-bound state or to be lost to the continuum.

Nevertheless, electron transmission spectroscopy (ETS)[23,24] is able to experimentally measure negative electron affinities, i.e., those molecular states that exist above the zero of energy in the continuum. ETS involves a scattering experiment in which electrons with kinetic energy equal to the LUMO energy level experience a resonance in transient metastable state and are scattered.

Since negative electron affinities are experimentally available, a number of "practical" methods for dealing with negative electron affinities theoretically have been proposed and used in the literature.[25,26] One is the use of small basis sets that confine the electron to the molecular framework and produce reasonable estimates of the relative (but not absolute) valence electron affinities.[10,25,26] Another is placing the molecule of interest in a sphere of charge to make the "virtual" states bound states and, after the calculation, to remove the effect of the charge.[25] In effect this is what solvation supplies to the molecular anion radical in solution. The original unstable state (negative electron affinity) of the molecule becomes stable in a solvent. Indeed, the Born equation gives a good estimate of the energy lowering of an ion in water. For a typical DNA base anion this should amount to several electronvolts, excluding specific hydrogen bonding contributions that also stabilize the anion. In this regard we note that the anion radicals of several

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TABLE 1: Electron Affinities (eV) Reported[a]

	experiment			theory				
	vertical		adiabatic	adiabatic			vertical	
ref no.	Aflatooni[6]	Periquet[7]	Schiedt[18]	Wetmore[9]	Wesolowski[10]	Sevilla[11]	Wetmore[9]	Sevilla[11]
G	−0.46[b]			−0.27	0.07	−0.7	−0.4	−1.23
A	−0.54	−0.45		−0.40	−0.17	−0.3	−0.7	−0.74
C	−0.32	−0.55	(0.13)	−0.06	−0.02	0.2	−0.5	−0.40
T	−0.29	0	(0.12)	0.14	0.16	0.3	−0.30	−0.32
U	−0.22		(0.15)	0.18	0.19	0.4	−0.3	−0.19

[a] Schiedt's data from extrapolation of hydrated bases, with ±0.12 eV error limits. Wetmore's data obtained at the B3LYP/6-311+G(2df,p) level; Wesolowski's at B3LYP/TZ2P++; Sevilla's at MP2/6-31+G(D), scaled results. [b] Enol tautomer.

TABLE 2: Electron Affinities (eV) Calculated by DFT (B3LYP) with Five Basis Sets[a]

	6-31G(D)	D95V(D)	6-31+G(D)	D95V+(D)	6-311++ G(2d,p)	D95V+(D) ϵ=78[b]	best estimate[c]
				Adiabatic (ZPE Corrected)			
U	−0.52	−0.13	0.18	0.22	0.20	2.14	0.20
T	−0.49	−0.15	0.20	0.22	0.22	2.06	0.22
C	−0.69	−0.36	−0.06	−0.01	−0.05	1.89	−0.05
I	−0.67	−0.31	−0.06	−0.02	−0.04	1.83	−0.04
A	−1.18	−0.81	−0.40	−0.34	−0.30(DB_2)	1.53	−0.35
G	−1.51	−1.17	−0.32 (DB_1)	−0.28 (DB_1)	−0.01 (DB_1)	1.01	−0.75
				Vertical (ZPE Uncorrected)			
U	−1.09	−0.69	−0.35	−0.32	−0.18 (DB_1)	1.67	−0.32
T	−1.05	−0.71	−0.29	−0.28	−0.22 (DB_1)	1.63	−0.28
C	−1.42	−1.04	−0.67	−0.63	−0.17 (DB_1)	1.44	−0.63
I	−1.21	−0.84	−0.55	−0.52	−0.18 (DB_1)	1.46	−0.52
A	−1.57	−1.20	−0.85	−0.80	−0.34 (DB_1)	1.36	−0.80
G	−2.07	−1.72	−0.41 (DB_1)	−0.37 (DB_1)	−0.07 (DB_1)	1.04	−1.25

[a] Values in which dipole-bound states significantly contribute are marked by DB_1 and we note that minor dipole-bound contributions may be presented for some calculations for A at the largest basis set (marked DB_2). Those values with significant dipole-bound contributions are not representative of estimates of the EAs sought in this work. [b] Solvated case (PCM method), ZPE uncorrected. [c] See discussion about "best estimates" for gas-phase valence EA values.

pyrimidine DNA bases have been observed in the gas phase when even one molecule of water is bonded.[17,18] In aqueous media all DNA base anions have been observed experimentally by electron spin resonance.[2c−e]

In this work, we employ the strategy of using small basis sets that confine the excess electron to the molecular framework to gain relative estimates of those DNA bases with negative valence electron affinities using the DFT method. We further calculate electron affinities with larger basis sets and show at which basis set size the excess electrons then fall into lower energy dipole-bound states. We also calculate valence EAs for DNA bases in a solvated environment. Our aim in this work is to obtain a set of estimates for valence EA's of the DNA bases as well as our best predictions of the relative order of valence electron affinities for the bases.

Methods

DNA/RNA single bases (guanine (G), adenine (A), cytosine (C), thymine (T), uracil (U), and hypoxanthine (I)) are optimized using DFT theory with the density functional B3LYP in combination with several commonly used basis sets, ranging from 6-31G(D) to 6311++G(2d,p). The Gaussian 98 program package was used throughout.[27] The optimizations were followed by frequency calculations at the same level to obtain zero point correction to energies (ZPE). A scaling factor[28] of 0.9804 is used throughout all frequency calculations.

The electron affinity is the energy of the neutral DNA base minus that of the anion radical ($E^\circ - E^-$). The calculation of the adiabatic electron affinity (AEA) is based on the optimized geometry of the neutral species and the optimized geometry of the anion radical species. The calculation of the vertical electron affinity (VEA) employs the optimized neutral geometry for both neutral and anion radical species.

To apply the solvent effect on the bases, we chose Tomasi's PCM model (keyword: SCRF=PCM) and performed single point energy calculation at the B3LYP/D95V+(D) level with structures optimized in the gas phase at the B3LYP/D95V(D) level. Water's dielectric constants, ϵ, of 78 and 100 points/sphere were specified.

Spartan 5.0[29] and GaussView[30] version 1.0 in conjunction with Gaussian 98[27] were used in the visualization of singly occupied molecular orbitals (SOMO) and spin surfaces. Due to software limitations, only the SOMO and spin density for the gas-phase calculations are presented.

Results

1. Basis Set Effect on Electron Affinities. Table 2 lists both the adiabatic and vertical electron affinities obtained at the B3LYP level with the use of the basis sets chosen for this study: 6-31G(D), 6-31+G(D), 6-311++G(2d,p), D95V(D), and D95V+(D), as well as the EAs in a solvated environment. As can be seen in the table, EA values for basis sets with diffuse functions ("+" signs) and the same bases sets without diffuse functions differ substantially. This is expected, as anions are usually better predicted with diffuse functions. In general, the EAs of purine bases are more sensitive to diffuse functions than those of the pyrimidine bases. Clearly, the adiabatic EA of guanine appears most sensitive to diffuse functions and we show below that this arises from mixing in of the dipole-bound state with the valence state. We find all the vertical EA's are dominated by dipole-bound state contributions for the largest basis set employed, 6311++G(2d,p), with guanine so affected even with the inclusion of a single diffuse function.

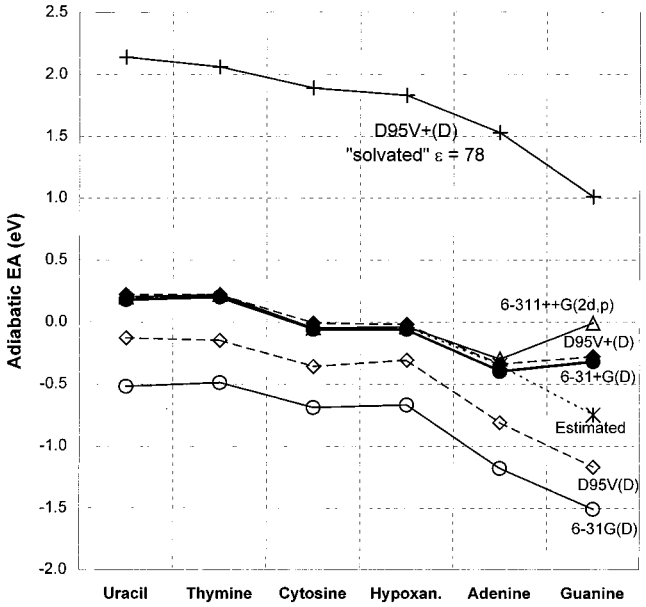

Figure 1. DFT-B3LYP calculated adiabatic electron affinities of the DNA/RNA bases at various basis sets. The trend lines show similar behavior for the compact basis sets but differ significantly for guanine when diffuse functions are included. In the solvated case we employed the D95v+(D) basis set and find the diffuse function does not have this effect. Our estimates of the gas-phase valence electron affinities are also plotted for A and G.

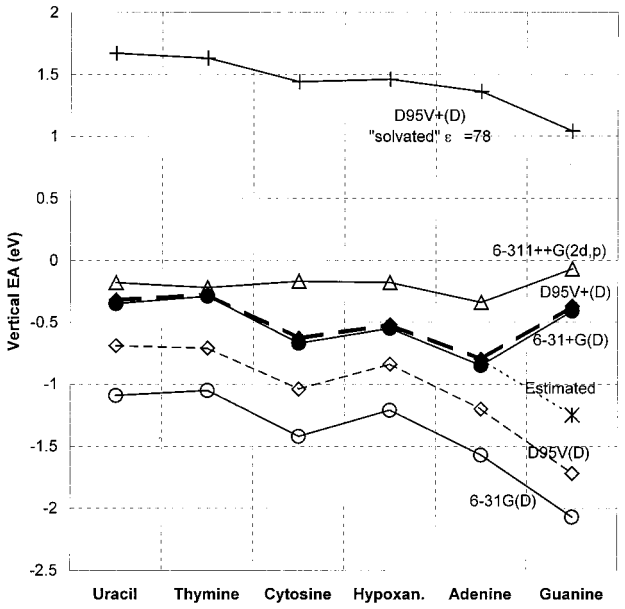

Figure 2. DFT-B3LYP calculated vertical electron affinities at various bases sets and trend lines for the DNA/ RNA bases. Our gas-phase vertical "valence" EA estimates are included for A and G.

Figure 1 (adiabatic) and Figure 2 (vertical) display the EA values of Table 2 in a fashion that clearly shows the trend lines in EA with basis set. As can be seen in Figure 1, the trend lines of the 6-31G(D) and D95V(D) basis sets and the solvated values are very similar in shape, we believe these lines show the relative trend of adiabatic EAs without mixing of dipole-bound states. The trend lines obtained with the three larger basis sets nearly overlap each other for U, T, C, and I. These lines are displaced to higher EA values but echo the trend of the smaller basis sets. However, calculations using these three larger basis sets with diffuse functions all slightly drift away from the trend line for A and much farther away for G, toward zero.

The EAs in the solvated environment were calculated using the PCM model ($\epsilon = 78$) at the B3LYP/ D95V+(D) level with geometries optimized at D95V(D) in the gas phase. These values (Table 2) are shown in the upper traces of Figures 1 (adiabatic) and 2 (vertical). As can be seen in the table, all EAs shift into positive values. In the figures we see inclusion of the effect of the dielectric continuum raises all values of the EA by about 2 eV. Further, the relative order of the solution EAs are those found in the gas phase calculations with compact basis sets. Even the EA for G is in a relative position near that found with the compact basis sets in the gas phase. Checking the molecular orbital coefficients for the SOMO suggests that valence states are found for all bases except for guanine where the dipole-bound state still is found to contribute to some extent. (Spin density contours are not available with the current software.) Since solvation is expected to stabilize the valence state so that it becomes favored over the dipole-bound state, we anticipate that improved solvent calculations would produce a full valence state for the guanine anion radical as found experimentally.

2. SOMO Surface and Spin Density of the Base Anion Radicals. When an electron attaches to a neutral molecule forming its anion radical, it occupies the SOMO. For the most part, the shape of the SOMO follows the spin density distribution of the anion radical. As we look into the SOMO surfaces and the spin density distributions of the base anion radicals, it becomes apparent that the presence of a diffuse function allows for the contribution of diffuse dipole-bound states. This is especially so in the case of guanine.

The spin density and SOMO surfaces for the guanine anion radical are found to substantially change with the inclusion of diffuse functions in basis sets. An extended investigation of such changes was conducted for various levels of theory, from PM3 and HF, up to DFT theories at different basis sets. The surfaces obtained can be roughly classified into two types (Figure 3): Type I includes those from PM3 and HF/6-31+G(D) to B3LYP/ 631G(D) and B3LYP/D95V(D). Type II includes all those obtained at the DFT level with basis sets from 6-31+G(D) to 6-311++G(2d,p). All surfaces of type I are confined to the molecular framework, and a diffuse function does not substantially change the shape of its SOMO surface at the HF level. While at DFT levels with the B3LYP functional, the SOMO and spin density surfaces (type II) are for the most part lost from the molecular framework when the diffuse function or even the extra orbitals on hydrogen are included, as in the 6-311G-(D) basis set. The spin density isosurface, when visualized at a lower 1/10 contour value of 0.0002 electron/au^3, shows a distribution that extends substantial distances from the molecular framework (Figure 3, D95V+(D) basis set). This diffuse distribution suggests the excess electron is tending toward a spatial distribution in accord with the dipole-bound state for the guanine molecule.[13,14] We do not suggest that these shapes are those of the true dipole-bound state or the wave functions used are appropriate for a dipole-bound state. Dipole-bound states are far more diffuse than can be accounted for by the basis sets used in our work.[13,14] We only point out that the diffuse functions allow for the mixing in of these states and do not therefore allow for the satisfactory computation of the valence EA's that we seek.

For each of the relaxed anions of A, T, C, U, and I, the SOMO surfaces and unpaired spin distributions remain nearly unchanged through the four basis sets: 6-31G(D), 6-31+G(D), D95V(D), and D95V+(D). Figure 4 shows the visualized SOMO surfaces and spin distributions of these nucleic acid bases

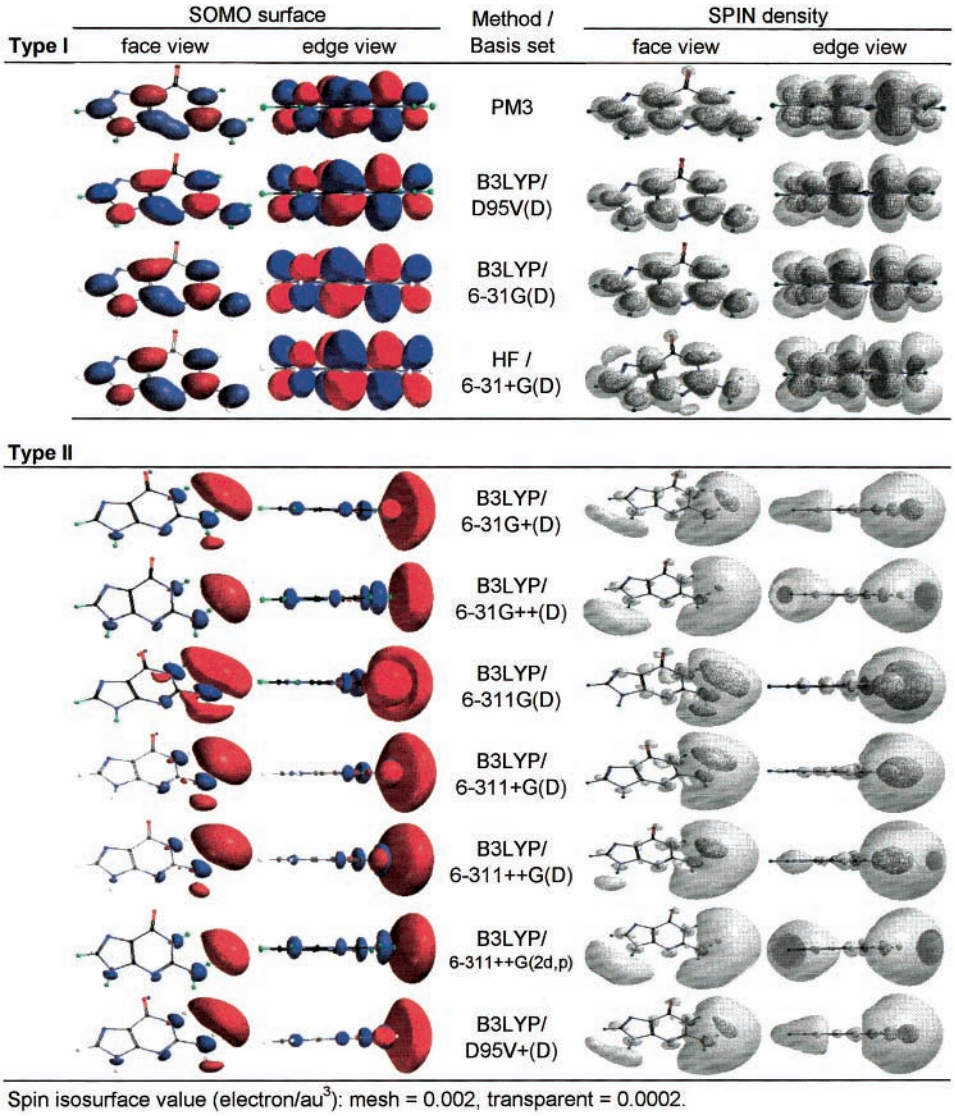

Figure 3. SOMO surfaces and SPIN density distributions of guanine anion radical. Type I represents valence-bound anions. Type II poorly represents the valence-bound anion, as they include significant contributions of the dipole-bound state. These include the D95V+(D) level and all those obtained at DFT level with basis sets containing diffuse functions. Spin isosurface value (electron/au^3): mesh = 0.002, transparent = 0.0002. We note that type II electron densities do not represent true dipole-bound states for guanine, as the basis sets are far too compact to fully represent these very diffuse states.

obtained with the D95V+(D) basis set. No significant dipole contributions are found for these molecules at these basis sets.

3. Contribution of the Excess Electron to Zero-Point Energy Correction of Anions. An anion radical is simply the neutral molecule plus an excess electron. The excess electron will cause a geometry reorganization in the structure; however, the larger the active space for excess electron distribution, the less contribution to changes in geometry there will be. The zero-point vibrational energy will be affected by the excess electron to the extent that the electron causes reorganization in the molecular framework. In the extreme that the electron is lost in continuum, there will be no change in the ZPE contribution before and after addition of the electron. We therefore use the difference in total ZPE correction between the anion and the neutral species as a measure of electron localization to the molecular framework. In effect, this ZPE difference equals the difference of electron affinity with and without ZPE correction.

Table 3 lists this difference in ZPE correction between the neutral molecule and the anion radical for each base calculated with 5 basis sets. As can be seen for U, T, C, and I, the values remain nearly constant with basis set, suggesting little change in the spacial distribution of the excess electron. The values for A and G decrease with increase basis set size, and those for G decease dramatically with inclusion of a diffuse function in the basis set, suggesting an increase in active space for the excess electron. At the 6-311++G(2d,p) basis set, the values of both A and G are close to zero, indicating a rather diffuse spacial distribution of the excess electron. The results in Table 3 further confirm that the gas-phase EAs of G and A calculated with basis sets containing diffuse functions are problematic, as they mix dipole-bound and valence states.

Best Estimates of the EAs and Discussion

Since the dipole-bound states are not believed to be relevant to aqueous systems and presumably biological events,[11] we confined our interest to the search for the valence-bound EAs of the bases in gas phase. We have tested five different basis sets in the gas phase as well as one with the effect of a continuous dielectric (solvated case) and found a set of DNA base EA values for each.

For guanine, the spin distributions clearly have dominant contributions from dipole-bound states whenever a diffuse

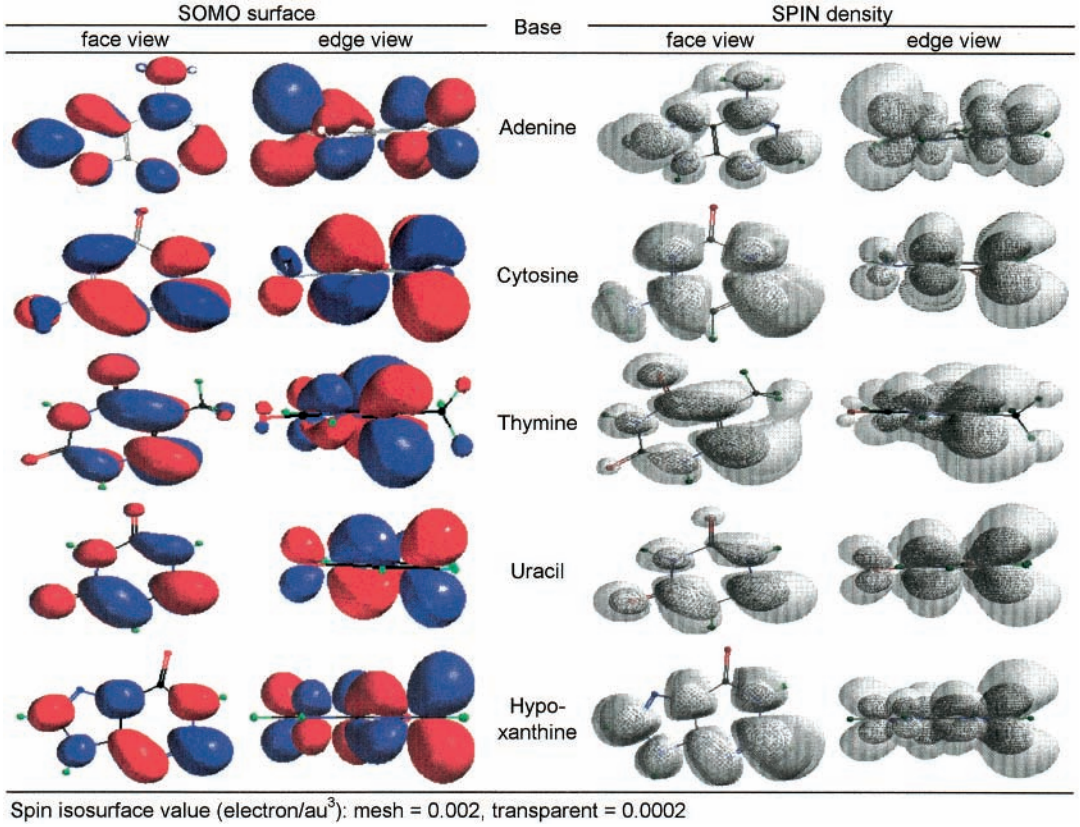

Figure 4. SOMO surfaces and SPIN density distributions of base anion radicals (adenine, cytosine, thymine, uracil, and hypoxanthine), obtained at the B3LYP/D95V+(D) level.

TABLE 3: ΔZPE in Gas Phase [ZPE Neutral − ZPE Anion] (eV)

basis set	U	T	C	I	A	G
6-31G(D)	0.17	0.17	0.10	0.20	0.20	0.27
D95V(D)	0.16	0.16	0.09	0.20	0.19	0.26
6-31+G(D)	0.17	0.16	0.10	0.20	0.12	0.06
D95V+(D)	0.17	0.16	0.09	0.20	0.12	0.06
6-311++G(2d,p)	0.17	0.17	0.10	0.21	0.03	0.04

function or extra set of orbitals on hydrogens are employed (Figure 3). And for adenine, the EA values obtained by 6-31+G-(D) and higher basis sets are problematic, as they are slightly higher than the expected trend predicted with smaller basis sets. There may be a small dipole-bound contamination, but this is not readily apparent in the spin distribution. However, for the four other DNA bases (U, T, C, I), the adiabatic EA values obtained by the 6-31+G(D), 6-311++G(2d,p), and D95V+-(D) basis sets are nearly identical, suggesting these values are close to the limit of accuracy for this theoretical method. The SOMO surfaces and spin densities shown in Figure 4, obtained with the D95V+(D) basis set, clearly show that the excess electron is covalent-bound in each anion of these bases. Thus, the EA values obtained by this basis set are probably the best theoretical estimates for these four bases (U, T, C, I). The other two basis sets are nearly equivalent in any case (Table 2).

Since dipole-bound contamination does not allow for calculation of the adiabatic EA of G with basis sets with diffuse functions, we estimate the value for G from the trends at lower basis sets. We note that the difference in adiabatic EA's calculated at D95V(D) and D95V+(D) are nearly constant at ca. 0.35 eV for U, C, and I and is slightly more for A at 0.47 eV. By lowering the value calculated at D95V(D) for G by 0.4 eV, we can gain an estimate of its "valence" adiabatic EAs. With this assumption, the estimated adiabatic valence EA's for G is ca. −0.75 eV. Thus in a condensed phase guanine is expected to provide the largest barrier for excess electron transfer in DNA by a substantial amount.

We believe that the best theoretical estimates from DFT theory provide good predictions of the ordering of the valence EA's. But what about the absolute values? First of all, we do not make any extraordinary claims to accuracy as we note there are some experiments that would suggest these values are 0.1 or 0.2 eV too high for the U and T.[16−18] Rather, these values are only the best estimates based on this level of theory. The theoretical EAs reported recently by Wesolowski et al.,[10] which were obtained at the B3LYP/TZ2P++ level (Table 1), show little difference with our estimate for cytosine (−0.02 eV vs −0.05 eV), uracil (0.19 vs 0.20), and thymine (0.16 vs 0.22). However, there are obvious and large discrepancies for adenine (−0.17 vs −0.35) and guanine (+0.07 vs −0.75). For U and T, their use of a larger basis set would suggest their slightly lower values may be more reasonable than ours, if no mixing of dipole-bound states are found. But for G, we have good reason to believe their value does not represent the valence-bound EA of guanine and likely adenine as well. Wetmore and co-workers' data[9] are in generally good agreement with our estimates on A (−0.40 eV), C (−0.06), T (0.14), and U (0.18), but not G (−0.27), which we again believe the excess electron is tending to the dipole-bound state as a result of the use of a larger basis set: 6-311+G(2df,p). Recently, another group[31] also reported a set of theoretical EA values obtained at the B3LYP/6-311++G** level, with A (−0.264), G (−0.004), C (0.006), and T (0.179). As can be seen, the value for G is near zero, a clear characteristic of the dipole-bound state.

Our estimate of the adiabatic EA of guanine (−0.75 eV) is clearly the most controversial, as several groups discussed above have reported far higher values; however, these efforts did not

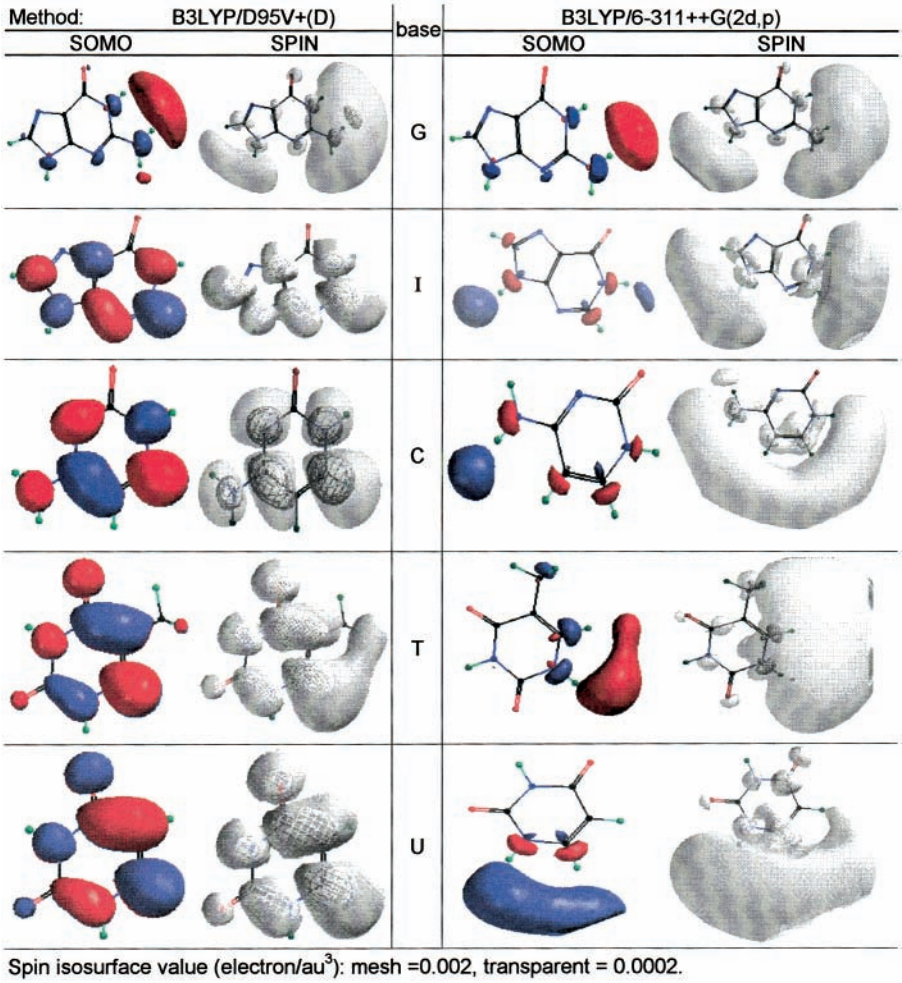

Figure 5. SOMO surfaces and SPIN density distributions of base anions in their neutral geometries (nonrelaxed anions), obtained at B3LYP with D95V+(D) and 6-311++G(2d,p) basis sets.

attempt to distinguish between dipole-bound and valence states of the anions. Since the valence-bound anion of guanine will be unstable, as inferred by the large negative electron affinity, experimental measurement of the valence EA can be a real challenge and only the vertical EA is likely to be measured. The only experimental vertical EA of guanine available is −0.46 eV, reported by Aflatooni et al.[6] and assigned to guanine's enol tautomer (Table 1). We calculated the enol form's vertical EA value to be −1.27 eV with the D95V(D) basis set. This compares with a vertical EA of −1.72 eV with D95V(D) for guanine in the usual form (Table 2). The results suggest that the enol tautomer is ca. 0.45 eV more electron affinic than the keto form. From this and the experimental vertical EA of the enol form we obtain an estimated vertical EA of guanine of ca. −0.9 eV. With an estimated relaxation energy of ca. 0.3 eV, this would make the adiabatic EA −0.6 eV, slightly larger than the −0.75 eV estimated by other means but still the least affinic of the DNA bases.

The vertical EAs of the bases cannot be appropriately corrected for ZPE's since they are not in their relaxed states as anion radicals. Thus, judging from the adiabatic EAs, these theoretical predictions are likely to be too low by roughly 0.1 eV. However, as can be seen in Table 2, the vertical EA values obtained by 6-31+G(D) and D95V+(D) basis sets are consistent with one another, and the values of T and U are close to the reported experimental values (see Table 1). From the trend lines shown in Figure 2, it appears that the smaller basis sets predict trends similar to the trend line found for the EAs for solvated systems. The trend lines for the 6-31+G(D) and D95V+(D) basis sets are nearly identical; however, for G they differ from the two smaller basis sets. Results found for the 6-311++G-(2d,p) basis set differ substantially from all other trends and tend toward zero. The SOMO and spin surfaces of the anions in their neutral geometries (nonrelaxed), obtained with the 6-311++G(2d,p) basis set (Figure 5), clearly show that the excess electron is displaced from the molecular frames of all pyrimidine and purine bases (We assume adenine is not an exception, although we could not obtain its surfaces). This is likely a result of the lack of relaxation of the anion molecular framework (nonadiabatic state) that makes the valence state energetically less competitive with the dipole-bound state. Theory thus suggests that in the gas phase an excess electron would initially be in the dipole-bound state for all DNA bases;[13,14,32] after relaxation, theory predicts valence-bound states for uracil and thymine bases (we note they are not found experimentally in the gas phase except for one report[8]), but in purine bases, excess electrons are predicted to remain in the dipole-bound state even after relaxation.

Thus, it appears that the D95V+(D) basis set provides a generally good estimate for the vertical valence EA values, as we believe it does for the adiabatic valence EA values of the bases, of course except for guanine. By following the trend line of lower basis sets, we estimate a set of vertical valence EA values (no ZPE correction, see Table 2). The experimental values reported[6,7] are all negative (Table 1), as we find, but somewhat more positive than our estimates without ZPE

corrections. The expected 0.1 eV ZPE corrections would make our calculated values more in line with experiment.

With the exception of one report of the uracil valence-bound anion, no DNA valence anion has been seen reported in the gas phase.[7,8] Hendricks et al.[16,17] have observed the dipole-bound anions of uracil and thymine and reported their adiabatic EA to be 0.069 eV (thymine) and 0.093 eV (uracil). Schiedt et al.[18] also reported their values for the dipole-bound adiabatic EA of pyrimidine anions to be 0.085 eV (cytosine), 0.062 eV (thymine), and 0.086 eV (uracil), respectively. Even though both groups had observed no conventional valence-bound anion of pyrimidine bases, both Hendricks et al. and Schiedt and coworkers[18] did measure the valence adiabatic EAs' of incrementally hydrated pyrimidine hydrates. Schiedt estimated that the valence-bound electron affinities of U, T, and C fall in the range 0−200 meV, which is supportive to our theoretical estimates (see Table 1). The question then is why they are not observed experimentally in the gas phase. One reason may be that they have EA's less than the dipole-bound energy of ca. 0.06−0.09 eV. The one experimentally reported value for uracil of 0.030 eV fits this description.[7,8] Also, theoretical calculations suggest that the first water of hydration should provide more EA stabilization than subsequent waters.[33] This would tend to make the extrapolations result in too high of an valence EA for the gas phases bases. These arguments based on experiment would suggest our calculated adiabatic EA values are high by ca. 0.16 eV. Although, we note that the broad photodetachment spectra make exact determinations of the absolute adiabatic EA's difficult.

Summary and Conclusions

In this effort to explain the diversity in the reported electron affinities of DNA/RNA bases, we employed the DFT method and tested five different basis sets in combination with the B3LYP functional and calculated values of the electron affinities in both the gas phase and solvated environment. By comparing the trends of EA values obtained with different basis sets, we clearly see that the values approach the limit of theoretical accuracy with the increase of basis set size to modest basis set sizes, i.e., D95V+(D) appears as predictive as 6-311++G(2d,p). On the other hand, by examining the SOMO surfaces and spin density distributions of the anion radicals, we found that inclusion of diffuse functions in the basis set can result in contamination of the valence-bound state with the dipole-bound state. This was especially so for the purine bases, with guanine showing the greatest tendency. The gas-phase ZPE difference between the neutral and the anion provides a measure of active space for the excess electron, i.e., its degree of association with the molecular framework. With inclusion of more diffuse functions in molecules with negative electron affinities, the excess electron leaves the molecular framework to dipole-bound or continuum states and results in a tendency of the electron affinity to approach zero. In the limit of basis set expansion to very diffuse functions, appropriate for dipole-bound states, the dipole-bound energy would be found (ca. 0.05−0.10 eV from experiment).[13,14,32]

General examination on the SOMO surface and spin density distribution shows guanine is most susceptible to dipole-bound contamination. An extended investigation of SOMO and spin density surfaces of the guanine anion at various computational levels from semiempirical (PM3), HF at 6-31+G(D) to DFT at B3LYP/6-311++G(D), shows that while inclusion of a single diffuse function does not result in diffuse states at the HF level, it does lead to significant dipole-bound state contribution at the DFT level without exception. As a consequence, we believe the EA values of guanine reported recently by the other groups[9,10] are in question, as they are neither representative of the valence state nor the dipole-bound state.

With two smaller basis sets, 6-31G(D) and D95V(D), the order of adiabatic valence EAs is predicted to be U ≈ T > C ≈ I > A > G. With three larger basis sets, the adiabatic EAs predicted for U, T, C, and I show no clear sign of dipole-bound contamination. Combining the trends predicted by smaller basis sets and the best values given by the larger basis sets, we proposed our best theoretical estimates of adiabatic valence electron affinities of the bases in gas phase to be U (0.20 eV) ≈ T (0.22 eV) > C (−0.05 eV) ≈ I (−0.04 eV) > A (−0.35 eV) > G(−0.75 eV).

Applying the same approach on vertical EAs, we estimate a set of vertical valence EA values (gas phase, without ZPE corrections) to be T (−0.28 eV) ≈ U (−0.32 eV) > I (−0.52 eV) > C (−0.63 eV) > A (−0.80 eV) > G (−1.25 eV). They are all negative as expected and in fair agreement with experimental values. But it should be pointed out that large basis sets, such as 6-311++G(2d,p) used in this work, fail to deal with nonrelaxed anion systems, as they are found to lead to diffuse states for every DNA base investigated. This results in vertical electron affinities that approach zero for all the DNA bases.

For systems with negative valence electron affinities, expansion in basis set size provides a more accurate estimate for valence-bound EA values up to a point at which further expansion leads to mixing of dipole-bound states and questionable values for valence EA's. Molecules with very negative valence electron affinities such as guanine fail at even smaller basis sets. In addition, calculations with nonadiabatic molecular frameworks fail well before adiabatic states.

The EAs for solvated DNA anion radicals calculated with the PCM model give the relative order of DNA bases' valence EA's under conditions where all bases have positive EAs. The importance of these calculations is that they include diffuse functions and that, although there was evidence for possible mixing in of dipole-bound state for G, we find the same relative order as calculated in the gas phase with smaller basis sets without diffuse functions. In aqueous solution, DNA base anion radicals are involved in specific hydrogen bonding with several water molecules that will further stabilize the anions.[33] The rather simple PCM model is insufficient to account for these affects, thus the solvated EAs reported here are likely to be smaller than the actual values. Accurate solution phase EA's especially for guanine await these and other improvements. While accurate values of the EA's of the DNA bases within DNA are not well-known yet, we believe our results should give good estimates of the relative order of the DNA base valence EA's even within DNA. Our results also explain previous experimental observations that the pyrimidine anion radicals, of cytosine and thymine, dominate the ESR spectrum of the DNA electron adduct with little contribution from adenine anion radical and no significant contribution from the guanine anion radical.[2a−c,34]

Finally, we note that improved techniques that can accurately describe both valence- and dipole-bound states are likely to be available for systems of DNA base size soon. For example, the electron-attached equation of motion coupled cluster (EA-EOMCC) method has had some success with the smaller nitomethane anion system.[35] With the availability of techniques to handle such mixed state systems some additional clarity shall be brought to these problems.

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Supporting Information Available: Optimized structures of bases, dipole moments of the DNA basis, and a complete list of SOMO/SPIN surfaces of DNA/RNA base anions are available free of charge via Internet at http://pubs.acs.org.

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