

Proton Affinities of Anionic Bases: Trends Across the Periodic Table, Structural Effects, and DFT Validation

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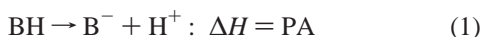
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Abstract: We have carried out an extensive exploration of the gas-phase basicity of archetypal anionic bases across the periodic system using the generalized gradient approximation of density functional theory (DFT) at BP86/QZ4P//BP86/TZ2P. First, we validate DFT as a reliable tool for computing proton affinities and related thermochemical quantities: BP86/QZ4P//BP86/TZ2P is shown to yield a mean absolute deviation of 1.6 kcal/mol for the proton affinity at 0 K with respect to high-level ab initio benchmark data. The main purpose of this work is to provide the proton affinities (and corresponding entropies) at 298 K of the anionic conjugate bases of all main-group-element hydrides of groups 14–17 and periods 2–6. We have also studied the effect of stepwise methylation of the protophilic center of the second- and third-period bases.

1. Introduction

Designing new (and optimizing existing) approaches and routes in organic synthesis requires knowledge of the thermochemistry involved in the targeted reactions. In this context, the proton affinity (PA) of a reactant or intermediate species B^- often plays an important role. This thermochemical quantity is defined as the enthalpy change associated with dissociation of the conjugate acid (eq 1):^{1–5}



Overall reaction enthalpies and reaction barriers (and thus reaction rates) are related to the PA, as soon as proton transfer occurs somewhere along the cascade of elementary steps of a reaction mechanism. This is often the case, as proton transfer is ubiquitous in organic reaction mechanisms, either as simple proton transfer (PT) or as part of a more complex chemical transformation, for example, base-induced elimination reactions that may compete with nucleophilic substitution.⁶

Here, we focus on the proton affinities of anionic bases in the gas phase. Gas-phase proton affinities are obviously directly applicable to gas-phase chemistry,^{3,4} but they are also relevant for chemistry occurring in the condensed

phase.^{1,7} On one hand, they reveal the intrinsic basicity of the protophilic species involved, and thus, they shed light on how this property is affected by the solvent. On the other hand, they can serve as a universal, solvent-independent framework of reference, from which the actual basicity of a species in solution can be obtained through an (empirical) correction for the particular solvent under consideration.⁸ Experimental gas-phase proton affinities are well-known for neutral and cationic organic bases.^{3,4} Less information is available for anionic bases, in particular, for anionic bases with a heavier, that is, third- and higher-period, atom as the protophilic center.^{4,5}

The present study has three purposes. First, we wish to evaluate the performance of various popular exchange-correlation functionals of density functional theory (DFT)⁹ ranging from the local density approximation (LDA) via the generalized gradient approximation (GGA) and hybrid functionals to meta-GGA functionals.^{9,10} This is done by computing the 0 K reaction enthalpies $\Delta_{\text{acid}}H_0$ of reaction 1 (i.e., PA^0 values) for a test set of 17 bases for which highly accurate benchmark data are available.^{11,12} It is anticipated here that the well-known BP86¹³ functional performs very reasonably, in fact, even slightly better than the B3LYP¹⁴ hybrid functional. Second, we aim at setting up a complete description of the proton affinities of the conjugate bases XH_n^- of all archetypal main-group-element hydrides XH_{n+1}

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of groups 14–17 and periods 2–6. Third, we have studied the influence of stepwise methylation of the protophilic center X in species $(\text{CH}_3)_m\text{XH}_{n-m}^-$ (for periods 2 and 3), for example, SiH_3^- , $\text{CH}_3\text{SiH}_2^-$, $(\text{CH}_3)_2\text{SiH}^-$, and $(\text{CH}_3)_3\text{Si}^-$. In addition to our computed BP86/QZ4P/BP86/TZ2P values for the 298 K reaction enthalpy $\Delta_{\text{acid}}H_{298}$ of all acids BH in eq 1 (that is, the proton affinity PA of all bases B^-), we also report the corresponding 298 K reaction entropies ($\Delta_{\text{acid}}S_{298}$, provided as $-\Delta_{\text{acid}}S_{298}$ values) and 298 K reaction free energies ($\Delta_{\text{acid}}G_{298}$).

Note that the series of, in total, 41 bases investigated in this study covers large parts of the periodic system as well as a number of important structural themes occurring in organic chemistry. To the best of our knowledge, this series of bases has never before been studied, in its full range, consistently with one and the same method, either experimentally or theoretically. We anticipate that the very consistency of our approach makes our data particularly suitable for inferring accurate *trends* in thermochemistry across the periodic system.

2. Methods

All calculations were performed with the Amsterdam Density Functional program developed by Baerends and others.^{15,16} Molecular orbitals were expanded using two different large, uncontracted sets of Slater-type orbitals: TZ2P and QZ4P.¹⁷ The TZ2P basis is of triple- ζ quality, augmented by two sets of polarization functions (d and f on heavy atoms; 2p and 3d on H). The QZ4P basis, which contains additional diffuse functions, is of quadruple- ζ quality, augmented by four sets of polarization functions (two d and f on heavy atoms; two 2p and two 3d sets on H). Core electrons (e.g., 1s for second period, 1s2s2p for third period, 1s2s2p3s3p for fourth period, 1s2s2p3s3p3d4s4p for fifth period, and 1s2s2p3s3p3d4s4p4d for sixth period) were treated by the frozen core approximation.¹⁶ An auxiliary set of s, p, d, f, and g Slater-type orbitals was used to fit the molecular density and to represent the Coulomb and exchange potentials accurately in each self-consistent field (SCF) cycle. Scalar relativistic corrections were included self-consistently using the zeroth order regular approximation.¹⁸

Energies and gradients were calculated using LDA (Slater exchange and VWN¹⁹ correlation) with nonlocal corrections¹³ due to Becke (exchange) and Perdew (correlation) added self-consistently. This is the BP86 density functional, which is one of the three best DFT functionals for the accuracy of geometries,²⁰ with an estimated unsigned error of 0.009 Å in combination with the TZ2P basis set. The restricted and unrestricted formalisms were used for closed-shell and open-shell species, respectively.

The energies of a range of other popular DFT functionals were calculated in a post-SCF fashion using the BP86/QZ4P//BP86/TZ2P orbitals and densities, to estimate the influence of the choice of DFT functional. These functionals include LDA,¹⁹ GGAs (BLYP, PBE, OLYP, and HCTH/407),^{13,21,22} meta-GGAs (VS98, BLAP3, TPSS, and τ -HCTH),^{13,23,24} and hybrid functionals (TPSSH, O3LYP, PBE0, B97, B1PW91, and τ -HCTHh).^{21,24,25} The resulting proton affinities at 0 K

and corresponding deviations from high-level theory data are provided in Table S1 in the Supporting Information.

Geometries were optimized using analytical gradient techniques until the maximum gradient component was less than 1.0×10^{-4} atomic units (see Table S2 in the Supporting Information). Vibrational frequencies were obtained through numerical differentiation of the analytical gradients.¹⁶ The enthalpy correction to the electronic energy of the systems was calculated from the vibrational frequencies using standard thermochemistry relations;²⁶ for example, enthalpy corrections at 298.15 K and 1 atm (ΔH_{298}) were calculated according to

$$\Delta H_{298} = \Delta E_{\text{trans},298} + \Delta E_{\text{rot},298} + \Delta E_{\text{vib},0} + \Delta(\Delta E_{\text{vib},0})_{298} + \Delta(\text{pV})$$

Here, $\Delta E_{\text{trans},298}$, $\Delta E_{\text{rot},298}$, and $\Delta E_{\text{vib},0}$ are the differences between the reactant (i.e., BH, the conjugate acid) and products (i.e., $\text{B}^- + \text{H}^+$, the anionic base and the proton) in translational, rotational, and zero-point vibrational energy, respectively; $\Delta(\Delta E_{\text{vib},0})_{298}$ is the change in the vibrational energy difference as one goes from 0 to 298.15 K. The vibrational energy corrections are based on our frequency calculations. The molar work term $\Delta(\text{pV})$ is $(\Delta n)RT$; $\Delta n = +1$ for one reactant BH dissociating to two products (B^- and H^+). Thermal corrections for the electronic energy are neglected.

3. Results and Discussion

3.1. Benchmarking and Validation of DFT. We begin with an extensive exploration of the performance of various density functionals covering LDA, GGA, meta-GGA, and hybrid DFT. To this end, we have computed the proton affinity at 0 K ($\text{PA}^0 = \Delta_{\text{acid}}H_0$) for a series of 17 anionic bases B^- , shown in Table 1, for which extremely accurate experimental data (with uncertainties of only 0.003 up to 0.7 kcal/mol)^{11,12} and ab initio theoretical benchmark values¹² are available. This series of bases covers PA^0 values ranging from 322.6 for Br^- through 415.2 kcal/mol for CH_3^- (see Table 1, exptl.). Table 1 compares our results for BP86, which emerges as one of the best functionals (vide infra), with earlier B3LYP/aug-cc-pVTZ and CCSD(T)/aug-cc-pVQZ//B3LYP/aug-cc-pVTZ benchmark calculations as well as with experimental results.^{11,12} Our results for the other density functionals are collected in Table S1 of the Supporting Information. As can be seen in Table 1, the CCSD(T) benchmark and experimental PA^0 values agree excellently, the latter showing a mean absolute deviation (MAD) from the former of only 0.4 kcal/mol.

First, we have explored with BP86 the effect of carrying out the DFT calculations with the TZ2P versus the very large QZ4P basis set (see Section 2). Already, with the “smaller” TZ2P basis, that is, at BP86/TZ2P, we find PA^0 values in reasonable agreement with the CCSD(T) benchmark, showing a MAD value of 2.8 kcal/mol with respect to the latter (see Table 1). There is one qualitative disagreement between BP86/TZ2P, on one hand, and CCSD(T) and the experimental results, on the other hand: the former yields the vinyl anion C_2H_3^- as slightly less basic than the amide anion NH_2^- ,

Table 1. Computed^{a,b,c} and Experimental^c Proton Affinities at 0 K PA⁰ (in kcal/mol) of Anionic Bases

base	BP86/TZ2P ^a	BP86/QZ4P ^b	B3LYP ^c	CCSD(T) ^{c,d}	exptl. ^c
CH ₃ ⁻	416.9	412.5	414.2	415.3	415.2 ± 0.7
C ₂ H ₃ ⁻	405.7	403.8	405.9	406.7	407.4 ± 0.3
NH ₂ ⁻	408.1	402.1	401.2	402.2	401.9 ± 0.1
C ₆ H ₅ ⁻	398.5	397.2	399.9		399.6 ± 0.4
H ⁻	400.1	398.3	398.1	399.6	399.5 ± 0.003
HCO ⁻	394.9	388.9	390.4	393.2	393.1 ± 0.1
OH ⁻	395.0	389.0	387.3	389.4	389.1 ± 0.02
CH ₃ O ⁻	376.6	375.4	377.8	381.0	380.7 ± 0.6
CH ₃ CH ₂ O ⁻	373.0	372.1	375.0		377.6 ± 0.7
C ₂ H ⁻	375.4	375.3	376.3	376.4	376.9 ± 0.1
(CH ₃) ₂ CHO ⁻	370.9	370.2	373.3		375.4 ± 0.6
(CH ₃) ₃ CO ⁻	370.3	369.9	372.7		374.6 ± 0.5
F ⁻	375.3	371.8	367.1	370.9	370.4 ± 0.003
SH ⁻	351.2	350.2	349.0	350.1	350.1 ± 0.01
CN ⁻	354.8	349.4	348.8	349.3	349.5 ± 0.2
Cl ⁻	334.9	332.6	330.8	332.7	332.5 ± 0.002
Br ⁻	323.4	323.4	321.6	324.3	322.6 ± 0.05
MAD/MD wrt CCSD(T) ^e	2.8/1.6	1.6/–1.4	1.7/–1.7	0	0.4/–0.2
MAD/MD wrt exp. ^f	2.3/–2.0	2.3/–2.0	1.6/–1.6	0.4/0.2	0

^a This work: BP86/TZ2P energies with ZPE correction at BP86/TZ2P. ^b This work: BP86/QZ4P//BP86/TZ2P energies with ZPE correction at BP86/TZ2P. ^c B3LYP/aug-cc-pVTZ from ref 12. ^d CCSD(T)/aug-cc-pVQZ//B3LYP/aug-cc-pVTZ from ref 12. ^e Mean absolute deviation (MAD)/mean deviation (MD) relative to CCSD(T). ^f Mean absolute deviation (MAD)/mean deviation (MD) relative to experiment.

whereas the two latter yield the reverse order, that is, NH₂⁻ as more basic than C₂H₃⁻ (see Table 1).

Further improvements can be achieved by going from the TZ2P to the QZ4P basis set. The QZ4P basis set is not only more flexible and better polarized it also contains more diffuse functions. One may, therefore, expect an improved description of reaction 1 in which we go from a neutral species BH to two (oppositely) charged species B⁻ + H⁺. In particular, the description of the expanding density (“breathing orbitals”) at the protophilic center (e.g., nitrogen in NH₃/NH₂⁻) benefits from going from the TZ2P to the QZ4P basis set. Thus, single-point calculations were done at BP86/QZ4P using the BP86/TZ2P geometries and enthalpy corrections. At this level of theory, that is, at BP86/QZ4P//BP86/TZ2P, we achieve a significant improvement of the MAD, which drops to 1.6 kcal/mol relative to the CCSD(T) benchmark data, which is comparable to the MAD value of 1.7 kcal/mol obtained earlier at B3LYP/aug-cc-pVTZ¹² (see Table 1). Furthermore, BP86/QZ4P//BP86/TZ2P yields correct relative PA⁰ values over the entire range of bases. None of the other density functionals (see Section 2) performs better than this BP86 approach, with MAD values ranging from 1.6 kcal/mol for PBE (the only other functional achieving this small MAD value) via 2.6 and 3.0 kcal/mol for BLYP and OLYP through 7.8 and 8.1 kcal/mol for O3LYP and LDA (see Table S1 in the Supporting Information).

We have verified that neither the geometry nor the enthalpy corrections differ significantly if they are also computed with the QZ4P basis set (data not shown). Thus, the full BP86/QZ4P//BP86/QZ4P energies differ by merely 0.04 kcal/mol or less compared to the BP86/QZ4P//BP86/TZ2P energies (tested for NH₂⁻ and F⁻), while the enthalpy corrections differ by only 0.05 kcal/mol or less (tested for CH₃O⁻ and F⁻).

In conclusion, BP86/QZ4P//BP86/TZ2P (with BP86/TZ2P enthalpy corrections) emerges as a reliable approach for studying trends in the basicity of anionic bases in the following section.

3.2. Proton Affinities of Main-Group-Element Hydrides. Using the BP86/QZ4P//BP86/TZ2P approach (see previous section), we have computed the proton affinities at 298 K (PA = Δ_{acid}H₂₉₈) and the corresponding entropies Δ_{acid}S₂₉₈ (provided as –TΔ_{acid}S₂₉₈ values) and reaction free energies Δ_{acid}G₂₉₈ of the anionic conjugate bases of all main-group-element hydrides of groups 14–17 and periods 2–6. The results are summarized in Table 2 and Figure 1.

Along the series of second-period bases, we obtain the well-known trend of a decreasing basicity as the PA falls from 414 to 404 to 390 to 373 kcal/mol along CH₃⁻, NH₂⁻, OH⁻, and F⁻ (see Table 2 and Figure 1). In each of the four groups (14–17), the PA decreases if one descends the periodic table. The largest reduction in PA occurs from the second to the third period. In group 14, for example, the PA decreases from 414 to 369 to 356 to 342 to 324 kcal/mol along CH₃⁻, SiH₃⁻, GeH₃⁻, SnH₃⁻, and PbH₃⁻ (see Table 2). Interestingly, the changes in PA descending group 14 are significantly larger than in the other groups, 15–17. Thus, as can be seen in Figure 1, the trend of a monotonic decrease in PA along the second (P2) and, already to a lesser extent, the third period (P3) changes for the fourth through sixth periods (P4, P5, and P6) into a trend where the PA along a period first *increases* from group 14 to 15 and then decreases again along groups 15, 16, and 17. The corresponding reaction entropies yield a relatively small (but not entirely constant) contribution –TΔ_{acid}S₂₉₈ of –5 to –9 kcal/mol for 298 K. As a consequence, the Gibbs free energies Δ_{acid}G₂₉₈ show the same trends as the corresponding PA values (see Table 2).

Table 2. Thermodynamic Acidity Properties (kcal/mol) for Anionic Bases $\text{Me}_m\text{H}_{n-m}\text{X}^-$ at $T = 298 \text{ K}^a$

group 14				group 15				group 16				group 17			
base	ΔH	$-\Delta S$	ΔG	base	ΔH	$-\Delta S$	ΔG	base	ΔH	$-\Delta S$	ΔG	base	ΔH	$-\Delta S$	ΔG
Period 2															
CH_3^-	414.0	-8.3	405.7	NH_2^-	403.6	-7.5	396.0	OH^-	390.2	-6.6	383.6	F^-	372.7	-5.7	366.9
MeCH_2^-	415.6	-8.7	406.8	MeNH^-	398.3	-7.4	390.8	MeO^-	376.6	-6.5	370.1				
Me_2CH^-	410.8	-7.9	402.9	Me_2N^-	387.1	-6.9	380.2								
Me_3C^-	403.9	-7.3	396.6												
Period 3															
SiH_3^-	369.1	-8.3	360.8	PH_2^-	366.2	-7.5	358.6	SH^-	351.4	-6.4	345.0	Cl^-	333.5	-5.4	328.2
MeSiH_2^-	376.2	-8.3	367.9	MePH^-	372.9	-7.6	365.4	MeS^-	357.5	-6.4	351.0				
Me_2SiH^-	381.2	-8.0	373.1	Me_2P^-	377.4	-7.2	370.2								
Me_3Si^-	383.7	-7.5	376.2												
Period 4															
GeH_3^-	355.9	-8.3	347.6	AsH_2^-	358.1	-7.5	350.6	SeH^-	341.9	-6.3	335.6	Br^-	324.3	-5.2	319.1
Period 5															
SnH_3^-	342.0	-8.2	333.9	SbH_2^-	348.5	-7.5	341.0	TeH^-	332.3	-6.2	326.1	I^-	315.9	-5.1	310.8
Period 6															
PbH_3^-	324.4	-8.1	316.3	BiH_2^-	345.0	-7.5	337.5	PoH^-	329.2	-6.2	323.0	At^-	313.5	-5.0	308.5

^a Computed at BP86/QZ4P//BP86/TZ2P for the reaction $\text{Me}_m\text{H}_{n-m}\text{XH} \rightarrow \text{H}^+ + \text{Me}_m\text{H}_{n-m}\text{X}^-$ with $n = 3, 2, 1$, and 0 for groups 14, 15, 16, and 17, respectively.

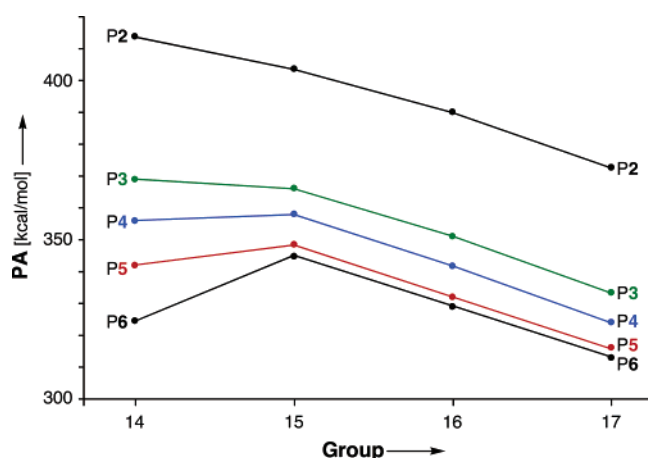
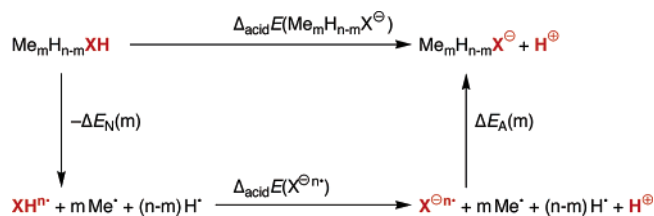


Figure 1. Proton affinities PA (at 298 K) of the anionic conjugate bases of main-group-element hydrides of groups 14–17 and periods 2–6 (P2–P6), computed at BP86/QZ4P//BP86/TZ2P.

3.3. Methyl Substituent Effects. Finally, we have studied the effect on the PA of a stepwise replacement of all hydrogen atoms in second- and third-period anionic bases H_nX^- by methyl substituents, that is, by a stepwise increase of m from 0 to n in $\text{Me}_m\text{H}_{n-m}\text{X}^-$ ($n = 3, 2, 1$, and 0 for group 14, 15, 16, and 17, respectively). The results are collected in Table 2. Strikingly, the PA of the second-period bases *decreases* while that of the third-period bases *increases* with the number of methyl substituents. For example, along NH_2^- , MeNH^- , and Me_2N^- , the PA decreases from 404 to 398 to 387 kcal/mol, which is in agreement with experimental gas-phase data,⁴ whereas along PH_2^- , MePH^- , and Me_2P^- , it increases from 366 to 373 to 377 kcal/mol (see Table 2). This may seem to suggest that a methyl substituent stabilizes the second-period base (e.g., NH_2^-) compared to a hydrogen atom and that it destabilizes a third-row base (e.g., PH_2^-).

Scheme 1. Relationship between PA Values and Methyl Substituent Effect (see Table 3)



This is, however, incorrect, as follows from a more detailed analysis.

To trace the origin of the opposite methyl-substituent effects on second- versus third-row bases, we have decomposed the proton-affinity energy $\Delta_{\text{acid}}E$, associated with acid dissociation of the conjugate acid $\text{Me}_m\text{H}_{n-m}\text{XH}$, into three partial reactions, as shown in the thermochemical cycle of Scheme 1.

The first step, which is associated with an energy change $-\Delta E_N(m)$, is the dissociation of all substituents of the neutral, conjugate acid $\text{Me}_m\text{H}_{n-m}\text{XH}$ (but not the acidic proton) to form the n -fold radical XH^{n*} (see Scheme 1; m = number of methyl substituents). The energy ΔE_N is the stabilization of the protophilic center X in the neutral conjugate acid $\text{Me}_m\text{H}_{n-m}\text{XH}$ by all substituents, that is, the interaction with m methyl groups (Me) and n hydrogen atoms (H). Next, the unsubstituted acid XH^{n*} is dissociated into $\text{X}^{\ominus n*} + \text{H}^+$ (see Scheme 1). The corresponding reaction energy is the proton-affinity energy $\Delta_{\text{acid}}E$ of the anionic base $\text{X}^{\ominus n*}$. The third and last step, which is associated with an energy change $\Delta E_A(m)$, is the addition of all substituents to the protophilic center $\text{X}^{\ominus n*}$ to form the base $\text{Me}_m\text{H}_{n-m}\text{X}^-$ (see Scheme 1; m = number of methyl substituents). The energy ΔE_A is the stabilization of the protophilic center X in the anionic base $\text{Me}_m\text{H}_{n-m}\text{X}^-$ by all substituents, that is, the interaction with m methyl groups (Me) and $n - m$ hydrogen atoms (H). The

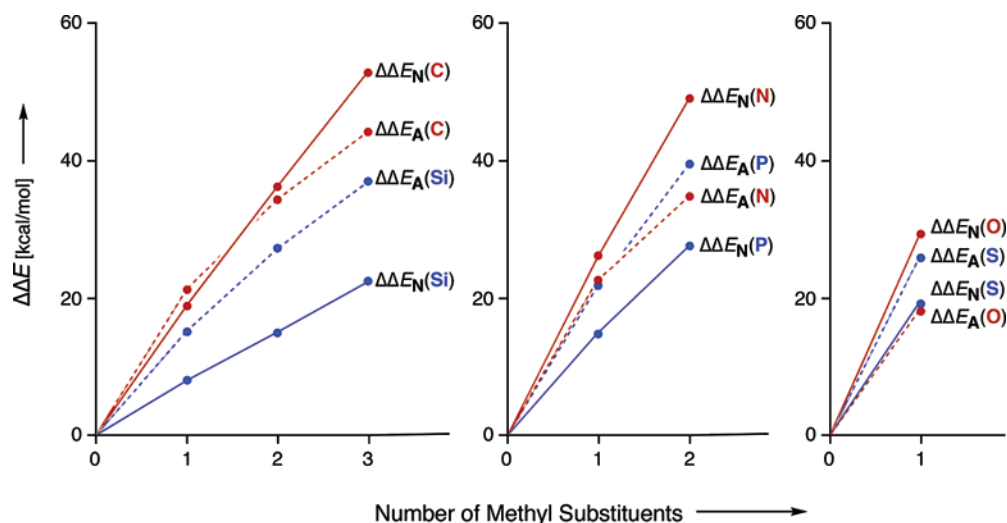


Figure 2. Effect of methyl substitution on the energy $\Delta E_N(X)$ of main-group-element hydrides H_nXH and the energy $\Delta E_A(X)$ of their anionic conjugate bases H_nX^- (see Scheme 1), computed at BP86/QZ4P//BP86/TZ2P (see Table 3).

Table 3. Analysis of the Methyl-Substituent Effect on PA Energies $\Delta_{\text{acid}}E$ in Terms of the Partial Reactions in Scheme 1^a

base	ΔE_N	ΔE_A	$\Delta_{\text{acid}}E$	base	ΔE_N	ΔE_A	$\Delta_{\text{acid}}E$
C ³⁻			350.00	Si ³⁻			314.65
CH ₃ ⁻	-357.13	-284.65	422.48	SiH ₃ ⁻	-289.11	-228.89	374.87
MeCH ₂ ⁻	-338.30	-263.41	424.89	MeSiH ₂ ⁻	-281.28	-213.96	381.97
Me ₂ CH ⁻	-320.94	-250.34	420.60	Me ₂ SiH ⁻	-274.14	-201.77	387.02
Me ₃ C ⁻	-304.20	-240.36	413.84	Me ₃ Si ⁻	-266.91	-191.94	389.62
N ³⁻			402.78	N ³⁻			369.69
NH ₂ ⁻	-217.43	-208.39	411.82	PH ₂ ⁻	-169.66	-167.92	371.43
MeNH ⁻	-191.32	-185.99	408.11	MePH ⁻	-154.92	-146.19	378.42
Me ₂ N ⁻	-168.43	-173.59	397.62	Me ₂ P ⁻	-142.01	-128.49	383.21
O ²⁻			387.48	S ²⁻			353.36
OH ⁻	-126.55	-117.21	396.82	SH ⁻	-96.49	-94.08	355.77
MeO ⁻	-97.47	-99.11	385.84	MeS ⁻	-77.48	-68.27	362.57

^a Computed at BP86/QZ4P//BP86/TZ2P. See also Figure 2.

computed proton-affinity energies' values $\Delta_{\text{acid}}E$, ΔE_N , and ΔE_A are collected in Table 3.

The relationship between the proton-affinity energy $\Delta_{\text{acid}}E(\text{Me}_m\text{H}_{n-m}\text{X}^-)$ of the anionic base and the other energy terms of the thermochemical cycle of Scheme 1 is summarized in eq 2 (m = number of methyl substituents):

$$\Delta_{\text{acid}}E(\text{Me}_m\text{H}_{n-m}\text{X}^-) = \Delta_{\text{acid}}E(\text{X}^{n-}) + \Delta E_A(m) - \Delta E_N(m) \quad (2)$$

Thus, the proton-affinity energy $\Delta_{\text{acid}}E(\text{Me}_m\text{H}_{n-m}\text{X}^-)$ of the base $\text{Me}_m\text{H}_{n-m}\text{X}^-$ is determined by the proton-affinity energy $\Delta_{\text{acid}}E(\text{X}^{n-})$ of the unsubstituted and deprotonated protophilic center X^{n-} plus the *difference* in stabilization $\Delta E_A(m)$ of X^{n-} in the base $\text{Me}_m\text{H}_{n-m}\text{X}^-$ and the stabilization $\Delta E_N(m)$ of XH^{n-} in $\text{Me}_m\text{H}_{n-m}\text{XH}$ by m methyl (Me) and n hydrogen substituents (H^{n-}). The methyl-substituent effect on the proton-affinity energy, that is, the change $\Delta\Delta_{\text{acid}}E(m)$ in this value if one goes from 0 to m methyl substituents, therefore, depends not only on the change $\Delta E_A(m) - \Delta E_A(0)$ in stabilization of the anionic base *but also* on the change $\Delta E_N(m) - \Delta E_N(0)$ in stabilization of the neutral conjugate acid.

This is the key to understanding the true origin of the opposite methyl-substituent effects on the PA of second- and third-period bases. In Figure 2, we have plotted the changes in stabilization by the substituents $\Delta\Delta E_A = \Delta E_A(m) -$

$\Delta E_A(0)$ and $\Delta\Delta E_N = E_N(m) - \Delta E_N(0)$ for the second- and third-period bases $\text{Me}_m\text{H}_{n-m}\text{X}^-$ and their conjugate acids $\text{Me}_m\text{H}_{n-m}\text{XH}$. Now it is clear that introducing a methyl substituent leads consistently, in all cases, to a destabilization of the system. Thus, the reason second-period bases become less basic and third-period bases more basic is *not* that a methyl group stabilizes second-period bases and destabilizes the third-period bases. In fact, the introduction of methyl groups *destabilizes*, in all cases, both the base and the conjugate acid. The opposite trends in basicity originate from the fact that a *second-period* base is destabilized less than its corresponding conjugate acid, whereas a *third-period* base is destabilized more than its conjugate acid. This behavior is reminiscent of the situation of the halomethyl anions CH_2X^- , the PA of which decreases along $\text{X} = \text{F}, \text{Cl}, \text{Br}$, and I . Very recently,²⁷ we have shown that this is not because of increasing α -stabilization of CH_2X^- by X . Rather, the latter continuously *decreases* along the series, *but more slowly* so than the α -stabilization of the conjugate acid CH_3X .

4. Conclusions

BP86, B3LYP, and PBE emerge from our exploration of 41 model systems as sound and computationally efficient alternatives to highly correlated ab initio methods for computing proton affinities and related thermochemical quantities of anionic bases across the periodic table. The BP86/QZ4P//BP86/TZ2P approach achieves a mean absolute deviation of 1.6 kcal/mol for the proton affinity at 0 K ($\Delta_{\text{acid}}H_0$) with respect to high-level ab initio benchmark data. This is slightly more accurate than B3LYP, and in combination with its higher computational efficiency, this makes us recommend the above BP86 approach for obtaining accurate proton affinities of organic and inorganic species that either escape direct experimental observation or are computationally too demanding for highly correlated ab initio methods such as CCSD(T).

The proton affinity along the archetypal second-period bases CH_3^- , NH_2^- , OH^- , and F^- decreases as valence 2p atomic orbitals of the protophilic atom become more compact and stable. This well-known trend changes if one descends in the periodic system to higher periods. In each group, the proton affinity decreases, but it does so significantly more pronouncedly down group 14 than down the other groups. This causes the proton affinities along third- and higher-period bases to first increase from group 14 to group 15 and then to decrease again until group 17.

Introducing methyl substituents at the protophilic center has opposite effects on second-period and third-period anionic bases: while the former become less basic as the number of methyl substituents increases (e.g., along NH_2^- , MeNH^- , and Me_2N^-), the latter become more basic (e.g., along PH_2^- , MePH^- , and Me_2P^-). Interestingly, the reason for this is *not* that a methyl group stabilizes second-period bases and destabilizes the third-period bases. In fact, the introduction of methyl groups *destabilizes*, in all cases, both the base and the conjugate acid. The opposite trends in basicity originate from the fact that a *second-period base* is destabilized less than its corresponding conjugate acid, whereas a *third-period base* is destabilized more than its conjugate acid.

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Supporting Information Available: Proton affinities for 17 bases computed with various density functionals and Cartesian coordinates of all species occurring in this study. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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