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Proton affinities of candidates for positively charged ambient ions in the boreal forest

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Abstract

The optimized structures and proton affinities of a total of 81 nitrogen-containing bases, chosen based on field measurements of ambient positive ions, were studied using the CBS-QB3 quantum chemical method. The results were compared to values given in the National Institute of Standards and Technology (NIST) Chemistry WebBook in cases where a value was listed. The computed values show good agreement with the values listed in NIST. Grouping the molecules based on their molecular formula, the largest calculated proton affinities for each group were also compared with experimentally observed ambient cation concentrations in the boreal forest. This comparison allows us to draw qualitative conclusions about the relative ambient concentrations of different nitrogen-containing organic base molecules.

1 Introduction

Electric charge plays a central role in atmospheric sciences. Sample ionization is employed in many measurement devices such as the chemical ionization mass spectrometer (CIMS) (Eisele and Tanner, 1991). In order to relate measurement results to actual atmospheric conditions, we therefore need to understand the possible effects of this ionization process on the molecules or clusters being charged as well as on the behavior of the ionized sample. Furthermore, the identification of ambient ions and ionization processes under different atmospheric conditions is essential in understanding the role of ions in atmospheric chemistry or in particle formation. Knowing which molecules will most likely carry a charge will aid the development of a comprehensive picture of these atmospheric processes. An easy way of assessing this question is to examine the proton affinities of molecules.

The proton affinity (PA) is the measure of gas-phase basicity of a molecule and an important thermodynamic quantity. In atmospheric ion-neutral collisions, molecules with the highest PA (bases) will end up collecting the positive charges, and the ones with

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the lowest PA (acids) will end up with negative charges. Unfortunately, absolute gas-phase PAs are hard to measure. Instead, measurements usually yield relative values. To reliably convert these relative values into absolute PAs, theoretical methods need to be used to anchor the PA scale. Theoretical methods can also be used to help interpret experimental data by directly calculating the desired PAs. However, theoretical results often depend on the method used, and the performance of the methods may vary with the type of molecule being studied. For this reason, theoretical calculations need to be combined with both benchmark calculations, and comparisons with experiments.

Our aim was to study the absolute values of PAs of atmospherically relevant bases using quantum chemical methods. These methods were applied to several molecular ion species, which were selected based on the experimental measurements of ambient ions in boreal forests (Ehn et al., 2010). Although the NIST WebBook contains data of over 40 000 compounds, several PAs with possible atmospheric relevance are missing. The values that are listed for the cases under study, are all evaluated values taken from a single review article (Hunter and Lias, 1998). Thus, the absolute values are useful by themselves, but we also wanted to see whether there was any correlation between the PAs and the observed mass spectrum peaks for the cations, which could help in interpreting the experimental results.

2 Methods and computational details

The molecules that were subjected to study were selected based on the molecular formula of the compounds identified in the paper by Ehn et al. (2010). For all 16 different molecular formulae (minus the proton) we first looked at cases that had a PA given in NIST and selected the isomers with the largest and the smallest PA along with a few others for comparison. For the three cases with the highest observed mean of 30 min ion concentration averages – labeled as pyridine, alkyl pyridine (1) and alkyl pyridine (2) in Figs. 1 and 2 in this work – we calculated the PA all isomers listed in NIST (except

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ones with additional molecule species such as deuterium or chloride) regardless of whether NIST gave a PA value for them or not.

Initial guesses of molecular geometries for all calculations were constructed by hand using ADF-GUI (ADF-GUI 2009.01, SCM), the graphical user interface of the computational chemistry program ADF. Some of the geometries were also optimized using the UFF (Rappe et al., 1992) method, which was the default in ADF-GUI, before running higher-level calculations. However, in some cases this led to unrealistic configurations. In such cases this initial optimization step was simply skipped.

Benchmarking calculations of the structures and proton affinities were performed using the quantum chemical methods W1BD (Martin and de Oliveira, 1999, Barnes et al., 2009), G2 (Curtiss et al., 1991), G3 (Curtiss et al., 1998), G4 (Curtiss et al., 2007), CBS-QB3 (Montgomery Jr. et al., 1999, 2000), CBS-APNO (Ochterski et al., 1996) and CBS-4M (Ochterski et al., 1996; Montgomery Jr. et al., 2000) implemented in Gaussian 09 (Frisch et al., 2009). The G2 calculations also provided G2MP2 (Curtiss et al., 1993) energies. Each method is a model chemistry method consisting of several computational steps, developed to provide accurate thermochemical values. The W1BD method is a variation of Weizmann-1 theory, where Brueckner doubles are used, and while strictly speaking it is not an ab initio method, its “empirical” parameter is actually derived from W2 calculations and not actual experiments. The Gaussian-n methods (G2, G3 etc.) are close to the CBS-methods: the Gaussian-n methods use high accuracy methods with medium-sized basis sets and then correct for errors using some empirical parameters, whereas the CBS-methods start similarly, but employ an extrapolation to reach the basis set limit and use empirical parameters to correct for systematic errors. The actual performance of the different methods may vary from case to case due to, e.g. fortuitous error cancellation, but from a purely theoretical standpoint, the W1BD method is the most accurate and computationally demanding of these methods, while the CBS-4M method is considerably faster than the other methods, but sacrifices some accuracy to achieve this. The G2, G3, G4, CBS-QB3 and CBS-APNO methods are generally of roughly comparable accuracy, but speed varies

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with CBS-QB3 proving to be the fastest method in our calculations and G4 being the slowest.

After the benchmarking, a quantum chemical study of the structure and proton affinities of several compounds with the molecular formulae C_4H_7N , $C_4H_{11}N$, C_5H_5N , C_5H_9N , $C_5H_{13}N$, C_7H_6 , C_6H_7N , $C_6H_{15}N$, C_7H_9N , $C_8H_{11}N$, C_9H_7N , $C_8H_{19}N$, $C_9H_{13}N$, $C_{10}H_9N$, $C_{10}H_{15}N$ and $C_{11}H_{11}N$ was performed using CBS-QB3. The CBS-QB3 method starts with a geometry optimization with the B3LYP (Lee et al., 1988; Becke, 1993) density functional and a 6-311G(2d,d,p) basis set, followed by a frequency calculation using a scaling factor of 0.99. The final CBS energies are then extrapolated based on single-point calculations at the CCSD(T) (Raghavachari et al., 1989), MP4SDQ (Trucks et al., 1988) and MP2 (Møller and Plesset, 1934; Head-Gordon et al., 1988) levels.

In all cases, proton affinities were calculated as the standard enthalpy change (that is, at 298.15 K and 1 atm reference pressure) change of the reaction $X+H^+ \rightarrow XH^+$. The enthalpy of the proton was taken to be exactly 2.5 RT, where R is the gas constant. Gas-phase basicities were calculated from the Gibbs free energy change of the protonation reaction. The Gibbs free energy for the proton was calculated with CBS-QB3 to be -0.01 hartree. Including the benchmarking calculations, a total of 81 proton affinities and gas-phase basicities were calculated in this study.

3 Results and discussion

The benchmarking results are shown in Fig. 1 and Table 1. Due to limitations in computational resources, we were unable to obtain a result for the PA of pyridine with the W1BD method. In the cases of methylamine, dimethylamine and trimethylamine, we compared all other methods with the W1BD. In the case of pyridine, all results were compared to the PA value listed in NIST. In the case of ammonia, all results were compared with the PA determined by Czako et al. (2008). This PA is the result of very high-level quantum chemical calculations. Due to the structural simplicity of the

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ammonia molecule, quantum chemical calculations can be expected to lead to quantitatively reliable values for this molecule, which means that ammonia is a good molecule for anchoring the PA scale.

Based on the benchmarking results, all of the CBS- and G-methods performed well, with most numerical results deviating from the W1BD value by less than 1 kcal mol^{-1} . The only clear exception is the CBS-4M result for the PA of ammonia, which is close to 2 kcal mol^{-1} greater than the W1BD result. Although the differences in the benchmarking calculations were relatively small, CBS-QB3 is a more accurate method than the CBS-4M while still being very fast. Also, the results for mono-, di- and trimethylamine suggest that the CBS-QB3 method will very slightly underestimate the PA, thus providing a lower bound. Furthermore, as this same method was used to calculate some PAs and gas-phase acidities as well as formation enthalpies and free energies in the paper by Ehn et al. (2010), our results should provide an interesting comparison. Therefore, we chose to use CBS-QB3 for the remainder of this study.

The CBS-QB3 proton affinity results are listed in Table 2. Including the benchmark calculations, a total of 52 of the molecules had a PA listed in NIST. As stated in the introduction, the values listed in NIST were all from a proton affinity review article by Hunter and Lias (1998), who evaluated absolute values for PAs. The exact details of this evaluation can be found in the original article, but the basic idea was to use computational PAs as well as experimental data in determining a suitable PA scale and then adjust experimental and relative PA values based on this scale. Since the computational values used to determine the PA scale play a key role in this kind of an evaluation, it should be noted that the computational values used by Hunter and Lias were calculated with a slightly modified G2 method (Smith and Radom, 1993). Based on our benchmarking calculations the standard G2 method is comparable in accuracy with the CBS-QB3 method, so the good general agreement with the evaluated results and CBS-QB3 results is not surprising. The differences between our results and those taken from the review article are mostly on the order of $1\text{--}2 \text{ kcal mol}^{-1}$, but as the G2

method is slightly different compared to the CBS-QB3 method and as the basis of the evaluated values is experimental values, some variation is to be expected.

There is one case where the CBS-QB3 proton affinity differs from the evaluated PA by a larger margin: tropylium, for which the difference between the two values is $\sim 20 \text{ kcal mol}^{-1}$. The reason for this discrepancy is most likely the fact that tropylium cation is not formed in a simple protonation reaction of the precursor neutral molecule, but by a process called the McLafferty rearrangement (McLafferty, 1959). Unfortunately, we were unable to resolve the issue. The difference between CBS-QB3 and NIST PAs is so large that the reliability of this value needs to be questioned. Because of this, tropylium has been omitted from Fig. 2, although the value can still be found in Table 2. Due to the general agreement with the NIST values, it is reasonable to assume that the calculated proton affinities, which had no corresponding value listed in NIST, remain reliable.

Figure 2 shows the experimentally observed mean of 30 min average concentrations in units of 1 cm^{-3} for each compound type (elemental composition) identified in the experiments of Ehn et al. (2010), with the largest computational proton affinity for the same compound types. Comparison between these two figures shows no clear correlation between the proton affinities and the observed ion concentrations. This is not surprising given that the ion concentration depends not only on the proton affinity, but also on the concentration of the neutral parent molecule. However, we can still extract some information from the individual values. A large observed concentration implies two possibilities: either the observed molecule species has a large proton affinity – which would lead to a large fraction of the molecules becoming charged – or the observed molecule species is abundant in the atmosphere – which could lead to a large number of charged molecules even when only a small or moderate fraction of the parent molecules would become charged.

The computed gas-phase basicities (GB) or proton affinities can be used to assess the relative abundances of neutral precursor molecules based on the measured ratios of the protonated ions. If the concentration of two molecules A and B are large enough

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that the collision frequency of neutral A and B with their protonated forms HA^+ and HB^+ are significantly larger than the loss rates of these ions (due to recombination with anions or scavenging onto aerosol particles), then the following equilibrium will hold:

$$\frac{[\text{A}]}{[\text{B}]} = e^{\frac{1}{RT}[\text{GB}(\text{A}) - \text{GB}(\text{B})]} \frac{[\text{HA}^+]}{[\text{HB}^+]} \approx e^{\frac{1}{RT}[\text{PA}(\text{A}) - \text{PA}(\text{B})]} \frac{[\text{HA}^+]}{[\text{HB}^+]} \quad (1)$$

where $\text{GB}(\text{A}) - \text{GB}(\text{B})$ and $\text{PA}(\text{A}) - \text{PA}(\text{B})$ are the differences in gas-phase basicities and proton affinities (respectively) of A and B, and the latter expression is usually valid because the number of gas-phase molecules does not change in a proton transfer reaction of the type $\text{HA}^+ + \text{B} \rightleftharpoons \text{A} + \text{HB}^+$, implying a rather small entropy change. Even in cases where the equilibrium expression does not strictly apply (e.g. due to too low concentrations of A or B), the quantities $\text{GB}(\text{A}) - \text{GB}(\text{B})$ or $\text{PA}(\text{A}) - \text{PA}(\text{B})$ can still be used as a qualitative indicator: if the proton affinity of A is much lower than that of B, then $[\text{A}]/[\text{B}]$ will be much lower than $[\text{HA}^+]/[\text{HB}^+]$.

Applying this reasoning to ambient ion measurements is complicated by the fact that a single molecular formula may correspond to several different structural isomers, with different proton affinities. The acyclic alkylamines with only a few carbon atoms have only a few isomers, and $\text{C}_5\text{H}_5\text{N}$ very likely corresponds solely to pyridine (according to our calculations, it also has the largest proton affinity of the isomers listed in NIST), but most other carbon-nitrogen-hydrogen compounds have multiple structural isomers. Thus, some information on the emission sources of neutral nitrogen-containing bases, or alternative chemical information such as gas chromatography data, is needed before extensive comparisons can be made.

Bearing this in mind, we can nevertheless use our computed proton affinities together with the three cation peaks with the highest concentrations in the measurements of Ehn et al. (2010) to tentatively conclude that pyridine likely has a higher concentration than any of the alkyl di- or triamines, since the concentration of protonated pyridine is so much higher despite a lower (or in some cases similar) proton affinity. Based on similar reasoning, if we assume that the peaks labeled as alkyl pyridine (1) and alkyl pyridine

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(2) indeed correspond to substituted pyridines rather than, e.g. anilines or nitriles, we can conclude that these compounds have much higher concentrations than either the acyclic amines or the more highly substituted pyridines. If these peaks instead correspond to protonated anilines or nitriles, then their neutral concentrations would need to be larger still, as these compounds have much lower proton affinities than the substituted pyridines. Similarly, methylpyridines likely have a higher concentration than either pyridine or 2-alkylpyridines. Many more similar arguments could be made using the peaks with lower concentrations (e.g. alkyl quinolines likely have lower concentrations than quinoline), but as the lower concentration values are likely more affected by random errors, conclusions drawn from them are likely less reliable.

4 Conclusions

The CBS-QB3 model chemistry method proved to be a quick and accurate way to obtain theoretical values for proton affinities. Several new proton affinities were determined and overall agreement with previous results was good. Comparing the obtained proton affinities and previous ambient ion measurements gave some indications of the relative atmospheric concentrations of the precursor neutral molecules.

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Table 1. An overview of the benchmark calculations. All values are in kcal mol⁻¹.

#		Ammonia	Pyridine	Proton affinity (kcal mol ⁻¹)		
				Methylamine	Dimethylamine	Trimethylamine
1	Czakó et al.	203.77629	—	—	—	—
2	NIST	204.01500	222.27500	214.86600	222.15600	226.79300
3	B3LYP/CBSB7	207.86000	—	—	—	—
4	B3LYP/CBSB7//RI-CC2/aug-cc-pV(T+d)Z	202.13000	—	—	220.38000	—
5	B3LYP/6-31++G(2df,2dp)//RI-MP2-F12/cc-pVDZ-F12	202.54049	219.60531	—	—	—
6	W1BD	204.06209	—	215.20163	222.46944	227.04712
7	CBS-QB3	204.18571	221.59971	214.96255	221.90970	226.24454
8	CBS-APNO	204.42040	222.36590	215.41185	222.56796	226.95488
9	CBS-4M	205.81096	221.78106	215.50409	222.28558	226.60535
10	G2	204.04013	222.23224	215.33969	222.69597	227.34330
11	G2MP2	204.00813	222.23789	215.39930	222.79135	227.43304
12	G3	204.61932	222.40732	215.64528	222.88046	227.36527
13	G4	204.36330	222.50458	215.40369	222.55353	227.14250

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Table 2. Proton affinities and gas phase basicities of all studied molecules. Values are in kcal mol⁻¹.

	Proton affinity (kcal mol ⁻¹)			ΔPA^a (kcal mol ⁻¹)	Gas phase basicity (kcal mol ⁻¹)
	CBS-QB3	NIST	Other		
NH ₃	204.18571	204.01500	204.06000 ^b	0.17071	196.78870
Methylamine	214.96255	214.86600	—	0.09655	207.40490
Dimethylamine	221.90970	222.15600	222.68200 ^c	-0.24630	214.39723
Trimethylamine	226.24454	226.79300	—	-0.54846	218.77097
Pyrroline	222.82649	—	221.27200 ^d	—	215.30524
3-Pyrroline	222.82085	—	222.51400 ^d	—	215.31591
Alkyl amine(4) (C₄H₁₁N):					
Ethanamine, N-ethyl-	227.11615	227.62900	—	-0.51285	219.61246
1-Butanamine	219.98137	220.24400	—	-0.26263	212.47078
Ethanamine, N,N-dimethyl-	228.81230	229.46900	—	-0.65670	221.37325
2-Propanamine, N-methyl-	227.56670	227.62900	—	-0.06230	219.86849
Pyridine (C₅H₅N):					
Pyridine	221.59971	222.27500	221.89300 ^e	-0.67529	213.96739
Bicyclo[1.1.0]butane-1-carbonitrile	192.57805	—	—	—	185.50296
Cis-1-cyano-1,3-butadiene	194.64569	—	—	—	187.94334
Cyclopropene-3-carbonitrile, 1-methyl-	197.86105	—	—	—	190.73450
2,4-Pentadienenitrile	194.64820	—	—	—	187.96969
4-Cyano-1-butyne	187.32831	—	—	—	180.10199
Trans-1-cyano-1,3-butadiene	194.64695	—	—	—	187.94836
Alkyl pyrroline(1) (C₅H₉N):					
Pentanenitrile	191.98443	191.77800	—	0.20643	184.74555
2-Propyn-1-amine, N,N-dimethyl-	224.98199	224.73700	—	0.24499	217.52411
Propane, 2-isocyanato-2-methyl-	207.25172	208.10200	—	-0.85028	199.71415
2,5-Dihydro-1-methylpyrrole	228.00784	—	—	—	220.36359
Alkyl amine(5) (C₅H₁₃N):					
1-Pentanamine	220.37795	220.72200	—	-0.34405	212.94769
N-ethyl-N-methylethanamine	231.14915	232.07500	—	-0.92585	223.59903
N,N-dimethyl-2-propanamine	231.22570	231.97900	—	-0.75330	223.66931
Tropylum	251.90526	232.07500	—	19.83026	244.35263
Alkyl pyridine(1) (C₆H₇N):					
2-Methylpyridine	225.59695	226.84000	—	-1.24305	217.90376
4-Methylpyridine	225.69107	226.38600	—	-0.69493	217.85230
Aniline	210.44511	210.92300	—	-0.47789	203.86575
3-Methylpyridine	224.81695	—	—	—	216.98885
1-Cyclopentene-1-carbonitrile	195.66289	—	—	—	188.66999

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Table 2. Continued.

	Proton affinity (kcal mol ⁻¹)			ΔPA^a (kcal mol ⁻¹)	Gas phase basicity (kcal mol ⁻¹)
	CBS-QB3	NIST	Other		
2-Cyclopentene-1-carbonitrile	194.02948	—	—	—	186.85398
3-Methylenecyclobutanenitrile	192.55672	—	—	—	185.42514
Bicyclo[2.1.0]pentane-1-carbonitrile	197.48580	—	—	—	190.66798
N-2-propynyl-2-propyn-1-amine	219.39528	—	—	—	211.61110
5-Hexynenitrile	189.48255	—	—	—	182.22987
7-Azenorbornadiene	228.60648	—	—	—	220.92709
2,4-Hexadienenitrile	197.80081	—	—	—	190.65857
Alkyl amine(6) (C₆H₁₅N):					
Triethylamine	233.79221	234.65600	—	-0.86389	226.18185
1-Hexanamine	220.58880	221.67800	—	-1.08920	213.16920
N,N,2-trimethyl-2-propanamine	233.23185	234.13000	—	-0.89815	225.84363
Alkyl pyridine(2) (C₇H₉N):					
2,6-Dimethylpyridine	229.29298	230.16300	—	-0.87002	221.83322
2,4-Dimethylpyridine	229.40530	230.13900	—	-0.73370	222.49210
o-Toluidine	211.85827	212.93000	—	-1.07173	205.14085
N-methylaniline	218.22121	219.07300	—	-0.85179	210.84679
p-Aminotoluene	212.84157	214.31600	—	-1.47443	206.28919
3-Methylbenzenamine	212.48326	214.10100	—	-1.61774	205.80287
3,5-Dimethylpyridine	227.80766	228.34600	—	-0.53834	220.08058
2,5-Dimethylpyridine	228.59268	229.15900	—	-0.56632	220.73445
2,3-Dimethylpyridine	228.58766	229.18300	—	-0.59534	221.14421
2-Ethylpyridine	227.06218	227.62900	—	-0.56682	219.24788
3,4-Dimethylpyridine	228.55879	228.80000	—	-0.24121	221.00239
3-Ethylpyridine	226.49680	226.43400	—	0.06280	219.02762
Benzylamine	220.85172	218.28400	—	2.56772	213.15728
4-Ethylpyridine	227.22094	227.31800	—	-0.09706	219.54532
Cyclohexenecarbonitrile	197.59185	—	—	—	190.64225
Bicyclo[3.1.0]hexane-1-carbonitrile	198.44275	—	—	—	191.48688
N-Methyl-di(2-propynyl)-amine	228.18856	—	—	—	220.11259
2-Cyclohexene-1-carbonitrile	192.92199	—	—	—	187.24931
4,4-Dimethyl-2-pentynonitrile	192.36093	—	—	—	185.49731
4-Cyanocyclohexene	193.53312	—	—	—	186.36013
1-Cyclopentylacetoneitrile	192.29818	—	—	—	185.31408
1-Allylpyrrole	227.52779	—	—	—	220.06113
Alkyl pyridine(3) (C₈H₁₁N):					
2,6-Xylidine	213.09885	215.51100	—	-2.41215	206.96251
2-(i-C ₃ H ₇)-pyridine	227.43116	228.58500	—	-1.15384	220.06364
2-Propylpyridine	227.33828	228.41800	—	-1.07972	219.71412
4-Isopropylpyridine	227.20149	228.41800	—	-1.21651	219.81327
3-Ethylaniline	212.48326	214.60300	—	-2.11974	206.11286

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Table 2. Continued.

	Proton affinity (kcal mol ⁻¹)			ΔPA^a (kcal mol ⁻¹)	Gas phase basicity (kcal mol ⁻¹)
	CBS-QB3	NIST	Other		
Quinoline	226.87142	227.82000	—	-0.94858	219.28428
Alkyl amine(8) (C₈H₁₉N):					
Diisopropylethylamine	236.82183	237.64300	—	-0.82117	228.45846
1-Octanamine	220.80968	222.01200	—	-1.20232	213.38444
(t-C ₄ H ₉) ₂ NH	234.67073	236.11400	—	-1.44327	227.08296
Alkyl pyridine(4) (C₉H₁₃N):					
2,6-Diethylpyridine	231.83941	232.38500	—	-0.54559	224.68776
N-ethyl-N-methyl-benzenamine	227.14752	225.16700	—	1.98052	219.32946
N,N,3-trimethyl-benzenamine	226.78106	224.42600	—	2.35506	219.18701
Alkyl quinoline(1) (C₁₀H₉N):					
1-Naphthalenamine	217.59181	216.77800	—	0.81381	210.51986
8-Methyl-quinoline	228.51926	—	—	—	220.78716
Alkyl pyridine(5) (C₁₀H₁₅N):					
N,N-diethylaniline	228.42325	229.39800	—	-0.97475	220.67923
N,N,2,6-tetramethylbenzenamine	228.46592	228.03500	—	0.43092	220.37426
N,N,3,5-tetramethylbenzenamine	228.30214	228.51300	—	-0.21086	220.83297
2-Methyl-4,6-diethylpyridine	234.42537	—	—	—	227.51155
Alkyl quinoline(2) (C₁₁H₁₁N):					
2,7-Dimethylquinoline	232.93441	—	—	—	226.07329

^a Proton affinity difference calculated as $\Delta PA = (PA_{\text{CBSQB3}} - PA_{\text{NIST}})$.^b W1 at 298 K, Parthiban and Martin (2001).^c G2 at 298 K, Smith and Radom (1993).^d Modified G2MS at 298 K, Elrod (2003).^e G2(MP2,SVP) at 298 K, Smith and Radom (1995).

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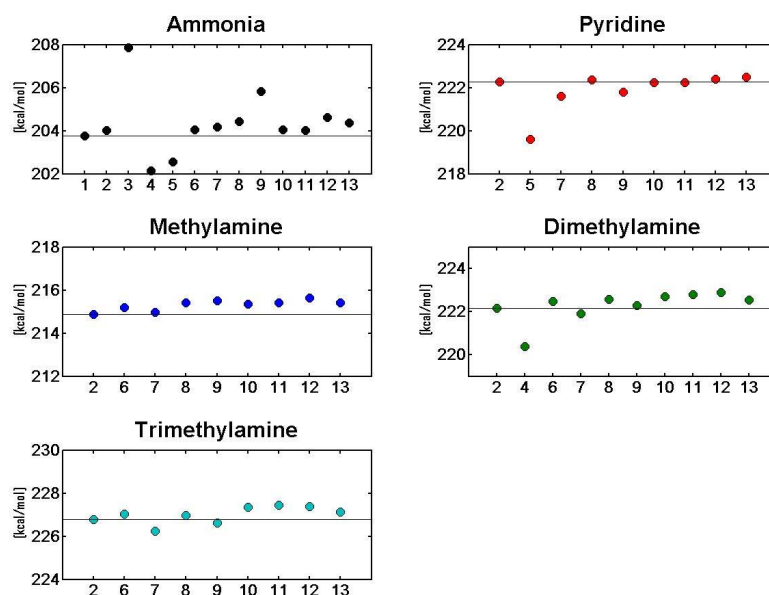


Fig. 1. Benchmark results. Values on the y-axis are in kcal mol^{-1} . Values on the x-axis are labels corresponding to the numbers assigned to different sources and methods in Table 1. Vertical lines mark the PA value given in NIST, except in the case of ammonia, where it marks the PA value calculated by Czako et al. (2008).

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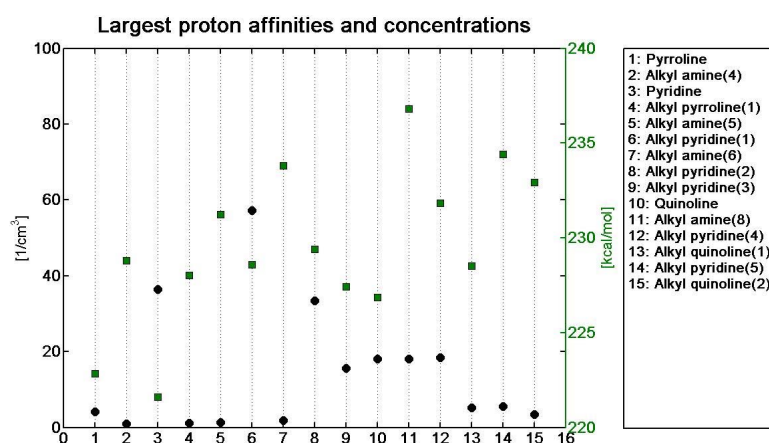


Fig. 2. Largest calculated proton affinities (green squares) for each compound and the mean of 30 min average concentrations over the measurement period (black circles, Ehn et al., 2010). The value of the x-axis is merely an index referring to the legend.

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