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How reliable are gas-phase proton affinity values of small carbanions? A comparison of experimental data with values calculated using Gaussian-3 and CBS compound methods

Witold Danikiewicz*

Institute of Organic Chemistry, Polish Academy of Sciences, ul. Kasprzaka 44/52, 01-224 Warsaw, Poland

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ABSTRACT

Gas-phase proton affinities (PA) of a series of 25 small, aliphatic carbanions were computed using different Gaussian-3 methods: G3, G3(B3LYP), G3(MP2) and G3(MP2, B3LYP) and Complete Basis Set Extrapolation methods: CBS-4M, CBS-Q, CBS-QB3, and CBS-APNO. The results were compared with critically selected experimental data. The analysis of the results shows that for the majority of the studied molecules all compound methods (Gaussian-3 and CBS), except for CBS-4M, give comparable results, which differ no more than ±2 kcal mol^{-1} from the experimental data. Taking into account the calculation time, G3(MP2) and G3(MP2, B3LYP) methods offer the best compromise between accuracy and computational cost. As an additional proof, the results obtained by these two methods were compared with the values obtained using CCSD(T) ab initio method with large basis set. It was found also that some of the published experimental data are erroneous and should be corrected. The results described in this work show that for the majority of the studied compounds PA values calculated using compound methods can be used with the same or even higher confidence as the experimental ones because even the largest differences between Gaussian-3 and CBS methods listed above are still comparable with the accuracy of the typical PA measurements.

1. Introduction

Carbanions are one of the most important groups of reactive intermediates in organic synthesis. Their reactions have been studied also in the gas phase [1–3]. Gas-phase ion-molecule reactions involving carbanions can give an important information about intrinsic reactivity of these species and, comparing with the reactions in condensed phase, can tell a lot about the role of solvation.

One of the most important thermodynamic parameters of carbanions is their basicity or, strictly related, acidity of the parent C–H acid, usually presented as pK_a values. In the gas phase, basicity of the carbanion is characterized by its proton affinity (PA). The acidity of the C–H acid is described by its gas-phase acidity (GA). PA or GA values are crucial for understanding many gas-phase ion-molecule reactions, especially those in which proton transfer is involved. From the theoretical point of view they are useful as a measure of the correlations between the acidity of organic compounds and their structure. In mass spectrometry they can help to rationalize fragmentation pathways of compounds of interest.

There are several methods used for measuring GA and PA but, especially for compounds of very low acidity, these methods require special equipment and their accuracy is often not very high [4,5]. The largest collection of the experimental PA and GA values is available on the NIST Website [6]. Analysis of the data published on this site shows that for compounds which were studied by several researchers, PA (and GA) values differ significantly – sometimes much more than suggested uncertainties of the measurements. For example, experimental PA data for acetonitrile range from 366.6 to 374.8 kcal mol^{-1} [6] and a typical uncertainty for them is declared to be about ±2 kcal mol^{-1}. Much better accuracy was obtained only for a few molecules, especially for those which form stable anions that cannot react with the parent neutral molecule in ways other than the proton transfer.

Taking into account a tremendous development in a quantum chemistry calculations which took place during the last 20 years, an important question appears: how reliable are calculated thermochemical data nowadays, especially for relatively small molecules for which the most sophisticated and accurate computational methods, yet available for personal computers, can be applied. Many researchers have addressed this question and their efforts are summarized in a recent review by Fabian [7]. The author concludes that the answer to the raised question is positive. This conclusion implies also the positive answer to the next important

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* Tel.: +48 22 3432211; fax: +48 22 6326681.
E-mail address: witold@icho.edu.pl.

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question concerning the applicability of the computational methods for testing the correctness of the experimental thermochemical data. This problem was especially interesting for us because, as it has been mentioned above, significant number of experimental PA values for carbanions are questionable.

Computation of the thermodynamic properties of molecules, ions and radicals has always been one of the most important applications of the quantum chemistry calculations. It is especially efficient for gas-phase species because they can be treated as free molecules. Among molecular properties which can be computed, proton affinity takes somewhat privileged position. The neutral molecule and its deprotonated form (anion) are both closed-shell species with the same number of electrons. This results in the cancellation of at least some of the intrinsic errors characteristic for a given computational method. Therefore, one can expect that the computed PA values should be quite accurate, comparing for example to the heats of formation or bond dissociation energies, which require calculations for the open-shell systems.

To obtain most accurate thermochemical results in a reasonable time, so-called compound methods were designed. The most popular at the present time are Gaussian-*n* and Complete Basis Set Extrapolation (CBS) families of methods, however a few other methods, designed either for higher accuracy for small molecules or the applicability for larger systems without significant loss of accuracy, can be found in the literature [7]. Among Gaussian-*n* methods Gaussian-3 (G3) and its variants are used most frequently at the present time [8]. G3 method, introduced in 1998, made obsolete its predecessors: G1 and G2 methods. The original G3 method [9] requires at lot of computer resources so its simpler, much faster and only slightly less accurate G3(MP2) variant has been developed [10]. In the original G3 and G3(MP2) methods the initial geometry and frequencies were calculated at the HF/6–31G(d) level. This method is known to give sometimes erroneous results so G3(B3LYP) and G3(MP2, B3LYP) methods were developed in which initial geometry and frequencies are calculated using B3LYP/6–31G(d) DFT method [11]. Extensive tests of G3 family of methods conducted on the set of 299 thermochemical data [11] showed the following mean absolute deviation (MAD) values (in kcal mol^{-1}): G3 – 1.01, G3(MP2) – 1.30, G3(B3LYP) – 0.99 and G3(MP2, B3LYP) – 1.25. For the rather small set of eight PA values the MAD were 1.34, 1.02, 1.22 and 0.89 kcal mol^{-1}, respectively. In practice, G3 methods can be used for molecules containing no more than about 10–15 heavy atoms. Recently G4 method has been introduced but it is not yet implemented in the commercial software packages [12].

Complete Basis Set Extrapolation (CBS) group of methods was developed by Petersson and co-workers [13–16]. The most popular variants of CBS are modified CBS-4 method (CBS-4M in Gaussian 03 software package) [16], CBS-Q [14], CBS-QB3 [15,16], and CBS-APNO [13,14] methods. The CBS-4M method is relatively fast but not very accurate. Much better results are obtained using CBS-Q and CBS-QB3 methods. These two methods differ only in the geometry optimization and frequency calculation steps (HF and MP2 for CBS-Q and B3LYP for CBS-QB3). On the set of 125 experimental energies they show the MAD of 0.98 and 0.87 kcal mol^{-1}, respectively, comparing to 3.26 kcal mol^{-1} for CBS-4 method. These methods are, however, quite demanding of computer resources and therefore are limited to about 10 heavy atoms from the first three rows of the periodic system (up to argon). The most accurate but very expensive is CBS-APNO method. It is limited to five heavy atoms from the first two rows (up to neon) but, for the molecules it can be applied, it gives results with the MAD of 0.53 kcal mol^{-1}.

The problem of the applicability of the various quantum chemistry methods for determination of the proton affinities of carbanions (or gas-phase acidities of the respective C–H acids) has been already studied by several researchers but either the number of compared methods or the number of compounds studied were quite limited. The most extensive studies were done by Shields and co-workers [17–19]. In a series of papers these authors described the performance of selected compound methods (CBS-QB3, CBS-APNO and G3) [17], several DFT methods [18] and some other sophisticated methods (CCSD(T), W1) [19] for PA calculations for 27 anions, including 8 carbanions. The most important criterion of the selection of model compounds was the availability of reliable experimental PA and/or GPA values with the uncertainty not exceeding ±1 kcal mol^{-1}. The authors found that all tested compound methods give quite accurate results. MAD values obtained for the subset of 17 anions (including 8 carbanions) were 1.26 kcal mol^{-1} for CBS-QB3, 0.92 kcal mol^{-1} for CBS-APNO and 1.03 kcal mol^{-1} for G3 methods [17]. Similar results were obtained for W1 and CCSD(T)/aug-cc-pVQZ methods. DFT methods were tested using aug-cc-pVTZ basis set for energy calculation and 6–31G(d) basis set for geometry and frequencies calculations. It was found that under these conditions the best results were obtained for PBE1PBE and B3P86 DFT methods (standard deviation 1.6 kcal mol^{-1} for both methods). The most popular B3LYP hybrid functional was found to be less accurate (standard deviation 2.2 kcal mol^{-1}). It has to be noted that the authors did not check the frequently used 6–311 + G(d, p) basis set and its more complex versions including multiple polarization functions.

Very interesting study, in which gas-phase acidities of many small molecules were investigated by both experimental and computational methods, has been published by Ervin and DeTuri [20]. In their work these authors had evaluated critically the most accurate available experimental data to obtain GA and PA values (at $T = 0$ and 298.15 K) for “benchmark” compounds which serve as the anchor points for constructing GA ladders. In the second part of their work, Ervin and DeTuri compared the experimental GA and PA values with ones obtained using G3(B3LYP), CBS-QB3 as well as B3LYP and CCSD(T)/B3LYP methods with different basis sets. Excellent results (MAD = 0.36 kcal mol^{-1}) were obtained for CCSD(T)/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ method. Even better results were obtained using aug-cc-pVQZ instead of aug-cc-pVTZ basis set but such calculations are possible for very small molecules only. G3(B3LYP) and CBS-QB3 methods gave also very good results (MAD = 1.0 and 0.96 kcal mol^{-1}, respectively). It has to be noted that all computations were performed for $T = 0$ K and their results were compared also to the 0 K PA values. It is possible, however, to compare these results with the experimental data obtained under standard conditions ($T = 298.15$ K) because the authors gave thermal correction factors for enthalpy of the studied compounds in the supplementary data for their paper. Unfortunately, the experimental GA and PA results obtained by these researchers are not included in the NIST database [6].

In our lab we are studying gas-phase reactions of various carbanions with electrophiles, so we are interested in having PA data accurate enough to estimate the thermochemistry of the studied processes. The number of available experimental data is quite limited and the quality of some of them is questionable so we decided to find the optimum calculation method (or methods) which will give us reliable PA values for small and medium-sized molecules in an acceptable time on a PC computer. The results of the first part of this project which includes the results of the PA calculations for a selection of 25 small carbanions (up to 5 heavy atoms) using a number of compound methods (G3 and CBS families of methods) are described in this paper.

2. Computational methods

The majority of calculations described in this paper were performed using two versions of Gaussian 03 suite of programs [21]: Gaussian 03W Rev. B.05 running under Microsoft Windows XP Professional operating system and Gaussian 03 Rev. E.01 running under SuSE Linux 10.3 64 bit version. It was tested on a few randomly selected molecules that both versions give exactly the same results.

Starting geometries of the molecules and ions were created using GaussView 3.0 program [22]. No symmetry restrictions were imposed on the starting geometries, i.e., all bond lengths, bond angles and dihedral angles were optimized independently. A few test calculations for the starting geometries with imposed symmetry restrictions show no differences comparing to the non-restricted starting geometries. For the molecules which can exist in more than one conformation, calculations were performed for all reasonable conformations and the results obtained for the lowest energy conformation were taken for final calculation of PA. All results of the geometry optimization were tested for the presence of the imaginary frequencies to make sure that the real minima were found.

Gaussian-3 methods: G3, G3(B3LYP), G3(MP2), G3(MP2, B3LYP) and Complete Basis Set Extrapolation methods: CBS-4M, CBS-Q, CBS-QB3 and CBS-APNO were invoked with their keywords. Single point CCSD(T) frozen-core calculations were performed using aug-cc-pVTZ basis set for the geometries optimized using B3LYP/aug-cc-pVTZ DFT method with scf = tight keyword. This last method was used also for computing the thermal correction factors for enthalpies. These factors were applied unscaled. It was found that to avoid too large size of the temporary scratch file, tran = iabc keyword has to added to the route section of the Gaussian input file for CCSD(T) calculations. Under these conditions the largest .rwf file did not exceed 50 GB which was acceptable on the 64 bit system. Without the tran = iabc keyword this file exceeded 250 GB and caused system to crash due to the low disk space.

Proton affinities of the carbanions at 298.15 K were calculated as the enthalpies of the reaction:

$$AH = A^- + H^+$$

using the equation:

$$PA = \Delta H_r^{298} = (H_{A^-}^{298} + H_{H^+}^{298}) - H_{AH}^{298}$$

The enthalpy of the proton at 298.15 K was taken as 1.48 kcal mol^{-1}, i.e., 5/2*RT*. The results are presented in kcal mol^{-1} (1 kcal mol^{-1} = 4.184 kJ mol^{-1}).

3. Results and discussion

The selection of C–H acids used in this work was based on three criteria. The first one was the size of the molecule. We decided to use small molecules, up to five heavy atoms, because this is the largest size of the molecule for which CBS-APNO method can be applied. Additionally, due to the limitations of the selected computational methods, we decided to limit our study to the elements belonging to the first three rows of the periodic system, i.e., up to chlorine. The second criterion was the availability of the experimental PA values. For practical reasons we selected our objects from those present in the NIST database [6]. Some additional, very accurate data were taken from the work of Ervin and DeTuri [20] which, unfortunately, was not included in this database. The last selection criterion was the maximum diversification of the structures of the studied molecules – from hydrocarbons to compounds containing halogens, oxygen, nitrogen and sulfur atoms.

3.1. Experimental PA values

All experimental PA values discussed in this paper are taken from the NIST database [6] (with exception of a few data from the paper of Ervin and DeTuri [20] – see Table 1). This is by all means the most comprehensive and reliable source of such data. Detailed description of the methodology of data collecting and presentation in the database can be found in the paper by Lias and Bartmess [5]. In this article the authors discuss also the reliability of the presented data, pointing out possible sources of errors. The most common of them are listed below.

- The measurements used for obtaining PA usually do not give their values directly and additional calculations requiring thermochemical data from the other experiments are necessary [4].

Table 1
Experimental PA values (in kcal mol^{-1}) for anions of the selected C–H acids.

Entry	C–H acid	Carbanion	Experimental data from NIST database [6][a]					Exp. data from Ref. [20]	"The best" value
1	Methane	$^{-}CH_3$	416.70 ± 0.70	418.0 ± 3.5				416.8 ± 0.7	**417.0**
2	Cyclopropane	$C_3H_5^-$	*416.9 ± 4.9*	410.7 ± 1.6	408.0 ± 5.0	411.5 ± 2.0	412.0 ± 2.0		**411.0**
3	Ethylene	$CH_2{=}CH^-$	409.40 ± 0.60	407.5 ± 2.0	407.0 ± 3.0	406.0 ± 2.0		408.8 ± 0.3	**408.0**
4	Propylene	$CH_2{=}CH{-}CH_2^-$	391.10 ± 0.30	389.1 ± 1.5	390.7 ± 2.1	390.20 ± 0.70			**390.5**
5	Cyclopentadiene	c-C_5H_5	353.9 ± 2.2	354.9 ± 2.9	353.6 ± 1.3				**354.0**
6	Acetylene	$HC{\equiv}C^-$	378.50 ± 0.20	378.00 ± 0.70	378.00 ± 0.50	379.80 ± 0.50	376.7 ± 2.1	378.3 ± 0.15	**378.5**
7	Formaldehyde	^{-}CHO	394.5 ± 0.1					394.5 ± 0.2	**394.5**
8	Acetaldehyde	$^{-}CH_2{-}CHO$	365.8 ± 2.2	366.5 ± 2.9					**366.0**
9	Acetone	$^{-}CH_2{-}CO{-}CH_3$	368.8 ± 2.0	369.1 ± 2.1	369.6 ± 2.6	367.6 ± 1.8			**369.0**
10	Methyl acetate	$^{-}CH_2{-}COOCH_3$	371.8 ± 2.1	*364.7 ± 2.6*	375.9 ± 3.5				**373.0**
11	Acetonitrile	$^{-}CH_2{-}CN$	372.9 ± 2.1	*369.0 ± 4.5*	373.3 ± 2.6	374.8 ± 2.0	*366.6 ± 4.6*		**373.5**
12	Malononitrile	$^{-}CH(CN)_2$	335.8 ± 2.1	336.0 ± 2.6					**336.0**
13	Acrylonitrile	$CH_2{=}(C^-){-}CN$	371.1 ± 2.2	*364.3 ± 4.6*					**371.0**
14	Cyanoacetylene	$^{-}C{\equiv}C{-}CN$	350.6 ± 2.1						**350.5**
15	Chloromethane	$^{-}CH_2Cl$	399.6 ± 2.5	*396.0 ± 3.1*	400.0 ± 2.0	399.1 ± 4.1			**399.5**
16	Dichloromethane	$^{-}CHCl_2$	375.7 ± 2.2	374.5 ± 3.1					**375.0**
17	Chloroform	$^{-}CCl_3$	357.6 ± 2.1	357.0 ± 6.1					**357.5**
18	Allyl chloride	$CH_2{=}CH{-}(CH^-){-}Cl$	375.4 ± 2.1	379.9 ± 4.1					**377.0**
19	Fluoromethane	$^{-}CH_2F$	409.0 ± 4.0						**409.0**
20	Difluoromethane	$^{-}CHF_2$	387.0 ± 7.0	389.0 ± 3.5					**389.0**
21	Trifluoromethane	$^{-}CF_3$	378.0 ± 1.4	376.9 ± 2.1	376.0 ± 4.5				**377.0**
22	Chloroacetonitrile	$Cl{-}(CH^-){-}CN$	357.7 ± 2.2	*348.2 ± 6.9*					**357.5**
23	Nitromethane	$^{-}CH_2{-}NO_2$	358.0 ± 5.0	356.4 ± 2.2	357.4 ± 2.9				**357.0**
24	Dimethyl sulfoxide	$CH_3{-}SO{-}CH_2^-$	373.5 ± 2.1	374.3 ± 2.3					**374.0**
25	Dimethyl sulfone	$CH_3{-}SO_2{-}CH_2^-$	365.8 ± 2.2	366.5 ± 2.9					**366.0**

[a] Data are presented in the same order as in the original database. A few values which are evidently erroneous are not included for clarity. Values in italics are unreliable for different reasons – see text for discussion. References to the original papers from which these data were taken can be found in the database.

This procedure is the source of additional uncertainty of the final PA value.

- PA is the enthalpy of the deprotonation reaction but some common types of measurements, e.g., direct measurement of the equilibrium of the proton transfer reaction give the Gibbs free energy of the deprotonation process, i.e., GA instead of PA. Consequently, additional measurements and/or calculations leading to the reaction entropy value are required. This, again, lowers the accuracy of the resulting PA value.
- PA measurements are usually relative to the selected reference compounds. Due to the very broad range of the PA values, a ladder of reference compounds has to be used rather than the single reference. Of course, every reference compound introduces its own uncertainty.
- In many proton transfer reactions more than one product can be formed, e.g., in the case when the molecule contains two or more different hydrogen atoms with very close acidity. For many compounds an important problem are also side reactions accompanying the deprotonation process, e.g., autocondensation of the carbonyl compounds or fragmentation of the carbanion. Neglecting the presence of such reactions can lead to serious errors.
- Some experimental methods are inaccurate by their principle. For example, so-called bracketing method gives only an estimation of the PA value with the uncertainty often exceeding 5 kcal mol^{-1}.

Screening of the NIST database allowed us to select 25 C–H acids, containing no more than 5 heavy atoms in their molecules, for which experimental PA data are available. These data are presented in Table 1.

Table 1 shows evidently that for many, even very simple compounds, the selection of the most reliable experimental PA value is not an easy task. There are no general rules which allow us to tell which data are “more” or “less” accurate, because even the results of the intrinsically very accurate measurements can give wrong PA results due to the reasons given above. In many instances the difference between the lowest and the highest PA values is much larger than the sum of the measurement uncertainties given by the authors. For example, in the case of acetonitrile this difference is about 8 kcal mol^{-1}. In such cases the only reasonable solution is to reject values which differ mostly from the average and take the average of the remaining data as the best estimate. When the number of independent measurements is too low to give meaningful average, the results of the measurements which are more accurate by their principle or, as the last resort, the newest results should be taken. Such values, given with the accuracy of 0.5 kcal mol^{-1}, are presented in the last column of Table 1. It is practically impossible to estimate the uncertainty of these values, however, taking into account typical uncertainties shown in Table 1, the value of ±3 kcal mol^{-1} seems to be reasonable. Such accuracy, though lower than so-called thermochemical accuracy, should be sufficient for many practical applications. In the following part of this paper these values will be taken as the reference for comparison with the calculated ones.

The problem with the wide scattering of the experimental PA results seems to be specific for carbanions. For example, screening of the PA values of the simple alkoxide anions (MeO$^-$, EtO$^-$, *n*-PrO$^-$, *i*PrO$^-$, *n*-BuO$^-$ and *t*-BuO$^-$) published in the NIST database show that the spread between the lowest and the highest values does not exceed 1.7 kcal mol^{-1}. The main reason is much higher gas-phase stability of the alkoxide anions comparing to carbanions, which can undergo fragmentation as well as ion-molecule reactions under experimental conditions.

3.2. *Calculated PA values*

As it was shown above, experimental PA values of carbanions are in some instances not very reliable due to the wide scattering of the results of different measurements. Taking into account a tremendous development of the computational methods observed recently the question arises which PA data are more reliable – experimental or computed ones? To answer this question we performed a series of PA calculations using compound methods from CBS and Gaussian-3 groups which were designed especially to give most accurate thermochemical data. Extensive benchmark calculations published in the literature show that the most advanced of these methods offer very high accuracy, usually with the mean error lower than ±2 kcal mol^{-1} (see Section 1). The results obtained by these methods are generally accepted to be quite reliable and in many comparative studies they are used as the “true” values when the experimental data are not available. Even more accurate are the results obtained by advanced ab initio methods using very large basis sets. As it was already mentioned in Section 1, Ervin and DeTuri [20] shown that CCSD(T)/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ method gives very accurate PA values at 0 K. Following this suggestion we decided to include the results of this type of computations as the final proof for both experimental data and the results obtained using the compound methods.

The results of the calculations are collected in Table 2, which contains also the best estimates of the experimental values from Table 1 and the differences between the calculated values and the experimental ones.

Data presented in Table 2 can be interpreted in several ways. The most evident observation is that all compound methods, except for the modified CBS-4 method (CBS-4M in Gaussian software package), give very consistent results. For practically all studied compounds PA values computed by these methods are quite similar to each other indicating that there are no significant differences between them. This can be clearly shown in Fig. 1 which contains the plots of the differences between calculated and “the best” experimental values taken from Table 1. For clarity, only data for B3LYP variants of CBS-Q, G3 and G3(MP2) methods, i.e., CBS-QB3, G3(B3LYP) and G3(MP2, B3LYP) are presented because there were no significant differences between these two groups of methods. It means also that for the studied compounds the method used for geometry optimization and frequency calculations is not important. B3LYP variants were selected because they give slightly better results both in this study (*vide infra*) and in benchmark studies [11].

The comparison between the compound methods and “benchmark” CCSD(T) method shows some significant features. For the smallest molecules (methane, ethylene, acetylene, formaldehyde, chloromethane and fluoromethane), i.e., those containing no more than two heavy atoms, CCSDT(T) method gives the PA values significantly lower than the compound methods. This regularity is not observed for larger molecules for which the results from CCSD(T) and compound methods are comparable. This problem will be discussed in more detail later.

Taking into account these results and relative computation times we decided to take the results obtained using G3(MP2, B3LYP) method for further analysis. This method seems to be the best compromise between accuracy and speed because an average deviation of the results obtained using G3(MP2, B3LYP) comparing to the “benchmark” CCSD(T)/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ method is equal to ±0.60 kcal mol^{-1} indicating very good consistency of them. Very similar average deviation shows also G3(MP2) method (±0.64 kcal mol^{-1}). On the basis of these results it is not possible to point out which method is better but literature data [11] favor the G3(MP3, B3LYP) one.

Much more important, yet more difficult is the comparison of the calculated and experimental PA values. Table 2 shows that for

Table 2

PA values and their deviations from "the best" experimental values (in kcal mol^{-1}) for anions of the selected C–H acids calculated using CBS and G3 groups of methods.

Entry	C–H acid	PA exp.	CBS-4M		CBS-Q		CBS-QB3		CBS-APNO[a]		G3		G3B3		G3(MP2)		G3(MP2)B3		CCSD(T)[b]	
			PA calcd.	Δ[c]	PA calcd.	Δ	PA calcd.	Δ	PA calcd.	Δ	PA calcd.	Δ	PA calcd.	Δ	PA calcd.	Δ	PA calcd.	Δ	PA calcd.	Δ
1	Methane	**417.0**	419.3	2.3	419.5	2.5	419.1	2.1	418.7	1.7	419.3	2.3	419.7	2.7	418.6	1.6	419.0	2.0	416.7	−0.3
2	Cyclopropane	**411.0**	414.4	3.4	413.9	2.9	413.3	2.3	413.9	2.9	414.3	3.3	414.0	3.0	413.3	2.3	412.9	1.9	412.8	1.8
3	Ethylene	**408.0**	409.4	1.4	409.1	1.1	408.8	0.8	409.1	1.1	409.5	1.5	409.3	1.3	408.8	0.8	408.6	0.6	407.8	−0.2
4	Propylene	**390.5**	392.3	1.8	391.6	1.1	391.4	0.9	391.0	0.5	392.0	1.5	391.7	1.2	391.3	0.8	390.9	0.4	390.9	0.4
5	Cyclopentadiene	**354.0**	351.2	−2.8	353.4	−0.6	353.3	−0.7	353.0	−1.0	355.0	1.0	355.1	1.1	354.4	0.4	354.4	0.4	355.0	1.0
6	Acetylene	**378.5**	378.2	−0.3	378.4	−0.1	378.3	−0.2	378.3	−0.2	378.7	0.2	378.9	0.4	377.9	−0.6	378.1	−0.4	377.3	−1.2
7	Formaldehyde	**394.5**	396.3	1.8	395.4	0.9	397.2	2.7	395.7	1.2	395.6	1.1	396.0	1.5	395.5	1.0	395.8	1.3	394.6	0.1
8	Acetaldehyde	**366.0**	368.4	2.4	367.2	1.2	367.3	1.3	367.3	1.3	367.5	1.5	367.5	1.5	367.2	1.2	367.2	1.2	367.5	1.5
9	Acetone	**369.0**	370.9	1.9	369.7	0.7	369.6	0.6	369.7	0.7	369.8	0.8	369.8	0.8	369.6	0.6	369.6	0.6	369.9	0.9
10	Methyl acetate	**373.0**	374.6	1.6	373.9	0.9	374.6	1.6	374.0	1.0	374.4	1.4	375.1	2.1	374.3	1.3	374.9	1.9	374.1	1.1
11	Acetonitrile	**373.5**	374.9	1.4	375.1	1.6	375.0	1.5	375.2	1.7	375.4	1.9	375.6	2.1	374.9	1.4	375.0	1.5	375.2	1.7
12	Malononitrile	**336.0**	335.1	−0.9	334.7	−1.3	335.2	−0.8	335.3	−0.7	335.5	−0.5	336.1	0.1	335.5	−0.5	336.1	0.1	336.2	0.2
13	Acrylonitrile	**371.0**	374.2	3.2	374.1	3.1	373.8	2.8	374.3	3.3	374.5	3.5	374.8	3.8	373.9	2.9	374.2	3.2	374.1	3.1
14	Cyanoacetylene	**350.5**	348.8	−1.7	348.8	−1.7	349.0	−1.5	348.9	−1.6	349.5	−1.0	349.9	−0.6	348.8	−1.7	349.2	−1.3	348.8	−1.7
15	Chloromethane	**399.5**	406.5	7.0	397.1	−2.4	397.7	−1.8	–	–	397.8	−1.7	398.8	−0.7	397.2	−2.3	398.2	−1.3	397.1	−2.4
16	Dichloromethane	**375.0**	385.3	10.3	376.9	1.9	377.3	2.3	–	–	377.6	2.6	378.7	3.7	376.8	1.8	377.7	2.7	377.4	2.4
17	Chloroform	**357.5**	365.6	8.1	358.7	1.2	359.4	1.9	–	–	359.7	2.2	361.2	3.7	358.6	1.1	359.8	2.3	360.0	2.5
18	Allyl chloride	**377.0**	388.7	11.7	382.0	5.0	381.3	4.3	–	–	381.5	4.5	382.1	5.1	381.0	4.0	381.5	4.5	381.4	4.4
19	Fluoromethane	**409.0**	411.8	2.8	412.2	3.2	411.4	2.4	411.3	2.3	411.2	2.2	411.3	2.3	411.2	2.2	411.3	2.3	409.8	0.8
20	Difluoromethane	**389.0**	400.1	11.1	400.5	11.5	399.9	10.9	400.0	11.0	399.4	10.4	399.5	10.5	399.8	10.8	399.8	10.8	398.6	9.6
21	Trifluoromethane	**378.0**	380.9	2.9	380.2	2.2	380.7	2.7	380.4	2.4	380.4	2.4	380.6	2.6	380.8	2.8	381.0	3.0	379.4	1.4
22	Chloroacetonitrile	**357.5**	363.6	6.1	360.4	2.9	360.7	3.2	–	–	361.0	3.5	361.7	4.2	360.7	3.2	361.3	3.8	361.5	4.0
23	Nitromethane	**357.0**	361.2	4.2	357.7	0.7	357.0	0.0	357.7	0.7	357.8	0.8	358.1	1.1	357.9	0.9	358.2	1.2	358.1	1.1
24	Dimethyl sulfoxide	**374.0**	378.1	4.1	376.3	2.3	376.3	2.3	–	–	376.2	2.2	376.1	2.1	376.1	2.1	375.9	1.9	376.6	2.6
25	Dimethyl sulfone	**366.0**	370.5	4.5	367.7	1.7	367.5	1.5	–	–	367.9	1.9	367.8	1.8	367.8	1.8	367.7	1.7	367.8	1.8
Average of $\lvert\Delta\rvert$				**4.0**		**2.2**		**2.1**		**2.0**		**2.2**		**2.4**		**2.0**		**2.1**		**1.9**
Average of $\lvert\Delta\rvert$ (without entries 18 and 20)				**3.3**		**1.7**		**1.7**		**1.4**		**1.8**		**1.9**		**1.5**		**1.6**		**1.5**

[a] CBS-APNO method is applicable only for molecules containing elements up to neon.

[b] CCSD(T)/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ.

[c] Δ = PA(calcd.) – PA(exp.).

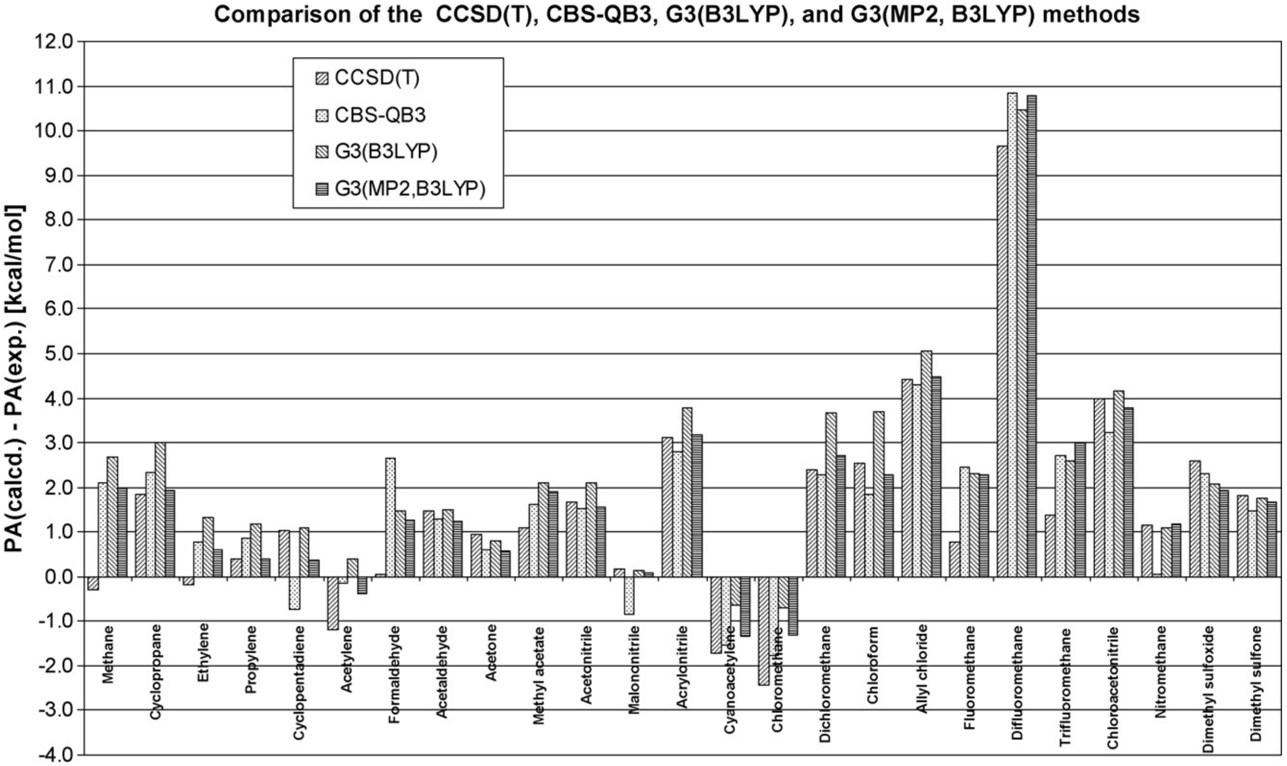

Fig. 1. Differences between PA values computed using CCSD(T)/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ, CBS-QB3, G3(B3LYP) and G3(MP2, B3LYP) methods and "the best" experimental values.

17 from 25 studied compounds PA values computed using G3(MP2, B3LYP) method lie within ±2 kcal mol^{-1} range from the experimental ones indicating very good agreement between the experiment and calculations. The PA values for the group of the next four carbanions lie within ±3 kcal mol^{-1} range from the experimental data which is still acceptable taking into account the discussion presented in the previous section of this paper. For comparison, these numbers for G3(MP2) method are 15 and 7, respectively. Differences exceeding ±3 kcal mol^{-1} are observed for four compounds for G3(MP2, B3LYP) and three for G3(MP2) methods.

The general conclusion which comes from the results described above is that, indeed, for small carbanions PA values computed using compound methods are – in most instances – accurate enough to replace the experimental ones. This is the case for all studied hydrocarbons, carbonyl compounds, nitriles as well as nitromethane, dimethyl sulfoxide and dimethyl sulfone. For all these compounds computed PA values lie either within ±3 kcal mol^{-1} range from the "the best" experimental value or, at least, within the range confined by the lowest and highest experimental PA values corrected by their experimental uncertainties (see Table 3).

As it comes also from Table 3, the most difficult cases are halogenated compounds. This is not a surprising result because it is quite difficult to measure accurately PA values of carbanions derived from them. α-Halocarbanions, especially chloro- and bromo-, are known to be relatively unstable because they readily eliminate halide anion yielding an appropriate carbene. This reaction and other possible processes, like halophilic reaction in which X^+ cation is transferred from the halogenated molecule to the carbanion, make PA measurements very difficult and often unreliable.

Taking this into account, the results shown in Tables 2 and 3 are quite reasonable. The only compound which shows really large discrepancy between experimental and computed PA values is difluoromethane (entry 20). The PA value for this compound was measured for the first time in 1977 by Sullivan using a bracketing method [23]. In 1990 this value was measured again by Graul and Squires [24]. They derived it from the measurement of the threshold energy of decarboxylation of the difluoroacetic acid anion. The results obtained by these two groups of researchers were quite similar: 387.0 ± 7.0 and 389.0 ± 3.5 kcal mol^{-1}, respectively. In 1998, Lee et al. [25] studied the gas-phase reaction of OH^- with CH_2F_2 by both experimental and computational means. They had not calculated PA value of $CHF_2{}^-$ anion explicitly, but from their data (obtained using G2 method) it is possible to estimate this value to be about 399 kcal mol^{-1}. This corresponds very well with our results (399.8 kcal mol^{-1} by G3(MP2, B3LYP) method). So the final conclusion is that the most likely PA value of $CHF_2{}^-$ anion is about 399 rather than 387–389 kcal mol^{-1}.

It is not possible to point out the source of this discrepancy, especially that all other PA values measured by Graul and Squires in the cited paper [24] are correct. To make sure that our calculations were made correctly we performed a number of tests and additional computations. We have tested that the calculated geometry of the $CHF_2{}^-$ anion represents the ground state and there is no singlet–triplet instability. To make sure that the geometry of both CH_2F_2 molecule and $CHF_2{}^-$ anion do not have a significant impact on the final energies we have repeated G3(MP2, B3LYP) calculation taking the geometries optimized using B3LYP/6–311 + G(d, p) method as the starting point for further calculations. The result obtained by the modified method – 400.1 kcal mol^{-1} – differs by 0.3 kcal mol^{-1} from the result of the original G3(MP2, B3LYP) method giving proof that the geometry of the neutral molecule as well as the anion have low influence on the final result.

To get one more proof that the calculations involving difluoromethane molecule can be quite accurate we have calculated the enthalpy of the following gas-phase reaction:

$$CH_4 + 2F_2 \rightarrow CH_2F_2 + 2HF$$

Table 3

Highest, lowest and “the best” experimental PA values (in kcal mol^{-1}) for anions of the selected C–H acids compared with values computed using G3(MP2)B3 method.

Entry	C–H acid	Carbanion	Experimental data[a]		“The best” value	G3(MP2)B3	Computed value lies	
			PA_{min}	PA_{max}			Within $PA_{min} - \Delta$ and $PA_{max} + \Delta$[b]	Within ±3 kcal/mol from “the best” value
1	Methane	$^{-}CH_3$	416.7 ± 0.7	418.0 ± 3.5	417.0	419.0	Yes	Yes
2	Cyclopropane	$C_3H_5^{-}$	408.0 ± 5.0	412.0 ± 2.0	411.0	412.9	Yes	Yes
3	Ethylene	$CH_2{=}CH^{-}$	406.0 ± 2.0	409.4 ± 0.6	408.0	408.6	Yes	Yes
4	Propylene	$CH_2{=}CH{-}CH_2^{-}$	389.1 ± 1.5	391.1 ± 0.3	390.5	390.9	Yes	Yes
5	Cyclopentadiene	c-C_5H_5	353.6 ± 1.3	354.9 ± 2.9	354.0	354.4	Yes	Yes
6	Acetylene	$HC{\equiv}C^{-}$	378.0 ± 0.5	379.8 ± 0.5	378.5	378.1	Yes	Yes
7	Formaldehyde	^{-}CHO	394.5 ± 0.2	394.5 ± 0.2	394.5	395.8	No	Yes
8	Acetaldehyde	$^{-}CH_2{-}CHO$	365.8 ± 2.2	366.5 ± 2.9	366.0	367.2	Yes	Yes
9	Acetone	$^{-}CH_2{-}CO{-}CH_3$	367.6 ± 1.8	369.6 ± 2.6	369.0	369.6	Yes	Yes
10	Methyl acetate	$^{-}CH_2{-}COOCH_3$	371.8 ± 2.1	375.9 ± 3.5	373.0	374.9	Yes	Yes
11	Acetonitrile	$^{-}CH_2{-}CN$	372.9 ± 2.1	374.8 ± 2.0	373.5	375.0	Yes	Yes
12	Malononitrile	$^{-}CH(CN)_2$	335.8 ± 2.1	336.0 ± 2.6	336.0	336.1	Yes	Yes
13	Acrylonitrile	$CH_2{=}(C^{-}){-}CN$	371.1 ± 2.2	371.1 ± 2.2	371.0	374.2	Yes	No
14	Cyanoacetylene	$^{-}C{\equiv}C{-}CN$	350.6 ± 2.1	350.6 ± 2.1	350.5	349.2	Yes	Yes
15	Chloromethane	$^{-}CH_2Cl$	399.1 ± 4.1	400.0 ± 2.0	399.5	398.2	Yes	Yes
16	Dichloromethane	$^{-}CHCl_2$	374.5 ± 3.1	375.7 ± 2.2	375.0	377.7	Yes	Yes
17	Chloroform	$^{-}CCl_3$	357.0 ± 6.1	357.6 ± 2.1	357.5	359.8	No	Yes
18	Allyl chloride	$CH_2{=}CH{-}(CH^{-}){-}Cl$	375.4 ± 2.1	379.9 ± 4.1	376.0	381.5	Yes	No
19	Fluoromethane	$^{-}CH_2F$	409.0 ± 4.0	409.0 ± 4.0	409.0	411.3	Yes	Yes
20	Difluoromethane	$^{-}CHF_2$	387.0 ± 7.0	389.0 ± 3.5	389.0	399.8	No	No
21	Trifluoromethane	$^{-}CF_3$	376.0 ± 4.5	378.0 ± 1.4	378.0	381.0	No	Yes
22	Chloroacetonitrile	$Cl{-}(CH^{-}){-}CN$	357.7 ± 2.2	357.7 ± 2.2	357.5	361.3	No	No
23	Nitromethane	$^{-}CH_2{-}NO_2$	356.4 ± 2.2	358.0 ± 5.0	357.0	358.2	Yes	Yes
24	Dimethyl sulfoxide	$CH_3{-}SO{-}CH_2^{-}$	373.5 ± 2.1	374.3 ± 2.3	374.0	375.9	Yes	Yes
25	Dimethyl sulfone	$CH_3{-}SO_2{-}CH_2^{-}$	365.8 ± 2.2	366.5 ± 2.9	366.0	367.7	Yes	Yes

[a] See footnote for Table 1; PA_{min} and PA_{max} are the lowest and highest experimental PA values, respectively.

[b] PA_{min} value decreased by the measurement uncertainty value and PA_{max} value increased by the measurement uncertainty value.

in two ways. In the first of them, absolute enthalpies of the reagents computed with the CBS-APNO method were used. The second one was based on the experimental enthalpies of formation. Both results were practically the same: −220.43 kcal mol^{-1} from the computed enthalpies and −220.46 from the experimental ΔH_f values. This results shows that there are no special problems with getting accurate thermochemical results for the fluorine containing neutral species.

An additional proof was given by the results obtained for CH_2F^{-} and CF_3^{-} anions (see Table 2). The PA values computed using the most accurate CCSD(T) method differ from the experimental ones by 0.8 and 2.4 kcal mol^{-1}, respectively, while for CHF_2^{-} anion this difference is 9.6 kcal mol^{-1}. It has to be noted that these experimental results come all from the same paper of Graul and Squires [24]. Taking into account all the results presented above it has to be concluded that the experimental PA values for CHF_2^{-} anion are erroneous for unknown reason and the computed values seem to be much more reliable in this case.

An interesting case is allyl chloride. The acidity of this compound was measured by two groups: Dahlke and Kass in 1991 [26] and Squires group in 1997 [27]. Both groups used bracketing method with a flowing afterglow instrument but their results were different. Dahlke and Kass reported that allyl chloride reacted with methoxide anion (PA = 382 kcal mol^{-1}) to give small amounts of chloroallyl anion but the proton transfer reaction was not observed for ethoxide (378.5), isopropoxide (376) and *tert*-butoxide (375) anions. The only anionic product was Cl^{-} in these cases. According to these results they proposed PA value for allyl chloride equal to 379 ± 4 kcal mol^{-1}. In contrast to these results, Squires and co-workers [27] found that under their experimental conditions allyl chloride reacted with all alkoxide anions mentioned above in a proton transfer reaction (the reaction with *t*-BuO^{-} was slow). These results allowed them to propose for allyl chloride GA = 368.0 ± 2 kcal mol^{-1} and PA = 375.4 ± 2 kcal mol^{-1}. It is difficult to explain the differences in the results obtained by these two groups. One possible rationalization is based on the observation that chloroallyl anion decomposes easily yielding chloride anion and neutral vinylcarbene. It is possible that Dahlke and Kass did not observe chloroallyl anion in the reactions of allyl chloride with alkoxide anions higher than methoxide because, under their experimental conditions, this anion, which was formed in a low yield, decomposed completely before reaching the detector of mass spectrometer. Taking into account the complexity of the flowing afterglow experiments another rationalization is possible. It is based on the observation that *m*/*z* 75 peak is often observed in the background in the negative ion spectra. One of the possible sources of this peak is the $CH_3O{-}CO{-}O^{-}$ anion which can be formed in the reaction of the methoxide anion with the traces of CO_2 which are present in the instrument.

If the first rationalization is correct, PA value for allyl chloride given by Squires et al. should be more accurate. The second rationalization favors the value given by Dahlke and Kass. Our calculations (381.0–382.1 kcal mol^{-1}, depending on the method) are closer to the value given by the last two authors, however this is by no means the conclusive result. Taking into account that all calculated PA values for α-halocarbanions, except of chloromethyl anion, are significantly higher than the experimental data (see Fig. 1) it is quite possible that for these species the compound methods exhibit a systematic, positive error. On the other hand, such error – negative in this case – can be an unavoidable feature of all PA measurements of α-halocarbanions which are known to be very reactive species. This example illustrates also very well how difficult are PA measurements for reactive carbanions.

As it was shown in the discussion presented above the experimental PA values for carbanions are in some instances not reliable so they cannot serve as a good test for the validity of different computational methods. To get one more proof that the G3(MP2) and G3(MP2, B3LYP) methods, we selected to be the most useful for PA calculations of the moderate size organic anions, are reliable, we decided to perform a series of calculations for OH^{-} and selected alkoxide anions: MeO^{-}, EtO^{-}, *i*PrO^{-} and *t*-BuO^{-}. The results are

Table 4
PA values and their deviations from the experimental [20] values (in kcal mol^{-1}) for OH^- and selected alkoxide anions calculated using CBS-APNO, G3(MP2), G3(MP2, B3LYP) and CCSD(T)/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ methods.

Anion	Exp.	CBS-APNO	Δ^a	G3(MP2)	Δ^b	G3(MP2, B3LYP)	Δ^a	CCSD(T)//B3LYP^b	Δ^a
HO^-	390.27 ± 0.02	390.3	0.0	391.4	1.1	391.6	1.3	390.3	0.1
MeO^-	381.9 ± 0.5	383.0	1.1	383.5	1.6	383.6	1.7	382.2	0.3
EtO^-	378.7 ± 0.8	379.5	0.8	379.9	1.2	379.9	1.2	379.0	0.3
iPrO^-	376.6 ± 0.7	376.8	0.2	377.2	0.6	377.2	0.6	376.6	0.0
t-BuO^-	375.8 ± 0.7	375.6	−0.2	376.0	0.2	376.1	0.3	375.7	−0.1

[a] Δ = PA(calcd.) − PA(exp.).

[b] CCSD(T)/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ.

presented in Table 4. Experimental data were taken from the paper of Ervin and DeTuri [20].

They show evidently that for alkoxide anions G3(MP2) and G3(MP2, B3LYP) methods give very accurate results. All of them lie within ±1.7 kcal mol^{-1} range from the experimental data, i.e., well within the typical measurement uncertainty limit. Even better are the results of the CBS-APNO calculations. For them the largest difference between the experimental and computed values is 1.1 kcal mol^{-1}. Almost perfect match (Δ_{max} = 0.3 kcal/mol) was obtained using the most advanced CCSD(T)/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ method confirming both the accuracy of the experimental results given by Ervin and TeTuri [20] and the applicability of the CCSD(T) method with large basis set as the benchmark computational method for small molecules. These results give in our opinion the final proof that the PA values computed using the compound methods can be used safely instead of experimental ones. It has to be noted that CCSD(T)/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ calculations for OH^- and alkoxide anions were done already by Ervin and DeTuri but they gave the results for 0 K only. Our results obtained for this temperature were identical with those described by the abovementioned authors.

The final, very important problem which has only been mentioned in the discussion presented above is the absolute sign of the mean error of the computed PA values. Fig. 1 shows that the PA values computed using compound methods are higher than the experimental ones for the majority of the studied molecules, i.e., these values have positive absolute error. Positive errors are observed also for the results obtained using compound methods for all but *t*-butoxide alkoxide anions (Table 4). Negative errors for the results obtained by all studied compound methods are observed only for cyanoacetylene and chloromethane, while the calculated PA values for acetylene and malononitrile oscillate around 0, depending on the method. One of possible conclusions which can be drawn from these results is that the compound methods give generally too high results and much better correlation between the experimental and computed PA values will be obtained by reducing the latter by about 1.5–1.9 kcal mol^{-1}, depending on the method. In favor for this solution are the results obtained by a “benchmark” CCSD(T) method for very small molecules (up to two heavy atoms) which are significantly lower than the average of the results obtained with compound methods (see Fig. 1 and Table 4). On the other hand, for larger carbanions the results from the calculations using CCSD(T) and compound methods are comparable to each other, yet significantly higher than the experimental ones. Taking into account all pros and contras we can suggest that it will be safer not to make any corrections to the computed PA values because it is not possible to predict in which cases they will help and in which they will make the results much worse than the uncorrected ones. It can be expected that for the calculation of the enthalpies of the gas-phase reactions the errors will cancel to some extent and the result will be accurate enough to enable drawing meaningful conclusions from them.

4. Conclusions

The analysis of the relations between experimental and computed PA values of small carbanions presented in this work leads to the following general conclusions:

- PA values for carbanions described in the literature and collected in the NIST database [6] are in some cases not reliable so they should be used cautiously.
- For small carbanions PA values computed using compound methods and advanced ab initio methods with large basis sets can be safely used instead of experimental ones. In some instances they are even more reliable than the experimental results.
- The most accurate PA values for small molecules (up to five heavy atoms) are obtained using CCSD(T)/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ method. For small molecules containing elements from the first two rows CBS-APNO method also give very accurate results and is significantly faster. For larger molecules G3(MP2) and G3(MP2, B3LYP) methods give acceptable results in a short time.
- It should become a common practice to check the experimental PA values by comparing them with the computed ones. On the modern PC computer with a 4-core processor it takes usually no longer than a couple of minutes for small molecules and a few hours for larger ones (up to about 12 heavy atoms).
- Our results indicate that for the majority of carbanions better correlation between the experimental PA values and the values calculated using G3(MP) or G3(MP2, B3LYP) methods can be obtained by reducing the latter by about 1.5 kcal mol^{-1} however it is not possible to predict in which instances this method will not work.

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