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Electron affinities of a homologous series of tertiary alkyl radicals and their C–H bond dissociation energies (BDEs)

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ABSTRACT

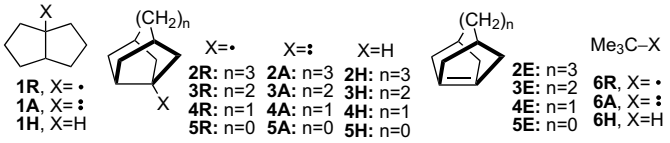
Heats of formation have been derived from G3(MP2)//B3LYP and G3MP2B3(+) atomization energies for *tert*-butyl radical (**6R**), cubyl radical, bicyclooctyl radical (**1R**), and tricyclo[3.3.*n*.0^{3,7}]alk-3(7)-yl (*n*=0–3, **2R**–**5R**) radicals, and their respective anions (**1A**–**6A**) and hydrocarbons (**1H**–**6H**). The electron affinity (EA) of **6R** is estimated at 1.5±2 kcal/mol and *tert*-butyl anion (**6A**) is likely to be bound. In the homologous series **2R**–**5R** the EAs range from 3.4±2 to 13.5±2 kcal/mol. The computed enthalpies of the acidities of the tricyclic hydrocarbons **1H**–**5H** are in the range 407–411 kcal/mol. Their C–H bond dissociation energies (BDEs) are in the range 97–110 kcal/mol. The increase of the BDEs in the homologous series **2H**–**5H** and the increase of EAs of **2A**–**5A** is attributed to the enhanced pyramidalization induced in radicals **2R**–**5R** by the shortening of the methylene chain connecting carbons C_3 and C_7.

1. Introduction

Calculations and experiments have shown that the methyl radical has a small electron affinity (1.8 kcal/mol),[1–3] In contrast, experimental data[4] suggest that other simple anions like ethyl, isopropyl, and *tert*-butyl anions are unstable toward loss of an electron, in agreement with published theoretical predictions.[5] On the other hand, sp^2 and sp-centered radicals have positive electron affinities. For example, the electron affinities of vinyl and ethynyl are 16.1[3] and 67.5 kcal/mol,[6] respectively. This can be attributed to the relatively high s character of the orbital that stabilizes the extra electron. Presumably for the same reason highly pyramidal radicals also have relatively high electron affinities. For example, the experimental electron affinity of the cubyl radical is 11.5±2 kcal/mol,[7] while that of 4-nortricylyl is computed to be about 4 kcal/mol higher.[8] A detailed computational study of various radicals concluded that 'the electron affinities of several secondary systems are clearly influenced by hybridization changes induced by bond angle compression, but not in a simple fashion'.[8]

Usually the electron affinities of alkyl radicals are derived from the gas-phase acidities of their corresponding hydrocarbons. Measuring the acidity of extremely weak acids is experimentally very challenging[4,9] and this is an area where computational studies can be of use.[3,5,8,10]

In this paper we examine computationally a homologous series of tricyclic pyramidal radicals (**2R**–**5R**), which are formally derived from **1R** (bicyclo[3.3.0]octyl radical) by connecting carbons 3 and 7 with a methylene bridge ($(CH_2)_n$, *n*=0–3). Derivatives of radicals **2R**–**5R** and their corresponding anions (**2A**–**5A**, respectively), are plausible intermediates in the generation of pyramidalized alkenes **2E**–**5E**, and therefore useful in understanding the mechanism for the formation of the latter.[11] Due to our interest in this class of alkenes[12] we examine at high levels of theory the electron affinities of radicals **2R**–**5R**, the acidities of **2H**–**5H** (to form anions **2A**–**5A**, respectively) and the C–H bond dissociation energies (BDEs) of **2H**–**5H** to form radicals **2R**–**5R**, respectively. The EA of the prototypical tertiary radical *t*-Bu (**6R**) is also examined.



2. Methodology

Calculations were carried out with the Gaussian 03[13] suite of programs and PQS software.[14] Structures were optimized at the B3LYP[15] level of theory with the 6-31G(d) and 6-31+G(d) basis sets.[16] Stationary points were characterized by vibrational analyses. G3(MP2)//B3LYP (G3MP2B3 for short) energies[17] were calculated and were converted to heats of formation using published procedures.[18] In addition, G3MP2B3(+) energies were obtained by carrying out the single-point calculations of G3MP2B3 at the B3LYP/6-31+G(d) optimized geometry and using the same HLC

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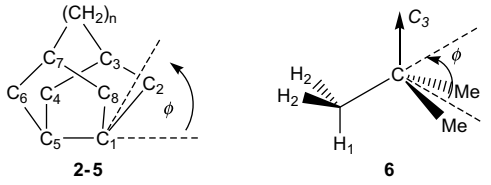
Table 1
G3MP2B3(+) energies (E, a.u.) at 0 at 298 K and derived heats of formation at 298 K ($\Delta H_{f\ 298}$, kcal/mol)

	E (0 K)	E (298 K)	$\Delta H_{f\ 298}$
1A	−312.0427	−312.0347	20.1
1R	−312.0392	−312.0311	22.4
1H	−312.6925	−312.6845	−22.0
2A	−428.5595	−428.5498	20.1
2R	−428.5512	−428.5416	25.2
2H	−429.2060	−429.1963	−19.9
3A	−389.3284	−389.3199	22.0
3R	−389.3177	−389.3092	28.7
3H	−389.9790	−389.9705	−20.6
4A	−350.0914	−350.0842	27.5
4R	−350.0779	−350.0708	35.9
4H	−350.7443	−350.7372	−16.6
5A	−310.8143	−310.8071	59.0
5R	−310.7900	−310.7829	74.2
5H	−311.4640	−311.4578	16.4
Cubyl anion	−308.2830	−308.2774	183.5
Cubyl radical	−308.2613	−308.2559	197.0
Cubane	−308.9278	−308.9223	144.5
tert-Butyl anion (**6A**)	−157.4810	−157.4745	9.9
tert-Butyl radical (**6R**)	−157.4768	−157.4695	13.1
Isobutane (**6H**)	−158.1306	−158.1240	−31.9
$CH3^-$	−39.7618	−39.7580	32.4
$CH_3^{\bullet}$	−39.7589	−39.7549	34.4
Methane	−40.4243	−40.4205	−17.6

factors and ZPE corrections as in the standard G3MP2B3 method (Table 1). Temperature corrections for quantities at 298 K were based on the B3LYP/6-31G(d) frequencies scaled by 0.9989.[19] The pyramidalization angle ϕ[11a] is defined as the angle formed by the extension of the C_5C_1 bond and the plane defined by the centers C_1, C_2, and C_8 (Scheme 1) can be taken as a measure of the degree of pyramidalization. For a perfectly tetrahedral radical ϕ=54.8°, and for a planar one ϕ=0°. Natural bond orbital analysis[20] was carried out to determine hybridization of orbitals (Table 2).



Scheme 1. Definition of pyramidalization angle φ in tricyclic systems **2**–**5** and **6**.

3. Results and discussion

The electron affinity of an alkyl radical R (EA(R), Eq. 2) can be derived from the gas-phase acidity of the corresponding alkane R–H (ΔH_{acid}(R–H), Eq. 4) in conjunction with the R–H bond dissociation energy (BDE(R–H)) (Eq. 1) and the ionization potential of the hydrogen atom (IP(H), Eq. 3) as indicated by the thermocycle of Figure 1 and expressed in Eq. 5.[21]

Table 2
Pyramidalization angles (φ, °) and %s character for radicals **1R**–**5R**, their corresponding anions **1A**–**5A** and hydrocarbons **1H**–**5H**[a]

R	φ (°)	%s[b]	R^-	φ (°)	%s[b]	R–H	%s[c]
1R	30.7	4.0	**1A**	54.9	14.0	**1H**	23.1
2R	42.2	6.9	**2A**	54.0	9.3	**2H**	23.7
3R	51.0	10.9	**3A**	62.9	14.8	**3H**	24.7
4R	58.2	15.2	**4A**	69.0	20.2	**4H**	26.1
5R	65.2	20.7	**5A**	75.1	28.4	**5H**	28.0

[a] Computed at the B3LYP/6-31+G(d) level of theory.
[b] Referring to the orbital containing the odd electron or electron pair, and which is largely localized on C_1.
[c] Referring to the orbital of the tertiary carbon forming the C_1–H bond (Scheme 1).

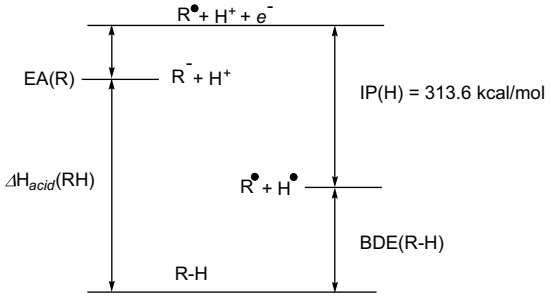


Figure 1. Thermocycle relating the BDE(R–H) with ΔH_{acid}(RH) and EA(R).

$$R{-}H \rightarrow R^{\bullet} + H^{\bullet}\ BDE(R{-}H) \quad (1)$$

$$R^- \rightarrow R^{\bullet} + e^-\ EA(R) \quad (2)$$

$$H^{\bullet} \rightarrow H^+ + e^-\ IP(H) \quad (3)$$

$$R{-}H \rightarrow R^- + H^+\ \Delta H_{acid}(R{-}H) \quad (4)$$

$$EA(R) = -\Delta H_{acid}(R{-}H) + BDE(R{-}H) + IP(H) \quad (5)$$

The electron affinity of the methyl radical was determined directly[1,3] with photoelectron spectroscopy at 1.8±0.7 kcal/mol. Based on the thermocycle of Figure 1, this corresponds to ΔH_{acid} (CH_4)=416.7±0.7 kcal/mol.[3] Usually, the electron affinities (EAs) of alkyl radicals are derived from gas-phase acidities with the help of Eq. 5.[2,9,23] In the cases studied by Squires carbanions are generated from the corresponding carboxylates and the assumption is made that the enthalpy of the decarboxylation reaction to produce the anion is equal to the threshold energy for appearance of the anion.[9] This appears to be a valid approximation, since in many cases the reverse reaction (the addition of a carbanion to CO_2) is believed to proceed essentially without barrier. However, with this technique, gas-phase anions with negative EAs (unbound with respect to the loss of an electron) cannot be formed. Such anions can be studied indirectly using kinetic methods[22–24] where product ratios from competing decompositions of a common intermediate are related to relative acidities.

DePuy has developed a kinetic method for determining the relative acidities of hydrocarbons based on the gas-phase reaction of alkyltrimethylsilanes with hydroxide anion.[4,23] The method has been applied to several hydrocarbons with acidities varying from 400.7 kcal/mol (benzene) to 420.1 kcal/mol (ethane). The method is useful in estimating electron affinities of small alkyl radical, which have non-bound anions. Using this method, the gas-phase acidity of isobutane was estimated at 413.1 kcal/mol and the electron affinity of *tert*-butyl radical was derived as −5.9 kcal/mol.[4] Early computational results at the SCF level of theory estimated that the electron affinity of **6R** is smaller than the EA of the methyl radical by 11.4 kcal/mol leading to the prediction EA(**6R**)=−9.6 kcal/mol.[5] More recent computational data gave conflicting results. Both MP2 and B3LYP levels of theory (with the 6-31+G(d,p) basis set) predict that the difference of electron affinities between **6R** and methyl radical is much smaller (1.2 and −4.5 kcal/mol, respectively) but in different directions, with B3LYP predicting that *tert*-butyl anion (**6A**) is not bound, and MP2 finding that it is slightly more bound than the methyl anion.[8] In light of the experimental data available at the time, it was noted that the performance of the MP2 method is inferior to that of DFT.[8] Increasing the basis set of B3LYP increases the EA of **6A**, but it still remains negative and smaller than that of methyl radical by at least 3 kcal/mol.[8,25]

Table 3
G3MP2B3(+) thermodynamic data at 298 K

R	EA(R$^{\bullet}$)[a]	BDE(R–H)	ΔH_{acid}(RH)
1R	2.3	96.4	409.3
2R	5.1	97.2	407.2
3R	6.7	101.3	409.8
4R	8.4	104.5	411.3
5R	15.2	109.9	409.8
6R (*tert*-Butyl radical)	3.2[b]	97.1	409.1
Cubyl radical	13.5	104.5	406.2
$CH_3^{\bullet}$[c]	2.0	104.0	417.2

[a] EAs of tertiary radicals are likely to be overestimated by about 1.7 kcal/mol, based on the discussion of EA(**6R**) in the text.
[b] Best estimate is 1.5±2 kcal/mol (see text).
[c] Experimental values for EA($CH_3^{\bullet}$), BDE(CH_4), and $\Delta H_{acid}(CH_4)$ are 1.8±0.7, 104.9±0.1, and 416.7±0.7 kcal/mol, respectively.[1,3,21]

The theoretically derived heat of formation for **6A** using the atomization method[38] is 9.9 kcal/mol when derived from the G3MP2B3(+) total energy.[26,27] Both G3MP2B3 and G3MP2B3(+) reproduce the known heat of formation of isobutane of −32.1 kcal/mol within 0.1 kcal/mol.[28] The heat of formation of **6R** has been reassessed recently at 12.8 kcal/mol.[29] This value assumed that the $\Delta H_{f\ 298}$ of the methyl radical is 35.6 kcal/mol. If the NIST recommended value of 35.1 kcal/mol for the methyl radical is used[28] then $\Delta H_{f\ 298}$(**6R**)=13.3 kcal/mol in excellent agreement with our computed value of 13.1 kcal/mol. This value is also in excellent agreement with the previous one computed by Radom and Smith (13.6 kcal/mol),[30] and is somewhat higher from the previous experimental data.[31]

With the above-mentioned experimental values for the heats of formation of isobutane and **6R**, the BDE of the 3° C–H bond of isobutane comes out as 97.5 kcal/mol, which is 1 kcal/mol higher than the recommendation.[21] A value of 96.5–97.5 kcal/mol for this BDE is between 2.9 and 3.9 kcal/mol higher than the one used to derive the experimental electron affinity of **6R**.[4] If this is taken into account, then Depuys' gas-phase data lead to EA(**6R**)=−2.0 to −3.0 kcal/mol. This revised value is still lower than the electron affinity of the methyl radical, but in better agreement with the computational data.[8]

At the G3MP2B3(+) level of theory, the EAs of methyl radical and **6R** are 2.0 and 3.2 kcal/mol, respectively (Table 3).[32] The former is just 0.2 kcal/mol above the experimental value. If this minor correction is taken into account, EA of **6R** is 3.0 kcal/mol, resulting in a bound anion. It is noteworthy that the computed difference of 1.2 kcal/mol between the EAs of methyl and *tert*-butyl radicals is almost entirely due to the zero-point energy (ZPE) corrections. If these are ignored the EA of **6R** is computed to be slightly smaller (by almost 0.1 kcal/mol) than that of the methyl radical.[33]

The G3MP2B3(+) acidity of methane (at 298 K) is 417.2 kcal/mol. At this level of theory the heat of formation of the proton is overestimated by 1.5 kcal/mol. If this correction is taken into account then the acidity of methane is predicted to be 415.7 kcal/mol. In both cases there is excellent agreement with the experimentally derived value of 416.7±0.7 kcal/mol.[1] At the same level of theory ΔH_{acid}(isobutane) is 8.1 kcal/mol lower than $\Delta H_{acid}(CH_4)$.[34] This is in disagreement with the gas-phase data,[4] which find the acidity of isobutane 3.5 kcal/mol lower than that of methane. The difference persists even at the CCSD(T)/aug-pvqz+ZPE level of theory where ΔH_{acid}(isobutane) is 6.1 kcal/mol lower than $\Delta H_{acid}(CH_4)$. This difference of 2.6–4.6 kcal/mol between theory and experiment regarding ΔH_{acid}(isobutane) is the origin of the discrepancy between the theoretically and experimentally[4] derived EA(**6R**). The reason for the disagreement is not clear yet, but steric effects could be important.[24,36,37]

In this context it is interesting to note that the acidity of cubane has been determined in two ways: (a) by DePuys' kinetic method of reacting (trimethylsilyl)cubane with hydroxide and estimating the relative acidities of methane and cubane[7] and (b) by using DePuys' desilylation reaction[41] to generate the cubyl anion from the gas-phase reaction of (trimethylsilyl)cubane with fluoride and subsequently measuring its proton affinity.[7] The acidity derived from the former method is 7 kcal/mol higher than our computed value of 406.2 kcal/mol, which is within the experimental error of the latter method (404±3 kcal/mol).

One may have expected that with an EA of 3.0 kcal/mol, the *tert*-butyl anion would have been detected in the gas-phase experiments of Squires.[9a,b] However, Squires estimated that the EA of a radical should be at least ∼2 kcal/mol[9b] and have a life time of at least ∼2 μs in order to be detectable under his experimental conditions. The value of 3.0 kcal/mol is not far off from the limit of 2 kcal/mol suggested by Squires, but at the same time the negative experimental result indicates that G3MP2B3(+) may be overestimating slightly the EA of **6R** and related radicals. Partial support for this overestimation is provided by the finding that the G3MP2B3(+) EA of cubyl radical (see below), although within the experimental error of ±2 kcal/mol, is 2 kcal/mol higher than the experimental value.[7]

An alternative way to estimate EA(**6R**) is based on Eq. 5 using a mixture of experimental and computational data. If the computed difference in acidities between methane and isobutane are used in conjunction with the experimental acidity of methane, ΔH_{acid}(isobutane) should be in the range of 408.6–410.6 kcal/mol. If the BDE of the 3° C–H bond of isobutane is taken as 97.0±0.5 kcal/mol, EA(**6R**) is in the range of −0.5 to 2.5 kcal/mol.

Given the experimental and theoretical uncertainties our best theoretical estimate for EA(**6R**) as a subjective average of the quantities discussed above is 1.5±2 kcal/mol.

The homologous series of tricyclic radicals **2R**–**5R** is tertiary radicals with various degrees of pyramidalization. As the length *n* of the methylene chain connecting carbons C_3 and C_7 becomes shorter, ϕ increases in a nearly linear fashion. In the parent radical **1R**, ϕ is considerably smaller (30.7°) and reflects the tendency of radicals for planar geometries. By comparison ϕ of *tert*-butyl radical is 19.9° implying that the five-membered rings of **1R** cause some geometrical strain at the radical center. According to the NBO analysis the %s character of the orbital containing the odd electron increases as pyramidalization of the radical center increases in the series **1R**–**5R** (Table 2).[38]

The pyramidalization angle of the parent anion **1A** is significantly larger than **1R** and similar to that of *tert*-butyl anion (55.9°), in agreement with the preference of anions for pyramidal geometries. For the homologous anions **2A**–**5A**, ϕ is around 10° larger than of the corresponding radical. Interestingly, the pyramidalizations angles ϕ of **1A** and **2A** are almost the same, and actually the former is slightly larger.[39]

The G3MP2B3(+) electron affinity of the parent radical **1R** is computed to be 1 kcal/mol less than that of *tert*-butyl radical (**6R**). With EA(**6R**)=1.5±2 kcal/mol, if **1A** is indeed bound its detection in the gas-phase is not expected to be easy. In contrast, the EAs of the pyramidal radicals **2R**–**5R** are likely to be measurable. The least pyramidal of them (**2R**) is estimated to have an EA of 3.4±2 kcal/mol. The computed EA increases with pyramidalization reaching 13.5±2 kcal/mol for the most pyramidal one in this series (**5R**).

The increased EA can be attributed to the increased %s character of the anion as the pyramidalization angle ϕ increases. It can also be linked to the strain induced by the pyramidalization. Figure 2 shows how the electronic energies of **6R** and **6A** depend on ϕ. In both cases, for angles higher than the corresponding equilibrium value of ϕ, the curves are to a good approximation parabolic. The cross-over point occurs at about 40°. Below this point the radical is expected to be less strained than its anion (if both have the same pyramidalization angle). If the EAs of radicals **1R**–**5R** were approximated as the difference in pyramidalization strain between

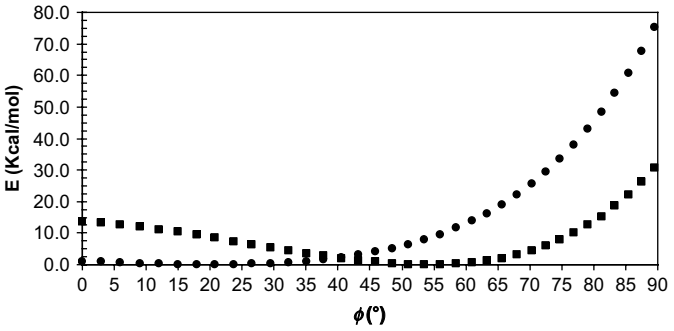
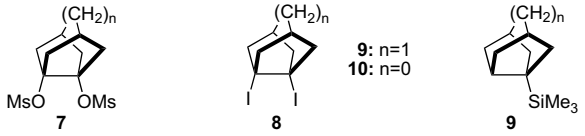


Figure 2. B3LYP/6-31+G(d) energies of **6R** (●) and **6A** (■) as a function of pyramidalization angle at C_{3v} symmetry.

the radical and its anion the estimated EAs (based on the data of Fig. 2) would be 0.5, 2.7, 5.3, 7.7, and 10.3 kcal/mol, respectively. These are in reasonable agreement with those of Table 3, suggesting that the pyramidalization strain induced by the methylene bridge on the radical center affects its EA.[40]

The computed EA of radical **5R** is remarkable and is almost 2 kcal/mol higher than that estimated for the cubyl radical (11.8±2 kcal/mol). The cubyl anion has been generated in the gas-phase and its EA determined at 11.5±2 kcal/mol.[7] This strongly suggests that anions **2A**–**5A** can also be generated in the gas phase. Given that compounds like **7**, n=2,3 and **8**, n=0,1 are known and have been used for the generation of pyramidalized alkenes **2E**–**5E** [11] silanes **9**, n=0–3 should be synthetically accessible and the previous prediction can be tested experimentally. These silanes are expected to react in the gas-phase with fluoride to form the bound anions **2A**–**5A**, whose proton affinity can then be determined with bracketing experiments. In addition the gas-phase reaction of these homologous series of silanes with hydroxide can shed light into the factors that are responsible for the shortcomings of this kinetic method in determining acidities of bulky alkyl groups.[6,25,41]



The 3° C–H BDEs of hydrocarbons **1H**–**5H** to form radicals **1R**–**5R**, respectively, increase from 96.5 to a remarkable 109.9 kcal/mol. This increase can be attributed to the formation of a more pyramidalized radical and perhaps to a stronger C–H due its higher %s character (Table 2). It is interesting that the 3° C–H BDE of **5H** is predicted to be around 5 kcal/mol stronger than that of cubane, which has been derived experimentally at 102±4 kcal/mol,[7] with previous calculations supporting the high end of the range.[6,42] The formally sp^3 C–H bond of **5H** is essentially as strong as the sp^2 C–H of ethylene.

The increase of C–H BDEs in the homologous series **2H**–**5H** may provide an explanation as to why room temperature reduction with sodium amalgam is possible for **7**, n=2,3 (and gives the corresponding pyramidalized alkenes **3E** and **2E**, respectively), but not for **7**, n=0,1 (to form **5E** and **4E**, respectively), even when the mesyl group (CH_3SO_2) is replaced by the trifyl (CF_3SO_2).[43] On the other hand the diiodides **8**, n=0,1 are easily reduced at room temperature under the same conditions. Since the mesyl anion is known to be several orders of magnitude better leaving group than iodide, one may have expected that successful reduction of the diiodides **8**, n=0,1 would imply the easy reduction of the corresponding dimesylates (**7**, n=0,1). To the extent that C–O BDEs correlate with C–H BDEs, the C–O BDEs in the homologous series **7**, are expected to increase as n decreases. Apparently, for n smaller than two, the C–O bond is strong enough to resist the reduction at room temperature. Reduction of the diiodides **8**, n=0,1 can then be attributed to the intrinsically weaker C–I bond as compared to a C–O bond.

The computed acidity (ΔH_{acid}) of hydrocarbons **1H**–**5H** ranges from 407 to 411 kcal/mol and does not seem to follow some specific pattern, despite the small but systematic increase of the %s character of the C–H bond in this homologous series. The lack of a good correlation between acidity and %s was noted previously by Sauers[8] for a variety of hydrocarbons. If Eq. 5 is re-written so as to express ΔH_{acid} in terms of the other quantities, it is seen that the acidity depends on the difference between the C–H BDE and the EA of the resulting radical. Since pyramidalization causes both quantities to increase, their difference tends to cancel out resulting in a much narrower range of acidities.

In conclusion, high level calculations predict that the *tert*-butyl anion is likely to be bound and in principle it should be observable in the gas phase. The homologous series of pyramidal radicals **2R**–**5R** is expected to give rise to bound anions. The most pyramidal of these (**5R**) is predicted to have a remarkable EA of around 13.5 kcal/mol, which is higher than the one measured for cubyl radical by about 2 kcal/mol. Pyramidalization of the resulting radical can also be associated with an increased C–H BDE in the series **1H**–**5H**. For **5H** a remarkably strong C–H bond (worth about 110 kcal/mol) is predicted.

Acknowledgements

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Supplementary data

G3MP2B3 energies and calculated geometries of the compounds in this report. This material is available free of charge via the Internet at http://pubs.acs.org. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.12.043.

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33. At 0 K and before ZPE corrections EA(**6R**)−EA($CH_3^{\cdot}$)=−0.3.
34. At the G3MP2B3 level of theory ΔH_{acid}(isobutane)=410.2 kcal/mol, because the stability of the anion is underestimated by 1.2 kcal/mol. At the G2 level of theory (where MP2/6-31G(d) optimized geometries are used) ΔH_{acid}(isobutane)=412. 2 kcal/mol.[35]
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39. A linear fit between %s character and ϕ for the homologous anions **2A**–**5A** has a regression coefficient (r^2) of 0.964, and extrapolation to zero %s character corresponds to ϕ=44.6°, quite far from the pyramidalization angle of the parent system **1A**.
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