

C–H Bond Dissociation Enthalpies in Norbornane. An Experimental and Computational Study

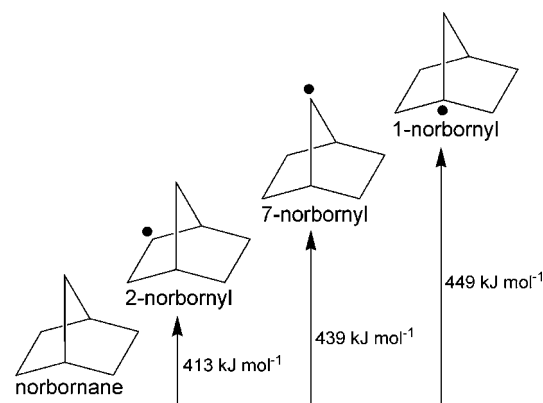
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ABSTRACT



Gas-phase C–H bond dissociation enthalpies (BDEs) in norbornane were determined by quantum chemistry calculations and the C2–H BDE was experimentally obtained for the first time by time-resolved photoacoustic calorimetry. CBS-Q and CBS-QB3 methods were used to derive the values $DH^\circ(C1-H) = 449 \text{ kJ mol}^{-1}$, $DH^\circ(C7-H) = 439 \text{ kJ mol}^{-1}$, and $DH^\circ(C2-H) = 413 \text{ kJ mol}^{-1}$. The experimental result $DH^\circ(C2-H) = 414.6 \pm 5.4 \text{ kJ mol}^{-1}$ is in excellent agreement with the theoretical value. The trend $DH^\circ(C1-H) > DH^\circ(C7-H) > DH^\circ(C2-H)$ is discussed.

Organic strained molecules, such as bicyclo-hydrocarbons, have long been the object of thermochemical studies.^{1–3} One of these molecules is norbornane (bicyclo[2.2.1]heptane), a

key compound in revealing how structural and energetic parameters are affected by a strained geometry.^{4,5} Despite this interest, the uncertainties of the experimental C–H bond dissociation enthalpies (BDEs) for this molecule are higher than the usual chemical accuracy limit (ca. 4 kJ mol⁻¹).⁶

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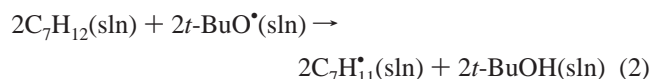
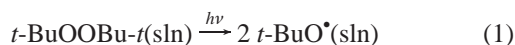
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This prompted us to determine the various C–H BDEs in norbornane, using both experimental and computational tools.

EPR studies showed that the photolysis of solutions of norbornane and di-*tert*-butylperoxide in cyclopentane generated 2-norbornyl (bicyclo[2.2.1]heptan-2-yl) radicals.⁷ Later, the rate constant for the hydrogen abstraction in norbornane by *tert*-butoxyl radicals in benzene solution was obtained using laser flash photolysis.⁸

In this work, we have used time-resolved photoacoustic calorimetry (TR-PAC)^{9–11} and quantum chemistry calculations to derive the three C–H bond dissociation enthalpies in norbornane.

The TR-PAC experiments were carried out using reactions 1 and 2. The photolysis of di-*tert*-butoxylperoxide in benzene solution produces a pair of *tert*-butoxyl radicals (reaction 1). Each *tert*-butoxyl radical reacts with a norbornane molecule (C₇H₁₂), producing the 2-norbornyl radical and *tert*-butanol (reaction 2).



The reaction enthalpy associated with reaction 2, $\Delta_r H_2^\circ$, is twice the difference between the C2–H BDE in norbornane and the O–H BDE in *t*-butanol. Hence, the C2–H BDE can be derived using eq 3:

$$DH^\circ_{\text{sln}}(\text{C2-H}) = \frac{\Delta_r H_2^\circ}{2} + DH^\circ_{\text{sln}}(t\text{-BuO-H}) \quad (3)$$

Using our experimental value for $\Delta_r H_2^\circ = -71.3 \pm 3.0$ kJ mol⁻¹ and the O–H BDE of *t*-butanol in benzene, $DH^\circ_{\text{sln}}(t\text{-BuO-H}) = 455.2 \pm 5.2$ kJ mol⁻¹,¹² we obtained $DH^\circ_{\text{sln}}(\text{C2-H}) = 419.6 \pm 5.4$ kJ mol⁻¹.

To calculate the gas-phase BDE for norbornane we must consider eq 4:

$$DH^\circ(\text{C2-H}) = DH^\circ_{\text{sln}}(\text{C2-H}) + \Delta_{\text{sln}} H^\circ(\text{C}_7\text{H}_{12;\text{g}}) - \Delta_{\text{sln}} H^\circ(\text{C}_7\text{H}_{11;\text{g}}) - \Delta_{\text{sln}} H^\circ(\text{H}^\bullet;\text{g}) \quad (4)$$

The difference between the solvation enthalpies of norbornane and the 2-norbornyl radical may be considered negligible.¹⁰ The solvation of the hydrogen atom can be estimated using the hydrogen molecule as a model, yielding

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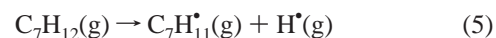
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$\Delta_{\text{sln}} H^\circ(\text{H}^\bullet;\text{g}) = 5 \pm 1$ kJ mol⁻¹ for organic solvents.^{13–16} Hence, we obtained $DH^\circ(\text{C2-H}) = 414.6 \pm 5.5$ kJ mol⁻¹.

The complete basis-set composite schemes CBS-Q and CBS-QB3^{17–19} were used to obtain the enthalpies of reactions 5 and 6. Reaction 5 represents the direct homolysis of the three different C–H bonds in norbornane, yielding 1-norbornyl, 2-norbornyl, or 7-norbornyl, and therefore its enthalpy is identified with $DH^\circ(\text{Cn-H})$, where $n = 1, 2, \text{ or } 7$, respectively. A more reliable method to obtain the three BDEs is provided by eq 7,²⁰ which uses the computed values of the enthalpies of the isodesmic and isogyric reaction 6 and of $DH^\circ(\text{C}_2\text{H}_5\text{-H}) = 423.0 \pm 1.7$ kJ mol⁻¹.²¹



$$\Delta_r H_6^\circ = DH^\circ(\text{Cn-H}) - DH^\circ(\text{C}_2\text{H}_5\text{-H}) \quad (7)$$

As noted in Table 1, the agreement between the results from reactions 5 and 6 is better than 3 kJ mol⁻¹. Also, the

Table 1. C–H Bond Dissociation Enthalpies (kJ mol⁻¹) in Norbornane, Determined by TR-PAC and Theoretical Methods, at 298.15 K

	$DH^\circ(\text{C1-H})$	$DH^\circ(\text{C2-H})$	$DH^\circ(\text{C7-H})$
TR-PAC		414.6 ± 5.5	
CBS-Q (reaction 5)	453.6	414.9	440.8
CBS-QB3 (reaction 5)	450.8	413.4	440.6
CBS-Q (reaction 6)	451.0	412.3	438.2
CBS-QB3 (reaction 6)	448.3	410.9	438.1
selected	449 ± 4	413 ± 4	439 ± 4

calculated values for the C2–H BDE are in excellent agreement with our TR-PAC experimental value. This agreement indicates that the theoretical values for C1–H and C7–H BDEs (which could not be determined by TR-PAC) are accurate. This is also supported by data calculated by Feng et al. using the G3B3 level of theory, viz., $DH^\circ(\text{C1-H}) = 450$ kJ mol⁻¹, $DH^\circ(\text{C2-H}) = 413$ kJ mol⁻¹, and $DH^\circ(\text{C7-H}) = 440$ kJ mol⁻¹.³

The early experimental values for $DH^\circ(\text{C1-H})$ shown in Table 2 are clearly low limits. Indeed, for instance, when

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Table 2. Experimental Values (kJ mol^{-1}) for the C1–H BDE in Norbornane

authors (year)	method ^a	$DH^\circ(\text{C1-H})$	ref
Applequist, Kaplan (1965)	SPK	408.8	24
O'Neal, Bagg, Richardson (1970)	GPK	403.3 \pm 9.6	25
Danen, Tipton, Saunders (1971)	GPK	416	22

^a SPK = solution-phase kinetics; GPK = gas-phase kinetics.

the C1–H BDE (416 kJ mol^{-1}) determined by Danen et al.²² is recalculated using recent data for C–H BDEs in *t*-Bu–H, Me–H, Et–H, *i*-Pr–H, and *s*-Bu–H,^{21,23} we obtained $DH^\circ(\text{C1-H}) = 427 \text{ kJ mol}^{-1}$.

The trend $DH^\circ(\text{C1-H}) > DH^\circ(\text{C7-H}) > DH^\circ(\text{C2-H})$ can be easily rationalized considering the relative stability of the resulting carbon-centered radicals. The 2-norbornyl radical is stabilized by hyperconjugation with the neighboring C1–H and C3–H bonds. This leads to a 6 and 4 pm shortening, respectively, in the C2–C3 and C2–C1 bonds in 2-norbornyl radical, relative to the corresponding bond lengths in norbornane (Figure 1). This shortening is in good agreement with previously reported bond length data.²⁶ On the other hand, as shown in Figure 1, the C1–C2–C3 angle in 2-norbornyl radical is about 5° wider than the same angle in norbornane. This seems to indicate that the radical center is trying to achieve a planar geometry but is constricted by the rigid carbon frame. Nonetheless, this is the largest angle widening for the three norbornyl radicals.

As expected, the 7-norbornyl radical is less stabilized by hyperconjugation than the 2-norbornyl radical. This is in keeping with the spin density values for the two radicals (Table 3). The spin density in the radical center of 7-nor-

Table 3. Spin Densities at the Radical Centers of Norbornyl Radicals and NBO Analysis Results for $p\%$ Character Associated with the C–H Bond in Norbornane and with the Odd Electron of the Radical Atom

	spin density	$p\%$ in norbornane	$p\%$ in radical
1-norbornyl	+0.907	0.75	0.83
2-norbornyl	+0.967	0.77	0.98
7-norbornyl	+0.970	0.76	0.93

bornyl is higher than the corresponding value for the 2-norbornyl. Both of these radicals may delocalize spin through two neighboring C–H bonds, but the hyperconju-

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gation is less effective in 7-norbornyl because of the geometrical constraints. As a result, the C7–C1 and C7–C4 bond distances shorten only by 3 pm. The C1–C7–C4 angle is about 4° wider than the same angle in norbornane. Again, the radical center is trying to attain a planar geometry but is hindered by a rigid structure. As a result, $DH^\circ(\text{C7-H}) > DH^\circ(\text{C2-H})$.

In the 1-norbornyl radical, hyperconjugation is achieved by delocalizing the spin through three C–H bonds. Therefore, the spin density at the radical center is smaller than in the other two radicals (Table 3), implying that the 1-norbornyl radical should be the most stable. However, spin density is not the only parameter required to explain the observed stability trend (see below). As a result of the rigid structure around C1, the radical cannot attain the optimal planar (or nearly planar) geometry. The bond distances around C1 shorten by 2–3 pm, but the rest of the bond distances become stretched by 1–2 pm. On the other hand, the angle at the radical center is wider than in norbornane, but an opposite trend is observed for several other angles. These changes make 1-norbornyl the least stable of the three norbornyl radicals and therefore the C1–H BDE has the highest value.

An alternative method to understand the stability trend of the norbornyl radicals, is using natural bond orbital (NBO) analysis to calculate the $p\%$ character associated with each one of the three C–H bonds in norbornane and with the odd electron of the corresponding radical atom. This has been proposed by Feng et al.,³ who showed that the C–H BDEs in hydrocarbons are dependent not only on the spin density but also on the hybridization of the radical and the parent molecule. Ring strain influences the hybridization in norbornane and in the corresponding radicals, as it forces these species to assume a certain geometry. The $p\%$ character data in Table 3 are in excellent agreement with the values computed by Feng et al. As observed, the $p\%$ character for the three carbon atoms is similar in norbornane but significantly different in the radicals. The smallest deviation from the pure p character in norbornyl radicals is observed for C2 in the 2-norbornyl radical, justifying a C2–H BDE smaller than C1–H and C7–H BDEs. On the other hand, the $p\%$ character in the radical center of 1-norbornyl has the highest deviation from a pure p orbital. Therefore, C1–H BDE has the highest value among the three BDEs. An intermediate situation is observed for C7. Hence, the C7–H BDE lies between the C1–H and C2–H BDEs.

Comparing the selected results in Table 1 with other C–H BDEs in simple hydrocarbons, we find that $DH^\circ(\text{C7-H})$ is similar to the C–H BDE in methane ($439.1 \pm 0.5 \text{ kJ mol}^{-1}$),²³ supporting the limited hyperconjugation of the C7 carbon with vicinal C–H bonds. The value for $DH^\circ(\text{C2-H})$ matches the C2–H BDE in propane ($412.5 \pm 1.7 \text{ kJ mol}^{-1}$)²¹ corroborating the conclusion that the 2-norbornyl radical is stabilized by hyperconjugation with both C1–H and C3–H bonds.

Remarkably, the $DH^\circ(\text{C1-H})$ is $\sim 10 \text{ kJ mol}^{-1}$ higher than the C–H BDE in methane but similar to the calculated bridgehead C–H BDEs in bicyclo[1.1.1]pentane and bicyclo[2.1.1]hexane.³ This is consistent with the hypothesis that

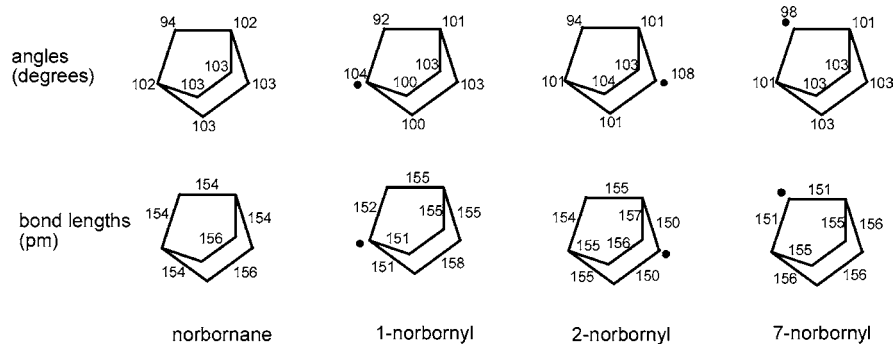


Figure 1. Bond lengths (pm) and angles (deg) for norbornane and for each norbornyl radical, calculated with B3LYP/cc-pVTZ.

bridgehead carbons have limited possibilities to change the geometry of the radical into a more stable one after the homolysis.

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Supporting Information Available: Experimental details (materials, photoacoustic calorimetry, theoretical calculations) and tables containing B3LYP/cc-pVTZ optimized geometries and total energies for norbornane and the norbornyl radicals. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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