# Experimental and Computational Bridgehead C–H Bond Dissociation Enthalpies

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Supporting Information

**ABSTRACT:** Bridgehead C–H bond dissociation enthalpies of 105.7 ± 2.0, 102.9 ± 1.7, and 102.4 ± 1.9 kcal mol<sup>-1</sup> for bicyclo[2.2.1]heptane, bicyclo[2.2.2]octane, and adamantane, respectively, were determined in the gas phase by making use of a thermodynamic cycle (i.e., BDE(R–H) =  $\Delta H^{\circ}_{acid}(H-X) - IE(H') + EA(X')$ ). These results are in good accord with high-level G3 theory calculations, and the experimental values along with G3 predictions for bicyclo[1.1.1]pentane, bicyclo[2.1.1]hexane, bicyclo[3.1.1]heptane, and bicyclo[4.2.1]nonane were found to correlate with the flexibility of the ring system. Rare examples of alkyl anions in the gas phase are also provided.



#### INTRODUCTION

Reactive intermediates formally derived from rigid hydrocarbons have been extensively studied because their lack of structural flexibility provides an ideal platform for probing geometry-dependent phenomena (e.g., orbital interactions, substituent effects, and reactivity), and their derivatives, while posing many synthetic challenges, are valuable in many practical contexts.<sup>1</sup> For example, adamantane-containing compounds have been used in the synthesis of polymers for electronic displays and in the treatment of influenza, HIV-1, leukemia, and Parkinson's and Alzheimer's diseases.<sup>2</sup> Likewise, bicyclo[2.2.1]heptanes and bicyclo[2.2.2]octanes are found in naturally occurring compounds and have been used to treat depression, cocaine abuse, and malaria.<sup>3</sup>

The bridgehead radicals of these rigid hydrocarbons have been generated by the thermolysis of peresters and azoalkanes as well as from tin hydride reductions of the corresponding halides.<sup>4</sup> On the basis of these studies, it is generally accepted that the 1-bicyclo[2.2.1]heptyl (1r), 1-bicyclo[2.2.2]octyl (2r) and 1-adamantyl (3r) radicals are harder to form than the *tert*butyl radical because they are thermodynamically less stable (i.e., BDE (CH<sub>3</sub>)<sub>3</sub>C-H < 3-H < 2-H < 1-H).<sup>5</sup> The C–H bond dissociation enthalpies of bicyclo[2.2.1]heptane (1H), bicyclo[2.2.2]octane (2H), and adamantane (3H), however, are uncertain despite considerable effort to determine these quantities.

Experimental measurements of the bond dissociation enthalpies for **1H** range from 96.7 to 101.8 kcal mol<sup>-1</sup>,<sup>1g,5b,6</sup> but recent computations give predictions spanning from 102 to 112 kcal mol<sup>-1,7</sup> The most reliable theoretical methods (CBS-QB3, G3B3, and G3) indicate that the BDE is 107–108 kcal mol<sup>-1,7c,d</sup> but these values, along with other computational predictions, are in poor accord with the experimental data. A similar situation applies for **2H** in that BDEs of 93.2 and 97.7 kcal mol<sup>-1</sup> have been reported,<sup>1g,5b</sup> whereas computational predictions range from 98.3 to 101.9 kcal mol<sup>-1</sup>, and the largest of these values comes from the most reliable procedure (i.e., a B3LYP/6-311++G(2df,p)//B3LYP/6-31(d) extrapolation to give a G3B3 prediction).<sup>7b,c</sup> For **3H**, the experimental C–H BDE is also not well established, and values spanning from 92.2 to 99.6 kcal mol<sup>-1</sup> have been reported.<sup>1g,5b,8</sup> The most recent experimental determination of the bond energy was carried out in 1998 and gave a value of 96.3 kcal mol<sup>-1</sup>, whereas a G3MP2 study three years later gave a prediction of 100.4 kcal mol<sup>-1</sup>. This computation suggests that the actual bond energy maybe at the high end of the experimentally reported range.

Two decades ago, Walton noted in his excellent review article on bridgehead radicals that bridgehead C–H bond energies are extremely valuable but not well established or generally available.<sup>1g</sup> This situation has not changed significantly in the intervening years. Consequently, in this study we report the bridgehead C–H BDEs of **1H–3H**. These values were determined from the gas-phase acidities ( $\Delta H^{\circ}_{acid}$ ) of these three hydrocarbons and the electron affinities (EA) of their bridgehead radicals by combining them in a thermodynamic cycle to afford the corresponding bond dissociation enthalpies (eq 1); IE(H) stands for the ionization energy of hydrogen atom and is well-known to be 313.6 kcal mol<sup>-1.10</sup> The experimental results were supplemented with G3 computations on **1H–3H** and a number of related bicyclic compounds.

$$BDE(HX) = \Delta H^{\circ}_{acid}(HX) - IE(H^{\cdot}) + EA(X^{\cdot})$$
(1)

# RESULTS AND DISCUSSION

**Bicyclo[2.2.1]heptane (1H).** Fluoride ion was used to deprotonate bicyclo[2.2.1]heptane-1-carboxylic acid  $(1CO_2H)$  in the gas phase, and the resulting conjugate base was transferred to the second cell of a dual cell Fourier transform mass spectrometer (FTMS) where it was fragmented by

Received:December 9, 2011Published:January 16, 2012

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energetic collisions with argon gas (i.e., collision-induced dissociation (CID)). It was anticipated that the bridgehead anion of bicyclo[2.2.1]heptane (i.e., 1a) would result from this process since other alkyl anions have been produced in this way.<sup>11</sup> To test this expectation, the decarboxylated (M - $(CO_2)^{-1}$  ion was isolated and allowed to react with a variety of neutral reagents. In accord with the known extreme basicity of alkyl anions,<sup>12</sup> the  $(M - CO_2)^-$  ion readily deprotonated water  $(\Delta H^{\circ}_{acid} = 390.27 \pm 0.02 \text{ kcal mol}^{-1})$  and ammonia  $(\Delta H^{\circ}_{acid} =$  $403.4 \pm 0.1$  kcal mol<sup>-1</sup>).<sup>13</sup> This places its conjugate acid at the high end of the gas-phase acidity scale (i.e.,  $\Delta H^{\circ}_{acid}$  > 403.4 ± 0.1 kcal mol<sup>-1</sup>), which is as expected for 1H. As a result, an alternative approach to equilibrium and bracketing measurements is needed for determining its acidity. This was accomplished by measuring the electron affinity (EA) of the bridgehead radical (1r) and taking advantage of a recently reported correlation between  $\Delta H^{\circ}_{acid}(RH)$  and EA(R) for hydrocarbons whose conjugate bases are localized anions.

Sulfur dioxide, chloropentafluorobenzene, and carbon disulfide were found to react with **1a** via electron transfer, whereas carbonyl sulfide, oxygen, and nitrous oxide, all of which have smaller electron affinities, did not (Table 1).<sup>15</sup> These

 Table 1. Experimental Determination of the Electron

 Affinity of 1-Bicyclo[2.2.1]heptyl Radical (1r)

ref compd	EA $(eV)^a$	electron transfer
SO <sub>2</sub>	$1.107 \pm 0.008$	yes
C <sub>6</sub> F <sub>5</sub> Cl	$0.82 \pm 0.11$	yes
CS <sub>2</sub>	$0.58 \pm 0.05$	yes <sup>b</sup>
COS	$0.46 \pm 0.20$	no <sup>c</sup>
O <sub>2</sub>	$0.448 \pm 0.006$	no
N <sub>2</sub> O	$0.22 \pm 0.10$	no

<sup>*a*</sup>Experimental values come from ref 10. <sup>*b*</sup>A small amount of sulfuratom transfer was also observed. <sup>*c*</sup>Sulfur-atom transfer and adduct formation were observed.

results indicate that the electron affinity of  $\mathbf{1r}$  is between that for O<sub>2</sub> and CS<sub>2</sub> or 0.51 ± 0.07 eV (i.e., 11.8 ± 1.6 kcal mol<sup>-1</sup>). This value is in accord with other alkyl anions which are known to be weakly bound.<sup>12</sup> It is also in between the measured electron affinities for dodecahedryl (0.17 ± 0.10 eV)<sup>16</sup> and 3*tert*-butyl-1-bicyclo[1.1.1]pentyl (0.64 ± 0.14 eV)<sup>17</sup> radicals as one might expect. A high level G3 theory<sup>18</sup> calculation gives a 298 K value of 0.453 eV (10.44 kcal mol<sup>-1</sup>), and this too is in excellent agreement with the experimental determination.

Substitution of the experimentally determined electron affinity of 1r into eq 2 affords  $\Delta H^{\circ}_{acid}(1H) = 407.5 \pm 1.2$ kcal mol<sup>-1</sup>; the given uncertainty is the statistical value, but a more conservative and arbitrary estimate is  $\pm 2-3$  kcal mol<sup>-1</sup>. This result is in reasonable accord with a G3 theory prediction of 411.9 kcal mol<sup>-1</sup> but is smaller than a preliminary estimate for this quantity of 414 kcal mol<sup>-1</sup> using the DePuy kinetic method (see below for a detailed description of this procedure).<sup>19</sup> The latter difference is not necessarily surprising, however, since 1-trimethylsilylbicyclo[2.2.1]heptane was used for the kinetic acidity measurement, and it was subsequently discovered that when the two substituents attached to silicon (1-bicyclo[2.2.1]heptyl and CH<sub>3</sub> in this case) differ sterically then acidities that are numerically too large can result. For example, cubane and dodecahedrane gave acidities that were too weak by 9 and 10 kcal mol<sup>-1</sup>, respectively.<sup>16,20</sup>

$$\Delta H^{\circ}_{acid}(RH) = (-0.613 \pm 0.022 \text{ kcal mol}^{-1})$$
$$\times \text{EA}(R) + (414.7 \pm 0.7)$$
$$\text{kcal mol}^{-1}$$
(2)

Combining  $\Delta H^{\circ}_{acid}(1H)$  and EA(1r) along with the wellknown ionization energy of hydrogen into the thermodynamic cycle given in eq 1 leads to 105.7  $\pm$  2.0 kcal mol<sup>-1</sup> for the bridgehead C–H bond dissociation enthalpy of bicyclo[2.2.1]heptane. This value is well reproduced by B3LYP/6-311+ +G(2d,p), CBS-QB3, G3B3, and G3 predictions of 104.0, 107.3, 107.6, and 107.9 kcal mol<sup>-1</sup>, respectively, and is also consistent with Allinger's estimate of 102.1 kcal mol<sup>-1.7</sup> A MP2/6-31+G(d) BDE of 112.0 kcal mol<sup>-1</sup>, however, is clearly too large.<sup>7b</sup>

Experimental determinations for the bridgehead C-H bond energy of **1H** of 96.7  $\pm$  2.5 and 99.4 kcal mol<sup>-1</sup> were originally reported in 1970 and 1971.<sup>5b,6</sup> The first of these energies was determined by reacting 1-iodobicyclo[2.2.1]heptane (II) with HI to afford bicyclo[2.2.1]heptane and I<sub>2</sub>, but as noted in Walton's 1992 review,<sup>1g</sup> measurements of this type subsequently were found to underestimate bond dissociation enthalpies by  $\sim 3$  kcal mol<sup>-1</sup> for tertiary C-H bonds. If one arbitrarily employs a 3.0 kcal mol<sup>-1</sup> correction for 1H as done by Walton, then a revised estimate of 99.7 kcal mol<sup>-1</sup> is obtained. The second bond energy was determined by comparing the polar-effect corrected relative iodine abstraction rates of phenyl radical with a series of alkyl iodides (RI) including 1I in which the reference compounds have known R-H bond dissociation enthalpies. Since updated C-H BDEs were available for the standards, a revised bond energy to 101.8 kcal mol<sup>-1</sup> was given by Walton. Both of these changes moved the original BDE determinations upward, but the resulting values are still  $\sim 5$  kcal mol<sup>-1</sup> too small. In the latter instance (phenyl radical abstraction of iodine), this appears to be a systematic error since the BDEs for several other compounds using this method are also  $\sim 5 \text{ kcal mol}^{-1}$  too weak; for further details, see below.

Bicyclo[2.2.2]octane (2H). We attempted to generate the bridgehead anion of 2H (i.e., 2a) in a similar manner as was done for 1a, but in this instance, as happens from time to time, a rearrangement to an unknown ion took place upon fragmentation of the bridgehead carboxylate anion. This was readily apparent in that the  $(M - CO_2)^-$  anion did not deprotonate NH3 or H2O nor did it undergo hydrogendeuterium exchange with ND<sub>3</sub>. These observations are inconsistent with all known alkyl anions and the G3 predicted acidity for 2H of 413.4 kcal mol<sup>-1</sup>. A less basic species such as the deprotonated allylic anion of vinylcyclohexane is a plausible structure, but this ion was not explored further. An alternative approach for the preparation of 2a was carried out instead by reacting fluoride anion with 1-trimethylsilylbicyclo[2.2.2]octane  $(2SiMe_3)$ . This methodology has been successfully employed in a similar case (bicyclo[1.1.1]pentane) where the loss of carbon dioxide from a carboxylate anion led to a rearrangement.<sup>17</sup> In this instance, however, even though 2SiMe<sub>3</sub> did give the desired  $(M - TMS)^{-}$  anion, it was produced in very small amounts. The resulting ion appears to be extremely basic which is consistent with the formation of 2a, but an insufficient signal kept us from collisionally cooling and reliably probing the reactivity of this ion. Our data does suggest, nevertheless, that 2a is bound with respect to electron loss as originally predicted by Sauer and subsequently indicated by the G3 computations reported herein.  $^{7\mathrm{b}}$ 

To determine the bridgehead acidity of **2H**, 1triphenylsilylbicyclo[2.2.2]octane was prepared from its corresponding bromide (eq 3), and the triphenylsilyl derivative,

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(3)

rather than the corresponding trimethylsilane, was used in a DePuy kinetic method determination.<sup>12a,b</sup> In this approach, a series of reference triphenylsilyl derivatives  $RSiPh_3$  were used in which RH has a known gas-phase acidity. By allowing these compounds to react with OH<sup>-</sup>, two product ions ( $Ph_3SiO^-$  and  $RPh_2SiO^-$ ) were produced (eq 4). A plot of the natural

$$Ph_{3}SiR + OH^{-} \longrightarrow Ph_{3}Si(OH)R^{-}$$

$$\longrightarrow [Ph_{2}Si(OH)R \cdot Ph^{-}] \longrightarrow Ph_{2}Si(R)O^{-} + PhH$$

$$\longrightarrow [Ph_{3}SiOH \cdot R^{-}] \longrightarrow Ph_{3}SiO^{-} + RH \quad (4b)$$

(4a)

logarithm of the statistically and isotopically corrected product ion ratio  $[\ln(3Ph_3SiO^-/Ph_2Si(R)O^-)]$  versus  $\Delta H^{\circ}_{acid}(RH)$ afforded a linear calibration line that can be used to obtain the acidity of an unknown acid. This methodology has been used most commonly with trimethylsilyl derivatives, but several large substrates (i.e., cubane and dodecahedrane) gave anamolously low acidities and this was attributed to the large steric difference between the two silicon substituents.<sup>16,20</sup> That is, pentacoordinate silconate **4a** is expected and was computed to be more stable than **4b** when R is large (Figure 1), but the



Figure 1. Trimethylsilyl pentacoordinate anion intermediates formed in the DePuy kinetic method.

latter species is the one that loses RH more readily. This leads to a reduced amount of  $(CH_3)_3SiO^-$  and a weaker acidity than would be obtained otherwise. If one replaces all three methyl groups in the tetraalkylsilane with larger phenyl rings, then the difference in stability between the two pentacoordinate anions should diminish and the resulting product ion ratio is more likely to reflect the thermodynamic acidity of RH. This was found to be the case for dodecahedrane, and it is for this reason that 1-triphenylsilylbicyclo[2.2.2]octane (**2SiPh**<sub>3</sub>) was employed in this work.

A five point calibration line was constructed using Ph<sub>3</sub>SiR compounds, where R = methyl, cyclopropyl, vinyl, phenyl, and 1-naphthyl (Table 2 and eq 5). The isotopically corrected ratio for **2SiPh<sub>3</sub>** was found to be 0.030  $\pm$  0.003, which leads to  $\Delta H^{\circ}_{acid}(2H) = 411.9 \pm 0.4$  kcal mol<sup>-1</sup>. This finding is in excellent accord with the G3 theory prediction of 413.4 kcal mol<sup>-1</sup>, and a previous estimate for this quantity of 414 kcal mol<sup>-1</sup> using the trimethylsilyl derivative.<sup>19</sup> It also leads to EA(2r) = 0.20  $\pm$  0.07 eV (4.6  $\pm$  1.6 kcal mol<sup>-1</sup>) via the correlation given in eq 2, and this too is well reproduced by the

Table 2. DePuy Kinetic Acidity Measurement Data for 1	1-
Triphenylsilybicyclo[2.2.2]octane and 1-	
Triphenylsilyladamantane	

RSiPh <sub>3</sub>	Ph <sub>3</sub> SiO <sup>-</sup> / Ph <sub>2</sub> Si(R)O <sup>-</sup> (ratio) <sup>a</sup>	$ln (3 \times ratio)$	$\Delta H^{\circ}_{ m acid}( m R m H)^{b}$
$R = CH_3$	$0.010 \pm 0.002$	-3.49	$416.7 \pm 0.7$
c-C <sub>3</sub> H <sub>5</sub>	$0.045 \pm 0.004$	-2.01	$411.5 \pm 2.0$
$C_2H_3$	$0.042 \pm 0.004$	-2.08	$409.4 \pm 0.6$
C <sub>6</sub> H <sub>5</sub>	1.00	0.00	$401.7 \pm 0.5$
1-naphthyl	$3.32 \pm 0.22$	2.30	$394.2 \pm 1.2$
1-bicyclo[2.2.2] octyl	$0.030 \pm 0.003$	-2.40	$411.9 \pm 0.4$
1-adamantyl	$0.021 \pm 0.003$	-2.79	$413.4 \pm 0.6$
<sup>a</sup> Observed ratio was	s isotopically corrected.	. <sup>b</sup> Values are	in kcal mo <sup>⊢1</sup> .

G3 value of 0.148 eV (3.42 kcal mol<sup>-1</sup>). By combining  $\Delta H^{\circ}_{acid}(2H)$  and EA(2r) via eq 1, one obtains 102.9  $\pm$  1.7 kcal mol<sup>-1</sup> for the bridgehead C–H bond of 2H. This value is also in excellent agreement with the G3 estimate for this quantity of 102.4 kcal mol<sup>-1</sup> but is larger than the B3LYP/6-311++G(2d,p) and MP2/6-31+G(d) predictions of 98.3 and 99.9 kcal mol<sup>-1</sup>, respectively.<sup>7b</sup>

$$\Delta H^{\circ}_{acid}(RH) = -3.90 \ln(3Ph_3SiO^{-}) + (402.6, r^2) = 0.987$$
(5)

An experimental value for **2H** of 93.2 kcal mol<sup>-1</sup> for the bridgehead C–H bond dissociation enthalpy was originally obtained by Danen using the phenyl radical abstraction method noted above.<sup>5b</sup> This bond energy was subsequently revised by Walton to 97.7 kcal mol<sup>-1</sup> using newer reference data,<sup>1g</sup> but it is still ~5 kcal mol<sup>-1</sup> too small as is the case for bicyclo[2.2.1]-heptane.

Adamantane (3H). Both 1-trimethylsilyl- and 1-triphenylsilyladamantane were synthesized from the commercially available bridgehead bromide to determine the acidity of adamantane and explore the effect of methyl vs phenyl substitution in the trialkylsilanes. To accomplish this, a fivepoint reference line was obtained using  $(CH_3)_3SiR$ , where R = $CH_2CH_3$ ,  $CH_3$ ,  $c-C_3H_5$ ,  $C_2H_3$ , and  $C_6H_5$  (Table 3, eq 6).

Table 3. DePuy Kinetic Acidity Measurement Data for 1-Trimethylsilyladamantane

RSiMe <sub>3</sub>	$\operatorname{Me_3SiO^-/ Me_2Si(R)O^-}_{(\operatorname{ratio})^a}$	$\ln (3 \times ratio)$	$\Delta H^{\circ}_{acid}(\mathrm{RH})^{b}$
$R = CH_3CH_2$	$0.13 \pm 0.01$	-0.95	$420.1 \pm 2.0$
CH <sub>3</sub>	1.00	0.00	$416.7 \pm 0.7$
c-C <sub>3</sub> H <sub>5</sub>	$0.98 \pm 0.06$	1.08	411.5 ± 2.0
$C_2H_3$	$2.43 \pm 0.08$	1.99	409.4 ± 0.6
C <sub>6</sub> H <sub>5</sub>	$8.93 \pm 0.62$	3.29	401.7 ± 0.5
1-adamantyl	$0.95 \pm 0.06$	1.04	411.9 ± 0.3
<sup><i>a</i></sup> Observed ratio	was isotopically corrected	. <sup>b</sup> Values ar	e in kcal mol⁻¹.

Subsequent measurements on both adamantane derivatives afforded  $\Delta H^{\circ}_{acid}(\mathbf{3H}) = 413.4 \pm 0.6$  (SiPh<sub>3</sub>) and  $411.9 \pm 0.3$  (SiMe<sub>3</sub>) kcal mol<sup>-1</sup> which are similar enough that both results were averaged to give our recommended value of  $412.7 \pm 0.8$  kcal mol<sup>-1</sup>. This quantity is well reproduced by the G3 estimate of 411.4 kcal mol<sup>-1</sup>. It leads also to EA( $3\mathbf{r}$ ) =  $0.14 \pm 0.08$  eV ( $3.3 \pm 1.8$  kcal mol<sup>-1</sup>) via eq 2, and this too is accurately predicted by G3 theory which gives a value of 2.1 kcal mol<sup>-1</sup> for this quantity. Both the experimental and the G3 electron

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affinities for 3r are numerically small values which is expected for an alkyl radical, but they are also larger than zero and this indicates that the anion is stable with respect to electron loss. This contrasts with a conclusion based upon B3LYP and other DFT functionals that indicated that 1-adamantyl anion is an unbound species with respect to its radical.<sup>21</sup> The sign of the electron affinity (positive or negative), consequently, can be viewed as an open question.

$$\Delta H^{\circ}_{acid}(RH) = -4.19 \ln(3Me_3 SiO^{-}) + (R(Me)_2 SiO^{-}) + 416.3, r^2 = 0.985$$
(6)

Our data leads to BDE(3H) =  $102.4 \pm 1.9$  kcal mol<sup>-1</sup> for the tertiary C–H bond, and this determination is in excellent accord with the G3 prediction of 100.6 kcal mol<sup>-1</sup>. It is larger, however, than a recent appearance energy measurement of 96.3 kcal mol<sup>-1</sup>,<sup>8b</sup> and it is ~5 kcal mol<sup>-1</sup> bigger than Danen's value of 97.0 kcal mol<sup>-1</sup>.<sup>5b</sup> The latter discrepancy is consistent with the experimental and computational findings for bicyclo[2.2.1]-heptane and bicyclo[2.2.2]octane, however, and suggests that all of the bond energies determined by phenyl abstraction of iodine are 5 kcal mol<sup>-1</sup> too small. Our bond dissociation enthalpy, on the other hand, is in excellent accord with Beauchamp's measurement of 100.2  $\pm$  1.3 kcal mol<sup>-1</sup> by photoelectron spectroscopy.<sup>8a</sup>

To put our bridgehead C–H bond dissociation enthalpies in a broader perspective, values for bicyclo[1.1.1]pentane (5H), bicyclo[2.1.1]hexane (6H), bicyclo[3.1.1]heptane (7H), and bicyclo[4.2.1]nonane (8H) were computed using G3 theory. All of these results are summarized in Table 4, and the resulting

Table 4. Experimental and Computed (G3) Bridgehead Bond Dissociation Enthalpies and Radical Stabilization Energies for Bicyclic Hydrocarbons 1H-3H and 5H-8Halong with Heteronuclear  $^{13}C^{-1}H$  Coupling Constants and a Measure of the Ring System's Flexibility<sup>*a*</sup>

			BDE (kcal mol <sup>−1</sup> )		
compd	$ \begin{pmatrix} J \\ {}^{13}\text{C} - {}^{1}\text{H}, \\ {}^{\text{Hz}} \end{pmatrix}^{b} $	$d (RH - \dot{R})^{c}$	expt	G3	RSE <sup>d</sup>
1H	141.0	0.072	$105.7\pm2.0$	107.9	$10.5 (9.2 \pm 2.0)$
2H	134.5	0.097	$102.9 \pm 1.7$	102.4	$5.0(6.4 \pm 1.7)$
3H	133.4	0.105	$102.4 \pm 1.9$	100.6	$3.2(5.9 \pm 1.9)$
5H	167.8	0.044	$109.7 \pm 3.3^{e}$	106.5	9.1
6H	151.8	0.034		109.1	11.7
7H	144.9	0.083		103.8	6.4
8H	-	0.181		97.4	0.0
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<sup>*a*</sup>Bond and radical stabilization energies are given in kcal mol<sup>-1</sup>. <sup>*b*</sup>All values come from ref 22. <sup>*c*</sup>The differences in the distances (in angstroms) between the bridgehead carbon and the plane defined by the three carbon atoms attached to it for the hydrocarbons and their corresponding radicals are given by *d*. <sup>*d*</sup>RSE = BDE(RH) – BDE((CH<sub>3</sub>)<sub>3</sub>C–H). The computed G3 energies are given first and the experimental values follow in parentheses. BDE ((CH<sub>3</sub>)<sub>3</sub>C–H) = 96.5 ± 0.4 kcal mol<sup>-1</sup> (expt, see ref 23) and 96.6 kcal mol<sup>-1</sup> (G3, ref 7c). <sup>*e*</sup>This value is for the 1-*tert*-butyl derivative (ref 17).

heats of formation and strain energies are given in Table S1 in the Supporting Information. One might expect these bond energies to correlate with the hybridization of the bridgehead C–H bonds or some measure of the flexibility of the ring systems. Heteronuclear  $^{13}C^{-1}H$  coupling constants for the bridgehead C–H bonds were used as a measure of their hybridization,<sup>22,24</sup> and the difference in the out-of-plane distance *d* between the bridgehead carbon and the plane defined by the 3 carbon atoms attached to it in the hydrocarbon and its radical was used as an indicator of the rigidity of the ring systems; more commonly employed out-of-plane angles were not used because most of the compounds in Table 4 do not have  $C_3$ -rotation axes and consequently more than one such angle can be defined. A plot of the BDEs versus the <sup>13</sup>C–<sup>1</sup>H coupling constants (Figure S1 in the Supporting Information) shows considerable scatter of the data points and only a loose correlation. In contrast, there is a good relationship between the bond dissociation enthalpies and the ability of the radicals to flatten out as given by the *d* values for the different ring systems (Figure 2).<sup>25</sup> This correlation is consistent with the



**Figure 2.** Plot of bridgehead bond dissociation enthalpies for 1H-3H and 5H-8H versus *d*, a measure of the flexibility of the ring system as described in the text.

commonly held assumption that the more rigid the ring system and the more pyramidal the radical the larger the bridgehead C-H bond dissociation enthalpy.<sup>1g</sup> The radical stabilization energies (RSEs, i.e., BDE(RH) – BDE((CH<sub>3</sub>)<sub>3</sub>C-H)<sup>26</sup> also track with the flexibility of the ring system (i.e., *d*), but the RSEs and BDEs only cover a 12 kcal mol<sup>-1</sup> range. M06-2X/aug-cc-pVDZ computations<sup>27,28</sup> were carried out

M06-2X/aug-cc-pVDZ computations<sup>27,28</sup> were carried out on the *tert*-butyl radical. When it is distorted from its equilibrium structure by carrying out partial geometry optimizations, the energy was found to change by less than 1.5 kcal mol<sup>-1</sup> when the same range in *d* spanned by the bicyclic hydrocarbons is used (i.e., 0.181 – 0.034 or  $\pm$  0.147 Å). This indicates that distorting (bending) the *tert*-butyl radical requires less energy than the bicyclic bridgehead radicals studied herein.

#### CONCLUSIONS

It appears that bridgehead anions from small strained ring systems such as bicyclo[1.1.1]pentane to larger and more flexible hydrocarbons such as bicyclo[2.2.2]octane and possibly even adamantane are stable with respect to electron detachment. This is in accord with weakly bound alkyl anions such as  $CH_3^-$  and  $(CH_3)_3CCH_2^-$  but contrasts with  $CH_3CH_2^-$ ,  $(CH_3)_2CH^-$ , and  $(CH_3)_3C^-$  which are unstable with respect to spontaneous electron detachment (i.e., the corresponding radicals are more stable than their anions). The electron affinity of 1-bicyclo[2.2.1]heptyl radical was large enough to be measured by a titration (bracketing) method (11.8 ± 1.6 [expt] and 10.4 [G3] kcal mol<sup>-1</sup>), whereas the 1-bicyclo[2.2.2]octyl and 1-adamantyl anions were too fragile for us to characterize them in the same way  $(EA(2\mathbf{r}) = 4.6 \pm 1.6 [expt] and 3.4 [G3] kcal mol<sup>-1</sup>, and EA(3\mathbf{r}) = 3.3 \pm 1.8 [expt] and 2.1 [G3] kcal mol<sup>-1</sup>). We therefore measured the acidities of their$ 

conjugate acids using a well-established kinetic method that correlates  $\Delta H^{\circ}_{acid}(R'H)$  to the product ratio of the reaction between hydroxide ion and a series of substituted silanes (i.e.,  $HO^- + R_3SiR' \rightarrow R_3SiO^- + R'H$  and  $R_2Si(R')O^- + RH$ ). Since it was important to use a large R group for dodecahedrane and cubane, a phenyl group was employed in this work. This may play a role for bicyclo [2.2.1] heptane  $(407.5 (R = SiPh_3) vs 414$  $(R = SiMe_3)$  kcal mol<sup>-1</sup>), but appears to be a small issue, if one at all, for bicyclo [2.2.2] octane  $(411.9 (R = SiPh_3) vs 414 (R =$  $SiMe_3$ ) and is unimportant for adamantane. The resulting acidities and the one electron affinity were substituted into a recently reported correlation between  $\Delta H^{\circ}_{acid}(RH)$  and EA(R) for localized carbanions to obtain the other quantity, and this enabled us to determine the homolytic bond dissociation enthalpies for 1H-3H. These bond energies are in accord with the previously proposed order  $(CH_3)_3C-H < 3-H < 2-H < 1-$ H and are consistent with high-level G3 computations. Additional bridgehead bond dissociation enthalpies for bicyclo[1.1.1]pentane, bicyclo[2.1.1]hexane, bicyclo[3.1.1]heptane, and bicyclo[4.2.1]nonane were also calculated using G3 theory and all 7 BDEs examined in this work were found to correlate with the ability of the ring system to flatten out upon formation of the radical. This intuitively reasonable finding suggests that bridgehead C-H bond energies are now finally well established to an accuracy of  $\pm 2-3$  kcal mol<sup>-1</sup>.

#### EXPERIMENTAL SECTION

1-Bromoadamantane and bicyclo[2.2.2]octane-1-carboxylic acid were purchased from a commercial supplier and the Florida Center for Heterocyclic Compounds, respectively, while bicyclo[2.2.1]heptane-1-carboxylic acid and 1-bromobicyclo[2.2.2]octane were kindly provided by Prof. William Adcock.<sup>29,30</sup>

1-Trmethylsilylbicyclo[2.2.2]octane (2SiMe<sub>3</sub>). A solution of trimethylsilylsodium was prepared under a stream of Ar by adding 0.36 mL (1.76 mmol) of hexamethyldisilane dropwise to a suspension of freshly prepared sodium methoxide (from 25 mg of Na and 1.0 mL of methanol) in 0.85 mL of anhydrous hexamethylphosphortriamide (HMPA). After the resulting red solution was stirred for 4 h at ambient temperature, a solution of 0.050 g (0.265 mmol) of 1bromobicyclo[2.2.2]octane in 0.25 mL of dry HMPA was added dropwise over ~10 min and then was allowed to stand overnight with stirring. The resulting reaction mixture was quenched with 3 mL of water and extracted with pentane  $(3 \times 10 \text{ mL})$ , and the combined organic layers were washed with water  $(3 \times 5 \text{ mL})$  and dried over MgSO<sub>4</sub>. Removal of the solvent was carried out by distillation at atmospheric pressure since the product is volatile and vacuum operations are best avoided.<sup>31</sup> Purification of the residue was carried out with a gas chromatograph equipped with a 16' long SE-30/ Chromosorb P column held at 140 °C to afford 10 mg (26%) of 1trimethylsilylbicyclo[2.2.2]octane (mp 66-67 °C (hexanes), lit.<sup>31,32</sup> mp 61–63 °C and 67–68 °C): <sup>1</sup>H NMR (300 MHz,  $CDCl_3$ )  $\delta$  –0.12 (s, 9H), 1.41–1.52 (m, 13H); <sup>13</sup>C NMR (75 MHz,  $CDCl_3$ )  $\delta$  –4.6, 15.6, 24.0, 26.0, 26.2.

**1-Triphenylsilylbicyclo**[2.2.2]octane (2SiPh<sub>3</sub>). A 30% dispersion of sodium in toluene (230 mg, 3.0 mmol) was placed in a roundbottomed flask, and the solvent was removed under vacuum. The pressure was restored to an atmosphere with argon and then 2 mL of dry ether was syringed into the flask. A solution of 221 mg (0.75 mmol) of chlorotriphenylsilane and 19.2 mg (0.15 mmol) of naphthalene in 1.5 mL of anhydrous ether was rapidly added to the reaction vessel.<sup>33</sup> The resulting mixture was stirred for 1 h before adding 0.31 mL (1.8 mmol) of HMPA. This solution turned deep green–black and was stirred for an additional 0.5 h before 56.7 mg (0.30 mmol) of 1-bromobicyclo[2.2.2]octane in 0.5 mL of ether was added by syringe over the course of 2 min. After 0.5 h, the reaction was quenched under argon by the careful dropwise addition of 1.0 mL of water to react away the excess sodium. The resulting solution was acidified with 1.0 mL of 10% HCl and diluted at the same time with 7 mL of CH<sub>2</sub>Cl<sub>2</sub>. After separation of the organic layer, the aqueous solution was extracted twice with 2 mL portions of CH<sub>2</sub>Cl<sub>2</sub>. The combined organic material was washed three times with 1 mL of brine, dried over MgSO<sub>4</sub>, and concentrated under aspirator pressure with a rotary evaporator. Purification of the residue by flash chromatography on a silica gel column with hexane as the eluent afforded 38 mg (35%) of 1-triphenylsilylbicyclo[2.2.2]octane with a melting point of 149–151 °C: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  1.53 (m, 6H), 1.57 (sextet, 1H), 1.82 (m, 6H), 7.34–7.38 (m, 6H), 7.39–7.43 (m, 3H), 7.54–7.57 (m, 6H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  18.8, 24.1, 26.1, 27.8, 127.8, 129.3, 134.9, 137.0; HRMS-CI (NH<sub>3</sub>) calcd for C<sub>26</sub>H<sub>32</sub>SiN (M + NH<sub>4</sub>)<sup>+</sup> 386.2304, found 386.2296.

**1-Triphenylsilyladamantane (3SiPh<sub>3</sub>).** The procedure above was followed using 215 mg (1.0 mmol) of 1-bromoadamantane to afford 188 mg (48%) of **3SiPh<sub>3</sub>** (mp = 167–168 °C): <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 1.78 (m, 6H), 1.88 (m, 3H), 2.03 (m, 6H), 7.34–7.47 (m, 9H), 7.59–7.63 (m, 6H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 24.1, 28.0, 37.6, 39.0, 127.8, 129.3, 134.5, 136.9; HRMS (EI) calcd for C<sub>28</sub>H<sub>30</sub>Si (M<sup>+</sup>) 394.2111, found 394.2100.

1-Trimethylsilyladamantane ( $3SiMe_3$ ). This substrate was prepared as previously described.<sup>34</sup> It had a melting point of 48–50 °C and a <sup>1</sup>H NMR spectrum that was the same as in the literature.<sup>35</sup>

**Gas-Phase Experiments.** A dual cell Fourier transform mass spectrometer (FTMS) equipped with a 3 T superconducting magnet and controlled by a Sun workstation running the Odyssey Software 4.2 package or a data system from Ion Spec running IonSpec99 Ver. 7.0 was used in these studies. A solid probe inlet kept at room temperature was employed to introduce solid samples into the FTMS. For the DePuy kinetic acidity method, hydroxide was prepared by electron ionization (6 eV) of water in the analyzer cell. The OH<sup>-</sup> ions were transferred into the source cell and after an argon pulse up to a nominal pressure of ~10<sup>-5</sup> Torr and a subsequent 700 ms delay, all of the product ions were ejected using a chirp broad band excitation.<sup>36</sup> The reaction of thermalized hydroxide with a static pressure of the neutral species (~2.0 × 10<sup>-8</sup> Torr) was then monitored over time (0.2–4 s) and the product ion ratio was found to be constant.

Fluoride ion was prepared by electron ionization of CF<sub>4</sub> at 7 eV. The resulting F<sup>-</sup> was used to deprotonate bicyclo[2.2.1]heptane-1carboxylic acid and bicyclo[2.2.2]octane-1-carboxylic acid in the source cell. The resulting carboxylate anions were transferred to the other cell where they were thermalized with an argon gas pulse up to a nominal pressure of ~10<sup>-5</sup> Torr. On-resonance collisionally induced dissociation (CID) of these ions resulted in the formation of  $(M - CO_2)^$ ions. The ion derived from bicyclo[2.2.1]heptane-1-carboxylate was isolated using a series of chirp and SWIFT excitations<sup>37</sup> and its reactions subsequently were examined as a function of time.

**Computations.** All of the calculations were carried out at the Minnesota Supercomputer Institute for Advanced Computational Research using the Gaussian suite of programs.<sup>38</sup> G3 energies were computed as previously described in the literature,<sup>18</sup> and M06-2X-augcc-pVDZ<sup>27,28</sup> partial optimizations on  $(CH_3)_3C$  were carried out in  $C_{3\nu}$  symmetry at fixed out-of-plane angles at the carbon radical center.

## ASSOCIATED CONTENT

#### Supporting Information

Computed MP2(full)/6-31G(d) geometries and G3 energies, heats of formation, and strain energies are provided along with experimental  $\Delta H^{\circ}_{\rm f,298\,K}$  values, a plot of bridgehead C–H BDEs vs  $^{13}C-^{1}H$  coupling constants, the  $^{1}H$  and  $^{13}C$  NMR spectra of **2SiPh\_3** and **3SiPh\_3**, and the complete citation to ref 38. This material is available free of charge via the Internet at http:// pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

#### ACKNOWLEDGMENTS

We thank Professor William Adcock for kindly providing us with samples of bicyclo[2.2.1]heptane-1-carboxylic acid and 1bromobicyclo[2.2.2]octane. Generous support from the National Science Foundation, the Petroleum Research Fund, and the Minnesota Supercomputer Institute for Advanced Computational Research are also gratefully acknowledged.

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