

FULL PAPER

μ -H-Bridged Bicyclo[3.3.3]undecyl Cations. Theoretical Calculations of Physical and Chemical Properties

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Abstract μ -H-Bridged carbocations **1** and **2**, which are still unknown experimentally, are structures with fascinating possibilities as intermediates for the synthesis of very strained in-bicyclic and tricyclic alkanes and alkenes. They are also expected to possess record high pK_a values. In conjunction with our experimental program to try to prepare **1** and **2**, we have carried out *ab initio* calculations on these structures and various reference compounds, with the aim of assessing just how stable these cations might be, and what physical and chemical properties they might possess. The results of these studies confirm that **1** and **2** should be viable species; they have energies similar to those of the conventional out-cations, and the μ -H bond distances are not very different from those calculated for known μ -H cations. The calculated ^1H NMR chemical shift for the μ -H of **1** is -12 ± 0.5 and -9.5 ± 0.5 for **2**, both values considerably more negative than in known μ -H cations. The possible effect of large amplitude motions of the μ -H on the ^1H NMR chemical shift was investigated and not found to be significant. The pK_a s for **1** and **2** are estimated to be 17-18 with respect to an alkene conjugate base, a virtually unimaginable size for a formally alkyl cation. The paper also discusses the possibility of the μ -H being involved in the acid-conjugate base chemistry, since this is shown to be a hugely exothermic reaction. Finally, the alkenes and alkanes associated with cations **1** and **2** have been calculated, the in-alkene **7** from cation **1** is shown, for example, to possess a large steric strain, yet this structure should be accessible *via* deprotonation of **1** with a strong base.

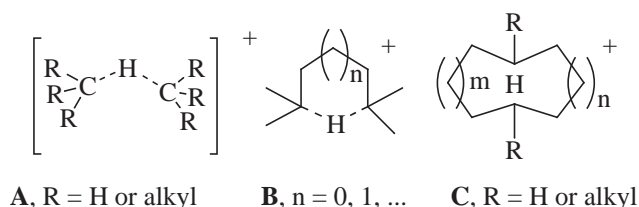
Keywords *ab initio*, μ -H-bridged carbocations, NMR shift calculations, In-bicycloalkenes, Carbocation pK_a

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Dedicated to Professor Paul von Ragué Schleyer on the occasion of his 70th birthday

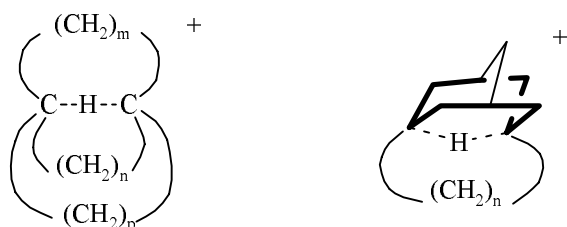
Introduction

A number of observable μ -H-bridged carbocation structures have been characterized as *in situ* solution species.[1,2] No acyclic examples **A** are known [3] in solution, nor have single ring structures **B** been observed.[4] For double ring structures **C**, μ -H-bridged ions have been prepared for cases where the carbon ring has a total of 8-11 atoms (medium rings).[1]



In bicyclic and tricyclic carbon frameworks, several μ -H cations have been described.[1] McMurry has described four systems having the **D** skeleton,[1,2] while Sorensen and Whitworth have studied [5] the tricyclic system **E**. As opposed to **A-C**, such caged structures potentially give one the opportunity to closely regulate the encapsulating distances

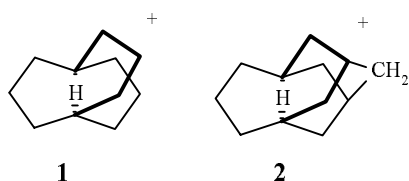
$\text{>C}^{\text{d}_1}\text{-H}^{\text{d}_2}\text{-C}^{\text{d}_3}\text{<}^+$ by varying the number of carbons in the m, n and p chains of **D**, or the value of n in **E**.



D (m + n + p = 12 or 13)

E, n = 5-8

This laboratory has recently been involved in attempts to prepare the μ -H-bridged bicyclo[3.3.3]undecyl cation **1**. With a total of 9 carbons in the m, n and p bridges of **D**, this structure represents a substantial leap in terms of compressing the volume available for the μ -H. A parallel approach has involved attempts to experimentally prepare the tricyclic cation **2** (**E**, with n = 3). In terms of the primary rings encapsulating the μ -H, **1** and **2** are identical, but "tying back" two of the rings potentially creates a larger opening into the encapsulating cavity.



1

2

In the study which follows we have carried out theoretical calculations involving cations **1** and **2**, and various other structures needed for comparison purposes. The main intent of the calculations can be summarized: (1) from an energy viewpoint, how stable are these structures? (2) how do the struc-

tures compare to the larger ring analogs? (3) in terms of possible *in situ* experimental preparation, what ^1H NMR chemical shift value might be expected for the μ -H, and how does this compare with the larger ring analogs? (4) finally, in anticipation of a possible isolation of salts of **1** or **2**, or the corresponding neutral products, what pK_a values would one estimate for cations **1** and **2**?

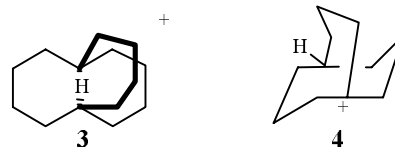
Details of the calculations

Unless indicated otherwise, all structures were optimized at the B3LYP/6-31G* level [6] using either the Gaussian 94 or 98 suite of programs.[7] In all cases, frequency calculations were performed to obtain ZPVE values and thermal corrections for 298K, using a 0.98 correction factor in each case. All ΔE and ΔG values include these corrections. ΔG_{298}^0 values were evaluated by including the calculated TS_{298}^0 term. NMR calculations employed the GIAO option with the 6-31G* basis set (B3LYP). Molecular mechanics (MM3) calculations were carried out using the Spartan program.[8]

Results and discussion

Geometry and energies of cations **1** and **2**

Cation 1 The structure of this cation in the most favorable conformation is shown in Figure 1, optimized at the B3LYP/6-31G* level of theory. The μ -H adopts a linear C—H—C geometry, and the C—H bond distances are both 1.176 Å (symmetrical μ -H bond). The hybridization of the bridgehead carbons is close to sp^2 , angle ($\mu\text{-H-C}_{\text{bridgehead}}\text{-CH}_2$) = 93.9°, meaning that the μ -H bonding involves nearly pure p_z orbitals on the two bridgehead carbons. Cioslowski has previously computed [9] the bicyclo[4.4.4]tetradecyl cation **3**, where the C—H—C distance is somewhat longer than calculated for **1** (1.23 Å), also with a linear geometry. The hybridization of the bridgehead carbons is intermediate between sp^2 and sp^3 . These parameters for **3** are similar to those calculated [3] for tBu—H—tBu⁺ and can therefore be regarded as typical for an unstrained μ -H bond in cations with tertiary end groups. It is clear from a comparison of **1** and **3** that the bicyclo[3.3.3]undecyl framework is imposing some bond compression and hybridization "strain" in the corresponding μ -H cation system **1**, but the energy consequences of this strain are unknown.



3

4

Table 1 Energy Comparisons (in kcal mol⁻¹) for Cations 1-4 and 2-5

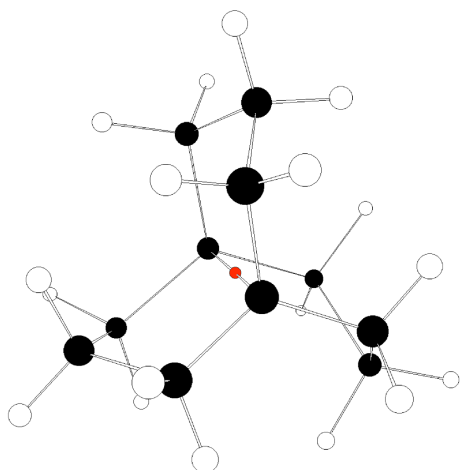
	1	4	2	5
Relative free energy B3LYP/6-31G*	+5.9	0	+17.0	0
MP2(Full)/6-311+G**// B3LYP/6-31G*	-3.0	0	+1.7	0

Another approach to assessing the energy of **1** is to compare this structure with the isomeric out-H monocation **4**. Cation **4** has been prepared *in situ* in superacid media,[10] and is a known solvolysis intermediate.[11] Energy comparisons are shown in Table 1, where one notes that the calculated energy difference between **1** and **4** is small, and that the MP2(Full)/6-311+G**//B3LYP/6-31G* energy calculation actually favors the μ -H structure **1**.

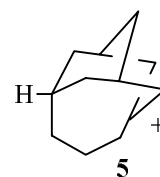
Although the bicyclo[3.3.3]undecyl ring system itself is quite strained, we conclude that the μ -H cation structure, i.e. presence of the internal hydrogen, is not creating much additional strain.

Cation 2 The optimized structure of cation **2** is shown in Figure 2. In this structure the μ -H is not entirely linear with respect to the associated bridgehead carbons, having C—H—C bond distances of 1.213 Å and a $\text{C} \begin{array}{c} \text{H} \\ \curvearrowright \end{array} \text{C}$ angle of 161.1°.

The angle $\mu\text{-H-C}_{\text{bridgehead}}\text{-CH}_2$ (three carbon bridge) is 88.8° which, like **1**, indicates an sp^2 hybridization of the bridgehead carbons and a μ -H bonding involving a nearly pure p_z orbital on each carbon. Like **1**, cation **2** should also mildly suffer from C—H—C bond compression steric strain, as well as a non-optimal bridgehead hybridization.

**Figure 1** Optimized geometry of μ -H cation **1** in the most stable conformer

In order to more accurately gauge the energy of **2**, we have carried out the identical comparison used for **1-4**, i.e. a comparison with the out-cation **5**, and these results are listed in Table 1. Cation **5** has not been reported previously, but has recently been prepared in this laboratory.

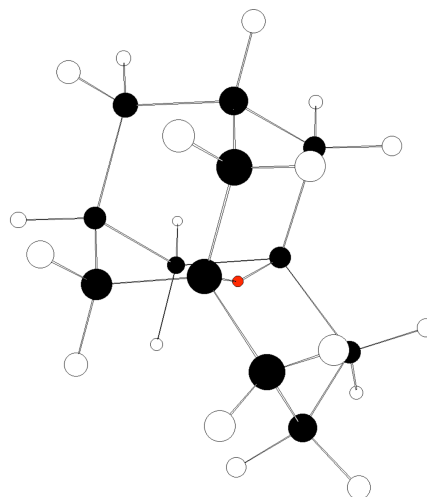


Overall, the comparison of **2** vs **5** is quite similar to that observed for **1** vs **4**, with the calculated μ -H structure **2** marginally less stable than **1** when compared to their corresponding out isomers.

Calculated physical properties of **1** and **2**

NMR chemical shift of the μ -H One possible route to the preparation of **1** (or **2**) would be to prepare the bridgehead dication, and then hope to abstract an external hydride into the inner dication mid-point. It was thought that even very minor amounts of **1** (or **2**) could be detected by ¹H NMR since it is known [1] that this hydrogen occurs at uniquely high fields (*ca.* -3 to -8 ppm) in other μ -H cations.

When this study was begun, there were indications from the work of Cioslowski,[9] and other unpublished results,[12] that calculated chemical shifts for μ -H's were much too negative compared to experiment, e.g. for the [4.4.4] structure **3**, calculated [9] (HF/6-311G*/GIAO-CPHF) -10.06, observed [2] -3.46, and this same trend initially looked as if it might

**Figure 2** Optimized geometry of μ -H cation **2** in the most stable conformer

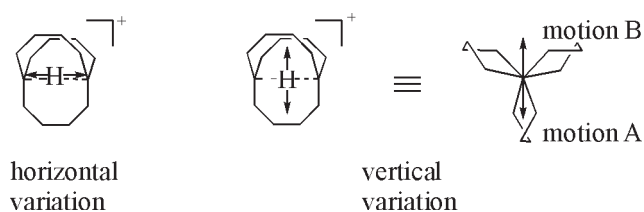


Figure 3 Fixed movement directions of the μ -H in cation **3** as employed in the calculations used to generate Figures 4 and 5

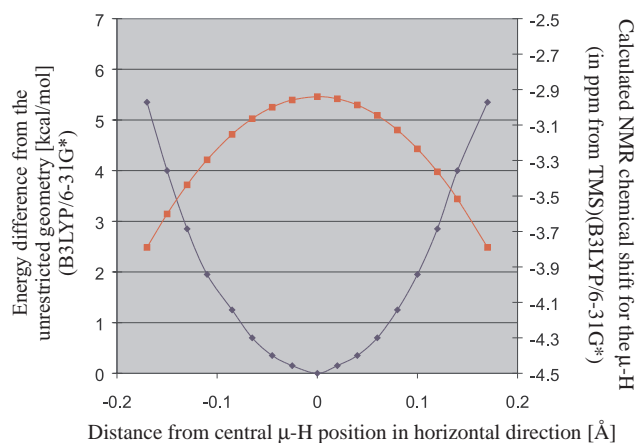


Figure 4 Chemical shift profile (red) and overall energy (blue) of cation **3** as the μ -H is moved in the horizontal direction

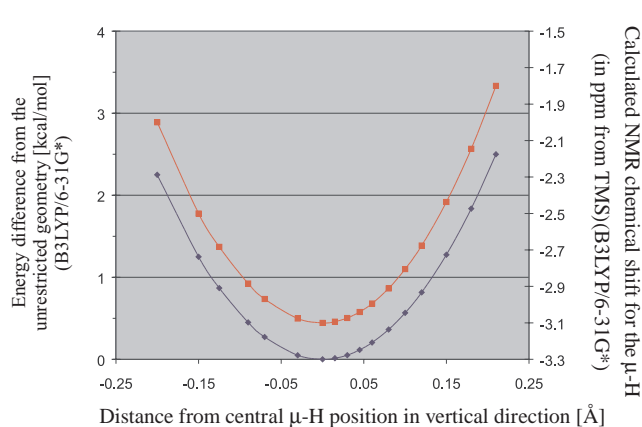


Figure 5 Chemical shift profile (red) and overall energy (blue) of cation **3** as the μ -H is moved in the vertical direction (motion B, positive numbers, motion A, negative numbers)

be true for **1** since values of *ca.* -12 ppm (see below) were calculated in our work (GIAO/B3LYP/6-31G*) for the μ -H of **1** (no comparison to experiment being possible).

Cioslowski had suggested that one possibility for the discrepancy between his calculated value for the μ -H of **3**

(-10.06) and the experimental value of -3.46 , was that since the potential energy surface (PES) for μ -H movement was very flat, the actual time-averaged μ -H position and that calculated for the Born-Oppenheimer surface was significantly different. We were interested therefore in following up on this suggestion.

A series of NMR calculations were performed with cation **3**, where the μ -H was artificially moved relative to the symmetric Born-Oppenheimer surface minimum. The μ -H was moved in three different directions, as shown in Figure 3, all other structural parameters being kept constant. One can argue that if the PES for μ -H movement is very flat, then other atoms may not change their positions significantly. The energy and NMR chemical shift profiles for the three movements are shown in Figures 4 and 5.

The major finding is that the chemical shift of the μ -H does not really change very much as a function of these geometry changes, particularly if one restricts the energy range to values typical of thermal motions. A second observation is that in-plane movement of the μ -H leads to slightly more negative δ values, while out-of-plane changes lead to less negative numbers, so that the overall effects tends to cancel.

However, the most unexpected observation was that the chemical shifts being calculated for **3** were all quite close to the experimental value. In recently reported calculations, Galasso [13] has also found that the newer NMR programs (the CSGT method in Guassian 94) give good agreement between experiment and theory.

Possibly because of the flat PES for the μ -H in cation **3**, the optimized geometries of this structure are slightly different at the B3LYP/6-31G* (present study) and the MP2/6-31G** (reference [9]) levels of theory. Specifically, the C---H---C distance for the latter method is 2.462 \AA vs 2.535 \AA for the former. A series of NMR calculations of the μ -H chemical shift were carried out, where the above distance was fixed at set values, and these results are shown in Figure 6. A separation of 2.493 \AA would exactly match the experimental value of -3.46 ppm. This distance is between those calculated with the above methods, which suggests that the B3LYP procedure slightly overestimates the distance, while the MP2 method underestimates it.

These detailed NMR calculations on the known [4.4.4] system **3** give one considerable confidence that the following NMR results calculated for the μ -H of cations **1** and **2** will also be close to experimental reality.

Calculated NMR chemical shift for cation 1 At the GIAO/B3LYP/6-31G* level, the μ -H of **1** was calculated as -12.02 ppm. As with cation **3** (previous section), we also looked at variations in this chemical shift in **1** as one moved the μ -H in the directions shown in Figure 7.

The results are shown graphically in Figures 8 and 9. As expected, the energy profile for the μ -H in **1** involves a much tighter encapsulating volume than in cation **3**. However, one sees the same effects, in-plane motion leads to more negative chemical shifts as opposed to the opposite trend for the out-of-plane motion, but overall these effects are fairly small and

Figure 6 Calculated chemical shift of the μ -H in cation **3** as a function of the bridgehead carbons separation

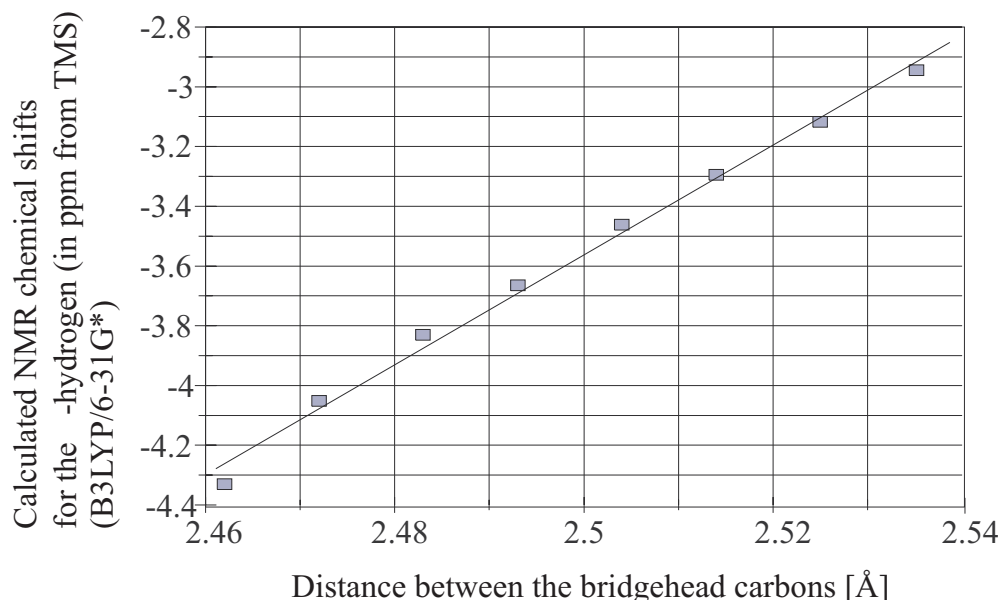
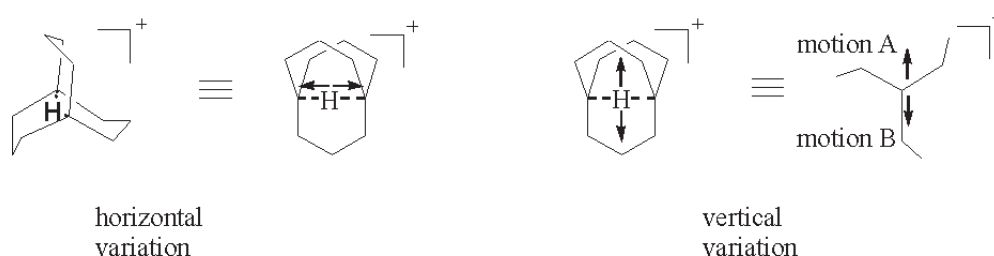


Figure 7 Fixed movement directions of the μ -H in cation **1** as employed in the calculations used to generate Figures 8 and 9



tend to cancel. A calculated value of -12 ± 0.5 ppm for the μ -H of **1** is thus expected to be a good estimate of the actual chemical shift and is about 4 ppm higher field than in any of the presently known μ -H cations.

Calculated NMR chemical shift for cation 2 The μ -H in cation **2** had a calculated chemical shift of -9.47 ppm, and movement of the μ -H (not shown) in the in-plane and out-of-plane directions produced similar results to those shown for **1**. Thus a chemical shift value of -9.5 ± 0.5 ppm is a good estimate of the expected experimental value. The μ -H in **2** is slightly displaced outside the shortest C—C line (see earlier discussion) and this may account for the somewhat lower field chemical shift compared to **1**.

*Estimated pK_a values for **1** and **2** and the possible synthesis of very strained inside-pyramidalized alkanes and alkenes*

Previous studies of the μ -H cations **3** and **6** have demonstrated that these structures are extraordinarily stable, in the pK_a sense, compared to normal alkyl cations [1] (pK_a s estimated *ca.* -1 to 4). This much weaker acidity arises from the ability of these cations to utilize the μ -H in a favorable bonding mode compared to that in the deprotonated alkenes, where the inside pyramidalized hydrogen causes a large steric strain.

Cations **1** and **2** are expected to show even more unusual pK_a behavior since these μ -H cations, while having some strain involving the μ -H, have conjugate base alkenes where the inner pyramidalization causes severe steric strain. In order to quantify this effect we undertook to calculate the ge-

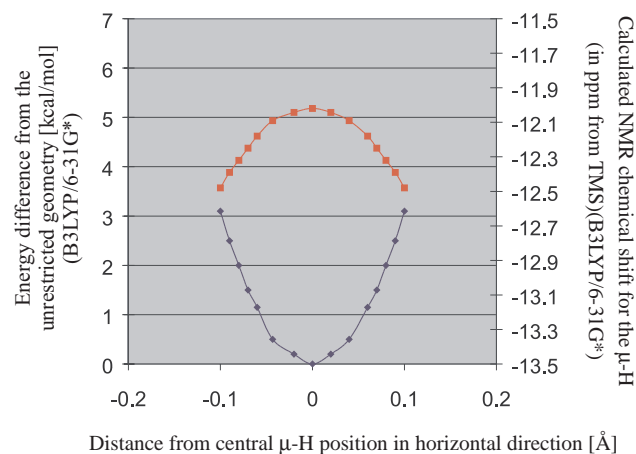
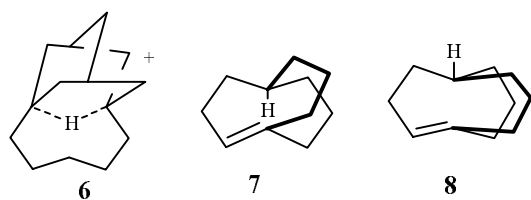


Figure 8 Chemical shift profile (red) and overall energy (blue) of cation **1** as the μ -H is moved in the horizontal direction

ometry and energy of the alkenes and alkanes associated with these cations. Also, in order to devise an approximate pK_a working curve for estimating the pK_a of **1** and **2**, we calculated the energies of several other carbocations and their alkene conjugate bases (including cations **3** and **6**).



Cation 1 system The structure of the most stable conformer of the alkene produced from the conventional deprotonation of **1** (structure **7**) is shown in Figure 10. The inner pyramidalized hydrogen is clearly well within van der Waals radii of other atoms in the molecule. An estimate of this strain energy ($38.1 \text{ kcal mol}^{-1}$) can be obtained by a comparison with the out-alkene **8**, as given in Table 2. This value does not represent the total strain present in **7** because **8** itself is quite strained ($45.5 \text{ kcal mol}^{-1}$ from MM3 calculations).

By way of contrast, known alkene **9** in the [4.4.4] system is calculated to be $6.8 \text{ kcal mol}^{-1}$ more stable than the out-isomer, in agreement with experimental results [2] and previous calculations at the molecular mechanics level.[14]

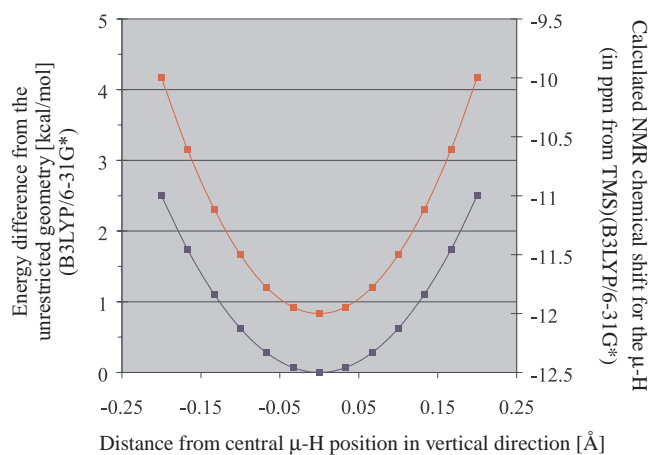
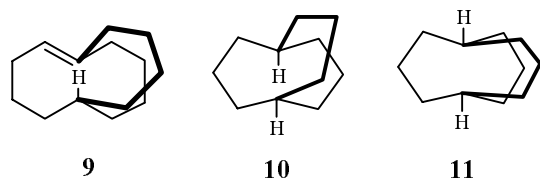
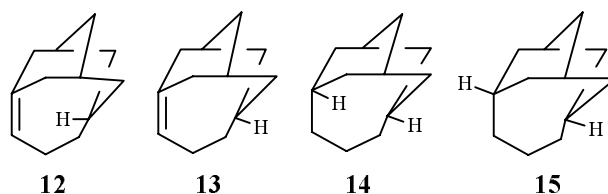


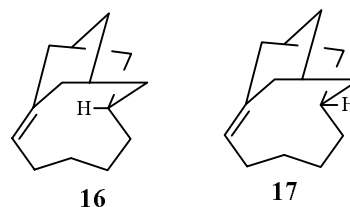
Figure 9 Chemical shift profile (red) and overall energy (blue) of cation **1** as the $\mu\text{-H}$ is moved in the vertical direction (motion B, positive numbers, motion A, negative numbers)

Acid-conjugate base relationships in cations can involve either a deprotonation to give an alkene (pK_a) or addition of a nucleophile (usually water) to give an alcohol (pK_{R^+}). Previous studies [1] with cations **3** and **6** showed no evidence for a pK_{R^+} -type equilibrium, presumably because an alcohol with in-H-pyramidalization is not much more stable (in a relative sense) than the alkene. Calculations on the [3.3.3] system bear this out, the two alkanes **10** and **11** (reasonable models for the corresponding alcohols) differ in energy by $32.0 \text{ kcal mol}^{-1}$, i.e. not very different from the alkene comparison **7** vs **8** (see Table 2).

Cation 2 system Cation **2** has two possible alkene conjugate bases, but formation of the double bond in the three carbon bridge is the more stable computed structure (**12**) and this is shown in Figure 11. Comparison to the out-isomer **13** yields a relative strain energy of $46.1 \text{ kcal mol}^{-1}$ (Table 2). The corresponding hydrocarbon comparison **14** vs **15** (Table 2) gives $34.7 \text{ kcal mol}^{-1}$ added strain.



These comparisons can be contrasted with the behavior of the known cation **6**, where the most stable alkene conjugate base **16** is computed to be only $7.0 \text{ kcal mol}^{-1}$ less stable than the corresponding out-isomer **17** (Table 2).



pK_a Estimates for **1** and **2**

In Figure 12 we show a plot of the calculated ΔG differences between carbocation and conjugate base alkene for several systems vs some experimental pK_a estimates. Gas-phase measurements of pK_a -like equilibria ignore both the sizeable (and variable) solvation energies of the cation and the proton (the a_{H^+} term in solution). However, there is expected to be some approximate linearity between calculated ΔG (cation-alkene)_g and experimental pK_a s, and we have used cations **3** and **6** in Figure 12 as “anchoring” systems, along with very approximate pK_a estimates for a substituted norbornyl system and the t-butyl cation.[15]

Table 2 Calculated Total Energies for Neutral Compounds 7-17 and 19-22 and of Cations 3, 6 and 18. Energy Comparisons of Isomeric Structures

Structure	Total E ^a	ZPVE ^b	H ^o ₂₉₈ -H ^o ₀ ^b	S ^o ₂₉₈ ^c	ΔG ^o ₂₉₈ ^d
7	-429.904797	169.2	6.5	91.8	38.1
8	-429.966762	170.0	6.5	91.7	0.0
9	-547.907999	224.2	8.7	108.1	0.0
9 (out-H)	-547.898296	224.9	8.8	108.3	-6.9
10	-431.157507	184.6	6.6	92.8	32.0
11	-431.209183	185.2	6.7	93.7	0.0
12	-468.015560	174.1	6.2	90.2	46.1
13	-468.090121	174.8	6.2	90.2	0.0
14	-469.269009	189.9	6.5	92.2	34.7
15	-469.324664	190.1	6.5	92.9	0.0
16	-546.708796	211.0	7.7	101.2	7.0
17	-546.720619	211.4	7.7	101.2	0.0
19	-507.359037	192.8	7.1	97.1	26.4
19 (out-H)	-507.401471	193.1	7.1	96.8	0.0
20	-430.024268	169.8	6.3	90.8	-74.3 vs 7
21	-546.751093	211.4	7.3	98.3	-25.7 vs 16
22	-468.125527	174.8	5.9	88.6	-68.2 vs 12
3	-548.286801	230.5	8.6	106.5	
6	-547.088677	216.8	7.8	101.2	
18	-507.767801	199.1	7.0	95.8	

[a] hartrees

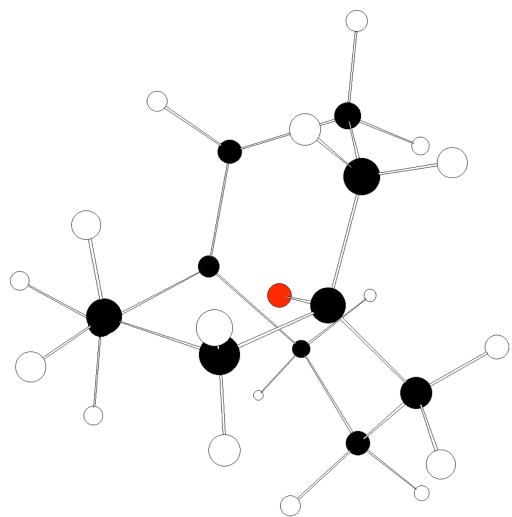
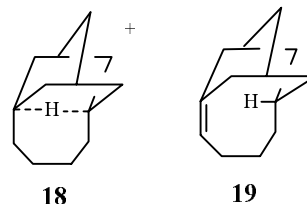
[b] kcal mol⁻¹

[c] cal/mol K

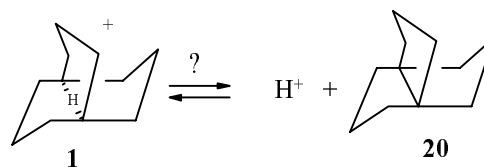
[d] HF + 0.98 (ZPVE+ (H^o₂₉₈-H^o₀)) -0.98 (298.15 S^o₂₉₈), compared to the corresponding out-isomer or as shown.. For a discussion of the 0.98 correction factor see ref. [16].

Although this correlation is admittedly very approximate, it seems clear that μ-H cations **1** and **2** would have high pK_a values of record breaking magnitude, ca. 17-18. Figure 12 also includes unknown cation **18** (and alkene **19**), a μ-H cation which would be expected to have a pK_a value intermediate

between cations **2** and **6**, and this is indeed what is calculated (see Figure 12).

**Figure 10** Optimized geometry of in-bicyclo[3.3.3]undec-1-ene 7. The in-hydrogen is only 1.551 Å from the other bridgehead carbon

One might wonder whether the μ-H of cation **1** could be involved in an acid ⇌ conjugate base equilibrium?



In the known cations **3** and **6**, there is no evidence that such equilibria are possible, see reference [1] for details. In this work we have calculated that the hypothetical equilibrium, **6** ⇌ H⁺ + **21**, would be 25.7 kcal mol⁻¹ more

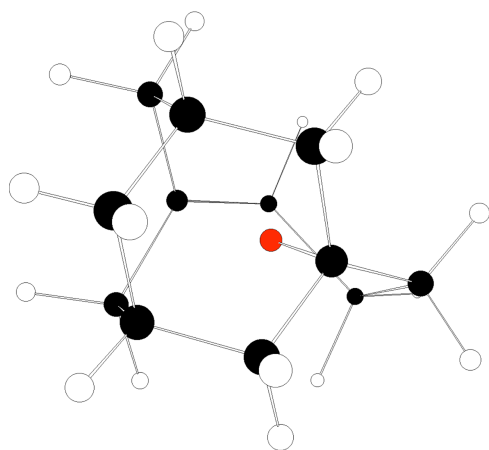
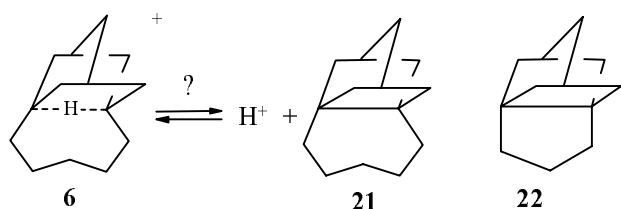


Figure 11 Optimized geometry of 7-in-tricyclo[5.3.1.1]-dodec-3-ene **12**. [3,9] The in-hydrogen is 1.595 Å from the opposite bridgehead carbon

favorable than that for the actually observed, $6 \rightleftharpoons H^+ + 16$, equilibrium. As expected, this energy difference becomes even larger in the case of cations **1** and **2**, where the corresponding hydrocarbons **20** and **22** are calculated to be 74.3 and 68.2 kcal mol⁻¹ more stable than the isomeric alkene conjugate bases **7** and **9** (Table 2). Because of the extreme exothermicity calculated for the $1 \rightarrow 20$, and $2 \rightarrow 22$ cases, compared to the alkenes, one cannot be totally confident that the μ -H loss as a proton would not occur, but we have previously discussed this reaction in terms of an unallowed HOMO-LUMO interaction.[1] A μ -H hydrogen is also sterically well protected.



Possible μ -H carbocation route to in, out-bicyclic and tricyclic structures

In,out-Bicyclo[3.3.3]undecane is an unknown structure and the synthesis of this compound by conventional approaches appears formidable. The synthesis of the corresponding μ -H cation **1** also represents a considerable challenge, particularly since known routes to these structures involve the prior preparation of the in-alkene or in,out-alkane. Obviously one needs new methodologies for the preparation of cation **1**, and as previously mentioned, a route in which a hydride equivalent is added internally to the known bridgehead dication would be one possibility.

Conclusions

In contrast to the large energy difference calculated for the in- and out-bicyclo[3.3.3]undec-1-enes **7** and **8** (38.1 kcal mol⁻¹), or the in,out- and out,out-bicyclo[3.3.3]undecanes **10** and **11** (32.0 kcal mol⁻¹), the corresponding μ -H carbocation **1** and its isomeric out-carbocation **4** have quite similar calculated energies, even favoring the μ -H cation at the MP2/6-311+G** level of theory. Thus a preparation of the μ -H cation **1** might be the most feasible approach for preparing the alkene **7** or alkane **9**.

A similar situation exists for the tricyclo[5.3.1.1]dodecyl system, [3,9] where the in- and out-alkenes **12** and **13**, and the in,out- and out,out-alkanes **14** and **15** are even more divergent in energy, 46.1 and 34.7 kcal mol⁻¹, respectively.

The ¹H NMR chemical shift for the μ -H in **1** (ca. -12 ± 0.5 ppm) and **2** (ca. -9.5 ± 0.5 ppm) has been calculated. The known μ -H bicyclo[4.4.4]tetradecyl cation **3** was used as a measure of the reliability of these NMR calculations, an exact fit of experimental vs calculated μ -¹H chemical shift occurring at a $\begin{matrix} C \cdots H \cdots C \\ \longleftarrow \quad \quad \longrightarrow \\ d \end{matrix}$ distance of 2.493 Å, a distance intermediate between that found for MP2/6-31G** (2.462 Å) and B3LYP/6-31G* (2.535 Å) optimized geometries.

It is shown in our NMR computational study that a combination of in-plane and out-of-plane motions of the μ -H in **1**, **2** or **3** would not cause much change in the averaged chemical shift of the μ -¹H peak.

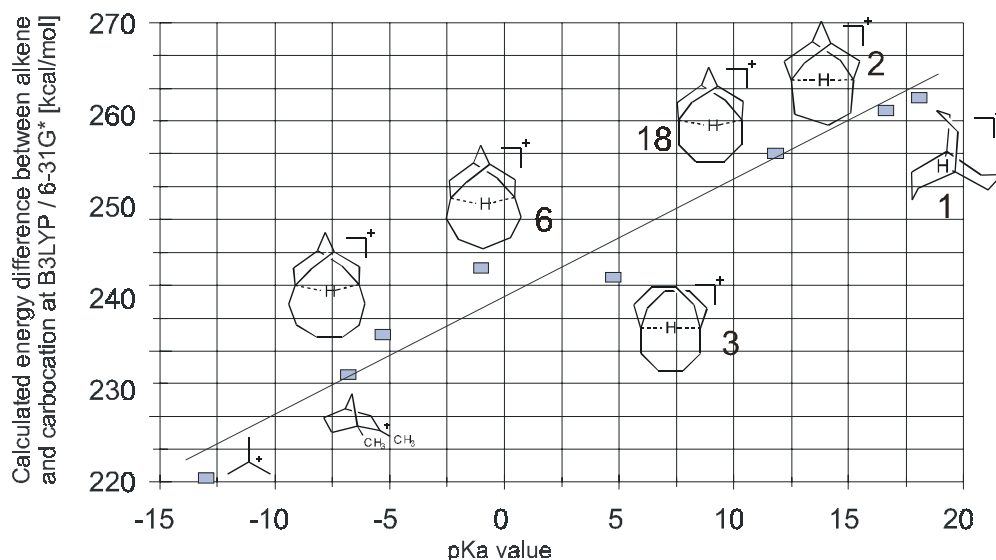
The pK_a of **1** and **2** has been estimated using an empirical correlation, both cations having a predicted pK_a of 17-18, i.e. stable in strong alkali.

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Figure 12 Plot of calculated ΔG_{298}^0 values (alkene-carbocation) vs some experimentally estimated pK_a values for model carbocations. The pK_a s for the unknown cations 1, 2 and 18 are extrapolated estimates



- (favoring $t\text{Bu}^+$) overcome the gas-phase stabilization energy that is being calculated.
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