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μ-Hydrido Bridging between Secondary and Tertiary "Carbocationic" Ends and the Analogy to Unsymmetrical Allyl Cations

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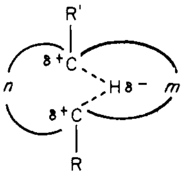
Abstract: From a detailed study of a series of observable tertiary 1-R-cyclooctyl$^+$ cations, R = OH, phenyl, c-Pr, Me, Et, *i*-Pr, and *t*-Bu, the first evidence for unsymmetrical μ-hydrido bridging between secondary–tertiary carbon ends, $\gt$C··H··CH$\lt^+$, is presented. Previously, only symmetrical bridging of the secondary–secondary and tertiary–tertiary type had been described. All of these bridged cations can be treated as nearly "open" three-center, two-electron σ-resonance systems, and the symmetrical and unsymmetrical subtypes can be compared to the rather analogous symmetrical and unsymmetrical π-resonance allyl cations. Both experimental and theoretical results confirm that the potential for the linear approach of a "secondary" H–C–H bond to a tertiary C$^+$ center is virtually flat and the consequence of this in medium-ring cycloalkyl cations is that only very subtle changes in the tertiary C$^+$ center (by varying R) are needed to cause a large variation in this $C_{sec}\cdots H\cdots C_{tert}{}^+$ bonding situation, which can be probed by using ^{1}H and ^{13}C chemical shifts, ^{13}C–^{1}H coupling constants, and a novel equilibrium deuterium isotope effect. The results in this paper are also relevant to a detailed understanding of more general hydride-transfer reactions.

Previously we have reported the in situ preparation of disecondary μ-hydrido-bridged carbocations,[1] **1**, R = R′ = H, and



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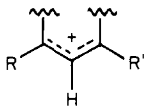
the corresponding ditertiary analogues,[2] **1**, R = R′ = CH_3 or alkyl. The prospects for observing the still missing secondary–tertiary counterpart, i.e., R = H and R′ = CH_3 or alkyl, did not appear on the surface very promising, since we naively imagined that the negatively charged μ-hydrogen might be rather precariously balanced only when the two carbon "ends" were equally charged, i.e., symmetrical, and that in hypothetical unsymmetrical cases the hydrogen would simply form a normal C–H bond to the secondary carbon end, leaving behind a "normal" tertiary carbocation. It is well-known that secondary carbocations are 10–15 kcal/mol less stable than isomeric tertiary analogues.[3]

However, when one visualizes these μ-hydrido-bridged carbocations in terms of a resonance system analogous to the allyl cation, the prospects look more promising. Secondary–tertiary allyl cations, e.g., **2**, R = H and R′ = CH_3, are well-known and generally conceded (I.C.R. studies,[4] theoretical calculations,[5] direct observation[6]) to involve a resonance interaction which, although smaller than in symmetrical cases, is nevertheless significant.



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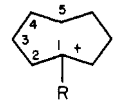
In any case, in a series of alkyl-substituted cyclooctyl cations (all formally tertiary), one observes very definite indications for partial μ-hydrido bridging of this unknown secondary–tertiary type. The actual delocalization is surprisingly dependent on the individual R alkyl group in **1** ($n = m = 3$). By varying R, we can observe a gradation of structural types beginning with the very weakest long-range transannular interaction all the way to situations nearly resembling the symmetrically bridged examples, in fact offering unique "stop action" spectroscopic glimpses at the probable progress of a normal hydride-transfer reaction $\gt C^+$ H–C$\lt$ $\rightarrow$ $\gt$C–H $^+C\lt$. The results of ab initio MO calculations, also carried out in this study, closely parallel the experimental observations.

Results

Initially in this study, we prepared a series of 1-R-cyclooctyl cations, **3**, where R = phenyl, OH, cyclopropyl, methyl,[7] ethyl,[8] isopropyl, and *tert*-butyl. The cations were then characterized by ^{1}H and ^{13}C NMR spectroscopy and the relevant chemical shifts are gathered together in Table I.



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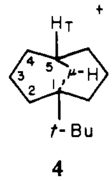
A difficulty in interpreting the experimental ^{1}H and ^{13}C NMR chemical shifts of new carbocations lies in the establishment of what one might term the "normal" or "expected" results, for comparison of course to various "divergent" experimental results. We refer in particular to the NMR (and other) properties of the 1-*tert*-butylcyclooctyl cation, **3**, R = *t*-Bu, which we confidently interpret in terms of an unsymmetrical μ-hydrido-bridged structure **4**.[9]



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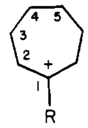

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(1) (a) Kirchen, R. P.; Sorensen, T. S. *J. Am. Chem. Soc.* **1979**, *101*, 3240. (b) Kirchen, R. P.; Sorensen, T. S.; Wagstaff, K. *Ibid.* **1978**, *100*, 6761.

(2) (a) Kirchen, R. P.; Sorensen, T. S. *J. Chem. Soc., Chem. Commun.* **1978**, 769. (b) Kirchen, R. P.; Ranganayakulu, K.; Rauk, A.; Singh, B. P.; Sorensen, T. S. *J. Am. Chem. Soc.* **1981**, *13*, 588.

(3) Arnett, E. M.; Petro, C. *J. Am. Chem. Soc.* **1978**, *100*, 5408 and references contained therein.

(4) Aue, D. H. Poster session, Sixteenth Conference on Reaction Mechanisms, Williamsburg, Va., June 1976.

(5) Mayr, H.; Förner, W.; Schleyer, P. von R. *J. Am. Chem. Soc.* **1979**, *101*, 6032.

(6) Olah, G. A.; Mayr, H. *J. Am. Chem. Soc.* **1976**, *98*, 7333.

(7) Kirchen, R. P.; Sorensen, T. S. *J. Am. Chem. Soc.* **1978**, *100*, 1487.

(8) Kirchen, R. P.; Sorensen, T. S.; Wagstaff, K. E. *J. Am. Chem. Soc.* **1978**, *100*, 5134.

(9) However, we do not want to make a big distinction between the *t*-Bu-substituted cation and some of the others since one has here an unparalleled view of the *gradual* way in which transannular μ-hydrido bridging develops in response to the increasing "need" for delocalization. This theme is developed later in this paper.

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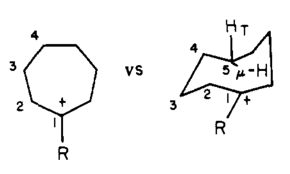
Table I. Relevant ^{13}C and ^{1}H NMR Chemical Shifts of the Cations[a]



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	R							
	Me	Et	*i*-Pr	*t*-Bu	Ph	c-Pr	OH	ketone
C-1 (7-ring)-^{13}C	327.5[b]	334.8	331.1[d]	332.9	263.3	292.1	252.9	215.0[f]
C-1 (8-ring)-^{13}C	334.3[b]	332.5[c]	313.0	249.7[e]	270.5	299.7	257.6	218.0
difference (ppm)	−6.8	+2.3	+18.0	+83.2	−7.2	−7.6	−4.7	−3.0
C-4 (7-ring)-^{13}C	27.5[b,g]	28.8[g]	28.8[d,g]	28.4[g]	28.8[g]	30.5,[g] 28.5[g]	29.6[g]	30.6[f]
C-5 (8-ring)-^{13}C	34.4[b]	37.9	56.1	105.7	29.7		26.7	24.9[f]
difference (ppm)	−6.9	−9.1	−27.3	−77.3	−0.9		+2.9	+5.7
H_T (8-ring)	2.56[h]	2.64[h]	3.85[h,i]	5.9	2.26[h]		2.38[h]	1.70[k]
μ-H (8-ring)	−0.72[i]	−0.84[i]	−2.38[j]	−6.3[j]	0.21[j]	0.5	0.62[j]	0.71[k]
difference (ppm)	3.28	3.48	6.23	12.2	2.05		1.76	0.99

[a] Shifts for ^{13}C in δ (ppm) relative to $CFCl_3$ (δ 117.9), ^{1}H shifts are also δ (ppm) relative to external Me_4Si or internal $CHCl_3$. The remaining peaks for unreported ions are listed in the Experimental Section together with some coupling constant data, temperatures, etc. [b] Previously reported.[7] [c] Previously reported.[8] [d] Small temperature dependence of the C-1 and α-CH carbons is indicative of a very small population of the exocyclic cation isomer. [e] Temperature dependent; see ref 13. [f] Previously reported.[37] [g] Previously we assigned the C-4 carbon to the highest field peak in the ^{13}C spectrum, but we have now reassigned this to C-3 on the basis of the 1,4-dimethylcycloheptyl cation spectrum. This point is unimportant for our analysis since both C-3 and C-4 will have similar chemical shifts, regardless of which is which. [h] Extrapolated from position of the averaged H_T–μ-H signal obtained at much higher temperatures. As discussed in the paper, all of the ions show a line-broadening interchange process, $H_T \rightleftarrows$ μ-H. The interchange kinetics do not vary much with changes in R substituent, $\Delta G^{\ddagger} \approx$ 7–8 kcal/mol, from a series of variable-temperature spectra. [i] Position also verified by moving the decoupler frequency in spin-saturation-transfer experiments at −120 °C. [j] In order to "freeze-out" these signals, the temperature was between −120 and −135 °C. [k] Reference 21.

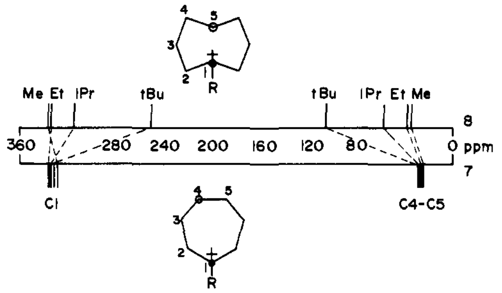

Figure 1. Comparison of ^{13}C shifts (δ) for the C-1 and C-4 carbons of 1-R-cycloheptyl cations with the C-1 and C-5 carbons of analogous 1-R-cyclooctyl cations.

Perhaps the best way of initially showing the gradually "divergent" nature of the ^{13}C shifts in **3** is to compare these with the correspondingly substituted cycloheptyl cations **5**, like cyclooctyl a strained ring, but one where we have found no evidence for any kind of observable transannular μ-hydrido bridging, symmetrical or otherwise.[10] A partial visual comparison of the two series is shown in Figure 1, which includes the C$^+$ carbons as well as a transannular one, C-5 in the cyclooctyl case and the identical C-4, C-5 carbons in the cycloheptyl series.

The following comments derive from Table I and Figure 1 comparisons.

(1) The reference 1-alkylcycloheptyl cations show C$^+$ ^{13}C shifts which are typical of at least 100 examples of ordinary aliphatic and monocyclic carbocations, i.e., δ 330 ± 10. Alkyl substituent changes, Me, Et, *i*-Pr and *t*-Bu, have surprisingly little effect on this parameter considering the usual deshielding effects of β substitution in the ^{13}C spectra of alkanes.[11]

(2) The transannular carbons at C-4, C-5 in the cycloheptyl series have ^{13}C shifts similar to those in hydrocarbons (δ 28.2[12]), reflecting their position four carbons from the positively charged center.

(3) *Both* the cycloheptyl and cyclooctyl cation series with R = OH, cyclopropyl, or phenyl have very similar NMR properties, which are in turn similar to those of analogous aliphatic analogues, e.g., α,α′-dimethylbenzyl cations as an R = phenyl model.

(4) The cyclooctyl cation with R = *t*-Bu is completely anomalous, the C$^+$ carbon falling at about δ 250, and perhaps even more telling, the transannular C-5 is found downfield at δ 106.[13] From Figure 1, one notes that with R = *i*-Pr, both these carbons are similarly shifted but to a much smaller extent.

These initial observations have prompted us to conduct a complete NMR characterization of the alkylcyclooctyl cations, particularly the R = *t*-Bu member, and to look closely at those properties (NMR and otherwise) in this series which reflect the gradual strengthening of a transannular μ-hydrido bridge (our interpretation of the anomalous spectra) as one goes from R = Me to R = *t*-Bu. The ^{1}H and ^{13}C NMR spectra of **3**, R = *t*-Bu, are shown in Figure 2, the completely decoupled ^{13}C NMR spectrum horizontal and the ^{1}H spectrum along the vertical axis. This arrangement permits one to illustrate the effects of specific ^{1}H decoupling on the ^{13}C spectrum.

The ^{1}H spectrum of **3**, R = *t*-Bu, is particularly diagnostic for the presence of the proposed μ-hydrido bridge, i.e., structure **4**. We note *one* very high-field peak at δ −6.3 and *one* low-field peak

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(10) Unpublished results from a study of the 1,4-dimethylcycloheptyl cation; see also ref 1a.

(11) Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972.

(12) Burke, J. J.; Lanterbur, P. C. *J. Am. Chem. Soc.* **1964**, *86*, 1870.

(13) The data are for a temperature of −130 °C. The ^{13}C shifts of the C-1 and C-5 carbons are quite temperature dependent, δ 244.9 and 108.8 at −140 °C and 252.5 and 103.9 at −118.5 °C. For an equilibrium

the temperature dependence would have been completely opposite. We believe that the C-1 and C-5 ^{13}C shifts are likely coupled to a low-frequency pseudorotation motion of the ring and that lower temperatures lead to the population of lower pseudorotational levels which involve, on the average, smaller C–H···C distances and hence "better" bridging.

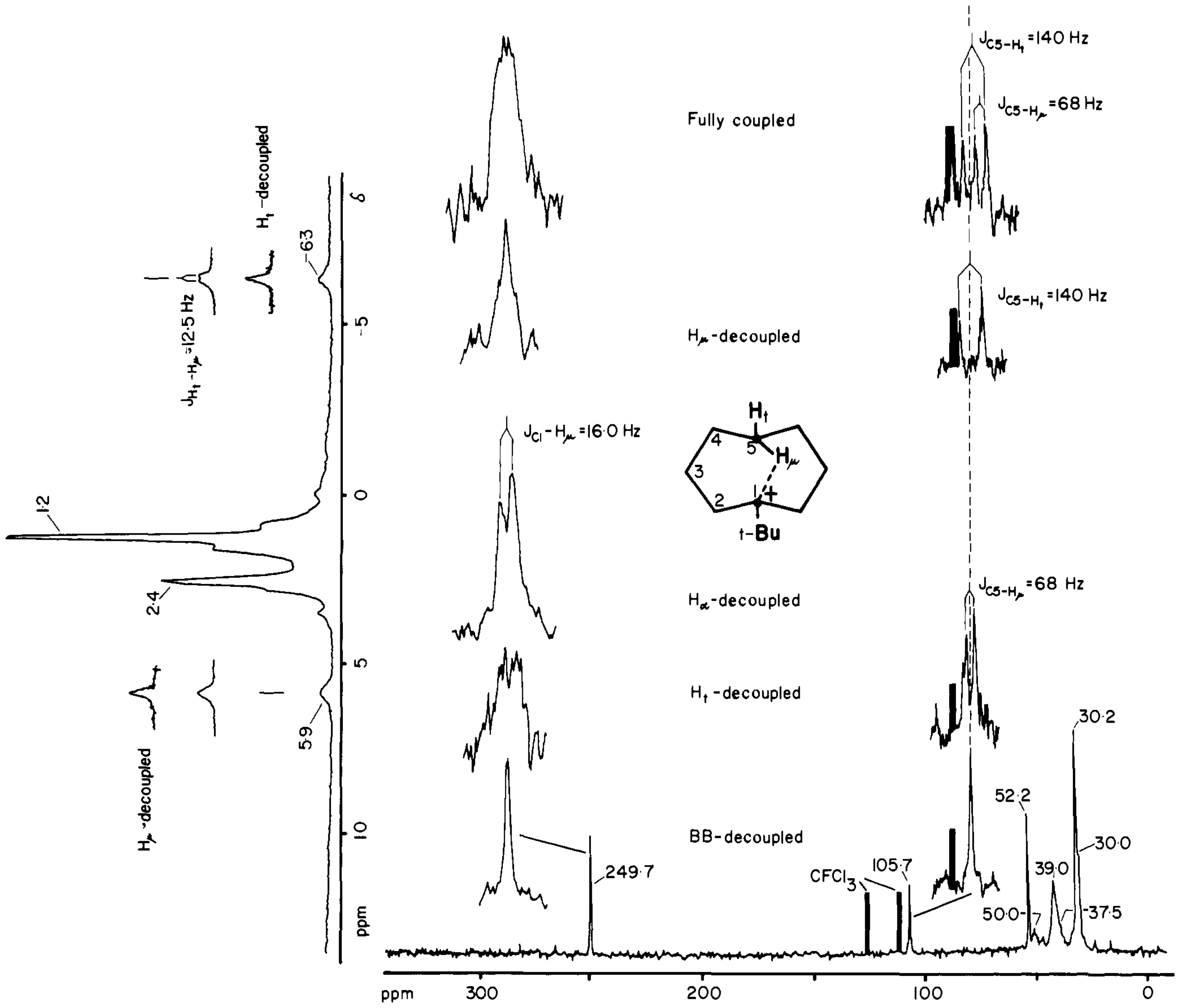
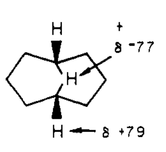


Figure 2. ^{13}C (horizontal) and ^1H (vertical) NMR spectra of the 1-*tert*-butylcyclooctyl cation. The bottom ^{13}C spectrum is broad-band decoupled, and the mounted inserts illustrate the effects of specific heteronuclear proton decoupling on the important resonances. Similarly, homonuclear decoupling effects involving H_T and μ-H are as illustrated in the ^1H spectrum.

at δ +5.9. This spectrum can be compared with the corresponding spectra for the symmetrical 1,5-μ-hydrido-bridged-cyclooctyl cation 6 (disecondary) and the 1,5-dimethyl-1,5-μ-hydrido-bridged cyclooctyl cation 7 (ditertiary).[14] The former has *one* high-field peak at δ −7.7 and *two* low-field protons at δ +7.9, while the latter cation has *one* high-field peak at δ −6.3 and *no* low-field protons. The very high-field peak is assigned to the μ-hydrogen and the low-field peak(s) to the terminal hydrogen(s). In Figure 3, these features are shown for comparison purposes.



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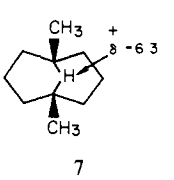

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The remaining protons in 4 are badly overlapped (Figure 2), and only the *t*-Bu group can be definitely assigned.[15]

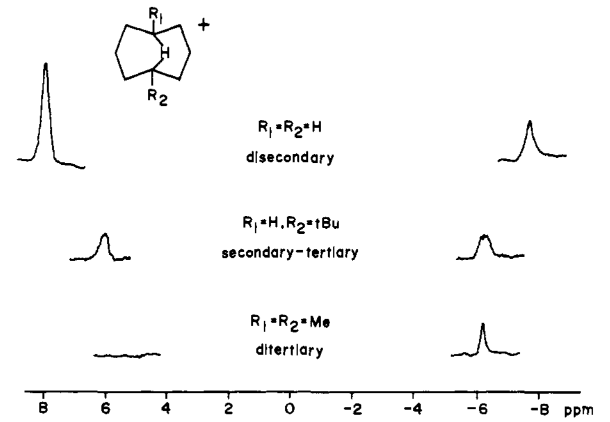

Figure 3. Diagnostic low- and high-field ^1H NMR signal patterns for the three presently known classes of μ-hydrido-bridged carbocations.

The assignment of these high- and low-field protons in the spectrum of 4 to the C-5 "methylene group" is further verified by correlating the ^{13}C and ^1H NMR spectra (next section). Thus, the C-5 carbon in 4 is by symmetry the only single intensity CH_2 carbon (see later discussion of conformational averaging effects) and hence is unequivocally identified. Furthermore, specific

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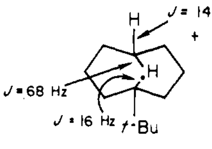
(14) Kirchen, R. P.; Ranganayakulu, K.; Singh, B. P.; Sorensen, T. S., submitted for publication in *Can. J. Chem.*

(15) The preparation of 4 is tempermental and in our hands is always accompanied by some rearrangement/decomposition since the μ-hydrogen integration is consistently less than 1 H, when being compared to all the remaining hydrogen absorptions in the "normal region" (which includes decomposition products).

deuteration results are completely consistent with these assignments. It should be noted also that not only C-1 and C-5 but also practically all of the ^{13}C shifts in **4**, befitting the unique structure, are different from those of the more "normal" cyclooctyl cations, e.g., the 1-methyl analogue.

Nature of the Partial μ-Hydrido-Bridge Bonding. Although the ^{1}H NMR results suggest a great deal of similarity between **4**, **6**, and **7**, this is not entirely borne out by the ^{13}C NMR results or by looking at the ^{13}C coupling constants involving this μ-hydrogen (nor would one expect exactly equal bonding in this secondary–tertiary bridge). For example, the ^{13}C shift of the two terminal carbons in **6** is δ 151.7 and in **7** δ 171.0. In cation **4**, the corresponding values are 250 and 106 ppm and these would average out at δ 178. The difference between the actual value of 250 ppm and this 178-ppm average (72 ppm) is very close to the difference between 250 and the normal 330 ppm (80 ppm) for a tertiary C^+ carbon. Similarly, δ 106 for C-5 in **4** is nearly midway between δ 178 (73 ppm) and a normal hydrocarbon value of ca. δ 30 (75 ppm). The hydrido bridging in the symmetrical ions **6** and **7** is postulated to involve a resonance system[2b] in which the bond order is approximately 0.5 for both bonds. The ^{13}C results for **4** can be naively interpreted in terms of a resonance system in which the μ-H–C_{tert} bond order is ca. 0.25 and the μ-H–C_{sec} value, 0.75.

Evidence for Partial μ-Hydrido Bridging from Coupling Constants. Coupling constants provide one with yet another tool in which to evaluate these bond orders. These bridged ions are ideal since the two C-5 "methylene protons" in **4** are separated by 12.2 ppm and hence easily specifically decoupled in the ^{13}C spectrum. These results are shown in Figure 2, in insets mounted above the decoupled ^{13}C spectrum. In the fully coupled spectrum, C-5 is a doublet of doublets, J = 68 and 140 Hz, and C-1 is simply broadened. Specific decoupling of μ-H reduces C-5 to a doublet, J = 140 Hz, and considerably sharpens C-1, thus establishing that a coupling exists between these centers (which are of course nonbonded in any interpretation not involving hydrido bridging). Specific decoupling of H_T also reduces C-5 to a doublet, J = 68 Hz, while low power decoupling of the C-2 (α) protons removes long-range proton coupling from C-1 and allows one to see clearly the C-1 doublet (J = 16 Hz) due *only* to the coupling with μ-H. The coupling constants thus determined are shown, with symmetrical ions **6** and **7** for comparison.



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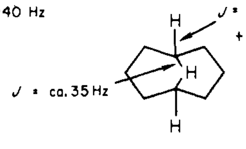

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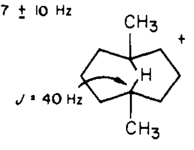

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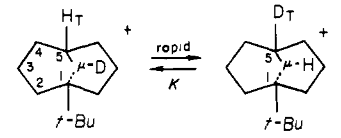
The μ-H–C coupling constant found for several symmetrical carbocations is ca. 35 Hz, and one notes that the 16-Hz value in **4** is about half of this, i.e., naively representing half of the "normal" 0.5 bond order. Similarly, 68 Hz falls between a "normal" C–H coupling of 125–130 Hz and the 35-Hz value. Thus, the coupling constant data is completely consistent with the "partial" bonding picture derived from chemical shift data.

The μ-H and H_T peaks in **4**, **6**, and **7** are characteristically broad, but in the case of **4**, this is partly because of mutual coupling, shown in Figure 2, with J = ca. ±12.5 Hz.

Theoretical calculations on the μ-hydrido-bridged cations suggest a bridge carbon hydridization in the symmetrical cases which is nearly half way between trigonal planar (sp^2) and tetrahedral (sp^3), and the resulting high "p character" in the bond to the μ-hydrogen is undoubtedly responsible for the overall low coupling constants (cf. analogous findings in boron chemistry[16]). In the case of **4**, one would expect that the hybridization would be intermediate as well but in an unsymmetrical way; thus C-1 is only slightly distorted toward tetrahedral and C-5 only slightly distorted toward planarity.

Other Evidence for μ-Hydrido Bridging. In searching for a more chemical verification of actual bonding between a C-5 hydrogen and C-1 in **4**, it is worthwhile to prepare the 5-monodeuterated cation, which can exist in two isomeric modifications, **4**-μ-D and **4**-D_T (eq 1). From prior rate measurements of degenerate

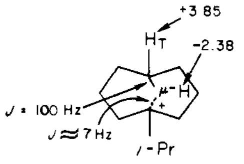


4-μ-D **4**-D_T (1)

conformational interchange in **4** (see later), we knew that the equilibrium would be rapidly established. Also, from prior work,[2b] it was expected that an μ-H-D_T combination would be favored (K > 1) over an H_T–μ-D arrangement.[17] The observation of an equilibrium isotope effect in **4** would surely indicate a bonding interaction between μ-H and C-1, particularly if the effect diminished along with the aberrant NMR properties as one varied the R alkyl group. Both ^{1}H and ^{2}D NMR spectroscopy were used to measure this equilibrium constant. In the ^{2}D spectrum, μ-$^{2}D/^{2}D_T$ was ca. 0.23 (−130 °C), while in the ^{1}H spectrum of the same solution, μ-$^{1}H/^{1}H_T$ was ca. 4.5 (−130 °C), in excellent agreement, i.e., K = **4**-D_T/**4**-μ-D = 4.5 ± 0.5 (−130 °C). This is a rather extraordinary equilibrium deuterium isotope effect since only C–H bonds are involved, i.e., typical of *primary* isotope effects in rate studies, but it becomes comprehensible when one realizes that the *ground state* involves C–H bonds which are very stretched, i.e., related to the imagined *transition state* in a hydride-transfer reaction.

The Diminishing μ-Hydrido Interaction Observed in 3 (R = *i*-Pr > Et ≈ Me > c-Pr ≈ Ph ≈ OH. From Figure 1, one notes that the 1-isopropylcyclooctyl cation is clearly a little divergent when C-1 and C-5 ^{13}C chemical shifts are compared to those of the cycloheptyl analogue or to those of the 1-ethyl- or 1-methylcyclooctyl cation. Surely we would then also expect a complementary change in the following, as befits a weaker sort of transannular interaction. (1) The μ-H chemical shift, compared to **4**, should decrease toward a more "normal" position. (2) H_T should increase. (3) The C-5-μ-H coupling constant should increase. (4) The C-1-μ-H coupling constant should decrease. (5) The equilibrium constant for the monodeuterated ion should decrease, i.e., approach K = 1.

All of these expectations are found experimentally. The μ-H and H_T protons are found at δ −2.38 and +3.85, respectively, both still unusual for a pair of "methylene" protons. The C-5-μ-H coupling is 100 Hz[19] and that between C-1 and μ-H is now too small to measure.[20] The equilibrium constant **8**-D_T/**8**-μ-D is 1.4 (−70 °C), the averaged H_T–μ-H peak position being used in this determination (see Experimental Section).



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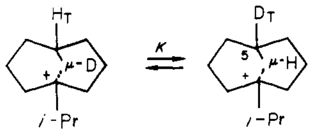

8-μ-D **8**-D_T

The 1-methyl- and 1-ethylcyclooctyl cations exhibit ^{13}C NMR spectra typical of ordinary alkyl cations, but the ^{1}H spectra are

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[16] (a) Hertz, R. K.; Johnson, H. D., II; Shore, S. G. *Inorg. Chem.* **1973**, *12*, 1875. (b) Saturinino, D. J.; Yamauchi, M.; Clayton, W. R.; Nelson, R. W.; Shore, S. G. *J. Am. Chem. Soc.* **1975**, *97*, 6063.

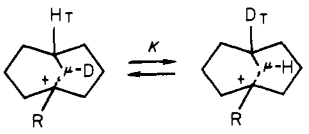
[17] In hydrogen bonding, isotope fractionation equilibria[18] favor –O–D + –O···H···O– over –O–H + –O···D···O–. The same arguments should apply to a bridging hydride assuming that μ-H and μ-D do indeed "sit" in a very loose potential well and that C–H_T and C–D_T involve normal carbon-hydrogen bonding.

[18] For a very recent discussion, see: Kreevoy, M. M.; Liang, T. M. *J. Am. Chem. Soc.* **1980**, *102*, 3315.

[19] In fully ^{1}H-coupled spectra of **8**, C-5 is badly overlapped by the isopropyl CH carbon and the C-2 and C-2′ ring carbon peaks. The μ-H–C-5 coupling constant was indirectly determined from off-resonance spectra.

[20] Decoupling the μ-H hydrogen reduces the C-1 line width (half-height) from about 20 to 13 Hz (~9 Hz for broad-band decoupling).

Table II. Equilibrium Isotope Effects



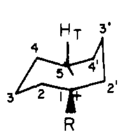
R	K	temp, °C	dev (K − 1)
t-Bu	4.5[a]	−130	
	3.0[b] (est)	−70	2.0
i-Pr	1.40 ± 0.05[c]	−70	0.4
Et	1.20 ± 0.05	−70	0.2
Me	1.15 ± 0.05	−70	0.15

[a] Determined directly from integration of μ-H and H_T in ^1H NMR and also μ-D and D_T from deuterium NMR, both on "frozen-out" spectra. [b] Using the van't Hoff relationship and assuming $\Delta H = \Delta G$, i.e., that $\Delta S = 0$, which seems reasonable in view of the similar structure of the two ions. [c] Determined from the change in the averaged chemical shift of the μ-H-H_T peak (population dependent), compared to the all-hydrogen case where the process is degenerate.

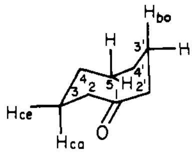
still somewhat unusual in showing one slightly high-field proton, δ −0.72 in the 1-methyl case and δ −0.84 in 1-ethyl. The equilibrium isotope effects also continue to decrease and to approach 1, i.e., δ 1.20 for 1-ethyl and δ 1.15 for 1-methyl, both measured at −70 °C. These latter results are compared for all four ions in Table II.

A single very slightly high-field proton is also observed in the 1-cyclopropylcyclooctyl cation, δ +0.5, the 1-phenylcyclooctyl cation, δ +0.2, protonated cyclooctanone (1-hydroxy), δ +0.62, and even cyclooctanone itself, δ +0.71.[21] The ^1H NMR transannular "interaction" thus seems to reach a sort of limiting situation. One could ascribe this interaction to several "through-space" phenomena (e.g., polarization), but even here there is probably a gradual merging with the onset of actual "bonding".

Conformational Considerations. Previous studies have already indicated a specific boat-chair conformation **9** for the 1-methylcyclooctyl cation, and the present studies are consistent with this conformation for all of the cyclooctyl cations.[7] This conformation is also found[21] for cyclooctanone **10**. In the ketone, there are two ring-conformational interchanges, a pseudorotation process ($\Delta G^{\ddagger}$ = 6.3 kcal/mol[21,22]) which interchanges chair and boat carbons (and hydrogens, i.e., $H_{ca} = H_{be}$ etc.) and an inversion process ($\Delta G^{\ddagger}$ = 7.5 kcal/mol) which interchanges the two hydrogens on C-5 and further averages the others, i.e., $H_{ca} = H_{ba}$ so that, for example, all four of the C-3 hydrogens are averaged. In the cyclooctyl cations, these two (?) barriers have identical values, within experimental error, $\Delta G^{\ddagger}$ = 7.2 and 7.1 kcal/mol, on the basis of computer simulations of line broadening in the 1-methylcyclooctyl cation, the former from ^{13}C data[7] and the latter from the interchange kinetics of the μ-H and H_T protons. Since small-temperature variations are difficult to control between different samples, we show in Figure 4 the ^1H spectrum of a mixture of all four alkylcyclooctyl cations (μ-H only), and the resulting line broadening due to the exchange with H_T. That this exchange is specifically H_T-μ-H ⇄ μ-H-H_T can be shown by spin-saturation-transfer experiments or in the R = Me, Et, or i-Pr cases, by observing the coalesced peak at much higher temperatures.



9



10

ba = boat-axial etc.

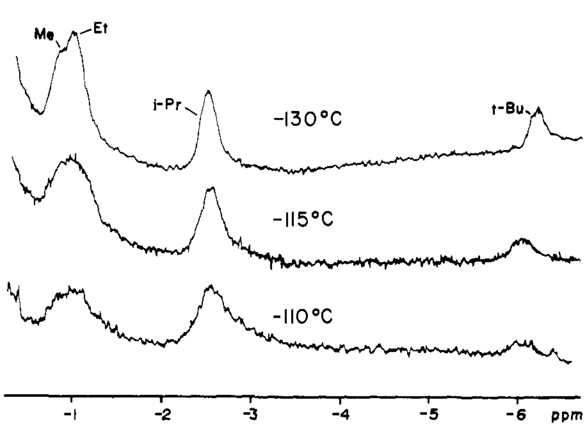
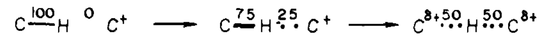


Figure 4. The μ-H protons (200 MHz) of a mixture of all four 1-R-cyclooctyl cations, R = Me, Et, i-Pr, and t-Bu. The figure illustrates the very similar line-broadening rates observed for the H_T–μ-H interchange in all four ions.

The most obvious way to interchange H_T and μ-H in models is to initially pull outward at C-1 and C-5 and then to rotate the molecule inside-out until the degenerate chair–boat structure is again formed (termed inversion[23]). From Figure 4, the amazing observation is that this conformational barrier is very nearly the same in all cases, i.e., independent of the R group[24] and thereby independent of the extent of transannular bridging! Since the direct result of the conformational change is to initially completely *break* and then *remake* the transannular bridge, how can the conformational barrier be so independent of bridging? For a more quantitative perspective of this, a rough calculation of the relevant bond strengths can be made as follows.

The energy of a normal C–H bond and *both* "bonds" in the delocalized three-center bonding of the C–H–C^+ must be similar,[25] i.e., ~100/2 = 50 kcal/mol for each of the latter in a symmetrical case. In our unsymmetrical case for R = t-Bu, this might be divided 75–25 kcal/mol (previous arguments), but even 25 kcal/mol for the μ-H to C^+ bond would completely overwhelm the observed 7.5-kcal/mol conformational barrier.

The obvious solution to this dilemma is in fact contained in the figures used above to derive these μ-hydrido bond strengths, i.e., the energy barrier for stretching the hydrogen in



$$\mathrm{C}\overset{100}{\text{—}}\mathrm{H}\;\overset{0}{}\;\mathrm{C}^{+} \longrightarrow \mathrm{C}\overset{75}{\text{—}}\mathrm{H}\overset{25}{\cdots}\mathrm{C}^{+} \longrightarrow \mathrm{C}^{\delta+}\overset{50}{\cdots}\mathrm{H}\overset{50}{\cdots}\mathrm{C}^{\delta+}$$

must be close to zero, a nearly flat potential energy curve. Coupling constant and chemical shift properties will depend however on the *actual representation present*, but changes in the conformational barriers are related to the *difference in energy between these structures*. In energy terms, the factors which promote the C···H···C^+ situation (as with R = t-Bu) over C–H···C^+ (e.g., R = Me) must be very subtle, probably less than 1 kcal/mol. It is conceivable (1) that hyperconjugative stabilization, Me > Et > i-Pr > t-Bu, would progressively decrease the "need" of the C-1 center for additional stabilization, in this case μ-hydrido bridging, (2) that steric factors, where t-Bu > i-Pr etc., force the

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(21) Anet. F. A. L.; St. Jacques, J.; Henrichs, P. M. *Intra-Sci. Chem. Rep.* **1970**, *4*, 251–56.

(22) We have rechecked this value by using a ^{13}C NMR line-broadening analysis and find a slightly higher barrier than that reported from the ^1H NMR analysis of the ketone-d_{13}.[21]

(23) Rounds, T. C.; Strauss, H. L. *J. Chem. Phys.* **1978**, *69*, 268.

(24) This rapid conformational interchange makes the ^{13}C NMR characterizations difficult. In the R = t-Bu case, for example, the ion solutions must be observed at temperatures of about −135 °C in order to "freeze out" the nonequivalent β (C-3 and C-3′) carbons (^{13}C NMR) and the μ-H and H_T protons (^1H NMR). Such low temperatures cause viscosity broadening of lines. In Figure 1, for example, the C-3 and C-3′ carbons of **4** (at −130 °C) are assigned to broad peaks at δ 50.0 and 37.5. On further cooling all peaks broaden because of the viscosity.

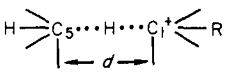
(25) This is based on the fact that intermolecular cation–hydrocarbon hydride transfers have close to zero activation enthalpy; see, for example: (a) Kramer, G. M. *J. Org. Chem.* **1969**, *34*, 2919; (b) Brownstein, S.; Bornais, J. *Can. J. Chem.* **1971**, *49*, 7; (c) Olah, G. A.; Mo, Y. K.; Olah, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 4939; (d) Dirda, D.; Rapp, D.; Kramer, G. M. *J. Org. Chem.* **1979**, *44*, 2619.

C-1 and C-5 carbons closer, or (3) that steric hindrance to solvation may cause the progressive "need" in 1.

We favor the arguments contained in 1 and/or 3 and note that in several different allyl cation equilibria, alkyl substituents stabilize in the order Me > Et > *i*-Pr > *t*-Bu.[26]

Medium-ring compounds commonly show enhanced solvolysis rates[27] *and* solvolysis products derived from transannular hydride transfer,[28] and there have naturally been suggestions that these observations have a similar origin.[29] However, the above results suggest that the μ-hydrido bridging can in some instances be associated with almost no change in the total energy of the carbocationic intermediates and hence that the two observations should not be very *correlatable*.[30]

Calculations on the Shape of the Hydrogen Potential in Unsymmetrical μ-Hydrido Bridging. Molecular orbital calculations performed on symmetrical μ-hydrido-bridged cation models show several features consistent with experimental results and these include (1) single potential minima for the hydride, centered between the two carbons, and (2) relatively modest stabilization energy for the interaction, decreasing in the order primary–primary > secondary–secondary > tertiary–tertiary. In our present unsymmetrical secondary–tertiary cases, the degree of bridging is very dependent on the R group and the most reasonable interpretation of this would involve changes in the overall



distance as one varied the R group. The chair–boat conformation 9 is certainly flexible enough[31] to "freely" allow this distance (and perhaps angle) to vary considerably, 2.5–3.5 Å being a reasonable range. As previously discussed, the experimental results suggest a virtually flat potential for changing "*d*", this "*d*" change of course being a function of the particular R group and remembering that the $\underbrace{>C-H}$ distance will naturally be "optimized" for a given "*d*" (hence R). However, only at short distances (poorer stabilizing R's) will we expect a gradual strengthening of the $-\mu$-H···C_1^+ bond and a weakening of the C_5–μ-H bond.

The unsymmetrical model systems chosen for computation were based on Me···H···Me$^+$, where the Me can be permutationally replaced by Et, *i*-Pr, and *t*-Bu. The systems Me···H···*i*-Pr$^+$, Me···H···*t*-Bu$^+$, Et···H···*t*-Bu$^+$, and *i*-Pr···H···*t*-Bu$^+$, under full optimization, are not computationally stable (MINDO/3).[32] However Me···H···Et$^+$ and Et···H···*i*-Pr$^+$ are stable at both the MINDO/3 and STO-4G[33] ab initio levels. Both ions yield similar profiles and that for the ab initio calculation on Et···H···*i*-Pr$^+$ is

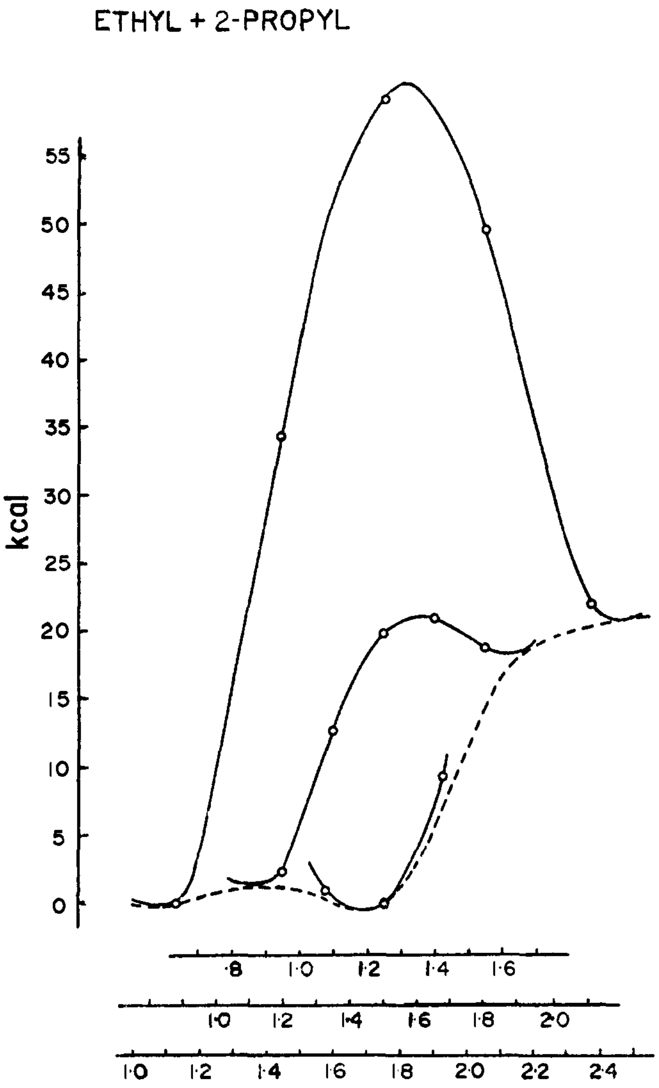


Figure 5. Theoretical calculation (STO-4G) of the CH_3CH_2···H- - -CH-$(CH_3)_2^+$ systems. The lower scale refers to a "*d*" separation of 3.5 Å and the highest curve, the middle scale to a "*d*" separation of 3.0 Å and the middle curve, and the upper scale to a "*d*" separation of 2.5 Å and the lowest solid curve. The circles in each curve indicate the C–H distances chosen for computation. The dashed line represents the *coupled* potential well function for simulataneously varying both the C···C and C–H separations.

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[26] (a) Sorensen, T. S. *J. Am. Chem. Soc.* **1967**, *89*, 3782 and 3794. (b) Ranganayakulu, K.; Sorensen, T. S. *Can. J. Chem.* **1972**, *50*, 3534. (c) Ananthanarayan, K. A.; Sorensen, T. S. *Ibid.* **1972**, *50*, 3550. (d) Hogeveen, H.; van Kruchten, E. M. G. A. *Top. Curr. Chem.* **1979**, *80*, 89.

[27] (a) Heck, R.; Prelog, V. *Helv. Chim. Acta* **1955**, *38*, 1541. (b) Brown, H. C.; Ham, G. *J. Am. Chem. Soc.* **1956**, *78*, 2735. (c) Brown, H. C.; Borkowski, M. *Ibid.* **1952**, *74*, 1894.

[28] First studied by Prelog and co-workers: (a) Prelog, V. *Rec. Chem. Prog.* **1957**, *18*, 247–60 and subsequently by many other workers. For reviews, see: (b) Prelog, V.; Traynham, J. G. In "Molecular Rearrangements"; de Mayo, P., Ed.; Interscience: New York, 1963; Vol. 1, p 593. (c) Cope, A. C.; Martin, M. M.; McKervey, M. A. *Q. Rev., Chem. Soc.* **1966**, *20*, 119.

[29] Most workers in the area, including Prelog, have discussed enhanced solvolysis rates in terms of possible "hydrogen participation" rather than the formation of discrete bridged *intermediates*. Early evidence based on H/D isotope rate studies proved negative, see: ref 28a, Roberts, A. A.; Anderson, C. B. *Tetrahedron Lett.* **1969**, 3883. Recently, however, such H/D rate evidence has appeared: Parker, W.; Watt, C. I. F. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1647. See also: Bartlett, P. D. "Nonclassical Ions"; W. A. Benjamin: New York, 1965; p 196.

[30] Our results, of course, apply only to potentially bridged secondary–tertiary systems, but even in secondary–secondary systems, the evidence shows that the symmetrical μ-hydrido-bridged cations are not much stabilized compared to "normal" secondary cycloalkyl cations,[1a] so that the same conclusions apply. The I-strain concept certainly appears responsible for the majority of the solvolysis rate enhancement found in medium rings, but we would also expect *small* effects from μ-hydrido bridging in the transition state.

[31] From MO calculations on the disecondary system (MINDO/3), the C–H···C bond is predicted to be somewhat bent (140°). With disecondary C–H bond distances of ca. 1.3 Å, this gives a C–C bond distance of 2.44 Å and corresponds essentially to the "open" bonding picture. The C–H···C distance in the chair–boat conformation can be varied by a simple twisting motion.

[32] Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1285–93.

[33] Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657–64

[34] The mechanism of hydride transfers between a carbocation and a hydrocarbon has been discussed extensively in the literature. Olah has stated:[25c] "These studies have shown that intermolecular hydrogen transfer involves not linear but triangular three-center-bonded pentacoordinate carbonium ion transition states (or intermediates)". In more recent work with methylated benzyl cations, the transfer is apparently proton acid catalyzed, leading the authors to postulate a termolecular transition state: van Pelt, P.; Buck, H. M. *J. Am. Chem. Soc.* **1976**, *98*, 5864. Notwithstanding, the "linear" transition state, as originally discussed by Swain et al., seems to be most in line with our results: Swain, C. G.; Wiles, R. A.; Bader, R. F. W. *J. Am. Chem. Soc.* **1961**, *83*, 1945.

[35] It should be noted that functionalization of a secondary position in a tertiary carbocationic intermediate is by no means unknown, even in the absence of bridging. However, the energetics of the process would provide the key factor in distinguishing our μ-hydrido-bridged cations (or allyl cations), since in "normal" cases a secondary cation can be formed from an appropriate tertiary species (by hydride shifts etc.) with an input of ca. 10–15 kcal/mol. With the formation of the resonance μ-hydrido bridge, one should require essentially no additional input of energy; i.e., the process should be much more facile than the "normal" case.

shown in Figure 5. The three solid lines are artificially constructed by fixing the

$$\underset{\longleftarrow\; d\; \longrightarrow}{\mathrm{C{-}H\cdots C^+}}$$

distance, 2.5, 3.0, and 3.5 Å, and then moving the hydrogen between the two carbons. The dashed line represents the potential function for the situation where both the C–C and C–H bond distances change such as might be caused by changing the R group in the cyclooctyl cations and is thus comparable to the experimental results. The gratifying conclusion is that changing "*d*" (and $\underbracket{\mathrm{C{-}H}}$), which we are equating with changing R in **3**, in the Et···H···*i*-Pr$^+$ cation results in a very flat potential, i.e., a conclusion identical with that reached for the cyclooctyl cation series **3** on the basis of the experimental data. Furthermore, we believe that the three distances, 3.5, 3.0, and 2.5 Å, might even correspond reasonably to **3**, R = Me or Et, R = *i*-Pr, and *R* = *t*-Bu, respectively. Specifically: (1) At short $\underbracket{\mathrm{C\cdots H{-}C^+}}$ distances, one gets a single unsymmetrical potential minimum produced; the net energy stabilization, as already inferred, is small. This situation would seem to fit our R = *t*-Bu ion **4**. (2) At longer separations, one develops a shoulder on the high-energy secondary side of the overall potential (Figure 5) and at even longer distances a second (high-energy) minimum. We suggest that the cyclooctyl cation, where R = *i*-Pr, might fall somewhere in this picture. (3) Even in the double minima case at 3.5-Å separation, the computed charge on the "*μ*-hydrogen" is substantially negative, compared to a normal C–H bond, and this case probably represents the R = methyl- or ethylcyclooctyl cations. These calculations have the virtue of reinforcing our contention[36] that the changes in structure are *gradual* as one varies the R group, and as just noted, we can do the same gradual changes computationally simply by varying the $\underbracket{\mathrm{C{-}H\cdots C^+}}$ distance. In fact, the series R-cyclooctyl$^+$, *R* = Me, Et, *i*-Pr, and *t*-Bu, is probably the best example yet of the common-sense notion that carbocation structure changes can be very gradual, in contrast to the typical classical–nonclassical dichotomy still prevalent in the literature.

Discussion

The results discussed so far in this paper are relevant to our basic understanding of organic molecular structure, but are they of any further use? It is too early to answer this question but they seem to relate to more general organic reactions in two ways: (1) they serve as possible models (electronic structure, geometry) for the transition state of hydride-transfer reactions, and (2) they suggest that ready transannular functionalization should be possible at *secondary* centers from the solvolysis of tertiary esters etc., in analogy to unsymmetrical allyl cations.

Organic hydride-transfer reactions encompass anionic, neutral, and cationic cases, and our observations are probably relevant only to carbocation abstractions. This reaction has been extensively studied from a kinetic viewpoint, but there are conflicting theories on the mechanism.[34] It seems reasonable to us that in simple alkyl cases at least, the transition state (or intermediate) would involve linear *μ*-hydrido bridging. In fact, the R-cyclooctyl$^+$ series offers one a probable series of "stop action" spectroscopic glimpses of the reaction course since we have just interpreted changes with R as involving changes in the "linear" $\underbracket{\mathrm{C{-}H\cdots C^+}}$ distance, the same distance which we would suggest is the reaction coordinate for a hydride-transfer process. The reaction "progress" is thus suggested to involve initial C–H polarization by C$^+$, gradual strengthening of C–H···C$^+$, formation of a single potential well intermediate, and then the reverse of these.

There is a close analogy between unsymmetrical allyl cations (unequal three-center, two-electron *π* bonding) and that involved in unsymmetrical *μ*-hydrido-bridged cations (unequal three-center, two-electron *σ* bonding). In allyl cations, nucleophile capture can occur at the less substituted center, and using this analogy, one might expect some similar functionalization at the *secondary* end of secondary–tertiary *μ*-hydrido-bridged cations. There seems, however, to be little evidence for this in the literature.[35] However, we have previously described[2b] the extremely facile H/D exchange in bridged cyclodecyl cations and have rationalized this in terms of "low-energy" unsymmetrical *μ*-hydrido-bridged cationic intermediates.

Experimental Section

The cations were prepared as previously described[7] from either the tertiary alcohol or the corresponding chloride or in the 1-hydroxy case, by protonating the ketone. Solvent and temperature conditions varied depending on the specific case: A, cycloalkanol, 3:1 or 4:1 SO_2ClF/SbF_5-FSO_3H at −120 °C; B, cycloalkyl chloride, 3:1:1 $SO_2ClF/SO_2F_2/SbF_5$ at ca. −140 °C; C, cycloalkanone, 4:1 SO_2ClF/FSO_3H at −120 °C. ^{13}C NMR spectra of cations were recorded on a Bruker WH-90 spectrometer as previously described.[7] ^1H NMR spectra were recorded mostly at 90 MHz but in some cases at 200 MHz, by using a Varian XL-200 spectrometer. ^2D NMR spectra were obtained at 13.84 or 30.7 MHz on the above instruments. The purity of the alcohol samples was monitored by ^{13}C NMR spectroscopy since GLC analysis is often accompanied by dehydration. In the following descriptions of the cations, additional NMR data not reported in Table I are given.

1-Methylcycloheptanol, 1-methylcyclooctanol, and **1-ethylcyclooctanol** and the corresponding cations **1-methylcycloheptyl, 1-methylcyclooctyl,** and **1-ethylcyclooctyl** have been reported[7,8] and characterized by ^{13}C NMR spectroscopy. ^1H data for the 1-methylcycloheptyl cation are as follows: δ 3.90 (4 H (2- and 2′-CH_2)), 3.37 (3 H (CH_3)), 1.65 and 1.39 (both 3 H (3- and 3′-CH_2 and 4- and 4′-CH_2)). These chemical shifts are representative of the very "normal" ^1H behavior observed for cycloheptyl cations. The ^1H data reported[7] for the 1-methylcyclooctyl cation were partly misinterpreted and are as follows: δ 3.73 (7 H (2- and 2′-CH_2 and CH_3)), 2.79 (4 H (3- and 3′-CH_2)), 1.60 (4 H (4- and 4′-CH_2)), 0.92 (2 H (averaged H_T and *μ*-H)) (−80 °C). The ^1H spectrum of the 1-ethyl analogue has δ 2.07 (2 H (CH_2 of ethyl)), 3.69 (4 H (2- and 2′-CH_2)), 2.63 (4 H (3- and 3′-CH_2)), 1.63 (d, *J* = 6 Hz, 7 H (4- and 4′-CH_2 and CH_3)), and 0.90 (2 H (averaged H_T and *μ*-H)) (−80 °C). **1-Ethylcycloheptanol,** ^{13}C peaks at δ 75.3 (C-1), 41.2 (C-2), 36.7 (CH_2 of Et), 30.5 and 23.1 (C-3 and C-4), and 8.1 (CH_3), has been reported.[38] The **1-ethylcycloheptyl cation** (preparation A) has ^{13}C peaks at δ 58.1 (C-2), 26.0 (C-3), 55.1 (CH_2 of Et), and 9.5 (CH_3) (−116 °C). **1-Isopropylcycloheptanol,** ^{13}C peaks at δ 76.9 (C-1), 39.7 (CH of *i*-Pr), 38.8 (C-2), 30.2 and 23.3 (C-3 and C-4), and 17.7 (CH_3), has been reported.[38] The **1-isopropylcycloheptyl cation** (preparation A) has ^{13}C peaks at δ 56.7 (C-2), 28.8 (C-3), 58.4 (CH of *i*-Pr), and 21.7 (CH_3) (−123 °C). **1-Isopropylcyclooctanol,** ^{13}C peaks at δ 75.95 (C-1), 35.7 (CH of *i*-Pr), 34.5 (C-2), 28.4 (C-4), 25.3 (C-5), 22.4 (C-3), and 16.8 (CH_3), has been reported.[39] The **1-isopropylcyclooctyl cation** (preparation A) has ^{13}C peaks at δ 49.4 ($J_{^{13}C-^1H}$ = 135 Hz (C-2 and C-2′)), 53.6 ($J_{^{13}C-^1H}$ = 145 Hz (CH of *i*-Pr)), 32.3, 29.5, 28.5, 26.7, and 22.8 (C-3, -3′, -4, and -4′ and CH_3's) (−128 °C) and ^1H peaks at δ 3.42 (4 H (2- and 2′-CH_2)), 2.66 (4 H (3 and 3′-CH_2)), 1.55 (10 H, d, *J* = 6.5 Hz (4- and 4′-CH_2 and CH_3)), 3.97, (1 H, heptet, *J* = 6.5 (CH of *i*-Pr)), and 0.74 (2 H (averaged H_T and *μ*-H) (−76 °C). **1-*tert*-Butylcycloheptanol,** ^{13}C peaks at δ 78.5 (C-1), 35.9 (C-2), 29.9, 23.1 (C-3 and C-4), 38.9 (C of *t*-Bu), 25.3 (CH_3), has been reported.[40] The **1-*tert*-butylcycloheptyl cation** (preparation B is best, see subsequent description of cycloalkyl chloride preparation) has ^{13}C peaks at δ 55.4 (C-2), 24.3 (C-3), 59.7 (C of *t*-Bu), and 28.4 (CH_3) (−130 °C). This cation is very unstable and the preparation is accompanied by a second set of ^{13}C peaks about 25% by area of those for the above cation. **1-*tert*-Butylcyclooctanol,** ^{13}C peaks at δ 77.5 (C-1), 32.2 (C-2), 28.7, 23.1 (C-3 and C-4), 39.4 (C of *t*-Bu), and 26.45 (CH_3), has been reported.[41] The **1-*tert*-butylcyclooctyl cation** (see Figure 2) is best prepared by using procedure B; see subsequent description for the chloride preparation. The cation is unstable above −120 °C. ^{13}C peaks are found at δ 39.0 (C-2 and C-2′), 37.5 and 50.0 (C-3 and C-3′), 30.0 (C-4 and C-4′), 52.2 (C of *t*-Bu), and 30.2 (CH_3) (−130 °C). For C-2 and -2′, $J_{^{13}C-^1H}$ = 135 Hz and for CH_3 of *t*-Bu, 133 Hz. For ^1H spectrum: δ 2.4 (C-2 and C-2′), 1.2 (CH_3 of *t*-Bu), additional shoulders on the δ 1.2 peaks (−130 °C). **1-Cyclopropylcycloheptanol,** ^{13}C peaks at δ 73.9 (C-1), 40.9 ((C-2), *J* = 125 Hz), 29.2 and

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(36) Schmitz, L. R.; Sorensen, T. S. *J. Am. Chem. Soc.* **1980**, *102*, 1645.

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(38) Borsdord, R.; Olesch, B. *J. Prakt. Chem.* **1967**, *36*, 165.

(39) Rowsell, D. G.; Spring, D. J.; Hems, R. *Chem. Abstr.* **1975**, *88*, P136919c.

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21.7 ((C-3 and C-4), J = 124 and 127 Hz), 21.7 ((α-CH), J = 163 Hz), and −0.5 ((β-CH_2); J = 159 Hz), has been reported.[42] The **1-cyclopropylcycloheptyl cation** (preparation A) shows no rotation of the cyclopropyl, resulting in a loss of symmetry in the cation, ^{13}C peaks at δ 53.9, 40.8 (C-2), 27.0, 25.2, 28.5 (C-3 and C-4), 52.7 (α-CH), and 48.8 (β-CH_2) (−115 °C). **1-Cyclopropylcyclooctanol**, ^{13}C peaks at δ 72.2 (C-1), 37.1 (C-2), 28.6 and 22.6 (C-3 and C-4), 25.2 (C-5), 21.2 (α-CH), and 0.0 (β-CH_2), has been reported.[42] The **1-cyclopropylcyclooctyl cation** (preparation A) has the possibility of forming two isomers, and the conformational process is not necessarily degenerate. The following ^{13}C NMR peaks were observed at −115 °C: δ 53.1, 49.6, 43.2, 39.8, 29.6, 28.4, 26.6, 25.5, 24.5. At −120 °C, ^{1}H peaks were observed at δ 2.53 (3-CH_2) and 1.82 (4-CH_2) and a series of unassigned peaks was observed at δ 4.0, 3.7, 3.5, 3.4, 3.25, 3.20, and 3.06 for the 2-CH_2 and cyclopropyl protons (200 MHz). **1-Phenylcycloheptanol**, ^{13}C peaks at δ 77.0 (C-1), 43.5 (C-2), 29.5 and 22.9 (C-3 and C-4), 126.5 (para), 151.5 (ipso), 128.2, and 125.0 (ortho and meta), has been reported.[43] The **1-phenylcycloheptyl cation** (preparation A) has ^{13}C peaks at δ 45.5 (C-1), 26.9 (C-2), 154.0 (para), 139.1 (ipso) 140.4, and 139.1 (ortho and meta) (−108 °C). **1-Phenylcyclooctanol**, ^{13}C peaks at δ 76.7 (C-1), 38.0 (C-2), 28.8 and 22.3 (C-3 and C-4), 24.8 (C-5), 150.0 (ipso), 126.6 (para), and 128.1 and 125.5 (ortho and meta), has been reported.[44] The **1-phenylcyclooctyl cation** (preparation A) has ^{13}C peaks at δ 45.6 (C-2 and C-2′), 36.6 (C-3 and C-3′), 28.5 (C-4 and C-4′), 153.4 (para), 139.1 (ipso), 133.0, and 139.1 (ortho and meta) (−69 °C). The cation has ^{1}H peaks at δ 3.67 and 4.43 (2 H each (2- and 2′-CH_2)), 3.15 and 3.04 (1 H each, 2.3, 2 H (3- and 3′-CH_2)), 1.88 (4 H (4- and 4′-CH_2)), 8.92 (2 H, d, J = 8 Hz (ortho), 8.65 (1 H, t, J = 8 Hz (para)), and 8.12 (2 H, t, J = 8 Hz (meta)) (−120 °C (200 MHz)). The **1-hydroxycycloheptyl cation** and the **1-hydroxycyclooctyl cation** (preparation C) have ^{13}C peaks at δ 44.1 (C-2) and 24.0 (C-3) and at δ 42.3 (C-2 and C-2′), 28.8 (C-3 and C-3′), and 26.7 (C-4 and C-4′), respectively (−108 °C and −78 °C). The 1-hydroxycyclooctyl cation has ^{1}H peaks (200 MHz) at δ 3.45 (2 H) and 3.28 (2 H (2 and 2′-CH_2)), 2.64 (2 H) and 2.26 (2 H (3- and 3′-CH_2)), and 1.86 (2 H) and 1.76 (2 H (4- and 4′-CH_2)) (−120 °C).

1-*tert*-Butylcycloheptyl chloride and **1-*tert*-butylcyclooctyl chloride** were made from the corresponding alcohols and require rather exacting conditions, otherwise the cycloalkene is the sole product. The alcohol (200 mg) in $CFCl_3$ (10 mL) was cooled to −80 °C and dry HCl bubbled in for 15 min. The solution was allowed to warm to room temperature whereupon the water droplets coalesce and float on the $CFCl_3$. The solution was recooled to −80 °C and filtered through glass wool to remove ice, the solvent was removed under reduced pressure (20 °C), and the residue was redissolved in 2-methylbutane and quickly dried (a few minutes) over $MgSO_4$. The solution was filtered, solvent removed under reduced pressure, and the product stored in the freezer. The products were conveniently analyzed by ^{13}C NMR spectroscopy at about −30 °C in $CFCl_3$ solvent. In several instances when room temperature conditions were employed, the solution spontaneously lost HCl. The seven-membered chloride has ^{13}C peaks at δ 87.1 (C-1), 39..0 (C-2), 30.4 and 24.7 (C-3 and C-4), 41.4 (C of *t*-Bu), and 27.1 (CH_3). The eight-membered ring shows peaks at δ 87.4 (C-1), 34.0 (C-2), 28.4 and 23.8 (C-3 and C-4), 24.0 (C-5), 41.4 (C of *t*-Bu), and 28.4 (CH_3). At about −70 °C, conformational line broadening starts to show up.

Deuterated Alcohols. The **1-R-5-deuteriocycloalkanols** were prepared from **5-deuteriocyclooctanone** and the corresponding alkyl lithium in the same way as for the unsubstituted alcohols. The ketone was prepared from the known secondary alcohol (Parker and Watts, ref 24) by using Jones oxidation. Mass spectral analysis of the ketone indicated 90% deuterium content. The ^{13}C NMR spectra of the alcohols were consistent with this, the C-5 carbon showing the expected slightly displaced triplet for ^{2}D coupling and a small ^{1}H isomer peak about one-fourth to half the size of each single ^{2}D-coupled peak. Further confirmation that the deuterium was only at C-5 was provided by a ^{2}D spectrum of the labeled 1-*tert*-butylcyclooctanol, which is a clean doublet, J = 2.5 Hz (geminal coupling to C-5 hydrogen). The cations were prepared as described for the undeuterated cases.

Measurement of the Equilibrium Isotope Effects. The *tert*-butyl-substituted cation analysis is straightforward since the H_T and μ-H signals are well resolved at −130 °C and can readily be integrated. The broad D_T and μ-D signals were partly overlapped with signals from decomposition products and required some curve resolution. In the other cations, the H_T (or D_T) peaks are "buried". Fortunately, at −70 °C, one can see the averaged H_T–μ-H peak. The equilibrium constant μ-^{1}H/^1H_T is easily calculated by the formula $2\,\delta_{H(av)} - \delta_{\mu\text{-}H} - \delta_{D(av)}/\delta_{D(av)} - \delta_{\mu\text{-}H}$, where $\delta_{H(av)}$ and $\delta_{D(av)}$ are the positions of the averaged H_T–μ-H peaks in the unlabeled and deuterium-labeled ions, respectively.

NMR Line-Broadening Calculations. The μ-H–H_T interchange rate was determined by matching computer calculated curves (modified Bloch equations, two-site exchange) with experimental spectra.

Theoretical Calculations. In the ab initio study,[45] the geometries of the systems were determined as follows. In the parent complex, $C_2H_7^+$, the two carbon atoms were held fixed at three separations, 2.5, 3.0, and 3.5 Å. For each representation, the equilibrium position of the bridging hydrogen was determined along the line separating the carbon atoms. At the minimum point and at several other points along the transfer coordinate, the angles at each carbon atom were independently optimized by using the extended 4-31G basis set.[46] The angles thus obtained were transferred to the R···H···R′$^+$ systems without further optimization. In the geometries corresponding to R–H (alkane) the internal C–C bond length of 1.54 Å was used. For R$^+$ (cation), C–C = 1.48 Å. At intermediate geometries, the C–C bond lengths were linearly interpolated.

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