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Dimethylcyclodecyl Cations. Evidence for μ-Hydrido Bridging

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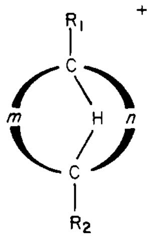
Abstract: The carbocations 1,5- and 1,6-dimethylcyclododecyl are postulated to have a μ-hydrido-bridged structure. This assignment is based on the observation of a single very high-field hydrogen in the ^{1}H NMR, anomalously low coupling constants involving this hydrogen, and very small isotope perturbation shifts using Saunders' criterion for equilibrating and resonance structural distinction. Both positional and conformational isomerization is possible in these bridged ions, but no evidence for cis-trans isomerization was found. The μ-hydrido bridging is best treated as an "open" three-center, two-electron resonance system involving a single potential minimum for the bridged hydrogen. The bridging hydrogen is not electrophilic, and the bridged ions cannot be prepared by protonating the central bond of decalins nor can the μ-hydrogen be removed as a proton. Numerous theoretical calculations have been performed and correlated with the experimental data.

We have recently reported the direct observation of a series of *secondary* medium-ring cycloalkyl cations for which a μ-hydrido-bridged structure **1** ($R_1 = R_2 = H$) was proposed.[1,2]



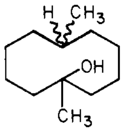
1, $m = n = 3$; $m = 3, n = 4$; $m = 3, n = 5$; $m = 4, n = 5$

Although these secondary cation investigations are very relevant in terms of previously observed transannular reactivity in medium rings,[3] they are not ideal species for looking in detail at the evidence for this μ-hydrido bridging. The corresponding *ditertiary* analogues, e.g., $R_1 = R_2 = CH_3$, have two major advantages: (1) they are thermally more stable, and (2) the proposed μ-hydrido bridge can be fixed geometrically simply by positioning the two alkyl groups in a known relationship.

In this work, we report a detailed investigation of the dimethylcyclodecyl system.[4]

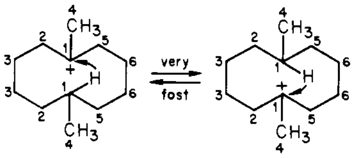
Results and Discussion

The 1,6-Dimethylcyclodecyl Cation The alcohol **2** was prepared



2

as a 60:40 mixture of isomers by treating the known ketone[5] with methyllithium. Ionization in either FSO_3H/SO_2ClF or 1:1 FSO_3H-SbF_5/SO_2ClF at temperatures of ca. −120 °C resulted in a single ionic species. The ^{13}C and ^{1}H spectra of this ion are shown in Figures 1 and 2. At first sight, the ^{13}C spectrum seems relatively normal for a rapidly equilibrating (on the NMR time scale) tertiary carbocation, e.g., eq 1, since there are six double

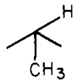


(1)

numbers illustrate the six peaks possible for a rapidly equilibrating system

intensity peaks present (NMR data for all the ions prepared in this work are gathered together in Table I) and it was expected that conformational preferences could make both "sides" of the ring nonequivalent, i.e., atoms 2 and 5 etc.[6] in eq 1. At first the ^{1}H spectrum, taken as usual over the normal sweep range, also seemed compatible with eq 1, but this situation rapidly changed when we were unable to specifically decouple the low-field carbon peak shown in Figure 1, irrespective of where we placed the proton decoupling frequency in the δ 1–4 region. This of necessity prompted a wider search, and a single intensity peak at the extremely unusual position of δ −3.9 was located (in general, carbocation ^{1}H spectra show deshielded chemical shifts). This *single* high-field proton feature has since been located in about 15 different cations.

For an equilibrating system, i.e., eq 1, one would have expected to find the



proton at ca. 1.5 ppm, i.e., typical of a saturated >C–H resonance in a hydrocarbon. Although the observed position in this case is shifted upfield by 5.5 ppm from the expected, in other recent cation examples this proton is shifted upfield by as much as 9 ppm.

This anomalous proton shift was accompanied by another gross abnormality in the NMR spectrum, namely, a coupling constant of only 35 ± 2 Hz between this high-field hydrogen and the two low-field carbons. For an equilibrating system, eq 1, this coupling would have been the average of the two couplings in a single structure, i.e., about $(130 + 0)/2$ Hz = 65 Hz. Numerous examples exist where such averaged values have indeed been found.[7]

These two observations led to the proposed μ-hydrido-bridged structure **3** for this cation. Close analogies exist between this cation

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[1] Kirchen, R. P.; Sorensen, T. S.; Wagstaff, K. *J. Am. Chem. Soc.* **1978**, *100*, 6761.

[2] Kirchen, R. P.; Sorensen, T. S. *J. Am. Chem. Soc.* **1979**, *101*, 3240.

[3] (a) Prelog, V.; Traynham, J. G. "Molecular Rearrangements"; de Mayo, P., Ed.; Interscience: New York, 1963; Vol. 1, p 593. (b) Cope, A. C.; Martin, M. M.; McKervey, M. A. *Q. Rev., Chem. Soc.* **1966**, *20*, 119.

[4] A preliminary report has appeared: Kirchen, R. P.; Sorensen, T. S. *J. Chem. Soc., Chem. Commun.* **1978**, 769.

[5] Prelog, V.; Küng, W. *Helv. Chim. Acta* **1956**, *39*, 1394.

[6] For example, this occurs at low temperature (∼−130 °C) in the 1-methylcyclodecyl cation (unpublished results).

[7] Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972; pp 345–347.

0002-7863/81/1503-588$01.00/0 © 1981 American Chemical Society

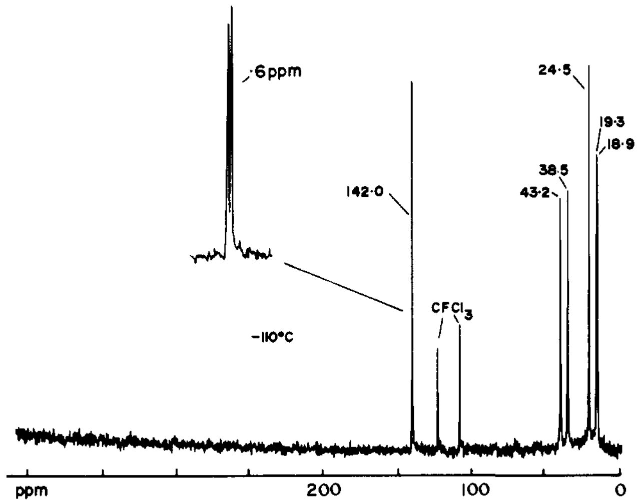


Figure 1. ^{13}C NMR spectrum (BB decoupled) of the μ-hydrido-bridged 1,6-dimethylcyclodecyl cation. The inset "doublet" is the δ splitting of the δ 142.0 peak caused by the isotope perturbation of a single CD_3 group.

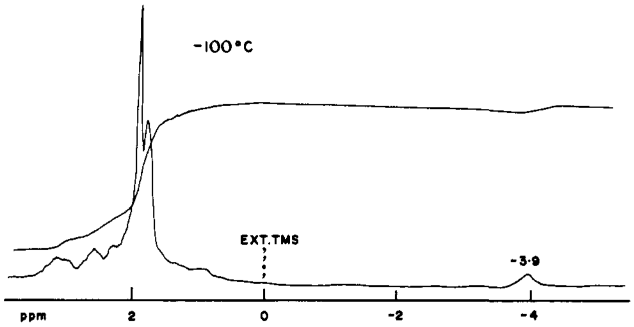
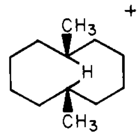


Figure 2. The 90-MHz ^1H NMR spectrum of the μ-hydrido-bridged 1,6-dimethylcyclodecyl cation.

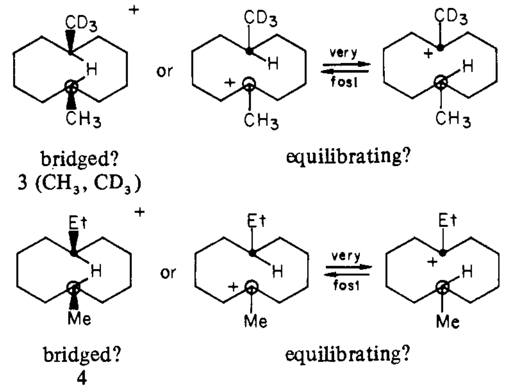
and isoelectronic μ-hydrido-bridged diboron anions,[8] e.g., a high-field μ-hydrogen and very reduced coupling constants.

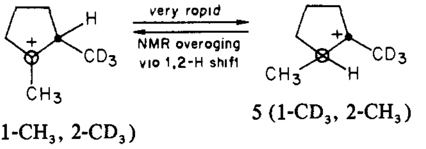


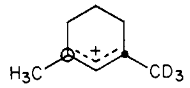
3

In order to obtain yet further experimental evidence for this μ-hydrido bridging, i.e., 3, we have now applied Saunders' "equilibrium deuterium isotope effect" criterion[9] and a similar test in which a methyl and an ethyl group are placed at the ends of the bridged system. These tests are specifically designed to distinguish between resonance systems and those involving very rapid equilibration, in our specific case between those in Scheme I. The proposed μ-hydrido-bridged ions are equivalent to resonance systems such as exist in allyl cations (see later). The Saunders' technique involves the determination of the ^{13}C peak separation (δ) of the "end" carbons (marked as ○ and ● above) in the unknowns, i.e., in 3 and 4, and then the comparison of the δ value to that for known resonance and known equilibrating models.[10] For the equilibrating model, we use their data for the 1-methyl-2-trideuteriomethylcyclopentyl cation 5, where the two averaged carbons marked ○ and ● are separated (δ) by 45.4 ppm at −45 °C, and this δ separation is very temperature dependent, e.g., δ 81.8 at −142 °C, as befits an equilibrium where the Boltzmann populations are changing. In contrast, the allyl cation resonance model 6 (this work) has a δ separation of only 0.30, with no measurable temperature dependence. The noise-decoupled ^{13}C spectrum of 3 (CH_3, CD_3) is shown as an inset in Figure 1, displaying only the critical low-field peak(s), the δ separation being 0.60, i.e., quite similar to that observed for the allyl cation 6. No measurable temperature dependence was found for this δ separation. The lower field of the two carbons can be assigned to that bearing the CD_3 group.[11]

Scheme I







6

For the Et/Me/cyclodecyl system 4, we first needed to prepare reference cations with known resonance and known equilibrating structures. Thus, the allyl cation 7 and the (expected to be) equilibrating 1-ethyl-2-methylcyclohexyl cation 8 were prepared. The δ separation for the marked carbons are shown under each structure. The experimental δ value for the Et/Me/cyclodecyl system 4 (which also shows the high-field μ-H at δ −3.6 and $J(^{13}C-^1H)$ couplings of ca. 36 Hz for both low-field carbons) was 6.3 ppm at −102 °C, and the small temperature dependence[13] observed for this δ is exactly opposite to that observed for the equilibrating system 8 but is in the same direction as that observed for the small δ vs. temperature variation in the allyl cation 7.[12]

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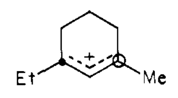
(8) (a) Brown, H. C.; Stehle, P. F.; Tierney, D. A. *J. Am. Chem. Soc.* **1957**, *79*, 2020. (b) Young, D. E.; Shore, S. G. *Ibid.* **1969**, *91*, 3497. (c) Hertz, R. K.; Johnson, H. D.; Shore, S. G. *Inorg. Chem.* **1973**, *12*, 1875. (d) Gaines, D. F. *Ibid.* **1963**, *2*, 523. (e) Clayton, W. R.; Saturnino, D. J.; Corfield, D. W. R.; Shore, S. G. *J. Chem. Soc., Chem. Commun.* **1973**, 377. (f) Saturnino, D. J.; Yamauchi, M.; Clayton, W. R.; Shore, S. G. *J. Am. Chem. Soc.* **1975**, *97*, 6063. (g) Brown, H. C.; Khuri, A.; Krishnamurthy, S. *Ibid.* **1977**, *99*, 6237. (h) Brown, C. A. *J. Organomet. Chem.* **1978**, *156*, C17.

(9) (a) Saunders, M.; Telkowski, L.; Kates, M. R. *J. Am. Chem. Soc.* **1977**, *99*, 8070. (b) Saunders, M.; Kates, M. R. *Ibid.* **1977**, *99*, 8071.

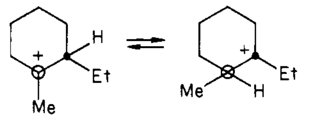
(10) Actually, the exact procedure is more complex, involving a comparison of δ/Δ values, where Δ is the shift calculated (or estimated) for a single equilibrium partner in the equilibrating case or a single resonance hybrid structure in the case of resonance systems. One should also calculate the effects on a per deuterium atom basis. Furthermore, δ values for resonance systems are defined in a more complicated way than we use in this paper. We feel justified in using this more qualititative approach because estimating Δ for μ-hydrido-bridged cations is very arbitrary. Other problems are cancelled out if we stick to CH_3–CD_3 models for our comparisons. It is also recognized that small $^{12}C/^{13}C$ isotope effects are possible since, on average, only one ^{13}C is present in any given cation molecule. Thus, although processes like that shown in eq 1 are usually labeled degenerate in ^{13}C NMR spectroscopy studies, this is strictly speaking not true.

(11) The lower field carbon is consistently smaller in size, expected under normal ^{13}C NMR measuring conditions because the NOE of CD_3 is smaller and T_1 relaxation less efficient (than for CH_3).

(12) An unusual temperature dependence of δ is observed in cation 7, δ 3.25 at −80 °C, 3.6 at −60 °C, and 3.8 and −40 °C.



7
δ 3.05 at −100 °C



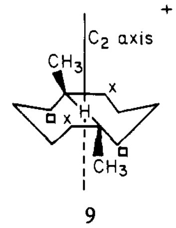
8
δ 37.3 at −125 °C,[14] δ 35.0 at −112 °C, δ 30.3 at −100 °C

It should be noted that a major contribution to δ in both the allyl cation **7** and the cyclodecyl cation **4** is the "β-substitution deshielding" present in the ethyl-substituted ^{13}C end (ca. −5 to −9 ppm expected from hydrocarbon data[15]).

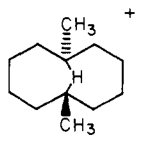
In summary, therefore, these 1,6-dialkylcyclodecyl cations behave similarly to known resonance systems and *not as equilibrating* cations. Thus, three separate criteria now all point to the μ-hydrido bridging: (1) very high-field ^1H chemical shifts, (2) very reduced ^{13}C–^1H coupling constants involving this μ-hydrogen, and (3) the similarity of δ to that of allyl cation models.

Both the first and second criteria are also found in secondary μ-hydrido-bridged cations, but it should be noted that Saunder's criterion could not easily be applied here, e.g., **1**, R_1 = H and R_2 = D, because of probable rapid H/D exchange with other hydrogens in the cations.

Conformational Aspects. A *cis*-decalin-type structure **9** is completely consistent with the pattern of the ^{13}C peaks since it predicts six double intensity peaks (a C_2 axis) and could account for the considerable chemical shift difference observed for the two sets of α-carbons (× and □ in **9**).[16] A trans geometry, **10**, would be predicted to show only four peaks since all four α-carbons would now be equivalent.[17] The *cis*-decalin geometry is written in the dichair conformation, and no line broadening indicative of chair–chair interconversions has been noted, $\Delta G^{\ddagger} \geq 10$ kcal/mol (in a possible ditwist boat conformation such a large barrier would be very unexpected). A diboron anion analogue of **9** has been characterized by X-ray crystallography and has the identical *cis*-decalin structure **11**.[8e,f]



9



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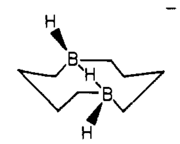
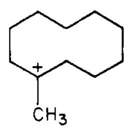


11

Rearrangement. When the cation **9** solution was warmed to −100 °C, the peaks of **9** in the ^1H or ^{13}C NMR spectrum slowly decrease. Since ring contraction reactions are known for the 1-methylcyclodecyl cation,[18] e.g., **12** → **13**, we initially considered the same possibility for **9**. However, the peaks which appear for



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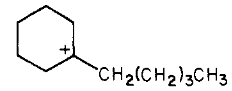
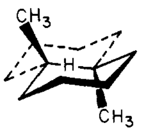


13

the rearranged cation are clearly those of a *second μ-hydrido-bridged species*, the key observation being an even higher field proton at δ −5.8 in the ^1H spectrum. This is shown in Figure 3. The ^{13}C spectrum showed a single, but very broad, low-field carbon peak and showed what appeared at first sight to be three high-field peaks, these also being broad—see Figure 4. The broad lines in the ^{13}C spectrum are easily explained because on cooling, the broad lines split up into a multiple series of peaks; i.e., the spectrum of this rearrangement cation at −100 °C has fortuitously a dynamic exchange rate in the NMR line-broadening region. Warming above −100 °C sharpens the averaged peaks, as expected. The high-field ^{13}C NMR pattern, under frozen-out conditions, is complex, but the low-field region clearly shows three peaks; see inset in Figure 4. Correspondingly, the "single" proton peak at δ −5.8 becomes three peaks at lower temperatures (200-MHz spectrum); see Figure 5. The areas for the ^1H and ^{13}C spectra match, and by specific decoupling it can be shown that the high-field protons are coupled to the low-field carbons. Indeed, the ^{13}C and ^1H spectra form a sort of "mirror-image" pattern. We tentatively assigned this rearranged ion to a *trans*-1,6-dimethylcyclodecyl cation, **10**, there being three possible conformers, viz., chair–chair (**14**), chair–twist boat (**15**), and twist boat–twist boat (**16**). Furthermore, MINDO/3 calculations[19] suggested that the cis and trans isomers were not very different in energy (see later). However, an independent synthesis of the 1,5-dimethylcyclodecyl cation proves that this latter species is the rearranged product.



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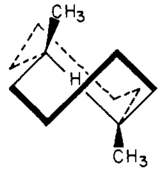
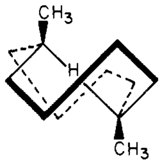
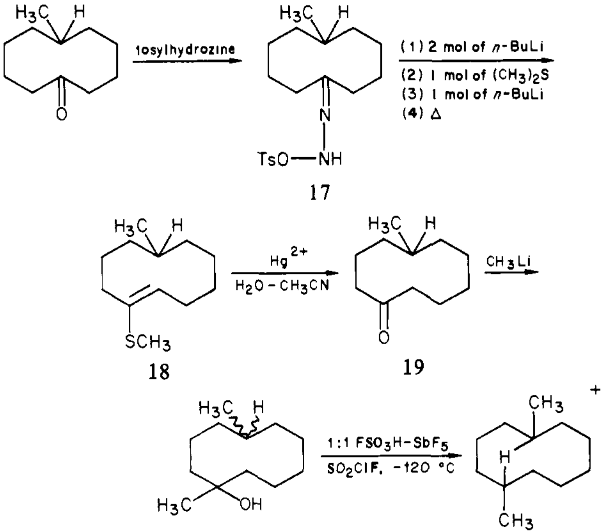




16

The *cis*-1,5-Dimethylcyclodecyl Cation. The 1,5-dimethylcyclodecyl system was conveniently prepared, eq 2, by first performing a carbonyl transposition on the 6-methylcyclodecanone, using the general procedure of Nakai and Mimura.[20]



20
55:45 mixture

21

(2)

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(13) The δ separation is temperature dependent, δ 6.8 at −92 °C, 5.9 at −110 °C, 5.5 at −117 °C, and 5.2 at −124 °C. The temperature dependence seems to decrease toward a limiting value at very low temperatures. Furthermore, although the two individual peaks in **4** move in opposite directions, the extent is different. We have no entirely satisfactory explanation for these results other than a feeling that the population of low-frequency vibrational states probably affects chemical shifts. It should be emphasized that the effects are much smaller than observed for the equilibrating systems, e.g., **8**, and are in the opposite direction.

(14) Judging from the small low-field shift of the $>C-^{13}CH_3$ carbon with increasing temperature, the right-hand cation in **8** is the more stable.

(15) Reference 7, pp 55–65.

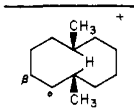
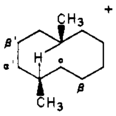
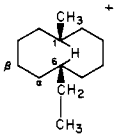
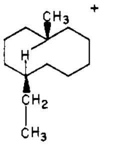
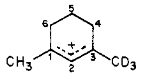
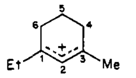
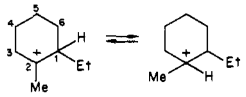
(16) Note that the symmetry proposed for **9** is different from that which would be involved in the equilibrating case, i.e., structure **3**.

(17) Strictly speaking, only if the C–H–C bonds are linear. However, the inversion barrier for a nonlinear bridge would likely be very small (see subsequent calculations on model systems).

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

(19) Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1285–1293.

Table I. NMR Spectral Data of Cations[a]

ion	description
	^{13}C: 142.0 (2 C, $J = 36$),[b] 43.2 and 38.5 (both 2 C, both $J = 126$ (α-C)), 19.3 and 18.9 (both 2 C, both $J = 129$ (β-C)), 24.5 (2 C, $J = 131$ (CH_3)) ^{1}H:[c] 3.15 (2 H, t, $J \approx 13$),[d] 2.65 (2 H), 2.27[e] (2 H, another 2 H buried under CH_3 peak (all α-CH_2 protons)), 1.79 and 1.38 (β-CH_2), −3.9[f] (μ-H)
	^{13}C:[g] 162.5[b] (2 C, $J = 37$), 40.0 (2 C, $J = 133$), 37.2 (2 C (α- and α′-C)), 34.7[h] (β′-C), 23.8 and 21.1[h] (β- and γ-C), 25.0 ($J = 130$ (CH_3)), ^{1}H:[g] 2.08 (CH_3), −5.6 (μ-H), remainder broad and unresolved
first minor conformational isomer	^{13}C:[j] 165.3[b] (2 C, $J = 37$) ^{1}H:[c] −6.1 (μ-H)
second minor conformational isomer	^{13}C:[j] 167.6[b] (2 C, $J = 37$) ^{1}H:[c] −6.2 (μ-H)
averaged spectrum of above isomers (−80 °C)	^{13}C: 41.7 (1 C (β′-C)), 39.8 (4 C (α-C)), 25.4 (2 C (CH_3)), 25.0 (3 C (β- and γ-C)) ^{1}H: −5.8 (μ-H)
	^{13}C: 147.4 (1 C, $J = 36$ (C-6)), 141.5 (1 C, $J = 36$ (C-1)), 43.1, 40.9, 38.3, 34.7, and 30.8 (all 1 C (α-C and CH_2 of Et),[k] 18.85 (4 C (β-C)),[l] 24.4 (1 C (CH_3)), 10.9 (1 C (CH_3 of Et)) ^{1}H: 2.0 (CH_3), 1.2 (t, $J = 6.5$ (CH_3 of Et)), −3.6 (μ-H), remainder broad and nondescript
	^{13}C:[n] ca. 162–173 (very broad or overlapping), 13.6 (CH_3 of Et)[p] ^{1}H:[m] 2.1 (CH_3), 1.2 (t, $J = 6.5$ (CH_3 of Et)), −5.4 (μ-H), remainder nondescript (some decomposition has also occurred)
	^{13}C:[q] 232.4 (C-3), 232.1 (C-1), 139.4 (C-2), 37.9 (C-4, C-6), 32.2 (CH_3), 20.3 (C-5)
	^{13}C:[r] 236.1 (C-3),[s] 232.4 (C-1), 137.1 (C-2), 39.3, 38.5, and 37.1 (CH_2 of Et, C-4, C-6), 32.6 (CH_3), 20.7 (C-5), 10.0 (CH_3 of Et)
	^{13}C:[t] 218.2 (C-1), 180.9 (C-2), 55.5 and 55.3 (C-3, C-6 or CH_2 of Et), 37.7, 35.6, and 35.1 (C-4, C-5 and one of preceding three), 26.4 (CH_3),[u] 9.8 (CH_3 of Et)

[a] ^{13}C shifts in δ (ppm) relative to internal $CFCl_3$ (δ 117.9), ^{1}H shifts in δ (ppm) relative to external Me_4Si in $CFCl_3$. J in Hz; most ^{13}C multiplicities confirmed by off-resonance decoupling. [b] Shown by heteronuclear decoupling to be specifically coupled to μ-H. [c] 200 MHz. [d] Becomes a doublet, $J \approx 16$ Hz, on irradiation at δ 1.79. [e] Becomes a doublet, $J \approx 15$ Hz, on irradiation of μ-H. [f] Characteristically broad, ca. 20 Hz at −90 °C (can be sharpened somewhat on decoupling methyls and α-CH_2's). [g] Major isomer. [h] Tentative assignment. [j] Additional peaks from these conformers found at δ 47.1, 44.7, 41.7, 39.8, 31.6, 30.3, and 27.2. [k] Lack of equivalence of any of the α-carbons is further evidence for a *cis*-decalin-type structure since the C_2 axis is now missing but not a potential symmetry plane. [l] Overlapping peaks, somewhat broad. [m] 90 MHz. [n] −95 °C. [p] It is difficult to pick out any distinctive features of this spectrum other than this peak, which is very characteristic of CH_3 in Et and therefore indicative that this group is still present. [q] ^{13}C and ^{1}H NMR data for the unlabeled cation have been reported: Olah, G. A.; Liang, G. *J. Am. Chem. Soc.* 1972, *94*, 6434. [r] −60 °C. [s] Could possibly be interchanged. [t] −125 °C. [u] See ref 14.

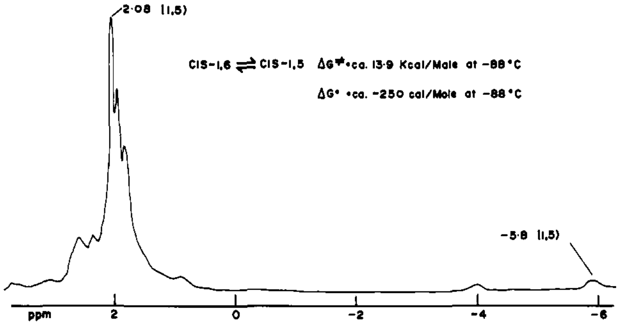


Figure 3. The 90-MHz ^{1}H NMR spectrum of a mixture of the μ-hydrido-bridged 1,5-dimethyl- and 1,6-dimethylcyclodecyl cations.

Addition of the alcohol **20** to 1:1 SbF_5–FSO_3H/SO_2ClF at −120 °C led to the pure 1,5-dimethylcyclodecyl cation **21**, in all respects identical with the rearranged ion starting from the 1,6-dimethyl isomer **9**. The μ-hydrido-1,5- and 1,6-dimethylcyclodecyl cations

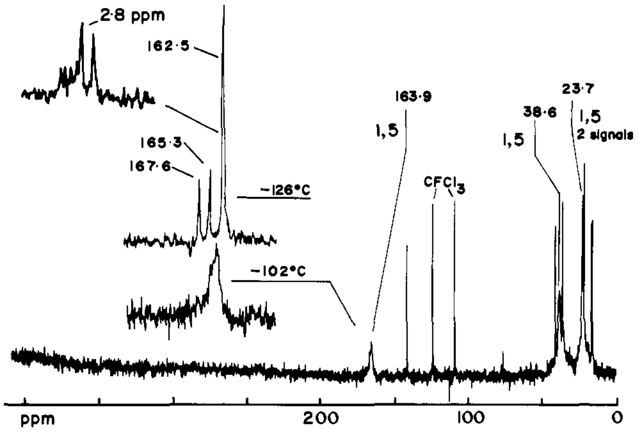


Figure 4. ^{13}C NMR spectrum (BB decoupled) of a mixture of the μ-hydrido-bridged 1,5-dimethyl- and 1,6-dimethylcyclodecyl cations. The first two insets show the temperature-dependent line broadening of the δ 163.9 peak (from the 1,5 isomer). The uppermost inset is the δ splitting of each of the δ 162.5, 165.3, and 167.6 peaks caused by the isotopic perturbation of a single CD_3 group.

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(20) Nakai, T.; Mimura, T. *Tetrahedron Lett.* **1979**, 531.

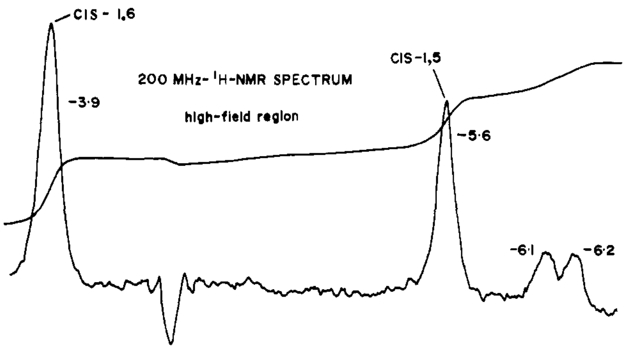
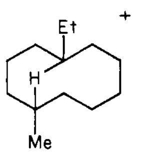


Figure 5. The 200-MHz ^{1}H NMR spectrum of the μ-hydrido region of a mixture of the μ-hydrido-bridged 1,5-dimethyl- and 1,6-dimethylcyclodecyl cations. The peaks at δ −5.6, −6.1, and −6.2 are assigned to three different conformations of the 1,5 system.

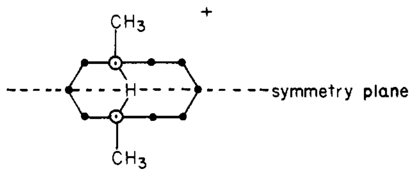
9 and **21** actually form an equilibrium mixture (approached by using either pure isomer) which favors the 1,5 isomer, K = 1,5/1,6 = 2.8 (−84 °C). The rate constant for the forward reaction 1,6 $\rightleftarrows$ 1,5 was $k_f = 1.3 \times 10^{-4}$ s^{-1} at −88 °C, $\Delta G^{\ddagger}$ = 13.9 kcal/mol.

The evidence for μ-hydrido bridging in **21** follows the same arguments used for **9**: viz., (1) a very high-field chemical shift for the μ-hydrogen at δ values equal to −5.6, −6.1, and −6.2 in the three different conformers, (2) the coupling of this μ-hydrogen to the ^{13}C terminal carbons is 37 Hz for the major conformer (the minor conformers coupled ^{13}C peaks are overlapping, but off-resonance splittings are identical, within experimental error, for all three conformers, so that indications are that all three have the same coupling constant), and (3) application of the Saunders isotopic perturbation technique yields δ splittings of 2.75, 1.1, and 1.1, respectively, as one goes to the lower field carbon of the mixture; see second insert in Figure 4. These numbers are significantly larger than found for **9** (0.6 ppm) or for the allyl cations, but they are still much closer to these latter models than to equilibrating models. The *cis*-1,6-ethylmethylcyclodecyl cation **4** also rearranges at about the same temperature as **9**, the μ-hydrido peak in **4** being replaced by one at δ −5.4 and assignable to the 1,5-ethylmethylcyclodecyl cation **22**. The conformational behavior of the latter was not further investigated, but the 1,5/1,6 equilibrium constant again favors the 1,5 isomer.



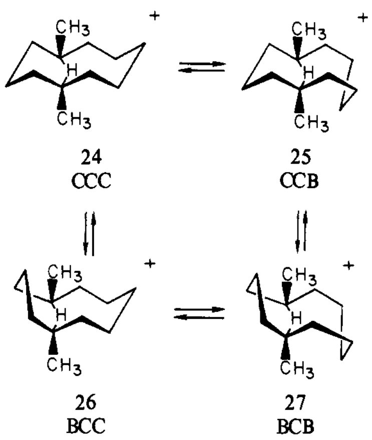
22

Conformational Analysis of 21. The appearance of three μ-hydrogens in **21** dictates the existence of at least three conformers, and since each conformer shows a *single* ^{13}C peak for *two* bridge carbons, it is very probable that each conformer has a symmetry plane (or very rapidly averages to this), i.e., **23**.



23

One other peculiarity of the observed line broadening is that three peaks average to one and this is impossible for a single rate process in the present context. A minimum of two rate processes is necessary, and these have to have nearly the same value. These requirements are nicely met when one examines the conformational choices involved in a 1,5 bridge. These are shown below in structures **24**–**27**, and one notes that *all* have a symmetry plane of the kind shown in **23**. At least three of these four conformers would be involved here, and B → C interconversions are likely to have similar barriers to C → B changes, if the ground-state energy levels are comparable (as is obviously the case, ratio is ca. 1:1:4; see Figure 5). By analogy to the conformation of cyclodecanone,[21] one might tentatively assign the major conformer to the BCB isomer. The cis geometry is quite clearly the more stable (molecular model studies), but MINDO/3 calculations on the various geometric and positional isomers give energies for **27** which are larger than those calculated for either *cis*- or *trans*-1,6-dimethyl-bridged ions (see later).



24
CCC

25
CCB

26
BCC

27
BCB

CCC = chair, chair, chair, etc.

A quantitative figure for the conformational free energy of activation, $\Delta G^{\ddagger}$, was obtained by matching a series of 200-MHz ^{1}H spectra, run at different temperatures, with computer-simulated line broadening, $\Delta G^{\ddagger}$ = ca. 7.7 and 8.1 kcal/mol for the two rates.[22]

Mechanism of the Interconversion of the 1,6/1,5 Isomers 9 and 21. The barrier for the interconversion of the title cations is $\Delta G^{\ddagger}$ = 13.9 kcal/mol, considerably lower than expected. For example, 1,2- and 1,3-dimethylcyclopentyl cations are interconverted with $\Delta G^{\ddagger}$ = 15.8 kcal/mol.[23] This latter figure reflects the fact that a tertiary$^+$ $\rightleftarrows$ [secondary]$^+$ step (ca. 10–15 kcal/mol[24]) is a prelude to the methyl shift, so that the transition state must be even greater than this. A possible rationale for this anomaly in the case of **9** and **21** would be the presence of partially bridged secondary–tertiary carbocations, where one could effectively lower the energy of the "secondary" intermediates, eq 3. Indeed, very definite evidence has now been obtained in cyclooctyl cation studies for such secondary–tertiary bridging.[25] The equilibrium mixture of **9** and **21** eventually decomposes at temperatures greater than −60 °C, but up to this temperature there is no evidence for the formation of 1,4- 1,3-, or 1,2-dimethylcyclodecyl cations.[26] The above interconversion of **9** and **21** also suggests that one should expect to see interchange of the μ-hydrogen with hydrogens on

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(21) Anet, F. A. L.; Cheng, A. K.; Krane, J. *J. Am. Chem. Soc.* **1973**, *95*, 7877. In 4,4,8,8-tetramethylcyclodecanone, a BCC conformation has been found: Borgen, G.; Dale, J. *Acta Chem. Scand., Ser. B* **1976**, *B30*, 711–715.

(22) On the basis of the assumption of only three populated conformers. The exchange matrix in which the large peak exchanges with both small peaks seems to fit the experimental spectrum better than the other two permutations. For example, this might correspond to the process

$$\underset{\text{minor}}{\text{BCC}} \rightleftarrows \underset{\text{major}}{\text{BCB}} \rightleftarrows \underset{\text{minor}}{\text{CCB}}$$

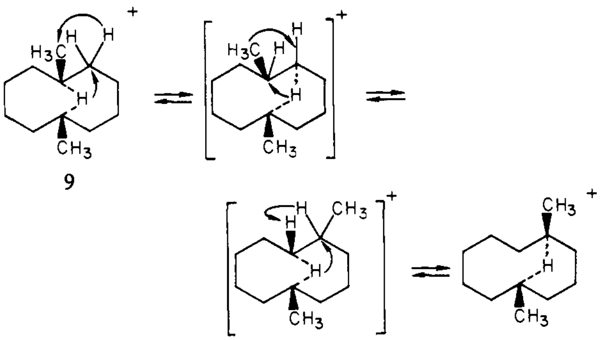
if one assumes that the major conformer has the BCB structure. The large barrier (8.1 kcal/mol) is calculated for the exchange of the major peak with the highest field of the minor peaks and other combinations of rates for this particular exchange permutation do not fit the experimental data as well.

(23) Hogeveen, H.; Gaasbeek, C. J. *Recl. Trav. Chim. Pays-Bas* **1969**, *88*, 1307.

(24) Arnett, E. M.; Petro, C. *J. Am. Chem. Soc.* **1978**, *100*, 5408–5416 and references contained in this article.

(25) Kirchen, R. P.; Okazawa, N.; Ranganayakulu, K.; Rauk, A.; Sorensen, T. S. *J. Am. Chem. Soc.* **1981**, *103*, 597.

(26) The formation of these by a mechanism equivalent to eq 2 would initially require 1,4 bridging, and no evidence has yet been found for this, either in observable ion work or in solvolysis studies.



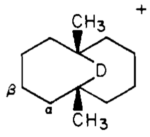
9

21

(3)

the adjacent carbons and in fact this can be seen in two different experiments.

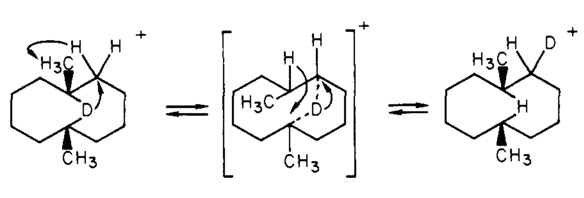
The μ-Deuterio-1,6-dimethylcyclodecyl Cation 28. The title



28

cation was prepared in the same way as the proton analogue, using a preparation of 6-methyl-6-deuteriocyclodecanone described by Prelog.[5] It had been intended to use this cation for vibrational spectroscopy studies, but unfortunately the deuterium is exchanged in a rapid but still measurable reaction. This exchange is easily monitored by using ^{2}D NMR; on initial preparation one has a spectrum with the deuterium largely in the μ-position. At −120 °C, this peak rapidly decreases and is replaced by a broad peak at the position for "normal" C–D resonances, k = ca. 1×10^{-3} s^{-1} at −120 °C, $\Delta G^{\ddagger}$ = ca. 10–11 kcal/mol. Complementary results are obtained from ^{1}H NMR spectra where an initially absent μ-H peak very rapidly "grows in" with time (−106 °C). A sizeable isotope effect favoring μ-H is indicated at equilibrium,[27] but we are not certain whether the deuterium is able to exchange with only the eight α-protons or whether all 16 ring protons are involved.[28] Significantly, *no deuterium exchange with solvent is found.*

The ^{13}C spectrum of the μ-deuterio ion has virtually identical chemical shifts compared to those of the proton analogue. Similarly, the ^{2}D NMR shifts, specifically the μ-hydrogen, are the same in both deuterio and protio isomers.[29] The barrier for the H/D exchange, $\Delta G^{\ddagger}$ = ca. 10–11 kcal/mol, is considerably less than that for the 1,6-dimethyl ⇄ 1,5-dimethyl interchange, $\Delta G^{\ddagger}$ = 13.9 kcal/mol, and this is consistent with previous studies where hydrogen shifts generally have a lower barrier than similarly positioned methyl shifts; i.e., the proposed mechanism in eq 4 starts out with the same intermediate as eq 3 but does not require a methyl shift.



(4)

Line Broadening in the μ-Hydrido-1,6-dimethylcyclodecyl Cation Involving the μ-H. If the equilibrium mixture of 9 and 21 is warmed beyond −70 °C, the μ-H peak (and others) in cation 9 begins to broaden (reversible on cooling). No such changes occur in cation 21. These observations are almost certainly due to the same process (the H/D exchange) discussed in the previous section, except that the rate is now in the NMR line-broadening range. The rate can be calculated by simulation and comparison of exchange spectra or by double-irradiation spin-saturation transfer, $\Delta G^{\ddagger}$ = ca. 10.2 kcal/mol, in good agreement with the H/D exchange result.[30] For unknown reasons, the corresponding exchange in the 1,5 isomer 21 must be too slow to observe, before eventual decomposition occurs on heating too high.

Correspondence of Experiment with MO Calculations. Molecular orbital (MO) calculations have been carried out on the model μ-hydrido-bridged cations $H_3C\cdots H\cdots CH_3^+$, $Et\cdots H\cdots Et^+$, and $i\text{-}Pr\cdots H\cdots i\text{-}Pr^+$ at both the STO-4G ab initio[31] and MINDO/3[19] levels, $t\text{-}Bu\cdots H\cdots t\text{-}Bu^+$ with MINDO/3 only. Some calculations have previously been reported in the literature for $C_2H_7^+$ (protonated ethane).[32] Our MO results can be summarized as follows.

(1) All of the above molecules are stable with respect to dissociation into alkane and carbocation.

(2) The stability decreases in the series Me > Et > i-Pr > t-Bu.[33]

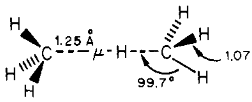
(3) The $\underbrace{C\cdots H\cdots C}$ bond distances increase in the order: Me, 1.21 Å, Et, 1.25 Å, i-Pr, 1.31 Å, and t-Bu, 1.37 Å (MINDO/3).

(4) The C–H–C bonding angle θ is close to 180° (linear) in all cases.

(5) The hybridization of the bridge carbons is intermediate between sp^2 and sp^3.

(6) The μ-hydrogen has a slight negative charge and sits in a very "loose" potential; it can be moved substantially up, down, or sideways with little overall change in the total energy.

(7) Where compared, both ab initio and MINDO/3 results give very similar optimized geometries. The optimized geometry for μ-bridged $C_2H_7^+$ is shown below,[34] and the potential well of the bridged proton in $i\text{-}Pr\cdots H\cdots i\text{-}Pr^+$ is shown in Figure 6.



charge on μ-H = −0.008

In order to look at the possible distortions to these simple structures present in the medium-ring μ-hydrido-bridged cyclodecyl cations, we have also carried out fully optimized geometries (MINDO/3) on the *cis*-1,6-μ-hydridocyclodecyl cation 29, the corresponding cis-1,5 isomer 30, and the trans-1,6 isomer 31. Pertinent bond lengths and angles are shown below. The calculated C···H···C angle in the cis-1,6 case 29 is fairly close to that observed in the crystal structure determination for the diboron anion 11 (140°).

Two aspects of these calculations can be related to the experiments reported here and elsewhere.

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[27] The equilibrium ratio, $^2D_{\text{normal}}/\mu\text{-}^2D$, is ≥25 at −115 °C.

[28] Since we see no evidence for 1,4-dimethylcyclodecyl cation formation, one would also not expect to see H/D interchange involving the eight "β" protons in 28.

[29] Recently, the shape of the O···H···O potential in hydrogen bonding has been probed by comparing ^{1}H, ^{2}D, and ^{3}T chemical shifts for otherwise identical systems. Similar studies might be fruitful for μ-hydrido bridging, but this will require much better chemical shift accuracy than we can presently obtain. Altman, L. J.; Laungani, D.; Gunnarsson, G.; Wennerström, H.; Forsén, S. *J. Am. Chem. Soc.* **1978**, *100*, 8264–8266.

[30] The kinetics for this μ-H interchange can only be approximately correct since we are not sure how many α- or β-protons are involved in the dynamic exchange. The calculations have assumed an exchange with eight α-protons.

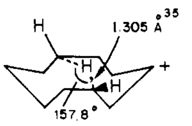
[31] Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657–2664.

[32] (a) Lathan, W. A.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 808. (b) Bischof, P. K.; Dewar, M. J. S. *Ibid.* **1975**, *97*, 2278–2280. (c) See also: Hiraoka, P.; Kebarle, P. *Adv. Mass Spectrom.* **1978**, *7B*, 1408.

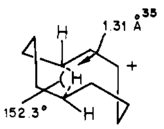
[33] The actual figures are 15.0, 9.25, and 6.0 kcal/mol for Me, Et, and i-Pr cases, on the basis of the ab initio results.

[34] The most stable bridged form, by 0.5 kcal/mol, is actually bent on an angle of 141.5° (ref 32a and this work). This illustrates the extremely loose nature of the calculated μ-hydrogen potential. The ion $C_2H_7^+$ is known from mass spectrometry[32c] and molecular beam studies, but the structural evidence available from the latter is apparently not compatible with a μ-H-bridged structure; see, for example: Weiner, J.; Smith, G. P. K.; Saunders, M.; Cross, Jr., R. J. *J. Am. Chem. Soc.* **1973**, *95*, 4115.

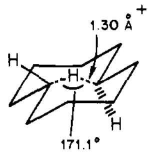
[35] In order not to prejudice the calculations, we imposed no symmetry restrictions. Consequently the two C–H–C$^+$ bond lengths are slightly different in most cases and exacerbated because the C–H–C potential is so flat. The data shown are approximate averages.



29
charge on μ-H = −0.094
charge on carbons = +0.28
ΔH = 148.6 kcal/mol



30
charge on H = −0.093
charge on carbons = +0.27
ΔH = 152.3 kcal/mol



31
charge on μ-H = −0.111
charge on carbons = +0.29
ΔH = 151.3 kcal/mol

(1) The μ-H sits in a very loose potential and has a small calculated negative charge. In experiments, one finds an ^1H peak at very high fields (implying more negative charge on hydrogen than in a C–H hydrocarbon case).

(2) The ^{13}C–^1H coupling constant to the terminal bridge hydrogens in secondary bridged ions is ca. 150 Hz,[2] appropriate for a hybridization of the carbons intermediate between sp^2 and sp^3, as also found in the calculations.

Formulation of μ-Hydrido-Bridged Cations as Open Three-Centered Resonance Systems. Three-center, two-electron bonding can exist in two distinct types, often referred to as "closed" and "open" geometries[36]

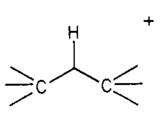
"closed"

"open"

although it is recognized that a continuum of intermediate geometries is also possible. The closed geometry appears to be preferred in many cases, e.g., in a number of single μ-H-bridged organometallics,[36] in H_3^+,[37] and in the formulation of protonated C–C and C–H single bonds.[38] However, the open geometry seems well established for μ-H-bridged diboron anions.[8,39] We believe that μ-hydrido-bridged carbocations basically have the "open" bonding. This is based on the following observations.

(1) The previously discussed calculations on model systems give essentially linear geometries. Even in cyclodecyl rings, C–H–C angles of 152 and 158° are calculated, two wide (~2.5 Å) to permit significant direct C–C overlap. This calculated distortion from 180° is undoubtedly caused by ring conformational effects. One must emphasize of course that these are not experimental observations.

(2) Perhaps more importantly, the properties of these cations are *not those expected for a protonated C–C bond*, for which a "closed" bonding has been postulated, i.e.



in Olah's notation.[38] This formulation implies that another approach to our μ-hydrido-bridged cations should be the C–C *protonation* of the 9–10 bond in decalins. Three separate experiments have therefore been performed, and these all show quite clearly that the μ-hydrogen does not have a facile electrophilic (H^+) character.

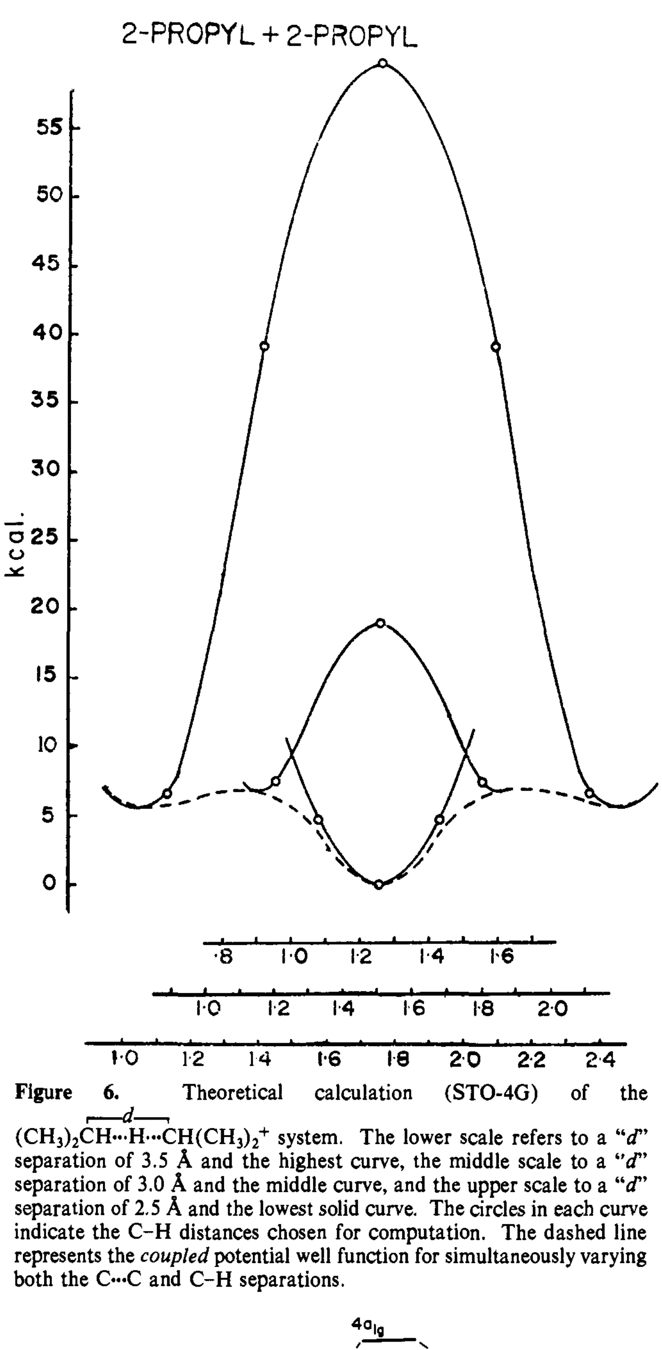


Figure 6. Theoretical calculation (STO-4G) of the $(CH_3)_2\overbrace{CH\cdots H\cdots CH}^{d}(CH_3)_2^+$ system. The lower scale refers to a "*d*" separation of 3.5 Å and the highest curve, the middle scale to a "*d*" separation of 3.0 Å and the middle curve, and the upper scale to a "*d*" separation 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 simultaneously varying both the C···C and C–H separations.

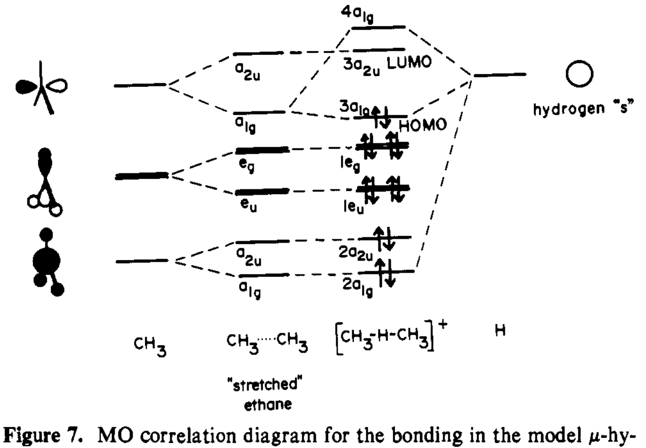


Figure 7. MO correlation diagram for the bonding in the model μ-hydrido-bridged cation $CH_3\cdots H\cdots CH_3^+$.

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[36] Bau, R.; Teller, R. G.; Kirtley, S. W.; Koetzle, T. F. *Acc. Chem. Res.* **1979**, *12*, 176–183.

[37] Christoffersen, R. E. *J. Chem. Phys.* **1964**, *41*, 960.

[38] (a) Olah, G. A.; Klopman, G.; Schlosberg, R. H. *J. Am. Chem. Soc.* **1969**, *91*, 3261. Hogeveen, J.; Bickel, A. F. *J. Chem. Soc., Chem. Commun.* **1967**, 635. (c) Olah, G. A.; Halpern, Y.; Shen, J.; Mo, Y. K. *J. Am. Chem. Soc.* **1971**, *93*, 1251.

[39] (a) Hall, J. H., Jr.; Marynick, O. S.; Lipscomb, W. N. *Inorg. Chem.* **1972**, *11*, 1326. (b) Hoheisel, C.; Kutzelnigg, W. *J. Am. Chem. Soc.* **1975**, *97*, 6970.

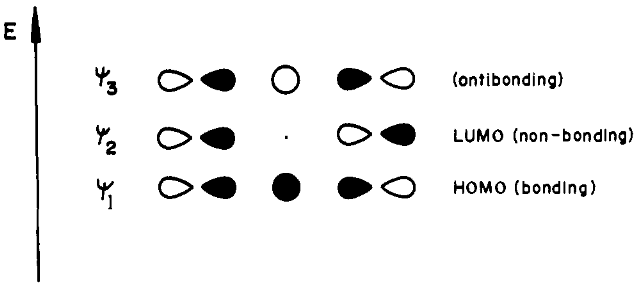
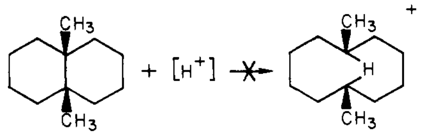


Figure 8. Frontier orbital interactions involved in μ-hydrido-bridged carbocations.

(a) Protonation attempts on *cis*-9,10-dimethyldecalin **32**,[40] using a wide variety of superacid systems, show no evidence for **9**. Note that one has a very good analytical measure for **9**, even in small concentrations, by looking in the high-field ^{1}H NMR region.[41]



32 9

(b) The μ-deuterio ion **28**, as previously noted, shows absolutely no exchange with a protic acid solvent system (1:1 FSO_3H/SbF_5).[41]

(c) Quenching the ion **9** in excess NaOMe/MeOH yields mainly 1,6-dimethylcyclodecene. A careful study of the total recovered material shows no evidence for μ-H deprotonation with formation of 9,10-dimethyldecalin **32**.

One can "picture" an "open" μ-hydrido-bridged ion in terms of a MO correlation diagram, and this is shown in Figure 7. The important frontier interactions are between the C $2p_z$ and H 1s orbitals, a bonding interaction (HOMO), an essentially nonbonding level (LUMO), and an antibonding level, as shown in Figure 8, more-or-less as written by Swain et al.[42] in discussing the transition state for a hydride-transfer reaction. This MO diagram also corresponds to that written for symmetrical hydrogen bonding,[43] except that two electrons are removed from the ψ_2 level. The bonding level in μ-hydrido bridging has a high electron density centered between the carbons and embedding the hydrogen atom. The extra two electrons in hydrogen bonding populate the end atoms and make it obvious why hydrogen bonding shows the opposite polarity to μ-hydrido bridging.

It may be possible in the future to probe the HOMO-LUMO separation if reliable electronic spectra can be measured and if the separation corresponds to an accessible wavelength. The resonance stabilization in these μ-hydrido-bridged cations cannot be large, probably <5 kcal/mol, but such resonance formulations are useful in that one can now make conceptual comparisons to the properties of the well-known allyl cation systems since there is an obvious analogy to the μ-bridged ions, in particular, the possibility of unsymmetrically μ-hydrido-bridged carbocations,[25] analogous to unsymmetrical allyl cations.

In conclusion, we have presented detailed evidence in support of the existence of μ-hydrido-bridged cations, probably with symmetric, single potential minima or something very close to this. We have shown that positional and conformational isomers (and isomerization) exist, although no evidence for cis-trans geometric isomerization has yet been found. The cations are best regarded as "open" resonance stabilized three-center, two-electron systems, with the μ-hydrogen showing no electrophilic character, even in transition-state behavior.

Experimental Section

6-Hydroxycyclodecanone: prepared both by the Criegee procedure[44] and by the acetic anhydride procedure of Holmquist et al.,[45] via 1-acetoxy-11-oxabicyclo[4.4.1]undecane, ^{13}C NMR: δ 168.4 (C=O), 108.1 (CO_2), 75.0 (C—O), 22.1 (CH_3), 39.7, 33.6, 30.0, 23.4 (all 2 $C(CH_2)$) (with the latter more convenient for large-scale preparations). As reported,[46] the NMR spectra of solutions show a mixture of free ketone and bicyclic acetal, ^{13}C peaks for the former: δ 214.3 (C=O), 69.5 (C—O), 42.5, 34.4, 24.0, and 23.6 (all 2 $C(CH_2)$). The latter: δ 103.3 (CO_2), 75.9 (C—O), 41.3, 34.6, 25.6, and 25.0 (all 2 $C(CH_2)$).

6-Methylcyclodecanone: prepared from 6-hydroxycyclodecanone as described by Prelog et al.[5] ^{13}C NMR: δ 211.2 (C=O), 30.0 (CH), 22.0 (CH_3), 42.1, 33.7, 24.3, and 23.9 (all 2 $C(CH_2)$).

1,6-Dimethylcyclodecan-1-ol (2): prepared in 70% yield by thrice treating the ketone with methyllithium (enolization!) at 0 °C, with the usual workup after each treatment; bp 79-80 °C (0.5 mmHg). Anal. Calcd for $C_{12}H_{24}O$: C, 78.26; H, 13.04. Found: C, 78.15; H, 12.90. NMR analysis indicates a mixture of cis and trans isomers (40:60). ^{13}C NMR: δ 75.0 (both C—O), 32.4 and 31.9 (CH), 30.1 and 29.9 (CH_3 on C-1), 22.6 (one CH_3 on C-6), 36.2, 36.1, 31.5, 31.1, 24.2, 24.0, 22.5, and 22.3 (all 2 $C(CH_2)$). ^{1}H NMR: δ 0.89 and 0.905 (both d, J = 6.5 Hz).

1-Ethyl-6-methylcyclodecan-1-ol: prepared from ethyllithium and the ketone (four treatments), as for the methyl analogue. ^{13}C NMR analysis shows a mixture of cis and trans isomers: δ 75.9 (both C—O), 32.5 and 31.9 (CH), 22.9 and 22.6 (CH_3), 7.5 (both CH_3 of Et), 34.2, 34.0, 33.9, 32.1, 31.2, 24.7, 24.3, 22.2 and 21.9 (all 2 $C(CH_2)$).

6-Deuterio-1,6-dimethylcyclodecan-1-ol: prepared from the correspondingly labeled ketone as described for the unlabeled alcohol. The ketone was prepared by a known[5] sequnce starting with 6-hydroxycyclodecanone. The detuerium content and position were checked by both ^{13}C and ^{2}D NMR. In the ketone, C-6 is "missing", and in the isomeric alcohols, peaks at δ 32.4 and 31.9 have likewise "disappeared". The ^{2}D NMR shows a major peak at δ 1.61, assignable to the C-6 deuterium, half-width 0.1 ppm, 90% area, and a smaller peak at 1.4 ppm, ca. 10%, which has obviously been introduced into another position. However, this product is certainly satisfactory for our experiments.

1-Methyl-*d*$_3$-6-Methylcyclodecan-1-ol: prepared from methyl-d_3-lithium and the ketone by using three treatments of the lithium reagent as for the unlabeled alcohol, bp 81-82 °C (0.6 mmHg).

6-Methylcyclodecanone tosylhydrazone: from 8.4 g (0.05 mol) of ketone, 9.46 g (0.055 mol) of tosylhydrazine, and 0.5 mL of HCl in 40 mL of 95% ethanol, there was obtained with heating to reflux and recrystallization from 95% ethanol 14.4 g (90%) of the title compound, mp 119-120 °C. Anal. Calcd for $C_{18}H_{28}N_2O_2S$: C, 64.28; H, 8.33; N, 8.33. Found: C, 64.47; H, 8.68; N, 8.29. ^{1}H NMR: δ 0.65 (d, J = 6 Hz, 3 H), 0.8-2.4 (b, 18 H), 2.3 (3 H), 7.81 and 7.23 (AB pattern, J = 9 Hz, 4 H).

1-Thiomethyl-7-methylcyclodec-1-ene. A solution of 3.21 g (0.01 mol) of the above tosylhydrazone in 25 mL of a 1:2 mixture of tetramethylethylenediamine (TMED) and THF was cooled to -50 °C. Under argon, 14 mL of 1.6 M *n*-BuLi in hexane (0.022 mol) was added dropwise with stirring, maintaining the temperature between -30 and -40 °C. The solution became yellow and then deep red, indicating the dianion. The solution was allowed to stand for 15 min at -30 °C, and then 0.94 g (0.01 mol) of dimethyl sulfide in 1 mL of 1:2 TMED/THF was added. The mixture was allowed to warm to 0-5 °C and held until the color turned pale yellow, ca. 30-45 min. The solution was again cooled to -50 °C, and 10 mL of 1.6 M *n*-BuLi in hexane was added with stirring, whereupon the solution became red again. The solution was allowed to warm to 25 °C and left for 15 h, whereupon evolution of N_2 is complete, the

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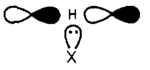
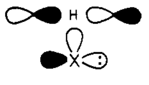
[41] Previously, it has been reported that hexamethylethane is also not protonated at the central C-C bond at -80 °C, and this is attributed to steric hindrance: Olah, G. A.; Halpern, Y.; Shen, J.; Mo, Y. K. *J. Am. Chem. Soc.* **1973**, *95*, 4960; Hogeveen, H.; Bickel, A. F. *Recl. Trav. Chim. Pays-Bas* **1969**, *88*, 371. However, it should be noted that the protonation or deprotonation of a μ-hydrido-bound atom will normally be *symmetry forbidden*, since the LUMO orbital contains a nodal point at the hydrogen, i.e., i. If one could tailor a base for this job, one would postulate an occupied p-type lone pair and an empty orthogonal orbital, i.e., ii.



i



ii

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solution changing from dark brown to pale yellow. Water (10 mL) was added, followed by 10 mL of saturated NH_4Cl, and the mixture extracted (3 × 30 mL) with ether. The ether extract was washed with 10 mL of 10% $NaHCO_3$, followed by 10 mL of brine, and these aqueous extracts were extracted with 2 × 20 mL of ether. After the mixture was dried ($MgSO_4$), the ether was removed under reduced pressure to yield 2.0 g of an oil, which is a 1:1 mixture (GLC, Carbowax 20M; NMR) of the above vinyl sulfide and an alkene (from the normal Bamford-Stevens rearrangement). ^1H NMR of the sulfide: δ 0.77 (d, J = 6 Hz, 3 H), 1.1–2.2 (b, 16 H), 2.32 (3 H, (S—CH_3)), 5.0–5.5 (m, 1 H).

5-Methylcyclodecanone (19). The above mixture was hydrolyzed without further purification by using $HgCl_2$, 6.0 g in 50 mL of 3:1 CH_3CN/H_2O, at 60 °C for 72 h. The reaction mixture was diluted with 50 mL of water, saturated with H_2S to precipitate the excess $HgCl_2$, and filtered, and the aqueous layer was extracted with 3 × 50 mL of ether. After the mixture was washed with aqueous $NaHCO_3$ and then brine and dried ($MgSO_4$), the solvent was removed under reduced pressure. The crude 5-methylcyclodecanone was purified by distillation through a 6-in. fractionating column: bp 63 °C (0.5 mmHg), semicarbazone; mp 178–179 °C. Anal. Calcd for $C_{12}H_{23}N_3O$ (semicarbazone): C, 64.0; H, 10.22; N, 18.66. Found: C, 63.66; H, 10.56; N, 18.78. ^1H NMR: δ 0.85 (d, J = 6 Hz, 3 H), 1.1–2.7 (m, 17 H). ^{13}C NMR: δ 214.0 (C=O), 41.84 (both α-C), 32.95, 32.55, 24.3, 23.45, 23.25, and 21.75 (CH_2), 29.75 (CH), 21.63 (CH_3).

1,5-Dimethylcyclodecan-1-ol (20). The ketone **19** (0.5 g, 0.003 mol) in 10 mL of pentane at −80 °C under argon was treated with 5 mL of 1.75 M methyllithium in ether. The reaction mixture was warmed to 25 °C, decomposed with 10 mL of saturated NH_4Cl solution, and worked up in the usual way. Three more treatments with methyllithium were required before most of the ketone had been reacted. The alcohol was purified by distillation: bp 83–85 °C (0.75 mmHg); yield 0.35 g (64%). Anal. Calcd for $C_{12}H_{24}O$: C, 78.26; H, 13.04. Found: C, 78.31; H, 12.81. ^{13}C NMR analysis shows a nearly equal mixture of the cis and trans isomers (two C—O peaks etc., 20 out of 24 resolved peaks in all).

1-Methyl-*d*$_3$-3-methylcyclohex-2-en-1-ol: prepared from the ketone and methyl-*d*$_3$-lithium. The unlabeled compound is known.[47] ^{13}C NMR: δ 136.5 (C-3), 128.4 (C-2), 68.1 (C-1), 37.3 (C-4), 29.9 (CH_3 at C-3), 23.4, and 19.6 (C-5 and C-6).

1-Ethyl-3-methylcyclohex-2-en-1-ol: kindly supplied by Mr. N. Myshok, University of Lethbridge. Anal. Calcd for $C_9H_{16}O$: C, 77.14; H, 11.42. Found: C, 76.99; H, 11.65.

1-Ethyl-2-methylcyclohexan-1-ol: prepared from 2-methylcyclohexanone and two treatments with ethyllithium and used without further purification. ^{13}C NMR analysis shows the presence of cis and trans isomers (ca. 20% of the minor isomer, in reasonable agreement with the literature[48]). The major isomer (alkyl groups trans) has the expected nine ^{13}C peaks at δ 73.0 (C—O), 37.2, 35.2, 33.0, 30.4, 25.7, 21.6, 14.6, and 7.8.

***cis*-9,10-Dimethyldecalin (32).** As reported,[40] conjugate addition of lithium dimethylcuprate to 10-methyl-1(9)-octalen-2-one gave *cis*-9,10-dimethyldecal-2-one (^{13}C NMR δ 208.7 (C=O), 50.9, 38.1, 36.0, 35.8, 34.4, 22.3, and 21.9 (CH_2), 40.7 and 35.5 (q), 23.7 and 23.3 (CH_3)), which was converted to the hydrocarbon via Wolff–Kishner reduction. The decalin is characterized by ^{13}C peaks at δ 37.4 and 33.7 (uncoalesced broad at 25 °C (α-C)), 24.2 (CH_3), 22.4 (coalesced broad at 25 °C (β-C)). This ^{13}C spectrum, δ-positions and broad peaks, was used in the unsuccessful search for this hydrocarbon in the quench products.

Quenching Experiments. The 1,6-dimethylcyclodecyl cation **9** was prepared at −120 °C from 500 mg of the alcohol by using $FSO_3H/SO_2ClF/SO_2F_2$ (1:3:1) as acid solvent. In one experiment, this mixture was added with vigorous stirring to a suspension of K_2CO_3 in 2-methylbutane cooled to −130 °C. The mixture was warmed to 25 °C, washed with water, with 5% $NaHCO_3$, and again with water, and dried over $MgSO_4$. Removal of solvent left a residue of 400 mg (>80% recovery); bp 103–110 °C (25 mmHg). GLC analysis (10% Carbowax 20M) showed the presence of two major peaks with retention times of 3.1 and 6 min (ratio 1:1.2). The "two" products were separated by preparative GLC (SE-30). Fraction 1, *m/e* 168.05, on NMR analysis, did not correspond to either *cis*- or *trans*-1,6-dimethylcyclodecane and may involve a ring-contracted product. The second fraction, *m/e* 166.15, showed the following major ^{13}C peaks: δ 135.2, 125.8, 34.7, 30.5, 28.8, 28.5, 26.0, 25.1, 24.9, 22.7, 21.9, and 19.9. The ^1H NMR showed peaks at δ 0.75 (d, J = 6 Hz, 3 H), 1.1–1.65 (b, 15 H), 1.7 (3 H), and 5.15 (m, 1 H). Both ^{13}C and ^1H spectra match well with those from an authentic sample of 1,6-dimethylcyclodec-1-ene (one major isomer is present, cis or trans?), prepared by dehydration of the alcohol **2** with thionyl chloride–pyridine. Numerous other smaller ^{13}C peaks are found in the quench product and also in the crude dimethylcyclodecene from the dehydration. None of these fit for *cis*-9,10-dimethyldecalin (**32**). Since 1,6-dimethylcyclodecene and 9,10-dimethyldecalin had identical retention times on several GLC columns, the quench product was hydrogenated to give a shorter retention product by ^{13}C NMR analysis identical with the product of hydrogenation of the authentic dimethylcyclodecene. No GLC peak any longer remained at the retention position for the decalin. The hydrogenation product from the "authentic" dimethylcyclodecenes appears quite "clean" by ^{13}C NMR and is undoubtedly a nearly equal mixture of *cis*- and *trans*-1,6-dimethylcyclodecane, seven of the eight possible ^{13}C peaks being found at δ 33.4, 31.8 (probably two overlapping), 29.8, 24.1, 24.0, 22.8, and 22.6. At 200 MHz, the ^1H spectrum shows a peak at δ 0.85 (d, J = 6 Hz). Quenches were also conducted by using $NaOCH_3$ (10 g) in methanol (100 mL) cooled in a pentane slush bath (as low as possible). Both GLC and ^{13}C NMR analysis showed the presence of some 1,6-dimethylcyclodecene and no evidence for *cis*-9,10-dimethyldecalin (**32**).

Protonation Attempts Using *cis*-9,10-Dimethyldecalin (32). Since the *cis*-1,6- or 1,5-dimethylycyclodecyl cations are irreversibly decomposed at >−60 °C, all experiments were conducted at temperatures lower than this. Three basic acid systems were tried: FSO_3H, 1:1 HF/SbF_5, and 1:1 FSO_3H/SbF_5. The solvent was SO_2ClF. In each case, the decalin was added at about −105 °C and the ^1H NMR spectrum measured. The mixture was then slowly warmed to −80 °C and again monitored by ^1H NMR. Particularly with the latter two acids, there were a large number of peaks different from those of the starting hydrocarbon; however, no μ-hydrogen peaks were discernible even under the high S/N conditions of the ^1H FT NMR.

Ion Preparations and Instrumentation. These followed previous descriptions.[18,49] Some ^1H NMR spectra were recorded at 200 MHz by using a Bruker WP-200 spectrometer.

Kinetic Measurements. Kinetics for the 1,6-dimethylcyclodecyl ⇄ 1,5-dimethylcyclodecyl cation were evaluated by using the standard reversible first-order rate expression, employing the area of the respective CH_3-carbon peaks for concentrations. Kinetics for the H/D exchange in the μ-D-bridged ion **28** were approximate and were based on the rate of area loss for the μ-D signal in ^2D NMR and on the growth of μ-H area with time. Standardized machine settings were employed for each point. The acid signal peak in the ^2D NMR case would have been well separated from the "normal" C–D resonances but no signal was observed. NMR line-broadening simulations for the conformational interchange in **24–27** are discussed in ref 22. The exchange of the μ-hydrogen in **9** is discussed in ref 30. Double irradiation spin-saturation-transfer experiments were also performed on **9** and confirm the μ-hydrogen exchange.

Theoretical Calculations. The ab initio molecular orbital calculations involved the same procedures and approximations discussed for the model secondary–tertiary-bridged carbocations reported in an accompanying paper.[25]

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