The 1,6-Dimethylcyclodecyl Cation. Nuclear Magnetic Resonance Evidence for a 1,6-μ-Hydrido Structure

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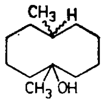
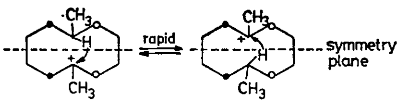
Summary The ^{1}H and ^{13}C n.m.r. spectra of the observable 1,6-dimethyl-cyclodecyl cation are consistent with a 1,6-hydrogen-bridged structure, a previously unknown class of observable carbocations of both historical and current interest.

Addition of 1,6-dimethylcyclodecan-1-ol† (**1**) to 1:1 FSO_3H-SbF_5 in SO_2ClF (1:4) at −120 °C results in the formation of a carbocation with some interesting and unusual n.m.r. properties. Six ^{13}C peaks are observed at all temperatures (−90 to −130 °C), each of two carbon intensity. However, this result in itself is not unexpected for a rapidly equilibrating pair of carbocations, *e.g.* (**2**), in which the α-carbons (and β) (marked ● and ○) could be non-equivalent.‡ An examination of the rather featureless 90 MHz ^{1}H n.m.r. spectrum, over the normal range, was not inconsistent with this picture; the 6H methyl peak is observable at δ 1·84 and the remainder of the signals form a broad overlapping band from δ 1 to 3.



(1)



(2)

It was only on attempted cross-correlation of the ^{13}C and ^{1}H assignment, by selective ^{1}H decoupling of the ^{13}C spectrum, that the startling features of the cation showed up: (i) the lowest field carbon peak was a doublet (as expected) but ν_2 irradiation anywhere in the δ 1—3 proton region completely failed to decouple this carbon; (ii) a coupled ^{13}C spectrum shows this carbon peak to be coupled to the single proton with J 36 Hz. At this point, a re-examination of the ^{1}H spectrum revealed a small broad peak at δ −3·9 and ν_2 irradiation at this unusual position did indeed collapse the ^{13}C doublet. For an equilibrating cation, *e.g.* (**2**), one would have expected a ^{13}C–^{1}H coupling of *ca.* 65 Hz (average of *ca.* 130 and 0 Hz).[1] Moreover, the proton involved in this equilibration process would be expected to have a chemical shift of δ *ca.* 2 (for a remote hydrocarbon ⩾C–H resonance).

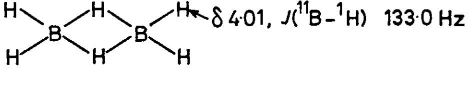


Figure 1. N.m.r. data for diborane.

These results become meaningful when one looks at the n.m.r. properties of diborane[2] (Figure 1), where the bridging hydrogens show abnormally small coupling and are found at high fields. In fact, the cation results are even more divergent than those in B_2H_6 and we suggest on this basis that the title cation exists in a symmetrical μ-hydrido-bridged structure (**3**) (Figure 2). The *cis*-geometry is

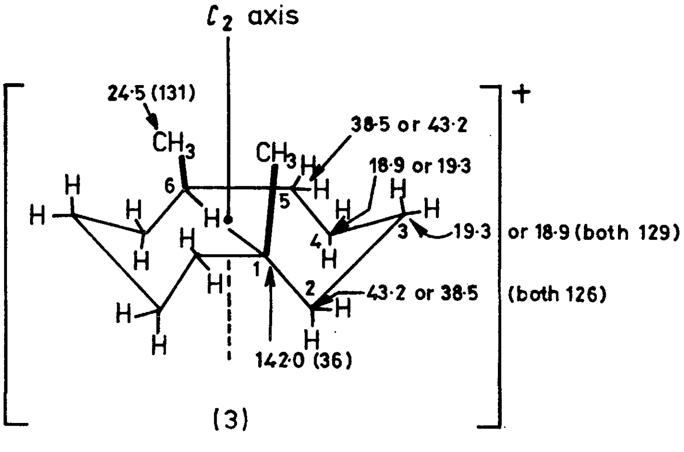


Figure 2. ^{13}C assignments for (**3**), with ^{13}C–^{1}H coupling constants in parentheses (in Hz).

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† Mixture of the *cis*- and *trans*-isomers.

‡ For example, this occurs at low temperature in the 1-methylcyclodecyl cation.[4]

preferred§ but no particular C–H–C angle is implied by (**3**), although some bending to improve the *cis*-decalin-type conformation would be expected. The remaining features of both the ^{1}H and ^{13}C n.m.r. spectrum of (**3**) are consistent with this structure and one should note that carbon equivalences are due to a C_{2v} rotation axis rather than the more obvious symmetry plane depicted in (**2**).

Hydrogen-bridged cations like (**3**) were at one time postulated as solvolysis intermediates but later evidence was unsupportive.[3] MO calculations have been carried out on various bridged species but these generally involve primary or secondary cations. That a 'tertiary' ion like (**3**) should form such a structure is unexpected but we suggest that the dominant factor is the release of steric strain in forming a relatively strainless decalin-type geometry from the strained cyclodecyl geometry.

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§ Above −90 °C, cation (**3**) slowly rearranges to form an equilibrium mixture containing a second bridged cation, this one having only four ^{13}C peaks at −80 °C. Such a pattern is more consistent with the *trans*-decalin-type geometry. In this case, the bridging hydrogen is found at δ −5·8.

[1] J. B. Stothers, 'Carbon-13 NMR Spectroscopy,' Academic Press, New York, 1972, pp. 345—347.
[2] J. B. Leach, C. B. Ungermann, and T. P. Onak, *J. Magnetic Resonance*, 1972, **6**, 74.
[3] V. Prelog and W. Küng, *Helv. Chim. Acta*, 1956, **39**, 1394.
[4] R. Kirchen and T. S. Sorensen, *Canad. J. Chem.*, in preparation.