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THE ^{13}C-^{1}H COUPLING CONSTANT AT THE APICAL CARBON ATOM OF A PYRAMIDAL CARBOCATION

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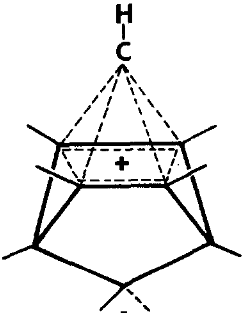
Since the original predictions of Williams[1] and of Stohrer and Hoffmann[2] that (CH)$_5^+$-type carbocations might have a pyramidal geometry with the apical carbon coordinated to more than four other atoms, at least eight examples[3-9] of such ions have been described.[10] In no instance, however, has the ^{13}C-^{1}H coupling constant at the apical carbon atom of such an ion been reported. The nature of the bonding at the apical carbon is of considerable interest, and since the magnitude of one-bond C-H coupling constants is related to the bond hybridization,[11] it seemed important to make such a measurement.[12]

We report and discuss here the ^{13}C-^{1}H coupling constant for the apical carbon in ion 1. The ion was prepared from alcohol 2 essentially as previously described.[4,13] The ^{13}C NMR spectra were recorded on two instruments, a Varian CFT-20 (20.00MHz), and a Bruker WH-180 (45.277 MHz); both spectra were necessary, for reasons described below. They were measured at -80°C, referenced to the central line of the CD_2Cl_2 quintet (53.80 ppm). Decoupled spectra were obtained before and after obtaining the coupled spectrum, to insure that the cation had not rearranged during data collection.[4] Portions of the coupled spectra are shown in the Figures.



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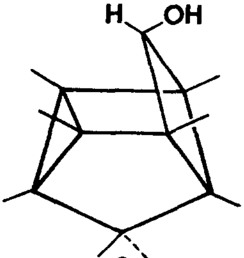

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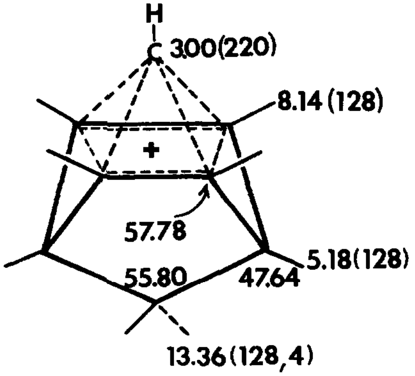
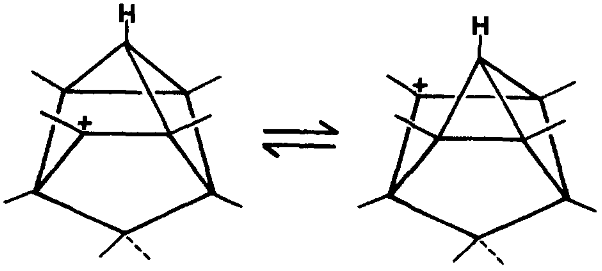
The chemical shifts agreed reasonably well with the literature values[4,14] and are shown with coupling constants in parentheses, on the structure. In the coupled spectra, the downfield signals due to the quaternary carbons were singlets, broadened due to 2- and 3-bond coupling to the methyl protons. The signals at δ 5.18 and 8.14 were sharp quartets (J = 128Hz), but the signal at δ 13.36 was a quartet of quartets (J = 128 and 4 Hz) due to some long-range coupling. In the spectrum obtained on the CFT-20 spectrometer (Figure 1A) only the upfield arm of the expected doublet due to the apical carbon atom was clearly visible, as a broadened peak; the

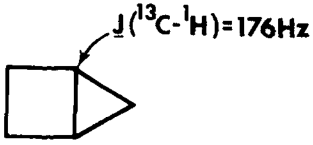


lower arm of this doublet was overlapped with the downfield central line of the quartet from the δ 5.18 signal. In the spectrum obtained on the WH-180 spectrometer the converse occurred. The downfield arm of the apical carbon doublet was clearly visible (Figure 1B) whereas the upper arm was concealed under the upfield outer line of the δ 5.18 quartet.

From the two spectra, the apical ^{13}C-^{1}H coupling constant was estimated as 220 ± 5 Hz. This value corresponds approximately to sp hybridization (common ^{13}C-^{1}H coupling constants are 125 Hz for sp^3, 160 Hz for sp^2 and 250 Hz for sp bonding [11]). It is much higher than might be predicted for a set of equilibrating classical tertiary cations (**1a**, **1b**, etc.) for which a suitable model



1a **1b**



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might be the ring juncture carbons in **3**.[15] It is also appreciably higher than what might be predicted for equilibrating homocyclopropenyl cations (**1c**, **1d**), for which a suitable model might be the trishomocyclopropenyl cation itself (**4**).[16] The value is, perhaps coincidentally nearly identical with that at C_7 of the 7-norbornenyl cation.[17] We believe that the coupling

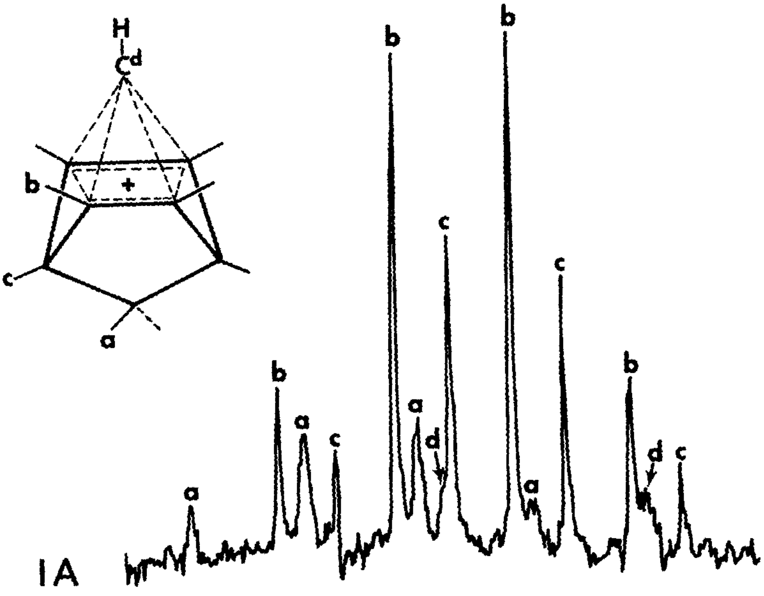


Figure 1A: Coupled ^{13}C spectrum (upfield portion) of ion 1 at 20.00MHz, with peaks assigned. a=δ13.36, b=δ8.14, c=δ5.18, d=δ3.00.

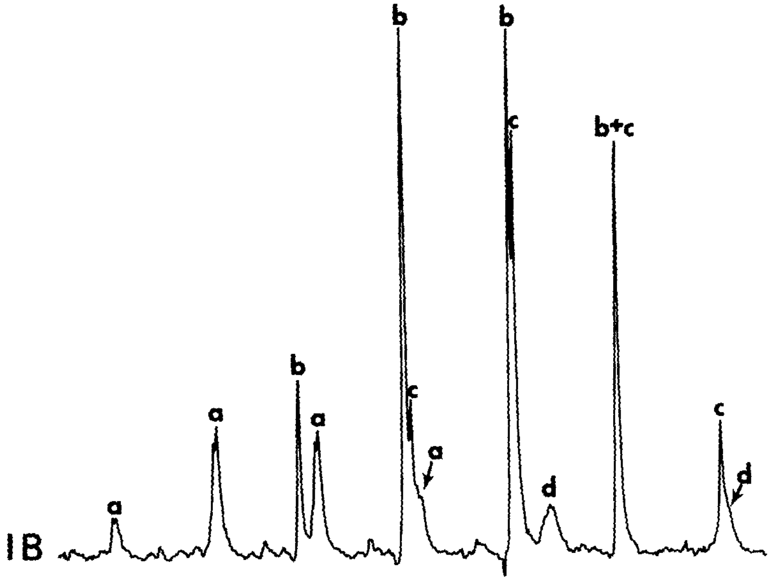
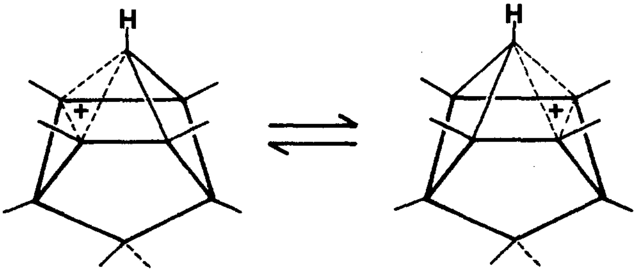
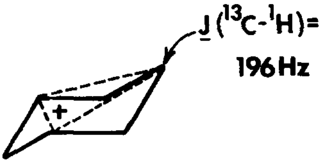


Figure 1B: Same as 1A, but at 45.277MHz.



1c 1d



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constant is consistent with the unique pyramidal structure 1, with nearly sp bonding at the apical carbon atom. This result for the bis-homo ion 1 is consistent with various theoretical models for $(CH)_5^+$ itself.[2,18]

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References and Notes

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