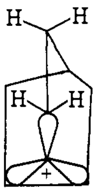
Several conformations of the bridging methylene protons can be envisaged. Since they appear to be equivalent in the low-temperature nmr spectrum (a small shift of less than 0.1 ppm would, however, not have been detectable), the conformation in which these protons eclipse two of the bridging methylene protons would appear to be preferred. The nature of the bonding could thus be best described as a three-center molecular orbital comprising a vacant lobe of the sp^3-hybridized bridging carbon and two orbitals from the remaining two carbons in the three-membered ring. The bonding would thus be analogous to the description of the bonding of the bridging methyl groups in alkyl organometallics such as the dimers of trimethylaluminum, dimethylberyllium, and dimethylmagnesium.[10,11] As with these compounds, however, the distinction between the protonated cyclopropane description and the alternative alkylated olefin approach (*i.e.*, π-complexed cyclopentenylethyl cation) is somewhat arbitrary. This is true, however, only in terms of an orbital description of the highly delocalized system. It can be seen that the chemical shifts of the bridging methylene and cyclopropane protons[12] are not in accordance with any "localized" π-complex nature of the ion.



The substantial difference in activation energies for the 3,2- and 6,1,2-hydrogen shifts (10.8 and 5.9 kcal/mol, respectively) observed in the stable "norbornyl cation" is, we feel, very significant. The 6,1,2-hydrogen shift is envisaged as proceeding *via* an edge-protonated cyclopropane (either as an intermediate or as a transition state) and since the "norbornyl cation" has the geometry of nortricyclene and therefore the 6,1, 6,2 and 1,2 C–C bond distances must be closely similar, this hydrogen shift will involve little if any change in the carbon skeleton. The 3,2 shift, on the other hand, must involve lengthening of the 6,2 C–C bond distance in the transition state, and the observed activation energy must therefore involve a contribution from the resultant loss in σ-delocalization energy. This would account for the high value for the activation energy observed. In the limiting case, when all the delocalization energy is lost prior to the transition state for the 3,2 shift, the classical ion could be considered an intermediate. A model for the 3,2 shift in the classical ion is the degenerate hydrogen shift in the cyclopentyl cation. From the nmr spectrum of the cyclopentyl cation at $-154°$, the activation energy for the hydride shift in this ion is known to be less than 5 kcal. Assuming the value to lie in the range of 2–4 kcal would lead to an estimated 7–9 kcal of σ delocalization in the norbornyl cation. This compares to a calculated value of 40 kcal.[4,12a] From this large discrepancy we would conclude that the classical ion[13] cannot be an intermediate and that σ delocalization is present in the transition state. The 3,2-hydrogen shift is in many respects the intramolecular analog of the attack on the norbornyl cation by an external nucleophile. Its significance, in this light, will be discussed in a forthcoming full paper.

In conclusion it is clear that we have observed the long-lived nonclassical norbornyl cation and demonstrated its identity with corner-protonated nortricyclene. The rates of hydrogen shifts measured in the stable ion and the establishment of its close structural relationship to nortricyclene rather than norbornane contribute toward a better understanding of the truly unique norbornyl cation. Winstein and Trifan have suggested in 1949 the nonclassical structure of the norbornyl cation. Winstein, Roberts, and many other investigators since have added much additional information supporting the structure of the ion under solvolytic conditions.[14a,b] ^{1}H and ^{13}C nmr as well as Raman spectroscopic studies of the long-lived ion now fully substantiate their views.

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cations in solution. In this latter case, however, no stable ions were observed: G. A. Olah and R. H. Schlosberg, *J. Amer. Chem. Soc.*, **90**, 2726 (1968); H. Hogeveen and C. J. Gaasbeek, *Chem. Commun.*, 635 (1967); G. A. Olah, G. Klopman, and R. H. Schlosberg, *J. Amer. Chem. Soc.*, in press.

[10] R. G. Vranka and E. L. Amma, *ibid.*, 89, 3121 (1967).

[11] Our studies on the trimethylaluminum dimer as a model for the bridging methylene in protonated nortricyclene show that the differences in proton shift (1.14 ppm), ^{13}C shift (4.0 ppm), and J_{CH} (1.5 Hz) for the bridging and terminal methyl groups are small. This justifies our previous assumption on the magnitude of J_{CH} for the bridging methylene.[1]

[12] The assignment of these protons is, at the present time, tentative. If the 7-norbornenyl cation[9b] is taken as a model, then the bridging methylene protons have to be assigned to the highest field peak (δ 3.05). It is at the present time, however, not finally established whether the 7-norbornenyl ion represents an adequate model for this case, and we are currently undertaking further experiments with a view to clarifying this point.

(12a) NOTE ADDED IN PROOF. Recent calculations (G. Klopman, personal communication) have shown that, in acyclic carbonium ions, it is necessary to decrease the sp^3–sp^2 C–C bond distance from the standard values used previously.[4] This results in a decrease in calculated energy for the ions. A similar treatment of the classical norbornyl cation brings its energy somewhat closer than 40 kcal to that of corner-protonated nortricyclene.

[13] For a summary and reference see H. C. Brown, *Chem. Eng. News*, **44**, 87 (Feb 13, 1969).

[14] (a) S. Winstein and D. S. Trifan, *J. Amer. Chem. Soc.*, 71, 2935 (1949). (b) For a summary and leading references see P. D. Bartlett, "Non-classical Ions," W. A. Benjamin, Inc., New York, N. Y., 1965.

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Stable Carbonium Ions. LXXXVIII. Hydrogen-1 and Carbon-13 Nuclear Magnetic Resonance and Laser Raman Spectroscopic Study of the 2-Methyl-, 2-Ethyl-, and 2-Phenylnorbornyl Cations[1]

Sir:

Raman and nmr studies of the norbornyl cation in super acid have shown that the ion exists as corner-protonated nortricyclene.[1,2] A logical extension of our work was the study of 2-alkyl- and 2-phenylnorbornyl cations. Nmr spectroscopic studies of the 2-phenyl-[3,4]

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[1] Part LXXVII: G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 3956 (1969).

[2] G. A. Olah, A. Commeyras, and C. Y. Lui, *ibid.*, **90**, 3882 (1968).

[3] P. von R. Schleyer, D. C. Kleinfelter, and H. B. Richey, Jr., *ibid.*, **85**, 479 (1963).

Table I. Pmr Parameters (δ) of 2-Methyl-, 2-Ethyl-, and 2-Phenylnorbornyl Cations at 100 MHz in FSO_3H-SbF_5-SO_2 Solution at −60° [a]

Ion	CH_3	CH_3CH_2	H_1	H_6 *exo*	H_3 *exo*, *endo*	H_4	H_7	H_5 *exo*, *endo*	H_6 *endo*
2-CH_3	3.00 (J = 3 tr)		4.64 (J = 6.5 d)	3.28 (br, m)	2.70	2.70	1.71	1.47	1.09
2-C_2H_5	1.28 (tr)	3.46 (m)	4.41 (J = 6.5 d)	3.46 (br, m)	2.82	2.82	1.78	1.60	1.28
2-C_6H_5 [b]			4.83 (J = 6.5 d)	2.81 (br, m)	3.49	3.20	2.04	1.41	2.00

[a] d = doublet; tr = triplet; br = broad; m = multiplet. J values in hertz. [b] In FSO_3H, as reported by Farnum and Mehta.[4]

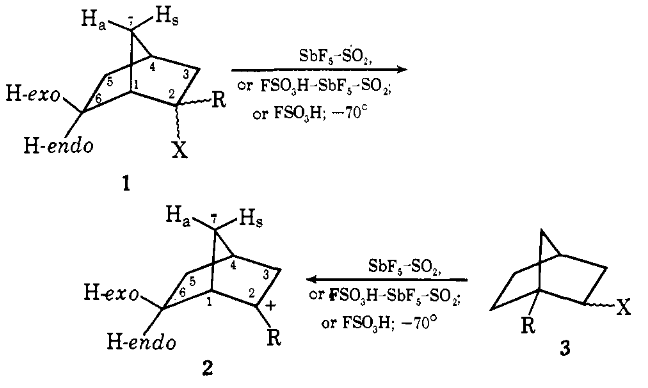
Table II. Main Raman Spectral Characteristics (cm^{-1}) of the 2-Methyl- and 2-Ethylnorbornyl Cations and Their Comparison with Raman and Ir[7] Data of Norbornane and Nortricyclene Models[a]

	C–H region			C–C region[a]			
2-CH_3	2984 (s)	2960 (s)	2855 (m)	911 (m)	880 (s; 0.24)	770 m	350 (m; 0.20)
2-C_2H_5	2980 (s)	2965 (s)	2870 (m)	920 (m)	884 (s; 0.24)	765 m	350 (m; 0.22)
Norbornane[1]	2964 (d)	2936 (s)	2873 (m)	920 (m, 0.25)	871 (s; 0.25)	753 w	
1-Methylnortricyclene[7a]		Complex			850 (s)	785 w	
Norcamphor	2964 (s)	2920 (s)	2882 (s)	938 (s)	880 (m)	786 m	
2-Methylnorbornane[7b]	2952 (s)	?	2869 (s)	923 (s)	873 (m)	719 m	
2-Ethylnorbornane[7b]	2947 (s)	?	2869 (s)	923 (m)	878 (m)	696 m	

[a] Values in parentheses are the polarization factors for the Raman bands. s = strong; m = medium; w = weak.

and 1,2-diarylnorbornyl cations[3] support a classical structure for these ions. An attempted nmr study[5] of the 2-alkylnorbornyl cation led to inconclusive results.

The 2-methyl- (**2**-CH_3), 2-ethyl- (**2**-C_2H_5), and 2-phenylnorbornyl cations were generated as shown.

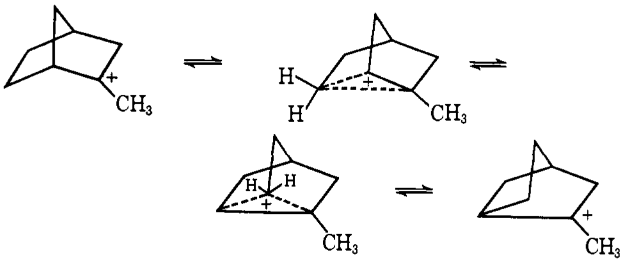


(X = F,Cl,Br,OH) R = CH_3,C_2H_5

The pmr parameters of the **2**-CH_3 and **2**-C_2H_5 ions are summarized in Table I, together with the related data of the 2-phenylnorbornyl cation (**2**-C_6H_5). With the exception of the chemical shifts of the H_6 *exo* protons, these spectra are very similar to that reported by Farnum and Mehta[4] for the 2-phenylnorbornyl cation generated in neat HSO_3F. Although in all three cases the H_6 *exo* proton is deshielded and shown by decoupling and isotopic labeling[4] experiments to be coupled strongly to the proton at the 1-bridgehead position, its chemical shift is at substantially higher field in cation **2**-C_6H_5 than in **2**-CH_3 or **2**-C_2H_5. However, this is expected since deshielding of the H_6 *exo* proton of these cations is due to overlap of the backside lobe of the sp^3 C_6–H *exo* orbital with the empty p orbital at C_2 in which the positive charge is substantially localized in **2**-CH_3 and **2**-C_2H_5 but to a lesser degree in **2**-C_6H_5 where delocalization into the neighboring phenyl group is significant. Thus, the observed large differences in the chemical shifts of the H_6 *exo* and H_6 *endo* protons of cations **2**-CH_3 and **2**-C_2H_5 can be accounted for by considering some C_6 to C_1 σ delocalization.

^{13}C nmr spectroscopy is considered to be particularly well suited to the study of the degree of neighboring group participation at carbonium ion centers because of the sensitivity of the shifts to changes in charge distribution. Using the INDOR method, the ^{13}C chemical shift of C_2 in the 2-methylnorbornyl cation has been obtained (in SbF_5–SO_2 solution at −80°), the value being −76.1 ppm (from $^{13}CS_2$). This shift is substantially to high field of that of the carbonium carbon shift in the *t*-butyl cation (−135.4 ppm in SbF_5–SO_2ClF solution at −20°) and the 1-methylcyclopentyl cation (−142.2 ppm in SbF_5–SO_2 solution at −60°), revealing the presence of σ delocalization resulting in a decrease in the positive charge at C_2 relative to the two "classical" model ions. The question of how much σ delocalization is present depends on a model being available for the fully nonclassical ion. Only an average shift has been determined in the symmetrically bridged norbornyl cation for the "cyclopropane" carbon atoms C_1, C_2, and C_6. However, we would estimate that C_2 would have a shift of 100–120 ppm in the fully delocalized 2-methylnorbornyl cation, and thus although σ delocalization is present, the ion is closer to the classical than to the completely nonclassical structure.

An important feature of the pmr spectrum of **2**-CH_3 is the long-range coupling (J = 3 Hz) of the methyl group with the C_3 methylene protons. This kind of long-range coupling is indicative of an sp^2-hybridized carbonium ion center. Similar long-range coupling is also observed in the **2**-C_2H_5 ion. When solutions of **2**-CH_3 and **2**-C_2H_5 are heated to −10°, reversible changes in the pmr spectra are observed. These changes approach those expected for the fast equilib-



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[4] D. G. Farnum and G. Mehta, personal communication; *J. Amer. Chem. Soc.*, in press.

[5] J. T. McFarland, Ph.D. Thesis, California Institute of Technology, Pasadena, Calif., 1969.

rium as shown above, possibly involving intermediate bridged ions as indicated.

Raman spectra for the solutions of **2**-CH_3 and **2**-C_2H_5 at −80° were obtained using a He–Ne laser, in conjunction with a Cary 81 spectrometer and low-temperature cell previously described.[6,7] The characteristic C–C and C–H stretching frequency region of the Raman spectra of the ions **2**-CH_3 and **2**-C_2H_5 (within the limitation of the significant absorption of the solvent in this region) are summarized in Table II. Lines observed for **2**-CH_3 and **2**-C_2H_5 in the C–H stretching frequency region are usually broad and weak, preventing detection of the lines from the methyl and ethyl groups, respectively.

The two intense highly polarized lines at 880–885 and 910–940 cm^{-1} and the three intense bands in the C–H stretching frequency region in the spectrum of norbornane and its derivatives can be interpreted as model bands indicating the **2**-CH_3 and **2**-C_2H_5 ions are "classical" or "semiclassical" (*i.e.*, some σ delocalization but not enough to significantly alter the over-all geometry of the carbon skeleton) norbornyl cations since these bands are due to skeletal deformations with band frequencies, relative intensities, and polarizations directly related to the symmetry of the bicyclo[2.2.1] skeleton.[2,8]

Alternatively, it can be argued that for an intermediary case involving partial σ delocalization (*vide supra*) of the positive charge at C_2, norbornane derivatives and nortricyclene derivatives are not necessarily suitable models for the stretching frequency region of the resulting cation since in this case the skeletal similarities may no longer exist. However, we believe that as a first approximation and within the limitation of the solvent bands, the Raman lines in the stretching and bending frequency regions of **2**-CH_3 and **2**-C_2H_5 do reflect an over-all skeletal similarity to the bicyclo[2.2.1] skeleton.

Only two strong Raman bands are observed in the C–C stretching frequency region of both ions **2**-CH_3 and **2**-C_2H_5 in HSO_3F–SbF_5–SO_2 solution with the more intense band occurring at 880 and 884 cm^{-1}, respectively, and the less intense at 911 and 920 cm^{-1}. The bands at 880 and 884 cm^{-1} are highly polarized with identical ρ factors of 0.24. Relatively strong acid solvent peaks at 920–960 cm^{-1} prevent measurement of polarizations of the cation signals in this region. However, the observation of two relatively intense Raman lines in the C–C stretching regions, the depolarization factor for the 880 and 884 cm^{-1} signals, and the three bands in the C–H stretching region indicate that cations **2**-CH_3 and **2**-C_2H_5 do not possess a molecular symmetry related to that of 1-methylnortricyclene. In addition, the highly polarized bands at 350 cm^{-1} ($\rho \approx 0.20$) in the spectra of **2**-CH_3 and **2**-C_2H_5 are very similar to those observed for several tertiary alkylcarbonium ions. These bands, which are apparently due[9] to A_1-type skeletal deformations (out of plane bending) about the sp^2 carbon, lead us to conclude that the positive charge in ions **2**-CH_3 and **2**-C_2H_5 is substantially localized on the C_2 carbon atom. The low values of the depolarization factors for these lines also indicate that there can be little deviation from planarity about the C_2 carbon atom.

We were not able to record Raman spectra of super acid solutions of the 2-phenylnorbornyl cation due to masking by intense fluorescence from impurities and very probably from the cation itself. We were, however, able to obtain the ^{13}C chemical shift of C_2 in the 2-phenylnorbornyl cation (in FSO_3H solution at +35°). This shift was found to be −65.8 ppm and compares to shifts of −61.1 ppm for the phenyldimethylcarbonium ion (SbF_5–SO_2 solution at −60°) and ∼−70 ppm for the 1-phenylcyclopentyl cation (neat FSO_3H at −20°). The near equality of these shifts provides a convincing demonstration that in the 2-phenylnorbornyl cation, σ delocalization is essentially absent, and the ion thus represents a model for a completely classical norbornyl cation.

The Raman and pmr results obtained for the super acid solutions of 2-methyl- and 2-ethylnorbornyl cations at −80° together with ^{13}C nmr studies demonstrate the norbornane-related structure of these ions and also indicate a degree of σ participation in these tertiary 2-alkylnorbornyl cations.[10]

Clearly σ delocalization in **2**-CH_3 and **2**-C_2H_5 is not as advanced as in the norbornyl cation itself (see preceding communication) in which the 6,2 bond distance is such as to give the ion over-all nortricyclene rather than norbornane skeletal symmetry. Carbonium ions obviously can display various degrees of σ delocalization ranging from completely bridged to weakly delocalized, partially bridged ions.

Restricting the term "nonclassical" to ions such as the norbornyl cation itself, in which completely symmetrical bridging is possible, is clearly too restrictive and it would seem more appropriate to discard these limiting terms altogether and to introduce a quantitative measure of the amount of σ delocalization present. Skeletal symmetry considerations observed in the present work together with ^{13}C nmr shifts appears to give a sensitive criterion of the various degrees of σ delocalization present in ions like **2**-CH_3, **2**-C_2H_5, and **2**-C_6H_5.

Raman, ^1H, and ^{13}C nmr studies of the 1,2-dimethyl- and other alkylnorbornyl cations are presently being carried out in our laboratories.

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(6) A. Commeyras and G. A. Olah, *J. Amer. Chem. Soc.*, **91**, 2929 (1969).

(7) (a) H. Hart and R. A. Martin, *J. Org. Chem.*, **24**, 1267 (1959); (b) V. T. Alexsanyan and Kh. E. Sterin, *Fiz. Sb. L'vovak. Gos. Univ.*, **1**, 59 (1957); *cf. Chem. Abstr.* **53**, 21158*a* (1959).

(8) Skeletal similarities and not over-all point group symmetries are responsible for the Raman spectral correlations (*e.g.*, Raman spectra of nortricyclene (and norbornane) derivatives closely resemble each other even when they are substituted at various positions around the skeleton). As long as vibrational distortions introduced by the substituent into the basic carbon skeletons are not too large, the skeletal vibrations are relatively unaffected.

(9) G. A. Olah, A. Commeyras, J. R. DeMember, and J. L. Bribes, *J. Amer. Chem. Soc.*, in press.

(10) When FSO_3H–SbF_5–SO_2, SbF_5–SO_2, or FSO_3H solutions of cations 2-CH_3 and 2-C_2H_5 were quenched, nearly quantitative yields of the corresponding 2-norbornyl derivatives were obtained, demonstrating that no rearrangements or ring closures occur during or after the ionization of the halide precursor in the solutions studied.

(11) Postdoctoral Research Investigator.