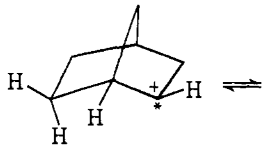
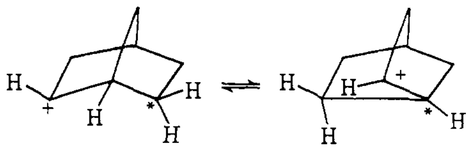
cyclopropane ring. This effect is also evident in the comparison of the proton spectra.

To account for both the proton and carbon nmr spectra in terms of a classical ion, the 1,2 Wagner–Meerwein rearrangement and the 6,2-hydride shift have to be fast with respect to the nmr time scale, **2a** ⇄ **2 b** ⇄ **2c**.[9] The observed shift will thus be the average of the shifts for the carbon bearing the positive charge and carbons one and two bonds removed. Using the isopropyl cation[4] as a model for the positively charged carbon and norbornane for the bridgehead methine and methylene shifts (see Table I) gives a calculated average shift of 65 ppm. An analogous calculation gives a calculated coupling constant of 47 Hz. This approach makes no allowance for the effect of the positive charge one and two bonds removed from the carbonium ion center, and if such corrections are made (from shifts observed in alkyl carbonium ions), the calculated shift is reduced to 50 ppm. Clearly the observed shift is incompatible with the equilibrating classical structure of the ion.



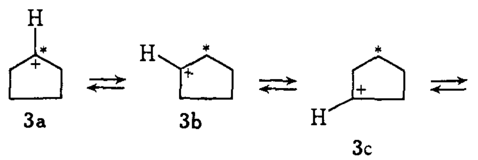
2a



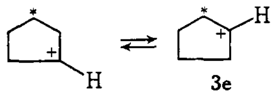
2b **2c**

As confirmation that the isopropyl cation is a reasonable model for estimating the chemical shift and coupling constant in the classical norbornyl cation, we obtained the ^{13}C spectrum of the closely related cyclopentyl cation **3**.[10]

The ion was prepared from chlorocyclopentane in SbF_5–SO_2ClF solution, and the proton spectrum of the ion at −70° consists of a single resonance at δ 4.48 (from internal TMS). The intensity of the ^{13}C satellites (~5% of the main peak) shows that complete equilibration of the nine protons among the five carbon atoms is occurring through equilibria **3a** ⇄ **3b** ⇄, etc., interconversions proceeding *via* the rapid 1,2-hydride shifts. The ^{13}C INDOR spectrum is a ten-line multiplet centered at +95.4 ppm with a coupling constant of 28.5 Hz.



3a **3b** **3c**



3d **3e**

The coupling constant observed is the average of one sp^2 and four sp^3 carbon–hydrogen coupling constants. This neglects long-range couplings which, however, will not only be small but should cancel out because of the opposing signs. Using the isopropyl cation (J = 169 Hz) and cyclopentane (J = 131 Hz)[7] as models gives a calculated coupling constant of $(169 + 8 \times 131/(9 \times 5)$ or 27 Hz, in excellent agreement with the observed value. Similarly the chemical shift will be the average of the isopropyl cation shift (−125 ppm) and four methylene shifts (cyclopentane 167 ppm)[7] giving a calculated value of 109 ppm. If allowance is made for the methylenes being one and two bonds removed from the cation center (using data for alkylcarbonium ions), this value is reduced to 95 ppm, again in excellent agreement with the observed value.

Protonated nortricyclene is the only structure in accordance with the low-temperature Raman, proton, and carbon nmr spectra of the stable norbornyl cation. The question still remains, however, as to whether it is edge- or corner-protonated and which of these forms represents an intermediate or transition state in the equilibrium observed. Both corner- and edge-protonated forms could be compatible with both the ^{13}C and Raman spectroscopic observations (see, however, the following communication). What we feel is the more important point, however, is that the "norbornyl cation" corresponds much more closely in geometry to nortricyclene than to norbornane, and in our view the observed stable, long-lived nonclassical norbornyl cation can be properly described as protonated nortricyclene (rather than implying a structural relationship to norbornane).

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[9] M. Saunders, P. von R. Schleyer, and G. A. Olah, *J. Amer. Chem. Soc.*, **86**, 5680 (1964).

[10] The pmr spectrum of this degenerate ion was known previously: G. A. Olah and J. Lukas, *ibid.*, **90**, 933 (1968).

The Proton Magnetic Resonance Spectrum of the Nonclassical Norbornyl Cation and Its Identity with Corner-Protonated Nortricyclene, a Stable Protonated Cyclopropane Containing a Pentacoordinated Carbon Atom[1]

Sir:

Since the first pmr observation of the 2-norbornyl cation,[2] various approaches have been used to elucidate its structure. Raman spectroscopy demonstrated that the cation has a geometry corresponding to that of nortricyclene rather than that of a 2-norbornyl derivative,[3] and it was proposed that the stable ion observed was protonated nortricyclene. In the preceding communication we have reported the complete ^{13}C nmr spectrum of the ion at −70° which is consistent only

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[1] Stable Carbonium Ions. LXXXVII. Part LXXXVI: G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 3954 (1969).

[2] (a) P. von R. Schleyer, W. E. Watts, R. C. Fort, Jr., M. B. Comisarow, and G. A. Olah, *ibid.*, **86**, 5679 (1964); (b) M. Saunders, P. von R. Schleyer, and G. A. Olah, *ibid.*, **86**, 5680 (1964).

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

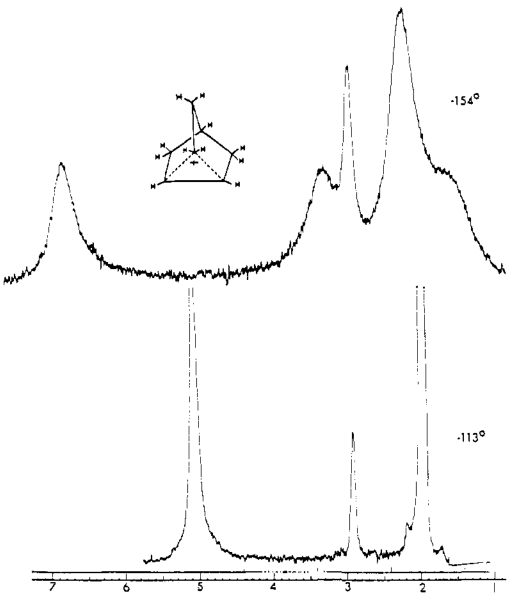

Figure 1. 100-MHz proton nmr spectra of the "norbornyl cation" in SbF_5–SO_2ClF–SO_2F_2 solution at temperatures between −113 and −154°.

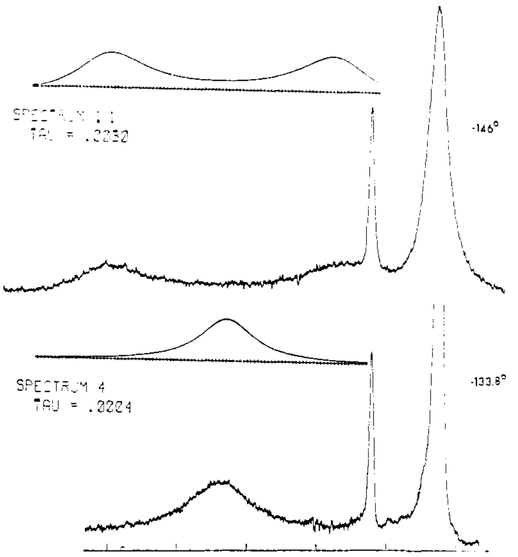

Figure 2. Computer-simulated and experimental spectra of the "norbornyl cation" for two temperatures before and after coalescence. The values of τ indicated refer to the mean lifetime in seconds.

with protonated nortricyclene and not with an equilibrating classical norbornyl ion structure.

Neither the Raman nor the ^{13}Cn mr spectra were, however, able to distinguish between the edge- or corner-protonated nortricyclene structures. Quantum mechanical calculations[4] on the norbornyl cation showed that face-protonated nortricyclene (the nortricyclonium ion) and the classical ion had a substantially higher energy than either the corner- or edge-protonated species; the latter differed in energy by only 3 kcal, compared to an estimated error in the calculations of ±10 kcal. Furthermore the calculations apply of course to the gas phase and thus take no account of solvation energies.

We now wish to report our success in "freezing out" on the nmr time scale the hydrogen shift[5] around the cyclopropane ring in protonated nortricyclene, the resulting spectrum showing the ion to be corner-protonated.

In the previous pmr study,[2b] the 60-MHz spectrum of the ion was obtained at temperatures down to −120°, and from the temperature dependence of the spectrum the rate of the "3,2-hydride shift" was obtained. Using a mixed SbF_5–SO_2ClF–SO_2F_2 solvent system we now have been able to observe the 100-MHz spectrum at temperatures down to −156°. At −120°, the spectrum was identical with that described previously; however, in the temperature range −128 to −150° significant changes in the spectrum occur. The low-field peak due to the four equilibrating protonated cyclopropane ring protons broadens and then separates into two resonances each of relative area 2 at δ 3.05 and 6.59.[6] The high-field resonance, due to the six methylene protons, also broadened, developing a shoulder at δ 1.70. The peak at δ 2.82 due to the single bridgehead proton remains unchanged. These changes are shown in the spectra reproduced in Figure 1. The temperature dependence of the low-field resonance was used to calculate the rate constants using a FORTRAN IV coded program based on the Gutowsky–Holm equations[7] (Figure 2). The activation energy from the Arrhenius plot is 5.9 ± 0.2 kcal mol^{-1} and the preexponential factor $10^{12.7}$ sec^{-1}.

These observations could be consistent with either (a) that the ion is classical and that the temperature dependence corresponds to the "freezing out" of the 6,2-hydride shift, the Wagner–Meerwein rearrangement still being fast at −156°, or (b) that the ion is nonclassical, the 6,1,2-hydrogen shift has been "frozen out," and that the structure of the ion is corner-protonated nortricyclene.[8] The latter observation is the only one compatible with the ^{13}C and Raman spectroscopic evidence and with the rates of the 3,2- and 6,2-hydrogen shifts. Thus the norbornyl cation represents one of the first examples of the observation of a stable, corner-protonated cyclopropane containing what amounts to a pentacoordinated carbon atom.[9a,b]

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[4] G. Klopman, *J. Amer. Chem. Soc.*, **91**, 89 (1969).

[5] We prefer in this case not to use the expression "hydride shift" which implies the involvement of a negatively charged hydrogen since the migrations involved can be equally well represented with transition states in which the hydrogen bears a positive charge. The term "hydrogen shift" seems to us a description which better represents the actual processes involved.

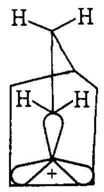
[6] Since TMS could not be used as a reference at these low temperatures, shifts were measured relative to the bridgehead methine proton, the shift of which is independent of temperature, and were then referred back to internal TMS.

[7] H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

[8] The alternative possibility, that the ion is edge-protonated, can be now eliminated since this species would not give the observed temperature dependence of the pmr spectrum. In this case the low-temperature spectrum would be expected to give a low-field resonance of area 1 due to the edge proton and two peaks at higher field in the ratio 2:1, due to the cyclopropane ring protons. The face-protonated ion is also inconsistent with the observed spectrum for the same reasons.

[9] (a) Previous attempts to observe protonated cyclopropane itself in FSO_3H–SbF_5–SO_2ClF solutions at −100° [G. A. Olah and J. Lukas, *J. Amer. Chem. Soc.*, **90**, 933 (1968)] were inconclusive, and it has since been shown that no long-lived protonated cyclopropane was observed. The major product observable is isopropyl fluorosulfate (unpublished results with G. Mateescu). (b) A related case is that of the 7-norbornenyl cation reported by Winstein [M. Brookhart, A. Diaz, and S. Winstein, *ibid.*, **88**, 3135 (1966)] and Richey [H. G. Richey, Jr., and R. K. Lustgarten, *ibid.*, **88**, 3136 (1966)] and that of the 7-norbornadienyl cation (P. R. Story, and M. Saunders, *ibid.*, **84**, 4876 (1962)). The recently studied solution chemistry of the methanonium ion (CH_5^+) is also considered relevant relating to pentacoordinated carbon

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.

Acknowledgment. Partial support of this research by the National Science Foundation and by the C. F. Mabery Fund of Case Western Reserve University is gratefully acknowledged.

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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.

[15] Postdoctoral Research Associate.

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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).