as prevalent as once believed".[42a] We are really left only with the question of the factor responsible for the high exo/endo rate ratio in 2-norbornyl and related secondary derivatives, a very small fragment of the original question.

For some 20 years I have been carefully examining many pieces of evidence purporting to support the formation of a highly stabilized 2-norbornyl cation. Invariably, the arguments and evidence have crumpled after careful study.[1b]

The heart of the 2-norbornyl question appears to be the thermochemistry. The nonclassical interpretation of the high exo/endo rate ratio in the solvolysis of 2-norbornyl derivatives requires nonclassical stabilization of the exo transition state by 6.0 kcal/mol and a somewhat larger stabilization of the free ion ($\sim$8.0 kcal/mol).

None of the three independent experimental approaches has detected any significant stabilization of either the transition states for secondary *exo*-norbornyl not present in the corresponding tertiary derivatives or in the free secondary cation not present in the tertiary cation. The 6.0–8.0 kcal/mol of nonclassical stabilization energy cannot be detected.

On the other hand, unsymmetrical 2-norbornyl cations have been captured in a number of reactions.[42b]

Meanwhile, various workers continue to publish papers purporting to have established the nonclassical nature of the 2-norbornyl cation in the gas phase (calculation,[43,44] stability,[32,45]), in the solid state (ESCA,[46] low-temperature NMR[47]), and in solution under stable ion conditions, (NMR,[48] isotope perturbation[49]). It is an interesting question as to what is the structure of the 2-norbornyl cation under these special conditions. However, I do not see that the results are pertinent to the question as to what is responsible for the high exo/endo rate ratio in the solvolysis of 2-norbornyl derivatives.[50]

None of the workers in this area has addressed the thermodynamic dilemma that has been the major point made in this Account. It will be of intense interest to see if any of the papers in this Symposium-In-Print addresses this question.

I believe that our data clearly reveal that the 2-norbornyl cation can be prepared and captured in an unsymmetrical state.[42b] It clearly does not have the nonclassical stabilization energy that has been postulated for so long. It ill befits serious scientific workers in this area to ignore these data and results.

(42) (a) Reference 1b, p 259. (b) Reference 1b, Chapter 12.

(43) Raghavachari, K.; Haddon, R. C.; Schleyer, P. v. R.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1983** *105*, 5915. See also: Yoshimine, M.; McLean, A. D.; Lin, B.; Defrees, D. J.; Binkley, J. S. *Ibid.* **1983**, *105*, 6185.

(44) Goddard, J. D.; Osamura, Y.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1982**, *104*, 3258.

(45) Saluja, P. P. S.; Kebarle, P. *J. Am. Chem. Soc.* **1979**, *101*, 1084.

(46) Olah, G. A.; Mateescu, D. G.; Riemeneschneider, J. L. *J. Am. Chem. Soc.* **1972**, *94*, 2529. It has been pointed out that the published spectrum analyzes for a 1:6 distribution of carbon atoms corresponding to a classical ion, not 2:5, as claimed. Kramer, G. *Adv. Phys. Org. Chem.* **1975**, *11*, 177.

(47) Yannoni, C. S.; Macho, V.; Myhre, P. C. *J. Am. Chem. Soc.* **1982**, *104*, 907.

(48) Olah, G. A.; Surya Prakash, G. K.; Arvanaghi, M.; Anet, F. A. L. *J. Am. Chem. Soc.* **1982**, *104*, 7105.

(49) Saunders, M.; Kates, M. R. *J. Am. Chem. Soc.* **1983**, *105*, 3571.

(50) In ref 49, the authors conclude that the cation under stable ion conditions differs considerably from the transition state under solvolytic conditions.

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# Conclusion of the Classical–Nonclassical Ion Controversy Based on the Structural Study of the 2-Norbornyl Cation[†]

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Facile skeletal rearrangements in the bicyclo[2.2.1]heptyl system attracted the interest of chemists, most notably Wagner,[1] who as early as 1899 studied the borneol–camphene rearrangement. The actual ionic nature of the camphene hydrochloride (**1**)–isobornyl chloride (**2**) rearrangement was first recognized by Meerwin and Van Emster in 1922.[2] Their interpretation replaced Ruzicka's earlier suggested neutral tricyclane type mechanism for the process.[3] This ionic path is now known as the Wagner–Meerwin rearrangement. Thus Meerwein's studies laid the foundation for modern carbocation chemistry.

George A. Olah is a native of Hungary, where he received his university education. He emigrated in 1956, was for 8 years with Dow Chemical Co. in Canada, and in 1965 moved to Western Reserve University as Professor of Chemistry. After the amalgamation he was C. F. Maybery Professor of Chemistry and Department Chairman at Case Western Reserve University. In 1977, he moved to the University of Southern California where he is Loker Distinguished Professor of Organic Chemistry and Scientific Co-Director of the Hydrocarbon Research Institute.

G. K. Surya Prakash, a native of India, is Research Associate Professor of Chemistry at the University of Southern California.

Martin Saunders came from Brooklyn, NY. He did undergraduate work at City College of New York and in 1956 took his Ph.D. at Harvard University. He moved directly to the Yale University faculty and is now Professor of Chemistry as well as Fellow of Branford College.

[†] Stable Carbocations. 249.

(1) Wagner, G.; Brickner, W. *Ber.* **1899**, *32*, 2307. *J. Russ. Phys. Chem. Soc.* **1899**, *31*, 680.

(2) Meerwein, H.; Van Emster, K. *Chem. Ber.* **1922**, *55*, 2500.

(3) Ruzicka, L. *Helv. Chim. Acta* **1918**, *1*, 110.

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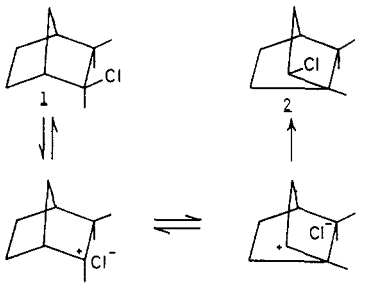
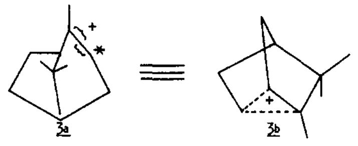


Bartlett and Pockel in 1938 pointed out[4] that the rearrangement of camphene hydrochloride to isobornyl chloride could not take place through the intermediacy of two ions suggested in Meerwein's scheme.[3] If that were the case, from the secondary ion a mixture of isobornyl chloride and bornyl chloride should result (exo and endo isomers). In fact, only isobornyl chloride was formed. Furthermore, it was observed that the solvolysis of isobornyl chloride in aqueous alcohol at 85 °C was $10^5$ times faster than that of bornyl chloride.

Wilson et al. in 1939,[5] in a study remarkable for the time, using exchange rates between camphene hydrochloride and radioactive deuterium chloride, reached the conclusion that "while the ion of Meerwein's scheme might be a real intermediate (i.e. the tertiary camphenyl cation), the secondary ion (possessing the isobornyl structure) can never attain the kinetic freedom.... Although the intermediate ion is represented as having the camphene structure, it is possible that it is mesomeric between this and the corresponding isobornyl structure". Wilson depicted the ion as **3a** or in currently more familar formulation **3b**. Such formulation of a mesomeric σ-delocalized carbocation intermediate, i.e., a nonclassical ion, was subsequently extended by Winstein to the structure of the parent 2-norbornyl cation. This became the focal point of the "classical–nonclassical ion controversy".[6]



In 1949 and 1952 Winstein and Trifan reported[7] solvolytic study of the parent *exo*- and *endo*-2-norbornyl brosylates (*p*-bromobenzenesulfonates) and postulated the intermediacy of a σ-delocalized, symmetrically bridged norbornyl ion intermediate. The endo reactant was found to solvolyze in acetic acid, aqueous acetone, and aqueous dioxane to give substituion products of completely exo configuration and with nearly complete racemization; 7–8% preservation of optical activity was observed in acetolysis at 75 °C. Titrimetric and polarimetric rates agreed, within experimental uncertainty, in the three media. The exo substrate produced only exo product but in this case with complete loss of optical activity and with polarimetric rates exceeding titrimetric rates by factors of from 1.40 in 75% aqueous acetone to 3.46 in acetic acid, at 25 °C. (The latter value was subsequently revised to 4.6.[7]) Furthermore, the *exo*-brosylate was markedly more reactive in acetolysis than the *endo*-brosylate by a factor of 350 titrimetrically or 350 × 4.6 = 1600 polarimetrically, at 25 °C.

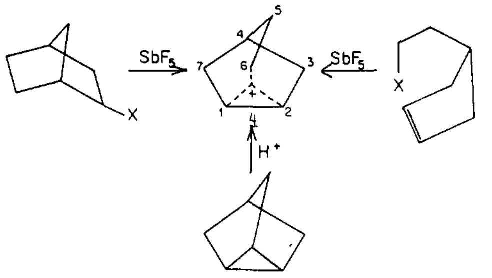
Winstein noted that the racemization results alone "could be due to dynamic equilibrium between two one-sided ("classical") cationic species", but that "further qualifications regarding these species and their reactions would be necessary to account for...the essentially exclusive formation of *exo* product and the enhanced solvolysis rate of the *exo*-bromobenzenesulfonate". Winstein concluded that "it is attractive to account for all of these results by way of the bridged formulation for the norbornyl cation".

In 1962 Brown initiated[8] his objection against the σ-bridged 2-norbornyl cation and other σ-bridged carbocations. He has maintained his position on the 2-norbornyl cation virtually unchanged since.[9]

One of us reviewed in a 1976 Account[10] evidence for the structure of 2-norbornyl cation available at the time, which seemed to be quite conclusive. It was hoped that it would put an end to the prolonged "nonclassical ion controversy". The controversy, however, was kept alive by Brown. In recent years, however, much additional evidence has been obtained that should answer any remaining questions and warrants the present Account.

## NMR Spectroscopic Studies

**$^1$H and $^{13}$C NMR Spectroscopic Studies.** The methods developed by Olah in the early 1960s to generate and observe stable carbocations in low nucleophilicity solutions[11] were successfully applied to direct observation of the norbornyl cation. Preparation of the ion by the "σ route" from 2-norbornyl halides, by the "π route" from β-Δ$^3$-cyclopentenylethyl halides, and by the protonation of nortricyclene all led to the same norbornyl cation.



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(4) Bartlett, P. D.; Pockel, I. *J. Am. Chem. Soc.* **1937**, *59*, 820; **1938**, *60*, 1585.

(5) Nevell, T. P.; deSalas, E.; Wilson, C. L. *J. Chem. Soc.* **1939**, 1188.

(6) (a) Brown, H. C. *Acc. Chem. Res.* **1973**, *6*, 377; (b) *Chem. Brit.* **1966**, 199; (c) *Chem. Eng. News.* **1967**, *45*, 86; (d) "Boranes in Organic Chemistry"; Cornell University Press: Ithaca, NY, 1972; Chapter 9, p 14. (e) Brown, H. C.; Morgan, K. J.; Chlouper, F. J. *J. Am. Chem. Soc.* **1965**, *87*, 2141. (f) Winstein, S. *Q. Rev., Chem. Soc.* **1969**, *23*, 1411. (g) Bartlett, P. D. "Nonclassical Ions"; W. A. Benjamin: New York, 1965. (h) Brown, H. C. "Nonclassical Ion Problem", with commentary by Schleyer, P. v. R.; Plenum Press: New York, 1977.

(7) Winstein, S.; Trifan, D. S. *J. Am. Chem. Soc.* **1949**, *71*, 2953; **1952**, *74*, 1147, 1159.

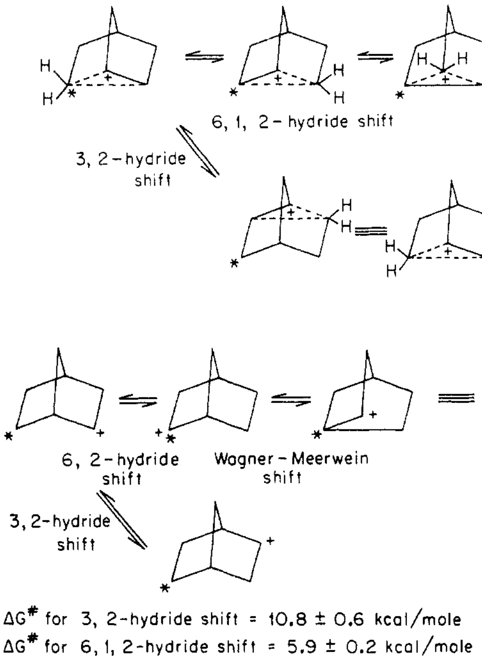
(8) Brown, H. C. *Spec. Publ.-Chem. Soc.* **1962**, *16*, 140, 174.

(9) Lectures by H. C. Bronw presented at following: (a) International Symposium on Carbocation Chemistry, Bangor, England, 1981; (b) the 6th IUPAC Conference on Physical Organic Chemistry at Université Catholique de Louvain, Louvain-la-Neuve, Belgium, 1982; (c) Symposium on Carbocation Chemistry, National Meeting of the American Chemical Society Seattle, WA, 1983.

(10) Olah, G. A. *Acc. Chem. Res.* **1976**, *9*, 41 and references given therein.

(11) (a) Olah, G. A.; Tolgyesi, W. S.; Kuhn, S. J.; Moffatt, M. E.; Bastien, I. J.; Baker, E. B. *J. Am. Chem. Soc.* **1963**, *85*, 1328. (b) Olah, G. A.; Baker, E. B.; Evans, J. C.; Tolgyesi, W. S.; McIntyre, J. S.; Bastein, I. J. *Ibid.* **1964**, *86*, 1360. (c) For reviews see: Olah, G. A. *Angew. Chem.* **1973**, *85*, 183; *Angew Chem., Int. Ed. Engl.* **1973**, *12*, 173; *Top. Curr. Chem.* **1979**, *80*, 211; *Chem. Scr.* **1981**, *18*, 97. (d) Olah, G. A.; Schleyer, P. v. R., Ed. "Carbonium Ions"; Wiley-Interscience: New York, 1968–1975; Vol. 1–5.

Scheme I
Degenerate Shifts in 2-Norbornyl Cation



The method of choice for preparation of the norbornyl cation (giving clean NMR spectra) is from *exo*-2-fluoronorbornane in $SbF_5$–$SO_2$ (or $SO_2ClF$) solution.

In a joint effort[12] in the early sixties, Olah, Saunders, and Schleyer first investigated the 60-MHz $^1H$ NMR spectrum of the 2-norbornyl cation. There followed detailed 100-MHz $^1H$ and 25-MHz $^{13}C$ NMR spectroscopic studies[13,14] in the early seventies at successively lower temperatures. From the detailed $^1H$ NMR investigation at various temperatures (ambient to −154 °C), the barriers for the 2,3 hydrogen shift as well as the 6,1,2 hydrogen shift were determined by line-shape analysis and found to be 10.8 ± 0.6 kcal/mol and 5.9 ± 0.2 kcal/mol, respectively[13] (Scheme I). More recently $^1H$ and $^{13}C$ NMR spectra of the 2-norbornyl cation at substantially higher fields (395-MHz $^1H$ and 50-MHz $^{13}C$) have been obtained at various low temperatures.[15]

The 395-MHz $^1H$ NMR spectra of 4 are substantially resolved (Figure 1) over those previously obtained at 100 MHz.[13] At −100 °C the 2-norbornyl cation 4 in $SbF_5/SO_2ClF/SO_2F_2$ solvent system shows three peaks at $\delta$ 4.92 (4 protons), 2.82 (1 proton), and 1.93 (6 protons), indicating that the 2,3 hydrogen shift is fully frozen, whereas 6,1,2 hydrogen and Wagner–Meerwein shifts (if any) are still fast on the NMR time scale. Cooling the same solution further to −158 °C results in significant changes in the spectrum. The peak at $\delta$ 4.92 develops into two peaks at $\delta$ 6.75 and 3.17 with a ratio 2:2. The high-field peak broadens and splits into two peaks at $\delta$ 2.13 and 1.37 in the ratio 4:2. The peak at $\delta$ 2.82 remains unchanged. This indicates that the 6,1,2 hydrogen shift is also fully frozen at this low temperature.

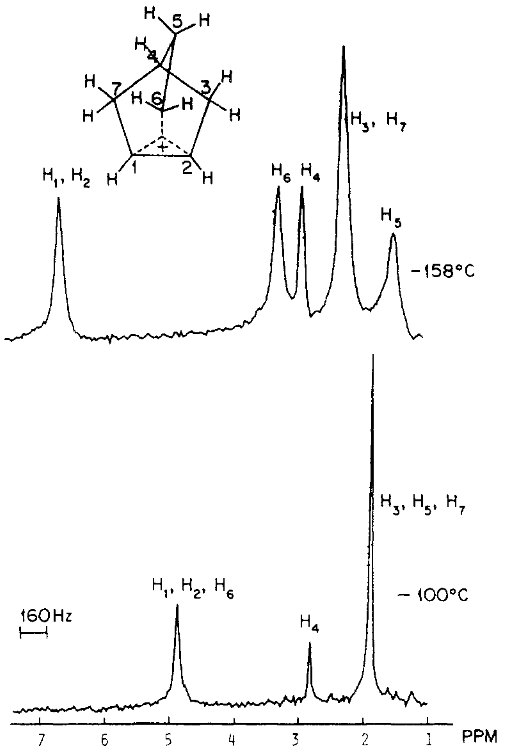
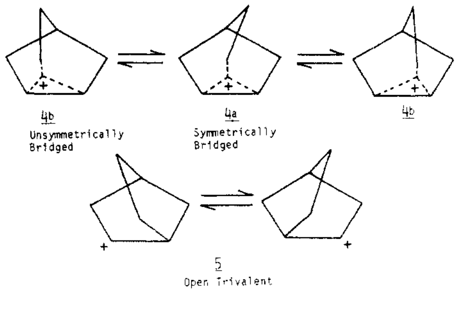


**Figure 1.** 395-MHz $^1H$ NMR spectra of the 2-norbornyl cation in $SbF_5/SO_2ClF/SO_2F_2$ solution.

One other significant aspect of the recent high-field study concerns the observed proton signal line widths at 395 MHz. The ≈60-Hz line width observed at −158 °C is rather small as compared to the one obtained previously at 100 MHz (≈30 Hz) at −154 °C. If the line width were due to any slow exchange process still occurring at such low temperature, the line should have broadened 15.6 times at 395 MHz over the one observed at 100 MHz. The observation of comparably narrow line widths at 395 MHz indicates either that the 6,1,2 hydrogen shift and the Wagner–Meerwein shift (if any) are completely frozen and the 2-norbornyl cation has the symmetrically bridged structure **4a** or that the 6,1,2 hydrogen shift is frozen and the so-called Wagner–Meerwein shift is still fast on the NMR time scale through a very shallow activation energy barrier (≤3 kcal/mol). The second possibility raises the question as to the nature of the ion undergoing equilibration. If such a process occurs, it must be exclusively between unsymmetrically bridged ions **4b** equilibrating through the intermediacy of the symmetrically bridged species **4a**.[10] Equilibrating open trivalent classical cations **5** cannot be involved.



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[12] Saunders, M.; Schleyer, P. v. R.; Olah, G. A. *J. Am. Chem. Soc.* **1964**, *86*, 5680.

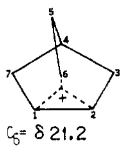
[13] Olah, G. A.; White, A. M.; DeMember, J. R.; Commeyras, A.; Lui, C. Y. *J. Am. Chem. Soc.* **1970**, *92*, 4627.

[14] Olah, G. A.; Liang, G.; Mateescu, G. D.; Riemenschneider, J. L. *J. Am. Chem. Soc.* **1973**, *95*, 8698.

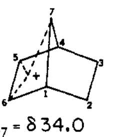
[15] Olah, G. A.; Prakash, G. K. S., Arvanaghi, M.; Anet, F. A. L. *J. Am. Chem. Soc.* **1982**, *104*, 7105. The published $^1H$ NMR spectra had the chemical-shift scale displaced by a unit, which is corrected in the present Account. The reported $^{13}C$ NMR data closely resemble the data at 25 MHz[14] in the low-field region. However, there were some ambiguities in the previously reported spectrum[14] in the assignment of the methylene region.

The 50-MHz $^{13}C$ NMR spectroscopic study of 2-norbornyl cation 4 generated from 95% $^{13}C$-enriched *exo*-2-chloronorbornane (the label corresponds to one carbon/molecule randomly distributed among C-1, C-2, and C-6) complements well the 395-MHz $^1H$ NMR study. At −80 °C, the 50-MHz $^{13}C$ NMR spectrum of the cation 4 (Figure 2) shows three absorptions at $\delta$ 91.7 (quintet, $J_{C-H}$ = 55.1 Hz), 37.7 (d, $J_{C-H}$ = 153.1 Hz), and 30.8 (t, $J_{C-H}$ = 139.1 Hz), indicating that the 2,3 hydrogen shift is frozen, but the 6,1,2 hydrogen and the Wagner–Meerwein shift (if any) are still fast on the NMR time scale. Cooling the solution down results in broadening and slow merger into the base line of the peaks at $\delta$ 91.7 and 30.8, but the peak at $\delta$ 37.7 remains relatively sharp. At −159 °C, the peaks at $\delta$ 91.7 and 30.8 split into two sets of two peaks at $\delta$ 124.5 (d, $J_{C-H}$ = 187.7 Hz), 21.2 (t, $J_{C-H}$ = 147.1 Hz) and $\delta$ 36.3 (t, $J_{C-H}$ = 131.2 Hz), 20.4 (t, $J_{C-H}$ = 153.2 Hz), respectively.

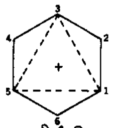
The observation of the C-1 and C-2 carbons at $\delta$ 124.5 and the C-6 carbon at $\delta$ 21.2 clearly supports the bridged structure for the ion. Five (or higher)-coordinate carbons generally show shielded (up field) $^{13}C$ NMR shifts. In fact, the higher coordinate carbons in the 7-norbornenyl,[16] trishomocyclopropenyl,[17] and 9-pentacyclononyl[18] (Coates' system) cations are observed at $\delta$ 34.0, 4.9, and 29.6, respectively.



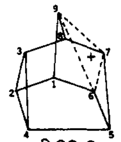
$C_6$ = $\delta$ 21.2



$C_7$ = $\delta$34.0



$C_1,C_3,C_5$ = $\delta$4.9



$C_6,C_7,C_9$ = $\delta$ 29.6

Applying the additivity of chemical shift analysis[19] to the 2-norbornyl cation 4 also supports the bridged nature of the ion. A chemical-shift difference of 168.0 ppm is observed between the ion 4 and its parent hydrocarbon, i.e., norbornane, whereas ordinary trivalent carbocations such as the cyclopentyl cation reveal a chemical-shift difference of ≈360 ppm.[19]

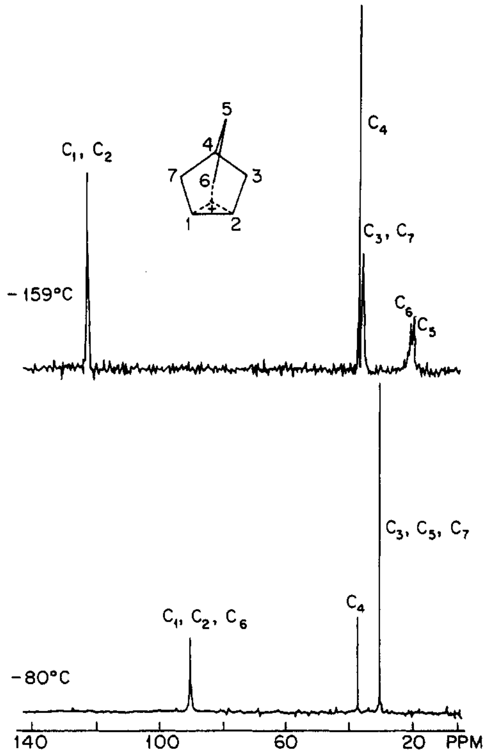


**Figure 2.** 50-MHz $^{13}C$ NMR spectra of the 2-norbornyl cation in $SbF_5/SO_2ClF/SO_2F_2$ solution.

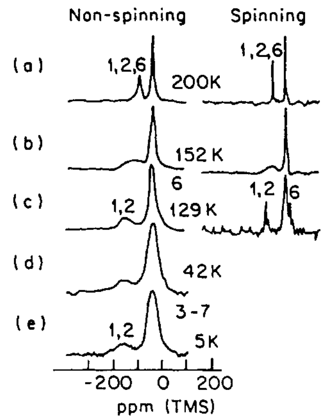


**Figure 3.** Representative solid-state $^{13}C$ NMR spectra of the 2-norbornyl cation according to Yannoni and Myhre.[21] Reprinted with permission from ref 21. Copyright American Chemical Society, 1982.

**Solid-State Cross-Polarization Magic Angle Spinning $^{13}C$ NMR Spectroscopic Studies at Very Low Temperatures.** Yannoni and Myhre[20] have obtained magic angle cross-polarization $^{13}C$ NMR spectra of the $^{13}C$-enriched 2-norbornyl cation 4 in $SbF_5$ solid matrix down to −196 °C. Their solid-state chemical shifts and the measured barrier for 6,1,2 hydrogen shift of 6.1 kcal/mol correlate well with our solution data. More recently they even[21] have obtained $^{13}C$ NMR spectra in the solid state at −268 °C (5 K). A remarkable achievement indeed. A fortuitous combination of large isotropic chemical shifts and small chemical shift anisotropies permitted them to obtain reasonable resolution of the positively charged carbon resonance without the need for magic angle spinning.

Comparison with their previous MAS spectra[20] down to −196 °C shows that the nonspinning spectra reflect slowing of 6,2,1 hydrogen shift. Since no change was observed in the positively charged carbon resonance (at $\delta$ 125) between −144 and −268 °C (Figure 3), the authors[21] concluded that, if the hypothetical 1,2 Wagner–Meerwein shift is still occurring, then it should be rapid and an upper limit for the barrier for such a process (involving structures 5) can be estimated to be 0.2 kcal/mol. This can be taken as the most definitive spectroscopic evidence besides the ESCA studies for the symmetrical $\sigma$-bridged structure of the 2-norbornyl cation, in good accordance with the previously discussed

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(16) Olah, G. A.; Liang, G. *J. Am. Chem. Soc.* **1975**, *97*, 6803.

(17) (a) Masamune, S.; Sakai, M.; Jones, A. V. K.; Nakashima, T. *Can. J. Chem.* **1974**, *52*, 855. (b) Masamune, S.; Sakai, M.; Jones, A. V. K. *Ibid.* **1974**, *52*, 858. (c) Olah, G. A.; Prakash, G. K. S.; Rawdah, T. N.; Whittaker, D.; Rees, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 3935.

(18) Coates, R. M.; Fretz, E. R. *J. Am. Chem. Soc.* **1975**, *97*, 2538.

(19) Schleyer, P. v. R.; Lenoir, D.; Mison, P.; Liang, G.; Prakash, G. K. S.; Olah, G. A. *J. Am. Chem. Soc.* **1980**, *102*, 683.

(20) Yannoni, C. S.; Macho, V.; Myhre, P. C. *J. Am. Chem. Soc.* **1982**, *104*, 907.

(21) Yannoni, C. S.; Macho, V.; Myhre, P. C. *J. Am. Chem. Soc.* **1982**, *104*, 7380.

low-temperature solution studies.

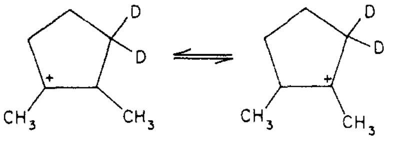
Yannoni and Myhre[22] also succeeded in freezing out the degenerate hydrogen shift in the cyclopentyl cation in the solid state at −203 °C (the ion is degenerate in solution even at −150 °C). The obtained chemical shifts at δ 320, 71.0, and 28.0 indicate the regular trivalent classical nature of the ion and are in good agreement with estimated shifts in solution based on the average shift data. These results also show the ability of very low temperature solid-state NMR methods to differentiate rapidly equilibrating secondary classical ion systems from their static counterparts even if the barrier involved is much less than 3 kcal/mol.

**Isotopic Perturbation of Resonance Studies.** The isotopic perturbation of resonance method developed by one of us is capable of providing a convenient means to distinguish the rapidly equilibrating from the bridged nature of carbocations.

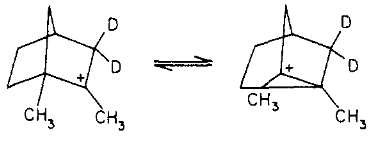
Saunders and Vogel in 1971 discovered[23,25] that by asymetrically introducing deuterium into some carbocation systems that were known to undergo degenerate, very rapid and reversible rearrangement processes, large splittings were produced in the NMR spectrum. Although the ions were interconverting extremely rapidly and still gave averaged spectra, the isotope made the energies of the two interconverting species slightly different, and thus the equilibrium constant between them was no longer unity. Each ion, therefore, spent a little more time on one side of the equilibrium barrier than on the other side. The weighted-average peaks of the two carbon atoms that were interchanged by the rearrangement process no longer coincided. Splitting values in the $^{13}C$ NMR spectrum of over 100 ppm were observed as a result of perturbation by deuterium.[26]

However, when deuterium was introduced into systems that were accepted as static, single-minimum, nonequilibrating species,[27] such as the cyclohexenyl cation, no large splittings were observed, and in contrast to the behavior of the equilibrating systems, there were no observable changes in the spectra with temperature. In fact, the isotope-induced changes in the spectrum were not very different from changes that occur in any simple molecule on introducing deuterium and were roughly 50 times smaller than the effects produced in the equilibrating systems.

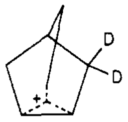
These observations led to the method of observing changes in NMR spectra produced by asymmetric introduction of isotopes (isotopic perturbation) as a means of distinguishing systems involving equilibrating species passing rapidly over a low barrier from molecules with single energy minima, intermediate between the presumed equilibrating structures. Applying this method[28] to the 2-norbornyl cation clearly supports its bridged nature. Since the 6,1,2 hydrogen shift has a barrier of only 5.9 kcal/mol, a certain amount of line broadening of the lowest field signal is observed in the $^{13}C$ NMR spectrum of the 2-norbornyl cation even at very low temperatures. Even in the ion with no deuterium, the downfield signal at δ 124.5 (C-2 and C-6 cyclopropane-like carbons) is 2 ppm wide. Nevertheless, no additional isotopic splitting or broadening was observed with either 2-monodeuterio or 3,3-dideuterio cations and therefore the isotopic splitting can be no more than 2 ppm. This is true even if a slow 6,2 hydride shift converts part of the latter ions to a symmetrical 5,5-dideuterio system that lacks an equilibrium isotope effect in the equilibrium process.



ΔδC = 104 ppm



ΔδC = 24 ppm



ΔδC < 2 ppm

The result, when compared to the significantly larger splitting observed[26] for deuterated dimethylcyclopentyl and dimethylnorbornyl cations (known to be equilibrating ions), is in accordance with the nonclassical nature of 2-norbornyl cation. Similar conclusions were recently reached,[29] based on the deuterium isotopic perturbation effect in the $^{1}H$ NMR spectrum of the 2-norbornyl cation obtained at higher temperatures.

Application of the method to the 1,6-dimethylcyclodecyl cation,[30] Coates' pentacyclononyl cation,[28] the cyclopropylcarbinyl cation,[31] and the hexamethylpyramidal dication of Hogeveen[32] shows good agreement with their studied nonclassical (bridged) structures.

**Application of $^{13}C$ NMR Spectroscopy to the Gassman–Fentiman Tool of Increasing Electron Demand.** The Gassman–Fentiman "tool of increasing electron demand"[33a] was applied by Richey et al. with the use of NMR spectroscopy in 1970[33b] to measure the electron demand of the electron-deficient cationic center of 7-aryl-7-norbornenyl cations. In 1977 Brown accepted[34] the existence of a nonclassical ion by using the "tool" in the solvolytic rate studies of 9-aryl-9-pentacyclo[4.3.0$^{2,4}$.0$^{3,8}$.0$^{3,7}$]nonyl *p*-nitrobenzoates. The very low methyl/hydrogen and phenyl/methyl rate ratios observed were taken as a criteria for a transition state stabilized by σ-bridging. However, he also stated "it should be pointed out that the application of the same criteria to the 2-norbornyl cation fails to reveal

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(22) Myhre, P. C., private communication.

(23) Saunders, M.; Jaffe, M. H.; Vogel, P. *J. Am. Chem. Soc.* **1971**, *93*, 2558.

(24) Saunders, M.; Vogel, P. *J. Am. Chem. Soc.* **1971**, *93*, 2559.

(25) Saunders, M.; Vogel, P. *J. Am. Chem. Soc.* **1971**, *93*, 2561.

(26) Saunders, M.; Telkowski, L. A.; Kates, M. R. *J. Am. Chem. Soc.* **1977**, *99*, 8070.

(27) Saunders, M.; Kates, M. R. *J. Am. Chem. Soc.* **1977**, *99*, 8071.

(28) Saunders, M.; Kates, M. R. *J. Am. Chem. Soc.* **1980**, *102*, 6867.

(29) Saunders, M.; Kates, M. R. *J. Am. Chem. Soc.* **1983**, *105*, 3571.

(30) Kirchen, R. P.; Ranganayakalu, K.; Singh, B. P.; Sorensen, T. S. *J. Am. Chem. Soc.* **1981**, *103*, 588.

(31) Saunders, M.; Siehl, H-U. *J. Am. Chem. Soc.* **1980**, *102*, 6868.

(32) Van Kruchten, E. M. G. A.; Hogeveen, H. *J. Org. Chem.* **1981**, *46*, 1350.

(33) (a) Gassman, P. G.; Fentiman, A. F., Jr. *J. Am. Chem. Soc.* **1970**, *91*, 1545; **1971**, *92*, 2549. (b) Richey, H. G., Jr.; Nichols, D.; Gassman, P. G.; Fentiman, A. F., Jr.; Winstein, S.; Brookhart, M.; Lustgarten, R. K. *Ibid.* **1970**, *92*, 3783.

(34) Brown, H. C.; Ravindranathan, M. *J. Am. Chem. Soc.* **1977**, *99*, 299.

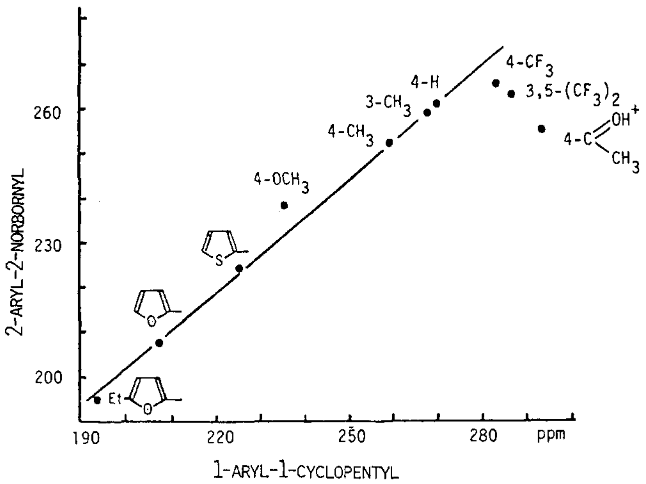


**Figure 4.** Plot of the $^{13}$C NMR chemical shifts of the cationic center of the 2-aryl-2-norbornyl cations vs. those of model 1-aryl-1-cyclopentyl cations.

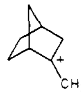
such a participation under solvolytic conditions".

Farnum and Olah's group, respectively, have extended the "tool" coupled with $^1$H and $^{13}$C NMR spectroscopy as the structural probe under stable conditions to show the onset of $\pi$-, $\pi\sigma$-, and $\sigma$-delocalization in a variety of systems.[35-41] The $^{13}$C NMR chemical shifts of the cationic carbon of a series of regular trivalent arylcyclopentyl, arylcyclohexyl, 2-aryl-2-adamantyl, 6-aryl-6-bicyclo[3.2.1]octyl, 7-aryl-7-norbornyl cations (so called classical cations) correlate linearly with the observed cationic carbon chemical shifts of substituted cumyl cations over a range of substituents[42-43] (generally from the most electron releasing $p$-OCH$_3$ to the most electron withdrawing 3,5-(CF$_3$)$_2$ groups).

However, systems such as 2-norbornyl show deviations from linearity in such chemical shift plots with electron-withdrawing substituents (Figure 4); this is indicative of the onset of nonclassical $\sigma$-delocalization and thus fully suports the nonclassical nature of the parent secondary cation. These conclusions were criticized by Brown.[44] In a recent paper[45] we have shown major flaws in Brown's arguments and we will not repeat them here. It was also shown that in some cases, such as phenyl- and cyclopropyl-substituted cationic systems wherein a similar deviation was observed, the origin of such effects may be entirely different.

Brown attempted to explain all observed deviations by an inductive $\pi$-polarization phenomenon.[46] This suggestion, however, is not compatible with many experimental findings,[45] and, moreover, the norbornyl framework in question lacks $\pi$-electrons to be polarized. Judicious application of the tool of increasing electron demand coupled with $^{13}$C NMR spectroscopy as the structural probe is useful to determine the onset of $\pi$-, $\pi\sigma$-, or $\sigma$-delocalization provided alternative explanations for the data are ruled out. No claim was ever made that the method was selective for $\sigma$-delocalization.

Table I
Binding Energy Differences of Carbocation Centers from Neighboring Carbon Atoms $dE_{b^+C-C}$

| ion | $dE_{b^+C-C}$ | approx rel C$^+$:C intensity |
|---|---|---|
| $(CH_3)_3{}^+C$ | 3.9 ± 0.2 | 1:3 |
|  | 4.2 ± 0.2 | 1:5 |
|  | 3.7 ± 0.2 | 1:7 |
|  | 4.3 ± 0.5 | 1:4 |
|  | 1.5 ± 0.2 | 2:5 |

However, it should be reemphasized that, since phenyl groups even with electron-withdrawing substituents can still delocalize charge into the $\pi$-system, the method is not sensitive enough to detect bridging in cases where structural changes are limited, including systems that are partially bridged or delocalized. For the same reasons the method must be considered ineffective in many solvolytic studies, since solvation significantly masks the electron demand of the cationic center in the solvolytic transition state unless the structural change is significant (as in the case of 7-norbornenyl, 5-norbornen-2-yl, or pentacyclononyl systems).

## Core Electron Spectroscopy (ESCA) Studies

Since the time scale of the ionization processes in electron spectroscopy is in the order of $10^{-16}$ s, definite ionic species are characterized, regardless of their possible intra- and intermolecular interactions (e.g., Wagner–Meerwein rearrangements, hydride shifts, etc.), even at rates equaling or exceeding those of vibrational transitions. Thus, electron spectroscopy can give an unequivocal answer to the question of the "classical" or "nonclassical" nature of the norbornyl cation.

In an ESCA study Olah et al.[14] succeeded in observing the ESCA spectrum of the norbornyl cation and compared it with those of the 2-methyl-2-norbornyl cation and other trivalent carbenium ions, such as the cyclopentyl and methylcyclopentyl cations. The 1s electron spectrum of the norbornyl cation shows no high binding energy carbenium center, and a maximum separation of less than 1.5 eV is observed between the two "cyclopropyl" type carbons, to which bridging takes place from the other carbon atoms (including the pentacoordinated bridging carbon). In contrast, the 2-methyl-2-norbornyl cation shows a high binding energy carbenium center, deshielded with the $\delta E_b$ of 3.7 eV

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(35) Olah, G. A.; Prakash, G. K. S.; Liang, G. *J. Am. Chem. Soc.* **1977**, *99*, 5683.

(36) Farnum, D. G.; Botto, R. E. *Tetrahedron Lett.* **1975**, *46*, 4013.

(37) (a) Farnum, D. G.; Botto, R. E.; Chambers, W. T.; Lam, B. *J. Am. Chem. Soc.* **1978**, *100*, 3847. (b) For preceding $^1$H studies, see: Farnum, D. G.; Wolf, H. D. *Ibid.* **1974**, *96*, 5166.

(38) Olah, G. A.; Berrier, A. L.; Arvanaghi, M.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1981**, *103*, 1122.

(39) Farnum, D. G.; Clausen, T. P. *Tetrahedron Lett.* **1981**, *22*, 549.

(40) For a comprehensive evaluation of the method, see: Olah, G. A.; Berrier, A. L.; Prakash, G. K. S. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 1998.

(41) Olah, G. A.; Berrier, A. L.; Prakash, G. K. S. *J. Org. Chem.* **1982**, *47*, 3903.

(42) Olah, G. A.; Porter, R. D.; Jeuell, C. L.; White, A. M. *J. Am. Chem. Soc.* **1972**, *94*, 2044.

(43) Brown, H. C.; Kelly, D. P.; Periasamy, M. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 6956.

(44) Brown, H. C.; Periasamy, M.; Kelly, D. P.; Giansiracusa, J. J. *J. Org. Chem.* **1982**, *47*, 2089 and references cited therein.

(45) Olah, G. A.; Prakash, G. K. S.; Farnum, D. G.; Clausen, T. P. *J. Org. Chem.* **1983**, *48*, 2146.

(46) Brown, H. C.; Periasamy, M. *J. Org. Chem.* **1982**, *47*, 4740, 4742.

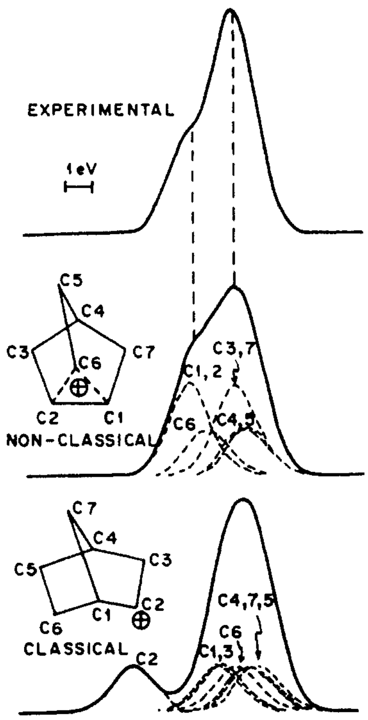

**Figure 5.** 1s core-hole-state spectra for the 2-norbornyl cation and simulated spectra for the classical and nonclassical ions according to Clark.[50] Reprinted with permission from ref 50. Copyright American Chemical Society, 1977.

from the other carbon atoms. Typical ESCA shift differences are summarized in Table I.

Recently, Grunthaner reexamined the ESCA spectrum of the norbornyl cation on a higher resolution X-ray photoelectron spectrometer using highly efficient vacuum techniques.[47] The spectrum closely matches the previously published spectra, demonstrating the reproducibility of the ESCA data of the norbornyl cation, despite speculation by Brown and Kramer[48] to the contrary. Furthermore, the reported ESCA spectral results are consistent with the theoretical studies of Allen and Goetz[49] on the classical and nonclassical norbornyl cation at the STO-3G and STO-4.31G levels. Using the parameters obtained by Allen and Goetz, Clark et al.[50] were able to carry out a detailed interpretation of the experimental ESCA data for the core-hole-state spectra at SCF STO-4.31G level and calculated equivalent cores at STO-3G level. Agreement between experimentally obtained and calculated spectra for the nonclassical cation are good and clearly different from that calculated for the classical cation (Figure 5).

## Thermochemical Calorimetric Studies

If the classical structure were correct, the 2-norbornyl cation would be a regular secondary carbocation with no additional stabilization provided by $\sigma$-delocalization (such as the cyclopentyl cation). The facts are, however, to the contrary. Direct experimental evidence for the unusual stability of the secondary 2-norbornyl cation comes from the low temperature solution calorimetric studies by Arnett and co-workers.[51] In a series of investigations they determined[51a] the heats of ionization ($\Delta H_i$) of secondary and tertiary chlorides in $SbF_5/SO_2ClF$ and more recently[51b] of alcohols in $FSO_3H:SbF_5/SO_2ClF$ solutions.

$$\text{R-Cl} + SbF_5 \xrightarrow{\Delta H_i} R^+SbF_5Cl^-$$

$$\text{R-OH} + FSO_3H{:}SbF_5 \xrightarrow{\Delta H_i} R^+SbF_5(FSO_3)^- + H_3O^+$$

They have found that, whereas the difference observed in the heats of ionization of 2-methyl-2-*exo*-norbornyl chloride and 2-*exo*-norbornyl chloride in $SbF_5/SO_2ClF$ solution is 7.4 kcal/mol, the same difference between the corresponding alcohols in $FSO_3H:SbF_5/SO_2ClF$ solution is only 2.5 kcal/mol, a remarkably small difference for the corresponding secondary and tertiary cations, which generally is at least 10 kcal/mol or larger. Thus, in the case of norbornyl there seems to be a 7.5 kcal/mol extra stabilization. It has been repeatedly pointed out by Arnett that caution must be exercised in directly comparing calorimetric data of tertiary and secondary ions without considering initial-state contributions and further that there are not many stable secondary ions available for comparison. Regardless, it is clear that the norbornyl cation resembles more tertiary and not secondary ions.

The most compelling thermodynamic evidence for the nonclassical stabilization of the 2-norbornyl cation also comes from Arnett, who measured heats of isomerization of secondary cations to tertiary cations.[52] The measured heat of isomerization of the 4-methyl-2-norbornyl cation (a secondary system) to the tertiary 2-methyl-2-norbornyl cation is 6.6 kcal/mol. In contrast, the related isomerization of the *sec*-butyl cation and *tert*-butyl cation involved a difference in $\Delta H_i$ of 14.2 kcal/mol. Taking this latter value as characteristic for isomerization of secondary to tertiary ions, one must conclude that the secondary norbornyl ion has an extra stabilization of about 7.6 kcal/mol. Farcasiu[53] questioned these conclusions, arguing that they neglected to account for extra stabilization by bridgehead methyl substitution as indicated by his molecular force field calculations. Schleyer and Chandrasekhar[54] have subsequently pointed out that Farcasiu failed to include corrections for $\beta$-alkyl branching. Correcting for this effect, there is an overall 6 ± 1 kcal/mol extra stabilization in the 2-norbornyl cation for which no reasonable explanation other than $\sigma$-bridging can be offered.

## Gas-Phase and Theoretical Studies

Gas-phase mass spectrometric studies[55,56] also indicate exceptional stability of the 2-norbornyl cation

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[47] The ESCA spectrum was obtained on an HP 7950 A ESCA spectrometer at the Jet Propulsion Laboratory of the California Institute of Technology, Pasadena, CA.

[48] (a) Brown, H. C.; Liu, K. T. *J. Am. Chem. Soc.* **1975**, *97*, 600. (b) Kramer, G. M. *Adv. Phys. Org. Chem.* **1975**, *11*, 177. (c) Rebuttal of Kramer's view was given in ref 10. It is surprising that our techniques were questioned only in the case of the 2-norbornyl cation but not with model trivalent cations.

[49] Goetz, D. W.; Schlegel, H. B.; Allen, L. C. *J. Am. Chem. Soc.* **1977**, *99*, 8118.

[50] (a) Clark, D. T.; Cromarty, B. J.; Colling, L. *J. Am. Chem. Soc.* **1977**, *99*, 8121. (b) Calculations by M. J. S. Dewar on the ESCA spectra were commented on in ref 10.

[51] (a) Arnett, E. M.; Petro, C. *J. Am. Chem. Soc.* **1978**, *100*, 2563. (b) Arnett, E. M.; Hofelich, T. C. *Ibid.* **1983**, *105*, 2889.

[52] Arnett, E. M.; Pienta, N.; Petro, C. *J. Am. Chem. Soc.* **1980**, *102*, 398.

[53] Farcasiu, D. *J. Org. Chem.* **1981**, *46*, 223.

[54] Schleyer, P. v. R.; Chandrasekhar, J. *J. Org. Chem.* **1981**, *46*, 225.

[55] (a) Kaplan, F.; Cross, P.; Prinstein, R. *J. Am. Chem. Soc.* **1970**, *92*, 1445. (b) Solomon, J. J.; Field, F. H. *Ibid.* **1976**, *98*, 1567. (c) Staley, R. H.; Weiting, R. D.; Beauchamp, J. L. *Ibid.* **1977**, *99*, 5964.

[56] Saluja, P. P. S.; Kabarle, P. *J. Am. Chem. Soc.* **1979**, *101*, 1084.

relative to other secondary cations.

Theoretical quantum mechanical calculations[57-59] have been performed on the 2-norbornyl cation at various levels. These calculations reveal significant preference for $\sigma$-delocalized nonclassical structures. The most recent and extensive calculation by Schaefer and co-workers[60] using full geometry optimization for symmetrically and unsymmetrically bridged systems showed a difference of only 1.0 kcal/mol between these structures. (Some confusion was introduced by Schaefer calling the unsymmetrically bridged ions "classical".) Similar high-level calculations including electron correlations (with a double-$\zeta$ plus polarization bases set) by Ragavachari et al.[61a] as well as by Liu[61b] indicate that the only minimum on the 2-norbornyl cation potential energy surface is the symmetrically bridged structure. The "classical" 2-norbornyl-like geometry does not represent a minimum on the potential energy surface. The extra stabilization of the bridged structure in the gas phase was estimated at $\approx$15 kcal/mol at this high level of ab initio theory.[61]

## Relevance to Solvolytic Studies

The original starting point of the norbornyl cation controversy was Brown's contention that exo- and *endo*-norbornyl esters undergo anchimerically unassisted ionization and that the singular rate and product characteristics of the system (i.e., high exo/endo rate ratios) are attributable to steric effects, specifically hindrance to ionization of the endo isomers. In his view exo systems are not accelerated by anchimeric assistance, as suggested by Winstein, but the endo are slowed down by steric hindrance. Raising this possibility as an alternative reason for the observed high exo/endo rate ratio was a valid point. However, none of Brown's own or any other studies ever showed that $\sigma$-participation is not involved in the solvolysis of parent secondary *exo*-norbornyl systems.

The scope of our Account excludes any detailed discussion of solvolytic data. For a relevant discussion the reader is referred to Schleyer's commentary in ref 6h and also the accompanying Accounts by Grob and Walling. However, we would like to briefly comment concerning the basic difference in views of Winstein and Brown regarding the observed high exo/endo rate ratios of the solvolysis of 2-norbornyl systems. To what degree solvolysis of secondary systems is "limiting" as suggested by Winstein is still not fully established. Only in "limiting" systems is the transition state ionlike, otherwise it can lie earlier. Knowledge of the structure of the intermediate ion directly relates to the transition state in the former case, but it does not necessarily reflect the nature of the transition state in the latter. In recent years, however, it has been established that distortions due to nucleophilic solvent assistance can be avoided (or minimized) by comparing data obtained in low nucleophilicity solvents such as hexafluoroisopropyl alcohol. Such rate data collected by Bentley, Schleyer, and co-workers[62] for the solvolysis of secondary tosylates relative to isopropyl tosylate make an interesting comparison. The relative rates at 25 °C are as follows: 2-butyl, 14.3; 2-pentyl, 17.4; 3-pentyl, 76; 4-heptyl, 140.9; cyclopentyl, 377.3; cyclohexyl, 24; 2-adamantyl, 133.6; and pinacolyl, 954.5. The secondary *endo*-2-norbornyl with the relative rate ratio of 99.1 compares well with other secondary systems, whereas the *exo*-2-norbornyl shows a relative ratio of 155 455, a very high exo/endo rate ratio indeed. Since the endo system behaves similar to other model secondary systems and indicates no slowing down due to assumed steric hindrance, the large increase in the relative rate ratio in the *exo*-norbornyl system must be due to reasons other than steric hindrance in the endo systems. $\sigma$-Participation in the exo system is the only reasonable explanation that can be offered. Thus Winstein's original views seem to be fully justified.

The effect of substituents on the solvolysis of 2-norbornyl derivatives has been reviewed by Grob,[63] and he discusses these in his accompanying Account. Adding substituents invariably distorts the parent norbornyl system and therefore data must be analyzed with care. The concept that there is a continuum of charge delocalization depending upon the substituents is certainly valid and has been emphasized before concerning stable ions.[10] It should also be pointed out that varying degrees of $\sigma$-delocalization (partial bridging) are possible in tertiary 2-norbornyl cations, such as the 2-methyl-2-norbornyl cation. The 2-phenyl-2-norbornyl cation seems to show competing $\sigma$- with $\pi$-delocalization only when substituted with strongly electron withdrawing substituents, decreasing (but not eliminating) $\pi$-participation. No dogmatic statement as to the lack of $\sigma$-participation in tertiary 2-norbornyl cations is thus warranted.

## Concluding Remarks

Results of recent experimental structural studies of the stable, long-lived 2-norbornyl cation are summarized in this Account, including high-field $^1$H and $^{13}$C solution NMR, solid-state $^{13}$C NMR at 5 K, isotopic perturbation studies, application of tool of increasing electron demand, ESCA, stable ion solution calorimetry as well as theoretical calculations. Data supplement and unequivocally substantiate previous studies reviewed earlier.[10] All the evidence is consistent, and we believe that there can be no doubt left as to the $\sigma$-bridged structure of the 2-norbornyl cation. Any further continuation of the classical–nonclassical ion controversy seems to be a futile exercise of semantics and not of relevant experimental facts.[64] Already too much effort has been expended on the study of this fascinating cation now considered notorious by many.

It is rather surprising that Brown recently has questioned[65] the relevance of structural studies of the 2-norbornyl cation to what he considers the unanswered

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(57) Dewar, M. J. S.; Haddon, R. C.; Komornicki, A.; Rzepa, H. *J. Am. Chem. Soc.* **1977**, *99*, 377.

(58) Wenke, G.; Lenoir, D. *Tetrahedron* **1979**, *35*, 489.

(59) Kohler, H. J.; Lischka, H. *J. Am. Chem. Soc.* **1979**, *101*, 3479.

(60) Goddard, J. D.; Osamura, Y.; Schaefer, H. *J. Am. Chem. Soc.* **1982**, *104*, 3258.

(61) (a) Ragavachari, K.; Haddon, R. C.; Schleyer, P. v. R.; Schaefer, H., *J. Am. Chem. Soc.* **1983**, *105*, 5915. (b) Yoshimine, M.; McLean, A. D.; Liu, B.; DeFrees, D. J.; Binkley, J. S. *J. Am. Chem. Soc.* **1983**, *105*, 6185.

(62) (a) Bentley, T. W.; Bowen, C. T.; Morten, D. H.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5466. (b) We are grateful to Professor P. v. R. Schleyer for comments on this and other parts of our Account and his constructive suggestions.

(63) Grob, A. C. *Angew. Chem.* **1982**, *94*, 87; also see the accompanying Account.

(64) For closing comments on the "Norbornyl Cation Debate", see letters to the editor by G. A. Olah and H. C. Brown in *Chem. Eng. News* **1983**, *61*, May 23.

(65) (a) Brown, H. C.; Liu, K. T. *J. Am. Chem. Soc.* **1975**, *97*, 2469. (b) Reference 9. (c) Accompanying Account.

major issue of the high exo/endo rates in solvolysis, and related energetics. Some years ago one of us[10] commented, "Knowing the structure of the intermediate in any reaction, including solvolysis, has obvious significance to understanding of the path and mechanism of the whole process. What can be argued is to what degree the transition state will resemble the intermediate". Nothing further needs to be added.

More importantly, rather than being rare, two-electron, three (or multi)-center bonding is characteristic of electron-deficient molecules, including nonclassical carbocations.[11] The real significance of the very thorough study of the nonclassical norbornyl cation lies in that it helped to establish that carbocations, the positive ions of hydrocarbons that play the key role in their acid-catalyzed reactions, belong to two major subclasses:[66] (a) trivalent ions such as the parent $CH_3^+$ or the *tert*-butyl cation, $^+C(CH_3)_3$, and (b) ions containing five- or six-coordinate carbons, of which the parent is $CH_5^+$. It also provided evidence for the close similarity of $\pi$- and $\sigma$-bond donor ability and thus helped to open the door to the general utilization of single-bond reactivity in electrophilic reactions of saturated hydrocarbons (including methane).

(66) Olah, G. A. *J. Am. Chem. Soc.* **1972**, *94*, 808.

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# An Innocent Bystander Looks at the 2-Norbornyl Cation

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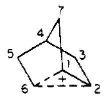
In 1949 Winstein and Trifan first reported the now long familiar facts about the acetolysis of 2-norbornyl arenesulfonates: exo isomers react much more rapidly than endo, both give solely exo products, and the products from optically active exo starting material are completely racemized.[1] They then stated "The facts are at present best accommodated by formulation of the intermediate ion from exo norbornyl derivatives as II".



II

Such a formulation was a plausible extension of Winstein's previous interpretation of neighboring-group effects, and the authors noted that such "bridged ions" had, in fact, been proposed or mentioned as possibilities by others in connection with several Wagner–Meerwein rearrangements. The next 15 years were very active ones in the study of both solvolyses and carbocation rearrangements, and similar structures were frequently invoked to account for the results in a variety of systems. As the field developed, so did the nomenclature. Winstein had originally referred to his postulated structure as "bridged" and, later, to the whole process of such neighboring-group interaction as "anchimeric assistance". Ingold proposed the name "synartetic ions" for such bridged species. However, the term "nonclassical ions" introduced by Roberts and Lee in 1951[2] has been most popular, at least in this country. Originally, its meaning was rather ill-defined, and it still seems to be used in two senses: to refer specifically to a symmetric bridged structure such as II or more generally to any cationic center on carbon, bonded to (or perhaps only interacting with) more than three other atoms. This leads to difficulties,[3] and I shall simply refer to all such structures as "bridged species".

By the 1960s, interest in such bridging phenomenon might have leveled off had it not been for a vigorous attack on the whole concept of "nonclassical" ions launched by Brown in 1962.[4] The number of contentious communications published in the next 10 years gives one some idea of the intensity of feeling aroused. The debate was vigorously pursued verbally in lectures, meetings, and seminars all over the U.S. and even abroad. The controversy has been fed by continual additional research, and, as other papers in this issue indicate,[5–7] interest in the subject continues to this day.

All this attention and activity has had consequences within the chemical community considerably beyond the significance of the question immediately involved. On the positive side, besides providing material for innumerable Ph.D. theses, it has clarified concepts, led to improved kinetic techniques, encouraged the gathering of thermochemical data, and, perhaps most important, sparked the development of techniques for the study of the NMR spectra of carbocations under "stable" conditions in highly acidic nonnucleophilic solvents over a wide range of temperature. On the negative side, the position of the chemical community as a whole appears to have moved from interest to a

Cheves Walling is Distinguished Professor of Chemistry at the University of Utah. He received his A.B. degree from Harvard (in 1937) and his Ph.D. at the University of Chicago with M. S. Kharasch. Although his chief field of research is free-radical reactions, he has been struggling to understand the broader aspects of physical organic chemistry and to explain them to students ever since. As Editor of the Journal of the American Chemical Society, 1975–1981, he estimates he had to make decisions on over 3000 physical organic manuscripts, not all (fortunately, in his view) involving 2-norbornyl systems.

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(1) Winstein, S.; Trifan, D. S. *J. Am. Chem. Soc.* **1949**, *71*, 2953.

(2) Roberts, J. D.; Lee, C. C. *J. Am. Chem. Soc.* **1951**, *73*, 5009.

(3) As in the familiar question, "is the 2-norbornyl cation nonclassical or two rapidly equilibrating classical ions?". A better form of the question would be "is it a symmetric bridged species, or two rapidly equilibrating species that may also be significantly bridged?".

(4) Brown, H. C. *Spec. Publ.–Chem. Soc.* **1962**, *16*, 140.

(5) Brown, H. C., accompanying paper in this issue.

(6) Grob, C. A., accompanying.

(7) Olah, G. A.; Prakash, G. K. S.; Saunders, M., accompanying paper in this issue.

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