The σ-Bridged 2-Norbornyl Cation and Its Significance to Chemistry[1]

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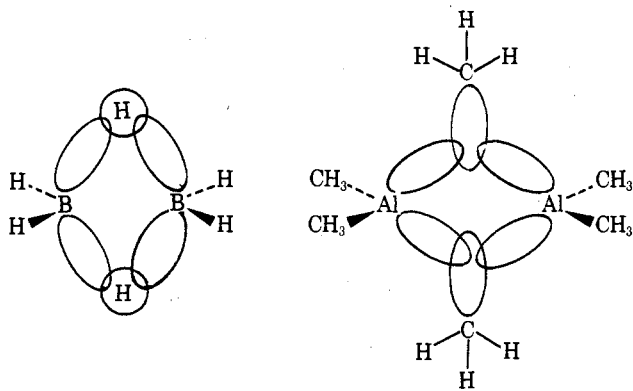
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Two-Electron Three-Center Bonding and Nonclassical Ions

One of the foundations of modern chemistry is the Lewis–Langmuir concept of the two-electron, two-atom covalent bond.[2] This treatment of bonding electrons as localized between two centers is now recognized through quantum mechanics to be an approximation, but one which has served well for interpretation of the chemical behavior of a great many compounds.

The properties of some molecules require, however, the formulation of bonds delocalized over more than two atoms. Most of these are conjugated unsaturated systems, which are discussed universally in terms of π-electron resonance. Other compounds have structures which indicate delocalized bent σ bonds. Well-known examples are diborane, where two-electron, three-center bonds result from overlap between the sp³-like boron orbitals and the hydrogen 1s orbital,[3] and the dimer of trimethylaluminum,[4] whose bridging bonds involve five-coordinate saturated carbons. In all cases bridging occurs toward fulfillment of the octet rule, structures with strained, electron-deficient bonds being preferred to those with open-sextet atoms.

Further and even more pertinent cases of two-electron, three-center bonding involving carbon can be found in carboranes.[3] The very stable 1,2-carboranes, such as the 1,2-, 1,7- and 1,12-dicarba-*closo*-dodecaboranes, for example, contain not only five-coordinated but six-coordinated carbon atoms.

Thus two-electron, two-center bonding is no longer the only recognized bonding, even for carbon compounds. Besides the quoted examples of stable, neutral carbon compounds containing five- or six-coordinated carbon atoms, carbocations exemplify the ability of carbon atoms to participate in two-electron, three-center bonding. I have devoted much time and effort, including the writing of a comprehensive review,[4] to emphasize this point, to summarize the extensive experimental evidence, and to point out the wide chemical implications. The latter include the general concept of σ-bond reactivity in electrophilic reactions, based on the understanding gained of carbocation intermediates.

Concerning carbocations, besides the familiar trivalent carbenium ions, containing an sp²-hybridized, electron-deficient carbenium center, of which CH_3^+ is the parent, there is a well-recognized and growing class of ions the structures of which cannot be adequately represented in valence bond terms by conventional two-electron, two-center bonds alone, but also necessitate two-electron, three- (or multi-) center bonds. Of these, CH_5^+ is the parent,[5] a five-coordinated carbonium ion. Carbon can also be six-coordinated, as in dications of the $(CCH_3)_6^{2+}$ type.[6] These are generally referred to as "nonclassical" ions, as contrasted to the trivalent "classical" ions. Sometimes nonclassical ions are alternatively referred to as σ-bridged ions, but this definition is less clear and less suitable.

My co-workers and I have explored the solution

(1) Stable Carbocations, 189. This Account is based on a lecture given at the EUCHEM Conference in Montpellier-LaGrande Motte, May 31, 1974, and related public discussion of the norbornyl cation problem with Professor H. C. Brown and Dr. G. M. Kramer.

(2) G. N. Lewis, *J. Am. Chem. Soc.*, 38, 762 (1916); "Valence and Structure of Atoms and Molecules", Chemical Catalog Co., New York, 1923.

(3) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3d ed, Wiley, New York, 1972, and references given therein.

(4) G. A. Olah, "Carbocations and Electrophilic Reactions", Verlag Chemie, Weinheim; Wiley-Interscience, New York, 1974.

(5) G. A. Olah, G. Klopman, and R. H. Schlosberg, *J. Am. Chem. Soc.*, 91, 3261 (1969).

(6) H. Hogeveen and P. W. Kwant, *Acc. Chem. Res.*, 8, 413 (1975).

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chemistry of the methonium ion, CH_5^+, and related alkonium ions[5] and have demonstrated them to represent the key to reactions of alkanes with electrophiles.[4] The isoelectronic boron analog of CH_5^+, namely BH_5, was also obtained and studied.[7] Evidence was also found in solution chemistry for H_3^+, for which J. J. Thompson in 1911 first discussed two-electron, three-center bonding.[8] Ingold later called it the parent synartetic ion,[9] and we now define it as the parent nonclassical ion. In deuterated superacid solution (e.g., $DF-SbF_5$) molecular hydrogen undergoes rapid exchange, indicating the intermediacy of H_3^+ in solution.[10] H_3^+ and other nonclassical ions (including CH_5^+) are also known in the gas phase. The characteristic, three-center bonded structures of some typical nonclassical ions are shown below.

H_3^+ methonium ion   norbornyl ion

corner   edge
protonated cyclopropane
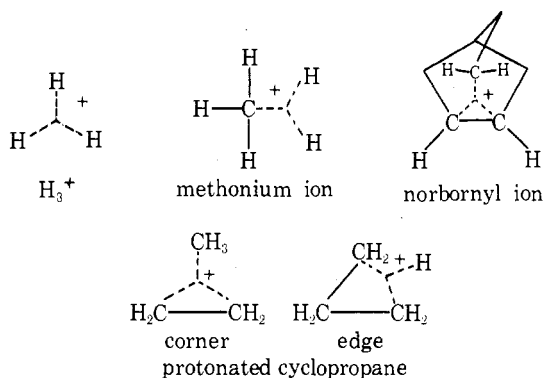
It should be recognized, however, that classical and nonclassical carbocations represent only the extremes of a continuum. It is frequently difficult to assign exactly the intermediate cases. Definition of limiting cases, i.e., carbenium and carbonium ions, should only be considered in this context.[5] It is also useful to recall that *hyperconjugation* is best defined as the overlap interaction of an appropriately oriented σ-bond orbital with a p orbital to provide electron delocalization involving the σ bond, with little or no accompanying nuclear reorganization. Nuclear reorganization accompanying σ-bond delocalization can range from little or no rearrangement (*hyperconjugation*), to partial reorganization of nuclei (σ *participation*), to more extensive or complete *bridging*.

The Norbornyl Cation Problem

The remarkable facility of skeletal rearrangements in the bicyclo[2.2.1]heptyl (norbornyl) system attracted the early interest of chemists. Wagner realized first in 1899 the general nature of the borneol-camphene type rearrangements and with great foresight related them to the rearrangement which takes place during the dehydration of pinacol to tetramethylethylene.[11] Semmler found tricyclanes in the products of Wagner rearrangements of terpenes.[12a] Ruzicka in 1918 suggested a tricyclane-type mechanism

for the Wagner rearrangement, without realizing the ionic nature of the process.[12b] Meerwein in 1922 reconsidered the mechanism and made the farsighted suggestion that the reaction proceeds through an ionic intermediate, a substituted norbornyl cation.[13] This mechanistic path is now known as the Wagner–Meerwein rearrangement.

The structure of the norbornyl cation became controversial, in the "classical–nonclassical ion" controversy,[14,15] following Wilson's original suggestion in 1939 of a mesomeric, σ-delocalized, carbonium ion intermediate in the camphene hydrochloride–isobornyl chloride rearrangement.[16]

In 1949 and 1952 Winstein and Trifan reported[17] a solvolytic study of the *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 substitution products of completely exo configuration and with nearly complete racemization; 7–8% preservation of optical activity was observed in acetolysis at 75°. 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.)[15] Furthermore, the *exo*-brosylate was markedly more reactive in acetolysis than the *endo*-, by a factor of 350 titrimetrically or 350 × 4.6 = 1600 polarimetrically, at 25°.

Winstein noted that the racemization results alone "could be due to a 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-p*-bromobenzenesulfonate". Winstein concluded that "it is attractive to account for all of these results by way of the bridged formulation for the norbornyl cation".

Winstein's formulation of the norbornyl cation as a σ-bridged species stimulated other workers in the solvolysis field to interpret results with a variety of systems in terms of σ-delocalized carbonium ions, in some cases with little independent evidence.

In 1962 H. C. Brown initiated[18] his well-known dissent against the σ-bridged 2-norbornyl cation and, for that matter, other bridged carbocations. He has maintained his position virtually unchanged over the years and continues to present his views forcefully.[15] In arguing against carbon σ bridging in solution he

(7) G. A. Olah, P. W. Westerman, Y. K. Mo, and G. Klopman, *J. Am. Chem. Soc.*, **94**, 7859 (1972).

(8) J. J. Thompson, *Phil. Mag.*, **21**, 225 (1911); **24**, 209 (1912).

(9) C. K. Ingold, "Structure and Mechanism in Organic Chemistry", 2d ed, Cornell University Press, Ithaca, NY, 1969, pp 766–787.

(10) G. A. Olah, J. Shen, and R. H. Schlosberg, *J. Am. Chem. Soc.*, **95**, 4957 (1973).

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

(12) (a) F. W. Semmler, *Ber.*, **35**, 1018 (1902); (b) L. Ruzicka, *Helv. Chim. Acta*, **1**, 110 (1918).

(13) H. Meerwein and K. Van Emster, *Chem. Ber.*, **55**, 2500 (1922).

(14) (a) M. C. Brown, *Acc. Chem. Res.*, **6**, 377 (1973); (b) *Chem. Brit.*, 199 (1966); (c) *Chem. Eng. News*, **45**, 86 (Feb 13, 1967); (d) "Boranes in Organic Chemistry", Cornell University Press, Ithaca, N.Y., 1972, Chapter 9, p 14; (e) H. C. Brown, K. J. Morgan, and F. J. Chlouper, *J. Am. Chem. Soc.*, **87**, 2141 (1965).

(15) (a) S. Winstein, *Q. Rev., Chem. Soc.*, **23**, 1411 (1969); (b) P. D. Bartlett, "Nonclassical Ions", W. A. Benjamin, New York, 1965.

(16) T. P. Nevell, E. de Salas, and C. L. Wilson, *J. Chem. Soc.*, 1192 (1939).

(17) S. Winstein and D. S. Trifan, *J. Am. Chem. Soc.*, **71**, 2953 (1969); **74**, 1147, 1159 (1952).

(18) H. C. Brown, *Chem. Soc., Spec. Publ.*, No. **16**, 140 (1962).

took the position, despite his pioneering work in boranes, that, if carbon were to participate in bridging, novel bonding characteristics would need to be attributed to it. For accurate representation of his position, I quote a few of his statements.

In 1967 Brown stated,[14c] "The second subclass consists of ions such as the bicyclobutonium and the norbornyl cation in its σ-bridged form, which do not possess sufficient electrons to provide a pair for all of the bonds required by the proposed structures. *A new bonding concept not yet established in carbon structures is required*" (italics mine).

Two years earlier he had said,[14e] "On the other hand, the norbornyl cation does not possess sufficient electrons to provide a pair for all of the bonds required by the proposed structures. *One must propose a new bonding concept, not yet established in carbon structures*" (again my emphasis).

In 1972 Brown again wrote:[14d] "The second subclass consists of ions, such as the *norbornyl cation in its σ-bridged form, that lack sufficient electrons to provide a pair for all bonds required by the proposed structure*".

In our public discussion in Montpellier in May 1974, Brown reiterated his position and extended it to criticism of my "assumed solution chemistry of CH_5^+, an unlikely species". The Brown "crusade", in numerous lectures, papers, private letters, and his recent "Norbornyl Newsletter" mailed to about 80 people, gave further expression of his position. I feel that these quotations do not misrepresent his position; if anything, they understate it.

In my judgment an unequivocal answer to the norbornyl ion controversy has been obtained in recent years in favor of the σ-delocalized structure for the 2-norbornyl cation, both as a solvolytic intermediate and under appropriate conditions as a long-lived stable species. This Account concentrates on structural study of the long-lived ion itself, but is preceded by brief remarks as to the present status of other studies, to put the topic into perspective. A more comprehensive review will be published.[19]

Present Status of Solvolytic Studies

Brown concluded that in solvolysis both exo and endo norbornyl substrates (e.g., brosylates) undergo anchimerically unassisted ionization, and that the singular rate and product characteristics of the system are attributable to steric effects, particularly hindrance to ionization of the endo isomers. From extensive solvolytic studies, he has concluded that high exo/endo rate and product ratios *do not necessitate σ* participation as the only possible explanation. However, *none of his studies ever showed that σ participation is not involved*.

In Brown's and other laboratories, a wide variety of substituted secondary *exo-* and *endo-*2-norbornyl substrates have been prepared for solvolytic rate comparisons with the unsubstituted compounds.[20]

Two approaches can be taken to evaluate the contribution from σ bridging to the sizable exo/endo rate

ratios for the parent system: (1) use of solvent systems with decreased nucleophilicity which might enhance delocalization in a bridged exo transition state and increase the exo/endo ratio; (2) substitution which would be expected to inhibit bridging in ionization of the exo epimer, and thus diminish the exo/endo ratio.

The Grunwald–Winstein m value[21] is a measure of the sensitivity of a substrate in solvolysis to the ionizing power of the solvent, according to

$$\log (k/k_0) = mY$$

in which k and k_0 are solvolysis rates for a compound in any solvent and in a standard solvent, respectively, and Y is a solvent parameter. For 2-adamantyl tosylate (p-toluenesulfonate), a model for "limiting" solvolysis without anchimeric or solvent assistance, m is 0.91, the highest value recorded for a secondary aliphatic tosylate.[22] In contrast, isopropyl tosylate has $m = 0.44$, a low value indicating much nucleophilic solvent assistance. *endo*-2-Norbornyl tosylate ($m = 0.69$) displays an intermediate value, consistent with weaker solvent assistance. The m value for 2-*exo*-norbornyl tosylate is 0.75.[22]

The fortuitous similarity of m values for the epimeric 2-norbornyl tosylates should make the exo/endo ratio somewhat insensitive to changes in solvent. The ratio increases, however, from 280 in acetic acid, a solvent of poor ionizing power and moderate nucleophilicity, to 1120 in trifluoroacetic acid[23] and 5200 in $CF_3COOH-SO_2ClF$, a low nucleophilicity medium of good ionizing power.[24]

Concerning substituent effects in 2-norbornyl systems, one must realize that substituent effects based on substituted π-aromatic systems, e.g., on solvolysis rates of cumyl chlorides, cannot be directly extrapolated to σ-donor hydrocarbons, such as norbornane. Substituent effects in pure σ-bonded systems cannot be simply derived from those for π systems. In σ systems, besides hyperconjugative and inductive effects of substituents, steric inhibition of σ participation is also very significant, for instance, in cases of fused-on rings or substituents at C.1 and C.6. These considerations were frequently overlooked by Brown, who was generally looking for substituent effects similar to those found in cumyl systems (σ^+). For that reason many of his conclusions in recent years concerning substitutent effects in norbornyl systems are questionable.[14a]

High exo/endo rates do not per se prove σ bridging in the 2-norbornyl system, but they are entirely consistent with it, and no experimental evidence to the contrary was ever provided. I find the solvent and substituent effects (as well kinetic isotope effects) studied entirely consistent with the concept of σ participation in the transition states of solvolysis of the exo derivatives, as originally suggested by Winstein. Detailed discussion will be presented elsewhere.[19]

(19) J. E. Nordlander, G. A. Olah, and P. v. R. Schleyer, *Adv. Phys. Org. Chem.*, in preparation.

(20) For a comprehensive review see G. D. Sargent in "Carbonium Ions", G. A. Olah and P. v. R. Schleyer, Ed., Vol. III, Wiley-Interscience, New York, 1972, pp 1099–1200.
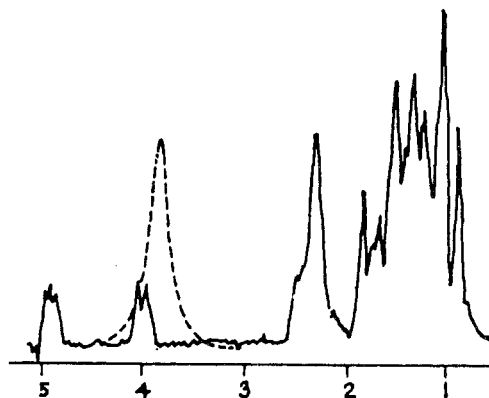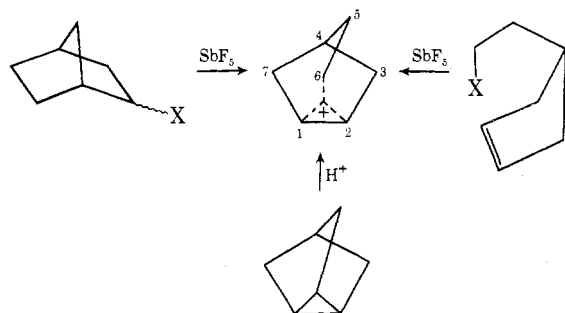
(21) E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, **70**, 846 (1948), and subsequent publications.

(22) P. v. R. Schleyer, *Acc. Chem. Res.*, manuscript in preparation (personal communication).

(23) J. E. Nordlander, R. R. Gutzmacker, W. J. Kelly, and S. P. Jindal, *J. Am. Chem. Soc.*, **96**, 181 (1974).

(24) G. Liang, Ph.D. Thesis, Case Western Reserve University, Cleveland, Ohio, 1973.

Figure 1. ^{1}H NMR spectrum (60 MHz) of the norbornyl cation at 35 °C (dotted line) and the precursor 2-*exo*-fluoronorborane (full line).

Figure 2. ^{1}H NMR spectrum (100 MHz) of the norbornyl cation in SbF_5–SO_2 solution at −80 °C. The insert shows the effect of irradiating the low-field septuplet on the one-proton peak at δ 2.82. A is the spectrum without irradiation and B is with irradiation.

Kinetic and stereochemical evidence predominated in early study of carbocations, but in recent years it became possible to prepare them as stable, long-lived species, and thus to study their structure and chemistry directly by physical and chemical methods.[5,25]

The Structure of the Long-Lived Norbornyl Cation. NMR Spectroscopic Studies.

The methods that we worked out in the early 1960's to generate and observe stable carbocations in low nucleophilicity solutions[5,26] 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.

The method of choice for preparation of the norbornyl cation (giving the best resolved NMR spectra, free of dinorbornylhalonium ion equilibration), is from *exo*-2-fluoronorbornane in SbF_5–SO_2 (or SO_2ClF) solution. With Saunders and Schleyer in a joint effort we first investigated the 2-norbornyl cation in 1964[27] and observed its ^{1}H NMR spectrum, having prepared the ion from *exo*-2-fluoronorborane in SbF_5–SO_2. At room temperature the ^{1}H NMR spectrum consisted of a single broad band at δ 3.75 (Figure 1) due to scrambling of all hydrogen atoms. The contrast between this single band and the complex spectrum of the progenitor, 2-*exo*-fluoronorborane, is striking. The equilibration of the hydrogen atoms is caused by fast 3,2- and 6,1,2-hydrogen shifts and by Wagner–Meerwein rearrangement.

Similarly at room temperature the ^{13}C spectrum of the ion shows a single broad absorption line centered at $\delta_{13C}134$[28] (from external Me_4Si to which all shifts are related).[29] When the temperature was lowered to −70 °C the ^{1}H NMR spectrum of the 2-norbornyl cation resolved into three peaks with relative areas 4:1:6 (Figure 2). The spectrum did not change when the temperature was further lowered to −120 °C.[28] Jensen and Beck obtained in $GaBr_3$–SO_2 similar spectra of good resolution.[30]

The spectrum was interpreted as evidence that the 3,2-hydrogen shift was frozen out, but the 6,1,2-hydrogen shift and the Wagner–Meerwein rearrangement are still fast even at the low temperature used (−120 °C). The rate of the slow 3,2-hydrogen shift was established from temperature-dependence studies, by comparing experimental spectra with those calculated for different rates. The activation energy of this shift is 10.8 ± 0.6 kcal/mol, with $A = 10^{12.3}$ sec[−1].[27]

When the ion is prepared at −78 °C in FSO_3D–SbF_5–SO_2 solution from nortricyclane, only one deuterium atom is incorporated, and in the ^{1}H NMR spectrum the relative area of the low-field peak is reduced from 4 to 3. No further inter- or intramolecular scrambling of the deuterium is observed during 1 h at −78°.

Preparation of the norbornyl cation by protonating nortricyclane, or from reaction of norbornyl fluoride or alcohol with SbF_5, precludes equilibration involving dinorbornylhalonium ions, but that complication can occur under certain conditions between norbornyl chloride or bromide and the norbornyl cation. We have studied equilibration of the norbornyl cation with excess norbornyl halides through the dinorbornylhalonium ions, and described its characteristics.

Subsequently we succeeded in "freezing out", on the NMR time scale, the fast 6,2-hydrogen shift.[28] Using a mixed SbF_5–SO_2ClF–SO_2F_2 solvent system,

(25) G. A. Olah and P. v. R. Schleyer, Ed., "Carbonium Ions", Vol. I–IV, Wiley-Interscience, New York, 1968–1973; Vol. V in preparation.

(26) G. A. Olah, *Science*, **168**, 1298 (1970); *Chem. Eng. News*, **45**, 36 (March 27, 1967).

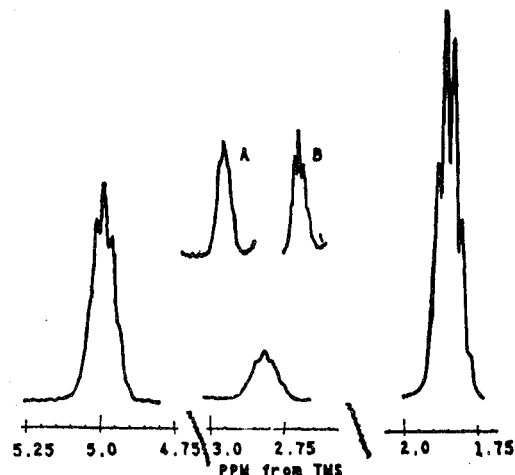(27) M. Saunders, P. v. R. Schleyer, and G. A. Olah, *J. Am. Chem. Soc.*, **86**, 5680 (1964).

(28) G. A. Olah, A. M. White, J. R. DeMember, A. Commeyras, and C. Y. Lin, *J. Am. Chem. Soc.*, **92**, 4627 (1970); G. A. Olah and A. M. White, *ibid.*, **91**, 3954, 3956 (1969); D. G. Farnum and G. Mehta, *ibid.*, **91**, 3256 (1969).

(29) In many of our earlier publications CS_2 was used as reference. The conversion, as determined and used in our laboratory, from CS_2 to Me_4Si is 193.8 ppm.
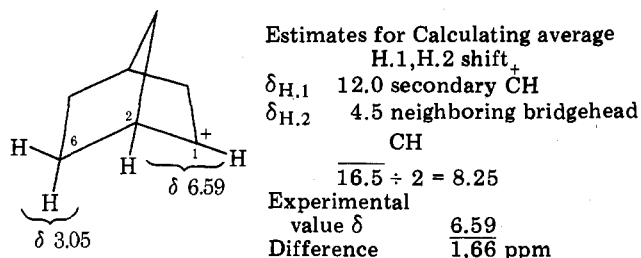
(30) F. R. Jensen and B. H. Beck, *Tetrahedron Lett.*, 4287 (1966).

Table I
^{13}C NMR Parameters of 2-Norbornyl Cation[a]

	Temp, °C	C.1 C.2	C.3	C.4	C.5	C.6	C.7
	−70	92	31.3	37.7	31.3	92	31.3
		(q, 53.3)[b]	(t, 140.2)	(d, 153.0)	(t, 140.2)	(q, 53.3)	(t, 140.2)
	−150	125.	48	33.4	28	22.4	48
		(d, 184.5)	(t, 153.5)	(d, 158.6)	(t, 160.2)	(t, 145.8)	(t, 153.5)

a ^{13}C NMR shifts are relative to capillary Me$_4$Si. b Multiplicities and coupling constants (J_{CH} in Hz) are given in parentheses: d = doublet, q = quintet, t = triplet.

Scheme I
Comparison of Calculated and Observed Average δ_H Shifts for Assumed Rapidly Equilibrating Classical Norbornyl Cation

Estimates for Calculating average H.1,H.2 shift$_+$

$\delta_{H.1}$ 12.0 secondary $\overset{+}{C}H$
$\delta_{H.2}$ 4.5 neighboring bridgehead CH

$\overline{16.5} \div 2 = 8.25$

Experimental value δ 6.59
Difference $\overline{1.66}$ ppm

we could observe the 100-MHz spectrum at temperatures down to −156 °C. At −120 °C, the spectrum was identical to that described at −78 °C, but between −128 and −150 °C significant changes in the spectrum occurred. The low-field peak due to the four equilibrating "protonated cyclopropane" ring protons broadened and then separated into two resonances, each of relative area two, at δ 3.05 and 6.59. The high-field resonance due to the six methylene protons broadened, developing a shoulder at δ 1.70. The peak at δ 2.82 due to the bridgehead proton remained unchanged (Figure 3). The temperature dependence of the low field resonance was used to calculate rate constants; the activation energy was 5.9 ± 0.2 kcal/mol^{-1} and the pre-exponential factor $10^{12.7}$ sec^{-1}.

These observations could be consistent with either of two interpretations: (a) that the ion is classical and that the temperature dependence corresponds to the "freezing out" of the 6,1,2-hydrogen shift, the Wagner-Meerwein rearrangement still being fast at −156°, or (b) that the ion is nonclassical, all rearrangements have been "frozen out", the structure of the ion being that of the methylene-bridged pentacoordinated ion.

If the first explanation were correct, the experimentally observed 6.59 δ shift must be that of the average of the H.1 and H.2 proton shifts. The average shift, as repeatedly shown in other systems, can be calculated from data for appropriate static model ions. Taking for the secondary $^+$CH shift a value of δ 12 (from the isopropyl and cyclopentyl ion shifts) and for the neighboring bridgehead CH a value of δ 4.5 (based on that in the 2-methyl and 2-phenylnorbornyl cations with the usual corrections for substituent effects), one obtains the values shown in Scheme I. ^{1}H NMR data on their own seem to eliminate a rapidly equilibrating classical ion, as the difference between the calculated and experimental shifts is unacceptably large. The shifts, however, fit very well the bridged structure (δ 3.05 for the pentacoordinated CH$_2$ carrying very little charge and 6.59
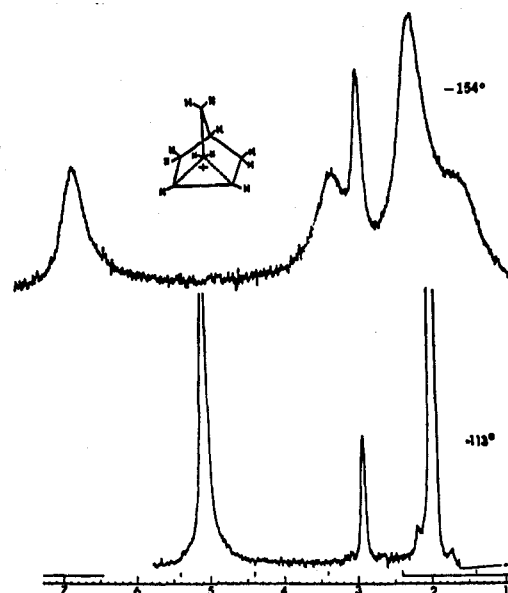

Figure 3. ^{1}H NMR spectra (100 MHz) of the "norbornyl cation" in SbF$_5$–SO$_2$ClF–SO$_2$F$_2$ solution at temperatures between −113 and −154 °C.

for the nortricyclane type CH, s delocalizing charge).

Carbon-13 spectroscopy provides even more convincing evidence for the structure of the norbornyl cation. Using first (with White) the INDOR method[28] and later (with Liang) the fast Fourier transformation method,[31] we obtained the complete ^{13}C NMR spectrum, with all the coupling constants and multiplicities both at −70 °C under conditions of rapid equilibration of the norbornyl cation, and at −150 °C as the static "frozen out" ion. The results are summarized in Table I.

The proton-decoupled FT ^{13}C NMR spectrum of the ion at −70 °C is shown in Figure 4A. It consists of three carbon resonances at δ_{13C} 92, 37.7, and 31.3, for equilibrating C.1, C.2, C.6, bridgehead C.4, and equivalent methylene carbons (C.3, C.5, and C.7), respectively. (Assignments were made by the off-resonance ^{13}C NMR spectrum, Figure 4B.) The most deshielded carbon resonance (δ_{13C} 92) shows a quintet indicating that each of the cyclopropane-like ring carbons couples with four equivalent protons, while the bridgehead carbon resonance and the methylene carbon resonance are a doublet and triplet, as they are coupled with one and two protons, respectively. At lower temperature (−150 °C) this resonance is separated into two components at δ_{13C} 125.3 (for C.1 and C.2) and 22.4 (for C.6). The bridgehead carbon (C.4) resonance is slightly moved to higher field at δ_{13C} 33.4. The methylene resonance is also separated

(31) G. A. Olah, G. Liang, G. D. Mateescu, and J. L. Riemenschneider, *J. Am. Chem. Soc.*, **95**, 8698 (1973).
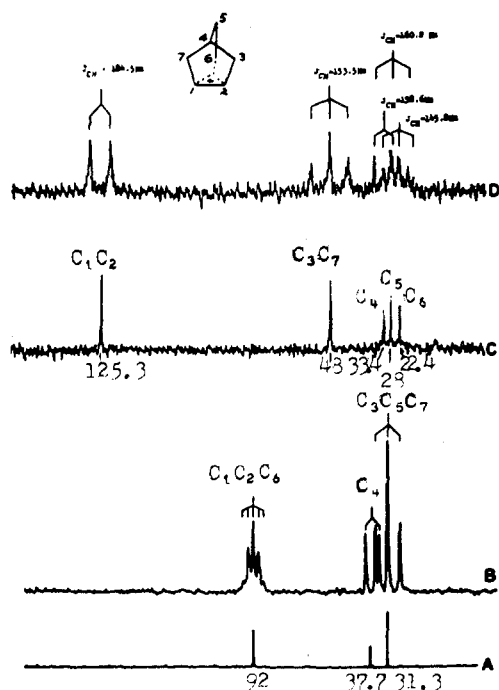(32) G. Kramer, *Ad. Phys. Org. Chem.*, in press as quoted by H. C. Brown in ref 36a.

Figure 4. Fourier transform ^{13}C NMR spectra of the 2-norbornyl cation: (A) at −70 °C, proton decoupled; (B) at −70 °C off-resonance; (C) at −150 °C, proton decoupled; (D) at −150 °C, proton coupled.

into two components at δ_{13C} 48 (for C.3 and C.7) and 28 (for C.5) (see Figure 4C). The C–H coupling constants (J_{CH}, in Hz) given in Table I were obtained directly from the proton-coupled ^{13}C NMR spectrum (Figure 4D). The pentacoordinated bridging methylene carbon atom is not deshielded (δ_{13C} 22.4), whereas the tetracoordinated carbons to which bridging takes place (and which consequently carry more positive charge) show more deshielding (δ_{13C} 125.3), but are still much more shielded than expected for an equilibrating classical ion, as shown in Scheme II.

In the proton-coupled ^{12}C NMR spectrum of the norbornyl ion (Figure 4D) no coupling was observed between the methylene hydrogens at the pentacoordinated carbon (C.6) and the cyclopropane-like carbons (C.1 and C.2). This is expected from the nonclassical structure since the two-electron, three-center bonds are longer and weaker than normal C_{sp^3}–C_{sp^2} bonds.

The ^{13}C NMR spectra show that the norbornyl cation is a nonclassical carbonium ion with a pentacoordinated bridging carbon atom. The magnitude of $J_{C.6-H} = 145.8$ Hz in the 2-norbornyl cation is smaller than those for $J_{C.1-H}$ in the 7-norbornenyl and 7-norbornadienyl ions (218.9 and 216.4 Mz, respectively). This is expected as the strained C.7 carbons in the latter have higher s character in the C–H bonds than has C.6 in the former (for an sp^3 carbon J_{CH} is about 125 Hz, corresponding to 25% s character). An increase of s character associated with the C–H bond is expected to increase the C–H coupling constant. Both ^{1}H and ^{13}C NMR spectra indicate that the bridging pentacoordinated methylene carbon C.6 in the norbornyl ion is tetrahedral in nature and carries little positive charge. The methine carbon atoms (C.1 and C.2) show resonances not much different (δ 125.3) than those of C.2 and C.3 in the norbornenyl
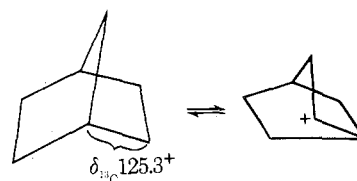
and norbornadienyl cations (δ 125.9 and 114.9, respectively).

If the norbornyl cation at −150 °C still underwent fast Wagner–Meerwein rearrangement (with all the hydride shifts frozen out), the average C.1–C.2 shifts would be the observed δ 125.3. To estimate the average shift expected for C.1 or C.2 according to this model, we use as δ_{13C} for the carbenium center a value of 300, estimated from comparison of ^{13}C NMR data of static 1-substituted (CH$_3$, Cl, F) cyclopentyl cations with those of the average observable shift of the rapidly equilibrating parent secondary cyclopentyl cation, and for the neighboring bridgehead CH a value of 70, from values of the 2-methyl and 2-phenylnorbornyl cations with usual corrections for substituent effects. The obtained values are shown in Scheme II. The difference between observed and calculated values is so large (60 ppm) as to exclude the possibility of an equilibrating pair of classical ions.

That the method of estimating average chemical shifts in rapidly equilibrating carbocations is satisfactory can be demonstrated in the case of the cyclopentyl cation, which was suggested as the closest model compound for the classical norbornyl cation. (The experimental shifts for the individual carbons in the assumed static ion were taken from the corresponding shifts of the static 1-methyl-1-cyclopentyl cation and corrected for the usual methyl substituent effect)

$$\delta_{13C}(av)_{calcd} = (300 + 2 \times 65 + 2 \times 28)/5 = 97$$
$$\delta_{13C}(av)_{obsd} = 99$$

A similar calculation can also be carried out concerning the J_{CH} coupling constant (Scheme III) using the same model compounds.

Again the difference from the experimental value is too great to be acceptable. Thus NMR studies of the norbornyl cation give conclusive evidence for the nonclassical, bridged structure of the ion, as contrasted with a pair of rapidly equilibrating classical ions. However, NMR is a relatively slow physical method. To obtain further structural evidence with fast physical methods, which could not be affected by any possible equilibration process, we also studied the ion through Raman and electron spectroscopy, as described below.

2-Substituted Norbornyl Cations. Because of

Scheme II
Assumed W–M Equilibration at −150°C in Classical Ion (All Hydrogen Shifts Frozen Out)

$\delta_{13C}.2,C.1$

Average $\delta_{13C}.1,C.2$ 125.3 (obsd)

Estimates for calculating average shift

$\delta_{13C}.2$ 300 secondary carbenium center
$\delta_{13C}.1$ $\underline{\ 70}$ neighboring bridgehead CH
$370 \div 2 = 185$

$\Delta\delta_{13C}.1,2$ obsd − calcd = 60.3

Table II
^{13}C NMR Shifts of Substituted 2-Norbornyl Cations

Ion	C.1	C.2	C.3	C.4	C.5	C.6	C.7	CH.3
2-CH$_3$[a]	80.8	271.1	55.6	42.8	23.6	35.8	40.2	28.3
2-C$_6$H$_5$[b]	59.8	257.3	51.0	40.1	34.6	41.8	25.8	

[a] The assignment of some shifts is reversed from that originally reported based on better resolution spectra in the overlapping region and deuterium labeling. The significant C.1 and C.2 shifts are, however, unchanged. [b] C$_{ipso}$ 133.9; C$_{ortho}$ 142.0; C$_{meta}$ 132.8; C$_{para}$ 152.7.

Scheme III
J_{CH} in Assumed W—M Equilibrating Classical Ion
(All Hydrogen Shifts Frozen Out)
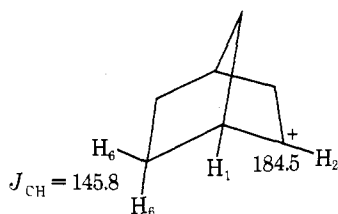
$J_{(CH).2,1\ obsd}$ 184.5 Hz
Estimates for calculating average
coupling from above-mentioned
model compounds

$J_{CH.1} = 160$ Hz
$J_{CH.2} = \dfrac{170\ \text{Hz}}{330 \div 2 = 165\ \text{Hz}}$
ΔJ_{CH} (obsd — calcd) = 19.5 Hz

space limitations, I will discuss only studies on the 2-methyl- and 2-phenyl-2-norbornyl cations, both of which have been investigated by proton[28] and carbon-13[33a] NMR spectroscopy. The 2-methyl-2-norbornyl cation can be characterized as a partially σ-bond (i.e., C.1–C.6) delocalized carbenium ion, while the 2-phenyl-2-norbornyl cation exhibits the properties of a classical carbenium ion with no significant σ delocalization (of course the positive charge is
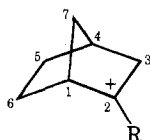
R = CH$_3$ and C$_6$H$_5$

extensively delocalized into the phenyl π system). These conclusions are particularly supported by comparing C.1 and C.2 carbon resonances in these two ions; the ^{13}C NMR shifts are shown in Table II along with their assignments. The difference in C.2 carbon resonances in the two ions is $\Delta\delta_{13C} = 271.1 - 257.3 = 13.8$, while the same difference between the related model cyclopentyl cations is 57.8. Also the carbon shift at the carbocationic center in the 2-methyl-2-

R	δ_{13C^+}
CH$_3$	335.8
C$_6$H$_5$	278.0
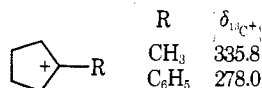
norbornyl cation is about 64 ppm less deshielded than that in the 1-methyl-1-cyclopentyl cation, while the carbon shifts are comparable in the corresponding phenyl substituted ions. These model ions are evidently classical carbenium ions without significant σ-bond delocalization. The discrepancy observed is

explained in terms of partial σ-bond delocalization through the C.1–C.6 bond toward the empty 2p orbital at C.2 in the 2-methyl-2-norbornyl cation. Such delocalization is, however, much more profound in the parent, unsubstituted 2-norbornyl cation.

Recently, Farnum and Wolf[33b] studied the relationship between NMR shifts and substituent effect in a series of substituted 2-aryl-2-norbornyl cations. With substituents increasingly more electron withdrawing, the "onset" of C.1–C.6 σ-bond delocalization or nonclassical stabilization was observed, due to increasing electron demand compared to the parent 2-phenyl-2-norbornyl cation, by a gradual and clear change of the NMR patterns.

Raman Spectroscopic Study

Raman spectroscopy is truly a fast physical method; obviously vibrational transitions are faster than hydrogen or alkyl shifts. With it the question of possible rapid equilibration vs. bridging becomes unimportant. Raman spectroscopic study of the stable norbornyl cation at −70 °C was carried out with use of a He–Ne laser.[28,34] In the C–C stretching frequency region there is only one strong line at 972 cm^{-1} ($\rho = 0.35$). The C–H stretching frequency region shows five lines, one of which is at 31.10 cm^{-1}.

The complexity and size of the norbornyl cation did not permit analysis of the Raman spectrum by normal coordinate analysis. The approach adopted was therefore to compare the spectrum with those of model compounds whose structure would be expected to show skeletal similarity to those of the nonclassical and classical ions. The models chosen were tricyclo[2.2.1.0]heptane[2,6] (nortricyclane) and bicyclo[2.2.1]heptane and their derivatives, respectively. The uncharged norbornyl derivatives have Raman spectra which differ markedly from that of the norbornyl cation, suggesting that the ion does not have a bicyclo[2.2.1]heptyl-type carbon skeleton. On the other hand, similarities between Raman spectra of nortricyclane, 3-bromonortricyclane, and the norbornyl cation indicate that the norbornyl cation is structurally related to a tricyclo[2.2.1.0]heptane[2,6] (nortricyclane) skeleton and, therefore, is best described as a protonated nortricyclane. This does not, however, imply the presence of an equilateral cyclopropane ring with identical C.1–C.2, C.1–C.6, and C.2–C.6 bond lengths. As a matter of fact the C.1–C.6 and C.2–C.6 bonds involved in three-center bond formation should be longer than the C.1–C.2 bond. The sensitivity of the Raman skeletal modes and hence the observed Raman spectral patterns to changes in the C–C bond lengths is not exactly known.

(33) (a) G. A. Olah and G. Liang, *J. Am. Chem. Soc.*, **96**, 195 (1974); (b) D. G. Farnum and A. D. Wolf, *ibid.*, **96**, 5166 (1974).

(34) G. A. Olah, A. Commeyras, and C. Y. Lin, *J. Am. Chem. Soc.*, **90**, 3882 (1968).

Claimed Equilibration with Rates as High as 10^{12} s^{-1}

Recently, on the basis of a relaxation theorem of Fong,[35] Brown seemingly has accepted the view that equilibration of the classical norbornyl ion can take place with rates similar to or exceeding those of vibrational transitions, i.e., ca. 10^{12} s^{-1}. Such a process would give the norbornyl ion a plane of symmetry, thus making it for all practical purposes symmetrically bridged, leaving little further reason for argument. Despite this Brown considers that such an ion still would be a classical equilibrating ion. He stated[36b] "The nonclassical ion does possess a plane of symmetry. However, a rapidly equilibrating pair of unsymmetrical classical cations can behave as though it possesses a plane of symmetry provided the rate of equilibration is rapid compared with the rate of reaction of the intermediate with solvent. Originally the solvolysis of such derivatives was interpreted as going through the formation of the free ions. It was considered inconceivable that the rate of equilibration could exceed the rate of reaction of secondary cation with solvent. There have been ... significant developments which require a reconsideration of this position ... Fong has applied relaxation theory to such equilibrating systems and has concluded that rates of equilibration as high as 10^{12} sec^{-1} are entirely feasible for 2-norbornyl and related equilibrating cations".

I feel that the foregoing suggestions lack chemical, as well as physical reality. Moreover, they are excluded by electron spectroscopic (ESCA) studies, for which the time scale of even such an unrealistic "equilibration process" can certainly be of no consequence.

The question of tunneling raised by Fong,[35] to explain the assumed uniquely fast equilibration of norbornyl cation, was previously considered in carbocation chemistry in another context, relating to CH-bond tunneling, by Mackor and MacLean in connection with 1,2 shifts in benzenium ions.[37] From H/D isotope effects they concluded that tunneling does not occur, and they explained that appreciable displacement of carbon atoms would necessarily be associated with the hydride shift.

Fong's assumption is even less plausible in the case of the norbornyl cation, for two reasons. First, Fong assumed a barrier of ~1 kcal for the fast equilibration in the norbornyl cation. However, the experimental barrier is 5.8 kcal, too high for any tunneling process. Would the experimentally observed ion at −150° still undergo rapid equilibration through a very low barrier (which is not in accordance with the reviewed spectroscopic findings), such a process could take place only between substantially σ-delocalized but somewhat unsymmetrical nonclassical ions, and not a classical ion pair, for which such a barrier must be significantly higher. For all practical purposes such a system would show symmetrical nature and the double energy minimum would be un-

distinguishible from a single minimum. Secondly, in order to account for the slow 2,3-hydrogen shift in comparison with the fast 6,1,2-hydrogen shift plus Wagner–Meerwein rearrangement, he is forced to suggest what amounts to selective carbon–carbon over carbon–hydrogen bond tunneling. As C–C bond tunneling itself is hypothetical and has no analogy, there can be no justification for this suggestion.

Core Electron Spectroscopy (ESCA) Studies

Since in electron spectroscopy the time scale of the ionization processes is on 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 equalling or exceeding those of vibrational transitions. Thus, electron spectroscopy can give an unequivocal answer to the long-debated question of the "classical" or "nonclassical" nature of the norbornyl cation, regardless of the rate of any possible equilibration processes.

Further, the gross atomic charge can be correlated with the electron binding energy (E_b) chemical shift in ESCA spectroscopy (i.e., of C 1s shifts in the case of carbocations). Electron deficiencies of different degrees in different carbocations are thus expected to give different carbon 1s binding energy shifts and E_b's. With Mateescu we have, indeed, found[38] that the trivalent trimethylcarbenium ion (classical *tert*-butyl cation), either as the isolated hexafluoroantimonate salt or in frozen superacid solutions, exhibits an ESCA spectrum showing two well-separated lines having approximately a 1:3 area ratio. The carbon 1s line of the highly electron-deficient carbenium ion center appears at 3.9 eV higher binding energy than the methyl carbon 1s line. The cyclopentyl and methylcyclopentyl cations also exhibit two distinct carbon 1s electron lines separated by 4.3 ± 0.5 and 4.2 ± 0.2 eV,[39] respectively. ESCA spectroscopy thus shows the cyclopentyl cation to be a classical ion, regardless of its fast equilibration. As in the *tert*-butyl cation, species with intensive charge localization always show a separate carbon 1s line for the carbenium center at higher (~4 eV) binding energies. A smaller ΔE_b (3.4 eV) was found in the case of the 1-adamantyl cation, in agreement with the expected charge delocalization in the "cage"-like structure of the adamantane skeleton. The 2-methyl-2-norbornyl cation also shows a slightly smaller separation (3.7 eV) indicative of some σ delocalization in an otherwise classical tertiary carbenium ion. Data are summarized in Table III.

An essentially different carbon 1s electron spectrum is obtained for the norbornyl cation.[39] The spectrum obtained with 100-V analyzer energy (Figure 5A) shows a single broad line with a pronounced shoulder on the higher binding energy side (corresponding to C.1 and C.2). A curve resolver analysis gave an approximate peak area ratio of 2:5 and a maximum separation of 1.7 eV. As even the slightest, inevitable carbon impurities (for example, from vacu-
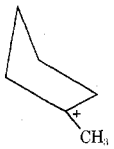
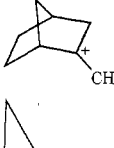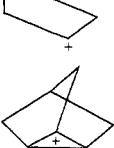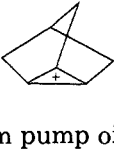(35) F. K. Fong, *J. Am. Chem. Soc.*, **96**, 7638 (1974).

(36) (a) H. C. Brown and K. T. Liu, *J. Am. Chem. Soc.*, **97**, 600 (1975); (b) *ibid.*, **97**, 2469 (1975).

(37) D. M. Brouwer, E. L. Mackor, and C. MacLean in "Carbonium Ions", G. A. Olah and P. v. R. Schleyer, Ed., Vol. II, Wiley-Interscience, New York, 1970, p 837, and references given therein.

(38) G. A. Olah, G. D. Mateescu, L. A. Wilson, and M. H. Gross, *J. Am. Chem. Soc.*, **92**, 7231 (1970).

(39) G. A. Olah, G. D. Mateescu, and J. L. Riemenschneider, *J. Am. Chem. Soc.*, **94**, 2529 (1972).

Table III
Binding Energy Differences of Carbocation Centers from
Neighboring Carbon Atoms $dE_b{}^+{}_{C-C}$

Ion	$dE_b{}^+{}_{C-C}$	Approximate relative $C^+:C$ intensity
$(CH_3)_3C^+$	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

Figure 5. Carbon 1s photoelectron spectrum of the norbornyl cation: (A) 100-V, (B) 30-V analyzer energy.

um pump oil) will increase the intensity of the major, lower binding energy signal, a slightly increased intensity of this peak is expected when studying carbon 1s carbon ESCA spectra.

Brown quotes Kramer[32] as having reexamined our spectra, integrating the peak ratio from the published spectrum closer to 1:6. In our hands, however, in three separate experiments, the peak area ratio was consistently found (from curve resolver analyses of the original spectra) to be closer to 2:5 than 1:6. Peak intensities, however, for reasons discussed never can be considered theoretical in carbon ESCA spectroscopic studies. The interpretation of the spectrum is primarily based on the relative (internal) chemical shift differences, which exclude any possibility for a classical, equilibrating norbornyl cation.

A considerable improvement of the above spectrum was obtained using lower, i.e., 30 V, analyzer energy (Figure 5B). It is noteworthy (Figure 5) that the ESCA spectra obtained at 100- and 30-V analyzer energy are identical in nature. They differ in that in the latter case an improved resolution was obtained (with some decrease in the signal-to-noise ratio, which is expected). Despite the facts Brown,[36a] quoting Kramer,[32] implied that we have published two different spectra and that they may be spectra of mixtures and even not be due to the norbornyl cation. However, all the samples were carefully checked before and after the experiments for identity of the ion by other spectroscopic methods. The possibility that samples deterioriated on the ESCA probe was eliminated by comparison with ESCA spectra of all possible hydrolysis or quenching products, which were found to be different from that of the ion. ESCA is, however, as is well recognized, an exceedingly sensitive surface method, and obtaining "clean" sample conditions is not easy. It is consequently well understood that in any ESCA study of sensitive compounds only one out of a number of attempted samples will give observable spectra. As, however, in other cases no spectra were observed, the reported
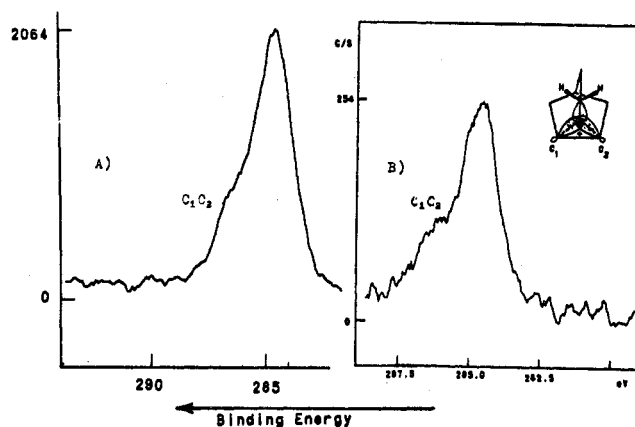
spectra of the norbornyl cation, as well as of other carbocations studied, are the only ESCA spectra obtainable, and they are reproducible. Further it would be remarkable if experimental difficulties would exist only in case of the norbornyl ion, as suggested by Brown and Kramer, but not with any of the other ions studied (see Table III).

Curve resolver analysis of the improved spectrum of the norbornyl cation obtained at 30 V gave an intensity ratio of 2:4.25, and more significantly a maximum internal peak separation of 1.47 eV. ESCA spectroscopy with its present resolution of about 0.5 eV can generally not differentiate between carbon atoms in organic compounds if they are not bound to strongly electron-withdrawing substituents (such as fluorine) or carry substantial free charge. Thus, no further resolution of the spectrum of the norbornyl ion than the observed two peaks can be expected. The results indicate that the norbornyl cation is of "nonclassical" carbonium ion nature since no high-binding energy line characteristic of a carbenium center is found. A classical ion equilibrating even at 10^{12} s^{-1} should give an electron spectrum identical with a static "classical" carbenium ion. As an example, the rapidly equilibrating, degenerate cyclopentyl cation shows the carbenium center line separated by 4.3 eV from the methylene carbons.

The ESCA spectroscopic results for the norbornyl cation are thus in excellent agreement with discussed carbon-13 and proton magnetic resonance (as well as Raman spectroscopic) data, indicating the methylene-bridged, nonclassical nature of the norbornyl cation.

Quenching of the Norbornyl Cation and Remarks Concerning the Claimed Capture of Unsymmetrical "Classical" Intermediates

Solutions of the norbornyl cation in superacids may be "quenched" by adding them to excess base in a solvent such as methanol. The products obtained depend on the nucleophile and on the efficiency of neutralization of the acid solution.[28] With MeOH–NaHCO₃ or NaOCH₃–MeOH, a mixture of nortricyclane and exo-2-norbornyl methyl ether is obtained (with some norbornylene as by-product). The proportions vary according to the procedure used. Quenching with pyridine on the other hand gave nortricyclane as the only identifiable product, in 80% overall

yield. When the acid solution of the ion is quenched with methanol in the absence of methoxide base, the product is *exo*-2-norbornyl methyl ether (with some norbornylene), but no detectable amount of nortricyclane is formed.

Quenching the stable ion thus gives either nortricyclane and/or an *exo*-2-norbornyl derivative depending on the conditions and the nucleophile. Complete deprotonation to nortricyclane takes place upon quenching in a tertiary amine (pyridine), no other nucleophile being present. Quenching the norbornyl cation with pyridine in methanol forms nortricyclane and methyl norbornyl ether in proportions depending on conditions. Hydrolysis or methanolysis without neutralization, on the other hand, gives practically quantitative yields of 2-*exo*-norbornyl products, showing the great ease of the acid-catalyzed opening of the cyclopropane ring under solvolytic conditions.

In my view the behavior of the norbornyl cation on quenching is entirely consistent with the structural studies. Brown's recent claims of quenching unsymmetrical ions faster than their equilibration (which, after Fong, he implied can have a rate as high as 10^{12} s^{-1}) lack physical reality. There is no need to suggest any excessive rates of quenching reactions; the nonclassical norbornyl ion clearly can give the observed quenched products. Further, the fact that nortricyclane was obtained even under solvolytic conditions, but in much higher amounts, by quenching the stable norbornyl cation would be difficult to explain without σ delocalization of the C.1–C.6 bond.

Rates of the 3,2- and 6,1,2-Hydrogen Shifts

The rate of the 3,2-hydrogen shift is abnormally slow compared with other 1,2-hydrogen shifts in secondary carbocations. In the cyclopentyl cation a maximum activation energy of 5 kcal (corresponding to a rate constant of 10^4 s^{-1} at −150 °C) can be estimated from the fact that no change in the spectrum in SbF$_5$–SO$_2$ClF–SO$_2$F$_2$ solution is observed down to this temperature. The 3,2-hydrogen shift barrier in the norbornyl cation is thus at least 5.8 kcal higher than that in the cyclopentyl cation, corresponding to a rate ratio of 10^{11} at −150° or 10^4 at 25 °C. Comparison of models of the two ions shows that torsional and steric effects alone cannot account for the large differences. The explanation for this marked difference in behavior is that the difference in activation energies represents loss of σ-delocalization energy in the nonclassical norbornyl cation upon reaching the transition state for the 3,2-hydrogen shift. The 3,2-hydrogen shift occurs exo–exo, and the transition state could be represented by
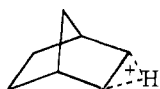
It is known than an electron donor at C.2 in the norbornyl cation (e.g., CH$_3$ or C$_6$H$_5$) drastically reduces the degree of σ participation. Since the 3,2-hydrogen shift transition state must involve delocalization of the positive charge from C.2 and C.3 (and

exo H.3), a substantial decrease in σ delocalization is expected. We can thus conclude that σ delocalization contributes at least 5.8 kcal to the stability of the norbornyl cation.

Concerning the nature of the frequently quoted 6,2-hydrogen shift, this shift as such could exist only in a completely classical, hypothetical ion, separately from the Wagner–Meerwein shift. The experimentally observed scrambling of the H.2, H.1, and H.6 hydrogen atoms as well of C.2, C.1, and C.6 carbon atoms seems to be in complete agreement with a protonated cyclopropane (in this case protonated nortricyclane) type mechanism. This process is analogous to the scrambling found in the parent propyl cation, which occurs via protonated cyclopropanes.[40] This equilibration process thus combines the 6,1,2-hydrogen and Wagner–Meerwein shifts.
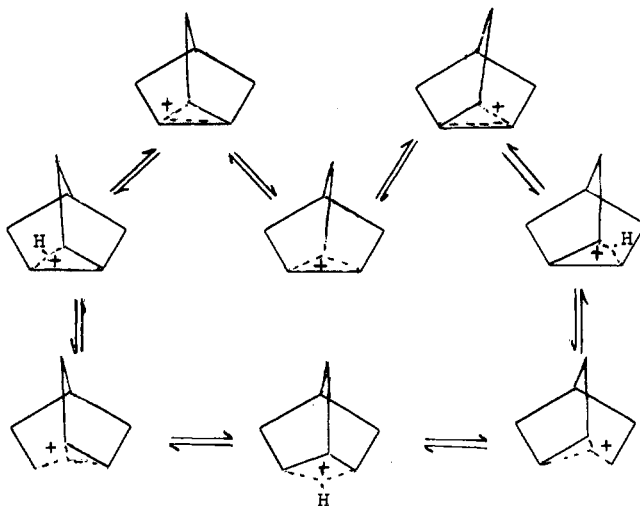
The experimentally observed activation energy of 5.8 kcal/mol would represent, in terms of equilibrating classical norbornyl cations, the overall energy for the fast 6,1,2-hydrogen shift (combined with the fast Wagner–Meerwein shift). In terms of the σ-bridged norbornyl cation the process is a threefold degenerate equilibration of the σ-bridged ion (as protonated nortricyclane).

For the "low" rate of the 2,3 shift the effect of orbital orientation can certainly be important, but it may not be the only or even the most important factor. In this connection we note that for the 1,2 shifts in benzenium ions (hexamethylbenzenium, prehnitenium ions) the combination of a moderately unfavorable orbital orientation and a strong charge delocalization results in a $\Delta G^{\ddagger} = \Delta H^{\ddagger} = 11$ kcal/mol.[36]

Relative Stabilities of Norbornyl and Related Model Ions

If the classical structure were correct, the norbornyl cation should be a regular secondary carbocation with no additional stabilization provided by σ delocalization (such as the cyclopentyl ion). The facts are, however, to the contrary. Several direct measurements related to the stability of the 2-norbornyl cation, such as Hogeveen's measurement of rates and equilibria of carbonylation[41] and the rates of hydro-

(40) For a review of protonated cyclopropanes see M. Saunders, P. Vogel, E. L. Hagen, and J. Rosenfeld, *Acc. Chem. Res.*, **6**, 53 (1973), and references therein.

(41) H. Hogeveen, *Adv. Phys. Org. Chem.*, **10**, 29–52 (1973), and references given therein.

genation,[42] Arnett, and Larsen's calorimetric data on the heats of formation of stable carbocations from alcohols in FSO_3H-SbF_5,[43a] as well as Arnett and Petro's preliminary measurements of related ionization of chlorides in $CH_2Cl_2-SbF_5$ solution,[43b] show the norbornyl cation to be substantially more stable (by 6–8 kcal/mol) than other secondary cations.

Regular secondary cations (other than the norbornyl cation), such as the isopropyl, *sec*-butyl, or cyclopentyl cations, are not stable in methylene chloride solution. However, Arnett was able to study in SbF_5-SO_2ClF solution (in which secondary alkyl cations are stable at low temperature) the heat of isomerization of the *sec*-butyl cation to the *tert*-butyl cation, and found it to be about 14 kcal/mol. This value is contrasted with the difference in heat of formation of the 2-methylnorbornyl and parent norbornyl cation, which is about 8 kcal/mol. Thus, the secondary norbornyl cation is substantially more stable than a simple secondary alkyl cation. The additional stabilization energy of the norbornyl ion is also in complete accord with the difference between the rates of the 2,3-hydride shifts of the norbornyl cation and 1,2-hydride shifts in usual secondary ions.

Solution studies, including direct comparison, through halonium ion formation, of stable ions with each other,[44c] are also in accord with recent gas-phase ICR and chemical ionization mass spectrometric measurements of relative ion stabilities.[45a,b] (In mass spectrometric work, of course, no structure for the ions involved can be assured.)

Space does not allow discussion of quantum mechanical calculations of the relative stabilities of the classical and nonclassical forms of the norbornyl cation. It must be noted, however, that neither ab initio or semiempirical studies allow at this time sufficient geometry optimization. Dewar's MINDO/3 calculations[44a] have found minima corresponding to both classical and nonclassical structures, differing by only 2–3 kcal mol^{-1}. Even when considering that these calculations relate only to the idealized gas phase and refinements may somewhat change values, the energy differences are relatively small, not unlike in the case of the $C_3H_7^+$ system. As, however, similar MINDO/3 calculations of the heat of formation of the parent neutral hydrocarbon, *i.e.*, norbornane, gave an error in excess of 20 kcal mol^{-1} compared with the experimentally measured value,[44b] it must be concluded that the limitations of theoretical calculations at the present time exceed the energy differences involved.

Conclusion of the Nonclassical Ion Controversy and Its Significance

Low-temperature NMR, as well as ESCA spectroscopy, demonstrate the methylene-bridged nonclassical carbonium ion structure of the norbornyl cation. Temperature-dependent NMR spectra also gave the activation barriers for the 2,3-hydrogen shift, $E_a = 10.8 \pm 0.6$ kcal/mol, and for the 6,2,1-hydrogen shift, $E_a = 5.8 \pm 0.2$ kcal/mol. There is no discrepancy between these results and solvolytic data, if appropriate corrections are made as to the temperatures at which the different experiments were carried out.[46]

The structural (spectroscopic) studies of the long-lived 2-norbornyl cation fully substantiate Winstein's original views. Until recently study of carbocation systems was based only on conclusions obtained from rate studies, stereochemical, and tracer investigations. It was on this basis that Winstein suggested the involvement of σ participation and formation of the bridged, nonclassical ion especially to explain the observed high exo/endo rate ratios in the solvolysis of 2-norbornyl esters.

Brown's criticism of this concept centered on the question of whether these data necessitate, as the sole explanation, involvement of the nonclassical ion, or can instead be explained on steric grounds, involving rapidly equilibrating classical norbornyl cations, and particularly hindrance to ionization of the endo isomer. In Brown's view the rate of solvolysis of the exo isomer is not accelerated; it is the rate for the endo isomer which is slow.

The last decade has seen rapid development of the direct experimental study of carbocations: long-lived ions were prepared in generally highly acidic (and therefore weakly nucleophilic) solvent systems, and their structures could consequently be established by spectroscopic (as well as chemical) methods. Study of the long-lived norbornyl cation has resulted in indisputable proof for the σ-bridged, nonclassical structure. As the identical ion was obtained from both the σ- and the π-precursor systems, it must be the intermediate of lowest energy in these systems. Whereas media of varying nucleophilicity obviously affect solvation of carbocations, the structure of ions observed under stable ion conditions cannot be basically different from that in solvolytic systems.

Brown[36b] recently questioned the relevance of direct studies of the norbornyl cation to the behavior of solvolytic systems: "Finally the point needs to be emphasized that it has not yet been established as to how pertinent are the results and conclusions for studies under stable-ion conditions to the behavior of cations under solvolytic conditions". I think the answer is obvious. 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.

As pointed out by Schleyer, solvolyses of secondary substrates are not necessarily of limiting SN1 type. Stable ion data, for which the ion is necessarily generated and stabilized in the absence of nucleophiles, cannot be directly extrapolated to solvolytic systems.

(42) D. M. Brouwer and H. Hogeveen, *Prog. Phys. Org. Chem.*, **9**, 179–240 (1972), and references given therein.

(43) (a) E. M. Arnett and J. M. Larsen in "Carbonium Ions", G. A. Olah and P. v. R. Schleyer, Ed., Vol. I, Wiley-Interscience, New York, 1968, p 441, and subsequent publications; (b) E. M. Arnett, personal communication of preliminary experimental data.

(44) (a) As quoted by L. Radon, D. Poppinger, R. C. Haddon, and P. v. R. Schleyer in the Chapter "Molecular Orbital Theory of Carbocations" in "Carbonium Ions", Vol. 5, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N.Y., in press; also personal communication by M. J. S. Dewar; (b) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97**, 1291 (1975); (c) G. A. Olah, "Halonium Ions", Wiley-Interscience, New York, 1975, pp 28–30.

(45) (a) R. D. Wietig, R. H. Staley, and J. L. Beauchamp, *J. Am. Chem. Soc.*, **96**, 7552 (1974); F. Field, personal communication.

(46) The question raised originally by Collins was in these terms clarified by J. A. Berson and M. Saunders, as quoted in ref 31, pp 8701, and acknowledged by C. J. Collins and C. E. Harding, *Justus Liebigs Ann. Chem.*, **745**, 124 (1971).

On the other hand, nucleophilic solvent participation into a developing carbocation center is the intermolecular counterpart of intramolecular neighboring group participation. The latter, in accordance with the general concept of carbocation behavior in electrophilic interactions,[5] can be by an n-donor group (such as halogen), a π donor (as in the cyclopentenylethyl route to the norbornyl cation), or a σ donor (the C.1–C.6 bond in forming the ion from norbornyl precursors). There can be competition between inter- and intramolecular nucleophiles, as, for example, recently discussed by Nordlander in solvolytic studies in trifluoroacetic acid.[23] All this, however, does not affect the structural conclusions reached concerning the norbornyl ion, which in my view finally ends the so-called "nonclassical ion controversy".[11]

Nonclassical carbonium ions containing two-electron, three-center bonded carbocation centers are now firmly proven to exist also as long-lived species. The differentiation of these ions from trivalent classical carbenium ions served a most useful purpose in defining these differing carbocations.[47] However, there always exists a continuum of charge delocalization depending on the characteristics of specific systems (comprising both inter- and intramolecular interactions).

The mode of charge delocalization in my view is a continuous process, with faster electronic movement being followed by slower nuclear reorganization.[4] There is, however, no reason to believe in a dichotomy of these processes, as once suggested by Traylor in his "vertical stabilization" concept.[48,49]

(47) G. A. Olah, *J. Am. Chem. Soc.*, **94**, 808 (1972).
(48) T. G. Taylor, W. Hanstein, H. J. Berwin, N. A. Clinton, and R. S. Brown, *J. Am. Chem. Soc.*, **93**, 5715 (1971).
(49) G. A. Olah and G. Liang, *J. Am. Chem. Soc.*, **97**, 1920 (1975).

The "classical–nonclassical ion controversy" is brought to conclusion not only by overwhelming chemical and structural evidence, but also by consideration of our present day understanding of chemical bonding and charge delocalization. Simply, there is no such thing as a completely "classical" type of carbocation. Charge is always delocalized to a significant degree whenever an electron-deficient center is formed in a molecule. Whether this happens through π-, n-, or σ-electron-pair interactions and to what a degree is dependent of the specific system, but not of principle. The norbornyl cation is only one of the many carbocations showing C–C σ-bond delocalization, and will be remembered in years to come as an interesting but by no means unique member of a substantial class of compounds.

Rather than being rare, the two-electron, three-center bond is characteristic of electron-deficient molecules, including nonclassical carbocations. The real significance of the nonclassical norbornyl cation is, however, that it provides evidence for the close similarity of intramolecular σ- and π-bond donor ability. Extending the same principle to intermolecular interactions raised the question as to whether σ-bond donor ability is a general phenomenon in organic chemistry. Our work since affirmed it, and has led to a rapid development of the reactions of saturated hydrocarbons with electrophiles.[4] Pentacoordinated carbonium ions, closely related in nature to the norbornyl cation, of which the methonium ion (CH_5^+) is parent, represent the key to all these reactions.[5,6]

Thione Photochemistry, and the Chemistry of the S_2 State[1]

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The study of the photochemistry of the carbonyl group dates from the earliest period of investigation of photic interactions with organic substances; that is, about the turn of the century. In contrast, the first study of a thiocarbonyl compound appears to have been reported in the thirties, and no systematic investigations were initiated until the late sixties.

The lack of interest may be variously interpreted. Certain thiones and thials have intimidating olefac-

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tory qualities;[2] they have ground states that are very reactive,[3] leading to the formation of dimers, trimers, or polymers; and those substances having an α hydrogen have a strong tendency to thioenolize. These undesirable characteristics are not possessed by all members of the group, however. In the last 8 years or so, it has become clear that the excited thione function has distinctive characteristics of its own, perhaps

(1) Photochemical Synthesis, 62. Publication No. 138 from the Photochemistry Unit, University of Western Ontario.
(2) E. Baumann and E. Fromm, *Ber.*, **22**, 2592 (1889); much, if not all, of the vile odor associated with thiocarbonyl compounds is to be attributed to impurities.
(3) For instance thioacrolein has recently[4] been prepared by flash thermolysis and is reactive even at the temperature of liquid nitrogen. Thiobenzaldehyde[4] is stable up to about −140°.