Stable Carbocations. CL.[1] Fourier Transform ^{13}C Nuclear Magnetic Resonance and X-Ray Photoelectron Spectroscopic Study of the 2-Norbornyl Cation

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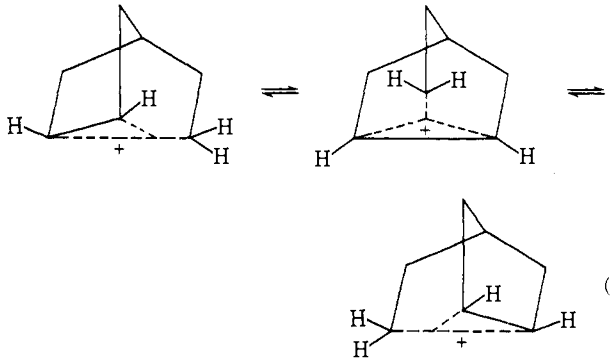
Abstract: The complete ^{13}C Fourier transform nmr spectra of the 2-norbornyl cation at −70° under conditions of rapid equilibration, and at −150° as a static, nonexchanging ion, were obtained. For comparison, we also studied the ^{13}C nmr spectra of the 7-norbornenyl and 7-norbornadienyl cations. The cmr data clearly indicate that all three ions at low temperature are present as the static bridged carbonium ions containing characteristic penta- and tetracoordinated carbon atoms. X-Ray photoelectron (ESCA) spectra of the norbornyl cation and related model ions were also obtained. Since in electron spectroscopy the time scale of the measured ionization process is on the order of 10^{-16} sec, electron spectra can characterize individual ionic species regardless of possible Wagner–Meerwein rearrangements or hydrogen shifts. It is concluded that the long standing controversy as to the nature of the 2-norbornyl cation is unequivocally resolved in favor of the nonclassical carbonium ion. The general importance of σ-bond delocalization in intra- and intermolecular systems is discussed, the latter representing the key to electrophilic reactions at single bonds.

The structure of the 2-norbornyl cation **1**[2] was the center of probably the most concerted research effort in physical organic chemistry of the last 25 years, and evoked strong controversy. The topic was repeatedly reviewed,[3] and the reader is referred to the available comprehensive reviews and the original literature quoted in them. Until the early sixties, investigations exclusively centered on kinetic (of solvolytic systems), stereochemical, and isotopic tracer studies. Winstein's views on the nonclassical (σ bridged) nature of the ion[4] were opposed by Brown's suggestion of rapid equilibration of the classical (trivalent) ion.[5]

The availability of methods found in our laboratory to generate stable, long-lived carbocations in low nucleophilicity solvents allowed direct spectroscopic studies of ion **1**.[6-8]

Results and Discussion

Fourier Transform Cmr Spectroscopic Studies. Besides the temperature-dependent pmr studies, we have reported previously the partial INDOR ^{13}C nmr spectra of ion **1** at −70° in SbF_5–SO_2, and at −150° in SbF_5–SO_2ClF–SO_2F_2 solution, respectively.[2,6] At −70°, three ^{13}C resonance absorptions were observed indicating fast intramolecular equilibration of the ion on the nmr time scale (eq 1), in accordance with the corresponding pmr spectrum.



(1)

At −150°, it was found possible to slow down the rate of this equilibration sufficiently to enable observation of the static nonclassical 2-norbornyl cation. Due to a poor signal-to-noise ratio in the pmr spectra at this temperature and insufficient concentration of the natural ^{13}C abundance species, only the C_1, C_6, and C_2 chemical shifts were obtained. C–H coupling constants and peak multiplicities could not be obtained. The bridging C_6 carbon and the two cyclopropane-like C_1 and C_2 carbons showed carbon resonances at $\delta_{^{13}C}$ +173 and +70, respectively.[2] From a consideration of the measured cmr parameters in the 2-norbornyl **1**, 7-norbornenyl **2**,[9] and 7-norbornadienyl **3**[9] cations, it was concluded that the positive charge resides mainly at the cyclopropane-like carbon atoms to which bridging takes place, rather than at the bridging carbon atoms.[3,10]

The development of Fourier transform nmr spectroscopy has now made it possible to obtain the complete

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[1] (a) Part CXLIX: G. A. Olah and P. W. Westerman, *J. Org. Chem.*, 38, 1986 (1973). (b) A preliminary communication appeared: G. A. Olah, Gh. D. Mateescu, and J. L. Riemenschneider, *J. Amer. Chem. Soc.*, **94**, 2529 (1972).

[2] (a) G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 3954 6883 (1969); (b) G. A. Olah, A. M. White, J. R. DeMember, A. Commeyras, and C. Y. Lui, *ibid.*, **92**, 4627 (1970).

[3] For reviews, see (a) G. D. Sargent, *Quart Rev., Chem. Soc.*, 20, 301 (1966); (b) G. D. Sargent in "Carbonium Ions," Vol. III, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1972, Chapter 24; (c) P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, New York, N. Y., 1965.

[4] (a) S. Winstein and D. S. Trifan, *J. Amer. Chem. Soc.*, 71, 2953 (1949); 74, 1146, 1149, 1154 (1952); (b) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *ibid.*, 77, 4183 (1955); (c) S. Winstein, *Quart. Rev., Chem. Soc.*, 23, 1411 (1969).

[5] For example, see H. C. Brown, "The Transition State," Symposium of the London Chemical Society, 1961, p 461; *Chem. Soc., Spec. Publ.*, No. **16**, 140 (1962); *Chem. Brit.*, 199 (1962).

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

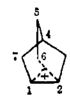
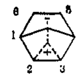
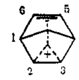
[7] G. A. Olah and A. M. White, *ibid.*, **91**, 3956, 5801 (1969).

[8] (a) G. A. Olah, A. Commeyras, and C. Y. Lui, *ibid.*, **90**, 3882 (1968); (b) G. A. Olah, J. R. DeMember, A. Commeyras, and J. L. Bribes, *ibid.*, **93**, 459 (1971).

[9] G. A. Olah and A. M. White, *ibid.*, **91**, 6883 (1969).

[10] Readers are referred to ref 2 and 7 for a detailed discussion of the norbornyl cation. See also G. A. Olah, *J. Amer. Chem. Soc.*, **94**, 808 (1972).

Table I. Cmr Parameters of 2-Norbornyl, 7-Norbornenyl, and 7-Norbornadienyl Cations[a]

Cation	Temp, °C	C_1	C_2	C_3	C_4	C_5	C_6	C_7
	−70	101.8 (q, 53.3)[b]		162.5 (t, 140.2)	156.1 (d, 153.0)	162.5 (t, 140.2)	101.8 (q, 53.3)	162.5 (t, 140.2)
	−150	68.5 (d, 184.5)		145.8 (t, 153.5)	160.4 (d, 158.6)	165.8 (t, 160.2)	171.4 (t, 145.8)	145.8 (t, 153.5)
 2	−70	135.8 (d, 173.0)	67.9 (d, 193.8)		135.8 (d, 173.0)	167.1 (t, 140.1)		159.8 (d, 218.9)
 3	−70	130.8 (d, 181.2)	78.9 (d, 192.3)		130.8 (d, 181.2)	71.8 (d, 177.3)		157.6 (d, 216.4)

[a] ^{13}C cmr shifts are relative to CS_2 (in ppm). More accurate chemical shifts and coupling constants are obtained due to the use of the Fourier transform method than the data obtained by the INDOR method previously.[2] [b] Multiplicities and coupling constants (J_{CH}, in Hz) are given in parentheses: d = doublet, q = quintet, t = triplet.

cmr spectrum of the 2-norbornyl cation (prepared as previously described[2]) at −70°, under conditions of rapid equilibration of the ion, and at −150° as the static "frozen out" ion. Furthermore, the complete cmr spectra of the related 7-norbornenyl **2** and 7-norbornadienyl **3** cations were also obtained. Results are summarized in Table I. The proton-decoupled FT cmr spectrum of ion **1** at −70° is shown in Figure 1A. It consists of three carbon resonances at $\delta_{^{13}C}$ 101.8, 156.1, and 162.5, which are assigned to the three equivalent cyclopropane-like ring carbons (C_1, C_2, and C_6), the bridgehead carbon (C_4), and the three equivalent methylene carbons (C_3, C_5, and C_7), respectively. (Assignments were made by the off-resonance cmr spectrum, Figure 1B.) As has previously been pointed out,[2] the most deshielded carbon resonance ($\delta_{^{13}C}$ 101.8) 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°) this resonance is separated into two components at $\delta_{^{13}C}$ 68.5 (for C_1 and C_2) and 171.4 (for C_6). The bridgehead carbon (C_4) resonance is slightly moved to higher field at $\delta_{^{13}C}$ 160.4. The methylene resonance is also separated into two components at $\delta_{^{13}C}$ 145.7 (for C_3 and C_7) and 165.8 (for C_5) (see Figure 1C). The C–H coupling constants (J_{CH}, in Hz) given in Table I were obtained directly from the proton coupled cmr spectrum (Figure 1D). The pentacoordinated bridging carbonium carbon atoms in ions **1**, **2**, and **3** all are highly shielded and exhibit chemical shifts in the range of $\delta_{^{13}C}$ +150 to +170, whereas the tetracoordinated carbons to which bridging takes place (and which consequently carry more positive charge) show shifts in the range of $\delta_{^{13}C}$ +68 to +80.

In the proton coupled cmr spectrum of ion **1** (Figure 1D), we did not observe coupling between the methylene hydrogens at the pentacoordinated carbon (C_6) with the cyclopropane-like carbons (C_1 and C_2). This is expected from the nonclassical structure **1**, since the two-electron three-center bonds are relatively longer and also weaker than normal C_{sp^3}–C_{sp^2} bonds.

The cmr spectra clearly indicate that all three ions **1–3** are carbonium ions having a characteristic pentacoordinated bridging carbon atom. The magnitude of $J_{C_6\text{–}H}$ = 145.8 Hz in the 2-norbornyl cation is smaller than those for $J_{C_7\text{–}H}$ in the ions **2** and **3**, which are 218.9 and 216.4 Hz, respectively. This is expected as the strained C_7 carbons in **2** and **3** have higher s character in the C–H bonds than has C_6 in **1**. (For 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 give an increase in the magnitude of the C–H coupling constant.[7] Both ^1H and ^{13}C nmr spectra indicate that the bridging pentacoordinated methylene carbon C_6 in ion **1** is tetrahedral in nature and carries little positive charge.[10] The methine carbons (C_1 and C_2) in ion **1** show slightly more de-

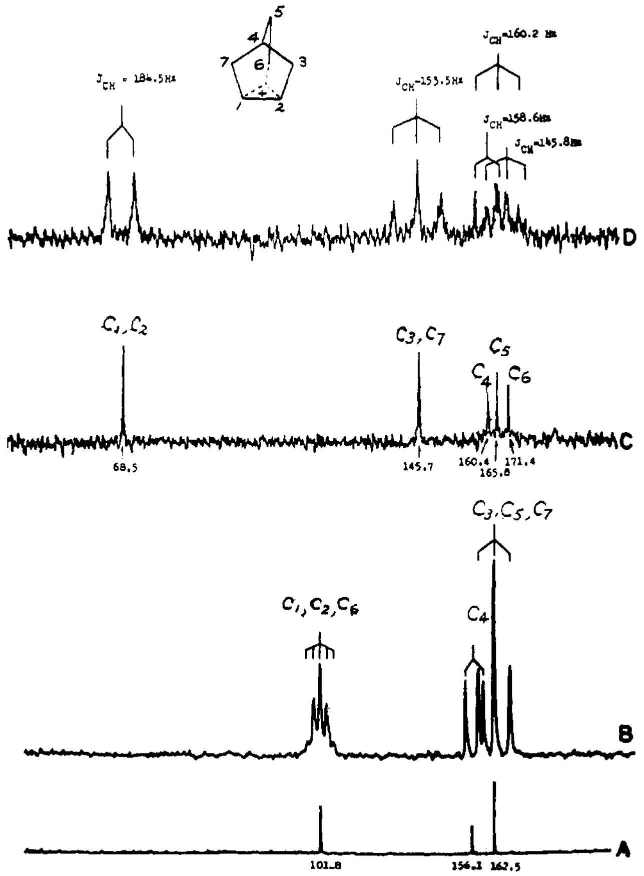


Figure 1. Fourier transform cmr spectra of the 2-norbornyl cation: (A) at −70°, proton decoupled; (B) at −70°, off-resonance; (C) at −150°, proton decoupled; (D) at −150°, proton coupled.

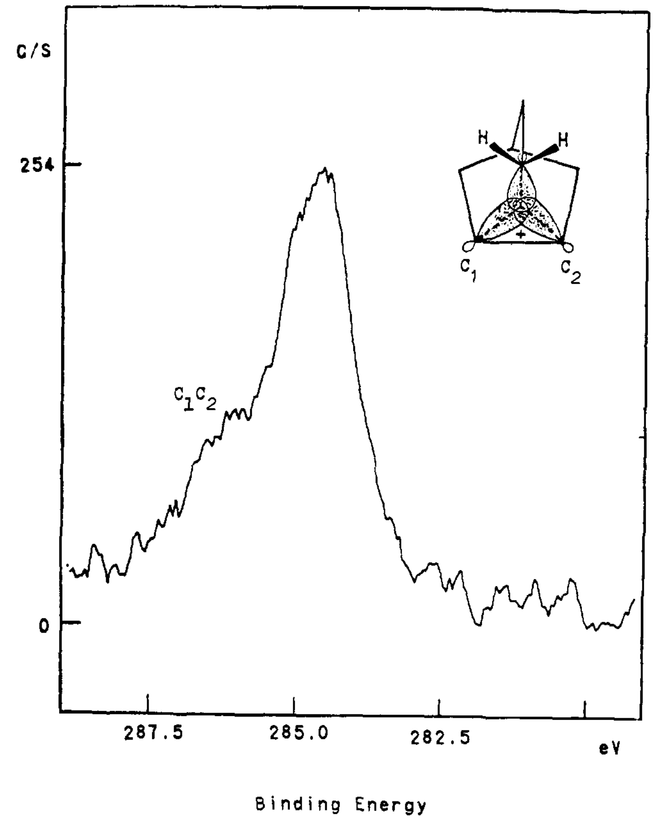


Figure 2. Carbon 1s electron spectrum of norbornyl cation **1** (30-V analyzer energy).

shielded resonances than those of C_2 and C_3 in ions **2** and **3**. The C–H coupling constants, however, are of similar magnitude as a result of a similar tetrahedral hybridization and charge distribution associated with these carbons. Considering the experimental difficulties involved in obtaining INDOR spectra in natural abundance at −150°, the FT cmr spectra show gratifying agreement with our previous data based on ^{13}C INDOR spectra.[2]

ESCA Studies. Since in electron spectroscopy the time scale of the measured ionization processes is on the order of 10^{-16} sec, definite ionic species are characterized, regardless of their possible intra- and intermolecular interactions (*e.g.*, Wagner–Meerwein rearrangements, hydride shifts, proton exchange, etc.). Thus, electron spectroscopy can give an unequivocal, direct answer to the long debated question of the "classical" or "nonclassical" nature of the norbornyl cation, independent of any possible equilibration processes.

Further, it is well established that the gross atomic charge can be correlated with the electron binding energy (E_b) chemical shift (in this case of carbon 1s electron lines).[11] Obviously, electron deficiencies of different degrees in different carbocations are expected to give different C1s binding energy shifts and E_b's. We have found, indeed, that the trivalent trimethylcarbenium ion (classical *tert*-butyl cation) exhibits an ESCA spectrum showing two well-separated lines having an approximately 1:3 area ratio.[12] The C1s line of the highly electron deficient carbenium ion center appears at 3.9 eV *higher* binding energy than the methyl C1s line. The cyclopentyl and methylcyclopentyl cations clearly exhibit two distinct carbon 1s electron lines separated by 4.3 ± 0.5 and 4.2 ± 0.2 eV, respectively. Thus, as in the *tert*-butyl cation, species with intensive charge localization will show a separated C1s line for the carbenium center at higher (~4 eV) binding energies. A smaller ΔE_b (3.4 eV) was found in the case of 1-adamantyl cation in agreement with the expected charge delocalization in the "cage"-like structure of the adamantane skeleton.[13] The 2-methylnorbornyl cation also shows a slightly smaller separation (3.7 eV)[1b] indicative of some σ delocalization in an otherwise classical tertiary carbenium ion.

An essentially different carbon 1s electron spectrum is obtained for the parent norbornyl cation **1**. The spectrum obtained with 100-V analyzer energy[1b] showed a single broad line with a pronounced shoulder on the higher binding energy side (corresponding to C_1 and C_2).[14] 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 carbon impurities (for example, from vacuum pump oil) will increase the intensity of the major, lower binding energy signal, a slightly increased intensity of this peak was expected. In three independent determinations, however, the peak area ratio was consistently found to be much closer to 2:5 than 1:6. More importantly, however, we emphasize that our interpretation of the spectrum is based essentially on the relative (internal) chemical-shift differences. In all determinations these were ~1.5 eV, thus clearly excluding the possibility of a classical norbornyl cation system.

A considerable improvement of the above spectrum has been obtained using lower, *i.e.* 30-V, analyzer energy (Figure 2). It should be emphasized that the ESCA spectra obtained at 100- and 30-V analyzer energy are identical in nature, only in the latter case a much better resolution was obtained (with some increase in the signal-to-noise ratio, which is expected). A curve resolver analysis gave an intensity ratio of 2:4.95, and a maximum 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 ion **1** than the observed two peaks is possible. The results clearly suggest that the ion **1** is of "nonclassical" carbonium ion nature since no high-binding energy line characteristic of a carbenium center is found. An equilibrating classical structure **1a** $\rightleftharpoons$ **1b** should give an electron spectrum identical with a static "classical" carbenium ion, even under conditions of extremely rapid equilibration.

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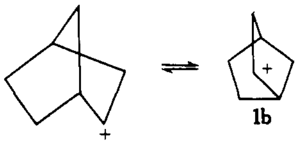
[11] K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S. Karlsson, I. Lindgren, and B. Lindberg, "ESCA, Atomic, Molecular, and Solid State Structure Studied by Means of Electron Spectroscopy," Almquist and Wiksells, Uppsala, 1967, p 108.

[12] G. A. Olah, Gh. D. Mateescu, L. A. Wilson, and M. H. Gross, *J. Amer. Chem. Soc.*, **92**, 7231 (1970).

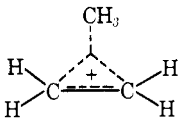
[13] Gh. D. Mateescu and J. L. Riemenschneider, Abstracts, 163rd National Meeting of the American Chemical Society, Boston, Mass., Apr 1972, No. ORGN-115.

[14] ESCA spectra of ion 1 were obtained in SbF_5, FSO_3H–SbF_5, and AsF_3 matrixes at liquid nitrogen temperature. Samples before and after the ESCA experiments gave identical pmr spectra with those reported for ion 1, thus showing that no deterioration of the ion took place during the ESCA experiment (see Experimental Section for details).



1a 1b

For example, the rapidly equilibrating, degenerate cyclopentyl cation clearly shows the carbenium center line separated by 4.3 eV from the methylene carbons. The results obtained for the norbornyl cation are in excellent agreement with reported carbon-13 and proton magnetic resonance (as well as Raman spectroscopic) data indicating the methylene bridged nonclassical carbonium ion nature of the norbornyl cation.[14] Moreover, *ab initio* calculations[15] on model $C_3H_7^+$ ions show that in structure **4** the difference in



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carbon 1s electron binding energy between bridged methyl and adjacent methylene groups is *ca.* 1.1 eV. This value is consistent with our experimental results.

Conclusion of the Nonclassical Ion Controversy and Its Significance. Low temperature nmr, as well as ESCA spectroscopy, clearly proved the methylene bridged nonclassical carbonium ion structure of the norbornyl cation. Temperature-dependent nmr spectra gave also 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, $E_a = 5.9 \pm 0.2$ kcal/mol.[2b] 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.[16]

The structural (spectroscopic) studies of the long-lived 2-norbornyl cation **1**, as well as of the related 7-norbornenyl **2** and 7-norbornadienyl **3** cations, fully substantiate Winstein's views of the norbornyl cation.[4] It should be noted that the study of carbocation systems until recently was based only on conclusions obtained from rate studies, stereochemical, and tracer investigations.[3] It was on this basis that Winstein suggested the involvement of σ participation and formation of the bridged, nonclassical ion to explain the observed high exo/endo rate ratios in the solvolysis of 2-norbornyl esters. Brown's questioning of this concept centered on the question of whether these data indeed necessitate, as the sole explanation, involvement of the nonclassical ion, or (as he suggested) can they be explained on steric grounds, involving rapidly equilibrating classical norbornyl cations, and particularly hindrance to ionization of the endo isomer.[5] (As Brown stated, the rate of solvolysis of the exo isomer is not accelerated at all by participation; it is the rate of the endo isomer which is slow.) The last decade has seen rapid development of a direct experimental approach to the study of carbocations: long-lived ions were prepared in generally highly acidic (and therefore low nucleophilicity) systems and their structure could consequently be established by spectroscopic (as well as chemical) methods. The study of the long-lived norbornyl cation **1** resulted (as summarized in this paper) in undisputable proof for the σ-bridged nonclassical structure of the ion. As the same common ion was observed from both σ- and π-precursor systems, it is obvious that ion **1** is the intermediate of lowest energy in these systems. Whereas media of varying nucleophilicity obviously effect solvation of carbocations, based on all available evidence, the structure of ions observed under stable ion conditions cannot be basically different from that in solvolytic systems. Knowing the structure of the intermediate of lowest energy thus clearly is of substantial consequence also in solvolytic systems. What can be argued is to what degree the transition state in any reaction will resemble the intermediate. This of course is also true for the norbornyl systems. As pointed out by Schleyer,[17] secondary systems should not be considered as necessarily SN1 type. Stable ion data, where by definition the ion state is reached and the ion then is kept stable by keeping it away from interaction with nucleophiles, cannot be directly extrapolated to solvolytic systems. On the other hand, solvent participation into a developing carbocation center is the intermolecular counterpart of intramolecular neighboring group participation.[10,18] The latter in accordance with the general concept of carbocation behavior in electrophilic interactions, can be by an n-donor group (such as halogen), a π-donor (such as the discussed case of the cyclopentenylethyl route to the norbornyl cation), or a σ-donor (the C_1–C_6 bond in forming ion **1** from norbornyl precursors). There can be obvious competition for interaction between inter- and intramolecular nucleophiles, as, for example, recently discussed by Nordlander[19] in solvolytic studies in trifluoroacetic acid. All this, however, is not affecting the structural conclusions reached concerning ion **1** which in our view finally end the so called "nonclassical ion controversy."

Nonclassical carbonium ions involving 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.[2,9] However, it must be clear that there always should be considered to exist a continuum of charge delocalization depending on specific systems (comprising both inter- and intramolecular interactions).

The mode of charge delocalization in our view is a continuous process, with faster electronic movement being followed by slower nuclear reorganization. There is, however, no reason to believe in a dichotomy of

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(15) J. Pople, L. Radom, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **94**, 5935 (1972).

(16) (a) C. J. Collins and C. E. Harding, *Justus Liebigs Ann. Chem.*, **745**, 124 (1971); (b) J. A. Berson and M. Saunders, personal communication, 1970.

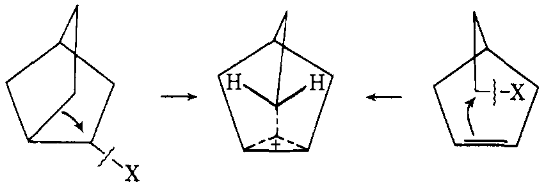
(17) (a) J. L. Fry, C. J. Lancelot, L. K. M. Lam, J. M. Harris, R. C. Bingham, D. J. Raber, R. E. Hall, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 2538 (1970); (b) J. L. Fry, J. M. Harris, R. C. Bingham, and P. v. R. Schleyer, *ibid.*, **92**, 2542 (1970); (c) P. v. R. Schleyer, J. L. Fry, L. K. M. Lam, and C. J. Lancelot, *ibid.*, **92**, 2544 (1970); (d) P. v. R. Schleyer, J. M. Harris, and R. E. Hall, *ibid.*, **93**, 2551 (1971).

(18) G. A. Olah, *Angew. Chem., Int. Ed. Engl.*, **12**, 173 (1973); *Chem. Brit.*, 8, 281 (1972); *Chimia*, **25**, 275 (1971); *Science*, **16**, 1298 (1970); *Chem. Eng. News*, **45**, 76 (Mar 27, 1967).

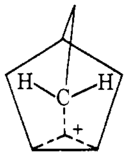
(19) (a) J. E. Nordlander, R. R. Gruetzmacher, W. J. Kelly, and S. P. Jindal, *J. Amer. Chem. Soc.*, submitted for publication; (b) J. E. Nordlander, R. R. Gruetzmacher, and F. Miller, *Tetrahedron Lett.*, 927 (1973).

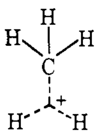
these processes, as suggested by Traylor[20] in his "vertical stabilization" concept. Participation of the σ-electron pair of the C_1–C_6 bond can reach different degrees,[21] but clearly the intermediate (*i.e.*, lowest energy) norbornyl cation is the pentacoordinated bridged ion **1**.

The real significance of the nonclassical norbornyl cation is, however, that it provides evidence for the close similarity of π- and σ-bond donor ability in the case of an intramolecular system (not much different from an intramolecular Friedel–Crafts alkylation).



By extending the same principle to intermolecular interactions the question could be raised, whether σ-donor single bond reactivity is a general phenomenon.[10,18] Experimental work, indeed, proved this assumption and led to a rapid development of the electrophilic chemistry of saturated hydrocarbons. 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 of these reactions.[22]

Experimental Section

Preparation of the 2-norbornyl cation has been previously described in detail.[2b]

Carbon-13 Nuclear Magnetic Resonance Spectroscopy. Cmr spectra were obtained using a Varian Associate Model XL-100 nmr spectrometer equipped with a broad-band proton decoupler, a Varian Fourier transform accessory, and a variable-temperature probe. The spectrometer was operated at 25.2 MHz, and was interfaced with a Varian 620-L computer. Chemical shifts were measured from the ^{13}C signal of ^{13}C-enriched TMS in a 1.75-mm capillary held concentrically inside the standard 12-mm sample tube, and were converted to ppm from $^{13}CS_2$. Multiplicities and couplings were obtained directly from the cmr spectra measured without proton decoupling.

ESCA spectra were obtained on a Varian VIEE-15 spectrometer. The probe was modified in order to rapidly obtain and maintain a temperature of about $-170°$ at the sample level. Varying the nitrogen flow allowed control of temperature. The probe was placed in a specially designed small drybox which allowed access from two sides. Through one side was introduced the bare cylindrical sample probe and high purity (dry) nitrogen under constant pressure. Through the other opening (which was also the exit site for the dry nitrogen) was introduced a pipet containing the cation solution in SbF_5–FSO_3H, SbF_5–AsF_3, or SbF_5–SO_2ClF. In contact with the cooled stainless steel probe the solution froze instantaneously in a uniform matrix. Then the probe was withdrawn into an attached polyethylene "glove bag" and brought, under continuous dry nitrogen flow, into the VIEE-15 analyzer. Measurements were performed at different temperatures and at two resolving powers (100- and 30-V analyzer energy, *i.e.*, at low and high resolution, respectively). AsF_3 has been found to be a good solvent since, due to its high freezing point, it diminishes the probability of water condensation and ice formation on the surface of the sample. Thus, the probability of quenching of the ions in the surface layer during the measurement is greatly reduced. As samples were checked before and after the ESCA experiments by nmr spectroscopy and gave identical spectra of the norbornyl cation **1**, we consider it proven that no deterioration of the ion took place during sample preparation and execution of the ESCA experiments. Moreover, ESCA spectra of 2-norborneol (the possible quenching product) and 2-chloronorbornane show only single broad lines, with no discernible separation or shoulder on the higher binding energy side. They are thus distinctly different from that of the norbornyl cation and could not have been present during observation of the ion.

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