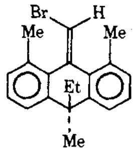
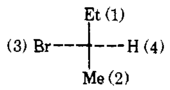
axial configuration of the 9-substituent is inferred by the NOE studies of the corresponding 10,10-dimethyl compounds.[5]

(9) The configuration nomenclature of **2** resembles that of alkylidenecyclohexane.[10] The enantiomer shown is (*R*)-(a)-ethyl-**2** whose substituents 1, 2, 3, and 4 describe a right-handed screw.



(*R*)-(a)-ethyl-**2**



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Stable Carbocations. CXCI.[1] Carbon-13 Nuclear Magnetic Resonance Spectroscopic Study of 7-Norbornenyl Cations Indicating Their "Nonclassical" Carbonium Ion Nature

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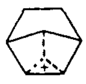
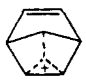
Abstract: A series of secondary and tertiary 7-norbornenyl cations were studied under stable ion conditions by carbon-13 NMR spectroscopy. The bridging carbon (C_7) in these ions is found substantially shielded. Substituents at C_7 do not greatly affect the carbon chemical shifts of the ions, except for C_7 itself which experiences a deshielding effect, by the attached substituent, indicating strong charge delocalization between C_2, C_3, and C_7. The carbon shift data and the characteristic and unusually large J_{C-H} coupling observed at C_7 in the parent 7-norbornenyl cation **1**-H (218 Hz) as well as at C_2 and C_3 in both secondary and tertiary ions (>190 Hz) suggest the nonclassical carbonium ion nature of these ions.

The structure of the 7-norbornenyl cations has been the subject of much interest[3] and controversy.[4] The high rate (10^{11} times that of related 7-norbornyl systems) and overall retention of configuration observed in the solvolysis of *anti*-7-norbornenyl *p*-toluenesulfonate were accounted for on the basis of a nonclassical 7-norbornenyl cation **1**-H[5] intermediate. Extensive solvolytic[6-10] and NMR spectroscopic studies[11] further confirmed the "bishomocyclopropenyl"[5a] type structure **1**-H. Delocalization and strain energy in the 7-norbornenyl cation also have been considered theoretically in agreement with the experimental results, favoring the nonclassical structure of the ion.[12]

Interested in the nature of carbocations,[2] we have previously reported both proton and carbon-13 NMR spectroscopic studies showing that the structure of the 7-norbornenyl cation **1** and the 7-norbornadienyl cation **2**, as well as that of the parent 2-norbornyl cation **3**, are those of typical nonclassical carbonium ions.[13]



1-H



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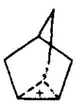

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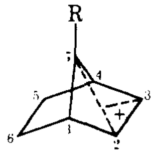
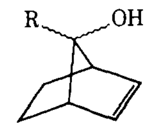
We now report our detailed ^{13}C NMR study of both secondary and tertiary 7-norbornenyl cations prepared under stable ion conditions to evaluate in full the structure of these ions.

Results and Discussion

Preparation of 7-Norbornenyl Cations. 7-Norbornenyl cations **1**-R[14] (R = H, CH_3, CH_2CH_3, C_6H_5, and OH) were prepared by slow addition solutions of appropriate alcohols **4**-R[15] or ketone **5**[15] in SO_2ClF to FSO_3H-SO_2ClF at Dry-Ice-acetone temperature (ca. −78°). The 1,2,3,4-tetrachloro-7-methoxy-7-norbornenyl cation (**6**) was prepared from the corresponding 7,7-dimethoxy-2-norbornene (**7**) in a similar way.[16] Ions were stable under the reaction conditions, and their ^1H NMR spectra were identical with those previously reported.[11,14]



1-R



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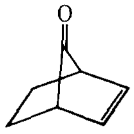

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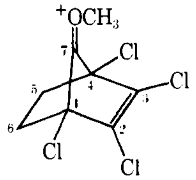

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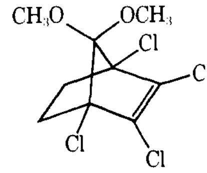

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Carbon-13 NMR Spectra. The proton-coupled FT ^{13}C NMR spectra and assignments of the 7-norbornenyl cations 1-R in FSO_3H-SO_2ClF solutions at −75° are summarized in Table I. Carbon shifts were obtained from their proton noise-decoupled ^{13}C NMR spectra. Multiplicities and coupling constants were obtained from the proton coupled ^{13}C NMR spectra. Typical are the spectra shown in Figure 1.

Table I. Carbon-13 NMR Parameters of 7-Norbornenyl Cations[a]

Ion	C_1, C_4	C_2, C_3	C_5, C_6	C_7	Others
1-H	58.0 (d, 173.0)	125.9 (d, 193.8)	26.7 (dd, 140.1, 138.7)	34.0 (d, 218.9)	
1-CH_3	57.1 (d, 167.4)	134.1 (d, 192.3)	24.8 (dd, 136.1, 132.1)	71.9 (s)	11.6 (CH_3) (q, 133.1)
1-CH_2CH_3	55.0 (d, 166.1)	132.2 (d, 193.2)	24.6 (dd, 138.1, 141.2)	80.5 (s)	18.9 (CH_2, t, 147.3) 12.1 (CH_3, q, 129.4)
1-C_6H_5	51.9 (d, 164.2)	140.1 (d, 191.6)	23.3 (dd, 136.1, 136.8)	109.8 (s)	120.2 (C_i, s);[b] 133.3 (C_o, d, 161.9) 130.0 (C_m, d, 161.9); 136.4 (C_p, d, 167.4)
1-OH	46.2 (d, 163.2) 45.5 (d, 163.7)	137.9 (d, 187.9) 136.9 (d, 187.0)	20.6 (dd, 142.8, 140.3)	225.5 (s)	
6	76.4 (s)	133.1 (s)	70.0 (t) 70.4 (t)	215.2 (s)	61.7 (OCH_3, q)

[a] Carbon-13 shifts are in parts per million from external Me_4Si (capillary). Multiplicities and coupling constants (J_{CH}, in Hz) are given in parenthesis. [b] d = doublet, dd = doublets of doublet, s = singlet, t = triplet, q = quartet. i = ipso, m = meta, o = ortho, and p = para carbons.

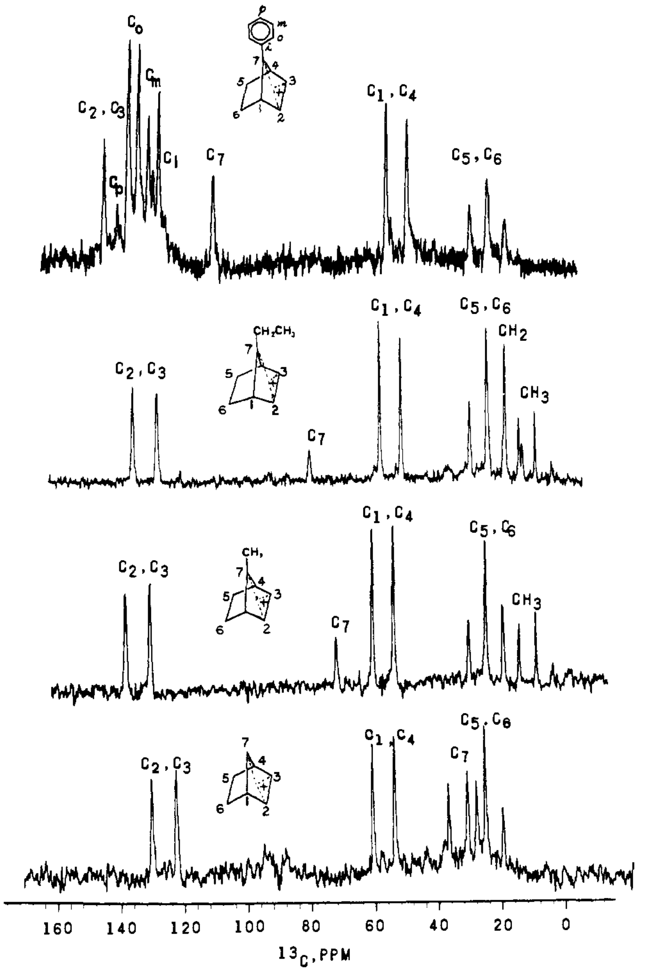
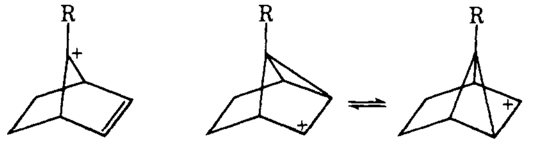


Figure 1. Proton coupled ^{13}C NMR spectra of 7-norbornenyl cations in FSO_3H-SO_2ClF at −75°.

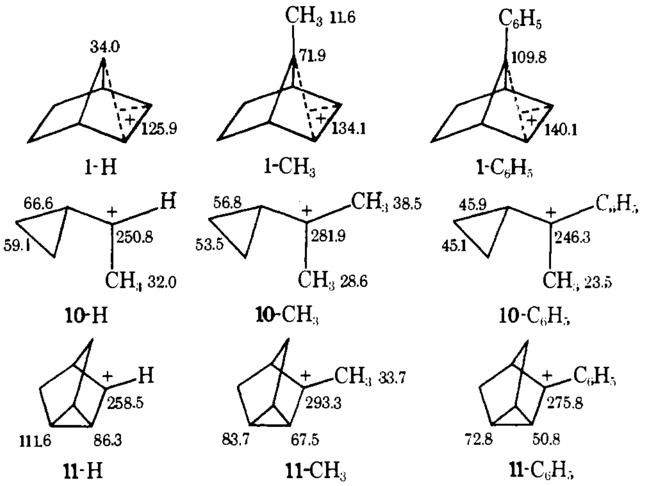
Besides the carbon resonances due to the substituents, there are four carbon resonances in the ^{13}C NMR spectra of all the 7-norbornenyl cations **1**-R. The bridge-head carbon signals (C_1 and C_4) are doublets, the methine bridge carbon signal (C_7) is a doublet in **1**-H and a singlet in the tertiary ions, the olefinic carbon signals (C_2 and C_3) are doublets, and the methylene carbon signals (C_5 and C_6) are doublet of doublets. Several interesting features are noticed in the ^{13}C NMR spectra of 7-norbornenyl cations: (a) the carbocationic centers are unusually *shielded* in both secondary and tertiary ions; (b) methyl and ethyl carbons in **1**-CH_3 and **1**-CH_2CH_3, respectively, are exceptionally shielded; (c) one-bond ^{13}C–H coupling constants at C_7 in the secondary ion **1**-H are unusually large for a trigonal carbon, likewise those at C_2 and C_3; (d) olefinic carbons (C_2 and C_3) becoming less deshielded going from secondary to tertiary ions, yet the change is small; (e) carbocationic centers in protonated ketone **1**-OH and the methylated ketone **6** are substantially more deshielded than those of other 7-norbornenyl cations.



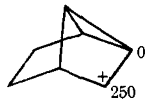
8 **9a** **9b**

The Structure of 7-Norbornenyl Cations. The extremely facile formation of 7-norbornenyl cations from their precursors indicates that these ions are stabilized by interaction involving the olefinic bonds. Static "classical" structure **8** is obviously not in accord with NMR data on the cationic species observed in superacidic solvents. The ^{13}C NMR spectroscopic data also eliminate the possibility of rapidly equilibrating ions **9a** ⇌ **9b** which would be cyclopropylcarbinyl type cations. There are by now many examples of long-lived cyclopropylcarbinyl type cations known.[17] ^{13}C NMR data for several typical examples are summarized in Scheme I in order to allow comparison between the 7-nor-

Scheme I

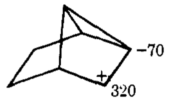


bornenyl cations and these ions. Carbocationic centers in both secondary and tertiary 7-norbornenyl cations are by more than 200 and 100 ppm, respectively, shielded than in the corresponding model cyclopropylcarbinyl type cations (**10** and **11**). We have previously reported that both secondary and tertiary cyclopropylcarbinyl **10** and 3-nortricyclyl **11** cations are of predominant *carbenium* ion nature with varied degree of charge delocalization into the cyclopropyl ring.[17] Evidently the π bond in the 7-norbornenyl cations plays an unusual role in delocalizing positive charge. Furthermore, rapidly equilibrating ions **9a** $\rightleftharpoons$ **9b** would result in averaged carbon shifts for C_2 and C_3. According to model ions, we could assume chemical shifts for C_2 and C_3 to be $\delta_{^{13}C}$ 250 and 80, respectively, in assumed static charge delocalized cyclopropylcarbinyl type structures **9a** or **9b**. The averaged values for C_2 and C_3 would be $\frac{1}{2}(250 + 80) = 165$ ppm which is 40 ppm from the experimental value for **1**-H. Using a value of $\delta_{^{13}C}$ 250 for C_2 and in order to be in agreement with the observed averaged shift, C_3 should have chemical shift of about $\delta_{^{13}C}$ 0, which clearly is not acceptable. Thus, both static and rapidly equilibrating carbenium ion-like structures for 7-norbornenyl cations must be ruled out.[3]



$\frac{1}{2}(250 + 0) = 125$

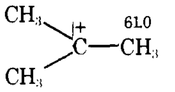
static with
charge delocalization



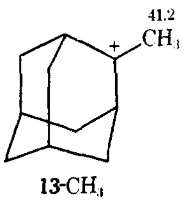
$\frac{1}{2}(320 + (-70)) = 125$

static without
charge delocalization

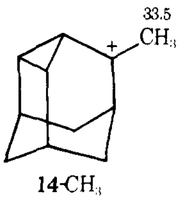
Methyl groups directly attached to carbenium ion centers generally experience substantial inductive deshielding effect from the neighboring electron deficient centers, causing substantial charge delocalization. For example, the methyl carbons in the *tert*-butyl cation (**12**-CH_3),[18] dimethylcyclopropyl (**10**-CH_3),[17] and 3-methyl-3-nortricyclyl (**11**-CH_3)[17] cations show resonances at $\delta_{^{13}C}$ 61.0, 28.6 (and 38.5), and 33.7, respectively. Going from these carbenium ions to the 7-norbornenyl cations (i.e., **1**-CH_3), the methyl carbon resonance is at $\delta_{^{13}C}$ 11.6. Further examples are seen in 2-methyl-2-adamantyl (**13**-CH_3),[19] 2-methyl-8,9-dehydro-2-adamantyl (**14**-CH_3),[20] 5-methyl-2,4-dehydrohomoadamantyl-2 (**15**-CH_3),[21] cations.



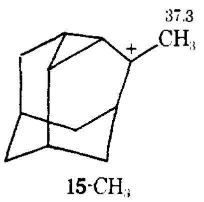
12-CH_3



13-CH_3



14-CH_3



15-CH_3

The 7-methyl-7-norbornenyl cation (**1**-CH_3), although a tertiary ion, also displays unusual charge delocalization similar to the parent secondary ion **1**-H. The 7-phenyl-7-norbornenyl cation (**1**-C_6H_5) is also showing similar behavior although the olefinic carbons (C_2 and C_3) are becoming more deshielded than those in **1**-H and **1**-CH_3.

In addition to the unusually shielded carbocationic center (i.e., C_7) in the 7-norbornenyl cations, consideration of the one-bond J_{CH} coupling is also significant. $J_{^{13}C\text{-}H}$ in the secondary 7-norbornenyl cation is 218.9 Hz which is considerably larger than the corresponding coupling observed in secondary carbenium ions, such as the isopropyl (169 Hz),[18] methylcyclopropylcarbinyl[17b] (165.0 Hz), 3-nortricyclyl (182.8),[17a] and 2,4-dehydro-5-homoadamantyl (174.6 Hz)[21] cations. Likewise, the olefinic carbons (C_2 and C_3) show unusually large coupling constants (~190 Hz) in all secondary and tertiary 7-norbornenyl cations. Substitution at C_7 does not apparently much affect their magnitude. Interaction between the carbocationic 2p orbital and the π bond is thus essentially the same in both secondary and tertiary ions.

Based on both carbon chemical shift data and coupling constants, we conclude that 7-norbornenyl cations are best represented as nonclassical carbonium ions involving delocalized two-electron, three-center bonded structures (shown by the triangular dotted lines) **1**-R.[2,13]

Through our continuing investigation of stable carbocations, particularly relating their charge delocalization, it became apparent that two distinct, limiting classes of carbocations exist, namely (1) trivalent ("classical") carbenium ions, the structure of which in valence bond terms can be described by using only conventional two-electron,two-center bonds, and which contain an sp^2 hybridized electron deficient carbon center, and (2) "nonclassical" carbonium ions, the structure of which in valence bond terms cannot be described utilizing only two-electron, two-center bonds, but also necessitates two-electron, three- (or multi-) center bonds.[2] 7-Norbornenyl cations are considered of nonclassical carbonium ion nature in order to explain the observed ^{13}C NMR data showing exceptionally shielded carbocation centers and large $J_{C\text{-}H}$ coupling constants. Other nonclassical carbonium ions, including the 2-norbornyl, 7-norbornadienyl, and cyclopropylcarbinyl cations as well as pyrimidal cations are known from the work of Masamune,[22] Hart,[23] and Hogeveen,[24] as well as our joint studies with Schleyer.[25] Charge delocalization between the electron-deficient center and neighboring groups (π, n, or σ donor nature) always results in dispersion of positive charge. Whereas bridging is not the only mechanism by which charge delocalization can occur, with suitably oriented π or σ bonds in geometrically favorable system formation of nonclassical carbonium ions can take place.[2] When the degree of charge delocalization is limited, carbocationic centers would retain their sp^2-like planar (or close to planar) configuration in accordance with predominant carbenium ion nature. When extensive overlap takes place between the empty p orbital and a suitable enriched π bond, as in the case of 7-norbornenyl cations, nonclassical ions are formed under long-lived ion conditions. It is thus apparent that there always exists a continuum of electron delocalization in carbocations[17] and definition of limiting cases, i.e., carbenium and carbonium ions, should only be considered in this context. It is also useful to recall that *hyperconjugation* is best defined as the overlap interaction of an appropriately oriented σ bond 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 complete formation of a fully delocalized three-center, two-electron bond (*σ bridging*).

Experimental Section

Materials. The precursor 7-norbornenyl derivatives **4**-R (R = H, CH_3, C_2H_5, C_6H_5) and **5** employed in this work were prepared according to literature procedures.[15,16]

Preparation of Ions. All 7-norbornenyl cations were prepared by the methods previously described by adding a solution of the corresponding alcohols **4**-R (R = H, CH_3, C_2H_5, C_6H_5) or ketone **5** in

SO_2ClF to a solution of FSO_3H in SO_2ClF at −78° to prepare an about 10 mol % solution of the ion.

^{1}H and ^{13}C Nuclear Magnetic Resonance Spectroscopy. ^{1}H NMR spectra of 7-norbornyl cations were obtained using a Varian Associates Model A56/60A NMR spectrometer equipped with a variable-temperature probe.

Carbon-13 NMR spectra were obtained on a Varian XL-100 NMR spectrometer equipped with a broad band proton decoupler, a Fourier transform accessory, and a variable-temperature probe. A continuous wavelength mode, pause delay (3.5 μsec), and pause width (35 μsec) were used. The need to provide multichannel excitation over the region of interest (10,000 Hz) limited the data acquisition time to 0.4 μsec. The number of spectra accumulated varied between 2000 and 5000, depending on ion concentration. A Varian 620L computer was used to accumulate data. Fourier transformation of the accumulated free induction signals gave the frequency spectrum, from which the chemical shifts relative to the external Me_4Si (capillary) signal ($\delta_{^{13}C}$ 0.0) were obtained. Multiplicities and coupling constants were obtained directly from the proton coupled ^{13}C NMR spectra.

Accuracies of the coupling constants (J_{CH}, ^{13}C NMR Hz) were determined by calibration to the measured J_{CH} value (118.5 ± 0.5 Hz) of the Me_4Si signal (5% ^{13}C enriched). Coupling constants of the parent ion **1**-H were also obtained from the spectrum of 7500 Hz sweep width, thus allowing higher accuracy. The variation of J_{CH}'s so obtained with 7500 Hz sweep compared with those obtained with 10,000 Hz sweep which was, however, small and the accuracy of the coupling constants are estimated as ±1.5 Hz.

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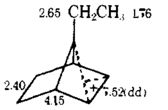

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