Stable Carbonium Ions. XCI.[1] Carbon-13 Nuclear Magnetic Resonance Spectroscopic Study of Carbonium Ions

George A. Olah and Anthony M. White[2]

Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. *Received April 1, 1969*

Abstract: ^{13}C nmr spectra have been obtained for a wide range of stable carbonium ions using the indor method. The normal substituent parameters appear to operate for the ions $(CH_3)_2{}^{13}C^+X$; $X = C_2H_5$ is at lowest field ($\delta_{^{13}\mathrm{CS_2}} = -139.2$) followed by $X = CH_3$ and $X = H$, the incremental ^{13}C shifts being 3.8 and 10.4 ppm, respectively. ^{13}C shifts for the ions $X = c\text{-}C_3H_5$, $X = C_6H_5$, and $X = OH$ show that hydroxyl and phenyl are similar in their abilities to delocalize the positive charge, both being considerably more effective than cyclopropyl. Di- and trihydroxycarbonium ions show the expected trend to higher field whereas the reverse is found for di- and triphenylcarbonium ions. This is interpreted in terms of the nonplanar character of the triphenylcarbonium ion. Scrambling of the ^{13}C label in the case of the isopropyl cation was found, indicating a protonated cyclopropane intermediate. In an extension of these results to the elucidation of carbonium ion structures, ^{13}C resonance is shown to be a powerful method for differentiating between bridged and equilibrating open-chain carbonium ions. The dimethylisopropyl-, dimethyl-*t*-butyl-, and methylethylcarbonium ions and the cyclopentyl cation are shown by this method to be rapidly equilibrating degenerate ions while the ethylenebromonium and ethylene-*p*-anisonium ions are shown to have the bridged structure. The norbornyl cation was found to be bridged, the results being consistent with a corner-protonated nortricyclene structure for the ion. σ delocalization is less pronounced but is still present in the 2-methylnorbornyl cation. It is essentially absent in the 2-phenylnorbornyl cation. ^{13}C spectra for the tetramethylethylenebromonium ion suggest that the bridged and open-chain ions have comparable stabilities or that partial bridging occurs.

Considerable data are now available on the proton magnetic resonance spectra of stable carbonium ions; however only a few studies of ^{13}C shifts in such ions have been reported. We have previously reported the ^{13}C chemical shifts of the electron-deficient carbon in protonated carboxylic acids and oxocarbonium ions.[3] The ^{13}C spectrum of trihydroxycarbonium ion (protonated carbonic acid) has been discussed and the shift compared to that of the sp^2 carbon atom in methyldihydroxycarbonium ion (protonated acetic acid), dimethylhydroxycarbonium ion (protonated acetone), and trimethylcarbonium ion (*t*-butyl cation) as well as their uncharged precursors.[4] A linear correlation of these shifts with calculated π-electron densities was found, the dependence being 360 ppm per electron.[4]

In other ^{13}C studies of positive ions, the ^{13}C spectra of the *t*-butyl cation,[5] the triphenylcarbonium ion,[6] the 2,4,6-trimethylbenzenonium ion,[7] and the tetramethylcyclobutenium dication[8] have been reported. The changes in ^{13}C shifts on protonation of amino acids[9] and a number of nitrogen heteroaromatic compounds have been discussed.[10,11] The ^{13}C shifts in protonated hydrogen cyanide,[12] acetonitrile,[12] diprotonated urea,[13] and protonated formaldehyde[14] have also been reported previously.

In addition to the above studies, proton–carbon spin–spin coupling constants in diphenylcarbonium ion,[15] isopropyl cation,[15] and 2,4-di-*t*-butyl-6-methylbenzyl cation[15,16] have been determined and show a close linearity with the s character of the C–H bond. This is in apparent contrast to the coupling constant in the cyclopropenium ion.[17]

In view of the large number of stable cations which can now be conveniently studied in solution we felt that a study of the ^{13}C spectra of some representative examples of these ions would lead to a greater understanding of the factors which determine ^{13}C chemical shifts and proton–carbon coupling constants in carbonium ions and to a more detailed knowledge of their structure and of the distribution of the unit positive charge.

The results obtained in this study are most conveniently presented in two parts. In the first part we will discuss carbonium ion ^{13}C data for ions whose structure is well established from previous work and examine the effect of substituents and hybridization on the ^{13}C chemical shifts and carbon–hydrogen coupling constants. These data are then applied in the second part in which we examine the results obtained for the ^{13}C spectra of ions whose structure is less well established. These ions are, in general, cases in which the possibility exists for the ion to be either a single bridged species or two or more rapidly equilibrating degenerate ions and we will show that the ^{13}C spectra of such ions enables, in many cases, a clear distinction between these two possibilities to be made. The application of this approach to the norbornyl, 2-methylnorbornyl, and 2-phenylnorbornyl

---

(1) Part XC: J. M. Bollinger and G. A. Olah, *J. Amer. Chem. Soc.*, **91**, in press.

(2) Postdoctoral Research Investigator.

(3) G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **89**, 7072 (1967).

(4) G. A. Olah and A. M. White, *ibid.*, **90**, 1884 (1968).

(5) G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. J. Bastien, *ibid.*, **86**, 1360.

(6) G. A. Olah, E. B. Baker, and M. B. Comisarow, *ibid.*, **86**, 1265 (1964).

(7) (a) V. A. Koptyug, I. S. Isaev, and A. I. Rezukhin, *Tetrahedron Lett.*, 823 (1967); (b) V. A. Koptyug, A. I. Rezukhin, E. Lippman, and T. Pehk, *ibid.*, 4009 (1968).

(8) G. A. Olah, J. M. Bollinger and A. M. White, *J. Amer. Chem. Soc.*, **91**, 3667 (1969).

(9) W. J. Horsley and H. Sternlicht, *ibid.*, **90**, 3738 (1968).

(10) R. J. Pugmire and D. M. Grant, *ibid.*, **90**, 697 (1968).

(11) R. J. Pugmire and D. M. Grant, *ibid.*, **90**, 4232 (1968).

(12) G. A. Olah and T. E. Kiovsky, *ibid.*, **90**, 4666 (1968).

(13) G. A. Olah and A. M. White, *ibid.*, **90**, 6087 (1968).

(14) A. M. White and G. A. Olah, *ibid.*, **91**, 2943 (1969).

(15) G. A. Olah and M. B. Comisarow, *ibid.*, **88**, 361 (1966).

(16) J. M. Bollinger, M. B. Comisarow, C. A. Cupas, and G. A. Olah, *ibid.*, **89**, 5687 (1967).

(17) R. Breslow, J. T. Groves, and G. Ryan, *ibid.*, **89**, 5048 (1967).

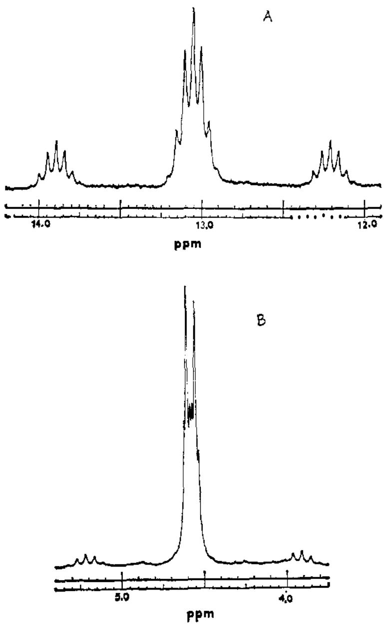


Figure 1. 100-MHz proton nmr spectrum of the isopropyl cation generated from isopropyl chloride with a 50% ^{13}C enrichment of C_1, in SO_2ClF–SbF_5 solution. The spectrum was recorded at −60°. Figure 1A shows the methine region and consists of a septuplet (J_{HH} = 5 Hz) with ^{13}C satellites 84.5 Hz on either side of the main resonance (J_{CH} = 169 Hz). Figure 1B shows the methyl region. The ^{12}C species gives a doublet in this region while the ^{13}C-labeled ions give a doublet of doublets due to the long-range CCH coupling of 3.3 Hz. Some scrambling of the ^{13}C label into the methyl groups is apparent in this spectrum giving small pentuplets 65.5 Hz on either side of the main resonance. The structure of these satellites arises from the fact that the three- and four-bond proton–proton coupling constants are similar in magnitude (5 and 6 Hz.

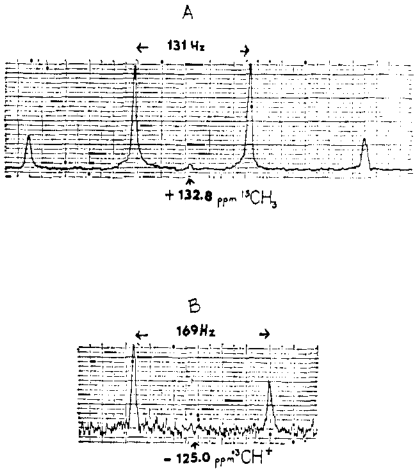


Figure 2. 25-MHz ^{13}C indor spectrum of the isorpopyl cation. The spectra were obtained at −20° by monitoring the signal intensity of the ^{13}C satellites shown in Figure 1 while sweeping the irradiating frequency. The peaks observed are the result of splitting of the satellite due to "tickling" of connected ^{13}C transitions. Figure 2A shows the quartet corresponding to the methyl ^{13}C and Figure 1B the doublet from the methine ^{13}C. The latter spectrum was obtained from the low-field ^{13}C satellite in the proton spectrum. The low-field ^{13}C transition is connected regressively and the high-field ^{13}C transition connected progressively to this transition leading to the observed asymmetry of the ^{13}C indor spectrum. This asymmetry is particularly apparent in indor spectra obtained using a low-amplitude "tickling" field.

cations was described in preliminary communications based on part of this work.[18]

A. ^{13}C Study of Carbonium Ions of Known Structure

Alkylcarbonium Ions. The ^{13}C shift of the ***t*-butyl cation,** $(CH_3)_3{}^{13}C^+$, was previously reported to be −146.5 ppm in neat SbF_5 solution.[5,19] For comparison with other alkylcarbonium ions the ^{13}C spectrum was obtained in SO_2ClF–SbF_5 solution at −20°, and a value of −135.4 ppm was found, with a long-range coupling to the methyl protons of 3.6 Hz. From the methyl ^{13}C satellites in the proton spectrum of the ion the long-range proton–proton coupling constant was found to be 3.5 Hz.

The ^{13}C shift of the **isopropyl cation,** under identical conditions, was found to be −125.0 ppm with a long-range coupling to the methyl protons of 3.3 Hz (Figures 1 and 2). The direct ^{13}C–H coupling constant was found to be 169 Hz in agreement with the value previously determined in SbF_5 solution.[15] From the ^{13}C satellite spectrum of the ion the long-range proton–proton coupling constant was found to be 6.0 Hz.

The effect of substituting the methyl group in the *t*-butyl cation by hydrogen is thus to cause an upfield shift of 10.4 ppm. The well-established relationship of ^{13}C shifts to electron density[20] leads to the conclusion that the central carbon atom in the *t*-butyl cation is slightly more positive than that in the isopropyl cation.

In alkanes, the effect of replacing hydrogen by a methyl group on the ^{13}C shifts is essentially the same as in the alkylcarbonium ions described above. In a treatment of the ^{13}C chemical shifts as a constitutive property, the replacement of methyl by hydrogen was found to consistently cause a shift to high field of 7 ppm per substitution in single bonds.[21] The factors effecting the shifts in alkanes have been discussed in terms of a valence-bond derivation of the chemical shift expression.[20d] Using this approach the effect of substitution of methyl for hydrogen can be accounted for essentially completely by the removal of electronic charge from the carbon under consideration. It is, of course, possible that the simplifying assumptions, appropriate to alkanes, are not fully applicable in the present study of carbonium ions. It is of interest to note, however, that the calculations by Hoffmann[22] using the extended Hückel theory are in agreement with the ^{13}C data for *t*-butyl and isopropyl cations. In spite of the fact that the *t*-butyl cation is calculated to be more stable than the isopropyl cation (by 4.70 eV) the charge on the central carbon atom in the *t*-butyl cation (+0.692) is more positive than in the isopropyl cation (+0.611). This difference, assuming a chemical shift dependence of 200 ppm per electron, gives a ^{13}C chemical shift difference of 16 ppm in reasonable agreement with the observed difference of 10.4 ppm.

The effect of an ethyl group on the ^{13}C shift of the carbonium ion center was found from the ***t*-amyl cation,**

---

(18) (a) G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 3954 (1969); (b) G. A. Olah, J. R. DeMember, C. Y. Lui, and A. M. White, *ibid.*, **91**, 3958 (1969).

(19) All ^{13}C chemical shifts are reported in parts per million from $^{13}CS_2$.

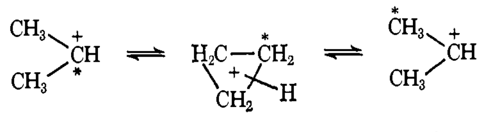
(20) (a) H. Spiesecke and W. G. Schneider, *Tetrahedron Lett.*, **14**, 468 (1961); (b) P. G. Lauterbur, *J. Amer. Chem. Soc.*, **83**, 1838 (1961); (c) *ibid.*, **83**, 1846 (1961); (d) B. V. Cheney and D. M. Grant, *ibid.*, **89**, 5319 (1967).

(21) (a) I. B. Savitsky and K. Namikawa, *J. Phys. Chem.*, **68**, 1956 (1964); (b) I. B. Savitsky, B. M. Pearson, and K. Namikawa, *ibid.*, **69**, 1425 (1965).

(22) R. Hoffmann, *J. Chem. Phys.*, **40**, 2480 (1964).

$C_2H_5C^+(CH_3)_2$. This shift was found to be −139.4 ppm, only 4 ppm to low field of the *t*-butyl cation. This is much smaller than the 17 ppm found in the case of the alkanes although the shift observed is in the same direction.

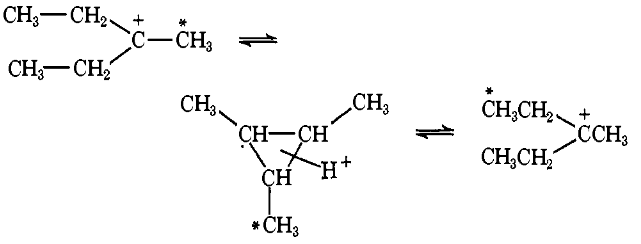
When the isopropyl cation was generated from 2-chloropropane with a 50% ^{13}C enrichment of the 2-carbon atom in $SO_2ClF-SbF_5$ solution at −78°, at −60° equilibration of the label was observed to occur, with a half-life (as determined by integration of the spectrum) of 1 hr. After several hours the label was distributed equally among the three carbon atoms. This observation confirms the interpretation of the temperature dependence of the proton spectrum of this ion in the temperature range −20 to −40° studied by Saunders[23] and his suggestion of a protonated cyclopropane being responsible for the proton scrambling mechanism.



On allowing solutions of the isopropyl cation to stand overnight at −20°, complete conversion to a mixture of hexyl cations was observed. The proton spectra of these ions has been described elsewhere.[24]

The ^{13}C spectra of the *t*-hexyl cations, **diethylmethylcarbonium ion** and the **dimethylisopropylcarbonium ion,** were obtained at −20°. The sp^2-carbon shift in the diethylmethylcarbonium ion was found to be −139.4 ppm, identical with that in the ethyldimethylcarbonium ion (*t*-amyl cation). Apparently the substituent effect on the shifts in this particular example is not additive, unlike substituent parameters observed in saturated hydrocarbons, indicative possibly of the role played by hyperconjugation in stabilizing these ions.

An interesting feature of the diethylmethylcarbonium ion is that, as in the case of the isopropyl cation, interchange of the methyl groups occurs. The equilibrium could be demonstrated by irradiation of the two equivalent methyl peaks in the proton spectrum, causing the peaks due to the methyl attached to positive carbon to rapidly decrease in intensity. On removing the perturbing field, the peak relaxed to its former intensity. This phenomenon[25] was used to confirm the assignment of the methyl shifts attached to the sp^2-carbon atom for the purpose of obtaining the ^{13}C chemical shift of this atom. The equilibration can be envisaged as involving intermediate formation of secondary carbonium ions or, more probably, a protonated cyclopropane intermediate. A scheme such as this has been proposed by Saunders to account for the temperature dependence of the proton spectrum of the related *t*-amyl cation.[26]



The ethylmethyl- and dimethylisopropylcarbonium ions are equilibrating ions and as such will be discussed in the second part of this paper.

Hydroxycarbonium Ions. The ^{13}C chemical shifts of some hydroxycarbonium ions were published in our previous work.[4] It is now possible to relate the effect of methyl substitution on the ^{13}C chemical shifts in hydroxycarbonium ions. The ^{13}C shifts of the ions are summarized in Table I. In the monohydroxycarbonium ions the effect of successivley replacing the methyl groups in protonated acetone by hydrogen is to cause a shift to higher field of 13.1 and 13.4 ppm as compared to 10.4 ppm between the *t*-butyl and isopropyl cation. In the dihydroxycarbonium ions the effect is 15.4 ppm, again to high field. The trend observed for the substitution of methyl groups by hydrogen in these ions is thus for an increased effect to be observed with decreasing positive charge at the central carbon atom. As has been reported previous, *t*-butyl cation, protonated acetone, protonated acetic acid, and trihydroxycarbonium ion as well as their uncharged precursors give a linear correlation of carbon chemical shifts with π electron charge density as calculated by a Hückel molecular orbital method.[4]

Table I. Carbonium ^{13}C Chemical Shifts of Alkyl- and Hydroxycarbonium Ions

Ion	Chemical shift[a]	Solvent[b]	Temp, °C
$(CH_3)C^+(C_2H_5)_2$	−139.4	A	−20
$(CH_3)_2C^+C_2H_5$	−139.2	A	−60
$(CH_3)_3C^+$	−135.4	A	−20
$(CH_3)_2CH^+$	−125.0	A	−20
$(CH_3)_2COH^+$	−55.7	B	−50
CH_3CHOH^+	−42.6	B	−50
H_2COH^+	−29.2	B	−50
$CH_3C(OH)_2^+$	−1.6	B	−30
$HC(OH)_2^+$	+17.0	B	−30
$C(OH)_3^+$	+28.0	B	−50
$CH_3OC(OH)_2^+$	+31.0	B	−30
$c\text{-}C_3H_5C^+(CH_3)_2$	−86.8	C	−60
$C_6H_5C^+(CH_3)_2$	−61.1	C	−60
$(C_6H_5)_2C^+H$	−5.6	C	−60
$(C_6H_5)_3C^+$	−18.1	C	−60

[a] In parts per million from $^{13}CS_2$ (shifts are for the sp^2-hybridized carbonium ion atoms). [b] A, $SO_2ClF-SbF_5$; B, $SO_2-FSO_3H-SbF_5$; C, SO_2-SbF_5.

Phenyl- and Cyclopropylcarbonium Ions. The ^{13}C chemical shifts of the sp^2 carbon in related phenyl and cyclopropyl carbonium ions was determined in order to establish the ability of the phenyl and cyclopropyl groups to stabilize an electron-deficient carbon.[27] The ^{13}C shift in cyclopropyldimethylcarbonium ion (−86.8 ppm) is 31.1 ppm to low field of protonated acetone and 38.3 ppm to high field of the isopropyl cation indicating that the ability of the cyclopropyl group to stabilize an electron-deficient carbon is approximately intermediate between hydrogen and hydroxyl. Similarly the shift in the phenyldimethylcarbonium ion, which was found to be 5.4 ppm to low field of protonated ace-

---

(23) M. Saunders and E. L. Hagen, *J. Amer. Chem. Soc.*, **90**, 6881 (1968).

(24) G. A. Olah and J. Lukas, *ibid.*, **89**, 4739 (1967); **90**, 933 (1968).

(25) R. A. Hoffman and S. Forsen, "Progress in Nuclear Magnetic Resonance Spectroscopy," Vol. 1, J. W. Emsley, J. Feeney, and L. H. Sutcliffe, Ed., Pergamon Press, Long Island City, N. Y., 1966, p 15.

(26) M. Saunders and E. L. Hagen, *J. Amer. Chem. Soc.*, **90**, 2436 (1968).

(27) The proton spectra and method of generation of these ions have been described previously: C. U. Pittman and G. A. Olah, *ibid.*, **87**, 2998 (1965); G. A. Olah, *ibid.*, **86**, 932 (1964).

tone, indicates phenyl to be slightly less effective than hydroxyl but substantially more effective than cyclopropyl in stabilizing a carbonium ion center.[28] In the diphenylcarbonium ion this relative order is maintained, the ^{13}C shift being 22.6 ppm to low field of protonated formic acid in which both phenyl groups are now replaced by hydroxyl. Comparing these shifts with the previously reported[6] shift of the triphenylcarbonium ion reveals the surprising result that the latter is 12.5 ppm to low field of the diphenylcarbonium ion, and 46.1 ppm to low field of the trihydroxycarbonium ion. Again assuming that these differences can be related to differences in charge density on the carbon under consideration, this result would indicate that there is a slightly higher positive charge on the carbonium carbon in the triphenylcarbonium ion than in the diphenylcarbonium ion. This is in contrast to stability data obtained from the ionization constants of the corresponding alcohols.[29] We suggest that the explanation for this observation is that the replacement of hydrogen by phenyl in the diphenylcarbonium ion reduces the conjugative interaction of the phenyl rings with the electron-deficient carbon due to the rings being twisted out of the plane—the effect being large enough to result in three phenyl groups being less effective than two in delocalizing the positive charge. This would be qualitatively in agreement with the conclusions reached by Deno[29] that the resonance energies of diphenyl- and triphenylcarbonium ions are similar, the differences in pK_R values of 6.7 being the result of release of steric strain on ionization in the case of the triphenylcarbonium ion.

The approach described above neglects the contribution of neighboring group anisotropies and the phenyl ring current to the chemical shift; however, the contributions will be small[20d] and the shifts observed undoubtedly will reflect to a large degree the effect of the substituent on the charge distribution in these ions.

sp-Hybridized Carbon. Protonated Nitriles and Oxocarbonium Ions. The ^{13}C shifts in protonated nitriles and oxocarbonium ions containing sp-hybridized carbon have been previously reported and are summarized in Table II.

The observation that protonation of nitriles causes a 10-ppm shift to high field is consistent with the effect on the α-C chemical shift in N heteroaromatics on protonation.[10,11] The upfield shift was attributed in these examples to bond order changes and it is reasonable to suppose that the same effect will be operative in the nitriles studied. We feel that the fact that the oxocarbonium ions are deshielded from the isoelectronic protonated nitriles is indicative of a lower charge density on carbon in the former ions. This would be consistent with the calculations using a NEMO method[30] for the methyloxocarbonium ion which indicated that the positive charge is carried by the sp-hybridized carbon and the methyl protons, both oxygen and methyl carbon bearing a slight negative charge.

Methyl ^{13}C Shifts. The methyl ^{13}C shift appears primarily to reflect the charge on the carbon atom and gives linear relationships with substituent electronegativity in substituted methanes.[31] We have determined the methyl ^{13}C shifts in a number of carbonium ions and the results are presented in Table III. It can be seen that the methyl shifts in alkylcarbonium ions occur at lowest field and in dihydroxycarbonium ions at highest field, monohydroxycarbonium ions being intermediate between these extremes. The methyl shift thus reflects the changing charge density of the adjacent, electron-deficient carbon although the effect on the ^{13}C shifts is highly attenuated. Within each of these categories, the substitution of methyl for hydrogen causes an upfield shift of the ^{13}C methyl resonance: 13.5 ppm in the case of alkylcarbonium ions (*t*-butyl and isopropyl cations) and 5.5 ppm in the case of monohydroxycarbonium ions (protonated acetone and protonated acetaldehyde). Interestingly, the observed order of methyl shifts in the *t*-butyl and isopropyl cations are predicted from Hoffmann's calculations described previously,[22] the charge density on the methyl carbons in the isopropyl cation (0.310) being 0.026 unit more positive than in the *t*-butyl cation (−0.336). Thus in this case the methyl carbon charge densities appears not to reflect the charge density on the adjacent electron-deficient carbon. In the carbonium ions studied containing two heteroatom

Table II. ^{13}C Chemical Shifts in sp-Hybridized Carbonium Ions

Ion	Chemical shift[a]	Uncharged model	Chemical shift
HCN^+H	−95.7	HCN	+83.7
CH_3CNH^+	+85.0	CH_3CN	+75.0
CH_3CO^+	+44.3		
$CH_3CH_2CO^+$	+44.1		
$C_6H_5CO^+$	+40.0		

[a] In parts per million from $^{13}CS_2$ for the sp carbon.

Table III. Methyl ^{13}C Chemical Shifts[a] and Coupling Constants in Methylcarbonium Ions

Ion	Solvent[b]	Temp, °C	$\delta_{^{13}C}$	$J_{^{13}CH}$
$(\mathit{CH}_3)_2CH^+$	A	−20	132.8	132.0
$(\mathit{CH}_3)_3C^+$	C	+30	146.3	132.0
$(\mathit{CH}_3)_2C^+C_2H_5$	C	−40	150.1	132.0
$(\mathit{CH}_3)_2CHC^+(CH_3)_2$	A	−20	151.8	132.0
CH_3CHOH^+	C	−40	159.4	132.7
$(\mathit{CH}_3)_2COH^+$	C	−40	162.0	132.0
			163.3	132.5
$(\mathit{CH}_3)_2\overset{+}{C}\text{-}c\text{-}C_3H_5$	C	−60	165.5	132.0
Tetramethylethylene-bromonium	C		168.0	132.5
$\mathit{CH}_3C^+(OH)(OCH_3)$	C	−20	173.3	134.8
$\mathit{CH}_3C(OH)_2^+$	C	−50	173.6	134.0
$\mathit{CH}_3C^+(OH)(NH_2)$	C	0	174.3	133.7
$\mathit{CH}_3C(OCH_3)_2^+$	C	−20	176.7	134.9
CH_3CO^+	C	−20	187.1	147.0
$\mathit{CH}_3OH_2^+$	C	−20	131.7	157.5
$(\mathit{CH}_3O)_2C^+CH_3$	C	−20	132.4	155.6
			133.5	155.2
$(\mathit{CH}_3O)C^+(CH_3)(OH)$	C	−20	132.6	155.8

[a] Referred to $^{13}CS_2$ as standard (shifts are for the methyl groups italicized). [b] See Table I.

---

(28) The opposite conclusions was reached by Deno: N. C. Deno, H. G. Richey, and J. O. Turner, *J. Amer. Chem. Soc.*, **87**, 4533 (1965).

(29) N. C. Deno and A. Schriesheim, *ibid.*, 77, 3051 (1955).

(30) F. P. Boer, *ibid.*, **88**, 1572 (1966); **90**, 6706 (1968).

(31) J. B. Stothers, *Quart. Rev.* (London), **19**, 144 (1965), and references therein.

electron donors, the methyl shift is essentially constant, suggesting that the charge density has reached a "saturation" value. Comparisons with the uncharged precursors to these ions (Table IV) show that within this group little, if any, change occurs on protonation. This is consistent with the interpretation of the α-carbon shifts on protonation of amino acids where a small upfield shift has been observed.[9] Also it has been found that ionization of acetic acid causes a 3.0-ppm downfield shift of the methyl ^{13}C resonance. These experimental observations were considered consistent with the self-consistent field theory predictions of charge transmission in NH_4^+ and H_3O^+, from the hydrogens in NH_3 and H_2O through the nitrogen and oxygen to the added proton.[9] The electronic charge densities of nitrogen and oxygen remain constant or increase upon protonation.

Table IV. Methyl ^{13}C Chemical Shifts and Coupling Constants in Precursors to Methylcarbonium Ions

Compound	$\delta_{^{13}C}$[a]	J_{CH}	Ref
$(\mathit{CH}_3)_2C{=}CH_2$	170.4	125.3	
CH_3CHO	164.7	128	b
$(\mathit{CH}_3)_2CO$	169.6	133	b
CH_3COOH	174.8	132.5	c
CH_3CONH_2		128.4	
CH_3COOCH_3		129.2	
CH_3CN	189.6	134	b
CH_3OH	146.3	141	c
CH_3OCH_3	134.5	140.0	
CH_3OOCCH_3		146.0	

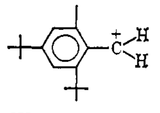
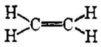
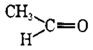
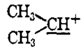
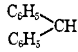
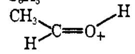
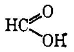
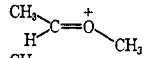
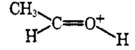
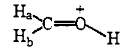
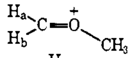
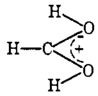
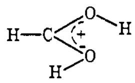
[a] In parts per million from $^{13}CS_2$ (shifts are for the methyl groups in italics). [b] H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 722 (1961). [c] G. B. Savitsky and K. Namikawa, *J. Phys. Chem.*, **67**, 2430 (1963).

In dihydroxycarbonium ions the same effect is observed as in protonated methylamine and the acetate anion, that is, the changes in the over-all charge upon protonation or ionization affect significantly only the proton charge densities and the charge density at the carbonyl carbon atom. In the monohydroxy- and alkylcarbonium ions, the strongly electronegative nature of the methyl substituent leads to the protons being no longer able to accommodate the positive charge, leading to a reduction in charge density at the methyl carbon.

In contrast to the observation that protonation of methylamine causes an upfield shift in the methyl resonance[9] we find that in methanol, on protonation, the methyl resonance shifts to low field. We find, however, that the shift in protonated methanol is virtually identical with that in dimethoxycarbonium ion and in protonated methyl acetate (Table III). The shift is also very close to that found in dimethyl ether (134.9 ppm) suggesting that in fact little or no change in charge density is occurring on protonation but that the shift in methanol (neat liquid) is anomalous due, most probably, to association.

Direct Carbon–Hydrogen Coupling Constants. The hyperfine contact interaction term, determining the carbon–hydrogen coupling mechanism, is sensitive not only to bond hybridization but also to bond polarization, variations in the carbon–hydrogen bond distance, and variations in the mean excitation energy.[32] In spite of only slight variations in hybridization as indicated by the bond angle data, the coupling constant in formyl compounds increases from 172 Hz in formaldehyde to 268.4 Hz in formyl fluoride.[33] A significant part of this increase is due to changes in the effective nuclear charge. This effect would be expected to increase on protonation, and this is indeed observed (Table V).

Table V. ^{13}C–H Coupling Constants in Carbonium Ions

Ion	J_{CH}, Hz	Uncharged model	J_{CH}, Hz
	169.0[a]		156.2[b]
			173.9[c]
	169.0		
	164.0		
	*Ca.* 203.0		225.1[c]
	190.0		
	193.3		
	198.4 (H_a) 209.8 (H_b)		
	195.0 (H_a) 210.0 (H_b)		
	235.8		
	244.8		
$HC\equiv\overset{+}{N}-H$	320.0		269.0[d]

[a] References 15 and 16. [b] D. M. Graham and C. E. Holloway, *Can. J. Chem.*, **41**, 2114 (1963). [c] SO_2 solution, −20°. [d] Reference 12.

The increase in the three protonated formyl compounds studied varies between 11 and 38 Hz. Evaluation of these increases in terms of the electronic properties of the groups in these ions is complicated by the fact that the magnitude of the carbon–hydrogen coupling constant is dependent on the orientation of the carbon–hydrogen bond with respect to the hydroxyl proton. This effect has been suggested to be due to interaction of the oxygen lone pair with the antisymmetric carbon–hydrogen bonding orbital.[14]

In view of the increases observed in coupling constants on protonation of formyl compounds it is surprising that the coupling constant observed in the isopropyl cation is only 12 Hz higher than that in ethylene. The effective nuclear charge term should differ significantly in the isopropyl cation, as compared to ethylene. The fact that the coupling constant is similar suggests that factors additional to hybridization and bond polarization are operative in this ion. A decrease in the

---

(32) D. M. Grant and W. M. Litchman, *J. Amer. Chem. Soc.*, **87**, 3994 (1965).

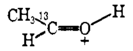
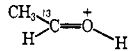
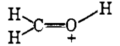
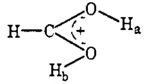
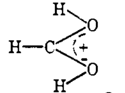
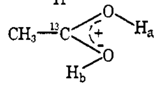
(33) Muller regards bond angle data to be misleading in this context since observed bond angles can differ from interorbital angles: N. Muller, *J. Chem. Phys.*, **36**, 359 (1962).

s character associated with the carbon–hydrogen bond and/or an increase in the bond length, counterbalancing the effect of nuclear charge, might be responsible for the magnitude of the coupling constant observed. Certainly both these factors might be expected to be operative in this ion but their magnitude is unknown. Unfortunately, attempts so far to isolate this ion in order to determine its structure by X-ray analysis have been unsuccessful.

No significant increase in the methyl C–H coupling constants is observed on protonation in spite of the highly polarizing nature of methyl substituent (see Tables III and IV). There are some exceptions to this observation and these occur in compounds in which the carbon is directly attached to a heteroatom. In methanol the increase is 11 Hz while in methylamine the increase is only 7 Hz.[9] Hydrogen cyanide provides an example of a proton attached to sp-hybridized carbon and in this case an increase of 51 Hz in the J_{CH} coupling is observed on protonation.

Long-Range Carbon–Hydrogen Coupling Constants. A correlation of ^{13}C–C–H coupling constants with C–C bond hybridization has been proposed and average values of 4.0, 5.9, and 10.6 Hz have been reported for sp^3, sp^2, and sp hybridization, respectively.[34] With the exception of the *t*-butyl and isopropyl cation, the J_{CCH} coupling constants observed follow this trend (Table VI). The sp^2-hybridized carbonium ions studied have values of 6.1–7.0 Hz and the sp-hybridized carbonium ions 9.3–9.8 Hz. While correlations of this kind are of somewhat questionable value,[35] the low values for the *t*-butyl and isopropyl cations could raise the question of the planarity of these ions. Evidence presented based on carbon chemical shifts and direct C–H coupling constants as well as Raman spectral studies of alkylcarbonium ions, including the *t*-butyl cation, however, leaves little doubt that alkylcarbonium ions are planar[36] and that factors other than hybridization must be responsible for the low value of the long-range carbon–proton coupling constant.

Table VI. Long-Range Coupling Constants in Carbonium Ions

Ion	J_{CCH}, Hz	J_{COH}, Hz
$(CH_3)_2{}^{13}CH^+$	3.3	
$(CH_3)_3{}^{13}C^+$	3.6	
$(CH_3)_2{}^{13}C^+OH$	7.0	6.5
	*a*	0.0
	6.1	7.9
		8.7[b]
		8.2 (H_a) 0.5 (H_b)
		0.5
	6.5	7.5 (H_a) 0.5 (H_b)
$CH_3{}^{13}CO^+$	9.3	
$CH_3CH_2{}^{13}CO^+$	9.3	
$CH_3{}^{13}CNH^+$	9.8	

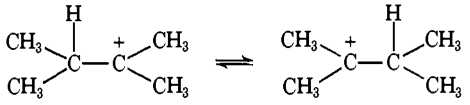
[a] Could not be determined in this isomer. [b] Shown to be negative (see ref 14).

As observed in an earlier paper in this series, the long-range COH coupling constants in hydroxycarbonium ions are very dependent on geometry. In protonated carboxylic acids, the near zero coupling is associated with the proton *cis* to the methine or methyl group. In protonated acetaldehyde the near zero coupling is associated with the isomer in which the hydroxyl proton is *cis* to the methyl group. Some rationale for these differences can be found in the molecular orbital theory approach to the magnitude of CCH coupling constants.[35b]

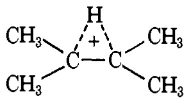
B. ^{13}C Study of Equilibrating or Bridged Carbonium Ions

In the previous part we have established the effect of substituents on the carbon shift of the electron-deficient carbon and the effect of forming a carbonium ion center on adjacent carbon shifts. In this section we will discuss how these parameters can be used to investigate the structure of carbonium ions in which the possibility exists for degenerate rearrangements to occur which are fast with respect to the nmr time scale and which lead to average shifts and coupling constants being observed in both the carbon and proton spectra. An example of such an ion is the **dimethylisopropylcarbonium ion** which is one of the hexyl cations formed on dimerization of the isopropyl cation (*vide supra*).

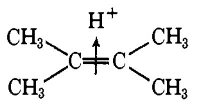
The proton spectrum, in which all four methyl groups are equivalent, does not allow a clear distinction to be made between a rapidly equilibrating pair of ions **1** or a static ion (which may be formulated as involving hydrogen bridging, **2**, or a π complex, **3**).[24]



1



2



3

The ^{13}C shift observed for the two central carbons in this ion is −3.4 ppm and the indor spectrum consists of a doublet (J_{CH} = 65 Hz). If the ion is a rapidly equilibrating pair of ions, the observed shift will be the average of the shifts in the two sites. A good model for estimating these shifts is the methyl ^{13}C shift and the central ^{13}C shift in the *t*-butyl cation. The average of these shifts is 6.2 ppm. The effect of the two additional methyl groups would be expected to decrease slightly both shifts from those in the model compound, as discussed previously, and thus the predicted and observed shifts for the rapidly equilibrating pair of ions are

---

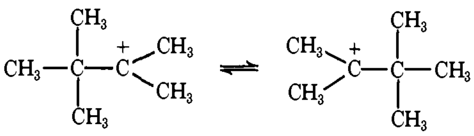
(34) (a) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press, Long Island City, N. Y., 1966, p 1027; (b) H. Dreeskamp and E. Sackman, "Nuclear Magnetic Resonance in Chemistry," B. Pesce, Ed., Academic Press, New York, N. Y., 1965, p 143.

(35) (a) G. J. Karabatsos and C. E. Orzech, *J. Amer. Chem. Soc.*, **86**, 3574 (1964); (b) K. A. McLauchlan and T. Schaeffer, *Can. J. Chem.*, **44**, 321 (1966).

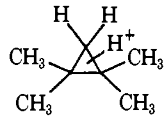
(36) G. A. Olah, A. Commeyras, J. R. DeMember, and J. L. Bribes, submitted for publication.

in excellent agreement. The coupling constant can be estimated, again using the *t*-butyl cation as a model compound, from the direct and long-range C–H coupling constants. The average of these values (assuming the long-range coupling to be negative as is usual in three-bond CCH coupling) is 64 Hz, again in excellent agreement with the observed value. While precise estimates of the shifts and the coupling constants in the two static formulations for this ion (see, however, later discussion of ions which adopt the bridged structure) cannot be made, the agreement of both the coupling constant and chemical shift with those predicted for the rapidly equilibrating ion are so good as to leave little doubt as to the nature of this ion. (Raman spectroscopic study of the ion also confirms this conclusion.[36])

Dimethyl-*t*-butylcarbonium Ion (Triptyl Cation). The dimethyl-*t*-butylcarbonium ion in FSO_3H–SbF_5–SO_2 solution has a proton nmr spectrum[24] consisting of a single resonance at δ 2.90. This chemical shift was considered indicative of a rapidly equilibrating structure **4** rather than the bridged structure **5**. The fact that only a single proton resonance is observed does not enable these structures to be distinguished since in the protonated cyclopropane structure equilibration of the methyls *via* the two classical ions as intermediates would be expected to occur. As in the case of the dimethylisopropylcarbonium ion we anticipated that the ^{13}C spectrum of this ion would provide additional evidence for its structure. The ion was generated from 2,3,3-trimethyl-2-butanol, with 56% ^{13}C enrichment at C_2, in FSO_3H–SbF_5–SO_2 solution. The proton spectrum consisted of a single peak at δ 2.90, the long-range coupling of the methyl protons to the ^{13}C being unresolved. A slight enhancement of this singlet was observed on irradiation of the ^{13}C nucleus enabling the ^{13}C chemical shift to be obtained.[37] The value of this shift, −11.5 ppm, is consistent only with the rapidly equilibrating structure. The chemical shift for this structure would be expected to be to low field of that observed in the dimethylisopropyl cation due to the additional methyl group deshielding and this is indeed found, the shift difference between the two ions being 8.1 ppm. The norbornyl cation (*vide infra*) provides a model for the methyl-bridged formulation of the ion. Although different equilibria are involved in the norbornyl cation and ion **5**, a shift of at least 100 ppm to high field of that actually observed can be estimated. The near-zero coupling between the methyl protons and the ^{13}C is also revealing. Since this ion is equilibrating, the observed coupling will be the average of the two- and three-bond proton–carbon coupling constants. The two-bond coupling constant in the *t*-butyl cation is 3.6 Hz and a similar value would be expected in this ion. For the observed coupling constant to be zero, the three-bond coupling must therefore have the same magnitude but opposite sign. Although the signs of only a few such couplings have been determined, such a sign alternation has been reported, the two-bond coupling being negative and the three-bond coupling positive.[38] It is of interest to note that this is a second example of a sign determination by investigation of a rapidly equilibrating system, the first example being the three- and four-bond proton–proton coupling constants in the related *t*-amyl cation.[25]

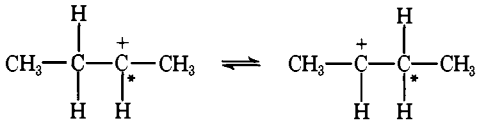


4



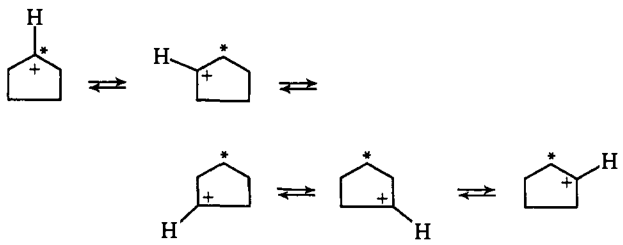
5

Ethylmethylcarbonium Ion (*sec*-Butyl Cation). The *sec*-butyl cation can be generated from *sec*-butyl chloride in SO_2ClF–SbF_5 solution at −78° without appreciable rearrangement to the *t*-butyl cation. The proton spectrum at −120° consists of two resonances at δ 3.2 and 6.7 of relative area 2:1. This is a result of a degenerate 1,2-hydride shift which at this temperature is fast with respect to the nmr time scale.[39]



The ^{13}C indor spectrum of the two central carbons (obtained in natural abundance) was found to be a quartet at 21.2 ppm with a carbon–hydrogen coupling constant of 70 ± 2 Hz. Using the shifts observed in the dimethylisopropyl- and dimethyl-*t*-butylcarbonium ions as models for the effect of methyl substitution in equilibrating ions (8 ppm) leads to a predicted shift of 13 ppm in reasonable agreement with the observed value. Using the isopropyl cation as a model gives an estimated coupling constant of 72 Hz. As in the two previous examples, the ^{13}C evidence clearly demonstrates that the *sec*-butyl cation is an equilibrating "classical" rather than a bridged "nonclassical" carbonium ion.

Cyclopentyl Cation. The proton spectrum of this ion in SbF_5–SO_2ClF solution at −70° consists of a singlet at δ 4.68. The ^{13}C satellites from this peak show a J_{CH} coupling constant at 28.5 Hz and have an intensity five times that normally observed. This is a result of the degenerate rearrangements that occur in this ion which, on the nmr time scale, leads to complete equilibration of the nine protons around the five carbon atoms. The ^{13}C indor spectrum is a ten-line multiplet at 95.4 ppm with a coupling of 28.5 Hz (Figure 3). This shift and coupling constant can be estimated from model compounds. The coupling constant will be the average of one sp^2- and four sp^3-carbon–



---

(37) From the decrease in line width on irradiation, the proton–carbon coupling was estimated to be about 0.2 Hz.

(38) (a) G. J. Karabatsos, J. D. Graham, and F. M. Vane, *J. Amer. Chem. Soc.*, **84**, 37 (1962); (b) G. Govil, *J. Chem. Soc., A*, 1420 (1967).

(39) M. Saunders, E. L. Hagen, and J. Rosenfeld, *J. Amer. Chem. Soc.*, **90**, 6882 (1968).

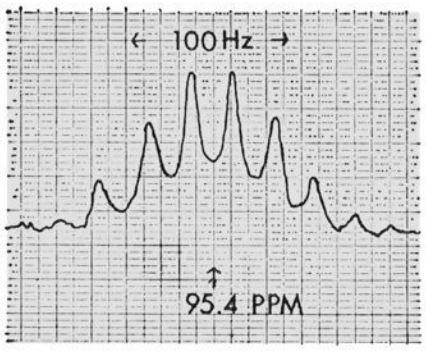
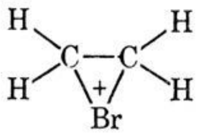


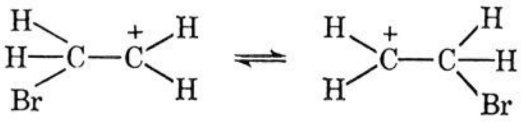
Figure 3. 25 MHz ^{13}C indor spectrum of the cyclopentyl cation obtained in natural abundance from cyclopentyl chloride in $SO_2ClF-SbF_5$ solution. The ten line multiplet (J_{CH} = 28.5 Hz) is a result of the degenerate rearrangements in this ion leading to complete scrambling of the nine protons among the five carbons on the nmr time scale. The observed shift and coupling constant are thus an average and can be predicted accurately from model compounds as described in the text.

hydrogen coupling constants.[40] Using the isopropyl cation (J_{CH} = 169 Hz) and cyclopentane (J_{CH_2} = 131 Hz) as models gives a calculated coupling constant of (169 + 8 × 131)/(9 × 5) or 27 Hz. Similarly the chemical shift will be the average of the isopropyl cation shift of −125 ppm and four methylene shifts (cyclopentane 167 ppm)[41] giving a calculated value of 108 ppm. If allowance is made for two of the methylenes being adjacent to the positive charge (from the isopropyl cation methyl shift compared to propylene) this shift is reduced to 95 ppm. Both coupling constant and chemical shift obtained in this way are thus in very close agreement with that observed showing clearly that the equilibria observed in this degenerate ion are as indicated above.

Ethylenebromonium Ion. The ^{13}C shift and J_{CH} coupling constant, 120.8 ppm and 185 Hz, respectively, provide good evidence for the three-membered ring nature of the ethylenebromonium ion **6** which shows a single peak in the proton spectrum.[42] If the ion were a rapidly equilibrating pair of primary carbonium ions, **7**, the observed chemical shift would be the average of the ^{13}C shift for the two sites. These shifts can be estimated from shifts observed in related compounds. Whereas no stable, long-lived primary alkylcarbonium ions are known, the shift of the primary carbonium ion center would be expected to be to higher field of that in the *t*-butyl cation and the isopropyl cation (*vide supra*); a reasonable predicted value would be −115 ppm. The other sp^3-hybridized carbon atom should have a shift close to that in ethylene dibromide (156 ppm) leading to an average shift of 13 ppm. This estimated shift differs so greatly from the experimentally observed shift that it strongly supports the bridged nature of the ion.



6



7

The larger J_{CH} coupling constant observed is also consistent with the three-membered-ring nature of this ion. Cyclobutane and higher homologous cycloalkanes show essentially "normal" J_{CH} coupling constants for sp^3-hybridized carbon (130 Hz) while in cyclopropane the value is substantially higher (162 Hz).[41] On forming a three-membered ring containing an electronegative substituent, bond polarization would be expected to increase this coupling constant, and this effect is indeed evident in ethylene sulfide (170.6 Hz) and ethylene oxide (175.7 Hz).[43] Br^+ would be expected to cause even greater bond polarization and thus the larger coupling constant is completely consistent with other three-membered-ring compounds.

The ^{13}C chemical shifts in cyclopropane, ethylene oxide, ethylene sulfide, and N-methylaziridine have been reported and also show a substantial electronegativity effect, ethylene oxide (δ_C = 154.6) being 42.3 ppm to low field of the ^{13}C shift in cyclopropane.[44] An approximately linear relation between CH coupling constants and carbon chemical shifts exists in the three-membered ring compound described above. An extrapolation to the coupling constant in the ethylenebromonium ion gives a predicted chemical shift of 125 ppm, in good agreement with the observed value.

The question remains as to whether the ethylenebromonium ion is best formulated as a covalent three-membered ring or as a π complex of the bromine cation with ethylene. The fact that the ^{13}C data fit well with that for other three-membered rings suggests that the former is most consistent with the experimental evidence; however, the possibility cannot be ruled out that the trend observed in the chemical shift and coupling constants on increasing the electronegativity of the substituent in the ring represents an increasing amount of π-complex contribution to the structure. We are inclined to the view, however, that the distinction between these two descriptions of the bonding is largely a matter of semantics.

The ^{13}C satellites in the proton spectrum of the ethylenebromonium ion provide information on the magnitude of the geminal and vicinal H–H coupling constants. These satellites, for the ions containing one ^{13}C atom, consist of two AA'BB' spectra which can be analyzed to a close approximation as AA'XX' cases, the "shift" difference being 92 Hz (J_{CH}–J_{CCH}). This treatment gives J_{gem} = 1.0 Hz and the two vicinal coupling constants 7.0 and 13.0 Hz, although there is some uncertainty in the value of J_{gem} due to the poor S/N ratio in the spectrum. These values are very close to those found in other halonium ions in which the larger of these coupling constants can be assigned to the *trans*-vicinal coupling constant.[42]

The long-range coupling constant, J_{CCH}, was found to be zero. Factors affecting J_{CCH} coupling constants are not well understood and, as was discussed previously, correlations with the s character of the C–C bond can be invalid.[35] The value of 0.0 Hz for this coupling constant in the ethylenebromonium ion is less than that for sp^3 hybridization (4.0 Hz) and is in approximate agreement with that predicted for sp^5 hybridization. An sp^5-hybridized C–C bond in cyclopropane has been reported from measurement of the C–C coupling constant.[45]

Tetramethylethylenebromonium Ion. The ^{13}C chemical shift in the tetramethylethylenebromonium ion[46]

---

[40] This neglects long-range couplings which, however, will be not only small but should cancel out due to sign alternation.

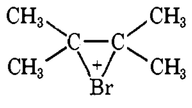
[41] J. Burke and P. Lauterbur, *J. Amer. Chem. Soc.*, **86**, 1870 (1964).

[42] G. A. Olah and J. M. Bollinger, *ibid.*, **90**, 2587 (1968).

[43] E. Lippert and H. Bragg, *Ber. Bunsenges Phys. Chem.*, **67**, 415 (1963).

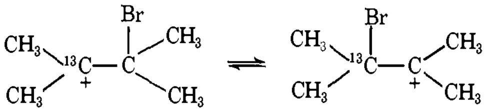
[44] G. E. Maciel and G. B. Savitsky, *J. Chem. Phys.*, **69**, 3925 (1965).

[45] F. S. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, **89**, 5962, (1967).



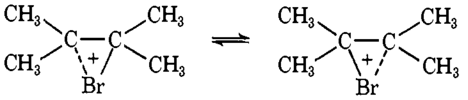
or

8



9

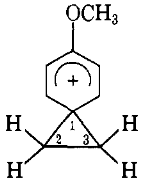
was found to be +55.2 or 65.6 ppm to low field of the ethylenebromonium ion. To evaluate the expected effect on the shift of the methyl groups, the ^{13}C shift of tetramethylethylene oxide was determined and found to be 21.2 ppm to low field of ethylene oxide. The tetramethylethylenebromonium ion is thus abnormal by comparison with the bridged ethylenebromonium ion. The open equilibrating ion would be expected to give a shift of about −10 ppm and we feel that the observed shift is incompatible with either a bridged **8** or equilibrating system **9**. Two possibilities remain, first that a mixture of approximately 50% each of the bridged and equilibrating ion is present; second, that the ion present is a rapidly equilibrating pair of partially bridged ions.



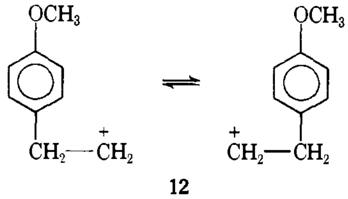
10

Either explanation would fit both the proton and ^{13}C data and at present we are unable to distinguish between the two possibilities. Work is in hand to study the Raman and ^{13}C spectra of a wide range of halonium ions with a view to clarifying this point.

Ethylene-*p*-anisonium Ion. Proton magnetic resonance studies of the *p*-anisonium ion indicated it to be a bridged ion **11** rather than a rapidly equilibrating pair of primary carbonium ions **12**.[47]



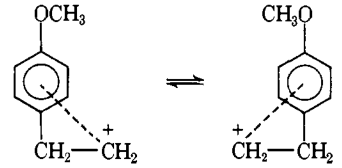
11



12

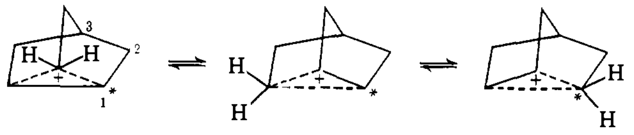
Using the ^{13}C satellites of the single cyclopropane hydrogen resonance the ^{13}C chemical shift of C_2 and C_3 was found to be 153.1 ppm (J = 176 Hz).[48] The relationship between the chemical shift and coupling constant in three-membered rings was discussed in the case of the ethylenebromonium ion and it can be seen that the shift and coupling constant in this phenonium ion are completely consistent with this correlation. The values observed are, in fact, virtually identical with those observed in ethylene oxide (δ_C = 154.6 ppm; J = 175.7 Hz) leaving no doubt but that the ion has the bridged structure **6**. If the ion were to have the rapidly equilibrating structure **7**, the expected shift and coupling constant (evaluated in the same manner as described for the ethylenebromonium ion) would be 15 ppm and 150 Hz, respectively.

Brown's suggestion[49] that phenonium ions are π-bridged equilibrating cations, **13**, can be similarly eliminated in the example shown. In the π-bridged ions, the average ^{13}C chemical shift of C_1 and C_2 will be similar to that of the classical equilibrating ions. Since in the bridged ion the average chemical shift is about 140 ppm more shielded than in the equilibrating classical ion, even allowing for some charge delocalization in the π-bridged ion could not lead to the observed shift. Carbonium ions obviously can have structures intermediate between limiting classical and nonclassical (see also ref 49), but clearly this phenonium ion is not such a case.



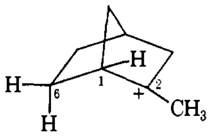
13

2-Norbornyl Cation (Protonated Nortricyclene). The low-temperature ^{13}C and ^{1}H nmr spectra of this ion have been described in preliminary communications.[18] ^{13}C spectra were obtained at −70° at which temperature the degenerate rearrangement **14** is fast on the nmr time scale. The ^{13}C shift of the three equivalent cyclopropyl carbons (C_1) was found to be +101.8 ppm (J = 53.3 Hz), that of the three methylene carbons (C_2) +162.5 ppm (J = 140 Hz), and that of the bridgehead carbon (C_3) +156.1 ppm (J = 153 Hz). For a full discussion of the significance of these results and their incompatibility with other structures of the ion, the reader is referred to ref 18.[49a]



14

2-Methylnorbornyl Cation. The complexity of the proton spectrum of the 2-methylnorbornyl cation at −80°[18b] did not allow a complete ^{13}C indor spectrum to be obtained for this ion. The satellites due to long-range coupling of the methyl group with C_2 and those due to the direct coupling to C_1 were, however, located and the ^{13}C shifts of these carbon atoms were obtained.



The C_2 chemical shift was found to be −76.1 ppm and the C_1 chemical shift +118.0 (J_{CH} = 168 Hz). The

---

(46) The proton spectrum and method of forming this ion have been described previously: G. A. Olah and J. M. Bollinger, *J. Amer. Chem. Soc.*, **89**, 4744 (1967).

(47) G. A. Olah, M. B. Comisarow, E. Namanworth, and B. Ramsey, *ibid.*, **89**, 5259 (1967).

(48) The satellites constitute the AA′ part of an AA′MM′X′ spectra but were not well-enough resolved to permit extraction of the geminal and vicinal proton coupling constants.

(49) H. C. Brown and C. J. Kim, *J. Amer. Chem. Soc.*, **90**, 2082 (1968).

(49a) NOTE ADDED IN PROOF. We have since succeeded in obtaining at −150° the "frozen-out" ^{13}C indor spectrum of the norbonyl cation. The ^{13}C shift of the bridging carbon is at δ_{13C} 173 ppm, that of the two cyclopropane type carbons at δ_{13C} 70 ppm: G. A. Olah and A. M. White, *ibid.*, in press.

proton spectrum of this ion at $-80°$ shows the 6,1-hydrogen shift to be slow at this temperature and the Raman spectrum shows the ion to correspond in structure to a norbornyl rather than a nortricyclene derivative,[18b] in contrast to observations on the unsubstituted norbornyl cation.[50] The ^{13}C shift of C$_2$, however, is substantially to high field of that of the carbonium carbon shift in the *t*-butyl cation (-135 ppm) and the 1-methylcyclopentyl cation (-142.2 ppm in SbF$_5$–SO$_2$ at $-60°$), revealing the presence of a certain degree of σ delocalization in this ion. Interaction between C$_2$ and C$_6$ would be expected to involve selective electron withdrawal from the bonding orbital involving C$_6$ and the *exo*-6 proton and this is substantiated by the deshielding of the *exo* compared to the *endo*-6 proton observed in the proton spectrum of the ion.[18b] 6,2 σ interaction would also account for the large C$_1$–H$_1$ coupling constant which is substantially higher than that in norbornane (140 Hz) and nortricyclene (148 Hz) and for the low chemical shift of this carbon (118.0 ppm compared to 157.6 ppm in norbornane).[18] The ^{13}C shift difference between C$_1$ and C$_2$ and the Raman spectrum of the ion show, however, that this delocalization is not as advanced as in the norbornyl cation in which the 6,2 bond distance is such as to give the ion over-all nortricyclene rather than norbornane skeletal symmetry.[50]

In contrast to these results for the 2-methylnorbornyl cation, the 2-phenylnorbornyl cation shows essentially no σ delocalization. The shift of C$_2$ was found to be -65.8 ppm (FSO$_3$H solution at $+35°$) which compares with -61.1 ppm in the phenyldimethylcarbonium ion and ~ -70 ppm (FSO$_3$H solution at $-20°$)[51] in the 1-phenylcyclopentyl cation. Clearly, in this case, conjugation with the phenyl ring is sufficiently advanced as to eliminate any substantial "nonclassical" interaction between C$_2$ and C$_6$. The classification of carbonium ions as either limiting classical or nonclassical thus presents difficulties in that, in the stable ions, a spectrum of varying degrees of σ delocalization can be present. We have ^{13}C evidence for a number of ions intermediate between "classical" and "nonclassical" behavior. These are the 2-methylnorbornyl cation, the tetramethylethylenebromonium ion, and *para*-substituted β-bromocumyl cations,[52] all being cases where partial bridging occurs at a tertiary carbonium ion center. It seems clear that many other examples of this type of behavior exist and we are actively pursuing studies in this field. Restricting the term "nonclassical" to ions such as the norbornyl cation itself in which completely symmetrical bridging is possible is clearly too restrictive and it would seem more appropriate to discard these limiting terms altogether and to introduce a quantitative measure of the amount of σ delocalization present. In solvolytic studies the contribution of σ delocalization to the energy of the transition state provide this measure. In the stable ions ^{13}C chemical shifts appear to represent at this time the most sensitive criterion of σ delocalization.

Experimental Section

Nmr Spectra. Proton spectra were obtained at 100 MHz using a Varian Associates Model HA 100 nmr spectrometer. Line positions were determined using the associated frequency counter and were referenced against external (capillary) TMS. Indor spectra were obtained by irradiation of the carbon-13 spectrum at 25.1 MHz. The instrumentation and technique employed in obtaining such spectra have been described in detail in a previous paper in this series.[14] ^{13}C shifts were obtained with respect to TMS as reference and converted to the ^{13}CS$_2$ standard by adding 194.6 ppm.[53] Carbon–hydrogen coupling constants were measured from the proton spectrum of the ion. Shifts are estimated to be accurate to within 0.2 ppm and coupling constants to within 0.2 Hz.

Preparation of the Ions. The ^{13}C shifts of ions in Tables I and II (with the exception of the phenyl- and cyclopropylcarbonium ions) were obtained using approximately 50% ^{13}C-enriched precursors obtained from Merck Sharp and Dohme of Canada Ltd. or synthesized using standard procedures. Other ^{13}C shifts reported were determined in natural abundance except where otherwise indicated in the text. All the ions discussed have been reported previously and procedures for their preparation, similar to those given in the references cited, were used throughout. In all cases the solutions used had proton spectra identical with those described previously.

Acknowledgment. Support of the work through grants of the National Institutes of Health, the National Science Foundation, and the Petroleum Research Fund (administered by the American Chemical Society) is gratefully acknowledged.

---

(50) G. A. Olah, A. Commeyras, and C. Y. Lui, *J. Amer. Chem. Soc.*, **90**, 3882 (1968).

(51) The indor spectrum from this ion (obtained by "sitting" on the resonance due to the *o*-phenyl protons) was very weak and broad and an error of ±2 ppm is estimated for this shift.

(52) G. A. Olah, C. L. Jeuell, and A. M. White, *J. Amer. Chem. Soc.*, **91**, 3961 (1969).

(53) A referee has commented that this conversion factor is probably too large by about 1.5 ppm, depending on solvent effects, etc. Since our arguments are based on relative ^{13}C shifts this will not affect any of the conclusions reached; however, for quantitative rigor it should be recognized that this error may be present in all of the quoted shifts.