was taken up in 2 ml of freshly distilled α-pyrone (110°, 26 mm).[51] The flask was protected from the atmosphere (Drierite-KOH) and pyrolyzed for 75 min in an oil bath maintained at 145°. Aliquots were removed periodically, acidified, and subjected to analysis on a 6 ft × 1/4 in. column of 10% DEGS on Chromosorb W. No indene was observed.

(B) The above procedure was repeated and aliquots of the gases from the reaction vessel were removed periodically during a 20-min period and analyzed (Porapak Q) indicating a nitrogen–carbon dioxide ratio of 1:120.

In the Presence of 1,2-Diazine. To 28 mg (0.21 mmol) of **9** and 160 mg (0.43 mmol) of 18-crown-6 ether in 2 ml of dry benzene was added 35 mg (0.88 mmol) of potassium hydride. The addition was carried out under nitrogen. After the bubbling ceased, the solution was filtered. The solvent was removed *in vacuo* and the dark residue was taken up in 2 ml of dry diazine in a 5-ml flask. The flask was fitted with a serum stopper and flushed with helium. The solution was pyrolyzed in an oil bath at 190°. Gas evolution ceased after 7 min. Gas samples removed through the serum cap showed the nitrogen–carbon dioxide ratio to be 1:1 by glpc (5 ft × 1/4 in., Porapak Q). Trapping the carbon dioxide with Ascarite gave 32% of the theoretical yield.

A portion of the solution was acidified with 5% HCl. No indene was observed by glpc (10% DEGS on Chromosorb W). Another portion was acidified with 1 equiv of HCl and treated with an ether solution containing an excess of diazomethane. No methyl ester was observed by glpc.

Acknowledgment. This research was supported by a grant from the National Science Foundation (NSF-GP 13331).

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(51) H. E. Zimmerman, G. L. Grunewald, and R. M. Paufler, *Org. Syn.*, **46**, 101 (1966).

Stable Carbonium Ions. LXXXV.[1] Laser Raman and Infrared Spectroscopic Study of Alkylcarbonium Ions[2]

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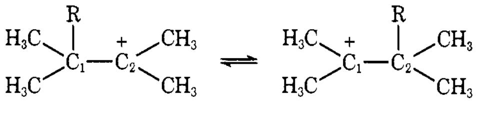
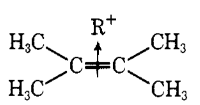
Abstract: Raman and infrared spectroscopic data of the *tert*-butyl cation (**1**) and their correlation with those of isoelectronic model trimethylboron provide direct spectroscopic evidence for the planarity of the $^{+}CC_3$ carbon skeleton. The nearly identical character of the Raman spectra of ion **1** and those of the *tert*-amyl cation (**3**), the dimethylisopropylcarbonium ion (**4**), andt he pentamethylethyl cation (**5**) reflects the generally classical nature of these ions.

The first nmr (^1H and ^{13}C) and infrared spectroscopic study of stable alkylcarbonium ions generated from ionization of alkyl fluorides in SbF_5 was reported in 1962.[3] This was followed by detailed studies of generation of the ions from other precursors in related superacid systems.[4] Pmr data observed for the *tert*-butyl cation (**1**) as well as *tert*-amyl[2] and isopropyl[3,4] cations were consistent with but not conclusive evidence for the planarity of the $^{+}CC_3$ (or $^{+}CHC_2$) carbon skeletons. For the dimethylisopropyl- (**4**) and dimethyl-*tert*-butyl- (**5**) carbonium ions, where the possibility exists for degenerate rearrangements (equilibrium I) and/or for a static bridged species (II, III), no clear differentiation was available on the basis of pmr data.

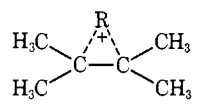
The high-energy (600–3100 cm^{-1}) ir spectra of *tert*-butyl and perdeuterio-*tert*-butyl cation have been reported.[4a] However, rigorous interpretation of these ir data was not possible since the low-energy ir and the Raman spectra of cation **1** were not available.



I, R = H, CH$_3$



II



III

Recently, we[5] have reported a cmr investigation of alkylcarbonium ions. On the basis of estimated average shifts and coupling constants, cmr results were indicative of an equilibrating classical pair of carbonium ions for both **4** and **5**, as shown in equilibrium I. Interestingly, although correlations between hybridization and long-range coupling constants are somewhat questionable,[6,7] the low values of $J_{^{13}CCH}$ obtained for the *tert*-butyl cation could raise the question of the planarity of this ion.[5] ("Planar," of course, refers always only to the arrangement of bonds at the positive carbon center and not to the overall geometry.)

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* Address correspondence to this author at Case Western Reserve University.

(1) Part LXXIV: G. A. Olah, J. A. Olah, and R. H. Schlosberg, *J. Org. Chem.*, **35**, 328 (1970).

(2) Presented in part at the Conference on Carbonium Ions, Cleveland, Ohio, Oct 23–25, 1968.

(3) G. A. Olah, Plenary Lecture, 9th Reaction Mechanisms Conference, Brookhaven National Laboratories, Upton, N. Y., Aug 1962.

(4) (a) G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. J. Bastien, *J. Amer. Chem. Soc.*, **86**, 1360 (1964); (b) G. A. Olah and J. Lukas, *ibid.*, **89**, 4739 (1967).

(5) G. A. Olah and A. M. White, *ibid.*, **91**, 5801 (1969).

(6) G. M. Karabatsos and C. E. Orzech, *ibid.*, **86**, 3574 (1964).

(7) K. A. McLauchlan and T. Schaeffer, *Can. J. Chem.*, **44**, 321 (1966).

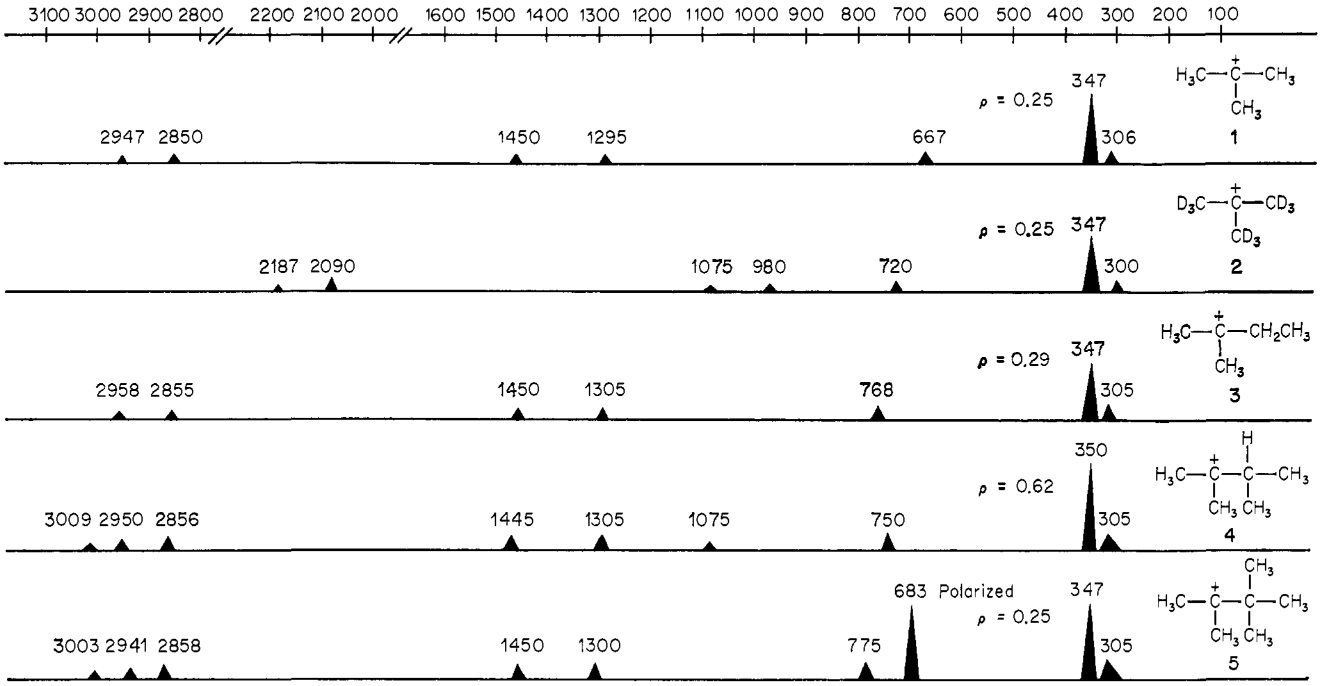

Figure 1. Schematic representation of Raman spectra of alkyl cations **1–5**.

Results

We report presently the Raman and low-energy infrared (600–250 cm^{-1}) spectra of the *tert*-butyl cation (**1**) (Figure 1; Tables I–III). We have obtained also the Raman spectra of the perdeuterated *tert*-butyl cation (**2**, Table II), the *tert*-amyl cation (**3**), the dimethylisopropylcarbonium ion (**4**), and the pentamethylethyl cation (**5**; all Raman spectral data are schematically summarized in Figure 1). Since trimethylboron is isoelectronic with ion **1** and is known to be planar, it, *a priori*, should be a model for both ir and Raman skeletal frequencies and the molecular symmetry of ion **1**. The Raman and ir spectral data of gaseous trimethylboron are, therefore, also shown in Table II and Table III with corresponding assignments.[8–10]

Table I. Raman Frequencies of *tert*-Butyl Chloride and Fluoride Solutions in FSO_3H–SbF_5–SO_2 Media, and Those of Control Solutions HF–FSO_3H–SbF_5–SO_2 and HCl–FSO_3H–SbF_5–SO_2[a]

Solution	$\Delta\tilde{\nu}$, cm^{-1} [c]																				
tert-BuCl–FSO_3H–SbF_5–SO_2[b]	**2947** **(s)**	**2850** **(s)**	**1450** **(m)**	1331	1237	**1295**	1144	1106	942	830	678	**667** **(m)**	650	600	560	525	487	437	387	**347** (s)	**306** **(m)**	294
tert-BuF–FSO_3H–SbF_5–SO_2[b]	**2947** **(s)**	**2850** (s)	**1450** **(m)**	1331	1237	**1295**	1144	1106	942	830	687	**667** **(m)**	653	600	560	525	487	437		**347** (s)	**306** **(m)**	294
HCl–FSO_3H–SbF_5–SO_2			1450 (vw)	1331	1237		1144	1106	942	830	678		650	600	560	525	487	437	387			
HF–FSO_3H–SbF_5–SO_2			1450 (vw)	1331			1144	1106	942	830	687		653	600	560	525	487	437				294

[a] For a detailed description of the Raman spectra of the acid solvent see ref 11. [b] Lines of the cation are shown in boldface type. [c] s = strong, m = medium, vw = very weak.

Table I shows the laser Raman spectra obtained for ion **1** generated in FSO_3H–SbF_5–SO_2 solution from both *tert*-butyl chloride and fluoride precursors. Also shown in Table I are Raman data obtained[11] for control solutions of HCl–FSO_3H–SbF_5–SO_2 and HF–FSO_3H–SbF_5–SO_2. The combined Raman data in Table I permit unambiguous assignment of the lines of ion **1** as 2947, 2850, 1450, 1295, 667, 347, and 306 cm^{-1}.

The absence of the characteristic lines observed for the C–Cl (C–F) bond of the precursor *tert*-butyl chloride (fluoride) and pmr spectra of the solutions indicate that formation of ion **1** is complete. In Table II the frequencies observed for ion **1** are shown to be coincident with several of those reported for trimethylboron. The frequencies of ion **1** are, therefore, assigned to the various modes shown in Table II on the basis of comparison with those assignments reported for $B(CH_3)_3$. In the Raman and ir spectra of ion **1**, the ν_3,

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(8) (a) J. Goubeau and H. J. Becker, *Z. Anorg. Allg. Chem.*, **268**, 1 (1952); (b) H. Siebert, *ibid.*, **268**, 13 (1952); (c) H. Siebert, *ibid.*, **271**, 65 (1953); (d) W. J. Lehmann, C. O. Wilson, Jr., and I. Shapiro, *J. Chem. Phys.*, **31**, 1071 (1959).

(9) See ref 8d and references therein.

(10) The uniquely low nucleophilicity of magic acid provides a solvent system where conditions are somewhat similar to those in the gas phase. This is exemplified by the good correlation between the frequencies of the vibrations of $B(CH_3)_3$ and $^+C(CH_3)_3$. Differences in the activity of the ν_{10} vibration of $B(CH_3)_3$ and $^+C(CH_3)_3$ on the other hand may be due to intermolecular association of the $^+C(CH_3)_3$ ion with the gegenion and/or solvent molecule (see text).

(11) A. Commeyras and G. A. Olah, *J. Amer. Chem. Soc.*, **91**, 2929 (1969).

Table II. Raman and Ir Frequencies of the *tert*-Butyl Cation and *tert*-Butyl-d_9 Cation and Their Correlation with Those of $(CH_3)_3B$ and $(CD_3)_3B$[a]

Species	Frequency of vibration, cm^{-1}											
	ν_1, ν_{12}, ν_7, ν_{19}	ν_2, ν_{13}	ν_{21}	ν_{14}	ν_{15}	ν_{17}	ν_5	ν_{16}	ν_6	ν_9	ν_{10}	ν_{18}
$(CH_3)_3C^+$ (**1**)	2947	2850		1450		1295			667		347	306
$(CH_3)_3B$	2975	2875	1060	1440	1300	1150	906	866	675	973 (486 ?)	*336*[c]	320
$(CD_3)C^+$ (**2**)	2187 [−760][b]	2090 [−760]		1075 [−375]		980 [−215]			720		347 [0]	300 [−6]
$(CD)_3B$	2230 [−745]	2185 [−690]		1033 [−407]	1018	1205 [−55]			620	870	(289)[d]	(276)[d]

[a] For a detailed discussion of the Raman and ir of $(CH_3)_3B$ and $(CD_3)_3B$ see ref 8 and references therein. [b] Numbers shown in brackets are isotope shifts; minus = frequency decrease. [c] The ν_{10} vibration of $(CH_3)_3B$ is ir active only; see ref 8 and Tables III and IV. [d] These are not observed, but calculated values (see Shapiro, *et al.*, ref 8d) for the ν_{10} and ν_{18} vibrations of $(CD_3)_3B$. It should be noted that there were considerable discrepancies between the observed and calculated frequencies for this molecule.

Table III. Raman[a] and Infrared[b] Fundamental Skeletal Vibrations of the *tert*-Butyl Cation and Its Isoelectronic Model, Trimethylboron[c,d]

Vibration	Assignment	$^+C(CH_3)_3$	$B(CH_3)_3$
ν_{18}	C–X–C def in plane	306 (Raman [dp]) 300 (ir)	320 (Raman [dp])[g] 320 (ir)
ν_{10}	XC_3 sym out-of-plane bending	347 (Raman [p]) 390 (ir)	336 (ir)
ν_6	XC_3 stretching sym	667 (Raman [?])[e] ? (ir)	675 (Raman [p])[g] 675 (ir)
ν_{17}	XC stretching asym	1295 (Raman [dp]) 1290 (ir)[f]	1150 (Raman [dp])[g] 1156 (ir)

[a] For complete experimental conditions see ref 11. [b] The ir spectrum was obtained for an ~30 mol % solution of *tert*-butyl chloride in neat SbF_5. Ion **1** was prepared initially in SO_2ClF at −78° and the solvent SO_2ClF was removed from the sample by evaporation with final traces of SO_2ClF removed by freeze–pump–thaw degassing. The resulting SbF_5 solution was lightly colored and was shown by nmr spectra to contain the *tert*-butyl cation in high purity. The film was placed between KRS5 plates separated by a 0.1-mm Teflon spacer and the spectrum was recorded on a Beckman IR-10 spectrophotometer. All manipulations were carried out in a drybox. [c] Spectra and assignments for gaseous trimethylboron as obtained by Shapiro, *et al.*; see ref 8d. [d] Activity of the ν_{18}, ν_{10}, ν_6, and ν_{17} modes are shown parenthetically with the state of polarization of the Raman active lines shown in brackets. [e] The ir activity and state of polarization of the Raman-active ν_6 vibration could not be obtained due to presence of strong solvent signals in this region. [f] As reported previously, see ref 4a. [g] Reference 8b.

ν_4, ν_5, ν_8, ν_{11}, ν_{15}, ν_{16}, ν_{20}, ν_{21}, and ν_{22} modes cannot be detected. This is essentially due to two factors: strong overlapping acid media lines and an inability to get a higher concentration of ion **1** in these solutions.

With the exception of the ν_6, ν_{17}, ν_{10}, and ν_{18} vibrations, the frequency shifts observed for ion **2** and $B(CD_3)_3$ relative to those of ion **1** and $B(CH_3)_3$ are analogous. On perdeuteration the ν_6 vibration of ion **1** shows a shift 53 cm^{-1} to higher frequency and that of $B(CH_3)_3$ shows a shift of 55 cm^{-1} to lower frequency. The observed frequency of the ν_{17} vibration shows a similar trend. Frequencies observed for the ν_{10} and ν_{18} vibrations are apparently insensitive to the substitution of deuterium for hydrogen.

The ν_{18}, ν_{10}, ν_6, and ν_{17} modes are the fundamental skeletal vibrations of the CC_3^+ carbon skeleton of ion **1** and the Raman and ir frequencies observed for these vibrations are shown in Table III along with those of $B(CH_3)_3$. For ion **1** in neat SbF_5, the ir spectrum (see Table III) displays two absorptions in the 600–250-cm^{-1} region (in addition to solvent bands). The ν_{18} and ν_{10} skeletal modes are observed at 300 and 390 cm^{-1}, respectively. The ir absorption at 1295 cm^{-1}, characteristic of the asymmetric ν_{17} stretching vibration, was observed as a broad medium intensity band. A very broad and intense band of the SbF_5 solvent covers the entire 580–700-cm^{-1} region preventing detection of the ν_6 skeletal mode of ion **1** in the ir spectrum. Since the ir spectrum of ion **1** was obtained in neat SbF_5, a resulting solvent shift of the frequencies observed for the CC_3^+ skeletal vibrations is, therefore, observed. Correlation between the frequencies, number of lines, and activity of the lines observed for the fundamentals of ion **1** and $B(CH_3)_3$ is evident. Relative to all other lines in the Raman spectra of ion **1**, the line at 347 cm^{-1} is sharp and intense. However, relative to the strong acid lines in the total spectrum, the line at 347 cm^{-1} is observed as a medium intensity signal. The lines at 320, 680, and 1295 cm^{-1} are relatively weak and broad.

Overall similarity in the Raman and ir spectra of ions **1** and **3**–**5** is obvious from Figure 1. In the C–C skeletal vibration regions (1200–1300 and 200–800 cm^{-1}), ions **1**–**4** each display a total of four lines. Ions **1**–**3** and **5** all show a strong and highly polarized line at 347 cm^{-1}. For ion **4** this line is shifted insignificantly to 350 cm^{-1} and is significantly less polarized.[12]

Expected small variation of the frequency of the ν_6 CC_3^+ skeletal vibration is consistent with the changes in structure of the ions. A strong line at 683 cm^{-1} is observed in the Raman spectrum of ion **5**. This line was identified by control experiments with neopentane and the chloride precursor of ion **5** to be due to the CC_4 skeletal vibration in ion **5**. Frequencies observed for the ν_{10} and ν_{18} vibrations of these ions show a remarkable lack of sensitivity to changes in substitution around the basic carbon CC_3^+ skeleton.

Discussion

The state of polarization, intensity, and sharpness of the line at 347 cm^{-1} in the Raman spectrum of ion **1** indicate that the skeletal vibration yielding this line is

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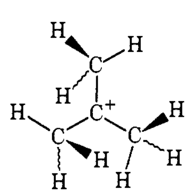
(12) (a) G. Herzberg, "Molecular Spectra and Molecular Structure, Vol. II. Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, Princeton, N. J., 1945, Chapter IV; (b) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N. Y., 1963, and references therein.

totally symmetric, as would be expected for the ν_{10} vibration of the planar *tert*-butyl cation.[12,13] The lines at 306 and 1295 cm^{-1} on the other hand are relatively weak and broad suggesting that these skeletal vibrations are not totally symmetric.[13]

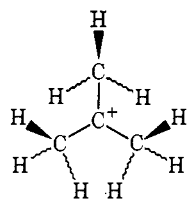
Correlation between the ir and Raman frequencies of the four fundamental skeletal modes of $B(CH_3)_3$ and $^+C(CH_3)_3$ is consistent with the identical character of their skeletal backbones, and is, therefore, evidence for the planarity[14] of the *tert*-butyl cation carbon skeleton. This correlation and the intensity, shape, and state of polarization of the Raman lines observed for ion **1** permit the assignment of the lines, 347 cm^{-1}, ν_{10}; 306 cm^{-1}, ν_{18}; 667 cm^{-1}, ν_6; and 1295, ν_{17}, to the corresponding skeletal modes.

The frequency reported for the ir-active and Raman-inactive out-of-plane bending vibration ν_{10} of $B(CH_3)_3$ (336 cm^{-1})[8d] correlates very well with the strong sharp and polarized Raman-active line observed at 347 cm^{-1} for ion **1**. Furthermore, the three relatively weak and broad lines of ion **1** and 320, 680, and 1295 cm^{-1} parallel significantly the frequencies observed for the ν_{18}, ν_6, and ν_{17} vibrations, respectively, of $B(CH_3)_3$. The predicted effects of perdeuteration of ion **1** on its vibrational spectrum are not easily determined. The effects of hyperconjugation and association with gegenion—not present for the isoelectronic model $(CH_3)_3B$—could be responsible for the substantial differences of $\Delta\nu$'s of the skeletal vibrations observed for perdeuterated ion **1** relative to those reported for perdeuterated $B(CH_3)_3$. The C–H stretching and bending frequencies of ion **1** and $B(CH_3)_3$ are shifted by approximately the same increments to lower frequencies on perdeuteration. The frequencies observed for the fundamental skeletal vibrations of ion **2**, on the other hand, show substantial differences relative to those observed for $B(CD_3)_3$. For both H and D, the effect of hyperconjugation should be to effectively increase the C–C bond strengths leading to frequency changes consistent with an increase of the force constant of the C-C bond. For H this effect would be expected to be more pronounced than for D and the effect would also be expected to be reflected similarly in the frequency shifts of both the C–H and C–C vibrations. However, neither of these predictions appears to be consistent with the data obtained. It is evident, therefore, that these anomalous shifts are probably not related to hyperconjugation in ion **1**. Alternatively, association with the gegenion remains as a possible explanation for these differences.

There are two molecular arrangements that can be expected to represent possible torsional minima for ion **1** and trimethylboron with a planar XC_3 backbone. Depending on the arrangement of the methyl hydrogens, these species can maintain preferred conformations leading to overall C_{3h} or C_{3v} point groups.[8,12,14,15]



C_{3h}



C_{3v}

The selection rules for the ir and Raman spectra of ion **1** and $B(CH_3)_3$ in these conformations are shown in Table IV.[8,13] It is evident from Table IV that the only theoretically predicted difference in the activity of the fundamental skeletal vibrations of ion **1** and $B(CH_3)_3$ in either a C_{3h} or a C_{3v} arrangement is the Raman inactivity of the ν_{10} skeletal vibration for the C_{3h} arrangement. Of course these selection rules are valid strictly only for the intramolecular valence vibrations of molecules in the gas phase. In solution, where intermolecular forces often play a fundamental role, violations of such selection rules are sometimes observed. However, since low nucleophilicity conditions in the solvent FSO_3H–SbF_5–SO_2 can somewhat be compared to those in the gas phase,[10] it is interesting to study the observed Raman and ir frequencies in relation to the activity predicted from Table IV.

Table IV. Selection Rules for the Fundamental Vibrations of Ion **1** and $B(CH_3)_3$

Vibration	Activity	
	C_{3h}	C_{3v}
ν_{18}	(Ir; Raman [dp])	(Ir; Raman [dp])
ν_{10}	(Ir only)	(Ir; Raman [p])
ν_6	(Ir; Raman [p])	(Ir; Raman [p])
ν_{17}	(Ir; Raman [dp])	(Ir; Raman [dp])

It has been pointed out[8d] that the ν_{10} vibration of $B(CH_3)_3$, being infrared active and Raman inactive, is evidence for a preferred overall C_{3h} molecular symmetry. On the other hand, the same, vibration, ν_{10}, for ion **1** is both ir and Raman active (polarized) consistent with an overall C_{3v} molecular symmetry (see Table IV). Thus, if the selection rules are valid for this system, the combined Raman and ir spectroscopic data indicate that the trimethylcarbonium ion in superacid solution prefers a conformation leading to overall C_{3v} group symmetry. The $^+C(CH_3)_3$ ion, therefore, probably exists in these solutions with a planar $^+CC_3$ carbon skeleton and primarily with one hydrogen atom of each CH_3 group above the CC_3^+ plane lying in the σ_v planes. The other two remaining hydrogen atoms of each methyl group are arranged symmetrically below the CC_3^+ plane to the right and left of the C_3 axis. Although this result may at first seem surprising, upon closer examination these differences are obviously related to the presence of positive charge on the central carbon atom of ion **1**. For ion **1** the driving force for preference of what is essentially a more energetic conformation (*i.e.*, C_{3v} rather than C_{3h}) can be interpreted in terms of the effect of "hyperconjugation" and association with the corresponding gegenion and/or solvent. In the C_{3v} arrangement the C–H bonds lying in the σ_v

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(13) See ref 12a, pp 270, 441, and 492.

(14) The sensitivity of the Raman and ir frequencies and their spectral character (*e.g.*, bond shape, intensity, and polarizability) to small deviations in planarity of the CC_3^+ skeleton is not known exactly. However, it is evident that *any significant loss of planarity* involving an equilibrating pair of nonplanar *tert*-butyl cations would be evidenced by substantial difference between the Raman and ir spectra of ion **1** relative to those of $B(CH_3)_3$.

(15) D_{3h} [L. A. Woodward, J. R. Hall, R. D. Dixon, and N. Sheppard, *Spectrochim. Acta*, 249 (1959)] and C_i [see ref 8a–c and references therein] point groups have also been considered for gaseous $B(CH_3)_3$. However, these are considered to be unlikely since free or nearly free rotation in the $B(CH_3)_3$ and $^+C(CH_3)_3$ systems does not appear to be feasible.

planes are aligned for "hyperconjugative" stabilization of the positive charge. In addition, the stabilized cation in solution can be pictured as approaching an ion pair interaction. This picture is best envisioned with the anion or polarized solvent molecule approaching the $^{+}C(CH_3)_3$ cation more closely on one face. Such an approach would be less hindered for a C_{3v} arrangement where six of the methyl protons on one face are arranged to the right and left of the C_3 axis lowering the steric barrier.

With the carbon skeleton of the *tert*-butyl cation verified as planar, we can now employ ion **1** as a structural model for the basic carbon skeleton of the related cations **3**–**5**. The Raman spectra of carbonium ions **3**–**5** reflect close $^{+}CC_3$ skeletal similarities to the *tert*-butyl cation as shown in Figure 1.[16]

An important additional feature of the Raman spectrum of ion **5** is the relatively intense line at 683 cm^{-1} which is characteristic of a neopentyl-like CC_4 fundamental skeletal vibration. This indicates that the $(CH_3)_3C_1$–C_2^{+} part of ion **5** remains essentially in the tetrahedral arrangement about C_1 that is present in the precursor (*vide supra*). For cation **5** the static bridged carbon skeleton of structure III would very closely resemble the skeleton of the three-membered ring in protonated cyclopropane. The Raman spectrum of ion **5** with structure III would not show, therefore, the intense line at 683 cm^{-1}, due to the loss of the tetrahedral CC_4 group. On the other hand, characteristic C–C and C–H cyclopropane vibrations would be expected. The "cyclopropane"-type C–H stretching vibrations of protonated nortricyclene yield a Raman line at 3100 cm^{-1}.[17] Such characteristic "cyclopropane" modes would also be expected for cation **5** with structure III. However, no lines are observed above 300 cm^{-1} in the Raman spectra of ion **5**.

Conclusions

The nearly identical Raman spectra of cations **1**–**5** and the evident planarity of the carbon skeleton of the *tert*-butyl cation strongly suggest that all of these cations are classical and maintain the planarity (or close to planarity) of the CC_3 skeleton.

Since the Raman and ir spectra provide direct evidence for the planarity of the carbon skeleton of the *tert*-butyl cation, factors other than hybridization must be responsible for the low value of the long-range nmr carbon–proton coupling constant in this ion.[5] The nearly identical Raman spectra of cation **1** and those of ions **3**, **4**, and **5** reflect the generally classical nature of these ions. This strongly indicates that the nmr equivalence of the methyl groups of cations **4** and **5** is observed as a result of the fast equilibrium I.[17a]

Experimental Section

Materials. Commercial antimony pentafluoride was purified by double distillation at atmospheric pressure in an all-glass apparatus. In a third distillation a constant-boiling fraction (bp 142–143°) was collected directly into a Teflon bottle. Fluorosulfuric acid was purified by double distillation at atmospheric pressure in an all-glass apparatus.

The mixtures of SbF_5–FSO_3H with SO_2 and RCl (Aldrich or Eastman) or $(CH_3)_3CF$[18] were prepared at low temperature (generally Dry Ice–acetone) to give a 20 mol % solution of the alkylcarbonium ion. Each constituent was weighed with a minimum accuracy of ±0.2 g.

Raman Spectra. Raman spectra were obtained on a Cary 81 Raman spectrophotometer with a laser source (50-mW gas laser using the 6328-Å He–Ne line) equipped with a variable-temperature Raman cell.[11]

Ir Spectra. Ir spectra were recorded on a Beckman IR-10 spectrophotometer (see Table III).

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(16) Although, because of the complexity of these molecular systems, it is not fully justified to attempt a rigorous interpretation of these Raman spectral correlations, we feel that some explanation for the exceptionally high depolarization ratio of the 350-cm^{-1} line of ion 3 is necessary. Raman spectra and especially the state of polarization, intensity, and shape of the line at 347 cm^{-1} in the spectra of ions 3 and 5 are consistent with overall torsional minima in these ions at a preferred C_s arrangement. This arrangement is also indicated by molecular models to be the least sterically crowded for ions 3 and 5. On the other hand, molecular models indicate considerable steric hindrance to the C_s arrangement for ion 3 and suggest that overall torsional minima for ion 3 at the C_1 arrangement is likely. For such an arrangement, the Raman line at 350 cm^{-1} in the spectrum of ion 3 would be expected to be considerably less polarized as observed (see, for example, ref 12 and 13).

(17) G. A. Olah, A. M. White, J. R. DeMember, A. Commeyras, and C. Y. Lui, *J. Amer. Chem. Soc.*, **92**, 4627 (1970).

(17a) Note Added in Proof. Pople, Schleyer, and their coworkers raised, since this paper was submitted, the question of rotational barriers in primary and secondary alkyl cations [L. Radom, J. A. Pople, V. Buss, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 6380 (1970)] and calculated preferred conformations (for the gas-phase ions). We see no discrepancy with our experimental observations, particulary when we consider that our Raman studies so far were centered on tertiary cations and futhermore, solvation of these ions in solution may play a major role relating to the preferred planar arrangement found at the carbonium ion center (a fact which, so far, could not be incorporated into theoretical calculations).

(18) Prepared from $(CH_3)_3COH$ and HF according to the procedure described by K. C. Cooper and E. P. Hughes in *J. Chem. Soc.*, 1183 (1937).