

The C₄H₉⁺ Potential Energy SurfaceStefan Sieber,[†] Peter Buzek,[†] Paul v. R. Schleyer,^{*,†} Wolfram Koch,^{*,‡} and José Walkimar de M. Carneiro[§]

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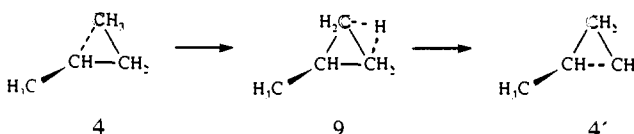
Abstract: The C₄H₉⁺ potential energy surface (PES) is investigated using high level ab initio molecular orbital theory. All structures were fully optimized at Hartree-Fock (HF) and correlated levels (HF/6-31G*, MP2(full)/6-31G*, and MP2(full)/6-31G**) followed by single point energy calculations at MP4sdtq/6-31G**//MP2(full)/6-31G**. The C₁, C_{3h}, C₂, and C_{3v} forms of the *tert*-butyl cation were investigated. At our final level, MP4sdtq/6-31G**//MP2/6-31G** + ZPE, **2** is more stable than **1** by only 0.1 kcal/mol. Nevertheless, better agreement between ¹³C chemical shifts computed using the IGLO (individual gauge for localized molecular orbitals) method, and experimental data were found with **1**. The stability and structure of *tert*-butyl cation is interpreted in terms of the bending of CH bonds due to their hyperconjugative interaction with the formally "vacant" p-orbital on the carbenium center. At our final level, **3** is 1.1 kcal/mol higher in energy than **2**. Of the five 2-butyl cation structures investigated, the symmetrically hydrogen-bridged minimum **5** (C₂ point group) is the more stable. However the C₁ methyl-bridged alternative **4** lies only 0.4 kcal/mol higher in energy. The IR spectrum of the H-bridged form **5** computed at MP2/6-31G* shows a 2100 cm⁻¹ frequency which is characteristic in the otherwise sparsely populated 2000-cm⁻¹ region. This is in good agreement with a peak at 2175 cm⁻¹ in the IR spectrum of the 2-butyl cation measured at -125 °C in a SbF₅ matrix. The computed spectrum of the alternative methyl bridged 2-butyl cation **4** has no frequency in the 1600-2800 cm⁻¹ region. The classical open chain isomer **7** is 2.3 kcal/mol less stable than **5**. H- and C-scrambling in the 2-butyl cation occurs via the edge protonated methylcyclopropane transition structure **9**, calculated to be 8.5 kcal/mol less stable than the minimum **5**. The activation barrier for the 2-butyl cation rearrangement into the tertiary isomer was calculated to be 19.6 kcal/mol in acceptable agreement with the 18 kcal/mol value derived from DNMR measurements. Besides these minima, two additional minima were found, i.e., edge protonated cyclobutane adopting a twisted (point group C₂) geometry **14** and a protonated methylcyclopropane **10**. However, protonated cyclobutane (**14**) is unfavorable energetically (35.9 kcal/mol less stable than the *tert*-butyl cation), while protonated methylcyclopropane (**10**) is only 8.6 kcal/mol higher in energy than the 2-butyl cation. The final relative stability ordering of butyl cations is predicted theoretically to be 0, 13.4, 22.0, 33.4, 35.7, and 35.9 kcal/mol for the *tert*-butyl (**1**), 2-butyl (**5**), protonated methylcyclopropane (**10**), isobutyl (**12**), 1-butyl (**13**), and protonated cyclobutane (**14**) ions, respectively. However, the isobutyl (**12**) and 1-butyl (**13**) cations are transition structures (rather than minima). The infrared spectra theoretically predicted at the MP2/6-31G* level also are reported.

Introduction

Carbocations, initially proposed as highly reactive intermediates in, e.g., rearrangement and substitution reactions,¹ are now well established species in organic chemistry.²⁻⁵ Their detection and study both in the gas-phase and in solution has increased the understanding of chemical processes which are influenced decisively by the nature and structure of the intermediate ion. Considerable amount of experimental data dealing with reactions, constitution, and stabilities of carbocations has accumulated.⁶⁻²⁶ However, detailed information about the energy and especially the structure requires theoretical investigations. In our systematic high level ab initio investigation of carbocations we have reported structures and energies of C₁-C₃,^{27,28} C₃H₇⁺,²⁹ C₄H₇⁺,^{30,31} and C₄H₉⁺^{32,33} systems recently. We now extend these studies by investigating the potential energy hypersurface of the C₄H₉⁺ cation more fully.

The *tert*-butyl and 2-butyl cations are the only experimentally observable C₄H₉⁺ species.²⁻⁵ Although the existence of alkyl cations was inferred from solvolysis and other experiments,^{1,2,6,7} the direct observation of stable aliphatic carbocations in superacid solutions was achieved by Olah and co-workers.⁴ The *tert*-butyl cation was obtained in solution from *tert*-butyl fluoride dissolved in excess SbF₅.^{7,8} This species can also be formed in many other ways, e.g., by olefin protonation,⁹ from alcohols by ionization,¹⁰ or by hydride ion abstraction from saturated hydrocarbons.¹¹ The high relative stability of the *tert*-butyl cation was evident from the first studies. Olah et al. reported that in the strongly acidic antimony pentafluoride solution, *n*-butyl, isobutyl, and 2-butyl fluoride all give the *tert*-butyl cation directly.⁸ Similar behavior

Scheme I



also observed for *n*-butane and isobutane¹¹ as well as for *n*-butanol, isobutyl alcohol, and 2-butanol¹⁰ in FSO₃H/SbF₅ solution. All

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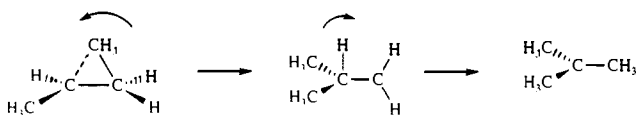
[§]Instituto de Química.

Table I. Heats of Formation of Butyl Cations^a

references			1-butyl	2-butyl	isobutyl	tert-butyl
Lossing et al.	1970	<i>b</i>				169
Franklin et al.	1972	<i>c</i>		183.2		
Lossing et al.	1976	<i>d</i>	201	183		
Rosenstock et al.	1977	<i>e</i>	201	183	199	169
Tsang	1978	<i>f</i>				166.5
Houle et al.	1979	<i>g</i>				162.9 ± 1.2
Traeger et al.	1979	<i>h</i>				162.1 ± 0.8
Bowers et al.	1979	<i>i</i>	201	183	199	164.0
		<i>i</i>				166.0
		<i>i</i>				165.1
Lias et al.	1980	<i>j</i>		176.7 ± 2.9		162.1 ± 0.8
Traeger et al.	1981	<i>k</i>				≤166.2 ± 0.8
Lias et al.	1984	<i>l</i>		183		166
Beauchamp et al.	1984	<i>m</i>	201.9 ± 3	181.0 ± 1.1	197.9 ± 3	164.8 ± 1.2

^aAll data in kcal/mol at 298 K. ^bLossing, F. P.; Semeluk, G. P. *Can. J. Chem.* **1970**, *48*, 955. ^cFranklin, J. L.; Chong, S. L. *J. Am. Chem. Soc.* **1972**, *94*, 6347. ^dLossing, F. P.; Maccoll, A. *Can. J. Chem.* **1976**, *54*, 990. ^e*J. Phys. Chem. Ref. Data* **1977**, *6*, Suppl. 1. ^fTsang, *Int. J. Chem. Kinet.* **1978**, *10*, 41. ^gHoule, F. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 4067. ^hMcLoughlin, R. G.; Traeger, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 5791. ⁱ*Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2. ^jLias, S. G.; Shold, D. M.; Ausloos, P. *J. Am. Chem. Soc.* **1980**, *102*, 2540. ^kTraeger, J. C.; McLoughlin, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 3647. ^l*J. Phys. Chem. Ref. Data* **1984**, *13*, 695. ^mSchultz, J. C.; Houle, F. A. *J. Am. Chem. Soc.* **1984**, *106*, 3917.

Scheme II



these species yielded the thermodynamically most stable *tert*-butyl ion. By using a special "molecular beam" apparatus at low temperatures (−110 °C), Saunders, Hagen, and Rosenfeld were first able to prepare the 2-butyl cation with very little *tert*-butyl cation contamination starting from 2-chlorobutane in SO₂ClF/SbF₅.¹² Even at this low temperature, only two peaks in the ¹H NMR spectrum of the 2-butyl cation were found, due to very rapid 2,3-hydride shifts. By warming the sample from −110 to −40 °C, a second process, which scrambles all the protons, was observed.¹² The activation energy is 7.5 ± 0.1 kcal/mol. This low barrier excludes the possibility of a reversible rearrangement via primary ions, which would involve an energy barrier more than twice as high, as is observed for scrambling in the 2-propyl cation.³⁴ The

Table II. Theoretical Relative Energies of Butyl Cations (kcal/mol)^a

references	tert-butyl	2-butyl	isobutyl	1-butyl	method
Kollmar et al.	0.0	14.0	43.0	38.0	CNDO/FK
Dewar et al.	0.0	12.0		38.0	MINDO/2
Schleyer et al.	0.0	18.0	36.0	39.0	STO-3G
Dewar et al.	0.0	3.7			MINDO/3
Tomás et al.	0.0	9.7	31.2		MINDO/3

^aSchaefer, H. F. *Applications of Electronic Structure Theory; Structural and Energetic Investigations*; Hehre, W. J., Ed.; Plenum Press: New York, 1977; p 317. Radom, L.; Poppinger, D.; Haddon, R. C. In *Carbocation Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Plenum Press: New York, 1968; p 2395. Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986; p 395.

mechanism proposed to explain the 2-butyl cation behavior involves cyclization to a protonated methylcyclopropane intermediate, followed by degenerate proton corner-to-corner rearrangement and reopening to give an equivalent 2-butyl cation (Scheme I).¹² A similar mechanism was proposed independently by Brouwer for the catalyzed isomerization of *n*-butane: in HF/SbF₅, [1-¹³C]-*n*-butane rearranges into [2-¹³C]-*n*-butane without formation of isobutane.³⁵ This result strongly supported the hypothesis of rearrangement via a protonated cyclopropane intermediate, with opening to the 2-butyl cation in contrast to opening to the less stable primary isobutyl ion. Various protonated cyclopropanes have now been established to be common in carbocation rearrangements.^{2,13}

At temperatures above −40 °C, rearrangement of the 2-butyl cation into the *tert*-butyl cation occurs with a barrier of roughly 18 kcal/mol. This implies the involvement of a primary carbenium ion structure as an intermediate or transition state (Scheme II).

Another process believed to involve an isobutyl cation transition structure was observed by studying H- and C-scrambling in the *tert*-butyl cation. Saunders and Rosenfeld first estimated the barrier for this process to be above 28 kcal/mol.¹⁴ Olah et al. observed C-scrambling in the *tert*-butyl cation to take place at 70 °C and evaluated the activation energy to be at least 30 kcal/mol.¹⁵ This corresponds to the energy difference between the *tert*-butyl and the primary isobutyl cation. Hence, the energy difference between the *tert*-butyl and the 2-butyl cation should be ca. 12 kcal/mol on the basis of the solution data.

The heat evolved during the rearrangement of the 2-butyl cation to the *tert*-butyl cation in a SbF₅/SO₂ClF solution has been measured directly in a calorimeter at −106 °C by Arnett et al.^{16,17}

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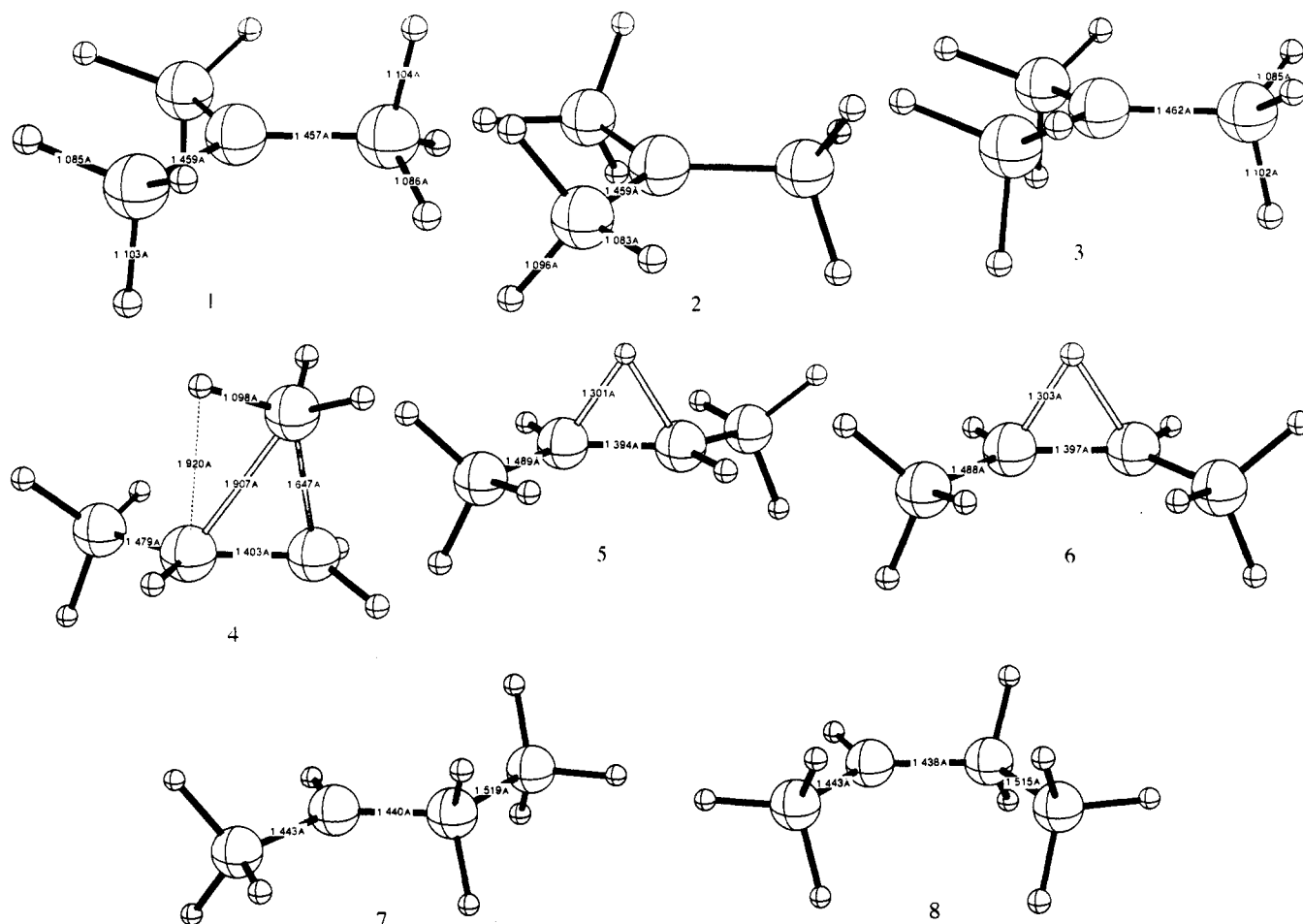


Figure 1. MP2/6-31G** optimized structures of the $C_4H_9^+$ isomers 1-8.

The average values for the rearrangement enthalpy based on two independent calorimetric techniques were 14.5 ± 0.5^{16} and 14.6 ± 0.7^{17} kcal/mol, respectively. Many gas-phase observations of butyl cations have been reported.^{18,19} In a pulsed ion cyclotron resonance experiment, Shold and Ausloos observed that branched chain precursors yielded primarily the *tert*-butyl ion. The isobutyl cation derived from isobutyl precursors rearranges immediately to the tertiary cation; only a small fraction isomerizes to the secondary species.^{18,19} The 2-butyl cation is formed from *n*-butyl or 2-butyl precursors. However, the *tert*-butyl cation is also detected as a consequence of the 2-butyl to *tert*-butyl rearrangement. The extent of this rearrangement was observed to be dependent on the fraction of the initially formed ions which have sufficient internal energy to overcome the energy barrier for isomerization.¹⁹ The more recent determinations give differences in heats of formation between the *tert*-butyl and 2-butyl cation which cluster between 14 and 17 kcal/mol (Table I).²⁰⁻²⁶

Some of the prior theoretical examinations of $C_4H_9^+$ species are summarized in Table II. We will comment on individual investigations of the *tert*-butyl and 2-butyl cation structures when discussing the respective species in the following sections. We call specific attention to a recent theoretical paper reporting an exhaustive investigation of the $C_4H_9^+$ potential energy surface, but only employing a very modest theoretical approach, the semiempirical MINDO/3 method.³⁶ In the present work we use much more sophisticated levels of ab initio theory with explicit consideration of electron correlation effects (also in the geometry optimization) to carry out a thorough and detailed computational investigation of the structures and energies of the various $C_4H_9^+$ isomers and the rearrangement.

Methods

The ab initio calculations have been carried out using the Gaussian 82,³⁷ 86,³⁸ 88,³⁹ and 90⁴⁰ as well as CADPAC 4.1⁴¹ programs. Standard 6-31G* (split valence including d-type polarization functions on carbon) and 6-31G** (which also includes p-type polarization functions on hydrogen) basis sets have been employed. The effects of dynamical electron correlation were included by means of Møller-Plesset (MP) perturbation theory. All geometries were fully optimized using analytical gradient techniques in the specified symmetry at the Hartree-Fock level using the 6-31G* (HF/6-31G*) basis set and at the correlated level using second order MP theory (correlating all electrons, MP2(full)), and the 6-31G* and 6-31G** basis set (MP2(full)/6-31G* and MP2(full)/6-31G**). The force constant matrix, the harmonic frequencies, and the IR intensities were computed analytically at the HF/6-31G* and MP2/6-31G* level (the latter using CADPAC) to characterize each stationary point as a minimum or saddle point, to determine the zero point vibrational energy (ZPE), and to provide computational predictions of the IR spectra of the $C_4H_9^+$ minimum structures.

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(38) Gaussian 86: Frisch, M. J.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Melius, C. F.; Martin, R. L.; Stewart, J. J. P.; Bobrowicz, F. W.; Rohlfing, C. W.; Kahn, L. R.; DeFrees, D. J.; Seeger, R.; Whiteside, R. A.; Fox, D. J.; Fluder, E. M.; Pople, J. A. Carnegie-Mellon Quantum Chemistry Publishing Unit, Pittsburgh, PA, 1984. The IBM version was used.

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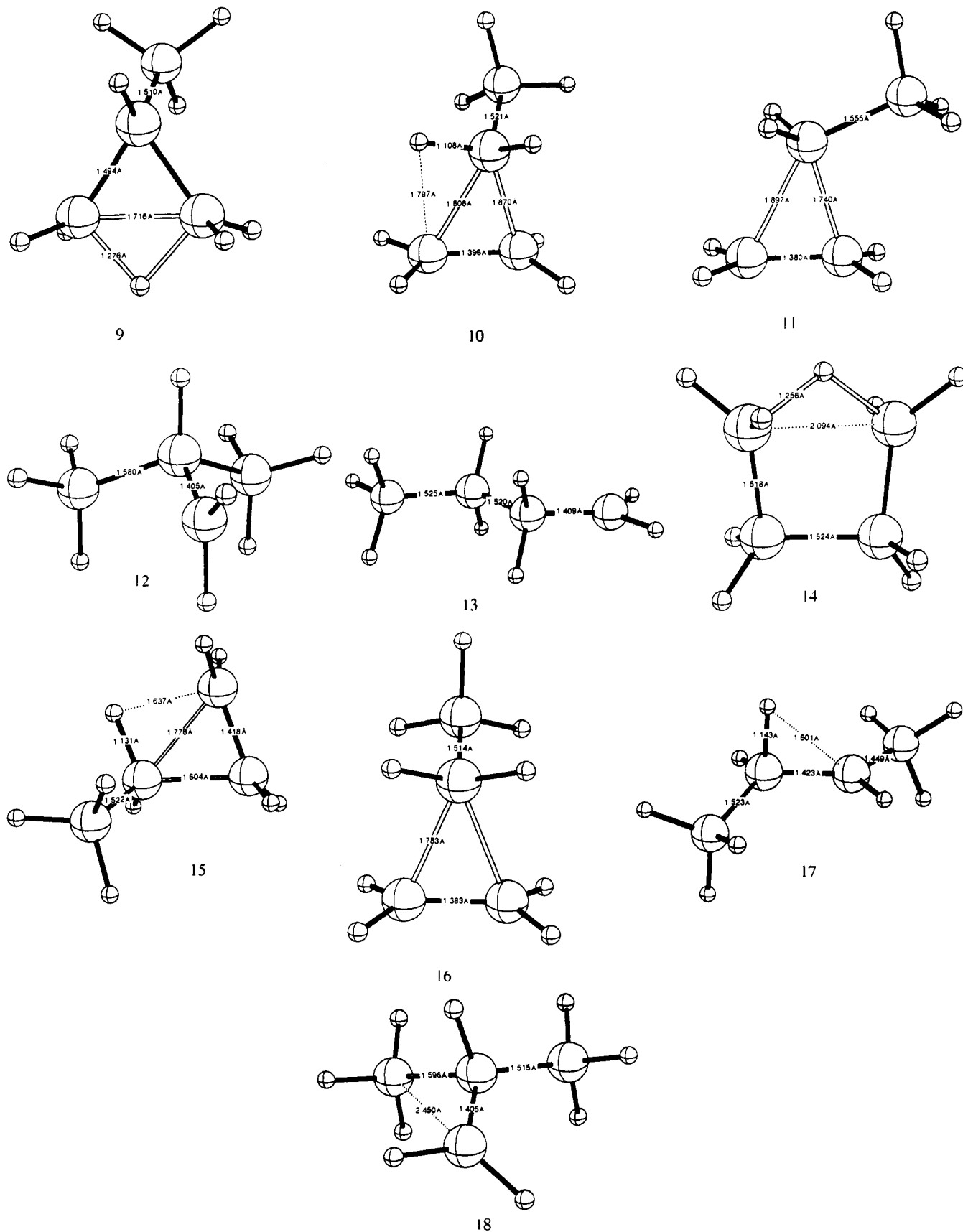


Figure 2. MP2/6-31G** optimized structures of the $C_4H_5^+$ isomers 9–18.

The optimized MP2(full)/6-31G** geometries were then subjected to single point energy determinations at our final level, MP4sdq/6-31G**//MP2(full)/6-31G** + ZPE (the “//” means “at the geometry of”). This includes also the corrections for the zero point energy computed at MP2/6-31G* (and scaled by 0.93⁴²). The basis sets, Møller-Plesset perturbation theory, and the computational procedures have been

described in detail.⁴² The most important structures are shown in Figures 1 and 2 (the MP2(full)/6-31G** geometries are plotted). Total

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Table III. Total Energies (-au)

species	theoretical level			
	6-31G*// 6-31G*	MP2(FU)/ 6-31G*// 6-31G*	MP2(FU)/ 6-31G**// 6-31G**	MP4sdtq/ 6-31G**// 6-31G**
1	156.442 549	156.959 665	157.030 308	157.081 054
2	156.442 413	156.959 542	157.030 085	157.080 895
3	156.440 714	156.957 486	157.028 035	157.079 021
4	156.420 808	156.942 150	157.013 269	157.061 850
5	156.414 196	156.938 210	157.010 856	157.060 719
6	156.412 349	156.936 782	157.009 422	157.059 301
7	156.419 153	156.933 716	157.004 449	157.055 919
8	156.418 484	156.934 492	157.005 178	157.056 546
9	156.392 381	156.927 985	157.001 452	157.048 497
10	156.398 999	156.929 901	157.001 681	157.049 465
11	156.395 416	156.922 803	156.993 883	157.042 764
12	156.390 438	156.906 769	156.978 035	157.029 584
13	156.388 240	156.901 213	156.972 403	157.024 142
14	156.375 078	156.902 742	156.976 712	157.027 362
15	156.394 554	156.928 672	157.001 522	157.049 018
16	156.398 530	156.929 166	157.000 549	157.048 581
17	156.420 327	156.936 009		
18	156.390 131	156.906 081	156.977 429	157.029 055

energies are listed in Table III. Relative energies are given in Table IV. As will be described later, we have determined the IR spectra of the *tert*-butyl and 2-butyl cations experimentally. These results are compared with calculated spectra for different forms of these species. Figure 3 shows the computed harmonic frequencies (scaled by 0.93⁴²) and IR intensities in the form of simulated IR spectra using a Lorentzian function for each band shape; the same width (20 cm⁻¹) was assumed for each band. A complete list of the computed harmonic frequencies (scaled by 0.93⁴²) and IR intensities of the four minimum ion structures is available as supplementary material.

The 2-butyl and the *tert*-butyl cations were generated in a cryogenic matrix using the method of Vančik and Sunko.³³

Energies and Geometries

A. The *tert*-Butyl Cation. Much less attention has been paid previously to the structure of the *tert*-butyl cation than to the nature of the 2-butyl cation. *tert*-C₄H₉⁺ has always been assumed to be the classical tertiary cation prototype, a reference standard for carbenium ion behavior.⁴³ Thus, there has been little consideration of its nature, in contrast to the complexities and uncertainties concerning the 2-butyl cation structure.³² Early theoretical studies,⁴⁴ using the minimal STO-3G basis set, favored a C_{3h} over a C_{3v} arrangement. This contradicted Olah's et al. conclusions, based on IR and Raman spectra, which were interpreted as favoring a C_{3v} symmetry structure (also see below).⁴⁵ Very recently, Yannoni, Myhre, and co-workers used nutation NMR techniques to determine the carbon skeleton of the *tert*-butyl cation experimentally. They concluded that the *tert*-butyl cation is "trigonal with a short central-carbon methyl bond length" (1.46–1.47 Å).⁴⁶

We computed three higher symmetry *tert*-butyl geometries, with C_s, C_{3h}, and C_{3v} point groups (1, 2, and 3, respectively). We also probed the C₃ geometry, but this optimized to C_{3h} at all levels employed. At the MP2/6-31G* level all three structures proved to be transition states by frequency analysis. Only a C₁ form was found to be a minimum, but its energy was identical to that of 1. This situation reflects the flat hypersurface for methyl group rotation. The lowest harmonic frequency of the C₁ form is very small (23 cm⁻¹). The C_{3v} and the C_s forms each have one imaginary frequency (a₂, 173i cm⁻¹ and a'', 27i cm⁻¹, respectively)

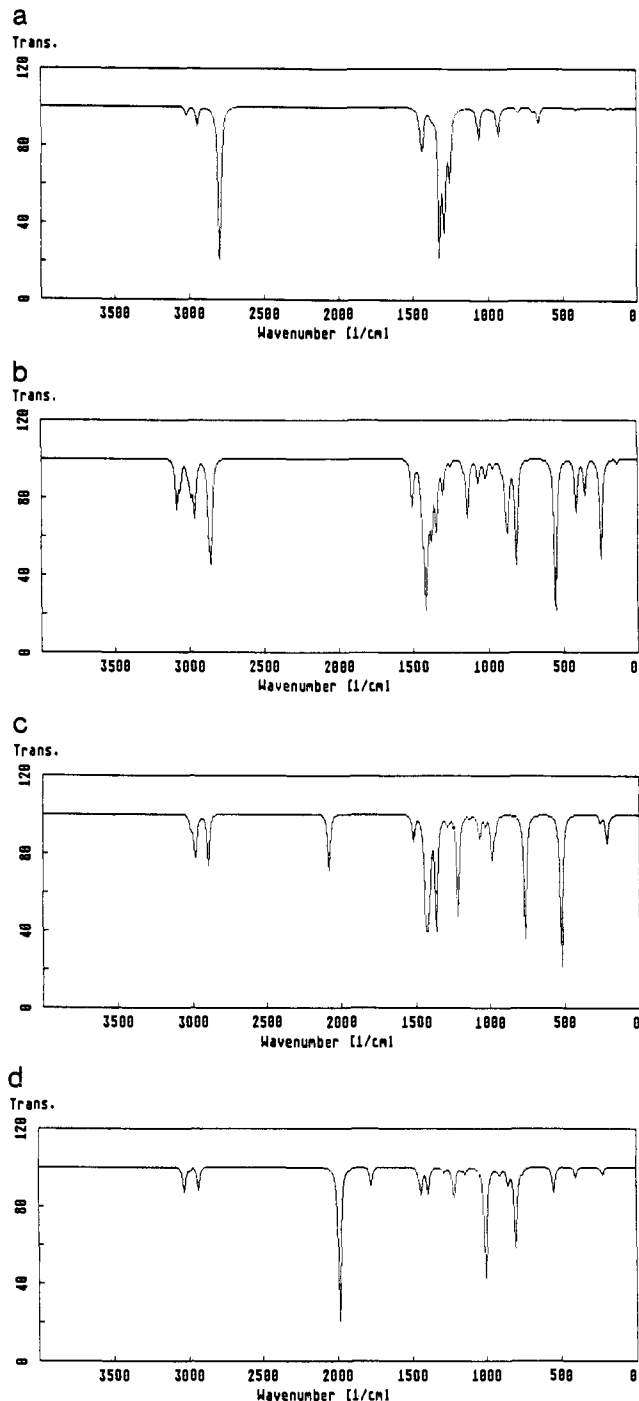


Figure 3. (a) Simulated IR spectrum of *tert*-butyl cation, C_s symmetry (MP2/6-31G*). (b) Simulated IR spectrum of 2-butyl cation, C₁ symmetry (MP2/6-31G*). (c) Simulated IR spectrum of 2-butyl cation, C₂ symmetry (MP2/6-31G*). (d) Simulated IR spectrum of protonated cyclobutane, C₂ symmetry (MP2/6-31G*). IR-Simulator is a program written by A. Haunschild.

and the C_{3h} form has a degenerate set (e'', 73i cm⁻¹). The C_s and C_{3h} forms also are virtually indistinguishable energetically. At the higher MP4sdtq/6-31G**//MP2(full)/6-31G** level, the C_s form 1 is more stable than 2 by 0.1 kcal/mol, but after correction for zero point vibrational energy, the order reverses and the C_{3h} form (2) is favored energetically by 0.1 kcal/mol over 1. This insignificant energy difference and the small values of the lowest harmonic vibrational frequencies again indicate the potential energy surface for rotation of the methyl groups to be extremely flat (rotational barrier ca. 0.1 kcal/mol). The C_{3v} form (3) is always higher in energy than the other structures (1 and 2) by at least 1 kcal/mol (Table IV) at all levels investigated.

(43) See, for example: Brown, H. C. (with comments by P. v. R. Schleyer) *The Non-Classical Ion Problem*; Plenum: New York, 1977.

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(45) Olah, G. A.; DeMember, J. R.; Commeyras, A.; Bribes, J. L. *J. Am. Chem. Soc.* **1971**, *93*, 459.

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The carbon skeleton geometries of all *tert*-butyl cations are very similar. At HF/6-31G*, the optimized C–C⁺ bond lengths vary from 1.472 to 1.475 Å. The carbon framework of the C_s and C_{3h} structures is planar and the central carbon atom in the C_{3v} form diverges from the plane of the three methyl carbon atoms only by 2°. The inclusion of electron correlation does not change this picture significantly. The C–C⁺ bond lengths are reduced a bit, to 1.458–1.460 and to 1.457–1.459 Å at MP2(full)/6-31G* and at MP2(full)/6-31G**, respectively. Again these are very similar and are in good agreement with Yannoni et al. experimental result of 1.46–1.47 Å.⁴⁶ One point deserves specific consideration. As we observed for other systems,^{29,47} there is always a small but definite preference for structures which offer better possibilities for stabilization through hyperconjugative distortion. Thus in the 2-propyl²⁹ and *tert*-pentyl⁴⁷ cations, the preferred structures are those which have C–H (or C–C) bonds aligned parallel to the “vacant” p-orbital at the formal carbenium ion center. This results in decreases in the corresponding bond angles. This situation also pertains in the *tert*-butyl cation (Table V). In the C_s structure, each methyl carbon has a C–H bond which is aligned parallel to the formally vacant p-orbital on the central carbon atom. Two of these are on one side of the carbon “plane” and the third on the opposite side (see 1). Distortion of the methyl groups increases this interaction. All three of these hyperconjugating hydrogens bend toward the central carbon. The C_{3h} *tert*-butyl cation has six symmetrically oriented C–H bonds which can hyperconjugate with the formally vacant orbital on the carbenium carbon, but the interactions are not optimal since these C–H bonds diverge by about 30° from the ideal alignment; hyperconjugative distortion also is ineffective when so many equivalent H's are involved. This interpretation is corroborated by analyzing the conformation around the methyl carbons.⁴⁸ In the MP2(full)/6-31G** optimized C_s structure the C–H bonds aligned with the p-orbital on the central carbon atom are elongated to 1.103–1.104 Å in contrast to the other C–H bonds, which are significantly shorter (1.084–1.087 Å). The C–C–H angles of the hyperconjugating bonds are 102.6–103.5°, while the other bond angles vary from 112.6 to 113.7°. The MP2(full)/6-31G** optimized C_{3h} structure shows these typical effects of hyperconjugation to a lesser extent. The C–H bond lengths are 1.096 and 1.083 Å for the hyperconjugating and the perpendicular bonds, respectively. The corresponding C–C–H angles are 107.9° and 114.4°. Elongated C–H bonds and H atom bending toward the formal cationic center (i.e., reduced C–C–H angles) are typical of systems stabilized by C–H hyperconjugation.^{47,48} This is now established to be a general feature of carbocation structures.

Why is not the C_{3v} structure hyperconjugatively stabilized, since three C–H bonds are ideally aligned with the “vacant” p-orbital? The MP2(full)/6-31G** optimized C_{3v} geometry does show the same features as the C_s form. The hyperconjugating C–H bonds are elongated to 1.102 Å; the other C–H distances are 1.085 Å.⁴⁹ However, in this case the remaining hydrogen atoms are in the same plane and there is a repulsive steric effect. This results in the deviation (2°) of the central carbon from the plane of the three methyl carbons. This effect results in the 1.2 kcal/mol energy difference of the C_{3v} structure (3) relative to the C_s conformer (1) at our final level. While the energies of 1 and 2 are very similar, we believe that the C_s structure (1), which is better suited for hyperconjugation, should be the global minimum. We present spectroscopic evidence in supporting these conclusions in the vibrational spectra section, below.

B. The 2-Butyl Cation. The 2-butyl cation structure has not yet been established experimentally.³² Indeed the conclusions based on experimental evidence appear to be contradictory.

Saunders and Kates investigated the 2-butyl cation at –140 °C and set a 2.4 kcal/mol upper limit for the 2,3-hydride shift.⁵⁰ The solid-state ¹³C–CPMAS–NMR results of Myhre and Yannoni show no evidence for a static 2-butyl cation at temperatures as low as –190 °C.⁵¹ Due to the often observed suppression of the rates of chemical processes in solid state,⁵² these authors suggested that the barrier for the 2,3-hydride shift in solution should be considerably less than 2.4 kcal/mol. In a comprehensive analysis of the ¹³C NMR spectrum of alkyl cations in superacid solution. Olah and Donovan, based on the observation of two quartets in the fully ¹H coupled ¹³C NMR spectrum, excluded a static hydrogen bridged 2-butyl cation intermediate,⁵³ as did Myhre and Yannoni's solid-state evidence.⁵¹ Olah and Donovan suggested that the best agreement with the NMR data is achieved by a model assuming a rapidly equilibrating system with the H-bridged and the two degenerate open chain cations being of similar stability, so that both types of intermediates would contribute to the averaged ¹³C NMR spectrum.⁵³

In contrast to these conclusions, solvolytic studies by Dannenberg et al. gave evidence interpreted to favor the H-bridged structure.⁵⁴ The solvolysis of 1,1,1,2-tetradeuterio-2-butyl tosylate yielded equal amounts of 1,1,1,2-tetradeuterio-2-butyl and 3,4,4,4-tetradeuterio-2-butyl derivatives, with only an insignificant formation of D-scrambled products. The authors felt that these results are strongly suggestive of a bridged ion intermediate.⁵⁴ Dietze and Wojciechowski⁵⁵ found ¹⁸O scrambling in labeled 2-butyl-4-bromobenzenesulfonate recovered after partial trifluoroacetylation. That optically active substrate did not racemize concurrently is consistent with a chiral 2-butyl cation ion pair intermediate, although this explanation was not considered by the authors. The most recent experimental observations have also led to different conclusions. Johnson and Clark generated the 2-butyl cation by deposition of 2-butene on a superacid surface in the source of an ESCA spectrometer.⁵⁶ The C 1s spectrum resulting did not have two peaks with 1:1 intensity ratio, as required for a system with only two carbon environments like the H-bridged structure 5. Indeed the spectrum can be better reproduced by assuming three peaks of intensity ratio 1:1:2 to be present, which was interpreted to favor a partially methyl bridged 2-butyl cation structure.⁵⁶ However, the ESCA spectrum was broad, and the possibility of contamination with neutral material or the presence of a second C₄H₉⁺ form was not excluded. Indeed, the separation of the main peaks corresponds to that calculated for the H-bridged cation 5. In addition, there is the possibility that the species observed on the surface may be different from that in the bulk. The second line of experimental evidence is not yet published in full. Based on temperature dependence of isotopic shifts of NMR ¹H and ¹³C spectra and isotopic perturbation of the 2-butyl cation, Saunders and Walker⁵⁷ concluded that the best fit with experimental results is obtained with a model assuming both methyl and H-bridged structures to be present. In contrast to Johnson and Clark, Saunders concluded that the H-bridged structure is more stable by 0.4 kcal/mol.^{56,57} Saunders repeated his isotopic perturbation experiments in 1991, which confirmed the former NMR investigations: The symmetrically bridged form is in equilibrium with a second unsymmetrical structure. Very recently a low-temperature IR investigation of the 2-butyl cation had been published by our group. Applying the matrix technique developed by Sunko et al.⁵⁸ clear evidence could be found for the C₂ symmetrical H-bridged form being at least the main isomer.³³ The IR spectrum of the 2-butyl cation measured at –125 °C in an SbF₅ matrix and calculated ab initio (MP2(full)/6-31G*) was

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(49) The MP2(full)/6-31G* optimized C–H bond lengths are usually longer than those at MP2(full)/6-31G**. The MP2(full)/6-31G* C–H bond lengths in the C_{3v} geometry are 1.101 and 1.089 Å while in the C_s form they are 1.108–1.109 vs 1.090–1.092 Å, respectively.

Table IV. Relative Energies (kcal/mol)

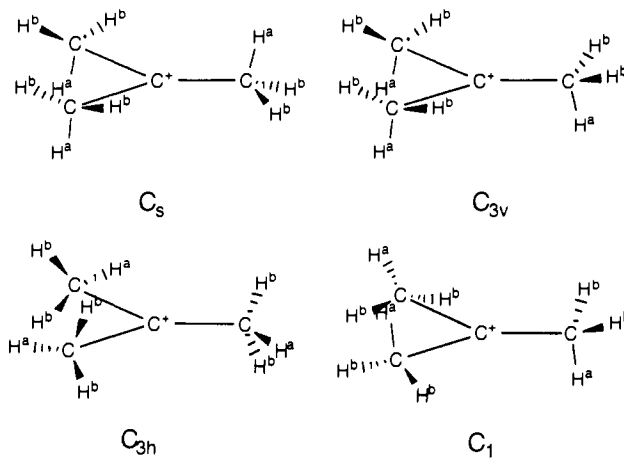
species	theoretical level			
	6-31G*// 6-31G*	MP2(FU)// 6-31G*	MP2(FU)// 6-31G**	MP4sdq// 6-31G**
	6-31G* ^a	MP2(FU)// 6-31G* ^b	MP2(FU)// 6-31G** ^b	MP2(FU)// 6-31G** ^b
1	0.00	0.00	0.00	0.00
2	-0.16	-0.16	-0.10	-0.14
3	1.03	1.24	1.30	1.14
4	14.58	12.78	12.48	13.83
5	17.65	14.10	12.84	13.39
6	18.88	15.00	13.74	14.28
7	14.71	16.22	16.16	15.70
8	15.17	15.74	15.70	15.31
9	32.64	21.35	19.58	21.90
10	29.25	20.85	20.13	21.99
11	31.40	25.62	25.34	26.51
12	33.53	34.28	33.89	33.38
13	34.22	36.72	36.37	35.75
14	43.81	37.93	35.84	35.89
15	31.56	21.18	19.80	21.83
16	29.40	21.05	20.58	22.28
17	14.26	14.88		
18	33.25	34.03	33.59	33.03

^aIncluding correction for ZPE calculated at 6-31G* (scaled by 0.89, see text). ^bIncluding correction for ZPE calculated at MP2/6-31G* (scaled by 0.93, see text).

characterized by a C(H)C peak at 2175 cm⁻¹ assigned to the nonclassical H-bridged structure. We discuss these results in full below.

Similar to experimental evidence, the early theoretical computations on 2-butyl cation isomers were not definitive. In a first attempt to characterize this cation, Radom, Pople, and Schleyer used a minimal STO-3G basis set to calculate a C₁ and a C_s classical structure.⁴⁴ At this very modest level, the C₁ form was found to be 2.2 kcal/mol more stable than the classical C_s isomer. Köhler and Lischka⁵⁹ still used the STO-3G basis set but included electron correlation through the CEPA approximation. Their final estimate is that the H-bridged structure is more stable than a classical C_s form by 8–10 kcal/mol. In a study related to the ESCA work, Clark and Harrison investigated 2-butyl structures at "STO-4-31G" using assumed, i.e., not explicitly optimized geometries.⁶⁰ These authors analyzed an open chain classical structure and forms with varying degrees of methyl bridging and concluded that the 2-butyl cation may adopt a partially methyl bridged structure.⁶⁰

We discuss five 2-butyl cation structures; the two H-bridged trans C₂ (5) and cis C_s (6), the C₁ (4), and the open chain classical trans (7) and cis C_s (8) forms. At HF/6-31G* only the C₁ structure (4) is a minimum; all the other structures have one imaginary harmonic frequency. However, subsequent characterization of the MP2(full)/6-31G* and MP2(full)/6-31G** geometries showed that, besides the C₁ structure (4), the H-bridged C₂ (5) and C_s (6) forms are minima as well.³² At the HF level, the C₁ structure (4) clearly has the lowest energy (Table IV). However, this is no longer the case when electron correlation effects are included. Even at MP2(full)/6-31G*//HF/6-31G* (i.e., using the HF geometry), the C₂ H-bridged structure (5) is more stable than the C₁ alternative (4). Optimization at the correlated MP2/6-31G* level distorts the C₁ geometry (4) strongly (see discussion below) and lowers the energy with respect to the *tert*-butyl cation (1) by 3.6 kcal/mol. In contrast the HF to MP2 energy reduction for the H-bridged C₂ form is only 0.5 kcal/mol. This situation alters the relative stability ordering, e.g., at MP4sdq/6-31G**//MP2(full)/6-31G** the C₁ form (4) is slightly more stable, 0.7 kcal/mol. When this value is corrected for zero point vibrational energies the order reverses, and the H-bridged C₂ form (5) becomes more stable by 0.4 kcal/mol. Harmonic frequency calculations at the MP2(full)/6-31G* level

Table V. Structural Data of the *tert*-Butyl Cation Isomers Calculated at MP2/6-31G**^a


isomer		<i>d</i> (HC) (Å)	<(HCC ⁺)	<(HCC ⁺ p) ^b
C _s	H ^a	1.103–1.104	102.5–103.4	0.0–1.0
	H ^b	1.085–1.087	112.7–113.6	64.9–65.4
C _{3v}	H ^a	1.102	104.2	0.0
	H ^b	1.085	113.0	64.5
C _{3h}	H ^a	1.083	114.4	90.0
	H ^b	1.096	107.9	34.0
C ₁	H ^a	1.102–1.104	102.6–104.1	5.8–9.8
	H ^b	1.084–1.088	111.9–114.1	57.1–72.0

^aThe C₁ geometry is the only minimum structure at this level. ^bDihedral angle between H, C, C⁺ and (empty) p-orbital on C⁺.

Table VI. IGLO ¹³C NMR Chemical Shifts (vs CH₄) for *tert*-Butyl Cation Isomers

point group	IGLO basis// geometry level	δ ¹³ C			H ₂ av	H ₄ av
		C ₁	C ₂	C ₄		
C _s	DZ//6-31G*	358.8	46.4	47.1	3.9	3.9
	II//6-31G*	360.0	40.2	41.3		
	DZ//MP2/6-31G*	346.9	45.9	47.0	4.1	4.1
	II//MP2/6-31G*	348.0	39.9	41.5		
C _{3h}	DZ//MP2/6-31G**	346.5	45.6	46.8	3.7	3.7
	DZ//6-31G*	364.0	46.5		4.0	
	II//6-31G*	365.0	40.8			
	DZ//MP2/6-31G*	352.4	46.0		4.2	
expt (vs TMS) ^a	II//MP2/6-31G*	354.0	40.5			
	DZ//MP2/6-31G**	353.0	45.7		3.9	
		335.2	47.5			

^aReference 46. ^bThe ¹³C absolute chemical shifts of CH₄ and TMS calculated with the DZ basis set differ by 0.2 ppm, absolute shifts calculated with the IGLO/II basis set differ by 5.7 ppm.

corroborate this result and confirm that the global 2-butyl cation minimum is the C₂ H-bridged structure 5.³² The potential energy surface in the vicinity of this minimum is not very flat. The frequency which corresponds to the symmetry-breaking CHC(↔) vibrational modes is rather high (565 cm⁻¹), the minimum lies in a deep well. As expected, the other three 2-butyl species are higher in energy than both of these minima. At our final level, the relative energy (vs 5) of the cis H-bridged C_s (6) as well as the open chain cis (8) and trans (7) forms are 0.9, 1.9, and 2.3 kcal/mol, respectively (Table IV). The open chain cis form (8) is favored over the trans (7) at all levels by about 0.3–0.5 kcal/mol. The energy difference between the trans (5) and cis (6) H-bridged isomers is almost identical to the experimental energy difference between *trans*- and *cis*-2-butene of 1.1 kcal/mol.⁶¹

The HF/6-31G* optimized C₁ structure, which has also been reported by Ibrahim and Jorgensen,⁶² is partially methyl bridged even at this level. The C₂⁺–C₃–C₄ angle already is quite small,

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Table VII. IGLO ^{13}C NMR Chemical Shifts (vs CH_4) for 2-Butyl Cation Isomers

description	IGLO basis// geometry level	angle ^a $\text{C}_2^+-\text{C}_3-\text{C}_4$	$\delta^{13}\text{C}$						
			C_1	C_2	C_3	C_4	$(\text{C}_1\text{C}_4)_{\text{av}}^b$	$(\text{C}_2\text{C}_3)_{\text{av}}^b$	
open chain (classical) methyl-bridged	DZ//6-31G*	116.7	45.5	360.8	52.3	7.8	26.7	206.6	
	DZ//6-31G*	102.4	43.5	335.0	49.1	9.3	26.4	192.1	
	II//6-31G* ^d		39.2	338.0	48.1	5.2	22.2	193.1	
	DZ//6-31G* ^e	97.0	40.2	316.6	51.4	6.9	23.6	184.0	
	DZ//6-31G* ^e	92.5	37.0	295.7	53.6	4.5	20.8	174.7	
	DZ//6-31G* ^e	87.0	31.6	255.6	52.5	-2.8	14.4	154.1	
	DZ//6-31G* ^e	77.0	23.2	180.1	61.8	-10.6	6.3	121.0	
	DZ//MP2/6-31G*	77.4	24.0	178.3	57.0	-13.7	5.2	117.7	
	II//MP2/6-31G*		20.5	178.0	52.7	-14.0	3.3	115.4	
	II//MP2/6-31G*		20.4	177.0	52.9	-13.4	3.5	115.0	
	DZ//MP2/6-31G**	76.9	23.0	174.2	55.1	-15.9	3.6	114.7	
	DZ//6-31G* ^e	67.0	18.9	117.9	108.0	-4.0	7.5	113.0	
	H-bridged	DZ//6-31G*		19.1	160.0				
		II//6-31G*		15.0	156.0				
DZ//MP2/6-31G*			19.8	161.2					
DZ//MP2/6-31G*+1p ^f			19.6	161.2					
DZ//MP2/6-31G**			19.1	161.2					
DZ//MP2/6-311G**			20.0	162.5					
II//MP2/6-31G*			15.8	157.0					
II//MP2/6-31G*			15.4	156.0					
expt (vs TMS) ^g			21.0	171.6					

^aAngles in deg. ^bAverage values for C_1 and C_4 . ^cAverage values for C_2 and C_3 . ^dIGLO calculations with basis II and II' by U. Fleischer. ^eGeometry fully optimized but $\text{C}_2^+-\text{C}_3-\text{C}_4$ angle fixed. ^fSingle p-function on the bridging hydrogen ($p\text{-exp} = 0.7$). ^gAveraged values: ref 4. The ^{13}C absolute chemical shifts of CH_4 and TMS calculated with the DZ basis set differ by 0.2 ppm, absolute shifts calculated with the IGLO/II basis set differ by 5.7 ppm.

102.4°. The C_2^+-C_3 and C_3-C_4 bond lengths are 1.447 and 1.584 Å, respectively, and the C_2^+-C_4 distance is 2.364 Å. Reoptimization at MP2(full)/6-31G* changes this geometry dramatically. Electron correlation strongly favors C-C hyperconjugation, and at the correlated level the C_1 structure has an almost symmetrically bridged geometry with the $\text{C}_2^+-\text{C}_3-\text{C}_4$ angle decreased to 77.4°. In addition, the bridging methyl group rotates to an eclipsed conformation (see 4). As observed for C-H hyperconjugation, the hyperconjugating C_3-C_4 bond elongates to 1.652 Å, the C_2^+-C_3 distance decreases to 1.403 Å, and the C_2^+-C_4 distance to 1.920 Å. These structural changes, already notable in the HF/6-31G* geometry,⁶² are very much accentuated by optimization at the correlated level. The deformed geometry of the C_1 structure (4) resembles a propene-methyl cation complex; it can also be considered to be an asymmetric corner protonated methylcyclopropane. We refer to 4 as the methyl-bridged 2-butyl cation, to differentiate from the trans H-bridged structure 5. The most stable 2-butyl cation form 5 has a *trans*-2-butene- H^+ complex-like geometry. The central C-C bond in 5 is 1.383 and 1.393 Å at HF/6-31G* and at MP2(full)/6-31G*, respectively. The distances between the bridging hydrogen atom and the midpoint of the C_2-C_3 bond are 1.110 and 1.105 Å at those levels. Inclusion of p-type polarization functions on all hydrogens (MP2(full)/6-31G**) does not influence the geometry, after reoptimization, significantly. At this level the $\text{C}_2^+-\text{C}_3-\text{C}_4$ angle in the methyl-bridged structure (4) reduces marginally to 76.9°, and the C_2^+-C_3 , C_3-C_4 , and C_2^+-C_4 bond lengths are 1.403, 1.647, and 1.906 Å, respectively. The C_2 hydrogen-bridged structure (5) has a central C-C bond length of 1.394 Å; the distance of the bridging H atom to the midpoint of the C_2-C_3 bond is reduced to 1.098 Å. The cis H-bridged structure 6 has a geometry similar to 5, with small deformations due to the steric interactions between the two methyl groups. The C_1 open chain structures 7 and 8 have more typical "classical" geometries.

At the MP2(full)/6-31G* level another 2-butyl cation minimum 17 could be obtained: this structure has one H at C_3 partly bridging the C_2-C_3 bond with a bond angle of 88.5° and a bond length of 1.143 Å. This clearly shows strong C-H hyperconjugation and is the only minimum in this region of the PES obtained at HF levels. However, such structures are artifacts, since they vanish from the PES at both the MP2(full)/6-31G** and MP2(full)/6-311G** levels. The recent experimental results from Saunders^{57a,b} stimulated us to search further for a minimum like 17. We started with the MP2/6-31G* geometry of 17 and used

a single p-function on the partially bridging hydrogen and also MP2/6-311G** for the whole molecule. Both calculations led to the symmetrically bridged C_2 form 5. Thus, partially bridged structures like 17 can definitively be ruled out as possible minima on the 2-butyl cation PES.

C. Protonated Methylcyclopropane. Besides the methyl bridged 2-butyl cation 4, a protonated methylcyclopropane, we have found five additional structures (9-11, 15, 16). Only one, the asymmetric 10, is a local minimum. At our final level 10 is only 8.6 kcal/mol higher in energy than the global 2-butyl minimum 5. The corresponding symmetric planar and perpendicular structures were characterized to be transition states. The edge protonated methylcyclopropanes 9 and 15 are the transition states for scrambling carbons C_1 and C_2 in the 2-butyl cation (Schemes I and III) and the rearrangement of 4 to 10, respectively. The local minimum 10, according to its geometry, can also be considered to be a π -complex of the ethyl cation with ethylene. The difference in energy between 10 and 16 is only ca. 0.3 kcal/mol, indicating a flat hypersurface for the ethyl group motion. The asymmetrical form 10 is favored over the symmetrical one (16) through insipient coordination of one of the C_3 hydrogens to C_1 (see Figures 1 and 2). This hydrogen migrates during rearrangement to the methyl bridged 2-butyl cation.

D. Protonated Cyclobutane. A fourth C_4H_9^+ species, which has elicited some interest in the literature,⁶³⁻⁷² is protonated cyclobutane. The special behavior and enhanced reactivity of protonated cyclopropanes is well-known. To what extent can special properties be expected in the protonated forms of the larger cycloalkanes? While, for example, protonated cyclopentane and protonated cyclohexane should hardly be any different from protonated acyclic alkanes, the strain energy of cyclobutane is nearly the same as that of cyclopropane. Hence, the proton affinity of cyclobutane might be enhanced, at least to some extent. However, gas-phase measurements⁶³ give $\Delta H_f^\circ(\text{gas}) = 223$ kcal/mol or a proton affinity of ca. 150.6 kcal/mol. This PA is considerably lower than that of cyclopropane (exptl 179.8) and may be compared with the PAs reported (in kcal/mol) for ethane (143.6), propane (150), isobutane (163.3), and cyclohexane (ca. 169).⁶⁴ Cacace et al. also reported evidence for the formation

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of protonated cyclobutane,⁶⁵ but this species rearranges rapidly in the gas phase to more stable isomers.¹⁸ The solution behavior of cyclobutane in strong acid media is similar. There is evidence for H^+/D^+ (or T^+) exchange,^{66,67} but ring opening products are observed frequently.^{68,69} One can infer from the experimental literature that protonated cyclobutane may be a high-lying minimum with a low barrier for isomerization into more stable ions.

Prior theoretical investigations on protonated cyclobutane were not carried out at the higher levels possible today and are inconclusive. Pakkanen and Whitten investigated both edge and corner protonated forms with partial geometry optimization and found a proton affinity (126 kcal/mol) which is much too low.⁷⁰ Lee et al. included cyclobutane in a comparative study of the protonation of cycloalkanes.⁷¹ In all these cases, only corner rather than edge protonated forms were investigated. The very modest 4-31G//STO-3G level gave a PA of 148.1 kcal/mol which is in reasonably good accord with experiment. However, this agreement is likely to be fortuitous, since unreasonably low values were found for cyclopentane and cyclohexane in the same study. Neither frequency analysis nor corrections for zero point energy differences were carried out. Employing the MP3/6-31G**//6-31G* level of theory, Wiberg and Kass investigated edge protonated as well as corner protonated cyclobutane. The latter structure was found to be considerably less stable than the edge protonated form.⁷²

We find an edge protonated cyclobutane minimum with a twisted geometry (**14**, point group C_2) to be the most stable protonated cyclobutane. However, the relative energy of 35.9 kcal/mol with respect to **1** (Table IV) is very high, and **14** probably cannot be detected as a stable species, in agreement with the (negative) experimental observations. Our PA value, 170.7 kcal/mol (see discussion below), while much higher than any of the previous estimates,^{63,71} is quite reasonable. Protonation leads to an elongation of CC bond length and a reduction in strain energy.

E. Other Structures. We have searched for additional stationary points on the $C_4H_9^+$ PES, in particular for the transition structures for the various rearrangement processes. No further minimum could be located; all the other stationary points were characterized as transition structures. These include the isobutyl cation **12** and the two 1-butyl structures **11** and **13**. The eclipsed transition structure **13** is that expected for a primary cation, but the perpendicular arrangement converges to the planar corner protonated methylcyclopropane **11** already mentioned in section C. The relative energies of these species will be discussed below.

IGLO ^{13}C Chemical Shift Calculations of *tert*-Butyl and 2-Butyl Cations. As described in the introduction, 1H and ^{13}C NMR experimental data furnish considerable information about structures and stabilities of stable carbocations. Only general structural information can be derived from NMR,^{53,73} details are available from theory. Ab initio calculations of magnetic properties as well as structures and energies afford an excellent opportunity for a coherent comparison between experimental and theoretical results. The IGLO (individual gauge for localized molecular orbitals) method⁷⁴ was first applied to carbocations in an extensive paper by Schindler.⁷⁵ However, in that work, most of the molecular geometries used were assumed or were deduced from lower theoretical levels. These were not adequate and did not provide accurate structures. Although Schindler's computed chemical shifts, using a basis set of double- ζ quality (DZ), for *tert*-butyl cation agree reasonably well with experimental data, he concluded

that solute-solvent interactions might be very important in localized carbenium ion systems.⁷⁵ We applied the IGLO method subsequently on structures obtained at high levels of theory and were able to reproduce the chemical shifts of a variety of carbocation species successfully.^{31,32,47,48} We report here the results for the *tert*-butyl and the 2-butyl cations. The computed ^{13}C NMR chemical shifts are very sensitive to small changes in geometry, and the very accurate structures as obtained from high level quantum chemical calculations are often a prerequisite to achieve good agreement between experimental and theoretically predicted ^{13}C NMR data.²⁹⁻³² As Olah also appreciated, solute-solvent interactions do not appear to be important. Tables VI and VII give the ^{13}C NMR IGLO chemical shifts for *tert*-butyl and 2-butyl cations, respectively. We investigated the two more stable *tert*-butyl structures, i.e., C_1 (**1**) and C_{3h} (**2**). The ^{13}C chemical shift of the carbonium carbon of both these species optimized at the HF/6-31G* level deviates by 25-30 ppm from the experimental value. The MP2(full)/6-31G* structures improve the theoretical values by more than 10 ppm, a consequence of the small, but significant, changes in the geometries on going from the HF to the MP2 level. MP2(full)/6-31G** optimization brings only slight additional improvement over those at MP2(full)/6-31G*. The ^{13}C chemical shifts of both structures reflect their similar geometries. The C_1 form **1**, with a conformation better suited for hyperconjugation, also gives better agreement with the experimental chemical shifts. The DZ//MP2(full)/6-31G** ^{13}C chemical shift of the central carbon lies about 11 ppm above the experimental value for the C_1 geometry, while for the C_{3h} structure this difference increases to 18 ppm (Table VI).

We recently discussed the ^{13}C IGLO chemical shifts of the 2-butyl cation.³² Here we would like to make only a few additional observations. The ^{13}C chemical shifts given in Table VII reproduce the geometrical changes discussed before. While the HF geometry (HF/6-31G*) of the C_1 structure **4** results in averaged chemical shifts which are larger than the experimental values, the geometries optimized at the MP2 levels (MP2(full)/6-31G* and MP2(full)/6-31G**) give averaged values which are smaller than experiment. This reflects the change in geometry. In contrast, the geometry of the C_2 structure **5** does not alter appreciably in going from the HF to the MP2 level, and the calculated chemical shifts are also not affected significantly. As in the *tert*-butyl cations, the chemical shifts calculated with the MP2(full)/6-31G*, MP2(full)/6-31G**, and MP2/6-311G** geometries are almost identical. A possible contribution to the error in theoretical chemical shifts is that the IGLO calculations are performed on equilibrium geometries, whereas the experimental NMR values pertain to vibrationally averaged states. When shallow vibrational surfaces are involved, the experimental values may pertain to structures, which differ from the equilibrium geometries.

Vibrational Spectra of $C_4H_9^+$ Cations. The computation of harmonic vibrational frequencies and the corresponding intensities allows IR spectra to be predicted. However, until recently, experimental vibrational spectra of carbocations were very scarce. Olah et al. reported the IR and Raman spectra of the *tert*-butyl cation in $H_2SO_4/SbF_5/SO_2$ superacid media.⁴⁵ Based on a comparison with the spectra of trimethylboron, $B(CH_3)_3$, they concluded that the *tert*-butyl cation spectrum is most consistent with a C_{3h} symmetry. While we identify the C_1 form of *tert*-butyl cation as the minimum energy structure, the very small rotational barrier of the methyl groups does not allow a definitive decision to be made. The computed (MP2/6-31G*) IR spectrum of **1** (Figure 3a) is in reasonable agreement with the early and necessarily cruder solution spectrum recorded by Olah et al.⁴⁵ Comparison of the experimental with the calculated data is restricted to the very intense peaks at 2830 cm^{-1} and 1290 cm^{-1} which are also found in the calculations (2803 cm^{-1} , 88 km/mol ; 2799 cm^{-1} , 125 km/mol ; 1296 cm^{-1} , 129 km/mol). The lowest C-H stretching vibration for the C_{3h} form is 2807 cm^{-1} , very close to that of **1** and 2842 cm^{-1} for the C_{3h} structure. A final decision

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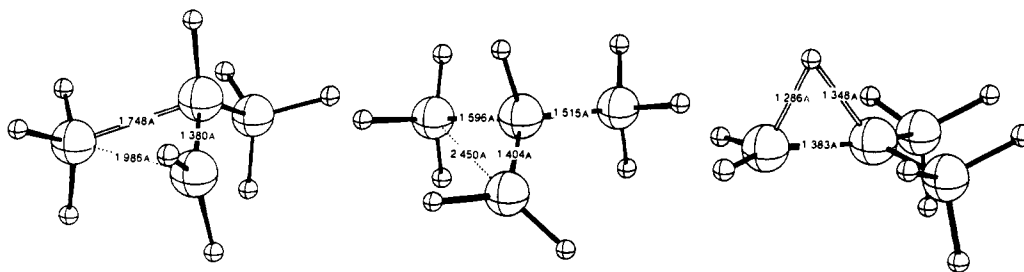


Figure 4. Optimized geometries for selected points along the intrinsic reaction coordinate calculated at the HF/6-31G* level. See Figure 5 for selected points.

about the real structure is not possible, because the *tert*-butyl cation is a highly fluctuating molecule. The IR spectrum of the 2-butyl cation is more instructive. Figure 3b,c shows many clear cut differences in the simulated IR spectra of the two 2-butyl cation isomers. Note in particular the presence of the 2085-cm⁻¹ absorption in **5** and its absence in **4**. Recently our group succeeded in generating the 2-butyl cation in a cryogenic SbF₅ matrix,³³ by using the method reported earlier.⁵⁸ SbF₅ and 2-chlorobutane were codeposited on the surface of a NaCl disc at -165 °C in a low-temperature vacuum IR cell. During warming to -60 °C a new peak at 2175 cm⁻¹ appears. While this vanishes quickly at higher temperature (due to rearrangement, see below), cooling to -125 °C just after the initial appearance of the peak, leads to the spectrum of the almost pure 2-butyl cation, only slightly contaminated with the *tert*-butyl cation. Upon warming to -10 °C, the 2-butyl cation completely rearranges to *tert*-butyl cation. The signal at 2175 cm⁻¹ provides striking evidence for H-bridging and corresponds to a CHC(1) symmetrical stretching vibration. Further applications of this new method were the comparison of computed and experimentally obtained IR spectra of the 2-norbornyl and cyclooctyl cation which demonstrated the usefulness of this combined approach to help identifying the minimum geometry of such species.⁷⁶ The IR data of the edge protonated cyclobutane **14** is given as a simulated IR spectrum in Figure 3d.

Rearrangements on the C₄H₉⁺ Potential Energy Surface. Elucidation of the rearrangement pathways on the C₄H₉⁺ potential energy surface is of particular interest. The central and methyl protons and carbons scramble in the 2-butyl cation with an activation energy of only 7.5 ± 0.1 kcal/mol.¹² The protonated methylcyclopropane postulated to be involved in this process is confirmed here to be the methyl bridged structure **4**. This is calculated to be only slightly less stable than the H-bridged structure, **5**. Interconversion of **5** to **4** occurs via the classical open chain isomers **7** (trans) and **8** (cis) by rotation around the C₂-C₃ bond axis with maximum barriers of 1.9 (via **8**) and 2.3 (via **7**). Hence, the highest energy transition structure for the scrambling process is that involved in the degenerate corner-to-corner hydrogen migration in **4** (Scheme I). The edge protonated methylcyclopropane **9** is calculated to lie 8.5 kcal/mol above **5**. Vibrational frequency calculations confirm that **9** is a transition state (one imaginary frequency), so that this species represents the saddle point for carbon scrambling in the 2-butyl cation. Another possible pathway for the C₁ and C₂ scrambling via **10** is indicated in Scheme III with a maximum barrier of 8.9 kcal/mol. Since the energetic difference between these possible pathways (i.e., via **9** and via **10**) is only 0.4 kcal/mol both may be involved. The primary cation **13** is 22.4 kcal/mol less stable than **5** and can be ruled out as a possible intermediate in this process.

The scrambling process in the 2-butylcation can be summarized as follows. The H- and methyl-bridged structures **5** and **4** are energetically similar with **5** more stable by merely 0.4 kcal/mol. Isomer **4** undergoes a degenerate corner-to-corner hydride shift via the edge protonated methylcyclopropyl cation **9**, to yield an

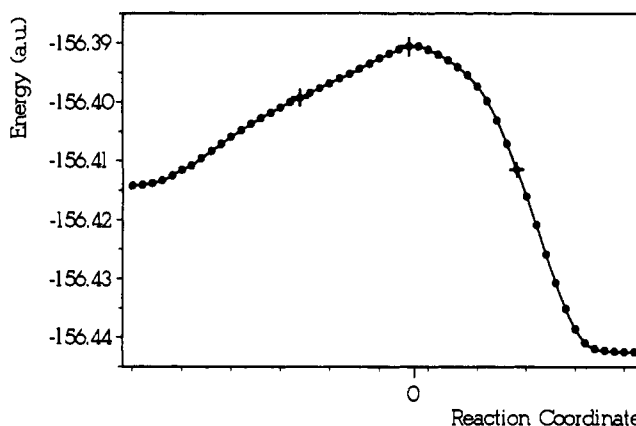


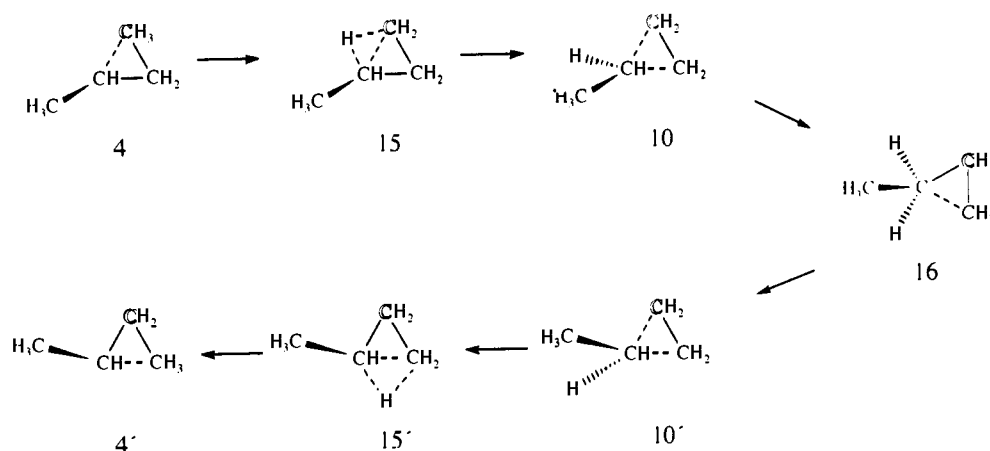
Figure 5. Potential energy profile along the reaction surface for the rearrangement of 2-butyl → *tert*-butyl at the HF/6-31G* level. The zero point along the reaction coordinate is the transition state.

equivalent structure. This can then rearrange back to **5**. As noted by Saunders,¹³ this process scrambles all protons but does not interchange all carbons. Each outside carbon exchanges with its inside neighbor but not with the other C's. This scrambling accounts for a single ¹H and ¹³C NMR peak, since the rapid 2,3-hydride shift makes both central and methyl carbons equivalent. It should be pointed out that the mechanisms proposed above represent only two possible pathways for the scrambling process and the 8.5 kcal/mol an upper limit for the activation energy. A less energetic pathway seems unlikely, since all the other protonated cyclopropane and cyclobutane structures we have examined are less stable than the C₄H₉⁺ species in the proposed mechanisms. Scrambling of the inner H's which interconverts C₁, C₂ and C₃, C₄ via **5** takes place by a rotation around the C₂-C₃ bond with a barrier of 3.5 kcal/mol or via **6** with a barrier of 2.2 kcal/mol. These barriers also are involved in the interconversion of the 2-butyl minima, **4** and **5**. The situation is similar in C₃H₇⁺, where there are two 1-propyl cation transition structures, one for H- and the other for C-scrambling.²⁹

Experimentally, the rearrangement of the 2-butyl to the *tert*-butyl cation occurs with an activation energy of ca. 18 kcal/mol.¹² This high value suggests that a primary carbocation transition structure should be involved. The methyl-bridged structure **4** can rearrange to the *tert*-butyl cation by opening the C₃-C₄ bond. This bond cleavage yields an isobutyl cation-like transition state **18** but does not involve the isobutyl cation **12** itself. This was proven by an intrinsic reaction coordinate calculation (IRC) to be the transition structure for the rearrangement of the asymmetric methyl-bridged 2-butyl cation into its stereoisomer. IRC also confirms **18** to be the desired transition state for the one-step rearrangement of the 2-butyl cation to the *tert*-butyl cation. Figure 4 shows characteristic points on the calculated reaction path. Except for **18**, the transition structure, the species shown are not stationary points on the PES. Figure 5 gives the energy profile along the reaction surface with the zeropoint of the reaction path being the transition state. The calculated activation energy of 19.6 kcal/mol agrees with the experimental value quite well. The reverse process has been observed by C scrambling in *tert*-butyl

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Scheme III

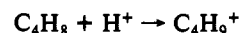


cation; the lower limit of the activation energy is 30 kcal/mol.^{15,50} Our final value for the energy difference between the *tert*-butyl 1 and the transition state 18 is 33.0 kcal/mol. Both rearrangements discussed above, scrambling in 2-butyl cation and rearrangement from 2-butyl to *tert*-butyl cation, fully characterize the $C_4H_9^+$ potential energy surface. Vibrational frequency calculations confirmed the character of the minima and the transition states involved in these processes. The calculated relative energies are in reasonable agreement with experimental values. The inclusion of electron correlation is very important for the determination of relative energies of nonclassical species, as already has been noted in earlier studies.^{27,31,59} Thus, while the energy, relative to 1, of the classical isobutyl cation 12 does not change very significantly from the HF to the correlated level, that of the bridged structure 9 is reduced by more than 15 kcal/mol. Similar behavior is observed for the other nonclassical structures as well (Table IV).

Relative Stabilities of Butyl Cations and Proton Affinities of Isobutene, *trans*-2-Butene and Cyclobutane. A compilation of experimental heats of formation, $\Delta H_f^\circ(298)$ for the various $C_4H_9^+$ isomers is presented in Table I. The most recent data of Lias et al. and Beauchamp et al. yield $\Delta H_f^\circ(298) = 166.0$ and 164.8 ± 1.2 kcal/mol for the *tert*-butyl cation and $\Delta H_f^\circ(298) = 183.0$ and 181.0 ± 1.1 kcal/mol for the 2-butyl cation, respectively.^{25,26} The heat of formation of protonated cyclobutane has been measured by Fiaux et al. as 223 kcal/mol.⁶³ Thus the energy difference between the two most stable $C_4H_9^+$ structures amounts to 17.0 and 16.2 ± 2.3 kcal/mol, respectively, while protonated cyclobutane is considerably less stable, 57–58 kcal/mol above the *tert*-butyl cation. The computed energy difference at our best level between the low-lying isomers is 13.5 kcal/mol, slightly smaller than the experimental data. On the other hand, we compute the relative stability of protonated cyclobutane with respect to *tert*-butyl cation as 35.9 kcal/mol, which discord with Fiaux et al. gas-phase measurements.⁶³ Beauchamp et al., using photoelectron (PE) spectroscopy, also report heats of formation for the higher energy isomers, isobutyl and 1-butyl cation.²⁶ Although these cationic species are not minima on the $C_4H_9^+$ surface and immediate rearrangement to the more stable *tert*-butyl or 2-butyl cation will take place, PE spectroscopy of the parent radicals can be expected to give reasonable thermodynamic quantities for the cations. The observed photoelectron process is limited by the accessible Franck–Condon region and thus the measured ionization energies refer to isobutyl- and 1-butyl-like

cationic structures.²⁶ The relative energies with respect to the *tert*-butyl cation of 33.1 ± 4.2 and 37.1 ± 4.2 kcal/mol²⁶ compare well with our theoretically predicted values, 33.4 and 35.8 kcal/mol.

We also computed the proton affinities for isobutene, *trans*-2-butene, and cyclobutane. On protonation, these give the *tert*-butyl, the 2-butyl cation, and protonated cyclobutane, respectively. The proton affinities (PA) at 298.15 K have been evaluated theoretically⁷⁷ using eq 1.⁷⁸ Standard statistical mechanics formulas and scaled harmonic vibrational frequencies computed at MP2/6-31G* (scaled by 0.93) have been used to determine ΔE_{vib}^{298} . The rotational and translational terms have been computed classically and amount to $\Delta E_{rot}^{298} = 0$ ($E_{rot}(C_4H_8, C_4H_9^+) = 1.5RT, E_{rot}(H^+) = 0$) and $\Delta E_{trans}^{298} = -3/2RT = -0.9$ kcal/mol. $\Delta(pV)_{298}$ was computed using the ideal gas law and is for the protonation reaction $-RT$, i.e., 0.6 kcal/mol. For isobutene we



$$-PA = \Delta H^{298} = \Delta E + \Delta E_{elec}^{298} + \Delta E_{vib}^{298} + \Delta E_{rot}^{298} + \Delta(pV)_{298} \quad (1)$$

compute a PA of 196.8 kcal/mol, and for *trans*-2-butene 184.9 kcal/mol. Using these values and the known experimental heats of formation of H^+ (365 kcal/mol²⁵), isobutene (-4.0 kcal/mol⁶¹), and *trans*-2-butene (-2.8 kcal/mol⁶¹) we compute ΔH_f° 's for the *tert*-butyl and the 2-butyl cation as 164.2 and 177.3 kcal/mol (cf. Table I), respectively. While the agreement with the experimental ΔH_f° is very good for the *tert*-butyl cation, the computed heat of formation of the 2-butyl cation is slightly lower than the experimental value. This reflects the difference between the experimental and theoretical relative stabilities of the 2-butyl cation with respect to *tert*-butyl cation discussed above. For cyclobutane, our computed PA is 170.7 kcal/mol, which is much higher than the PA of 150.6 kcal/mol reported experimentally. As a consequence, the theoretical heat of formation of protonated cyclobutane (using $\Delta H_f^\circ(298)$ cyclobutane = 6.8 kcal/mol⁶¹) also is much lower than the experimental data, i.e., 201.1 versus 223 kcal/mol.⁶³ The theoretically predicted relative stabilities of the neutral C_4H_8 isomers at 298 K show good agreement with experimental data also for cyclobutane, which lends further support to the reliability of our computations. Isobutene is the most stable form, 0.9 (computed) or 1.2 (exptl) kcal/mol more stable than *trans*-2-butene, while cyclobutane is 8.3 (computed) or 10.8 (exptl) kcal/mol energetically less favorable than isobutene. We conclude that the PA and the heat of formation of protonated cyclobutane is in need of a downward revision by roughly 20 kcal/mol. An enhanced PA of 170.7 kcal/mol for cyclobutane would also be in line with the expected similarity of cyclobutane and cyclo-

(77) Isobutene $E(MP4sdq/6-31G^{**}/MP2(full)/6-31G^*) -156.76044$ au, $ZPE(HF/6-31G^*) 64.6$ kcal/mol (scaled), $E_{vib}^{298}(HF/6-31G^*) 65.9$ kcal/mol (scaled); *trans*-2-butene $E(MP4sdq/6-31G^{**}/MP2(full)/6-31G^*) -156.75906$ au, $ZPE(HF/6-31G^*) 64.6$ kcal/mol (scaled), $E_{vib}^{298}(HF/6-31G^*) 65.9$ kcal/mol (scaled); cyclobutane $E(MP4sdq/6-31G^{**}/MP2(full)/6-31G^*) -156.74880$ au, $ZPE(HF/6-31G^*) 66.3$ kcal/mol (scaled), $E_{vib}^{298}(HF/6-31G^*) 66.9$ kcal/mol (scaled), 1 $E_{vib}^{298}(HF/6-31G^*) 71.7$ kcal/mol (scaled), 5 $E_{vib}^{298}(HF/6-31G^*) 72.4$ kcal/mol (scaled), 9 $E_{vib}^{298}(HF/6-31G^*) 72.4$ kcal/mol (scaled).

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propane due to the similar ring strain of both molecules.

Conclusions

The $C_4H_9^+$ potential energy surface has been investigated thoroughly at correlated levels of ab initio molecular orbital theory. A C_s symmetric structure **1** of the *tert*-butyl cation represents the global minimum on the $C_4H_9^+$ PES with a C_{3h} isomer being very close in energy. Both species benefit from C-H hyperconjugative stabilization, as shown by the elongation of the C-H bonds aligned parallel to the formally vacant 2p orbital on the central carbon and the decrease of the corresponding (HCC) angles. The 2-butyl cation, the second stable $C_4H_9^+$ species, is 13.4 kcal/mol less stable than the *tert*-butyl cation. 2-Butyl cation favors a symmetrically H-bridged C_2 structure, a protonated *trans*-2-butene **5**. A methyl bridged isomer of the 2-butyl cation **4**, which profits from C-C hyperconjugative stabilization, is only marginally higher in energy. Agreement between ^{13}C chemical shifts computed with the IGLO method for the *tert*-butyl and 2-butyl cation with the experimental data confirm this assignment. Several other stationary points have been located on the $C_4H_9^+$ surface, but only two additional minima could be found: one, **14**, corresponds to an edge protonated cyclobutane, 35.9 kcal/mol above the *tert*-butyl cation, the other, **10**, is a corner protonated methylcyclopropane, 22.0 kcal/mol above the *tert*-butyl cation. All other stationary points located, such as the isobutyl cation **12** and the 1-butyl cation **13**, are saddle points. Proton and carbon scrambling in the 2-butyl cation occurs either through an edge protonated cyclopropane with an activation barrier of 8.5 kcal/mol (exptl: 7.5 ± 0.1 kcal/mol) or via a corner protonated cyclopropane with a calculated activation barrier of

8.9 kcal/mol. Rearrangement from 2-butyl to the more stable *tert*-butyl cation has a theoretically predicted activation energy of 19.6 kcal/mol, also in good agreement with the experimental estimate of ca. 18 kcal/mol.

The computed relative stabilities of the various $C_4H_9^+$ species and the predicted proton affinities of *trans*-2-butene and isobutene are in good agreement with the experimentally known data. Considerable deviations are found only for protonated cyclobutane **14**. It seems likely that the experimental determination underestimated the stability of this cation by about 20 kcal/mol.

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Supplementary Material Available: A complete list of the computed harmonic frequencies (scaled by 0.93⁴²) and IR intensities of the four minimum ion structures (4 pages). Ordering information is given on any current masthead page.

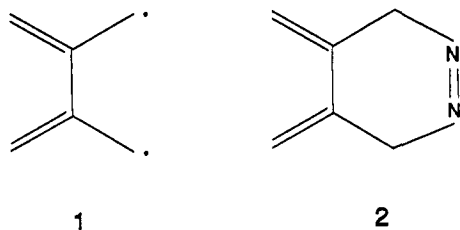
Theoretical Study of the Low-Lying Triplet and Singlet States of Tetramethyleneethane: Prediction of a Triplet below Singlet State at the Triplet Equilibrium Geometry

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Abstract: CI calculations are used to characterize the twisting potentials of the lowest singlet and triplet states of tetramethyleneethane. It is found that the triplet state, at its optimized geometry, lies 1.0-1.5 kcal/mol below the singlet state.

The two frontier orbitals of tetramethyleneethane (TME) (**1**) are close in energy, and, as a result, TME has low-lying singlet (S) and triplet (T) states.¹ The photochemical decomposition of the azo precursor (**2**) in low-temperature matrices gives rise to an EPR spectrum which has been attributed to the triplet state of TME.² The Curie-Weiss plot indicates that either the triplet state is the ground state or lies only slightly (≤ 0.1 kcal/mol) above



the singlet state. On the other hand, the theoretical calculations carried out to date have predicted that TME has a singlet ground state, lying about 1.4 kcal/mol below the triplet state.^{3,4}

A common feature of the previous theoretical studies of TME is that electron correlation effects involving excitations external to the valence space were excluded. In the present study it is shown that the inclusion of such correlation effects stabilizes the T state relative to the S state and that at the minimum in its twisting potential (for rotation of one allyl fragment relative to the other) the T state lies energetically below the S state.

In order to obtain estimates of the dependence of the energies of the S and T states on the dihedral angle, α , between the two allyl fragments (described below) were carried out for the planar (D_{2h} , $\alpha = 0^\circ$), perpendicular (D_{2d} , $\alpha = 90^\circ$), and D_2 ($\alpha = 59^\circ$) structures. In each case, geometrical parameters obtained from MCSCF(6,6)/3-21G⁵ optimizations of the singlet

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(5) The MCSCF(6,6) procedure allows for all arrangements of the six π electrons in the space of the six π and π^* orbitals.