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Secondary and Tertiary 2-Methylbutyl Cations. 3. Theoretical Study of Structures and Interconversions of $C_5H_{11}^+$ Ions in the Gas Phase[1a]

Dan Fărcaşiu* and Steven H. Norton[1b]

Department of Chemical and Petroleum Engineering, University of Pittsburgh, 1249 Benedum Hall, Pittsburgh, Pennsylvania 15261

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The structures, relative energies, and interconversion barriers and pathways for several isomeric $C_5H_{11}^+$ carbocations were investigated by high level *ab initio* MO calculations with inclusion of electron correlation. The energy minima found were two conformations of the tertiary 2-methyl-2-butyl cation (**2**), bisected (**2$_b$**) and asymmetric (**2$_{as}$**), and three 1-protonated (corner-protonated) cyclopropanes: *trans*-2,3-dimethyl (*trans*-**8**), *cis*-2,3-dimethyl (*cis*-**8**), and 1,2-dimethyl (**9**).The bridged ions *trans*-**8**, *cis*-**8**, and **9** are higher in energy than the tertiary ion by 8.3, 9.2, and 10.6 kcal/mol, respectively, at the MP4SDTQ(FC)/6-31G**//MP2(FC)/6-31G** level, or 9.6, 10.6 and 12.4 kcal/mol after correcting for the zero-point energies (ZPE). Various conformations of the "open" 3-methyl-2-butyl cation correspond to transition states for the interconversion of the tertiary ion **2$_{as}$** and the two 1-protonated-2,3-dimethylcyclopropanes. Hydrogen shift in 2$_{as}$ can lead only to the *cis*-2,3-dimethyl isomer, *cis*-**8**; *trans*-**8** is formed only from the *cis* isomer by ring opening and reclosure. The 1,3-protonated-1,2-dimethylcyclopropane (**10**) (edge-protonated) is the transition state for the interconversion of *trans*-**8**, and the third corner-protonated cyclopropane isomer (1-protonated-1,2-dimethylcyclopropane, **9**). The latter can be regarded as the cyclic form of the 2-pentyl cation or of the 2-methyl-1-butyl cation. The calculations thus agree with the results of the experimental study on the cations generated in trifluoroacetic by predicting the existence of more than one "2-methylbutyl" cation, but disagree on another point, by predicting that the other cation besides **2** has a symmetrical structure, **8**.

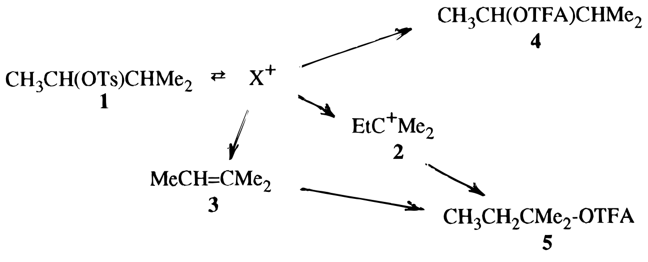
Introduction

A previous study in our laboratory of the solvolysis of 3-methyl-2-butyl tosylate (**1**) in trifluoroacetic acid (TFAH)[2] indicated the existence of two intermediates along the reaction coordinate, as shown in Chart 1. Whereas most of the product was formed from the tertiary 2-methyl-2-butyl cation (**2**), the latter was preceded by another carbocation, X. Ion X was formed from **1** together with TsO^- in a tight ion pair which underwent internal return to the extent of at least 50%. The part which did not return partitioned in the rate-determining step between elimination to 2-methyl-2-butene (**3**) (ca. 25%), capture by the solvent to form 3-methyl-2-butyl trifluoroacetate (**4**) (1.5%), and rearrangement to ion **2**. Both **2** and **3** reacted with the solvent in fast reactions and led to 2-methyl-2-butyl trifluoroacetate (**5**).[2]

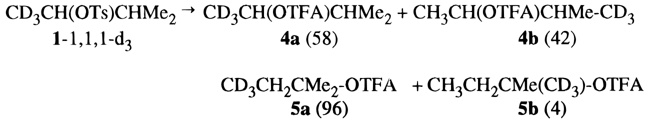
In another work, Collin and Herrman had shown that gas-phase protonation of 3-methyl-1-butene (**6**) by the conjugate acid of xenon gave a $C_5H_{11}^+$ cation which had a long lifetime compared with the collision frequency and was thermalized before isomerizing to ion **2** with an activation energy (E_a) of 2.1 kcal/mol.[3] It is not possible, however, to ascertain whether their $C_5H_{11}^+$ cation was the same as our ion X.

In trying to establish the nature of ion X, we found that solvolysis of **1**-1,1,1-d$_3$ gave products with the label scrambled to the extent shown in Scheme 1 (in parentheses), indicating that rearrangement, extensive before trapping and minor before hydrogen shift, had occurred in ion X.[2]

Chart 1



Scheme 1



The results of the labeling study indicated that the ion X cannot have a symmetrical structure. The same conclusion was reached from a study of the addition of TFAH (neat, or containing potassium trifluoroacetate, or mixed with acetonitrile) and TFAD to alkene **6** and its isomers, 2-methyl-1-butene and 2-methyl-2-butene.[1]

The exact structure of ion X could not be deduced, however, from rate and product studies. In an attempt at obtaining a description of this reactive intermediate we resorted to high level *ab initio* MO calculations[4] of $C_5H_{11}^+$ ions and of their interconversions by intramolecular rearrangements.

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(1) (a) Part 2: Fărcaşiu, D.; Marino, G.; Hsu, C. S. *J. Org. Chem.* **1994**, *59,* 163. (b) Department of Chemistry, University of Pittsburgh 1208 Chevron Science Center, Pittsburgh, PA 15260.

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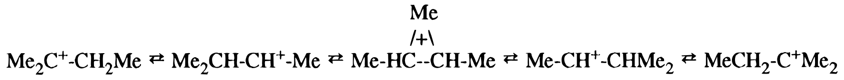
Scheme 2



$$\mathrm{Me_2C^{+}\text{-}CH_2Me} \rightleftarrows \mathrm{Me_2CH\text{-}CH^{+}\text{-}Me} \rightleftarrows \overset{\overset{\mathrm{Me}}{/+\backslash}}{\mathrm{Me\text{-}HC\text{--}CH\text{-}Me}} \rightleftarrows \mathrm{Me\text{-}CH^{+}\text{-}CHMe_2} \rightleftarrows \mathrm{MeCH_2\text{-}C^{+}Me_2}$$

2 **7** **8** **7'** **2'**

Computational Method

The calculations were conducted with the programs Gaussian 90[5] and Gausian 92.[6] Electron correlation was handled with the Møller−Plesset perturbation theory of the second (MP2), third (MP3), and fourth order (MP4).[7]

Full geometry optimization was achieved at the MP2(FC)/3-21G, MP2(FC)/6-31G*, and MP2(FC)/6-31G** levels, and then single point MP3(FC)/6-31G**//MP2(FC)/6-31G** and MP4SDTQ(FC)/6-31G**//MP2(FC)/6-31G** calculations were conducted for a more complete description of the electron correlation. No symmetry constraints were placed upon any of the structures investigated in the optimization runs. Structures optimized at the MP2(FC)/6-31G* level were confirmed as local minima or transition states by means of analytical frequency calculations, which also provided zero-point energies. The structures of endpoints (local minima) associated with each transition state were established by means of intrinsic reaction coordinate (IRC)[8] tracking at the same level of theory, followed by full optimization of the local minima thus located.

Results and Discussion

1. Comparison of Theoretical Approaches for Description of $C_5H_{11}^+$ Ions. One $C_5H_{11}^+$ ion has been thoroughly investigated as a long-lived species in superacid solution: the tertiary pentyl (2-methyl-2-butyl) cation **2**.[9] Scrambling of methyl groups in **2** was observed by NMR and rationalized by Scheme 2.[9b,10] An activation enthalpy of 13.6 kcal/mol[9b,10a] or 14.7 kcal/mol[10b] was measured for the overall process.

The intermediates in Scheme 2 are the "open" secondary 3-methyl-2-butyl cation (**7**) and the symmetrical, "bridged" ion, 1-protonated-2,3-dimethylcyclopropane (**8**). The latter can exist as two stereoisomers, *cis* and *trans*.

Preliminary semiempirical calculations with the MINDO-3 method[11] indicated that *cis*-**8** and *trans*-**8** (both energy minima) are formed by the ring closure of two different conformations of the open ion **7**, which are also energy minima. Both *cis*- and *trans*-**8** are not symmetric: the distances from the methyl carbon to the CH carbons are unequal. In each case, the bridging methyl group of **8** had one hydrogen in the plane of the ring, an arrangement similar to that of the parent protonated cyclopropane.[12] The calculations thus predicted the existence of two pathways, *cis* and *trans*, for Scheme 2. Along the *cis* pathway, the highest barrier (12.9 kcal/mol above **2**) is for conversion of **7** to *cis*-**8**, along the *trans* pathway, the highest barrier is for conversion of **2** to **7** (12.6 kcal/mol above 2).

The *ab initio* calculations at the HF level gave a similar picture, qualitatively, with the semiempirical calculations. As soon as electron correlation was introduced, however, in the optimization runs, at the MP2 level, the open ions were no longer energy minima, but transition states for the interconversion of various bridged ions with each other and with the tertiary ion **2**. Therefore, the results of the HF calculations will not be discussed in any detail here. Comparable results were obtained with the 3-21G, 6-31G*, and 6-31G** basis sets, but the smaller basis sets gave less symmetrical bridged species. Whereas introduction of electron correlation (MP2) had major effects on geometry optimization, essentially reversing the order of energies of the bridged and open secondary cations, reoptimization with electron correlation of the same order and larger basis set resulted in little change of geometries, in agreement with our observations in other cases.[13] Likewise, the differences between MP2(FU) and MP2(FC) structures and energies were negligible where examined. After full geometry optimization at the MP2(FC)/6-31G** level, single point energy calculations at the MP3(FC)/6-31G**//MP2(FC)6-31G** and MP4SDTQ(FC)/6-31G**//MP2(FC)6-31G** level were conducted for the optimum geometries thus found.

2. Tertiary Pentyl Cations. Our results on the tertiary ion **2** can be compared with the literature data on the same species at a similar level of theory.[14] In the previous study it was assumed that two conformations (geometries) could be adopted by ion **2**: a bisected geometry, $\mathbf{2_b}$, with dihedral angles φ(C1−C2−C3−C4) = −φ(C5−C2−C3−C4) (the C2C3C4 plane bisects the C1−C2−C5 angle) and a planar geometry, $\mathbf{2_p}$, in which all the carbon atoms are coplanar. Both geometries had C_s symmetry. An earlier study had considered only the bisected conformation, because the goal of that work was to compare C−C with Si−C hyperconjugation.[15] In the bisected form the symmetry-equivalent methyl groups C1 and C5 are eclipsed. This arrangement differs from that reported for the 2-propyl cation, for which in the minimum energy conformation C1 and C3 were staggered (chiral 2-propyl cation).[16] In the planar form $\mathbf{2_p}$, one hydrogen in each of the three methyl groups is situated

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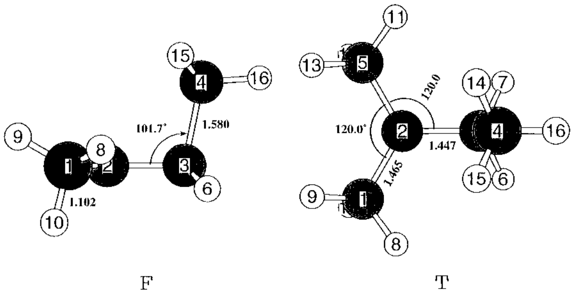

Figure 1. Optimized [MP2(FC)/6-31G*] geometry of the bilaterally symmetric (C_s, bisected) 2-methyl-2-butyl cation, $\mathbf{2_b}$. F: front view (C1 closest to the viewer); T: top view.

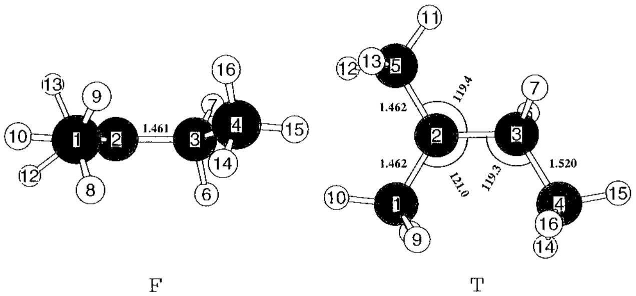

Figure 2. Optimized [MP2(FC)/6-31G*] geometry of the asymmetric 2-methyl-2-butyl cation, $\mathbf{2_{as}}$. F: front view (C1 closest to the viewer); T: top view.

in the plane of the five carbon atoms. According to the frequency analysis at the HF/631G*//HF-631G* level, conformer $\mathbf{2_b}$ was an energy minimum and conformer $\mathbf{2_p}$ was a transition state. A calculation of isotropic chemical shifts by the IGLO scheme[17] showed proper agreement (differences of less than 10 ppm) with experiment for C1, C3, C4, and C5 of both conformers, but only $\mathbf{2_b}$ matched the experimental value for C2 (C^+) within 0.3 ppm; $\mathbf{2_p}$ was off by 17.5 ppm.[14]

It was also found, however, that the two rotamers, $\mathbf{2_b}$ and $\mathbf{2_p}$, have the same energy (the difference of 0.03 kcal/mol is within the limit of uncertainty of the calculations) at the highest level pursued, MP4SDTQ/6-31G**//MP2-(FU)/6-31G* + ZPE,[14] thus making the assignment of one as a minimum and the other as transition state potentially problematic. Even if this was the case, the transition state theory[18] postulates that the initial state and the transition state are in equilibrium, therefore near-equality in energy requires near-equality in population, meaning that at any moment both conformers should be present in nearly equal amounts, and a time-averaged NMR signal should result, reflecting the contribution of both structures. The calculated chemical shift is then the average of the chemical shifts for $\mathbf{2_b}$ and $\mathbf{2_p}$, which does fit the experimental spectrum, the differences being 1.7(C1, C5), 8.9(C2), 7.6(C3), and 1.4 ppm(C4). Note that a deviation of 0.1 and one of 9.9 ppm are equally good fits for a method with uncertainty of 10 ppm. The averaged chemical shifts should not be temperature-dependent.

In our hands, optimization of the bisected conformation at the MP2(FC)/6-31G** level without any symmetry constraint gave a geometry essentially identical to the reported $\mathbf{2_b}$. The calculated energy was also basically the same with that reported,[14] the small difference being probably due to comparison of MP2(FC) with MP2(FU) results.This structure is shown in Figure 1 in two projections (front and top). An interesting feature, not discussed in previous analyses of $\mathbf{2_b}$[14,15] is that in each of the α methyl groups (C1 and C5) one hydrogen is reasonably albeit not perfectly positioned for providing H−C hyperconjugation with C^+ (C2), which adds to the C−C hyperconjugation assured by C4−C3.[19] These hydrogens, identified in Figure 1 as H10 and H12, are situated on the other side of the C1C2C3C5 plane from C4 and have dihedral angles $\varphi(\text{H12}-\text{C5}-\text{C2}-\text{C3}) = -\varphi(\text{H10}-\text{C1}-\text{C2}-\text{C3}) = 97.7°$. Their bond angles C^+-C-H (105.3°) are smaller than the corresponding bond angles of the other hydrogens bonded to C1 and C5 (113°), but their bond lengths are only slightly increased (1.107 Å compared to 1.092 Å). For comparison, the bond angle C4−C3−C2 is 101.7°, and the bond length C3−C4 is 1.583 Å for a dihedral angle $\varphi(\text{C1}-\text{C2}-\text{C3}-4) = 90.3°$, in agreement with the literature.[14] (The difference of 0.3° in the dihedral angle from the value of 90° is negligible.) The reduction of the C4−C3−C2 bond angle was described as a distortion toward bridging,[14] but we believe that the results are more appropriately rationalized by considering that hyperconjugation and bridging are different types of interaction[20] and maximum hyperconjugative stabilization is achieved for a C^+-C-C or C^+-C-H angle of 90° (and a dihedral angle $C-C^+-C-C$ or $C-C^+-C-H$ of 90°).

Starting from the transition state for the hydrogen shift (first step of Scheme 2) discussed below and following the IRC,[8] we found another energy minimum, somewhat close to $\mathbf{2_p}$, but with C4 slightly off the C1C2C3C5 plane. This displacement results in an asymmetric structure, $\mathbf{2_{as}}$, with a dihedral angle $\varphi(\text{C1}-\text{C2}-\text{C3}-\text{C4})$ of about 14.5° (MP2(FC)/6-31G**). This structure is shown in projections in Figure 2. No β bond exhibiting "excess" hyperconjugation is evident in this form, as the only "suitable" dihedral angles are $\varphi(\text{C1}-\text{C2}-\text{C3}-\text{H6}) = 107.2°$ and $\varphi(\text{C1}-\text{C2}-\text{C5}-\text{H13}) = 74.9°$.[19] The bond lengths of these imperfectly hyperconjugating hydrogens are not much increased compared with other hydrogens at the same carbons (1.109 *vs* 1.096 Å at C3, 1.102 *vs* 1.090 and 1.085 Å at C5), but the bond angles are reduced to 104.1° (C2−C5−H13) and, remarkably, to 100.4° (C2−C3−H6). The reduction in the latter bond angle does not represent, however, a distortion toward hydrogen bridging. As found for ions **8**, below, bridging produces a small pyramidalization of the "bridgehead" carbon, away from the bridging group, but in $\mathbf{2_{as}}$ C5 deviates from the C1C2C3 plane by 0.027 Å *in the direction of* H6. The

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Table 1. Relative Energies of the Optimized Geometries of $C_5H_{11}^+$ Ions (kcal/mol)

ion	MP2(FC)/6-31G*	MP2(FC)/6-31G**	MP3(FC)/6-31G**// MP2(FC)/6-31G**	MP4SDTQ(FC)/6-31G**// MP2(FC)/6-31G**	ZPE[a]	MP4SDTQ(FC)/6-31G**// MP2(FC)/6-31G**+SZPE[b]
$\mathbf{2_b}$	−0.79	−0.78	−0.20	−0.57	94.2	−0.02
$\mathbf{2_{as}}$	0.00[c]	0.00[d]	0.00[e]	0.0[f]	93.6	0.00[g,h]
7(0°)	15.2	15.1	15.7	15.0	94.2	15.6
7(±60°)	14.0	13.8	14.3	13.7	93.8	13.9
7(±120°)	15.6	15.4	15.6	15.2	93.7	15.2
7(±180°)	13.3	13.2	13.9	13.1	94.1	13.6
cis-**8**	7.2	7.2	10.1	9.2	95.1	10.6
trans-**8**	6.5	6.4	9.2	8.3	95.0	9.6
9	9.5	9.1	11.7	10.6	95.5	12.4
10	16.3	14.8	18.2	17.2	95.0	18.5

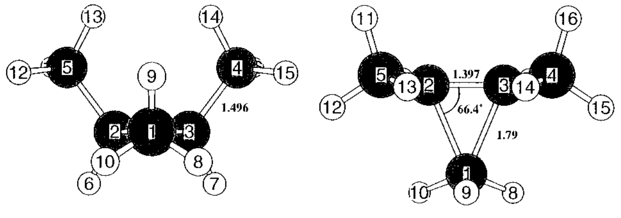
[a] From analytical MP2(FC)/6-31G*//MP2(FC)/6-31G* frequency calculations. [b] ZPE-s scaled by a factor of 0.9646, as recommended in ref 22. [c] Absolute value - 196.1098660. [d] Absolute value - 196.1952513. [e] Absolute value - 196.2535160. [f] Absolute value - 196.2832336. [g] Absolute value - 196.1393361. [h] Absolute energy values in Hartree; 1 Hartree = 627.5095 kcal/mol.

C2−C3−C4 angle, 119.4°, also exhibits a large deviation from the expected value, which can be safely assigned to the severe steric interaction with C1. The more rigid sp^2 bonds are also distorted, but to a lesser extent. such that the C1−C2−C3 angle is increased to 121.0°, whereas the C1−C2−C5 and C3−C2−C5 angles are reduced to 119.6° and 119.4°, respectively. The equilibrium C1···C4 distance in $\mathbf{2_{as}}$ is only 2.978 Å, to be compared with the C1···C4 distance calculated for *gauche* butane (3.199 Å) and eclipsed butane (2.961 Å).[21] The reduction of the C2−C3−H6 angle (to 100.4°) arises as the compensation for the increase of the C2−C3−C4 angle, rather than from a strong hyperconjugative interaction, in agreement with the less than optimum orientation shown by the value of the C1−C2−C3−H6 dihedral angle. The net effect is that H6 is favorably placed for the 1,2-shift.

It is noteworthy that despite the steric strain and the loss in hyperconjugative stabilization by the β C−C bond, the energy of $\mathbf{2_{as}}$ is not much different from the value for $\mathbf{2_b}$, even before applying the ZPE correction for both. In fact, the relative energy of $\mathbf{2_{as}}$ is similar to that of the symmetry-constrained planar form of Schleyer et al.[14] After ZPE correction with the appropriate scaling factor,[22] the two conformers are equal in energy (Table 1). Since upon a 360° rotation of the C2−C3 bond one encounters two minima with conformation $\mathbf{2_b}$ and four minima with conformation $\mathbf{2_{as}}$, the tertiary cation **2** is predominantly (67%) in the latter conformation. This result reduces the reliability of the reported chemical shift calculations, which considered only $\mathbf{2_b}$.[14]

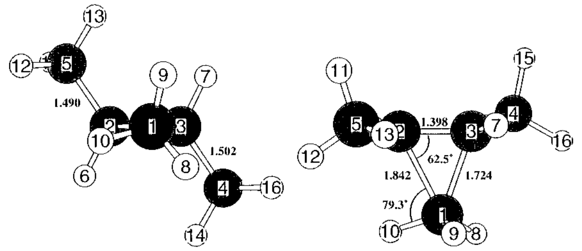
3. Secondary and Bridged Methylbutyl Cations.

Three C_5H_{11} cations with bridged structures were identified as energy minima: *cis*-**8**, *trans*-**8**, and the positional isomer 1-protonated-1,2-dimethylcyclopropane, **9**. Their calculated geometries are presented in Figures 3−5. *cis*-**8** exhibits a staggered conformation at the bonds connecting the methyl substituents with the ring. The bridging methyl is rotated by about 30° from the position in the parent, unsubstituted protonated cyclopropane, and the cation has, therefore, C_s symmetry (Figure 3). By contrast, *trans*-**8** is asymmetric. One of the hydrogens of the bridging methyl (labeled as H10) is almost in the plane of the ring: the dihedral angle φ(H10−C1−C2−C3) is 165.1°, just a little smaller than 180°. The two bridging bonds are unequal, the one facing H10 (C1−C2) is the longer of two. The two methyl substituents are again in staggered conformation (Figure 4). Likewise,the bridging CH₂Me group of the third isomer, **9**, is positioned with one of its hydrogens facing the most substituted bond of the ring, C1−C2 bond, which is then the longest (and presumably weakest) bond of the ring (Figure 5), suggesting some incipient C--H--C bonding. Breaking of this bond leads (in principle) to the 2-pentyl cation and products with the *n*-pentane skeleton.



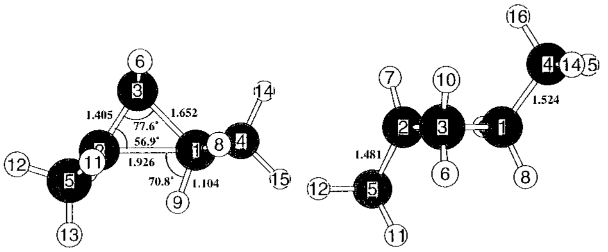
F T

Figure 3. Optimized [MP2(FC)/6-31G*] geometry of 1-protonated-*cis*-2,3-dimethylcyclopropane, *cis*-**8**. F: front view; T: top view.



F T

Figure 4. Optimized [MP2(FC)/6-31G*] geometry of 1-protonated-*trans*-2,3-dimethylcyclopropane, *trans*-**8**. F: front view; T: top view.



F T

Figure 5. Optimized [MP2(FC)/6-31G*] geometry of 1-protonated-1,2-dimethylcyclopropane, **9**. F: front view; T: top view.

The secondary 3-methyl-2-butyl cation (**7**) was not an energy minimum (MP2), but a few conformations of it were optimized as transition states. They are distin-

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(21) (a) Engler, E. M.; Andose, J. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 8005. (b) Engler, E. M. Ph.D. *Thesis*, Princeton University: Princeton, 1973.

(22) Pople, J. A.; Scott, A. P.; Wong, M. W.; Radom, L. *Isr. J. Chem.* **1993**, *33*, 345.

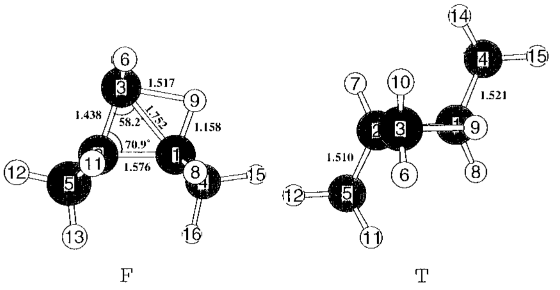

Figure 6. Optimized [MP2(FC)/6-31G*] geometry of 1,3-protonated-*trans*-1,2-dimethyl-cyclopropane (edge-protonated cyclopropane), **10**. F: front view; T: top view.

guished by the values of the dihedral angle φ(H−C2−C3−H): **7**(0.0°), **7**(60.4°), **7**(118.2°), and **7**(179.2°) which are close to 0°, 60°, 120°, and 180°. Finally, the (1,3)-protonated-1,2-dimethylcyclopropane, **10** (edge protonated), was also optimized as a transition state and its geometry is shown in Figure 6. This species, as well as **9**, does not appear in Scheme 2.

The energies obtained for each level of calculation of the several structures examined are presented in Table 1. As mentioned above, the conformers of the open ion **7** are identified by the value of the dihedral angle φ(H−C2−C3−H). Both the total energies and the energies relative to the tertiary cation are given. It can be seen that inclusion of polarization functions on hydrogen (MP2(FC)/6-31G** compared with MP2(FC)/6-31G* basis set) lowered all the relative energies by 0.1 to 0.4 kcal/mol, except for that of the edge-protonated **10**, which decreased by 1.5 kcal/mol. Inclusion of MP4 terms reduced the relative energies of the four conformers of the open form **7** by 0.1−0.2 kcal/mol and increased those of the bridged isomers **8**−**10** by 1.5−2.4 kcal/mol. At the highest level of theory shown in Table 1, *trans*-**8** is 8.3 kcal/mol higher in energy than $\mathbf{2}_{\mathbf{as}}$ and *cis*-**8** is only 0.9 kcal/mol less stable than *trans*-**8.** It is also seen that the carbocation resulting from proton attachment to a methyl-carrying carbon in 1,2-dimethylcyclopropane, **9**, is by10.6 kcal/mol higher in energy than $\mathbf{2}_{\mathbf{as}}$, therefore **9** is less stable than the two isomers **8**. Application of the correction for the ZPE energy[22] again reduces the energy differences between the bridged structures **8**−**10**) and the open structures **7**, as shown in Table 1.

Following the intrinsic reaction coordinate[8] allowed us to connect the various intermediates in the family of isomers with the appropriate transition structures. The orientation of the C−H bonds at C3 in $\mathbf{2}_{\mathbf{b}}$ is not favorable for the hydrogen shift. Ion **7**(60.4°) represents the transition state for the reaction (hydrogen shift and ring closure) which interconverts the asymmetric conformation of the tertiary ion, $\mathbf{2}_{\mathbf{as}}$, and *cis*-**8**. At the highest level of theory investigated here and after ZPE correction (Table 1) this reaction has a barrier of 13.9 kcal/mol in the endothermic direction and 3.3 kcal/mol in the exothermic direction. The latter barrier is somewhat higher than the value of 2.1 kcal/mol obtained from the study of protonation of 3-methyl-1-butene in the gas-phase.[3]

The rotamer **7**(118.2°) appeared as the transition state for a process interconverting the stereoisomers *cis*-**8** and *trans*-**8**. The ZPE-corrected barrier for stereoisomerization of *cis*-**8** to *trans*-**8**, 4.6 kcal/mol, is higher than the barrier for hydrogen shift in the former, leading to $\mathbf{2}_{\mathbf{as}}$. By virtue of its symmetry, *cis*-**8** can open equally at C2 and C3 upon returning to $\mathbf{2}_{\mathbf{as}}$, thus achieving the methyl interchange in the latter. We were not able to locate a transition state connecting *trans*-**8** with **2**. Intuitively, we had expected that opening *trans*-**8** to **7**(118.2°) should continue in that direction, but **7**(118.2°) closed to *cis*-**8**, instead.

In addition to the reaction steps connecting **2** with **8** via **7**, the calculations have revealed a pathway of ring opening of **8** followed by ring closure, which conserves the *cis* or *trans* stereochemistry and interchanges the bridging methyl with one of the substituent methyl groups. Structures **7**(0.0°) and **7**(179.2°) are the transition states of this transformation for *cis*-**8** and *trans*-**8**, respectively. This particular methyl scrambling in *trans*-**8** (4.0 kcal/mol ZPE-corrected barrier) is easier than the other two reactions available to this isomer, namely conversion to *cis*-**8** and to **9**. This mechanistic feature is of no consequence for the isomerizations originating with **2**, but could be important if *trans*-**8** were generated by the ionization of a 3-methyl-2-butyl precursor. The same energetic considerations suggest that protonation of 3-methyl-1-butene in the gas phase[3] should not involve **7**(179.2°) and *trans*-**8**, because the calculated energy barrier for the isomerization of the latter to the tertiary cation, 5.6 kcal/mol, is too high. The barrier for the corresponding scrambling in *cis*-**8**, 5.0 kcal/mol, is higher than the barriers for both return to $\mathbf{2}_{\mathbf{as}}$ and isomerization to *trans*-**8**. The calculations thus predict that reaction of 3-methyl-1-butene with XeD^+ should give **2** containing deuterium only or mostly at C4.

The calculations have also revealed a pathway for the intramolecular gas-phase isomerization of the branched cation **2** to the straight chain isomer, 2-pentyl cation (**11**). (The straight chain reaction products might be formed, however, directly from ion **9**.) The highest point (18.5 kcal/mol above **2** after ZPE correction) along that reaction coordinate is the edge-protonated cyclopropane **10**, which is the transition structure for the step connecting *trans*-**8** with the positional isomer, **9**. The *trans*-**8** $\rightleftarrows$ **9** step also achieves the exchange of hydrogen atoms between the methylene and methyl groups of ion **2**. This exchange is responsible for the complete hydrogen scrambling observed in superacid solution at temperatures above 100 °C.[23]

On the basis of the difference in energy between *cis*-**8** and *trans*-**8** and on the examination of the geometry of **10** (Figure 5), we estimated that the analog of **10** starting from *cis*-**8** should be higher in energy, therefore, we did not study it. Finally, the hydrogen shift from C1 to C2 in **9** (automerization) has no chemical consequence, because the methyl groups are scrambled earlier, in the $\mathbf{2}_{\mathbf{as}}$ $\rightleftarrows$ *cis*-**8** step or in the *trans*-**8** $\rightleftarrows$ **7**(179.2°) $\rightleftarrows$ *trans*-**8** step; it was also not investigated. The reaction pathways starting from $\mathbf{2}_{\mathbf{as}}$ which were identified in our calculations are shown in Chart 2 (the energies shown were corrected for ZPE). The conformer $\mathbf{2}_{\mathbf{as}}$ should be connected to $\mathbf{2}_{\mathbf{b}}$ by a rotation with a small barrier, but this process is not shown in the chart.

The identification of the pathway involving **9** and **10** by calculations allows us also to formulate a verifiable prediction for the isomerization of isopentane labeled with carbon-13 at C1, under conditions which would preclude a bimolecular pathway involving C_{10} cations as intermediates.[24] The first, fastest reaction to be observed should be the degenerate isomerization (automerization) of isopentane, transfering the label from C1 to C4 and

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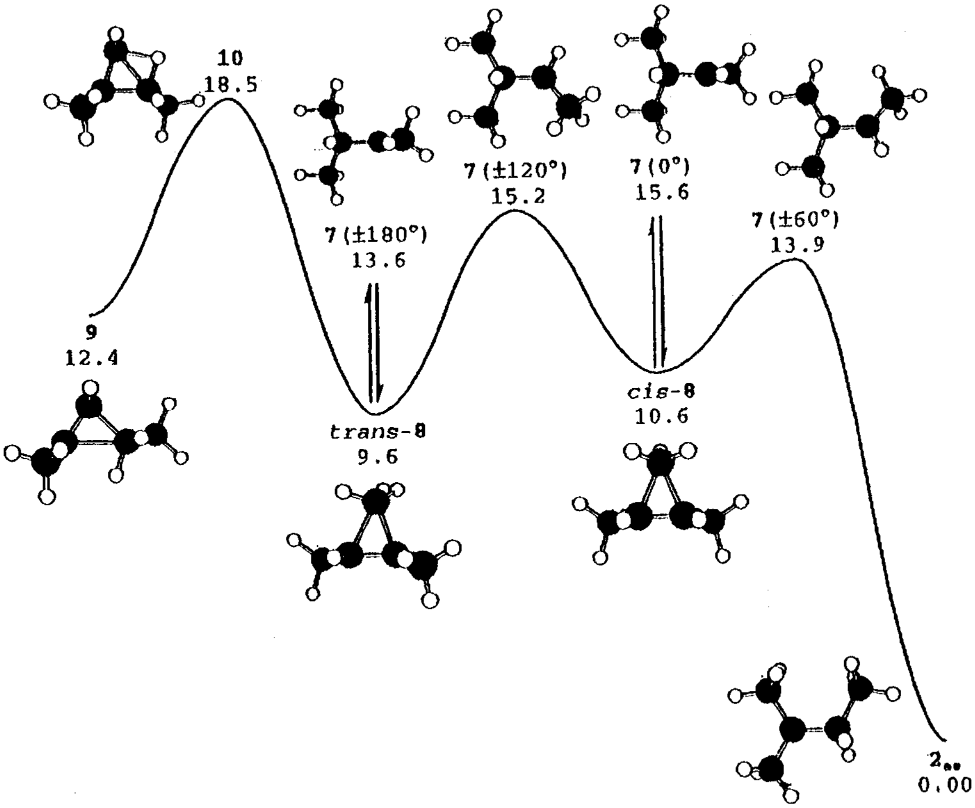
(23) Saunders, M.; Rosenfeld, J. *J. Am. Chem. Soc.* **1969**, *91*, 7756.

Chart 2



C5, according to Scheme 2, a reaction already studied experimentally for the ions in superacid.[9b,10] As a slower process, isomerization to *n*-pentane should be observed, giving a product labeled to a similar extent at C1 and C3, but unlabeled at C2. Determination of the label distribution in the product should serve to validate the mechanism. Rate measurements on the skeletal rearrangement at several temperatures would give an activation entalpy which could be compared with the potential energy barrier of 18.5 kcal/mol obtained from the calculation of the transition state **10** in this work.

Conclusions

Two equally stable conformers with the structure of *tert*-pentyl cation exist as energy minima, $\mathbf{2_b}$ ("bisected") and $\mathbf{2_{as}}$ (asymmetric). The latter is 2:1 favored by entropy. This finding casts doubts upon the published NMR chemical shift calculations, which considered only $\mathbf{2_b}$. Three other minima on the energy surface are the protonated dimethylcyclopropanes *cis*-**8**, *trans*-**8**, and **9**. Various conformations of the "open" 3-methyl-2-butyl cation are the transition states for the interconversion of the bridged ions **8** with each other and with $\mathbf{2_{as}}$. Thus, the results of the calculations reported here are in agreement with the studies on $C_5H_{11}^+$ cations in the gas-phase[3] and in TFAH solution[1,2] to the extent that they predict the existence of at least one other reaction intermediate with this formula, in addition to the tertiary cation **2**. They disagree with the conclusion of the work in TFAH, which indicated that the "other", less stable, cation was nonsymmetrical, because it scrambled the methyl groups during its lifetime incompletely and to different extents when the precursors were different.[1,2]

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Supporting Information Available: Table with absolute energies and Gaussian archive files (with figures) for all species investigated (11 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(24) (a) Brouwer, D. M.; Oelderik, J. M. *Rec. Trav. Chim.* **1968**, *87*, 721. (b) Karabatsos, G. J.; Vane, F. M. *J. Am. Chem. Soc.* **1963**, *85*, 729 and subsequent papers.