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Theoretical Studies of Carbocations in Ion Pairs. 5.[1] Structures and Interconversion of the 3-Methyl-2-butyl Cation and 2,3-Dimethyl-1-Protonated Cyclopropane

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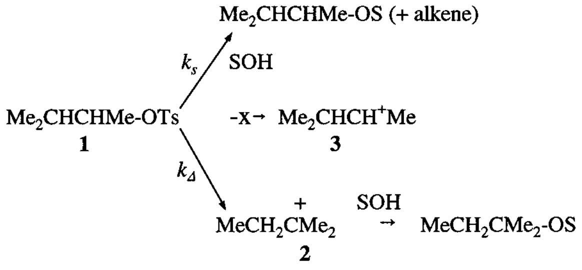
Abstract: The structures of carbocations formed in the ionization of 3-methyl-2-butyl precursors were investigated by high level ab initio MO calculations. The relative stability of the 3-methyl-2-butyl cation (**3**) increased upon placement in a dielectric medium using SCRF calculations, but the 2,3-dimethyl-1-protonated cyclopropanes (**5**) were still more stable, as they were in vacuum. Introduction of negative point charges in single-point calculations on the structures of isolated ions made the open ion more stable than the bridged isomers and increased the stability difference favoring *trans*-**5** over *cis*-**5**. The structure and stabilities of **3** and *trans*-**5** in ion pairs were examined with two counterions successfully used in previous studies, trihydrofluoroborate (FBH_3^-, **A**) at short interionic distances (d) and dihydrolithiate (LiH_2^-, **B**) at longer distances. Optimization (MP2/6-31G*) of *trans*-**5.A** with the anion free to move in a plane parallel to the C1C2C3 plane at $d = 2.3$ Å gives **3.A** as the only energy minimum. The position of the anion is determined by electrostatic interaction with C2 and hydrogen atoms at C1 and C5. At 2.6 Å, *trans*-**5.A** also opens, but the anion in the resulting **3.A** moves toward C1 and forms 3-methyl-1-butene by elimination. Rotation of the cation to the conformation in which the hydrogen at C3 of **3.A** faces the anion at $d = 2.6$ Å leads to 2-methyl-2-butene. Optimization at longer interionic distances with the anion (**B**) placed above C2, along a line perpendicular to the C1C2C3, plane, shows **3.B** as the only stable entity up to $d = 3.25$ Å. Both **3.B** and *trans*-**5.B** were optimized at $d = 3.3$ Å, where **3.B** was more stable by 2.11 kcal/mol (MP4SDTQ(FC)/6-31G**//MP2(FC)/6-31G** + ZPE). At greater separation, rotation of C2−C3 brings one hydrogen at C5 closer to the anion. At $d = 3.8$ Å, ring closure in **3.B** occurs with participation of C5, rather than C4 which should bridge in an anchimerically assisted ionization. Another orientation of the anion was tested, placing B on a line perpendicular to the C2,C3,C5 plane. Optimization of *trans*-**5.B** at $d = 4.0$ Å led to **3.B**, but *trans*-**5.B** could be optimized at $d = 4.5$ Å, where it was 7.1 kcal/mol less stable than **3.B**. The calculations indicate that there should be no anchimeric assistance by either methyl or hydrogen upon ionization of a 3-methyl-2-butyl precursor to ion pairs, in agreement with the previous study of this process in trifluoroacetic acid.

Introduction

The carbocations of 2-methylbutane have attracted interest since Winstein and co-workers found that in the acetolysis of 3-methyl-2-butyl tosylate (**1**) over 95% of the products result from the rearranged 2-methyl-2-butyl cation (**2**) as intermediate.[2] A large kinetic isotope effect (KIE), $k_H/k_D = 2.24$ at 25 °C, in the reaction of **1**-3-*d* led Winstein et al. to describe the process as a competition between a minor solvent-assisted reaction, k_s, and a major anchimerically assisted reaction, k_Δ (eq 1). The secondary ion **3**, or a kinetic equivalent of it, was considered not to form.[2b] This view was supported by MINDO3 calculations indicating that secondary carbocations with the charge adjacent to a tertiary carbon are converted to the tertiary cation by a hydrogen shift without an energy barrier.[3]



(1)

The existence of only one carbocation with the formula $C_5H_{11}^+$ was challenged by Collin and Herrman, who showed that gas-phase protonation of 3-methyl-1-butene (**4**) 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.[4] Likewise, the methyl group scrambling in ion **2** in superacid was described by eq 2, in which at least one of two species, **3** and the bridged ion **5**, was an intermediate.[5]

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(1) (a) Part 4: Fărcaşiu, D.; Hâncu, D. *J. Am. Chem. Soc.*, **1999**, *121*, 7173. (b) This is also part 4 in the series "Secondary and Tertiary 2-Methylbutyl Cations. For part 3, see: Fărcaşiu, D.; Norton, S. H. *J. Org. Chem.* **1997**, *62*, 5374. (c) Department of Chemistry, University of Pittsburgh, 1208 Chevron Science Center, Pittsburgh, PA 15260.

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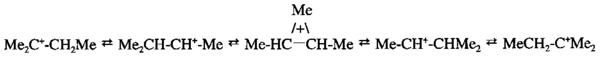

$$\underset{\mathbf{2}}{Me_2C^+\text{-}CH_2Me} \rightleftarrows \underset{\mathbf{3}}{Me_2CH\text{-}CH^+\text{-}Me} \rightleftarrows \underset{\mathbf{5}}{Me\text{-}HC\overset{\overset{Me}{/+\backslash}}{-}CH\text{-}Me} \rightleftarrows \underset{\mathbf{3'}}{Me\text{-}CH^+\text{-}CHMe_2} \rightleftarrows \underset{\mathbf{2'}}{MeCH_2\text{-}C^+Me_2} \quad (2)$$

2 **3** **5** **3'** **2'**

Other experiments indicated that the case for the mechanism of eq 1 was less clear-cut than desired. Thus, even though product analysis suggested that the k_Δ pathway was the predominant reaction course, no substantial rate acceleration attributable to the anchimeric assistance was found.[2b,6] Also, a small nucleophilic assistance was revealed for the reaction of **1** in aqueous ethanol, a solvent about 2 orders of magnitude more nucleophilic (by the N parameter[7]) than acetic acid,[6b] but the response of rates to changes in the solvent ionizing power (Y) and nucleophilicity was better correlated with the $k_s - k_c$ mechanistic description than with the $k_s - k_\Delta$ representation.[8] A rate study in formic acid, which has the same nucleophilicity ($N = -2.05$)[9] but a much higher ionizing power than acetic acid ($Y = 3.04$ compared with -0.61 for AcOH)[10] showed no solvent nucleophilic participation.[11] An intriguing result was that a very small extent of methyl scrambling had occurred in the tertiary ester obtained from the acetolysis of the labeled tosylate, **1**-1-^{14}C.[12]

These discrepancies prompted us to investigate the solvolysis in trifluoroacetic acid (TFA) of **1** and several derivatives specifically labeled with deuterium. This solvent is much less nucleophilic and better ionizing ($N = -5.55$,[9] $Y = 4.57$[10]) than formic acid.[13a,b] In a parallel study, addition of TFA and TFA-*d* to **4**, 2-methyl-1-butene, and 2-methyl-2-butene (**6**) and also addition of TFA containing toluenesulfonic acid (TsOH) to **4** were investigated.[13a,c]

The first observation was that the solvent effects on the KIE for deuterium in various positions did not fit the predictions for a $k_s - k_\Delta$ competition mechanism.[13a,b] Next, at least 50% of the ion pairs resulting from ionization of **1** underwent internal return back to **1**.[13a,c,14] Thus, the postulated[2] anchimeric assistance by hydrogen in the ionization of **1** did not exist.[13a,c] The fraction of ion pairs which did not return partitioned in the rate-determining step between elimination to **6** (~25%), capture by the solvent to form 3-methyl-2-butyl trifluoroacetate (**7**) (1.5%), and rearrangement to ion **2**. Both **2** and **6** reacted with the solvent in fast reactions and led to 2-methyl-2-butyl trifluoroacetate (**8**). Furthermore, solvolysis of **1**-1,1,1-d$_3$ gave products with the label scrambled to the extent shown in eq 3 (in parentheses).[13]

$$\begin{array}{l} CD_3CH(OTs)CHMe_2 \rightarrow \\ \quad \mathbf{1}\text{-}1,1,1\text{-}d_3 \\ \quad \underset{\mathbf{7a}\ (58)}{CD_3CH(OTFA)CHMe_2} + \underset{\mathbf{7b}\ (42)}{CH_3CH(OTFA)CHMe\text{-}CD_3} \\ \quad \underset{\mathbf{8a}\ (96)}{CD_3CH_2CMe_2\text{-}OTFA} + \underset{\mathbf{8b}\ (4)}{CH_3CH_2CMe(CD_3)\text{-}OTFA} \end{array} \quad (3)$$

We concluded that the species formed in the tight ion pair by ionization of **1** was **3** and methyl shift in **3** competed with hydrogen shift and elimination. The extent of scrambling in **8** required that at least 9% of **2** was formed from **3** which had survived long enough to undergo methyl shift.[13]

High-level ab initio calculations[15] were conducted to describe the $C_5H_{11}^+$ energy surface and to establish the structures of energy minima and of the transition structures for the interconversions of those ions.[1b] Those calculations have treated the isolated carbocations. Because the solvolysis of **1** represents tight ion pair chemistry in solution, we also conducted computations on ion pairs of **3** and **5** and report our results here.

Computational Method

The calculations were conducted as described earlier,[1] with the programs Gaussian 92[16] and Gaussian 94.[17] Electron correlation was handled with the Møller−Plesset perturbation theory of the second (MP2) and fourth order (MP4).[18] Because of the size of the systems investigated, we did not introduce diffuse functions in the basis sets used. It has been shown that their use has an insignificant effect on the $C_3H_7^+$ carbocation structures.[1a] Full geometry optimization of all parameters inside the cation and the anion was performed at the MP2(FC)/6-31G* level; it was found for the lower homolog, $C_3H_7^+$, that only small changes in the geometry found at this level occurred upon reoptimization with the MP2/6-311G** basis set.[1a] A further check was provided by MP2(FC)/6-31G** optimization and MP4SDTQ(FC)/6-31G**//MP2(FC)/6-31G** single-point calculations of two selected structures in the present work. No symmetry constraints were placed in the optimization runs upon any of the structures investigated. Structures optimized at the MP2(FC)/6-31G* level were confirmed as local minima by means of analytical frequency calculations, which also provided zero-point energies.

To follow easily the interconversion of the bridged and "open" species, the same numbering of carbon atoms was used for both: The sp^2 carbon of the open ion is C2; in the bridged ion it carries the longer bridging bond. C2 is bonded to C1 (methyl) and C3 (CH). The methyls bonded to C3 are C4 (bridging) and C5. The interionic distances are measured from the nearest atom in the anion: the proximal H in LiH_2^- and F in FBH_3^-.

In the calculations which allowed the anion an unrestricted plane parallel movement above the cation, the distance and orientation of

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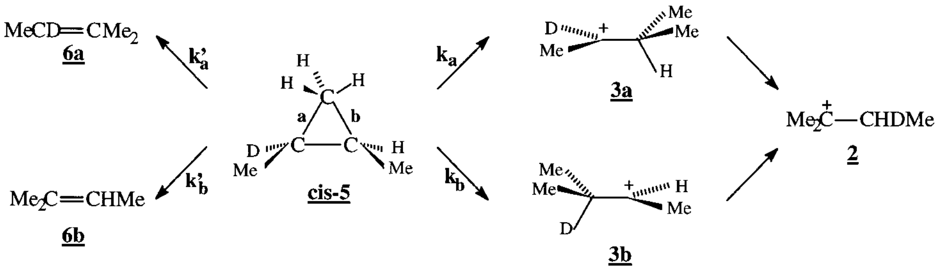
Chart 1



the anion relative to the cation was controlled with the use of two "dummy" atoms.[1a] The first, X1, was placed in the C1C2C3 plane, such that the angles θ(C1−C2−X1) and θ(X1−C2−C3) were equal. The second, X2, was placed on a line perpendicular to C1,C2,C3 passing through X1, and at a distance X1−X2 = d (the interionic distance). The anion was then positioned such that F−X2 was perpendicular to X1−X2 and B−F was antiparallel to X1−X2. The distance F−X2 and the dihedral angle φ(F−X2−X1−C2) were fully optimized, as were all of the geometrical parameters of the cation and anion. In this manner, the "dummy" atoms acted as a hinge. The runs in the series *4.d.* were conducted in the same way, only that the C2C3C5 plane was used to define the position of the "dummy" atoms.

Results and Discussion

1. Evaluation of Calculations for Isolated Ions. The calculations for isolated $C_5H_{11}^+$ ions indicated that the secondary cation **3** was not an intermediate (local minimum) on the $C_5H_{11}^+$ energy surface but only the transition state for interconversion of **2** and **5** and of stereoisomers of **5**.[1b] Those calculations described the automerization of ion **2** in superacid as involving the *cis*-2,3-dimethyl-1-protonated cyclopropane (*cis*-**5**) as intermediate and **3**(60°), the conformer of the secondary ion **3** with a dihedral angle φ(H−C2−C3−H) close to 60°, as the transition state structure connecting *cis*-**5** and **2** (right-hand side of eq 4). The stereoisomer *trans*-**5** cannot be formed directly from **2**, but only from *cis*-**5**, with an energy barrier higher than for the interconversion of the latter with **2**.[1b]

Application of the calculations for isolated cations to solvolysis results requires that ionization of **1** leads to one of the stereoisomers of **5**, which then undergoes internal return or partitions among the pathways leading to **6**, **7**, and **8**. The unequal content of **7a** and **7b** in the product (eq 3) can be rationalized by the slight asymmetry of **5**, if the longest bond in the cycle connects the pentacoordinated carbon with the carbon originally carrying the leaving group, which is thus by a slight margin the preferred site of nucleophilic attack.[1b] The same reactivity ratio should, however, be exhibited by the two positions toward the anion in the internal return, which should, therefore, produce the same amount of scrambling in the returned **1** as in **7**. Considering that the extent of internal return in the trifluoroacetolysis of **1** is at least 50%,[13] there is no way to explain the large difference between the levels of scrambling in **7** and **8** observed (eq 3). In addition, the intervention of **5** as intermediate cannot explain the different extent of deuterium scrambling found in **7** formed from solvolysis of **1**-2-*d* and from TFA-*d* addition to **4**.[13]

The ionization of **1** directly to **5** is also incompatible with the large (and, except for acetic acid as solvent,[2] constant) βH KIE found in solvolysis of **1**-3-*d* in solvents ranging from 80% ethanol to TFA.[2,6,13] The isotope effect manifests itself in the rate-determining step, which in this mechanism is the ring-opening of **5**, with hydrogen migration (k, 75%) or elimination (k', 25%). These pathways are shown in Chart 1 for the *cis*-**5** species resulting from **1**-3-*d*. The relative energies (kcal/mol) calculated at the highest level of theory employed in the previous paper for the relevant structures as isolated ions, identified in eq 4 as intermediates or transition structures, are shown in the first line of data under that equation.[1b] The conformers of **3** are identified by the dihedral angle φ(H−C2−C3−H) given in parentheses and the conformer of the tertiary cation chosen as standard is the "asymmetric form," $\mathbf{2}_{as}$, which results after the hydride shift from *cis*-**5**.[1b]

$$[\mathbf{3}(180°)]^‡ \rightleftarrows \textit{trans}\text{-}\mathbf{5} \rightleftarrows [\mathbf{3}(120°)]^‡ \rightleftarrows \textit{cis}\text{-}\mathbf{5} \rightleftarrows [\mathbf{3}(60°)]^‡ \rightleftarrows \mathbf{2}_{as} \tag{4}$$

	[3(180°)]‡	trans-5	[3(120°)]‡	cis-5	[3(60°)]‡	2as
MP4SDTQ(FC)/ 6-31G**//MP2(FC)/ 6-31G** + ZPE	13.6	9.6	15.2	10.6	13.9	0.0
MP2(FC)/6-31G*	15.2	6.5	15.6	7.2	14.0	0.0
SCRF-MP2(FC)/6-31G*// MP2(FC)/6-31G*:	14.5	6.8	14.7	7.3	13.2	0.0

In the all-protio molecule, the two paths for ring opening, *a* and *b*, are equivalent, because the rotation of the bridging methyl in *cis*-**5** at the top of the 2-butene base should require less energy than the 3.3 kcal/mol barrier calculated[1a] for ring-opening, *cis*-**5** → $\mathbf{3}(60°)^‡$ → **2** (first line of data under eq 4).[19] Not considering at first the position of the transition state along the path *cis*-**5** → **2**, we find that the reaction rate is $2(k_a + k'_a)$ for the protio molecule and $(k_a + k_b + k'_a + k'_b)$ for the deuterated molecule, which means that a KIE ≥ 2, as observed in AcOH,[2,6a] is not possible. The problem is even more complicated, because the calculations predict that ring opening and hydrogen shift in the step *cis*-**5** → **2** are not synchronous but occur before and after the transition state, respectively, whence there is no KIE in this step ($k_a = k_b$). All of the measured KIE should then originate in the elimination pathway. Introducing also the experimental result $k_a/k'_a = 75/25$, we find KIE = $8\ k'_a/(7k'_a + k'_b)$, which requires $1 <$ KIE $< 8/7$ (for $1 < k'_a/k'_b < \infty$).

Alternatively, ionization of **1** can lead to *trans*-**5** as the first intermediate, over **3**(180°) as transition structure. As the latter resulted from calculations as the lowest-energy conformer of the open ion **3**, this is predicted as the preferred pathway. No KIE should be observed for the hydrogen shift step, because it occurs after the rate-determining step *trans*-**5** → *cis*-**5**. A KIE is possible only if elimination takes place entirely from *trans*-**5**, but then maximum value is, again, 8/7.

2. Effect of Medium on Carbocation Relative Energies. To reconcile the calculations with the experiment, we addressed two shortcomings of the standard calculations[1b,19,20] on carbocations: neglect of medium effects and ion-pairing effects. The first is addressed by the self-consistent reaction field (SCRF, spherical cavity)[21] option of the programs.[16,17] We conducted

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such calculations with a dielectric constant of 39, at the MP2-(FC)/6-31G* level, on the geometries optimized at the same level (SCRF-MP2(FC)/6-31G*// MP2(FC)/6-31G*), for the species involved in the interconversion of **2**$_{as}$ and *trans*-**5**. The results are shown in the third line of data under eq 4 and can be compared with the data for these ions at the same level of theory in a vacuum, given in line 2 of data under eq 4.

It is seen that the differences in energy between the bridged and open secondary cations decrease by about 1 kcal/mol in solution relative to the gas phase, but the bridged isomers are still more stable. It is possible, albeit unlikely, that the relative stability might be reversed for the dielectric constant of HF (80),[22] but our calculations had to rationalize the results of solvolyses conducted in TFA,[13] which has a dielectric of 8−9.[23] Therefore, the solvent effects could not explain our findings,[13] at least in the approximation treating the solvent as a continuum.[16,17,24] The answer was to be given by the consideration of ion pairing.[1a,25] Some preliminary results were reported, but not in significant detail.[26]

3. Effect of a Negative Point Charge on the Stability of Isomeric Cations. In the first approximation, single-point calculations (MP2(FC)/6-31G*) were conducted for the gas-phase structures *cis*-**5**, *trans*-**5**, and a conformer of **3** (**3**(120°)) coupled with a negative point charge Z of unit value, placed at 2.5 Å from the C2−C3 bond. There was little change in the stability of *cis*-**5** and *trans*-**5** when the counter-charge was above C2, above C3, or midway. Their relative stabilities were somewhat different than found for the isolated ions (*trans*-**5** more stable than *cis*-**5** by about 2 kcal/mol, to be compared with 0.7 kcal/mol in eq 4). On the other hand, **3** with the point charge closest to the tricoordinated carbon C2 (d(Z...C2) = 2.5 Å) was more stable than *trans*-**5** by 2.4 kcal/mol when the charge was close to the C1C2C3 plane (dihedral angle φ(Z,C3,C2,C1 = 132°) and by 11.5 kcal/mol when the charge was placed such that Z...C2 was perpendicular to that plane. Moving the charge in the same way outside the cyclopropane plane had little effect on the stability of *cis*-**5** and *trans*-**5**.

4. Calculations on Ion Pairs. To conduct geometry optimization it was necessary to replace the point charge by a real anion, the choice of which was very important for the study. Previous computational studies of intermolecular effects on carbocations had examined (MINDO/3) ion−molecule pairs of hydrogen chloride and carbocations[27a−c] and, recently, the complex of 2-norbornyl cation and a water molecule (ab initio).[27d] A system claimed to represent the optimized structure of the *tert*-butyl chloride ion pair with four molecules of water, reveals itself upon inspection (bond lengths and angles) as O-protonated *tert*-butyl alcohol.[27e]

The choice of anion was also important for the consideration of solvent effects. Previous work has shown that formation of carbocations by solvolysis and their existence at equilibrium in superacids is conditioned by the stabilization of the anion through complexation with a Lewis acid or strong interaction with a solvent (anion stabilizing solvent); the specific solvation of the cation is nucleophilic and hinders its formation.[28] Multimolecule simulations by other workers have confirmed that interactions of solvent molecules with the negatively charged leaving group and entering group are important in both S_N1[29a,b] and S_N2 solvolyses.[29c]

The electrophilic solvation of the anion was taken into account in our calculation by the use of a complex anion, to ensure that only a part of the negative charge would face directly the cation.[1a,25] It was important, however, not to use a very stable anion when trying to model the type of interaction occurring in ionization in solvolytic media which provide good anion stabilization but have both low dielectric constants and some nucleophilicity (e.g., TFA). The more extensive comparisons were made with the smaller 2-propyl cation,[25a,b] and, to a more limited extent, *tert*-butyl cation.[30] The very high energy required for heterolysis (perhaps 100 kcal/mol) is in good part compensated by the complexation energy, 44 kcal/mol for $[F^-HF]^-$,[31a] 54kcal/mol for $[H^-LiH]^-$,[31b] 64kcal/mol for $[F^-BH_3]^-$,[31c] and 71kcal/mol for $[F^-BF_3]^-$,[31d] bringing the difference (bond cleavage minus complexation) within the range of energy barriers for ionization in solution.

It was found that (a) the structure of the cation in the ion pair is different from that of the free ion, (b) the nature of the anion does not influence significantly the cation structure if the anion is beyond the distance where a reaction between ions in the ion pair occurs, (c) the less stable anions (lower complexation energy) react with the cation by elimination or recombination at a longer distance than the more stable anions,[25a] and (d) geometry optimization at fixed interionic distances gives the correct structures for carbocations in ion pairs or aggregates.[25c] It was also found (e) that the nature of the interionic reaction, elimination or recombination is determined by the relative orientation of the ions approaching each other for the reaction within the ion pair.[1a,25a] The same relative orientation controls the hydrogen shift converting the 1-propyl cation to the 2-propyl cation.[1a] Thus, we found that nucleophilicity and basicity of the anion, gauged by the interionic distance at which elimination or recombination takes place in our calculations, varies inversely with the complexation energy, but at distances at which no interionic reaction occurs the carbocation structure is the same, irrespective of the anion in the pair.

The smaller specific solvation involving the carbocation, was shown by different methods to favor the “open ions” by a small margin.[27a,b,32]

The anions employed in this work were trihydrofluoroborate (**A**)[33] and dihydrolithiate (**B**).[34] Because of the size of the cation, an extensive study with anion **A** as counterion, as done in the

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Table 1. Carbon−Carbon Bond Lengths (a and b, Chart 1) to the Bridging Carbon in *trans*-5.B (fixed anion position) for Various Interatomic Distances, *d*[a]

d		7.0	6.0	5.0	4.0
D(a)[b]	1.735[c]	1.719	1.701	1.690	1.663
D(b)[b]	1.840	1.856	1.874	1.887	1.936

[a] All the distances are in Å; calculations at the MP2/6-31G* level. [b] D(a), D(b) = distances (a) and (b) as defined in Chart 1, i.e., the bond b is connected to C2 and the anion is opposite to it. [c] Isolated carbocation.

$C_3H_7^+$ case,[1a,25a] was not possible in the present work. Its use was limited to the tight ion pairs, and anion **B** was used for the investigation of the two forms of $C_5H_{11}^+$ cations, **3** and **5**, in “looser” ion pairs (longer interionic distances). The previous experience indicated that at the interionic distance used in the single point calculations on the cation-negative charge systems discussed above, elimination should occur with anion **B**.[25a] Because *trans*-**5** was the predicted first intermediate if the ionization of precursors were anchimerically assisted (see above) and, furthermore, the higher stability of *trans*-**5** over *cis*-**5** was more pronounced in the cations paired with negative point charges than in the isolated (gas phase) cations, only *trans*-**5** was investigated in ion pairs.

An additional complication with the larger cation is that it is difficult to guess the best position of the anion relative to the cation. It is possible that there is more than one “preferred” relative orientation of the partners in the ion pair for either cation structure. This potential multiplicity of relative orientations may be important in the looser ion pairs, but not in the tight ion pairs formed immediately after ionization.

4.a. Bridged Ions at Long Interionic Distances. In the first series of calculations, we examined the effect of an anion upon the geometry of the bridged ion, *trans*-**5**. For that purpose, the LiH_2^- anion (**B**) was placed in the plane of the three-membered ring, opposite to the bridging methyl, on a line drawn from C2 and perpendicular to the C2−C3 bond (see Computational Method for numbering). The interionic distance *d*, (C2.....**B**, see Computational Methods) was held constant in each run of calculations. An alteration in geometry was observed already at *d* = 7 Å. Most affected were the C−C bond lengths of the bridging carbon: the one opposite to the anion (C2−C4) increased, the other one (C3−C4) became shorter. Values of these two bond lengths for various distances *d* are shown in Table 1. This finding shows a higher sensitivity to the anion for the $C_5H_{11}^+$ system than for the lower homologue $C_3H_7^+$, for which the geometry of the protonated cyclopropane was not distorted by the anion present at distances greater than 3.5 Å.[1a]

4.b. “Open” Secondary Ions at Short Interionic Distances. In the second stage, optimization of the ion pair with **A** as anion at *d* = 2.30 Å (defined as the distance from the C1C2C3 plane), in which the anion was allowed a free plane-parallel movement at the top of the cation, gave the “open” structure **3.A** as the only energy minimum. As established in the study of the 1-propyl cation, the criteria to distinguish between an open and a methyl-bridged ion are the $C^+{-}C{-}CH_3$ bond angle (with 90° as the divide) and, most important, the conformation at the $(C^+{-})C - CH_3$ bond.[1a] Attempted optimization of the bridged ion pair *trans*-**5.A**, led to the same “open” structure, shown in three projections in Figure 1. It is seen that the cation layout in the C1,C2,C3 part is similar to that of the 2-propyl cation[28] and in the C2,C3,C4 part to that of the 1-propyl cation.[1a] The main geometrical parameters are listed in Table 2. The C3−C4 bond length and the C2−C3−C4 bond angle are similar to the corresponding parameters for the bisected form of the 2-methyl-2-butyl cation, $\mathbf{2_b}$.[1b,20] The equality of the C1−C2 and C2−C3 bond lengths is also worth noting. As in the other cases,[25a,c] the structure is very much controlled by the electrostatic interaction of the anion with the positively charged hydrogen atoms (here the ones bonded to C1 and to C5) and with C2. The orientation of C4 and C5 relative to the anion results from their position in the neutral precursor, 2-fluoro-3-methylbutane (C5 gauche, C4 trans to the fluorine). The anion is slightly displaced in the

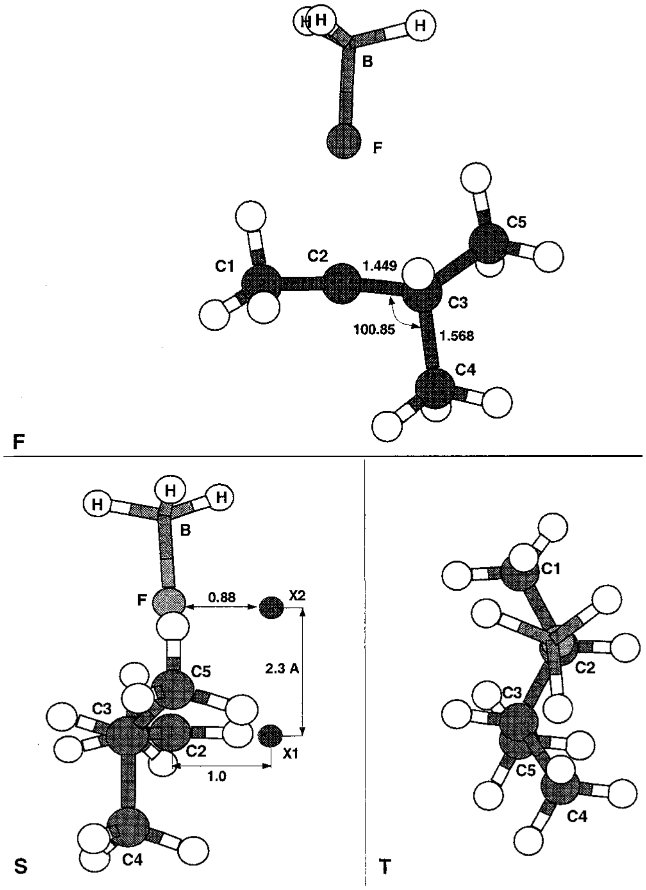

Figure 1. Optimized [MP2(FC)/6-31G*] geometry of the **3.A** ion pair with the anion allowed an unrestricted plane−parallel movement (see text) at *d* = 2.3 Å. **F**: front view; **S**: side view, **T**: top view.

Table 2. Main Geometrical Parameters of **3a.A** Ion Pair Optimized with the Anion Allowed an Unrestricted Plane−Parallel Movement (see text) at *d* = 2.3 Å

parameter	value
d(C1−C2)	1.449
d(C2−C3)	1.449
d(C3−C4)	1.568
d(C1−H1)	1.111
d(C5−H5)	1.090
d(C2−X1)	1.0
d(F−X2)	0.881
θ(C1−C2−C3)	124.65
θ(C2−C3−C4)	100.66
θ(H1−C1−C2)	97.70
φ(C4−C3−C2−C1)	91.81
φ(F−X2−X1−C2)	−4.38
φ(H5−C5−C3−H3)	−60.23

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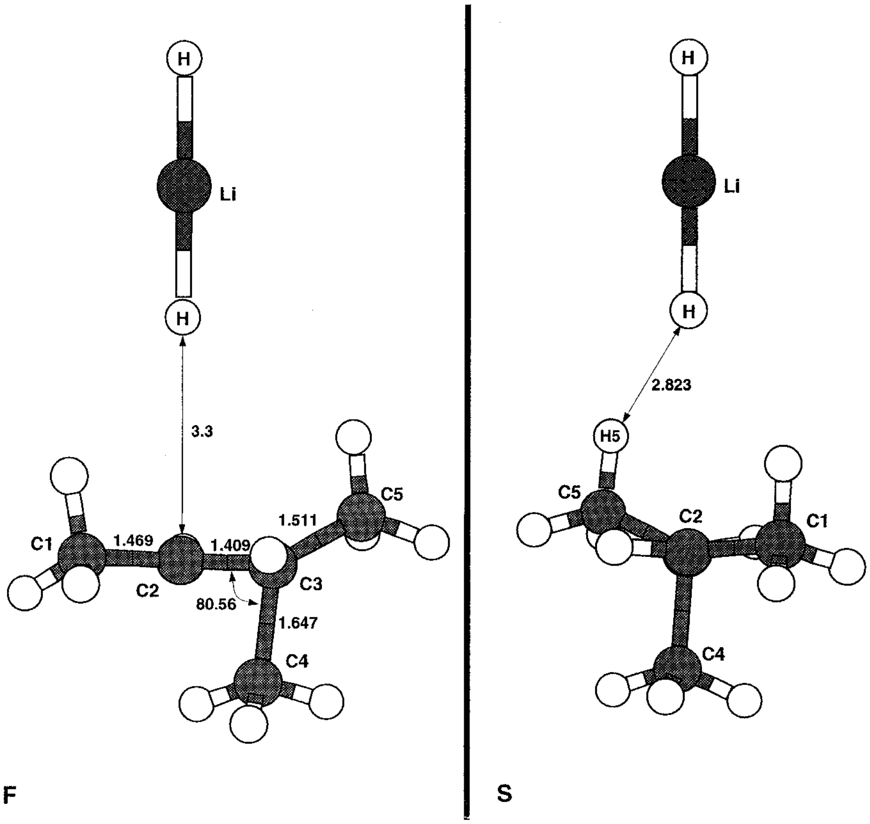


Figure 2. Optimized [MP2(FC)/6-31G*] geometry of the *trans*-**5**.**B** ion pair with the anion in a "fixed" position (see text) at $d = 3.3$ Å. **F**, **S**, as in Figure 1.

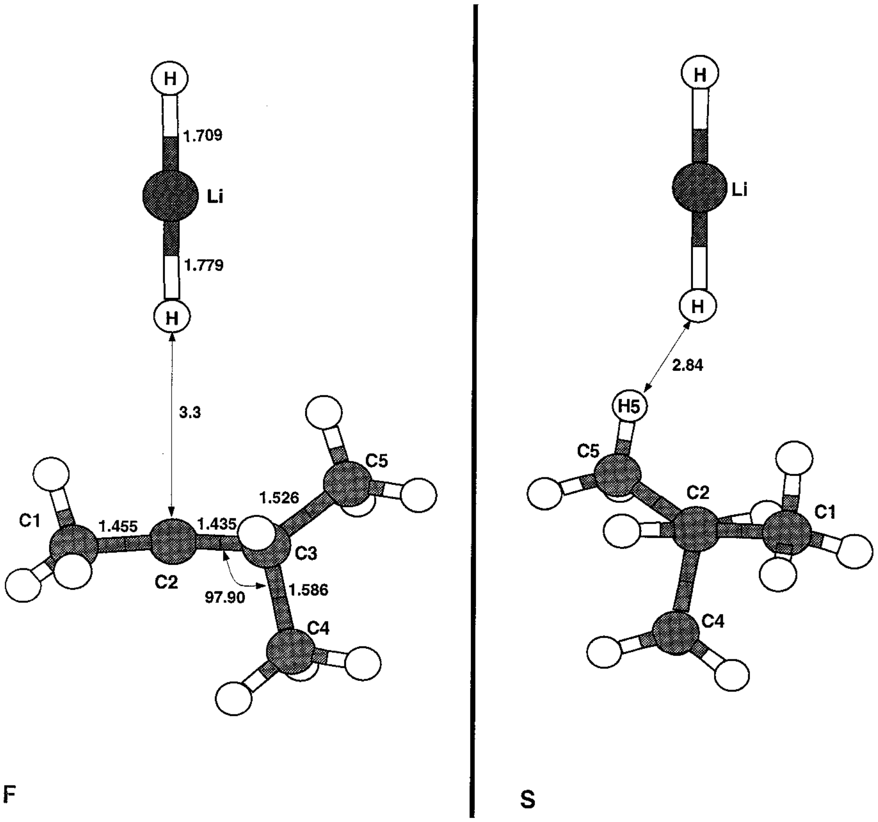


Figure 3. Optimized [MP2(FC)/6-31G*] geometry of the **3**.**B** ion pair with the anion in a "fixed" position (see text) at $d = 3.3$ Å. **F**, **S**, as in Figure 1.

direction of C1, the dihedral angle φ(C2−X1−X2−F) being 4.38° (X1 and X2 are "dummy atoms," see Computational Methods and Figure 1). Because of the interaction with the *syn* hydrogen at C5 the anion equilibrium position is over the

Table 3. Relative Energy of **3.B** and *trans*-**5.B** Ion Pairs Optimized with the Anion Fixed along a Line B−C2 Perpendicular to the C1,C2,C3 Plane (see text and Figures 2 and 3), at $d = 3.3$ Å

level of calculation	relative energy *trans*-**5B** − **3B**[a]
MP2(FC)/6-31G*	0.96
MP2(FC)/6-31G**	0.65
ZPE[b]	0.15
MP4SDTQ(FC)/6-31G**//MP2(FC)/6-31G**	1.96
MP4SDTQ(FC)/6-31G**// MP2(FC)/6-31G**+ ZPE[b]	2.11

[a] In kcal/mol. [b] The individual values (after scaling by a factor of 0.9676.[35]) were 99.46251 kcal/mol for *trans*-**5B** and 99.31258 kcal/mol for **3B**.

"outside" of the C1−C2−C3 angle, by 0.119 Å. This is at variance with the finding for the 2-propyl cation, for which the anion in the equilibrium position projected inside the C1−C2−C3 angle, because of electrostatic interactions with hydrogens at C1 and C3. In turn, the "outside" position of the anion is responsible for the existence of the ion pair at an interionic distance (2.30 Å) at which elimination occurred from the 2-propyl cation.[25a] *Thus, the presence of the C5 methyl group has significant consequences for the chemistry of this system.*

The bridged cation pair *trans*-**5.A** could not be optimized even at $d = 2.60$ Å, a distance at which the lower homologue protonated cyclopropane is lower in energy than the 1-propyl cation,[1a] confirming the prediction that a methyl substituent has a greater stabilizing effect in an open ion than in the bridged counterpart. As lengthening of d increases more the distance from anion to C2 than to the hydrogen at C1 in this relative orientation of the ions, ring opening is followed at $d = 2.60$ Å by the movement of the anion toward H−C1 and ultimately by elimination forming 3-methyl-1-butene, **4** (eq 5).

$$\mathbf{3.A} \rightarrow H_3B + HF + \underset{\mathbf{4}}{CH_2{=}CH{-}CHMe_2} \qquad (5)$$

Optimization of **3.A** at $d = 2.60$ Å with an eclipsed C1,C3 conformation of the cation (H at C3 facing the anion), resulted in the elimination from C3 and formation of 2-methyl-2-butene, **6** (eq 6).

$$\mathbf{3.A} \rightarrow H_3B + HF + \underset{\mathbf{6}}{CH_3{-}CH{=}CMe_2} \qquad (6)$$

4.c. "Open" and Bridged Ions at Intermediate Distances. In the third series of calculations, at longer d, the counterion (**B**) was positioned as in series *4.a*, with the added constraint that φ(Hp-C2−C3−C1) = − φ(Hp-C2−C3−H2), where Hp is the proximal hydrogen of the anion and H2 is the one bonded to C2. This orientation does not favor proton loss from C1. The starting point was the *trans*-**5.B** structure obtained in series **4.a**, at $d = 4$ Å. Upon moving the ions closer, the bridged form opened up at 3.25 Å, and the structure optimized was that of **3.B**. This confirms the greater sensitivity to the anion of the $C_5H_{11}^+$ cation than that of the $C_3H_7^+$ cation, for which the open and bridged cations coexisted at equilibrium in ion pairs for interionic distances d between 2.25 and 2.6 Å, at the same level of theory (MP2/6-31G*).[1a]

The two isomeric ion pairs, **3.B** and *trans*-**5.B**, could each be optimized for $d = 3.3$ Å, where the open form is more stable by 0.96 kcal/mol (MP2/6-31G*). These ion pairs are shown in Figures 2 and 3, respectively, and the main geometrical parameters of the carbocations are listed in Table 3. For a better comparison, the geometries of the isomers were also optimized at the MP2(FC)/6-31G** level and single-point MP4SDTQ(FC)/6-31G**//MP2(FC)/6-31G** calculations were conducted. The relative energies, including ZPE correction with the appropriate scaling factor,[35] are also shown in Table 3.

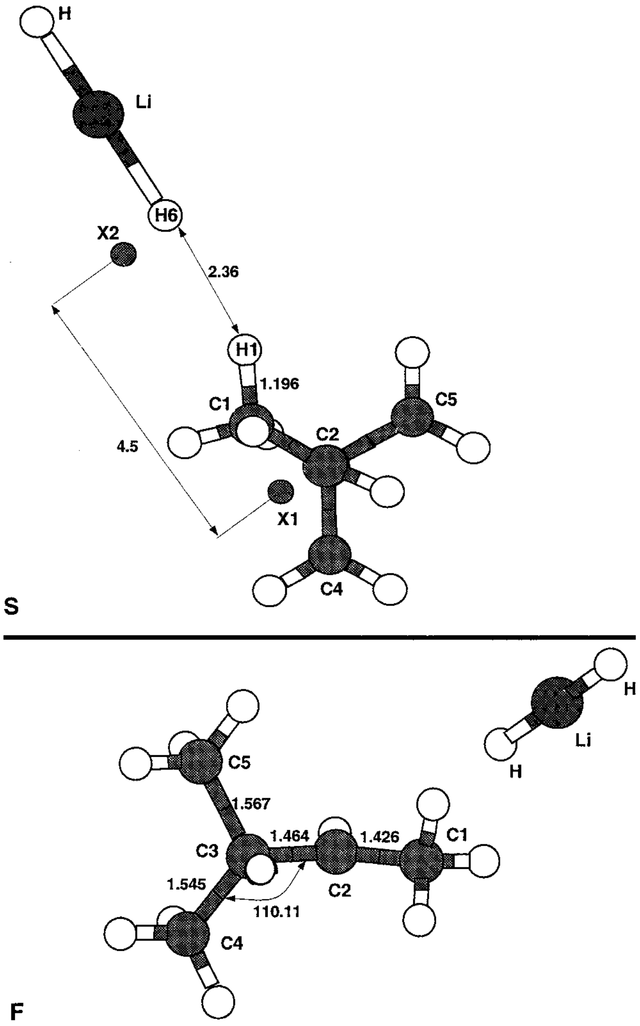
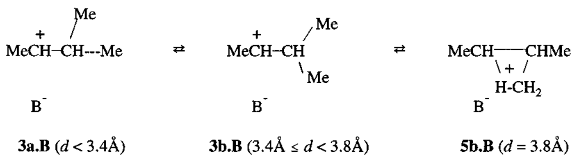


Figure 4. Optimized [MP2(FC)/6-31G*] geometry of the **3.B** ion pair with the anion allowed an unrestricted plane-parallel movement at the top of the C2C3C5 plane (see text) at $d = 4.5$ Å. **F**, **S**, as in Figure 1.

The complications introduced by the larger cation were evidenced, however, upon repeating the geometry optimizations at increasing values of d, when the energy difference variation was not monotonic as in the ion pairs of the $C_3H_7^+$ cations. The flexibility of the system allows a fine balance between the hyperconjugation by the "distal" (referring to the anion) methyl group, C4, and the electrostatic interaction of the anion with the *syn* hydrogen at C5 (the "proximal" methyl group), both β to the sp^2 carbon, C2, through the rotation of the C2−CH bond. The biggest energy difference favoring **3.B**, 2.5 kcal/mol (MP2/6-31G*), was calculated for $d = 3.4$ Å. The two isomers coexisted up to $d = 3.8$ Å, where ring closure of **3** → **5** occurred,



$$\underset{B^-}{\overset{+}{MeCH}{-}\overset{Me}{CH}{\cdots}Me} \rightleftarrows \underset{B^-}{\overset{+}{MeCH}{-}CH(Me)_2} \rightleftarrows \underset{B^-}{MeCH{-}CHMe\ (\overset{+}{\ }H{-}CH_2)} \qquad (7)$$

3a.B (d < 3.4Å) **3b.B** (3.4Å ≤ d < 3.8Å) **5b.B** (d = 3.8Å)

with the participation of the "proximal" methyl group. This process is sketched in eq 7.

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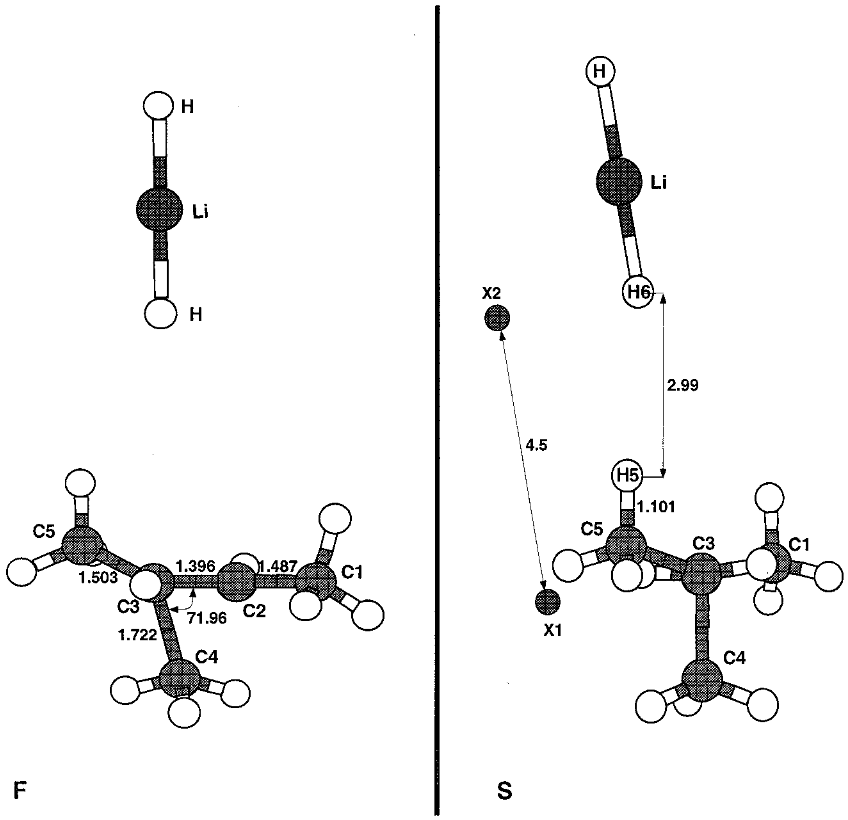

Figure 5. Optimized [MP2(FC)/6-31G*] geometry of the *trans*-**5.B** ion pair with the anion allowed an unrestricted plane-parallel movement at the top of the C12C2C3 plane (see text) at $d = 4.5$ Å. **F**, **S**, as in Figure 1.

It is noteworthy that the open ion **3** is the preferred structure in ion pairs up to such long interionic distances. This is not so surprising, however, in light of our results obtained for the lower homologue, $C_3H_7^+$, for which the point of equal stability of the open (primary) and bridged isomers in the ion pairs corresponded to $d = 2.47$ Å (MP4(FC)/6-311G**//MP2(FU)/6-311G** + ZPE). The stabilizing effect of methyl substituents is much larger in open ions than in bridged ions. For isolated ions, the preference for the bridged ion over the primary ion in the $C_3H_7^+$ ions was calculated as about 12 kcal/mol,[19] but it was only 4 kcal/mol for the bridged ion over the secondary ion in the $C_5H_{11}^+$ isomers.[1b]

4.d. "Open" and Bridged Ions at Intermediate Distances, in a Different Orientation. In this series of calculations, the geometry description of series **4.b** was applied to the bridged ion pair *trans*-**5.B**, at $d = 4$ Å. At this distance the main electrostatic interaction of the anion was with the "proximal" hydrogens of the methyl groups, C1−H1 and C5−H5. Because the anion was at a fixed distance from the C1C2C3 plane, its plane−parallel movement was controlled by the interaction with C5−H5; therefore, the anion moved toward that hydrogen, away from C2. This movement was followed by the cleavage of the C3−C4 bridging bond, instead of the one originally opposite to the anion, and the formation of the methyl-migrated ion pair, **3.B**. Renumbering the atoms to keep C2 tricoordinated showed that the anion was then free to glide in a plane parallel to the C2C3C5 plane. This arrangement prevented the movement of the C5-methyl toward the anion by the rotation of the C2−C3 bond as in the third series of calculations. Instead, rotation of the C2−C3 and movement of the anion brought the latter to the proximity of the C1 methyl group. In the equilibrium position, the distance between the proximal H of the anion (H6) and the nearest hydrogen at C1 (H1) was only 1.99 Å, and the H6....C2 distance was 4.08 Å. The C1−H1 bond length was 1.25 Å, whereas the C1−C2 bond (1.409 Å) was shorter than the C2−C3 bond (1.475 Å). If not kept separated, the ions would react by elimination.

Definition of the anion position relative to the C2C3C5 plane also allowed optimization of the "open" ion pair **3.B** at $d = 4.5$ Å (Figure 4). The distance from H1 to the proximal hydrogen of the anion (H6, Figure 4) was now 2.36 Å, the C1−H1 bond length was 1.196 Å, and the H6....C2 equilibrium distance was 4.52 Å. The C1−C2 (1.426 Å) and C2−C3 (1.464 Å) bond lengths are less different than at $d = 4$ Å. *It is seen that the "open" ion exists and it is even the preferred form at rather long distances from the anion and for various relative orientations of ions in the ion pairs*. At the same distance ($d = 4.5$ Å), the bridged ion pair *trans*-**5.B** with the position of the anion defined as in the previous paragraph was also an energy minimum, 7.12 kcal/mol higher in energy (MP2/6-31G*) than **3.B**. It had the anion on the side of the ring cis to C5, almost at the top of that methyl group, as shown in Figure 5.

5. The Mechanism of Ionization of 3-Methyl-2-butyl Substrates. For the solvolysis of the 3-methyl-2-butyl substrates (e.g., **1**), hydrogen participation[2] in the ionization step was ruled out by earlier work and our experimental studies of labeled compounds in TFA, which showed that the process involves reversible dissociation to ion pairs, prior to the hydrogen shift and elimination.[13] The alternative mechanism involving methyl participation was also shown above to be incompatible with the data. Now we find from ab initio calculations that the only form existing as an intermediate in tight ion pairs is the "open" 3-methyl-2-butyl cation, **3**. The calculations thus predict that the ionization of precursors of both 1-propyl[1a] and 3-methyl-2-butyl cations should take place without anchimeric assistance. This prediction has no bearing on solvolysis reactions of the former, which react by the S_N2 mechanism, but it is relevant for their reaction in HF−SbF$_5$. In addition, the hydrogen and carbon exchanges in the 2-propyl cation in superacid[36] may be rationalized most satisfactorily as occurring in tight ion pairs and involving both the open 1-propyl cation and the protonated cyclopropane as intermediates.[1a]

It appears that both the carbocation structures and the "internal" reactions of the ion pair depend on the distance and relative orientation of the two ions. Thus, for the ion pairs of **3**, the internal return is favored by the position of the anion "outside" the C1−C2−C3 angle of the cation, predicted by the calculations for the tight ion pair. At a slightly greater separation of the ions, $d > 2.5$ Å, recombination, elimination from C1, from C3, and hydride shift can occur. Elimination from C1 is minor or nonexistent in solvolyses,[2,13] whereas the last two reactions occur from the same orientation of the ions, but at different interionic distances. This dependence of the competition between elimination and hydrogen shift upon interionic distance was also evidenced by the calculations on the 1-propyl cation in ion pairs.[1a] We can refine, therefore, the picture of solvolysis of **1** by saying that 25% of the ion pairs which do not recombine (return) react at intermediate distance by elimination and most of the rest undergo hydrogen shift after further separation, before adding solvent and being trapped by the solvent, respectively. The methyl shift, which is concerted with the movement of the anion in the opposite direction, has to occur at an interionic distance at which the bridged isomer **5** is either a transition state or is higher in energy than the "open" ion **3**. The methyl shift competes effectively with the trapping by solvent, leading to the significant scrambling in the product **7** shown in eq 3, but neither methyl shift nor solvent trapping competes well with elimination or hydrogen shift, hence the low amount of **7** in the product mixture (1.5%).[13a,b]

Our previous calculations indicated that the first carbocation formed in the reaction of 3-methyl-1-butene with XeH^+ in the gas phase[4] was the bridged species **5**.[1b] It is gratifying that we have now an agreement between theory and experiment for the generation of these carbocations in solution as well.

Acknowledgment. Our research in strong acid catalysis is supported by the Grant CTS-9812704 from NSF. A number of grants of supercomputer time were obtained from the Pittsburgh Supercomputing Center in 1989−1990 for preliminary studies at Clarkson University and during the period 1992−1996 at the University of Pittsburgh We are indebted to Professor Kenneth D. Jordan and Dr. Carlos Gonzales for many helpful discussions.

Supporting Information Available: A table with the absolute and relative energies of *trans*-**5B** and **3B**, at $d = 3.30$ Å (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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