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Theoretical Studies of Carbocations in Ion Pairs. 4.[1] The Interconversion of the 1-Propyl Cation and Protonated Cyclopropane

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Abstract: The structure of the 1-propyl cation in the ion pair with the model anion trihydrofluoroborate, proven in earlier work to be appropriate for such studies, was investigated by ab initio calculations at the level previously reported to give the definitive structure of carbocations. In previous work, it was shown that the carbocation structure does not change with the nature of the anion. The cation structure is determined, however, by the distance between the cation and anion, d, and their relative orientation. At infinite interionic distance the only stable chemical species (energy minimum) is the protonated cyclopropane, **1**. As the ions move toward each other, the cyclopropane bond opposite to the anion becomes progressively longer and eventually it breaks up in the contact ion pair. Three domains of cation stability are identified as a function of d: at long distances, ion **1** is the only energy minimum; at intermediate distances **1** and the 1-propyl cation **2** are both energy minima; at short distances, ion **2** is the only energy minimum. Thus, ionization of 1-propyl precursors forms the tight ion pair of **2** as the first intermediate. Isomers **1** and **2** differ in both the C1—C2—C3 angle and the conformation of the C2—C3 bond; the transition structure for their interconversion has been determined by calculations. At the MP4(FC)/6-311G**//MP2/6-311G** level, the two isomers have the same energy content for $d = 2.40$ Å, but correction for the zero-point energies obtained from the vibrational frequencies calculated at the MP2/6-311G** level reduces the energy of **2** relative to **1**, thus requiring a slight upward correction in the value of d for equal stability of isomers. The interconversion of **1** and **2** is observed for a position of the anion essentially in the same plane as the three carbon atoms. Movement of the anion above the same plane results in hydrogen shift with the formation of the 2-propyl cation, **3**. Some literature results in which primary carbocations could intervene as intermediates are discussed. In particular, the data on carbon and hydrogen scrambling in **3** in superacid solution are better accounted for by the results of calculations for ion pairs, with both **1** and **2** as intermediates, than by the results of calculations for isolated ions.

Introduction

In our work on acid strength and mechanism of action of acid catalysts, we emphasized that on catalytic sites carbocations can be formed only in tight ion pairs,[2] but we noted that all theoretical descriptions of structure and reactivity of carbocations had examined isolated ions in the gas phase, with few considerations of possible solvent effects. Testing the effects of counterions on carbocation structures was desirable. As already stated,[1a,c] another incentive for theoretical work on carbocations in ion pairs was the discrepancy observed between the predictions of high-level ab initio calculations on the

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methylbutyl cations[3] and the results of studies of these ions in trifluoroacetic acid (TFAH),[4a,b] a medium of low dielectric constant but high anion stabilizing ability,[5] where the reaction pathways were determined by the formation and conversion of these carbocations in tight ion pairs.[4] The need to test the computational technique on ion pairs and the concern about the choice of the counterion, for which the size of the $C_5H_{11}^+$ cation did not allow many choices, led to the examination of the 2-propyl cation, for which the developmental work for these calculations was conducted.[1c] This species is also the smallest carbocation stable enough to be studied in superacid solution.[6] Another test of our approach was the study of the *tert*-butyl cation in a five-ion aggregate,[1a] the results of which could be matched with X-ray diffraction data.[7]

It was found that the interionic distance has an important effect on the cation geometry and recombination of the ions occurs at different distances for different anions, because of the different nucleophilicities of the latter. At distances beyond the recombination range, *the cation structure did not change, however, when the anion was changed.*[1]

As a significant result, the geometry of the 2-propyl cation changes in the presence of an anion as far as 6 Å away.[1c] Extensive calculations of the principal components of the NMR chemical shift tensor of the sp^2 carbon, for which experimental results existed,[8] of the 2-propyl cation ion paired with various anions and in larger ionic aggregates mimicking the crystal were also successfully conducted.[1b] Furthermore, geometry optimization on the isolated *tert*-butyl cation had indicated that the only energy minimum was an asymmetric conformation close to the C_{3h} form,[9] yet the IR spectrum measured in the solid state was matched with the simulated spectrum of the C_s conformation. It was pointed out that the energy surface was flat, with very small energy differences between conformers.[1] In that case, however, the energy absorption should occur from all conformations and the spectrum should show lines corresponding to them all, the strongest being the one corresponding to the energy minimum. For line separations of 25 cm^{-1}, averaged IR bands would be seen for residence times shorter than about 10^{-12} s. The C_s form resulted, however, as the energy minimum from the optimization of the aggregate modeling the crystal.[1a] Our results thus provided the justification for the choice made earlier in the simulation of the IR spectrum.[9]

It appears, therefore, that theoretical calculations on isolated carbocations are not adequate for describing cationic chemistry in condensed media, where ion pairing plays an essential role.[10] We tested further that possibility through ab initio calculations on ion pairs of protonated cyclopropane (**1**) and 1-propyl cation (**2**), the higher energy isomers of the previously studied 2-propyl cation (**3**).

Carbocationic chemistry of C_3H_7X precursors was early described in terms of two possible intermediates, the primary ion **2** and the secondary ion **3**. After the existence of **1** was demonstrated by Baird and Aboderin,[11] it was found that this ion and its substituted derivatives[12] intervene quite unexceptionally as reaction intermediates. These three relatively small ions became the subject of intensive computational scrutiny. Ab initio[13] calculations using the Hartree−Fock (HF) single-determinant form of the wave function and small basis sets[14] predicted **2** to be of lower energy than **1**, but calculations with larger basis sets favored "bridged" ions in general and **1** over **2** in particular.[15] Furthermore, inclusion of electron correlation increased the stability of bridged ions over their "open" counterparts,[16] a feature verified for **1** and **2**.[17] Finally, MP2/6-311G** geometry optimization and single-point calculations at the MP4(FC)/6-311G** level[18] indicated that **1** is the only energy minimum in addition to **3** and the most stable conformation of **2** is a transition state, 12.1 kcal/mol[19] higher in energy than **1**. The results of the calculations at this level were considered so accurate that discrepancies of 1.7 kcal/mol from the experimental values were said to warrant a revision of the accepted experimental values.[18,20] Even though this estimate of accuracy of calculated proton affinities of unsaturated hydrocarbons might be too optimistic, the comparison of closely related species might be as accurate as claimed. In any event, calculations at this level were reported to provide the definitive characterization of the potential energy surface for gas-phase $C_3H_7^+$ ions.[18] These highly reliable calculation results constituted the starting point of our study.

Computational Method

The calculations were conducted with the program Gaussian 92,[21] in the manner described previously.[1] As a rule, imposition of symmetry constraints to the calculated structures was avoided.

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The control of geometry by "dummy" atoms was presented in the previous papers.[1a,c] In this work, the position of the anion relative to the cation was defined with the use of two "dummy" atoms, X1 and X2. Two orientations of the anion were examined. In orientation A (B−F bond parallel with the C1C2C3 plane, Figure 1), X2 was connected to C1 by a "bond" 1.0 Å long, perpendicular to the C1C2C3 plane. X1 was connected to X2 by a "bond" of length d (held constant in any given optimization run) perpendicular to C1−X2 and forming a dihedral angle φ(X1−X2−C1−C2) of 90° (X1 on the other side of C1−C2 than C3). The fluorine atom of the anion was connected to X1 by a bond of variable (optimized) length at a (fixed) F−X1−X2 angle of 90° and a variable dihedral angle φ(F−X1−X2−C1). The F−B bond was held perpendicular to X1−F and antiparallel to X1−X2 (i.e., φ(B−F−X1−X2) = 180°). In orientation B (B−F bond perpendicular to the C1C2C3 plane), X2 was placed in the C1C2C3 plane, away from C3, and the X1−X2 "bond" was perpendicular to that plane. The F−X1−X2 angle was 90° and the F−B bond was antiparallel to X1−X2, as in orientation A.

Assignment of calculated frequencies to specific vibration modes was conducted with the computer program MOLDEN, available from QCPE.[22] Its application to the results obtained for both **1**·FBH$_3^-$ and **2**·FBH$_3^-$ showed three imaginary frequencies (negative eigenvalues in the force constant matrix) in each case, namely stretching of the F⋯C1 and bending of the F−B bond relative to the F⋯C1 "bond" in two perpendicular directions, all originating from the imposition of a fixed interionic distance and orientation of the anion relative to the cation. These are not actual vibrations. The eigenvalues for all actual vibrations of the cation and anion were positive.

The approximate location of the transition state along the reaction coordinate was determined with the program LST.[23] After that, the transition structure was optimized by the standard procedure.[3]

The projections of the molecular geometry shown here were generated with the computer program XMOL.[24] The diagrams shown in the article (Figures 2 and 6) were constructed with the program SigmaPlot, available from Jandel Scientific.

Results and Discussion

In the first study of modeling of carbocations in ion pairs it was found that the structure of the cation does not change with the anion, if the interionic distance is long enough to prevent reaction between ions (elimination, recombination). Also, examination of the *tert*-butyl cation in a five-ion aggregate Li$^+$·A$^-$·Me$_3$C$^+$·A$^-$·Li$^+$, which does not undergo ion recombination, and in a triple ion A$^-$·Me$_3$C$^+$·A$^-$, which does, showed that geometry optimization at fixed interionic distances gives the correct structures for carbocations in ion pairs or aggregates.[1a] The approach was also successful in modeling ^{17}O NMR chemical shifts of hydronium and dihydroxonium fluoroborates.[25]

All the calculations in the present work were conducted with fluorotrihydroborate[26] as the counterion. The smaller, cheaper to use, lithium dihydride[1b,27] reacts with the cation at short distances and can be a choice only for modeling carbocations in looser ion pairs.[27] To avoid recombination or elimination, the anion was held above the cation at a fixed distance and in a fixed orientation. Otherwise, the anion was fully optimized and also allowed an unrestricted plane-parallel movement at the top of the cation. Geometry optimization was conducted for a

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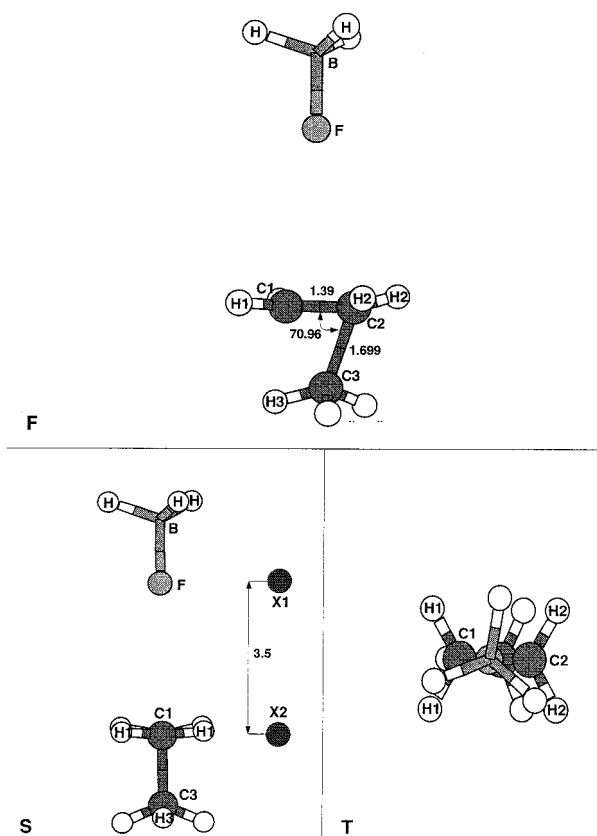(25) Fǎrcaşiu, D.; Hâncu, D. *J. Phys. Chem., A* **1999**, *103*, 754.

Figure 1. Geometry of the protonated cyclopropane−trihydrofluoroborate ion pair (**1**·BH$_3$F$^-$) at long interionic distance (d = 3.5 Å): F, front view, dummy atoms not represented; S, side view (C1 closest to the viewer), X1, X2, dummy atoms; T, top view, dummy atoms not represented.

series of values of the interionic distance, d. As it was observed that the changes in the calculated geometries of the cations from the MP2/6-31G* level to the MP2/6-311G** level range from unimportant to imperceptible,[1] an extended series of calculations was conducted with the smaller basis set. On the basis of the results of these calculations, certain values of d were selected for examination with the larger basis set.

As the starting point of the calculations, we took the most stable structure determined for the protonated cyclopropane **1** as an isolated ion.[18] The addition of the anion at a distance of 4 Å had no effect on the geometry of this cation. This result contrasts with the behavior of the 2-propyl cation, **3**, for which addition of the counterion changed the geometry from C1,C3 staggered[18,28] to C1,C3 eclipsed even at an interionic distance of 6 Å.[1c] The difference reflects a higher energy involved in the distortion of the bridging bonds of **1** than in the conformational changes in **3**. The anion positioned itself upon optimization above the C1−C2 bond.

As the anion, held in orientation A, is moved closer, the changes in the cation geometry are negligible at d = 3.5 Å. The geometry of the ion pair of **1** at this interionic distance is shown in Figure 1. The geometry modification becomes important, however, when the separation decreases further. It was observed that the bridging methyl (C3) is not equidistant from C1 and C2 even for the isolated ion **1**. The latter has a C_s symmetry with the C1−C2−C3 plane as the symmetry plane and one of the hydrogens at C3 is located in this plane, "leaning" somewhat toward C1. The C1−C3 bond is longer than the C2−C3 bond.[18] Reduction of the interionic distance increases this asymmetry by shortening the C2−C3 bond and lengthening the

Table 1. Geometrical Parameters for the Protonated Cyclopropane$-BH_3F^-$ Ion Pair at MP2(FC)/6-31G*, for Different Interionic Distances, d (Å)

d	$D(C1,C2)^a$	$D(C2,C3)^a$	$D(C1,C3)^a$	$\theta_1{}^b$	$\varphi_1{}^c$	$D(X2,C1)$	$D(X1,F)$
4.0	1.391	1.699	1.808	70.82	30.95	1.000	1.16
3.5	1.390	1.699	1.811	70.96	30.93	1.000	1.16
3.3	1.390	1.691	1.818	71.56	29.79	1.000	1.14
3.1	1.390	1.686	1.823	71.99	28.49	1.000	1.13
2.9	1.390	1.677	1.8400	73.05	25.61	1.000	1.08
2.5	1.398	1.636	1.936	78.87	7.413	1.000	1.00
2.45	1.402	1.627	1.965	80.53	3.60	1.000	0.976
2.4	1.406	1.618	2.003	82.67	0.66	1.000	0.994
2.3	1.420	1.598	2.135	89.87	4.44	1.000	0.99

[a] $D(C_i,C_j)$ = distance (C_i-C_j). [b] θ_1 = bond angle (C1,C2,C3). [c] φ_1 = dihedral angle (F,X1,X2,C1).

C1$-$C3 bond, thus opening the C1$-$C2$-$C3 angle. At a distance d of 2.4 Å, the C1$-$C2$-$C3 angle is 82.67° and the C1$-$C3 bond is 2.003 Å; at $d = 2.3$ Å the two values are 89.97° and 2.135 Å. It is noteworthy that for the isolated ion, the corresponding species with an angle of 83.4° and a C1$\cdots$C3 distance of 2.048 Å (the latter calculated by us from the other published geometrical parameters[14]) was previously discussed as a distorted C2,C3-eclipsed 1-propyl cation (open ion).[14] Indeed, one could reasonably argue that very little bonding exists between C1 and C3 at a distance of 2.048 Å, not to speak of 2.135 Å. Nonetheless, we interpret this geometry of the ion as bridged (i.e., **1**) even at $d = 2.3$ Å, although it could be considered very much distorted toward the open carbocation structure. The reason for our choice in classification is presented below.

A summary of the values for the most important geometrical parameters of **1** at several values of d is presented in Table 1. At the same time with the changes in the geometry of the cation, the position of the anion relative to the cation changes. As seen in Figure 1 the anion is not located over the middle of the C1$-$C2 bond even at distances where it does not affect the geometry of the cation, but it is closer to C1: at $d = 4.0$ Å, the distances from the projection of F on the C1$-$C2 bond to C1 and C2 are 0.600 and 0.791 Å, respectively. When d decreases, the anion moves above the C1$-$C2 bond in the direction of C1, such that at the short interionic distances it is positioned roughly at the top of C1. This movement is described in Table 1 by the change in values of the dihedral angle $DI_1 = \varphi(F-X1-X2-C1)$ and of the distance from X1 to F, where X1 and X2 are dummy atoms introduced to allow the movement of the anion relative to the cation in the manner described above.

Opening of the cyclopropane ring occurs at $d = 2.25$ Å and it is manifested not only by an increase in the C1$-$C2$-$C3 angle over 90° (to 104.21°) but also by a change in conformation through the rotation of the C2$-$C3 bond to achieve the C2,C3 staggered conformation. For this and shorter interionic distances the only energy minimum is the open ion **2**, present in an ion pair with the anion in orientation A. This orientation would result from the ionization of 1-fluoropropane by coordination of the fluorine with a Lewis acid.

Starting with the geometry obtained at $d = 2.25$ Å as input, the geometry of the ion pair was next optimized for increasing values of d. It was found that the ion pair containing **2** represents another energy minimum coexisting with the ion pair of **1**. At short distances the former ion pair has a lower energy content

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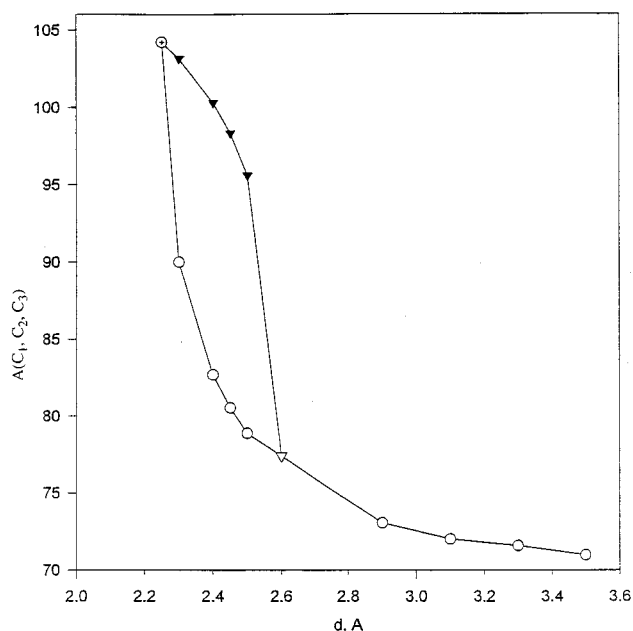
Table 2. Geometrical Parameters for the 1-Propyl$^+$·BH_3F^- Ion Pair at MP2(FC)/6-31G*, for Different Distances between the Ions

geometrical parameters^a	distance between the ions, d (Å)			
	2.3	2.4	2.45	2.5
$D(C1,C2)$	1.440	1.430	1.424	1.415
$D(C2,C3)$	1.569	1.580	1.587	1.597
$D(C1,C3)$	2.358	2.312	2.280	2.236
$\theta(C1,C2,C3)$	103.14	100.28	98.30	95.59
$D(X2,C1)$	1.000	1.000	1.000	1.000
$D(X1,F)$	0.992	1.001	1.001	1.000
$\varphi(F,X1,X2,C1)$	-3.32	-0.60	0.91	2.59
relative energy^b	-0.7926	0.1200	0.7957	1.506

[a] Meaning of symbols D, θ, and φ as in Table 1. [b] Kcal/mol, relative to **1**·BH_3F^- (cyclic isomer) taken as 0.0.

than the latter, but as the interionic distance increases the order of stability reverses itself. The geometry of **2** also changes monotonically with d. Thus, the C1$-$C2$-$C3 angle decreases, such that at $d = 2.5$ Å it is down to 95.59°, and the distance between C1 and C3 decreases as well, from 2.376 Å at $d = 2.25$ Å to 2.358 Å at $d = 2.3$ Å and 2.236 Å at $d = 2.5$ Å. The anion is in all cases located above C1 (it is noteworthy that the position of the anion relative to the cation in the ion pair of **1** is about the same as that in the ion pair of **2** at these interionic distances). The most important geometrical parameters of **2** in the ion pair at various values of d are listed in Table 2. Optimization at $d = 2.6$ Å leads to ring closure forming **1**, with a C1$-$C2$-$C3 angle of 77.4°. On the other hand, at distances smaller than 2.2 Å the fluorine "jumps" from boron to carbon and 1-fluoropropane results. This process is the reverse of the ionization of a 1-propyl precursor. The distance at which a reaction (either recombination or elimination) between the cation and the anion occurs is determined by the stability of both the cation and the anion. For lithium dihydride as anion this internal reaction occurs at interionic distances around 3.5 Å even for the secondary ion **3**.[1a] For anions such as $Sb_2F_{11}^-$ or $Sb_3F_{16}^-$, which are nonnucleophilic enough to allow experimental studies of unstable carbocations, the reversible reaction within the ion pair between **2** and the counterion will probably occur at less than 2 Å.

During the early optimization studies of **1** in the ion pair, seeing that the geometry changed significantly with the interionic distance d, we sought a criterion to determine whether a structure is bridged or open and decided that a C1$-$C2$-$C3 angle of 90° should be an appropriate structural divide. There could be a dilemma with that approach as to whether a certain structure should be called a partially bridged (distorted) open ion or a partially open (distorted) bridged ion. If we naively consider ideal structures, however, the corner protonated cyclopropane should have two equal carbon$-$carbon bonds and the 1-propyl cation should have a C1$-$C2$-$C3 bond angle of 112.4°, as in propane, therefore *all* cations have distorted structures. Furthermore, in such terms propane itself is distorted from the

Figure 2. Variation of the C1−C2−C3 angle with the interionic distance, d, at the MP2(FC)/6-31G* level: ○, protonated cyclopropane trihydrofluoroborate (**1**·BH$_3$F⁻); ▼, 1-propyl−trihydrofluoroborate (**2**·BH$_3$F⁻); ▽, cation geometry started as **2** (angle C1−C2−C3 > 90°), optimized as **1**; ⊙, cation geometry started as **1** (angle C1−C2−C3 < 90°), optimized as **2**.

tetrahedral bond angle of 109.5°. Having accepted that even among saturated hydrocarbons the bond lengths and bond angles deviate significantly from the ideal values we should not expect that the only change upon conversion of a C−H to a C⁺ be the change in bond lengths and angles for the atom undergoing the change of hybridization to the *ideal* values for an sp² carbon. The potential dilemma has been eliminated, however, by the results indicating the coexistence of two isomers at certain interionic distances. One of them is certainly bridged, the other is certainly open. Description of each of them as being partially the other one is counterproductive.[29]

The domains of existence of the carbocations **1** and **2** in the ion pairs are presented in Figure 2, which plots the C1−C2−C3 angle as a function of the interionic distance, d. It is seen that **2** exists for 2.2 Å < d < 2.6 Å and **1** for d > 2.25 Å. For values of d between 2.25 and 2.6 Å, the two isomers coexist. The manner in which each of them was optimized at distances d within this range indicated two clearly defined energy minima, rather than a flat energy surface.

The interconversion of the ion pairs of **1** and **2** was examined at the distance d = 2.4 Å, where the two isomers had about the same energy. Reaction coordinate tracking for this process, followed by geometry optimization of the transition structure, showed that both the C1−C2−C3 bond angle and the conformation of the C2−C3 bond change more or less continuously during this transformation. Thus, both the bond angle and the φ(H−C2−C3−H) dihedral angle of the transition structure are close to midway between the values for **1** and **2**. The main geometrical parameters of the transition structure (at the MP2/6-31G* level) are listed in the last column of Table 3 and its

(27) Fărcaşiu D.; Norton, S. H.; Hâncu, D. Paper in preparation.

(28) Schleyer, P. v. R.; Koch, W.; Liu, B.; Fleischer, U. *J. Chem. Soc., Chem. Commun.* **1989**, 1098.

(29) If we take this position, we can say that at the same level of theory (MP2/6-31G*) the 1-propyl cation **2** in the ion pair at d = 2.35 Å is "bridged" to the same extent as the isolated tertiary pentyl cation in the bisected conformation: Schleyer, P. v. R.; Carneiro, J. W. de M.; Koch, W.; Forsyth, D. A. *J. Am. Chem. Soc.* **1991**, *113*, 3990. See also ref 3.

projections are shown in Figure 3. The imaginary frequency in the transition structure was found to consist mostly of the C2−C3 bond rotation.[22] It is thus conceivable that the difference in conformation at the C2−C3 bond is the main reason for the barrier between ions **1** and **2**. The height of the barrier is 0.46 kcal/mol above **2**·FBH$_3$⁻ (0.41 kcal/mol after correcting for ZPE calculated at the MP2/6-31G* level). As the energy difference between isomers increases in either direction, the height of the barrier for the exothermic process decreases until it vanishes and only one energy minimum exists.[30]

In the next step, geometry optimizations were conducted with an expanded basis set for two interionic distances, d = 2.25 and 2.40 Å. The variation of geometrical parameters for **1** at d = 2.4 Å with the basis set is shown in Table 3 (first three columns). One sees in this series a lengthening of the C2−C3 bond, a shortening of the C1−C3 bond, and a reduction of the C1−C2−C3 bond angle at MP2(FC)/6-311G** relative to MP2-(FC)/6-31G*. There is no change in the C1−C2 bond length or in the position of the anion. Optimization at MP2(FU)/6-311G** (with consideration of the core electrons of C, F, and B) does not bring significant changes from the geometry found in the "frozen core" calculation. It is also noteworthy that the bridged ion **1** could be optimized as a minimum at d = 2.25 Å with the MP2/6-311G** basis set and shows an angle C1−C2−C3 of 87.20°, but ring opening still takes place before recombination occurs upon movement of the cation and anion toward each other. The geometry of **1**·FBH$_3$⁻ calculated with the largest basis set at the two interionic distances is presented in Figure 4. Interestingly, the bond length most sensitive to the variation of the interionic distance belongs to the C3−H bond located in the C1C2C3 plane (C3−H3 in Figures 1 and 4).

Optimization of the **2**·FBH$_3$⁻ ion pair at the MP2(FC)/6-311G** level also gives a somewhat shorter C1···C3 distance, a longer C2−C3 bond, and a smaller C1−C2−C3 angle than found with the smaller basis set. The anion moves slightly outside the C1−C2 bond. The main geometric parameters for d = 2.40 Å are listed in Table 4. Again, reoptimization at the MP2(FU)/6-311G** level produced negligible changes in geometry (and in energy difference between isomers) from the values obtained with the "frozen" core electrons. The structure of this ion pair optimized at the highest level of theory for d = 2.40 and 2.25 Å is shown in Figure 5. As discussed above, the main element distinguishing **1** from **2** is the conformation along the C2−C3 bond: staggered for **2** and eclipsed for **1**. The C1−C2−C3 bond angle is always greater than 90° for **2** and smaller than 90° for **1**, but the differences from this divider are in some cases rather small. The distances or lengths of bonds between the same pairs of atoms are not very different in the two isomers, but the differences are in the expected direction in each case. The transition structure for **1** ⇌ **2** is about midway between **1** and **2**.

Introduction of diffuse functions in the basis set (MP2(FC)/6-31++G*) had no significant effect on the geometries of **1** (Table 3) or **2** (Table 4), in agreement with the earlier results for the 2-propyl cation in ion pairs.[1c]

Another item of comparison of the two isomeric structures is the level of coplanarity of the bonds at C1. For a protonated cylopropane it is intuitively expected that the orientation of hydrogens at C1 and C2 is the same; this is not true even at large separations of ions within the ion pair, because the H$_2$C1−C2 group of **1** is nearly coplanar. At shorter distances

(30) Smirnov, S. N.; Golubev, N. S.; Deniksov, G. S.; Benedict, H.; Schach-Mohammedi, P.; Limbach, H.-H. *J. Am. Chem. Soc.* **1996**, *118*, 4094.
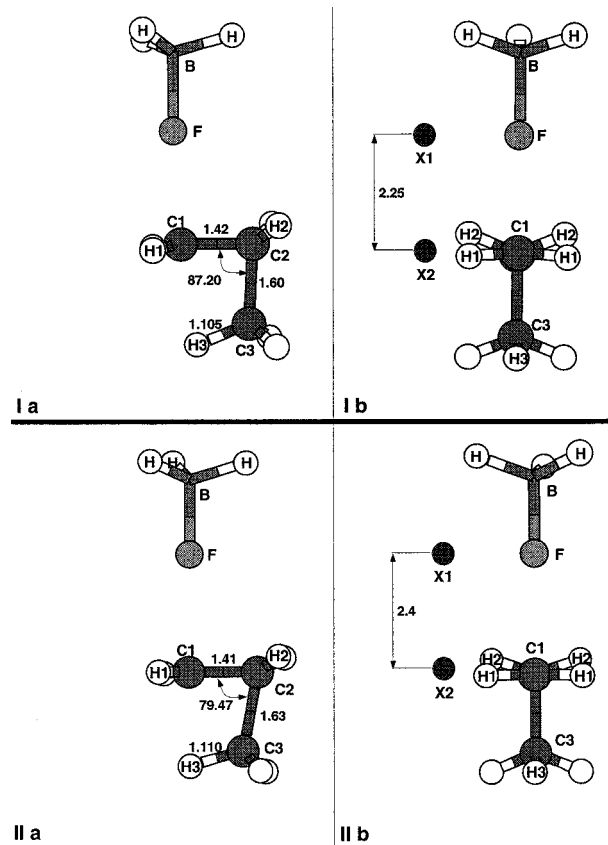
Table 3. Geometrical Parameters for Protonated Cyclopropane·BH₃F⁻ Ion Pair at Different Levels of Theory and for the Transition Structure for the Interconversion **1** ⇌ **2**, All at d = 2.4 Å

	level of calculation				
geometrical parameters[a]	protonated cyclopropane·BH₃F⁻				TS[b]
	MP2(FC)/6-31G*	MP2(FC)/6-31++G*	MP2(FC)/6-311G**	MP2(FU)/6-311G**	MP2(FC)/6-31G*
D(C1,C2)	1.406	1.406	1.407	1.406	1.416
D(C2,C3)	1.618	1.624	1.629	1.625	1.602
D(C1,C3)	2.003	1.986	1.950	1.945	2.170
D(X2,C1)	1.000	1.000	1.000	1.000	1.000
D(X1,F)	0.994	1.004	1.000	1.005	1.018
θ(C1,C2,C3)	82.67	81.53	79.60	79.46	91.74
φ(H3,C3,C2,C1)	0.00	0.06	0.00	0.00	33.58
φ(F,X1,X2,C1)	0.66	−6.48	0.26	0.39	−0.75

[a] Meaning of symbols D, θ, and φ as in Table 1. [b] Transition structure.
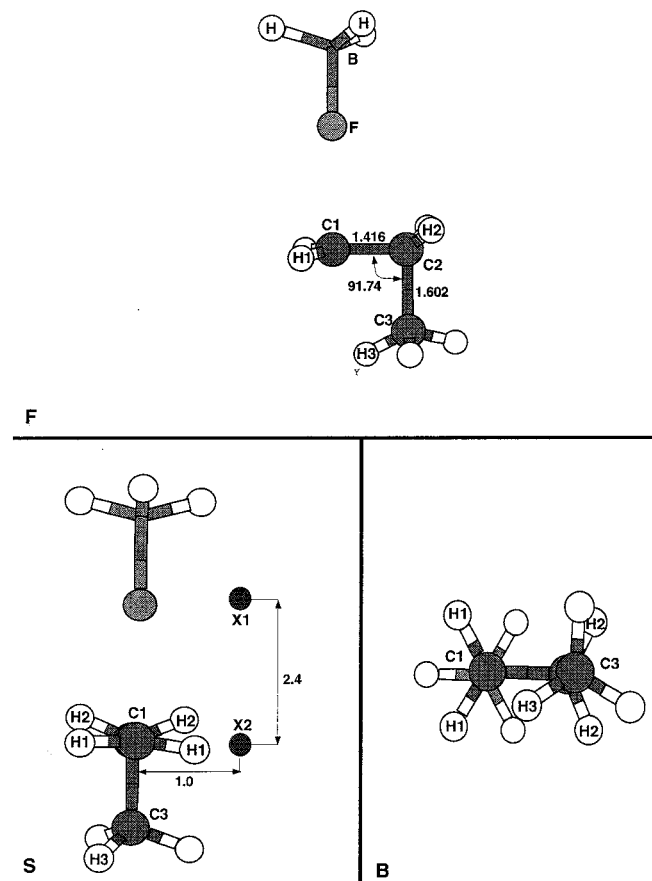
Figure 3. MP2(FC)/6-31G* geometry of the transition structure for the interconversion of **1**·BH₃F⁻ and **2**·BH₃F⁻ at d = 2.40 Å (F and S as in Figure 1; B, bottom view).

Figure 4. MP2(FU)/6-311G** geometry of the protonated cyclopropane−trihydrofluoroborate ion pair (**1**·BH₃F⁻) at d = 2.25 Å (I) and 2.40 Å (II) (F and S as in Figure 1).

Table 4. Geometrical Parameters for the 1-Propyl·BH₃F⁻ Ion Pair at d = 2.4 Å, for Different Levels of Calculation

	level of calculation			
geometrical parameters[a]	MP2(FC)/6-31G*	MP2(FC)/6-31++G*	MP2(FC)/6-311G**	MP2(FU)/6-311G**
D(C1,C2)	1.430	1.427	1.423	1.422
D(C2,C3)	1.580	1.588	1.595	1.592
D(C1,C3)	2.312	2.286	2.258	2.256
D(X2,C1)	1.000	1.000	1.000	1.000
D(X1,F)	1.001	1.006	1.001	1.000
θ(C1,C2,C3)	100.28	98.46	96.69	96.78
φ(H3,C3,C2,C1)	62.19	62.39	62.47	62.50
φ(F,X1,X2,C1)	−0.60	−6.03	−2.67	−2.66

[a] Meaning of symbols D, θ, and φ as in Table 1.

the hydrogens tilt "inwards" (toward C3), such that the dihedral angles φ(H11−C1−C2−C3) and φ(H12−C1−C2−C3) are −89.34° and 89.34° at d = 2.4 Å, and −84.86° and 84.82° at d = 2.25 Å. As a matter of fact the level of tilting at this interionic distance is the same in **1** as in the open ion **2**, for which φ(H11−C1−C2−C3) and φ(H12−C1−C2−C3) at d = 2.25 Å are given by our calculations as −84.78° and 84.79°, respectively. At the larger interionic distance, d = 2.40 Å, a slightly greater tilting in **2** is indicated by the calculations: φ(H11−C1−C2−C3) = −83.58° and φ(H12−C1−C2−C3) = 83.58°. It is noteworthy that inward tilting had been found in calculations with smaller basis sets for structures described as open (1-propyl cation) in the previous studies of isolated ions, both for the eclipsed and for the staggered conformation at

C2,C3. The level of tilting found there was slightly greater for the structure with a larger C1−C2−C3 angle (staggered at C2,C3).[14b]
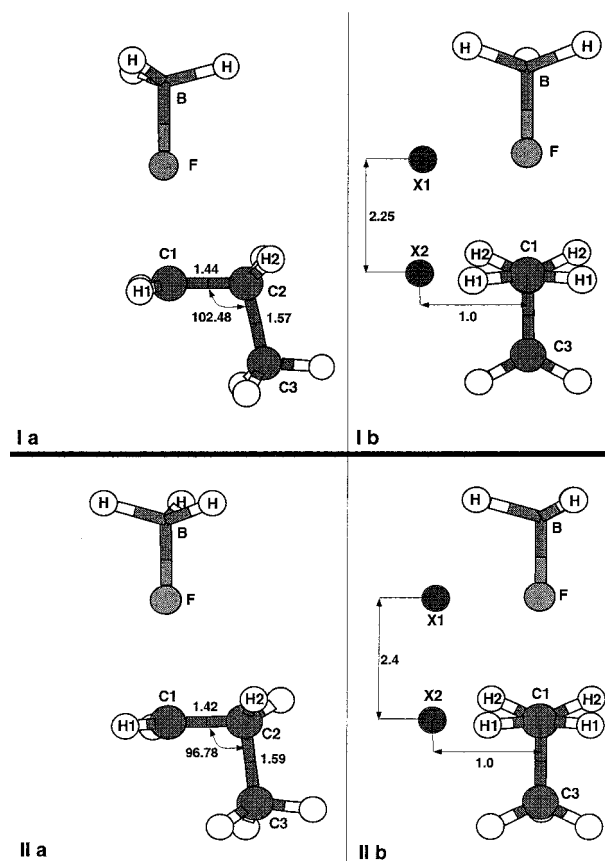
Figure 5. MP2(FU)/6-311G** geometry of the 1-propyl−trihydro-fluoroborate ion pair ($2 \cdot BH_3F^-$) at $d = 2.25$ (I) and 2.40 Å (II) (F and S as in Figure 1).

Table 5. Charge Distribution in $1 \cdot BH_3F^-$ and $2 \cdot BH_3F^-$ at $d = 2.4$ Å and the MP2/6-311G** Level

atom	**1**	**2**	atom	**1**	**2**
C1	0.096	0.234	F	−0.562	−0.574
C2	−0.154	−0.226	B	0.334	0.332
C3	−0.347	−0.351	H	−0.226	−0.217
H11	0.213	0.207	H	−0.227	−0.223
H12	0.213	0.207	H	−0.236	−0.213
H21	0.199	0.192	C1H₂	0.522	0.648
H22	0.199	0.191	C2H₂	0.244	0.157
H31	0.178	0.164	C3H₃	0.151	0.087
H32	0.178	0.137	FBH₃	−0.917	−0.895
H33	0.142	0.137			

With the caveat that these numbers are crude approximations, the Mulliken charge distributions in isomers $1 \cdot FBH_3^-$ and $2 \cdot FBH_3^-$ at $d = 2.40$ Å are shown in Table 5. There is a significant difference between charges at C1, a less important but notable difference between charges at C2, and essentially no difference between charges at C3. Considering groups, rather than atoms, the charge distribution within the two ions is rather similar and most of the positive charge is concentrated at the C1H₂ group. The charge imbalance among the three regions of the cation is less marked in **1** than in **2**. The bridging methyl group carries the least amount of positive charge in **1** (the methyl group of **2** carries less than one tenth of the total charge of the cation).

It is interesting to compare the geometries adopted by the primary ion **2** and by the secondary isomer **3**. Ion pairing brings the latter into an eclipsed C1,C3 conformation, with one hydrogen each at C1 and C3 pointing toward the anion and the two C−H bonds almost parallel to the F−B bond,[1c] because the electrostatic interaction between the anion and the two

Table 6. Energy Difference (kcal/mol) between 1-Propyl·BH₃F⁻ and Protonated Cyclopropane·BH₃F⁻ Ion Pairs at $d = 2.25$ and 2.4 Å, at Different Levels of Calculations

level of calculation	ΔE^a		position of the crossing point (Å)
	$d = 2.25$ Å	$d = 2.4$ Å	
MP2(FC)/6-31G*	−0.79[b]	0.12	2.38
MP2(FC)/6-31++G*	−0.44[b]	0.82	2.33
MP2(FC)/6-311G**	−0.816	1.36	2.31
MP2(FULL)/ 6-311G**	−0.816	1.439	2.3
MP4(FC)/6-311G**// //MP2/6-311G**[c]		0.05265	2.4
ZPE[d]		−0.34228	-
total	-	−0.277	~2.47[e]

[a] $\Delta E = E(2) - E(1)$. [b] At 2.30 Å. [c] Single point calculation. [d] ZPE was corrected with a factor of 0.964. [e] Value predicted from the relative energy (ΔE) at 2.4 Å.

positive hydrogens is much stronger than the gain from stronger hyperconjugation possible in the alternative conformation with one hydrogen at C1 up and one hydrogen at C3 down relative to the C1C2C3 plane (C_2, chiral conformation[18,28]). By contrast, the B−F bond in the ion pair of **2** bisects the projection of the H−C2−H angle in the plane perpendicular to C1−C2. The C2−C3 bond in $2 \cdot FBH_3^-$, antiperiplanar with the F−B bond, is situated in an optimum position for hyperconjugation with the empty orbital at C1.[31]

As shown in the last entry in Table 2, the isomers **1** and **2** are closest in energy at the MP2(FC)/6-31G* level for an interionic distance of 2.40 Å. This distance was selected for single-point calculations at a higher order of electron correlation on the geometries optimized with the MP2/6-311G** basis set. The calculated energy differences between the two isomers at different levels of theory and the zero-point vibrational energy correction at $d = 2.4$ Å deduced from the frequencies calculated at the MP2/6311G** level are listed in Table 6. It is seen that the larger basis set favors somewhat the bridged isomer, but this tendency is reversed in the calculation with the fourth-order perturbation treatment. Indeed, the two ion pairs are essentially equal in energy at this level for $d = 2.40$ Å. Introduction of the zero-point energy correction with the most recently proposed scaling factor[32] favors again the open ion in the ion pair, such that in the end $2 \cdot FBH_3^-$ is more stable by about 0.3 kcal/mol at this interionic distance.

Because the determination of the domains of existence of the isomeric ion pairs at the higher levels of theory would use too much computer time, we postponed that study for later. A good idea about this point can be gathered, however, from the examination of the interionic distance at which the two isomeric ion pairs have the same energy, extracted from the crossing points in Figure 6, which plots the energy difference between the two species as a function of d. This evaluation benefited from the choice to calculate the MP4(FC)/6-311G**//MP2/6-311G** energy for $d = 2.40$ Å, which just happened to be the crossing point at that level. The d values for the crossing points are also listed in the last column of Table 6. It can be evaluated that after ZPE correction the crossing point moves to $d \approx 2.47$ Å, as is also indicated in Figure 6.

Our results show that ion pairing stabilizes the open structures of carbocations such that even a simple ion like **2** can be a reaction intermediate and at short interionic distances (tight ion

(31) Hoffmann, R.; Radom, L.; Pople, J. A.; Schleyer, P. v. R.; Hehre, W. J.; Salem, L. *J. Am. Chem. Soc.* **1972**, *94*, 6221.

(32) (a) Pople, J. A.; Scott, A. P.; Wong, M. W.; Radom, L. *Isr. J. Chem.* **1993**, *33*, 345. (b) A very similar value was proposed by DeFrees (DeFrees, D. J.; McLean, A. D. *J. Chem. Phys.* **1985**, *82*, 233) and was used in ref 18.
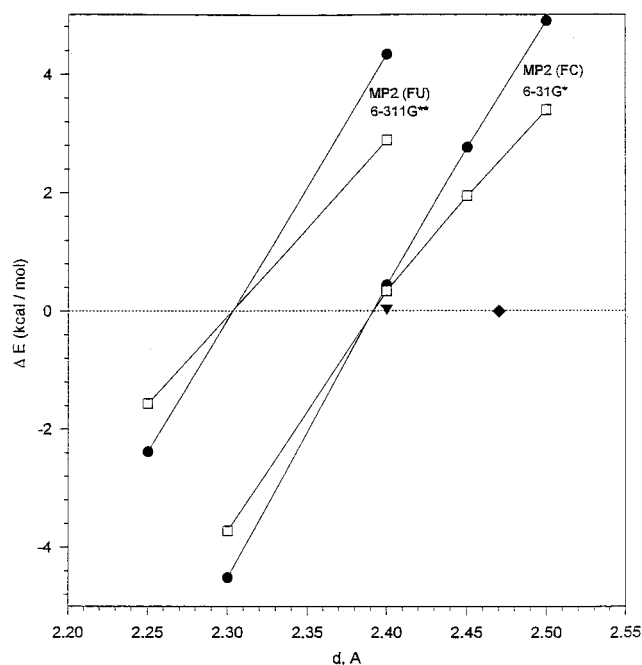
Figure 6. The relative energy (ΔE) scaled to the point of equal energy content of isomers (crossing point) as a function of the interionic distance, d: $\square$, $\mathbf{1}\cdot BH_3F^-$; $\bullet$, $\mathbf{2}\cdot BH_3F^-$; $\blacktriangledown$, crossing point at MP4(FC)/6-311G**//MP2(FU)/6-311G**; $\blacklozenge$, estimated crossing point after ZPE correction.

Figure 7. The 1-propyl−trihydrofluoroborate ion pair ($\mathbf{2}\cdot BH_3F^-$) at the MP2(FC)/6-31G* level in orientation B (before C1−C2 bond rotation and hydrogen shift from C2 to C1 to form the 2-propyl ion pair): F, S, and T, as in Figure 1 (dummy atoms not represented in any projection).

pairing) it can be more stable than its bridged counterpart. Stabilization of open carbocation structures by interaction with HCl as a model of polar solvent was shown before by MINDO3 semiempirical calculations.[33] We approached with some caution those results, however, because we saw that MINDO3 indicated the two rotamers of the isolated open ion 3-methyl-2-butyl cation to be reaction intermediates (energy minima), whereas ab initio calculations showed that under those conditions (gas phase, isolated ions) these species should be only the transition states for various conversions involving protonated 1,2-dimethylcyclopropane isomers.[3] In addition, the C···Cl distances calculated in the MINDO3 study for the R^+···Cl−H complexes were 1.9, 2.0, and 2.1 Å for primary, secondary, and tertiary carbocations, respectively, not much longer than the typical C−Cl covalent bond of 1.75 Å. In fact, it was pointed out that at least for the primary cations the aggregates are better considered as protonated alkyl chlorides.[33a] We note that the typical C−F bond is only 1.35···1.4 Å, yet recombination occurred in our calculations for interionic distances shorter than 2.2 Å in the ion pair $\mathbf{2}\cdot FBH_3^-$. Nonetheless, the trend observed in the interaction with HCl is real and it is in full agreement with our findings on the effect of the counterion on the structure of the carbocation.[34]

Calculations at the MP2/6-31G* level were also conducted for $\mathbf{2}\cdot FBH_3^-$ in orientation B, explained in the Computational Method section, above, and shown in Figure 7. Optimization for $d = 3...6$ Å led to the rotation of the C1−C2 bond, in the same way as in the 2-propyl cation, because of attraction between the anion and the β hydrogen.[1c] For $\mathbf{2}$, however, this rotation brings the β-H into the proper alignment with the empty orbital at C1 and a hydrogen shift from C2 to C1 concerted

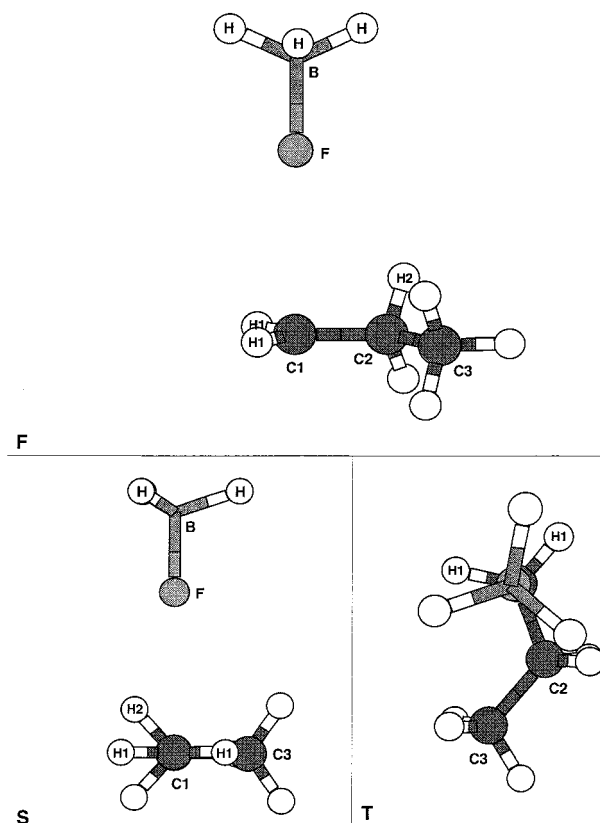with the movement of the anion in the opposite direction occur, leading to the secondary ion pair $\mathbf{3}\cdot FBH_3^-$, with the cation in the stable C_s form.[1c] The reverse process, conversion of $\mathbf{3}\cdot FBH_3^-$ to $\mathbf{2}\cdot FBH_3^-$ consists of hydrogen shift from C1 to C2 followed by or coupled with rotation of the C1−C2 bond such as to bring the C2−C3 bond antiperiplanar to the F−B bond (orientation A within the ion pair). The structure shown in Figure 7 may be close to the transition state for this process, but this transition state structure was not pursued further at this stage of our investigations.

Optimization of orientation B for d values below 2.5 Å resulted in elimination, forming propene and HF. Recombination to form 1-fluoropropane did not occur for this relative orientation of ions in the ion pair. This result is again similar with our findings for the 2-propyl cation where recombination and elimination occurred from different orientations of the ions in the ion pair.[1c,35] The distance at which the reaction pathway changes from elimination to intramolecular hydrogen shift is determined by the basicity of the anion, in addition to the stability of the secondary cation.

Primary Carbocations as Reaction Intermediates. It has been thoroughly proven that when a carbocationic reaction would involve a primary ion as intermediate, the reaction normally proceeds by an alternative pathway. There are examples, however, in which the data do not substantiate such an alternative pathway. Therefore, primary cations should be considered bona fide reaction intermediates.

Thus, primary carbocation intermediates have been proposed for the solvolysis of *N*-(1-alkyl)-5,6,7,8-tetrahydro-7-phen-
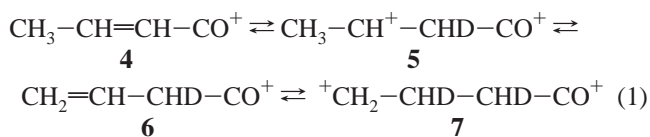
(33) (a) Jorgensen, W. L. *J. Am. Chem. Soc.* **1977**, *99*, 280. (b) Jorgensen, W. L.; Munroe, J. E. *Tetrahedron Lett.* **1977**, 581. (c) Jorgensen, W. L. *J. Am. Chem. Soc.* **1977**, *99*, 4272.

(34) The model of primary carbocation used in ref 33a,b was ethyl. We preferred in the first stage of our work to study the more complex case of propyl, for which experimental data in superacid exist, allowing some interpretation of the computational results.

(35) A more extensive study of the pathways for recombination and elimination in the ion pairs of carbocations is in progress in our laboratory.

yldibenzo[*c,h*]acridinium cations as better accounting for both rates and reaction products than the alternatives in which ionization would be anchimerically assisted and the intermediate ions would be bridged.[36]

Multiple H−D exchange was observed in the 2-butenoyl cation (**4**) in DF−SbF$_5$, involving the 1,3 *sec*-alkyl acyl dication **5** and the 3-butenoyl cation (**6**) as intermediates. The latter also adds a deuteron at C3, forming a cation that can be formulated as **7** ($k_{(6\rightarrow5)} = 35k_{(6\rightarrow7)}$).[37]

$$CH_3-CH{=}CH-CO^+ \rightleftarrows CH_3-CH^+-CHD-CO^+ \rightleftarrows$$
$$\quad\quad\quad \textbf{4} \quad\quad\quad\quad\quad\quad\quad\quad\quad \textbf{5}$$
$$CH_2{=}CH-CHD-CO^+ \rightleftarrows {}^+CH_2-CHD-CHD-CO^+ \quad (1)$$
$$\quad\quad \textbf{6} \quad\quad\quad\quad\quad\quad\quad\quad\quad \textbf{7}$$

Subsequent work has shown that the intermediate was, indeed, the acyl-primary alkyl cation **7**, rather than the 1-protonated cyclopropanemethanoyl cation alternative.[38] Note that the ionization of the 4-chlorobutanoyl cation (**8**) in HF−SbF$_5$ was more than 10^6 times slower than the ionization of the 4-chloropentanoyl cation (**9**),[39] which is reasonable for the effect of an α methyl group on the generation of a carbocation.

The most appropriate example for a discussion of effects of tight ion pairing is the exchange (scrambling) of atoms in the persistent[5c] 2-propyl cation, **3**. In cation **3** labeled with ^{2}H and ^{13}C, H scrambling was faster than C scrambling. The results were interpreted to mean that both **1** and **2** are intermediates for the intramolecular exchange of carbon and hydrogen atoms, respectively.[6]

The computations of isolated C$_3$H$_7^+$ ions identified two primary ions as transition states (one imaginary frequency in each). One of them appears to have the HC1H group within the C1C2C3 plane,[14b] corresponding to our orientation B (named here B$_i$, for isolated). From its representation, it seems that the second corresponds to our orientation A with the C1C2 bond rotated by an unstated angle (A$_{rot}$); if that angle is significant, A$_{rot}$ might lay between A$_i$ and B$_i$. Both A$_{rot}$ and B$_i$ have the C2−C3 bond rotated by 60° from the conformation in proto-

nated cyclopropane. The form B$_i$ had a lower calculated energy than A$_{rot}$ and was thus considered to be the transition state for hydrogen scrambling in **3**. It was noted, however, that the calculated barriers were 3 kcal/mol too high.[18]

It seems most likely to us that the energy barrier discrepancy reflects a lowering of the energy barrier resulting from ion pairing. Even if the secondary ion **3** might enjoy some autonomy in superacid, it does not probably go beyond solvent-separated ion pairs. A large, positive activation entropy for hydride transfer from neopentane (with rearrangement) to **3** in SbF$_5$−SO$_2$FCl indicated that **3** "is strongly solvated to a number of SbF$_5$ molecules",[40] that is, strongly ion-paired with a Sb$_n$F$_{5n+1}^-$ anion. The hydrogen shift to form a much less stable intermediate requires that the two ions come together in an even tighter **3**·Sb$_n$F$_{5n+1}^-$ ion pair. As discussed earlier, the anion in the latter has its equilibrium position in the bisector plane of the C1−C2−C3 angle, but oscillates easily across this plane, between positions above the hydrogens facing it at C1 and C3.[1b] The hydrogen shift from C1 to C2 occurs at the same time with the movement of the anion from the center to the position above C1 and gives the ion pair in the orientation B of Figure 7, continuing then until it reaches the energy minimum as the **2**·Sb$_n$F$_{5n+1}^-$ ion pair in orientation A. This intermediate interconverts with the third isomer, **1**·Sb$_n$F$_{5n+1}^-$; if the interionic separation d is less than 2.47 Å, this equilibration favors **2**·Sb$_n$F$_{5n+1}^-$. Each elementary reaction exchanges hydrogen (**3**·Sb$_n$F$_{5n+1}^-$ $\rightleftarrows$ **2**·Sb$_n$F$_{5n+1}^-$), but only the continuation to the second step (**2**·Sb$_n$F$_{5n+1}^-$ $\rightleftarrows$ **1**·Sb$_n$F$_{5n+1}^-$) exchanges the carbon atoms as well, whence the faster scrambling of hydrogen than of carbon, experimentally observed.[6]

It was stated that nucleophilic solvation does not appreciably affect the relative stabilities of bridged and open ions.[41] A similar statement cannot be made about ion pairing, at least at the currently available level of theory and complexity of models of ion pairs which we can currently use.

(36) (a) Katritzky, A. R.; El-Mowafy, A. M. *J. Org. Chem*. **1982**, *47*, 3506 (b) Katritzky, A. R.; Dega-Szafran, Z.; Lopez-Rodriguez, M. L.; King, R. W. *J. Am. Chem. Soc*. **1984**, *106*, 5577.

(37) Fărcaşiu, D.; Bologa, U. L. *J. Org. Chem*. **1996**, *61*, 8860.

(38) Fărcaşiu, D.; Miller, G.; Bologa, U. L.; Katritzky, A. R.; Carpenter B. K. *J. Chem. Soc., Perkins Trans. 2* **1998**, 2659.

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