Theoretical Studies of Carbocations in Ion Pairs. 8.[1] Search for Anchimeric Assistance in the Ionization of 2-Butyl Cation Precursors

Dan Fărcaşiu* and Rodica Leu

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

Received: June 28, 2007; In Final Form: September 18, 2007

The structures of carbocations formed in the ionization of 2-butyl precursors were investigated by high level ab initio MO calculations on the reaction of 2-butyl fluoride (**1**) with borane, which gives a $C_4H_9^+$ cation paired with trihydrofluoroborate (FBH_3^-, **A**). Two conformations of the "open," secondary cation (**2**) in the ion pair resulted from two conformations of **1**, with F *gauche* and *trans* to C4 (**2**-*g* and **2**-*t*, respectively). No anchimeric assistance by hydrogen (in **1**-*g*) or methyl (in **1**-*t*) was evidenced. In fact, attempts at optimizing the geometry of the H-bridged (**3**) and methyl-bridged (**6**) cations at short interionic distances (*d*) led to the corresponding conformations of **2**. Upon ion separation, proton transfer from **2** to the anion occurred at intermediate interionic distances, consonant with experimental observations in trifluoroacetic acid. Elimination was prevented by addition of a lithium cation to the ion pair, i.e., running computations on triple ions (**2.A.Li**$^+$). Cation **6** became an energy minimum beyond $d = 2.5$ Å and **3** beyond 2.8 Å. Cation **2**-*g* was still the most stable isomer at $d = 3.2$ Å, which was greater than the interionic distance in the crystals of the isomeric *tert*-butyl cation salts (3−3.1 Å). Thus, spectral determinations of 2-butyl cations in the solid state should be interpreted with **2**-*g* as the main component of the ion mixture. When the ions became separated ($d \geq 4$ Å), only the bridged ions were energy minima. In this process, bridging did not occur opposite to the leaving group to assist the ionization, but on the same side with it, being controlled by the electrostatic interaction with the anion, as it departed from the vicinity of the cation. Such behavior was also noted in the ionization of the 3-methyl-2-butyl homolog.

Introduction

The carbocationic mechanism has long been established for reactions of hydrocarbons under acid catalysis, the intermediates being the same as in carbocationic solvolyses.[2] It turns out that most if not all carbocationic reactions in solution are controlled by ion pairing,[3] whereas on solid acids, carbocations can intervene only tightly paired with anionic sites on the surface,[4] or the reaction may not involve fully formed carbocations, but cationoidic species, in which the cation is still partially bonded to the anion.[5] The reaction features (product distribution, kinetics, structure−reactivity relationships) in the latter case are similar to those of conversions involving ion pairs in solution.[5]

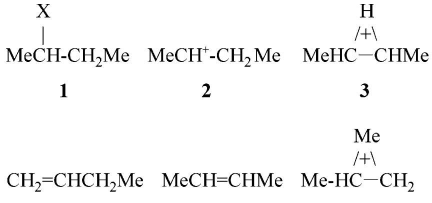
Earlier, we noted that existing computational treatments of carbocationic reactions had considered isolated carbocations and the calculations[6] made predictions occasionally at variance with the experimental findings.[7] We conducted, therefore, ab initio calculations[8] of carbocations ion-paired with various anions. Those calculations[1c] gave a satisfactory account of the results of solvolysis experiments.[7] Computations on carbocations placed in larger ionic aggregates gave good predictions for NMR[9a] and X-ray diffraction spectra[9b] of solid carbocation salts, whereas the average distance between ions in the ion pairs in solution was deduced from calculations and published Raman spectra.[1b] The same approach allowed us to establish the aggregation of a hydronium salt in a nonpolar environment and predict correctly its NMR spectrum.[10] We have looked in most cases at changes in the carbocation structure (2-propyl,[11] 1-propyl,[1d] *tert*-butyl,[1b] 3-methyl-2-butyl[1c]) under the influence of an anion approaching from infinity to the tight ion pair distance. Later, we have also examined the generation of the carbocation in the ion pair in the ionization of 2-propyl fluoride upon interacting with a Lewis acid.[1a]

We extended then our computational study to the 2-butyl cation. The structure of this species as intermediate in the solvolysis of 2-butyl sulfonates was considered in several studies. Thus, the absence of multiple hydrogen shifts in the trifluoroacetolysis product of the tosylate **1a** was thought to argue against an "open," secondary ion, **2**, and for a 2,3-hydrogen bridged structure, **3**, that is, for anchimeric assistance to ionization by a β hydrogen.[12] Another study in the same solvent (TFA), finding racemization with 7% inversion in the product and some racemization in **1a**, concluded that a 2-butyl cation (**2**) tosylate ion pair is the main intermediate and some internal return from it occurs.[13] The intermediacy of the hydrogen-bridged ion[12,14] could not give a simple prediction of the results.[13] Next, the ^{18}O-labeled bromobenzenesulfonate (**1b**) underwent oxygen scrambling in trifluoroethanol, without racemization. A sigmatropic rearrangement or a very short-lived ion pair of **2**, in which the anion rotates before recombination, was considered possible.[15] (A choice between the two might be made through an investigation of solvent polarity effect on scrambling rate.[15b]) Finally, application of Shiner's test of recombination from intimate ion pairs,[3e] generating the latter by reaction of 1-butene (**4**) with toluene-*p*-sulfonic acid in TFA, showed that roughly two-thirds of the ion pairs generated by ionization of **1a** recombine. Of the ion pairs that do not

---

* Address all inquiries to this author, at dfarca@optonline.net. Tel.: 516-484-7157.

10.1021/jp0750553 CCC: $40.75 © 2008 American Chemical Society
Published on Web 03/08/2008



1 **2** **3**

4 **5** **6**

a. X = OTs; **b**. X = OBs; **c**. X = O-CO-CF$_3$; **d**. X = F

recombine, at least 30% undergo elimination to 2-butene (**5**) and the rest are trapped by the solvent and form 2-butyl trifluoroacetate (**1c**).[16] The return ratio is greater than the ratio between the polarimetric and spectrophotometric rate constants for the reaction of **1a**.[13] The excess includes the ion pairs that scramble the oxygen but do not racemize;[15] therefore a sigmatropic rearrangement is unlikely for that process. The data point out to a reversible ionization to **2**, rather than **3**, in the ion pair, with the competition between hydrogen shift, elimination, and solvent trapping in the following step(s).[11] It was, of course, possible that product forming steps are preceded by the evolution to solvent-separated ion pairs[3b] as the rate-determining step.[3e,11]

Investigations of persistent cations in superacids did not give a clear picture. Proton[17] and solid-state ^{13}C NMR spectra[18] were compatible with **3**, or with **2** undergoing a 2,3-hydride shift with a very low barrier. The fully coupled (high resolution) ^{13}C NMR spectrum excluded a static cation **3** but was consistent with **3** in rapid equilibration with **2**, the latter predominating.[19] The broad ESCA pattern of a material obtained by deposition of 2-butene on frozen superacid was assigned to a third isomer, 2-methyl-1-protonated cyclopropane (**6**), possibly mixed with some hydrogen-bridged ion **3** and other species (polymeric ions? neutrals?).[20] Isotopic perturbation of NMR spectra was also considered to indicate a mixture of **6** and **3**, but the methyl-bridged ion **6** was held as the less stable. Finally, the IR and the NMR spectra of the cation generated in solid matrices were computationally (ab initio MO) assigned to structure **3**.[21a,c]

Of the several MO treatments (both semiempirical and ab initio) of C$_4$H$_9^+$ species, the report of results based on MP2-(FU)/6-31G** geometry optimizations, MP4/6-31G** single point energy calculations and MP2/6-31G* zero point energy calculations employed the most advanced methodology and can be taken as the work of reference.[21a,b] Only **3** (two conformations, corresponding to protonated *cis*- and *trans*-butene) and **6** were identified as energy minima. Isomer **2** was a transition structure, 1.9 kcal/mol (MP4SDTQ/6-31G**//MP2(FU)/6-31G** + ZPE) higher in energy than the most stable isomer, **3**.[21a] As anchimeric assistance of ionization requires the displacement of the β group (hydrogen or methyl) concerted with the cleavage of the bond to the leaving group, such that the tightest ion pair contains a bridged carbocation, it would follow that the latter should be the only species present not only in isolated ions but also in ion pairs at all interionic distances.

We have found, however, that calculations conducted on isolated ions do not describe accurately the structures of ions resulting after ionization of solvolysis precursors, or present as persistent carbocations under conditions that induce tight ion pairing.[1] Computational examination of **2**, **3**, and **6** in ion pairs could help choose among the contradictory conclusions reached in the experimental investigations. We report here the results of such calculations.

Computational Method

The calculations were conducted with the program Gaussian 98,[22] as described.[1] Electron correlation was handled with the Møller–Plesset perturbation theory of the second (MP2) and fourth order (MP4).[23] Because of the size of the systems investigated, we did not introduce diffuse functions in the basis sets used. It had been shown that their use has an insignificant effect on the C$_3$H$_7^+$ carbocation structures.[1d] Full geometry optimization of all parameters inside the cation was performed at the MP2(FC)/6-31G** level; insignificant changes in the geometry found at this level occurred upon reoptimization with the MP2/6-311G** basis set for the lower homolog, C$_3$H$_7^+$; in fact, there were little changes even from the optimization at MP2/6-31G*.[1d] MP4SDTQ(FC)/6-31G**//MP2(FC)/6-31G** single point calculations and MP2/6-31G** calculations of zero point energies were conducted in a few cases. The ZPE values were then corrected with the appropriate scaling factor.[24] 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, **2**, is C2, as it is in the precursor **1**; in the methyl-bridged ion **6**, it carries the longer bridging bond. C2 is bonded to C1 (methyl) and C3 (CH$_2$). The methyl carbon bonded to the methylene group of **2** retains its index (C4) when it becomes the bridging carbon in **6**.

The anion of the ion pair was FBH$_3^-$ (**A**),[25] in most calculations. The less basic anion BF$_4^-$ (**B**) was employed in a few cases. The stronger B–F bond in the latter (71 kcal/mol,[26a] compared with 64 kcal/mol for **A**[26b]) reduces the tendency of fluoride transfer to the cation,[1a] as discussed in detail elsewhere.[1c] It was shown that for a given interionic distance the nature of the anion does not change the cation structure, only the variation of its basicity changes the distance at which a proton transfer from the cation to the anion (elimination) occurs.[1,11] As an artifice to reduce the basicity and nucleophilicity of the anion, a series of calculations were conducted on a triple ion, in which a lithium cation was placed on the other side of anion **A**.[1a,9b] The lengths and angles for the B–H bonds in anion **A** and B–F(distal) bonds in **B** were held constant in most calculations. In selected cases, the anion geometry was also fully optimized.

The interionic distance, *d*, was normally defined as the distance between two parallel planes: one containing C1, C2, and C3 and another in which the fluorine atom of **A** or the proximal fluorine atom of **B** was allowed to move.[1,9,11] The distance between C2 and the proximal atom of the anion may be slightly longer than *d*. To allow the anion an unrestricted plane parallel movement above the cation, the distance and orientation of the anion relative to the cation was controlled with the use of two "dummy" atoms.[1d] The first, X1, was placed in the plane containing the fluorine; the second, X2, was placed in the C1,C2,C3 plane, usually at 5 Å from C2, such that X1–X2 was perpendicular on the two parallel planes, so X1–X2 was the interionic distance, *d*. Then, F–X1 was perpendicular to X1–X2, i.e., θ(F–X1–X2) = 90°. X2 was placed such that the angles θ(C1–C2–X2) and θ(X2–C2–C3) were equal (C2–X2 bisected the exterior angle C1–C2–C3). In the most restrictive mode, the distances d(X2–C2) and d(X1–F) were kept equal and the dihedral angle $\angle$(F,X1,X2,C2) was 0°, that is, F was atop C2 (d(C2–F) = *d*). In a more relaxed mode, the fluorine atom was kept in the plane bisecting the C1,C2,C3 angle, by keeping $\angle$(F,X1,X2,C2) = 0° and optimizing d(X1–F). In the freest mode, both d(F–X1) and $\angle$(F,X1,X2,C2) were optimized, the "dummy" atoms acting as a hinge. The F–B bond was kept parallel to X1–X2, by imposing θ(B–F–X1) = 90° and $\angle$(B,F,X1,X2) = 180°, or the inclination of the B–F bond over the cation was varied, when desired, by optimizing θ(B–F–X1) starting with values less than 90° (*out* orientation) or more than 90° (*in* orientation).[1a]

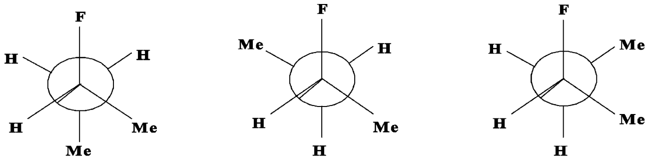
Reading of geometrical parameters in output was accomplished with the computer program MOLDEN.[27]

Results and Discussion

1. Evaluation of Calculations for Isolated Ions. An MP2/6-31G** geometry optimization of structures of the isolated ions **3** and **6**[21] was conducted by us to obtain the input data for some of our calculations. A few comments on structure **6** seem appropriate. Similar to homologs looked at previously,[1c,28] **6** features a very long C2−C4 bond (1.912 Å, in our calculation). Thus, rigorously speaking, C2 is not bonded to C4. The C3−C4 bond was 1.649 Å. In fact, the two carbon−carbon bridging bonds are not quite equal even in the parent protonated cyclopropane ($C_3H_7^+$) and the bond-length inequality increased when an anion approached the cation.[1d] We had arbitrarily named "bridged" the species with the angle opposite to the long bond smaller than 90° and "open" the ions with that angle greater than 90°.[1d] An objective criterion, however, was found in the conformation of the shorter "bridging" carbon−carbon bond, staggered in the "open" ions and eclipsed (or nearly so) in the "bridged" ions. In some cases, the two isomers may have the same value for the bond angle opposite to the longest carbon−carbon distance.[1c,d,28] For **6**, the dihedral angle ∠(H*syn*,C4,C3,C2) was 7.58°. Notably, the positioning of the C4−H*syn* bond is such that d(C2−H*syn*), 1.924 Å, is about equal to d(C2−C4). C2 is actually closest to the middle of the C4−H*syn* bond (1.835 Å). To establish the true nature of the interaction, a determination of the electron density distribution within the space enclosed by the three nuclei (C2, C4, and H*syn*) is required. Anyway, naming these species (except possibly those corresponding to 1-alkyl cations) corner-protonated cyclopropanes seems a simplified representation.

As reported,[21] the overall energy minimum on the potential energy surface for **2**, **3**, and **6** is the *trans* form of **3**. That was the structure for which calculated IR and NMR spectra had been fitted to the experimental spectra.[21] The isomer **6**, however, was only 0.4 kcal/mol higher in energy.[21] We note that **6** has two forms (C1 bridging and C4 bridging), each of them chiral. The *trans* form of **3** is also chiral, but it has a 2-fold symmetry axis.[29] (The *cis* form of **3**, 0.9 kcal/mol higher in energy,[21] is also less favored entropically.) Thus, on the basis of the calculations,[21] there should be enough of **6** in the mixture at the temperature at which the IR spectrum was scanned (148 K) to show its strong absorptions that do not coincide with those of **3**, in the C−H and C−C stretching regions. Also, observation of only one set of NMR signals would indicate interconversion of the two forms. Then, the theoretical (IGLO) ^{13}C NMR spectrum should be obtained as the average of the spectra for **3** (major) and **6** (minor). The chemical shifts thus computed deviate more from the experimental values than the values of pure **3** chosen in the comparison.[21] Moreover, the amount of **6** in the isomer mixture should change, possibly from less than one-tenth at 80 K to more than one-third at 200 K; therefore the ^{13}C chemical shifts, especially for the (C2,C3) signal, should vary markedly with temperature. No such variation was observed for the spectra in solution,[17,19] or between them and the spectra in the solid state at a much lower temperature.[18] Most likely, the carbocations are ion-paired or move in ionic aggregates even in solution and their structure and NMR chemical shifts are much affected by the electrostatic interactions with anions.[9a] Even the geometry of the bridged ions (e.g., the C2C3C4 angle in **6**) should vary with the distance and orientation of the anion.[1c,d] We note also that to model theoretically the solid-state ^{13}C NMR spectra, one should determine the principal components of the chemical shift tensor[30] and compare them with the calculated values.[1d,30]

CHART 1



1d (*t*) **1d** (*g*) **1d** (*gg*)

2. Ionization Process (Ion Pairs at Short Interionic Distances). It was asserted that ionization of a 2-butyl substrate (**1a** or **1b**), leads to the bridged ion **3**, which means it is anchimerically assisted by the *β* hydrogen.[12,14] Other experimental studies reached different conclusions.[13,16] To mimic the ionization, we optimized first the geometry of 2-fluorobutane (**1d**) with two dummy atoms. There are three conformations of **1d** (Chart 1): F and C4 *anti* (giving the *t* ion pair, see below); F and C4 *gauche*, C1 and C4 *anti* (*g* series); F and C4 *gauche*, C1 and C4 *gauche* (*gg* series). The *t* conformation is prone to methyl bridging; the *g* and *gg* conformations, to hydrogen bridging. Conformer *g* is 0.82 kcal/mol lower in energy than *t*.[31]

Coordination of a borane molecule did not change significantly the geometry of any conformer. We then stretched the C−F bond to 1.9 Å, keeping the coordinating BH_3 molecule on the other side[1a] and conducted the geometry optimization as discussed in the Computational Method section. This was the shortest interionic distance considered, because in the detailed study of the ionization of 2-fluoropropane we had established that ionization occurred at a C···F distance of 1.8−2.0 Å.[1a] Indeed, the geometry around the tricoordinated carbon indicated that the ion pair was formed at this distance for **1** as well.

Three orientations of the anions were tested: with the F−B bond perpendicular on the C1,C2,C3 plane (*top*), with the F−B bond tilted such that B is above the smaller C1C2C3 angle (*in*), and with the F−B bond tilted such that B is above the larger C1C2C3 angle (*out*).[1a] Just as found earlier for the 2-propyl cation, the *in* and *out* orientations are lower in energy than the *top* orientation. It was shown, however,[1a] that the *top* orientation is stabilized to the greatest extent and the *in* orientation becomes the least stable when the ion pair is imbedded in a dielectric medium.[32] We found that conformations of the C1−C2 and C2−C3 bonds and the lengths of *β* C−H bonds are sensitive to anion orientation, as they are to the charge density at the nearest atom in the anion (below), but the geometry of the tricoordinated carbon is not. Therefore, most calculations were conducted for the *top* orienation of the anion. The resulting cation structure was in all cases **2**, rather than **3** or **6**. The calculations thus show the absence of anchimeric assistance in the ionization of **1**.

Hyperconjugative stabilization by a *β* bond at C3 on the side of the cation opposite to the anion (connecting the distal hydrogen or carbon to C3 in *g* and *t* forms, respectively) alters its bond lengths and angles. Thus, at $d = 1.9$ Å (anion orientation *top*), the C3−C4 bond and the C2C3C4 angle measured 1.542 Å and 109.6° in the *t* conformation, but 1.526 Å and 114.3° in the *g* conformation. (The wide CCC$^+$ angle for a nonhyperconjugating carbon was also seen in the CCSD/6-31G** optimization of the isolated 4-methyl-2-pentyl cation.[28]) Likewise, a distortion of the hyperconjugating C−H bonds at C1 in both **2**-*t*.**A** and **2**-*g*.**A** and at C3 in **2**-*g*.**A** (bond lengthening by 0.001−0.015 Å, bond angle reduction by 3−4°, from the values for the nonhyperconjugating C−H bonds at the same carbon atoms) was observed for all orientations of the anion.

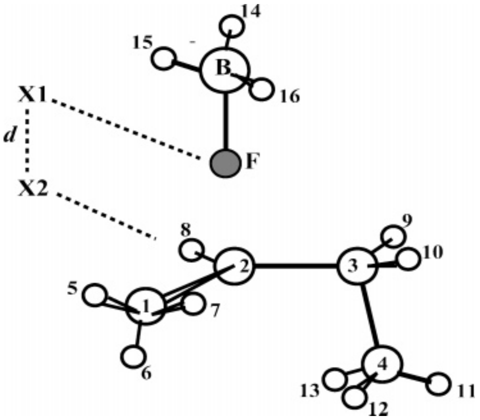


Figure 1. Representation of **2**-*t*.**A** at $d = 1.9$ Å.

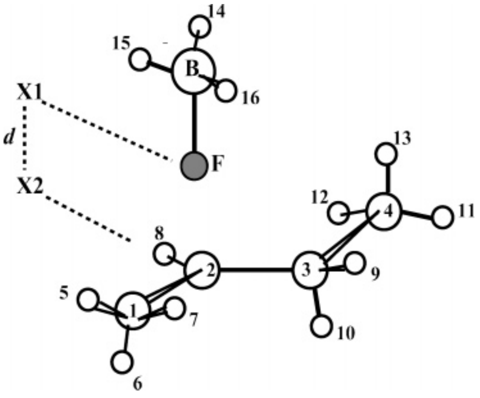


Figure 2. Representation of **2**-*g*.**A** at $d = 1.9$ Å.

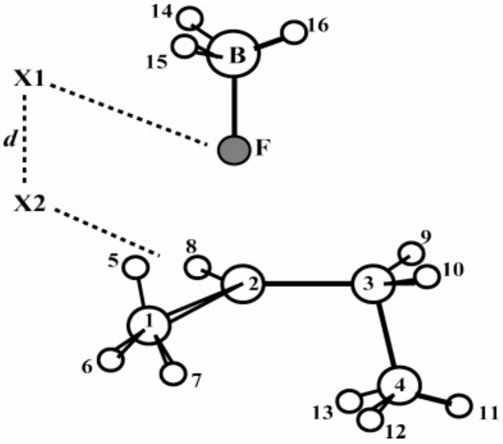


Figure 3. Representation of **2**-*t*.**A** at $d = 2.25$ Å and beyond.

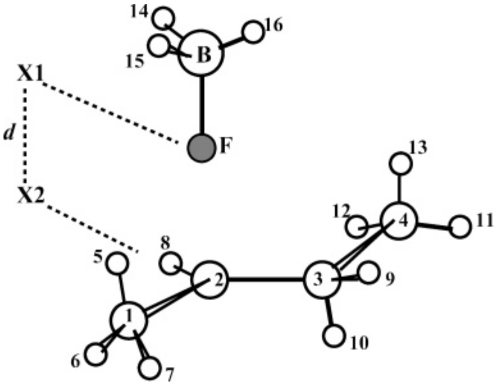


Figure 4. Representation of **2**-*g*.**A** at $d = 2.25$ Å and beyond.

The ion pairs **2**-*t*.**A** and **2**-*g*.**A** (anion orientation: *top*) are represented in Figures 1 and 2, respectively. The alignment of the hyperconjugating C−H bonds with the empty orbital axis is not optimal: the dihedral angle H6−C1-C2−C3 in both **2**-*t*.**A** and **2**-*g*.**A** deviates by 5−10°, and the dihedral angle H10−C3-C2−C1in **2**-*g*.**A** by 10−20° from 90°, for all orientations of the anion. The conformations of the C1−C2 and C2−C3 bonds respond more to the electrostatic interaction of the anion with the *syn* hydrogens of **2** than to hyperconjugation.

The *g* form was more stable than the *t* form, by 0.44 kcal/mol (MP2/6-31G** data for the *out* anion orientation in which the B−F bond length was optimized and the BH_3 group was allowed to rotate around B−F, with its bond lengths and angles frozen at 1.223 Å and 106.8°, respectively).

3. Ion Separation (Ion Pairs and Triple Ions at Long Interionic Distances). Starting with the geometries at $d = 1.9$ Å, the optimization was repeated for increasing values of *d*. Upon separation of ions with the anion in *top* or *in* orientation, the α methyl group (the C1−C2 bond) began to rotate to increase the electrostatic interaction of one of its hydrogens with the anion.[1a] At $d = 2.2$ Å, the C1−C2 bond had rotated by about 30°. At $d = 2.25$ Å, the methyl group (C1) had rotated by about 60° so that one of its hydrogens faced the anion. The orientation of this (proximal) hydrogen was favorable to hyperconjugation with the empty orbital at C2. The bond on the other side of the sp^2 carbon (C2−C3) does not rotate much at these short interionic distances, however, so hyperconjugative stabilization is provided by the C3−C4 bond in **2**-*t* and by a C3-H bond in **2**-*g*, on the side opposite to the anion in each case.[33] The distortion of the β C−H bond in the C1 methyl group of **2**-*g*.**A** (bond angle 98.1°) is greater than that of the β C−H bond at C3 (bond angle 100.5°). This feature is more pronounced at a longer distance, $d = 2.35$ Å. The rotation of the C1−C2 bond upon ion separation does not occur for the anion in the orientation *out*.

The ion pairs **2**-*t*.**A** and **2**-*g*.**A** at these longer interionic distances (anion orientation: *top*) are represented in Figures 3 and 4, respectively.

Attempted geometry optimization of **2**-*g*.**A** with both C1−C2 and C2−C3 rotated by 60° (C4 “below” the C1,C2,C3 plane), at $d = 2.2$ Å and 2.25 Å, led to the same conformation, with the hyperconjugating hydrogens “up” at C1 (facing the anion) and “down” at C3 (C4 “above” the C1,C2,C3 plane, Figure 4). The difference in energy favoring the *g* over *t* conformation (Table 1), is greater than for the contact ion pair discussed above.

The *gg* conformation (*cis* 2-butyl cation[21]) was found an energy minimum at $d = 2.25$ Å only for the *in* orientation of the anion, with C4 below the C1,C2,C3 plane and a hydrogen at C3 (H10 in Figure 5) facing the anion. The electrostatic interaction of H10 (proximal hydrogen, Hp) with the fluorine, at 2.15 Å, and with a hydrogen in the anion (H16), at 1.54 Å, stabilizes this conformation of the cation. The C3−Hp bond is stretched to 1.138 Å and its bond angle θ(C2C3Hp) reduced to 95.0°. Anion attraction moves Hp beyond optimal orientation for hyperconjugation, the dihedral angle ∠(Hp,C3,C2,C1) being −76.8° (283.2°) instead of −90° (270°). The conformation of the C1−C2 bond stays the same as in the cation immediately after the ionization, with the hyperconjugating hydrogen below the C1,C2,C3 plane (distal hydrogen, Hd). This conformation is by 2.45 kcal/mol higher in energy, however, than the *g* form with the same orientation of the anion (MP2/6-31G**, $-BH_3$ group free to rotate but its geometry is fixed, d(B−H) = 1.223 Å, θ(FBH) = 106.8°, in both cases). Moreover, as noted above, the ion pair of the 2-propyl cation with orientation of the anion

TABLE 1: Relative Energy of 2-*g*, 2-*t*, 3.A (*anti*), and 6.A (*anti*), with the Anion (A) Free To Move in a Plane Parallel to and at a Distance *d* from the C1,C2,C3 Plane, and B−F Perpendicular to That Plane[a]

	MP2(FC)/6-31G**	MP4SDTQ(FC)/6-31G**//MP2(FC)/6-31G**	MP4SDTQ(FC)/6-31G**//MP2(FC)/6-31G** + ZPE[b]
d = 2.25 Å			
relative energy[c]			
2-*t*.**A** − **2**-*g*.**A**	3.00	3.16	3.38
d = 2.8 Å[d]			
relative energy[c]			
2-*t*.**A** − **2**-*g*.**A**	0.75	0.94	0.98
6.**A** (*anti*) − **2**-*g*.**A**	0.72	1.76	2.84
d = 3.2 Å[d]			
relative energy[c]			
2-*t*.**A** − **2**-*g*.**A**	1.31		
6.**A** (*anti*) − **2**-*g*.**A**	0.97		
3.**A** (*anti*) − **2**-*g*.**A**	1.72		

[a] All the geometrical parameters of the anions were optimized as well. [b] ZPE scaled by a factor of 0.9676.[24] [c] kcal/mol.[31] [d] Triple ion (a Li^+ ion added on the other side of the anion, at 2.0 Å from boron).

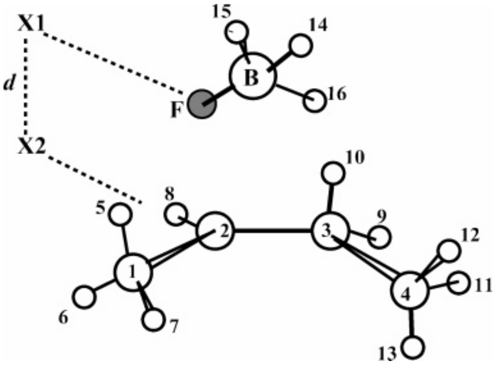


Figure 5. Representation of **2**-*gg*.**A** at d = 2.25 Å.

in was significantly destabilized in a dielectric medium relative to the *top* and *out* anion orientations, even for dielectric constants as low as those of dichloromethane or trifluoroacetic acid.[1a]

We did not examine the *gg* form at other interionic distances, but only the *t* and *g* forms. In the family of isolated ions, the open ion **2** is more stable in the *gg* conformation than in the *g* conformation, whereas for the bridged ion **3**, the *g* form is more stable than the *gg* form. Thus, we examined the case most favorable to anchimeric assistance.

The simulation of heterolytic carbon−fluorine bond cleavage did not evidence backside bridging either by hydrogen, as inferred in the first solvolytic studies[12,14] (in **2**-*g*), or by methyl (in **2**-*t*), immediately after ionization (d = 1.9 Å) or later (d = 2.25 Å). In fact, geometry optimization of the ion pairs expected to result from an anchimerically assisted ionization at d = 2.25 Å, **3**.**A**. (*anti*) and **6**.**A** (*anti*), with the geometries of isolated ions **3** and **6** as input, resulted in the "open" forms, **2**-*g*.**A** and **2**-*t*.**A**. The cation did not stay "bridged" even when optimization was conducted with the anion fixed atop the middle of the C2−C3 bond of **3**.**A** (*anti*).[1d]

The simulation of ionization of 2-fluoropropane with borane evidenced an elimination zone for interionic distances between 2.3 and 2.8 Å, varying slightly with the position and orientation of the anion.[1a] This observation is relevant for the ionization in solution, because elimination within tight ion pairs occurs to a large extent in the trifluoroacetolysis of secondary substrates,[3e,7] including 2-butyl tosylate.[16]

To obtain information on the cation structure at these interionic distances, we ran a few calculations on a triple ion with a lithium cation on the other side of the anion (at 2.0 Å from B).[1a,9b] This artifice lowered the tendency for proton transfer, by reducing somewhat the negative charge at fluorine. Also, the total charge of the aggregate remains the same (+1) after the proton transfer. For the 2-propyl cation at certain interionic distances, this approach led, however, to hydrogen bridging from methyl to C2, on the side of the anion.[1a] Thus, *syn* hydrogen bridging at intermediate interatomic distances is a frustrated elimination. We observed the same tendency here. The use of tetrafluoroborate as anion in this work, at d = 2.8 Å, had the same effect on a hydrogen at C1.

The *g* conformation was lower in energy than the *t* conformations at all interionic distances (up to d = 3.6 Å). Thus, there are two pathways of ionization of 2-butyl precursors, *g*, and *t*, the former of lower energy. Crossover from one pathway to another should require crossing an energy barrier.[1d] The ion pair resulting from the putative anchimeric assistance by hydrogen becomes an energy minimum only beyond 2.8 Å. Likewise, the isomeric ion pair resulting from a methyl-assisted ionization (not claimed in the solvolytic studies[12,14]), **6**.**A** (*anti*) becomes an energy minimum beyond 2.5 Å. A comparison of the energies of **2**-*g*.**A**, **2**-*t*.**A**, and **6**.**A** (*anti*) at d = 2.8 Å is also presented in Table 1, as is a less extended calculation at d = 3.2 Å, including **3**.**A** (*anti*).

Whereas not directly addressing the point, our calculations are relevant for the structure of 2-butyl cation in crystals. Stacking a carbocation between two anions should diminish even more its tendency toward bridging. The distances between the *t*-butyl cations and the anions on its two sides in the crystal were measured as 2.93 and 3.11 Å (hexafluoroantimonate salt).[34] It is then likely that at least one of the conformations of the "open" ion (*g*) was present in the solids on which the spectra (NMR,[18] ESCA,[20] IR[21]) of "2-butyl cation salts" were recorded. Theoretical calculations of the spectra, however, should consider the ion in higher aggregates[9] and were outside the scope of the current study.

If fluorobutane is represented as in Figure 2 (removing BH_3), with the C2···X2 distance 5 Å, the calculated distance X1···X2 (d) is 0.879 Å and X1···F, 3.898 Å (giving a C−F bond length of 1.410 Å). After ionization, the fluorine (now part of anion **A**) moved toward the "inside" C1C2C3 angle. At d = 1.9 Å, X1···F is 4.73 Å (C2···F, 1.93 Å). It interacted the strongest with H8 (at 2.33 Å), but H5, H7, H9, and H10 in **2**-*t*.**A**, H5, H7, H9, and H13 in **2**-*g*.**A**, were all at similar distances from it (2.4−2.7 Å). As expected,[35] the positive charge concentrated preferentially in these hydrogen atoms facing the anion. Upon ion separation, the "forward" displacement of the anion continued. The fluorine was roughly above C2 at d = 2.35 Å and then it moved to the region above the smaller

TABLE 2: Conformation of the C2−C3 Bond in 2-*g*.A as a Function of the Interionic Distance, *d*, and Its Consequence on the Distance between the Anion and the Terminal Methyl Group (C4)[a]

d, Å	1.9[b]	2.2[c]	2.25[d]	2.35[d]	2.5[d,e]	2.8[d,e]	3.2[d,e]	3.6[d,e]
∠(C4,C3,C2,C1)	199.9[f]	205.2	209.6,[g] 200.4[e,g]	210.1[f]	207.3[g]	221.6[g]	251.7[g]	
						215.7[h]	224.9[h]	236.1[h]
∠(H10,C3,C2,C1)[i]	79.4[f]	86.1	90.6,[g] 84.1[e,g]	90.8[f]	92.0[g]	105.4[g]	136.2[g]	
						99.8[h]	109.1[h]	121.5[h]
distance F···X1	4.725[f]	4.860	4.847,[g] 4.673[e,g]	4.998[f]	4.837[g]	5.238[g]	5.494[g]	
						5.0[h]	5.0[h]	5.0[h]
distance F···H5	2.568[f]	2.392	2.041,[g] 2.559[e,g]	1.942[f]	2.203[g]	1.993[g]	2.293[g]	
						2,209[h]	2.508[h]	2.899[h]
distance F···H7	2.639[f]	2.987						
distance F···H13	2.400[f]	2.323	2.268,[g] 2.509[e,g]	2.271[f]	2.446[g]	2.432[g]	1.918[g]	
						2.347[h]	2.273[h]	2.204[h]

[a] *Top* position of the anion (B−F bond perpendicular on the C1C2C3 plane), B−H bonds frozen at 1.223 Å, angles F−B−Hi frozen at 106.8°. [b] Figure 2. [c] Figure 2, with C1−C2 rotated 30° toward conformation of Figure 4. [d] Figure 4 (∠(H7,C1,C2,C3 close to 0°). [e] Triple ion (Li^+ placed on the other side of the anion). [f] MP2/6-31G*. [g] B−H bond lengths and F−B−H angles fully optimized. [h] Anion fixed atop C3. [i] A value of 90° is optimal for hyperconjugation.

C1C2C3 angle. When the dihedral angle ∠(F,X1,X2,C3) was also optimized, the fluorine moved at first within the bisector plane but increasingly deviated from it toward C1 at $d = 2.5$ Å and beyond. Thus, the pathway of the leaving group (anion) is determined by the electrostatic interaction with the hydrogen atoms of the carbocation.

Upon ion separation, the conformation of the C2−C3 bond in **2**-*g*.**A** was also affected by the interaction of the anion with the hydrogens at C4 (especially H13, Figure 4). As shown in Table 2, the dihedral angle ∠(C4,C3,C2,C1) increased with d, to bring H13 closer to the departing anion. At the same time, the hyperconjugating hydrogen, H10, on the side of C1 at $d = 1.9$ Å, moved to the side of H8 at longer interionic distances (cf. values of ∠(H10,C3,C2,C1) in Table 2). The electrostatic interactions trumped hyperconjugation. The conformational change was smaller for the triple ion, in which there was less negative charge at the fluorine. (Compare in Table 2 the values for the ion pair and triple ion at $d = 2.25$ Å; also the values for the ion pair at $d = 2.35$ Å and for the triple ion at $d = 2.5$ Å.) At $d = 3.2-3.6$ Å, the cation is better described as **2**-*t*.**A** with the anion facing the end methyl group (C4). Bridging by methyl *on the side of the anion*, giving **6**.**A** (*syn*), occurred beyond this distance. Along the **2**-*t*.**A** ionization pathway, the cation had also closed to **6**.**A** (*anti*), at $d = 4.0$ Å. Thus, at very long interionic distances, the present calculations predict the same structure as for the isolated 2-butyl cation (with somewhat distorted geometrical parameters). Interestingly, the most stable isomer of the isolated cation, **3**, is not reached by the normal ionization pathways of 2-butyl precursors. Formation of **3**.**A** (*syn*), the most stable form at long interionic distances requires rotation of the C2−C3 bond in **2**-*t*.**A** over an energy barrier. As our purpose was to probe for anchimeric assistance in the ionization, the interconversion of isomeric ions at long interionic distances was left for a future study.

Conclusions

The calculations show that the ionization of 2-butyl precursors forms an "open" 2-butyl cation (**2**), with no anchimeric participation of the β hydrogen or methyl group. It thus confirms the conclusions of some[13,16] and refutes other previous experimental studies.[12,14] The "bridged" carbocation structures (**3** and **6**) are not energy minima in tight ion pairs.

There are two ionization pathways possible, named by the conformation of the precursors, *t* and *g*, leading to the corresponding conformations of **2**. The *g* pathway is lower in energy. The trajectory of the leaving group after ionization (anion) is controlled by the electrostatic interactions with the hydrogen atoms closest to it in the carbocation. At first, it is above the larger C1C2C3 angle and within the bisector plane of it; then it moves above the smaller C1C2C3 angle and in the direction of C1. In turn, the departing anion changes the conformation of the carbocation; thus, the C2−C3 bond of **2**-*g* is gradually rotated to maximize the interaction of the anion with the hydrogens of the terminal (C4) methyl group, until it is converted to conformer **2**-*t* with C4 facing the anion. Finally, at long distances, the departing anion induces bridging (to **6**) *syn* to the anion. The *t* pathway leads ultimately to **6** (*anti*). The H-bridged isomer, **3**, is not formed upon ion separation along either pathway; its formation requires bond rotation over an energy barrier, but that barrier should not be high.

At least one form of the "open" ion, most likely **2**-*g*, should be the predominant species in solid salts of the 2-butyl cation.

Finally, we note that MP2 calculations, as employed here, are biased toward bridged structures, even "missing" nonbridged energy minima evidenced at higher levels of correlation (CCSD).[28] This fact strengthens our conclusions.

Acknowledgment. Grants of supercomputer time were obtained from the National Center for Supercomputing Applications (NCSA) in Urbana, IL, and at the University of Kentucky. We are indebted to Prof. Kenneth D. Jordan for helpful discussions. For many years, Herbert C. Brown has presented arguments challenging the existence, or at least generality, of anchimeric assistance in carbocationic solvolysis. This paper is dedicated to his memory.

Supporting Information Available: A table with the geometrical parameters of **2**-*t*.**A** and **2**-*g*.**A** at $d = 2.25$ Å. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Part 7: Fărcaşiu, D.; Vinslava, A. *J. Mol. Struct., THEOCHEM* **2001**, *548*, 1. (b) Part 6: Fărcaşiu, D.; Lukinskas, P. *J. Phys. Chem. A* **2000**, *104*, 1944. (c) Part 5: Fărcaşiu, D.; Norton, S. H.; Hâncu, D. *J. Am. Chem. Soc.* **2000**, *122*, 668. (d) Part 4: Fărcaşiu, D.; Hâncu, D. *J. Am. Chem. Soc.* **1999**, *121*, 7173.

(2) (a) Condon, F. E. In *Catalysis*; Emmett, P. H., Ed.; Reinhold Publishing Co.: New York, 1958; Vol. 6, Chapter 2. (b) Nenitzescu, C. D. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley: New York, 1968; Vol. 1, Chapter 1. (c) Pines, H. *The Chemistry of Catalytic Hydrocarbon Conversions*; Academic Press: NewYork, 1979.

(3) See, for example: (a) Hammett, L. P. *Physical Organic Chemistry*; McGraw-Hill: New York, 1940; pp 171ff. (b) Winstein, S.; Appel, B.; Baker, R.; Diaz, A. In *Organic Reaction Mechanisms*; Chemical Society Special Publication No. 19; Chemical Society: London, 1965. (c) Raber, D. J.; Harris, J. M.; Schleyer, P. v. R. In *Ions and Ion Pairs in Organic*

Chemistry; Szwarc, M., Ed.; John Wiley: New York, 1974; Chapter 3. (d) Bentley, T. W.; Schleyer, P. v. R. *Adv. Phys. Org. Chem.* **1977**, *14*, 1. (e) Shiner, V. J., Jr.; Dowd, W. *J. Am. Chem. Soc.* **1969**, *91*, 6528. (f) Sneen, R. A. *Acc. Chem. Res.* **1973**, *6*, 46.

(4) (a) Fărcaşiu D.; Ghenciu, A. *Prog. NMR Spectrosc.* **1996**, *29*, 129. (b) Fărcaşiu, D.; Ghenciu, A.; Li, J. Q. *J. Catal.* **1996**, *158*, 116. (c) Ghenciu, A.; Fărcaşiu, D. *J. Mol. Catal. A* **1996**, *109*, 273.

(5) (a) Fărcaşiu, D.; Lukinskas, P. *Rev. Roum. Chim.* **1999**, *44*, 1091. (b) Fărcaşiu, D. *Catal. Lett.* **2001**, *71*, 95. (c) For reactions involving partially or "weakly" coordinated carbocations in the gas phase, see: Williams, D. H. *Prepr. Pap.—Am. Chem. Soc. Div. Petrol. Chem.* **1983**, *28*, 252.

(6) Fărcaşiu, D.; Norton, S. H. *J. Org. Chem.* **1997**, *62*, 5374.

(7) (a) Fărcaşiu, D.; Marino, G.; Harris, J. M.; Hovanes, B. A.; Hsu, C. S. *J. Org. Chem.* **1994**, *59*, 154. (b) Fărcaşiu, D.; Marino, G.; Hsu, C. S. *J. Org. Chem.* **1994**, *59*, 163.

(8) (a) Pople, J. A. *Acc. Chem. Res.* **1970**, *3*, 217. (b) Pople, J. A. *Int. J. Mass Spectrom Ion Phys.* **1976**, *19*, 89. (c) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab initio Molecular Orbital Theory*; Wiley-Interscience: New York, 1986.

(9) (a) Fărcaşiu, D.; Hâncu, D.; Haw, J. F. *J. Phys. Chem. A* **1998**, *102*, 2493. (b) Fărcaşiu, D.; Lukinskas, P. *J. Phys. Chem. A* **1998**, *102*, 10436.

(10) (a) Fărcaşiu, D.; Lukinskas, P.; Hâncu, D. *J. Mol. Modeling* **2000**, *6*, 171. (b) Fărcaşiu, D.; Lukinskas, P. *Phys. Chem. Chem. Phys.* **2000**, *2*, 4219.

(11) Fărcaşiu, D.; Hâncu, D. *J. Phys. Chem. A* **1997**, *101*, 8695.

(12) (a) Dannenberg, J. J.; Weinwurzel, D. H.; Dill, K.; Goldberg, B. J. *Tetrahedron Lett.* **1972**, 1241. (b) Dannenberg, J. J.; Goldberg, B. J.; Barton, J. K.; Dill, K.; Weinwurzel, D. H.; Longas, M. O. *J. Am. Chem. Soc.* **1981**, *103*, 7764.

(13) Allen, A. D.; Ambidge, C.; Tidwell, T. T. *J. Org. Chem.* **1983**, *48*, 4527.

(14) Dannenberg, J. J.; Barton, J. K.; Bunch, B.; Goldberg, B. J.; Kowalski, T. *J. Org. Chem.* **1983**, *48*, 4524.

(15) (a) Dietze, P. E.; Wojchiekowski, M. *J. Am. Chem. Soc.* **1990**, *112*, 5240. (b) A rate *vs* solvent polarity study was discussed with the authors of ref 15a, but neither they, nor we, had the resources to do it.

(16) Fărcaşiu, D. *J. Chem. Soc., Chem. Commun.* **1994**, 2611.

(17) (a) Saunders, M.; Hagen, E. L.; Rosenfeld, J. *J. Am. Chem. Soc.* **1968**, *90*, 6882. (b) Saunders, M.; Kates, M. R. *J. Am. Chem. Soc.* **1978**, *100*, 7082. (c) Walker, G. E. Thesis, Yale University, 1983.

(18) Myhre, P. C.; Yannoni, C. S. *J. Am. Chem. Soc.* **1981**, *103*, 230.

(19) Olah, G. A.; Donovan, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 5026.

(20) Johnson, S. A.; Clark, D. T. *J. Am. Chem. Soc.* **1988**, *110*, 4112.

(21) (a) Sieber, S.; Buzek, P.; Schleyer, P. v. R.; Koch, W.; Carneiro, J. W. de M. *J. Am. Chem. Soc.* **1993**, *115*, 259. (b) Carneiro, J. W. de M.; Schleyer, P. v. R.; Koch, W.; Raghavachari, K. *J. Am. Chem. Soc.* **1990**, *112*, 4046. (c) Buzek, P.; Schleyer, P. v. R.; Sieber, S.; Koch, W.; Carneiro, J. W. de M.; Vančik, H.; Sunko, D. E. *J. Chem. Soc. Chem. Ccommun.* **1991**, 671.

(22) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Daprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, P.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(23) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

(24) Foresman, J. B.; Frisch, A. *Exploring Chemistry with Electronic Structure Methods*, 2nd ed.; Gaussian, Inc.: Pittsburgh, 1996; p 64.

(25) (a) Aftandilian, V. D.; Miller, H. C.; Muetterties, E. L. *J. Am. Chem. Soc.* **1961**, *83*, 2471. (b) Runtz, G. R.; Bader, R. F. W. *Mol. Phys.* **1975**, *30*, 129.

(26) (a) Murphy, M. K.; Beauchamp, J. L. *Inorg. Chem.* **1977**, *16*, 2437. (b) Anane, H.; Boutalib, A. *J. Phys. Chem.* **1997**, *101*, 7879.

(27) Schaftenaar, G. *MOLDEN. A Portable Electron Density Program*. Available at: ftp ftp.caos.kun.nl Name: anonymous.

(28) Fărcaşiu, D.; Pamidighantam, S.; Lukinskas, P. *J. Phys. Chem. A* **2002**, *106*, 11672.

(29) Benson, S. W. *Thermochemical Kinetics*; John Wiley: New York, 1968.

(30) Nicholas, J. B.; Xu, T.; Barich, D. H.; Torres, P. D.; Haw, J. F. *J. Am. Chem. Soc.* **1996**, *118*, 4202.

(31) 1 cal = 4.184 J.

(32) (a) Wong, M. W.; Frisch, M. J.; Wiberg, K. B. *J. Am. Chem. Soc.* **1991**, *113*, 4776. (b) Wong, M. W.; Wiberg, K. B.; Frisch, M. J. *J. Am. Chem. Soc.* **1992**, *114*, 1645.

(33) Hyperconjugative stabilization by bonds at C1 and C3 on opposite sides of the cation plane was deduced computationally for the isolated 2-propyl cation: (a) Koch, W.; Liu, B.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1989**, *111*, 3479. (b) Schleyer, P. v. R.; Koch, W.; Liu, B.; Fleischer, U. *J. Chem. Soc., Chem. Commun.* **1989**, 1098. (c) Koch, W.; Schleyer, P. v. R.; Buzek, P.; Liu, B. *Croat. Chem. Acta* **1992**, *65*, 655.

(34) (a) Hollenstein, S.; Laube, T. *J. Am. Chem. Soc.* **1993**, *115*, 7240. (b) Laube, T. *Chem. Rev.* **1998**, *98*, 1277.

(35) Fărcaşiu, D.; Lezcano, M.; Lukinskas, P.; Waldeck, D. H. *J. Phys. Chem. A* **2000**, *104*, 5190.