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Theoretical Studies of Carbocations in Ion Pairs. 1.[1] The 2-Propyl Cation

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Ab initio calculations with large basis sets and electron correlation were applied to the study of geometry of the 2-propyl cation in ion pairs with trihydro fluoroborate (**A**) or dihydrolithiate (**B**) as anion. The goal was to model the ion pair formed by ionization in a solvent with good anion-stabilizing properties, but of low dielectric constant, like trifluoroacetic acid (TFA). The effect of the anion, seen already at long distances, was that the preferred cation conformation changed from C1,C3 staggered as in the isolated carbocation (chiral 2-propyl cation, **1**) to C1,C3 eclipsed (C_s symmetry, **2**). The optimized cation geometry was essentially the same at the MP2(FC)/6-31G*, MP2(FC)/6-31++G*, and MP2(FU)/6-311G** levels, but the position of the anion above the cation was somewhat more sensitive to the basis set. The preferred anion position was in the plane bisecting the C1−C2−C3 angle of **2** and in the region "inside" that angle. This "inside" displacement became more pronounced as the interionic distance, d, was made shorter; at the same time, the anion moved slightly off the bisecting plane. Elimination within the ion pair to form propene occurred at $d < 2.5$ Å. When the anion was allowed to "fall" freely, the reaction pathway was determined by the initial position of the anion: elimination for a position "inside" the C1−C2−C3 angle and recombination to 2-fluoropropane (occurring at $d = 1.5-1.7$ Å) for a position "outside" the C1−C2−C3 angle. The equilibrium cation geometry did not change significantly in **2.B** relative to **2.A**, but the distortions toward elimination occurred at longer distances for the more basic anion **B** and elimination itself took place at $d = 3.5$ Å. The energy difference beween **1.A** (optimized with the methyl groups held staggered) and **2.A** at $d = 3.4$ Å was 2.39 and 3.25 kcal/mol at the MP2(FC)/6-31++G* and MP2(FU)/6-311G** levels, respectively. The equilibrium position of the anion paired with **1** was above the C1−C2 bond, close to the syn hydrogen at C1. Thus, methyl rotation along the lowest-energy pathway involves also a movement of the anion relative to the cation.

Introduction

The earliest studies of carbocations were conducted in solution, starting with the observation of a colored species being formed from triphenylmethyl derivatives in sulfuric acid,[2] or rather with the rationalization of this color as belonging to the triphenylmethyl cation.[3] Carbocation chemistry began when alkyl and cycloalkyl cations were indicated as intermediates of chemical reactions.[4] The understanding of reactivity and structure of these species was developed for many years based on solvolytic reactions. Through experiments and rationalizations highly ingenious and often aesthetically pleasing, a good description of this area of the organic chemistry emerged.[5] Nonetheless, all the information about these critical intermediates obtained during that period was per force indirect. Even though some carbocation salts had been isolated earlier in the solid state,[6] it can be said that the modern era of carbocation chemistry began with the NMR as method of investigation, first of arenium ions,[7] then, in quick succession, of triphenylmethyl,[8] alkenyl,[9] and finally alkyl cations.[10] The experiments on reactive carbocations conducted in nonnucleophilic, superacidic media offered for the first time an independent evaluation of reaction intermediates postulated earlier in the solvolytic reactions. On a different line, knowledge about carbocations in the gas phase was acquired through the investigation of metastable ions in the mass spectra, through high-pressure mass spectrometry, and through ion cyclotron resonance spectroscopy (ICR).[11] Valuable information was also obtained from radiochemical studies.[12]

The theoretical description of carbocations by MO calculations was developed following the direct observation of these species and sought to explain the experimental observations. As the computer power increased, the early studies employing π-electron approximation[13] were succeeded by all-electron (at least all-valence electron) calculations, both semiempirical and ab initio.[14] The latter approach[15] has now reached a level at which the accuracy of calculated structural parameters and energy is said to rival that of best experimental determinations.[16] The calculations refer to isolated ions, as they are encountered in the gas phase, but they have been used to describe these species under all circumstances, based on the report that the energy differences between carbocations are practically the same in the gas phase, superacid, or solvolytic media.[17]

We found, however, that the results of high-level ab initio calculations on cations with an isopentane carbon skeleton[18] and the results of studies conducted in our laboratory on these cations generated solvolytically in trifluoroacetic acid (TFA)[19] disagreed in some key conclusions. An attempt at taking into account the solvent by introducing a dielectric medium in the calculations[20] was able to correct only part of the discrepancy.[21] We noted then that the experimental results, in particular a high level of internal return, indicated that the chemistry in TFA is controlled by ion pairing, as most carbocationic solvolyses are.[22] Along another line of investigation, our work on mechanism of catalysis by strong solid acids indicated that there, too, the chemistry is determined by carbocations tightly paired with the anion of the catalytic site.[23] We concluded, therefore, that the existing ab initio calculations on isolated carbocations cannot be considered satisfactory and we initiated a study of the structure and energy of carbocations in ion pairs. Altogether,

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our calculations took several years, commensurate with our resources, and required a few developmental steps;[18,21] some partial results were reported, but not in significant detail.[24] A particular concern was that the size of the system forced some simplifying choices, particularly what anion could be employed. We developed our methodology on a simple system, the 2-propyl cation, which is the smallest carbocation stable enough to be investigated in superacid solution[25] and to intervene as intermediate in solvolyses in TFA.[22c,d] We found that, indeed, ion pairing influences in an important manner the structure of this carbocation.

Computational Method

The calculations were conducted with the program Gaussian 92,[26] in the manner described in the previous paper.[18] Because of the size of the systems investigated, we did not introduce diffuse functions in the basis sets used in most calculations, but diffuse functions were added for critical cases and found not to alter the conclusions. Because the structure of the anions is less important for us at this juncture, it will not be commented upon. We might return to it in a future publication. No symmetry constraints were imposed on the structures during calculation, in most cases.

The position of the anion relative to the cation was defined with the use of two "dummy" atoms, X1 and X2. The latter was placed within the C1C2C3 plane and on the bisector of the C1−C2−C3 angle, toward "outside", being connected with C2 by a "bond" of fixed length (1.5 or 2.0 Å). X1 was connected to X2 by a "bond" of length *d* (held constant in any given optimization run) perpendicular to the C1C2C3 plane (θ(X1X2C2) $\equiv$ 90°, φ(X1X2C2C1) $\equiv$ 90°). When the anion was FBH_3^- (**A**), 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 (optimized) dihedral angle φ(F−X1−X2−C2). Finally, the F−B bond was held perpendicular to X1−F and antiparallel to X1−X2 (i.e., φ(B−F−X1−X2) $\equiv$ 180°). When the anion was LiH_2^- (**B**), one hydrogen atom in the anion was connected to X1 in the same way as F was in **A**, and the H−Li bond was held antiparallel to X1−X2. By this procedure, the distance between cation and anion and the relative orientation of the two were kept constant, but the anion was allowed an unrestricted plane-parallel movement ("glide") above the cation.

The projections of the molecular geometry shown here were generated with the computer program XMOL.[27]

Results and Discussion

The first matter to be addressed when starting the study of a carbocation in an ion pair was the identity of the anion. It has been well established that ionization of a precursor takes place only upon electrophilic attack at the leaving group, such that the resulting anion is either coordinated by a Lewis acid or strongly hydrogen bonded with the solvent, the two possible forms of anion stabilization.[28] Therefore, a complex, rather than monatomic, anion had to be used in the calculation in order to ensure that only a part of the negative charge would directly face the cation. It was important, however, not to use a very stable anion when trying to model the type of interaction occurring in ionization in solvolytic media that provide good anion stabilization but have both low dielectric constants and some nucleophilicity (e.g., TFA).[19,28] At the same time, it was necessary that the anion be as small as possible to allow calculations at an adequate level of theory. Thus, our calculations were not meant to describe behavior in superacid solutions, although a comparison of the results with findings about carbocations in such media could indicate whether the cations are ion-paired there.

The first choice of anion was the dihydrolithiate, LiH_2^- (**B**). Because of its small size, this ion has been the subject of several computational investigations seeking to determine its structure and stability.[29] The calculations have determined that anion **B** is a bonded species, of $D_{\infty h}$ symmetry (sp hybridization at Li), with the negative charge distributed beween the two hydrogen atoms. In addition, the tendency to transfer an electron to the cation and thus form a pair of free radicals is very low.

An ion pair R^+.**B** formally results from a hydride abstraction by LiH as Lewis acid from the parent hydrocarbon, RH, which makes anion **B** a rather crude model. Note also that the Li−H bond is not very strong even in the parent lithium hydride (56.9 kcal/mol[30]).[31] Nonethelesss, we felt that it is useful to employ more than one anion to allow for some comparison.

Another anion which we examined extensively as counterion for the 2-propyl cation in the ion pair was the trihydrofluoroborate (**A**). Anion **A** combines a size manageable for calculations on smaller cations such as **1** with a realistic stability, established both experimentally[32] and computationally,[33] and an appropriate charge distribution. It is also less basic than **B**. An ion pair R^+.**A** formally results from the heterolysis of R−F by reaction with the Lewis acid BH_3. The B−F bond is a strong bond; its bond dissociation energy measured in BF_3 is 183 ± 3 kcal/mol.[34] Examination of both R^+.**A** and R^+.**B** allowed us to assess the effect of the anion on the structure of the cation.

The isolated 2-propyl cation has been the subject of extensive ab initio calculations.[16,35] The most recent study, in which geometry optimization was conducted at the MP2(FU)/6-311G** level, was considered to provide the "definitive characterization of the $C_3H_7^+$ potential energy surface".[16] Good agreement was found between the calculations and experimental studies of the cation in the gas phase.[36] The results of that computation were also used later to calculate the ^{13}C chemical shift tensor of the 2-propyl cation, which was then compared with the experimental values for the cation in frozen SbF_5.[37] Theoretical investigations at such a level can even reveal properties of the species which are difficult or impossible to examine by the experimental techniques available to date. An example was the determination of the preferred conformation of the 2-propyl cation.[16] Examination of five conformers of this ion showed that the C_2 structure, with C1 and C3 staggered (chiral structure, **1**), had the lowest energy. Frequency analyses[15c] performed on the five conformations of the cation showed that **1** was the only energy minimum; but the barrier for the rotation of the methyl groups was at most 0.5 kcal/mol, therefore not observable experimentally.[38]

The starting point of our calculations was the minimum energy structure **1** of the isolated ion, to which we added the anion at the rather long distance (*d*, defined under Computational Methods) of 5 Å on the same side with the hyperconjugating hydrogen at C1 (H1). To our surprise, this conformation was no longer an energy minimum at any level of calculations from STO-3G up. Instead, geometry optimization led to the rotation of the C2−C3 bond until the conformation with C1,C3 eclipsed (φ(H1−C1−C2−C3 = −φ(H3−C3−C2−C1), **2**) was reached. The latter was the energy minimum for the 2-propyl cation in the ion pair.[1] A partial optimization with the C−H bond lengths frozen showed this to be the case even for $d = 6$ Å.

The most important geometrical parameters of the ion pair **2.A**, calculated at the MP2(FC)/6-31G* level, are presented in Table 1. It is seen that at $d = 5$ Å the C−C bonds in the cation (1.438 Å) and the bond lengths of the two hyperconjugating hydrogens H1 and H3, now facing the anion (1.121 Å), were

TABLE 1: Geometrical Parameters for the 2-Propyl−BH_3F^- Ion Pair (2.A) at Different Interionic Distances, *d* (in Å), at the MP2(FC)/6-31G* Level

	$d = D(\text{X1−X2})^a$					
	5	4	3.7	3.4	3.4^b	3.4^c
D(C1−C2)	1.438	1.436	1.434	1.431	1.433	1.431
D(C2−C3)	1.438	1.435	1.434	1.433	1.435	1.433
D(C1−H1)	1.121	1.128	1.132	1.137	1.133	1.138
D(C3−H3)	1.121	1.128	1.132	1.135	1.130	1.134
D(H2−C2)	1.093	1.092	1.091	1.091	1.092	1.091
D(C2−X2)[a]	1.5	1.5	1.5	2.0	2.0	2.0
D(F−X1)	1.833	1.991	2.039	2.555	2.459	2.487
θ(H2−C2−X2)	7.46	9.41	10.26	11.14	10.15	11.63
θ(C1−C2−C3)	125.53	125.07	124.78	124.57	124.91	124.91
θ(H1−C1−C2)	100.89	98.16	96.61	94.76	94.48	93.18
θ(H3−C3−C2)	100.89	98.08	96.62	95.38	97.22	94.2
φ(F−X1−X2−C2)	0.04	0.03	−0.04	−0.46	−0.66	−0.48
charge at H1	0.33	0.35	0.35	0.35	0.37	0.25
charge at H3	0.33	0.35	0.35	0.35	0.37	0.25

[a] This distance was frozen during the optimization. [b] Optimization conducted at the MP2(FC)/6-31++G* level. [c] Optimization conducted at the MP2(FU)/6-311G** level. Frequency analyses at this level found no imaginary frequency in cation or anion.

not changed from the values in the isolated ion, 1.437 and 1.121 Å, respectively. The bond angles H1−C1−C2 and H3−C3−C2 opened from 92.7° to 100.89° (a value of 99−100° is expected at the highest level of theory, as discussed below). Thus, both the cation and the ion pair have C_s symmetry. An interesting feature is the deviation from the C1C2C3 plane of the hydrogen atom bonded to C2 (labeled H2 in Table 1) in the direction of the anion, described in Table 1 by the angle θ(H2−C2−X2). Also worth noting is that the anion is not located at the top of C2, but 0.333 Å (expected ca. 0.25 Å at the highest level of theory) "inside" the C1−C2−C3 angle. This offset of the anion is obtained as the difference beween *D*(X1−F) and *D*(X2−C2). Whereas the structure of the isolated ion **1** is largely controlled by hyperconjugation,[38] the most important factor in the ion pair appears to be the electrostatic interactions between the anion and the points of highest positive charge density in **2**, that is, H1, H3, H2, and C2.

The changes in the geometry of **2.A** with the interionic distance, *d*, are also shown in Table 1. As *d* decreases, the bond lengths C1−H1 and C3−H3 increase, their bond angles decrease, the carbon−carbon bond lengths decrease, and the bending of the H2−C2 bond in the direction of the anion increases. At the same time, the anion moves farther inside the C1−C2−C3 angle, which decreases but slightly. Most notably, the anion moves very slightly off the bisecting line, toward one of the methyl groups (C1 in Table 1). This movement is accompanied by a slight asymmetrization of the cation **2**: the C1−C2 bond becomes shorter than C2−C3, the C−H1 bond becomes longer than C3−H3, and the H1−C1−C2 angle becomes smaller than the H3−C3−C2 angle. The latter changes may appear insignificant, but they are important for the pathway for the elimination reaction within the ion pair, leading to olefin, as it will be discussed below. The ion pair **2.A** at *d* = 4.0 Å is represented in three projections, front (F), side (S), and top (T), in Figure 1.

Extensions of the basis sets for geometry optimization were sought along two lines. First, diffuse functions were introduced in MP2(FC)/6-31++G* calculations of the ion pair **2.A** for *d* = 3.4 Å, which gave the results for the geometrical parameters of the energy minimum shown in the second to last column in Table 1. The main changes were a slight movement of the anion toward "outside" (by 0.096 Å) and off the bisecting plane (by 0.20°) accompanied by the reduction of θ(H1−C1−C2) and increase of θ(H3−C3−C2). Then, a reoptimization of the geometry of **2.A** at *d* = 3.4 Å was conducted at the MP2(FU)/6-311G** level, and its results are shown in the last column of Table 1. It is seen that the only geometrical elements which changed significantly were the angle H1−C1−C2 and H3−C3−C2 (by ca. 1.5° inward) and the position of the anion (by 0.07 Å toward "outside"). In addition, the calculated positive charge densities at H1 and H3 are lower for the larger basis set, but the charge density estimates are approximate.

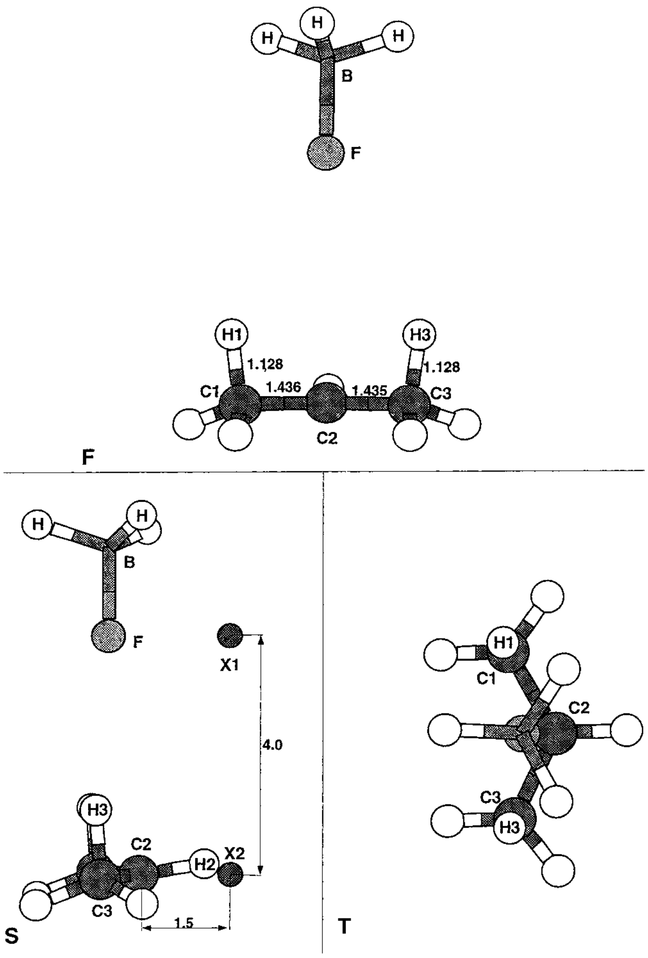

Figure 1. Geometry of the 2-propyl−trihydrofluoroborate ion pair (**2.A**) calculated at the MP2(FC)/6-31G* level for an interionic distance *d* = 4.0 Å. **F**: front view, dummy atoms not represented. **S**: side view (C3 closest to the viewer), X1, X2, dummy atoms. **T**: top view, dummy atoms not represented.

Optimization of a trihydrofluoroborate ion pair in which the cation has the same conformation as in the isolated ion (**1.A**) could be achieved by freezing the methyl groups in the staggered position. The optimization was conducted at an interionic distance *d* = 3.4 Å, and the main geometric parameters obtained at two levels of theory are presented in Table 2. It can be seen that the asymmetry is increased significantly by ion pairing, with the methyl C−H bond syn to the anion (C1−H1) lengthened and the anti methyl C−H bond (C3−H3) shortened relative to the values in the isolated ion, whereas the C1−C2 bond is shorter than the C2−C3 bond by 0.03 Å. Likewise, the bond angle H1−C1−C2 closes somewhat, and the bond angle H3−C3−C2 opens up to a greater extent. These two angles are the only elements in the geometry of the cation to change noticeably from MP2(FC)/6-31G* to MP2(FU)/6-311G**. It is thus seen again that the electrostatic interaction with the anion is more important for the structure of the carbocation than hyperconjugation. The preferred position of the anion is at the top of the C1−C2 bond, close to the syn hydrogen atom, H1, which has a significantly greater positive

TABLE 2: Main Geometrical Parameters and Atomic Charges for the C1,C3 Staggered (Originally C_2) Structure, 1,[a] of the 2-Propyl Cation in the Ion Pair at D(X1−X2) = 3.4 Å

	ion pair **1.A**	
geometric element	MP2(FC) 6-31G*	MP2(FU) 6-311G**
D(C1−C2)	1.417	1.416
D(C2−C3)	1.448	1.447
D(X1−F)	2.587	2.48
D(X2−C2)	2.000	2.000
D(C1−H1)	1.162	1.162
D(C3−H3)	1.114	1.116
D(H_2−C_2)	1.092	1.092
θ(H1−C1−C2)	92.9	90.28
θ(H3−C3−C2)	100.08	97.96
θ(C1−C2−C3)	124.57	124.58
θ(H2−C2−X2)	2.51	2.38
φ(F−X1−X2−C2)	−18.78	−15.95
charge at H1	0.38	0.27
charge at H3	0.25	0.15

[a] See text.

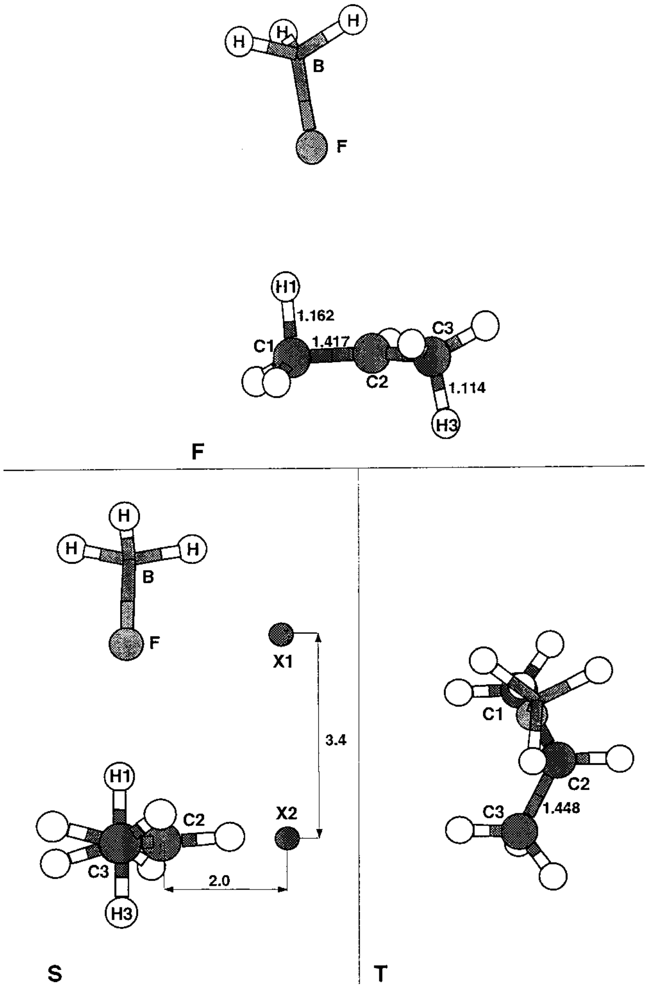

Figure 2. Geometry of the 2-propyl−trihydrofluoroborate ion pair with the cation held in the C1,C3 staggered (originally C_{2v}) conformation (**1.A**), calculated at the MP2(FC)/6-31G* level, for an interionic distance d = 3.40 Å (II). **F**, **S**, and **T** as in Figure 1.

charge density than the anti hydrogen, H3. The position of the anion is influenced more noticeably by the basis set than the geometry of the cation. The calculated geometry of the **1.A** ion pair is shown in Figure 2. Starting with this geometry and releasing the constraints, we obtained upon reoptimization the geometry **2.A** again.

The total energies and the relative energies of ion pairs **1.A** and **2.A** calculated for d = 3.4 Å are listed in Table 3. It can be seen that the energy difference between the two forms, representing the barrier for the rotation of the methyl group of the cation in the ion pair, changes very little with the increase in the basis set. Considering that, for isolated ions, **1** was more stable than **2** by ca. 0.5 kcal/mol,[38] it is seen that ion pairing reverses the stability of the conformers by almost 3 kcal/mol. The methyl rotation barrier in the ion pair, though even greater than that for the isolated ion, is still too small to be measured experimentally by a convenient procedure. It is important to note that methyl rotation also involves the movement of the anion at the top of the cation. This process can be envisioned as the rotation of one methyl group with the anion moving from the bisecting plane to the side of the nonrotating group and back for each 120° of rotation or the alternative rotation of the two methyl groups by 120° synchronized with a pendulating movement of the anion from one side to the other of the bisecting plane. It is conceivable, however, that rotation should occur not only by the path of minimum energy crossing the saddle point but also by a path in which the anion stays close to its position of equilibrium in **2.A**, that is, close to the plane bisecting the C1−C2−C3 angle. The latter, higher-energy, pathway of conformational transformation is more likely when the anion is heavy and particularly in the solid carbocation salts.

TABLE 3: Total and Relative Energy of the Optimized Geometries of Ion Pairs 1 and 2[a]

level of calculation	structure **1.A** (hartree)[b]	structure **2.A** (hartree)[b]	$\Delta E_{(1-2)}$ (kcal/mol)
MP2(FC)6-31G*	−244.027 18	−244.032 23	3.17[c]
MP2(FC)6-31++G*	−244.062 29	−244.223 39	2.39[d]
MP2(FC)6-311G*	−244.223 39	−244.228 56	3.24
MP2(FU)6-311G**	−244.316 19	−244.321 37	3.25

[a] Interionic distance, d = 3.4 Å; see text. [b] 1 Ha = 627.5095 kcal/mol. [c] 2.24 kcal/mol at d = 4.0 Å with FHF^- as anion. [d] 2.42 kcal/mol with FHF^- as anion.

TABLE 4: Geometrical Parameters for the 2-Propyl−LiH_2^- Ion Pair (2.B) at Different Interionic Distances, d (in Å), at the MP2(FC)/6-31G* Level

	d = D(X1−X2)	
	4.0	3.7
D(C1−C2)	1.431	1.427
D(C2−C3)	1.432	1.429
D(C1−H1)	1.140	1.149
D(C3−H3)	1.138	1.145
D(C2−X2)[a]	1.5	1.5
D(H8−X1)	2.217	2.305
D(H2−C2)	1.091	1.092
θ(H2−C2−X2)	10.9	11.98
θ(C1−C2−C3)	124.48	124.09
θ(H1−C1−C2)	96.72	95.03
θ(H3−C3−C2)	97.05	95.78
φ(F−X1−X2−C2)	−0.43	−0.76
charge at H1	0.34	0.33
charge at H3	0.34	0.33

[a] This distance was frozen during the optimization.

The effect of the anion on the structure of the cation in the ion pair was examined by replacing anion **A** with anion **B** (LiH_2^-) in the optimized structure at d = 4.0 Å. Reoptimization (MP2(FC)/6-31G*) required only a few cycles. As shown in Table 4, the structure of the carbocation changed very little, but the changes were of the nature seen in Table 1 for the cases when the anion moved closer to the cation. Indeed, the carbocation geometry in **2.B**, with d(C1−H1) = 1.140 Å, d(C3−H3) = 1.138 Å, θ(H1−C1−C2) = 96.72°, and θ(H3−C3−C2) = 97.05°, is similar to the geometry found for **2.A** at d = 3.4 Å. The ion pair **2.B** at d = 4.0 Å is represented in three projections in Figure 3.

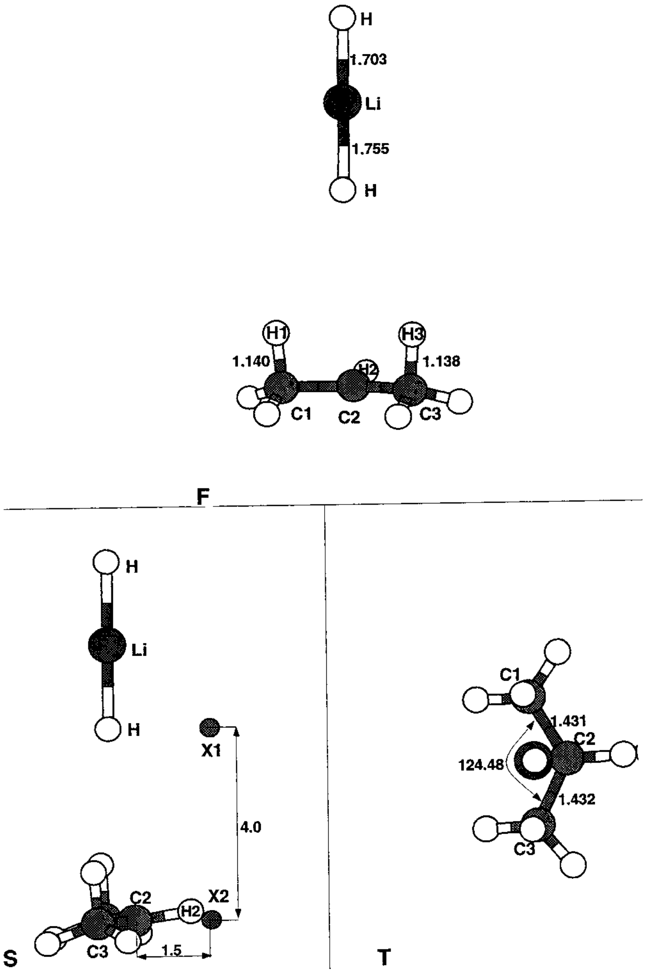

Figure 3. Geometry of the 2-propyl−dihydrolithiate ion pair (**2.B**) calculated at the MP2(FC)/6-31G* level, for an interionic distance $d = 4.0$ Å. **F**, **S**, and **T** as in Figure 1.

When the ion pair **2.B** becomes tighter, at $d = 3.7$ Å, the C−H bonds facing the anion become even longer (1.149 and 1.145 Å, respectively) and their bond angles smaller (95.03° and 95.78°, respectively), whereas the anion is inside the C1−C2−C3 angle by 0.805 Å from the position above C2 and off the bisecting plane by φ(H8−X1−X2−C2) = 0.76° (H8 is the hydrogen of **B** facing the cation), all at the MP2(FC)/6-31G* level (last column of Table 4). It is seen that the anion moves toward the hydrogen which is going to be eliminated more by movement inside the angle of the cation than away from the bisecting plane of that angle. Attempted optimization of **2.B** for $d = 3.5$ Å resulted in elimination with formation of propene, H_2, and LiH. As two different equivalent geometries may be identified at $d = 3.7$ Å with dihedral angles φ(H8−X1−X2−C2) of ±0.76, it is apparent that starting from the "loose" ion pair of C_s symmetry elimination can occur along two enantiomeric pathways. Elimination from the ion pair **2.A**, containing a less basic/nucleophilic anion and which forms propene, HF, and BH_3, occurred for d shorter than 2.5 Å. It can be predicted, therefore, that for a truly nonnucleophilic anion, like $Sb_2F_{11}^-$ or perhaps $Sb_3F_{16}^-$, for which the isopropyl cation is stable even in the solid state and does not undergo elimination,[37] the cation retains the C_s symmetry even in the tightest ion pair.

In summary, our results show that both anions **A** and **B** can be employed to calculate the structures of carbocations in ion pairs, but the less stable and more basic/nucleophilic **B** has to be used at a larger distance, in somewhat "looser" ion pairs, to avoid interionic reactions, especially elimination. Down to an interionic distance just slightly longer than required for the reaction of the carbocation with the anion, the structure of the carbocation in an ion pair does not change when the anion is changed. At that distance, slight alterations of the geometry of the cation, as if anticipating the reaction, are observed.

A few calculations were also conducted with FHF^- as the anion in the ion pair (see footnotes *c* and *d* under Table 3).[37,39] Qualitatively, the results are similar to those with **A** as anion, but FHF^- interacts stronger with H1 and H3 (longer C1−H1 and C3−H3 bonds, farther displacement of the anion "inside" the C1−C2−C3 angle for $d = 3.4$ Å at the MP2(FC)/6-31++G* level) than **A**, indicating incipient elimination. Moreover, the search of the plane at $d = 3.4$ Å above the cation has located a second energy minimum for **2.**FHF $^-$, with the anion at the top of C1, 0.88 kcal/mol *lower* in energy than the usuall minimum with the anion in the bisecting plane (deviation: 0.007 Å). This second minimum is brought about by a strong interaction with H1 (C1−H1, 1.251 Å; H1−F, 2.202 Å; θ(H1−C1−C2), 76.79°) and does not exist for **2.**A.[40]

It can be observed that the optimization at decreasing interionic distances, d, maps the lowest energy pathway of reaction of the carbocation with the anion in the ion pair. It was unexpected that this reaction should give only elimination, when it is known that recombination is the favored reaction of the intimate ion pairs formed in solvolyses of secondary alkyl substrates.[41] The cation−anion reaction within the ion pair was therefore examined by placing the anion in various positions on the plane at an interionic distance $d = 3.4$ Å and releasing the constraint $D(X1-X2) \equiv d$. It was found that whenever the starting position of the anion was "inside" the C1−C2−C3 angle, that is, when $D(X1-F) > D(X2-C2)$, the reaction which took place was elimination. When the anion started from "outside" the C1−C2−C3 angle or from a point exactly above C2, that is, $D(X1-F) \leq D(X2-C2)$, the reaction to occur was recombination at an interionic distance of 1.5−1.7 Å. In both cases, the reaction was the same, whether the initial position of the anion was in the bisecting plane of the C1−C2−C3 angle or not. Looking at the reaction pathway from the other direction, the calculations thus suggest that in solvolysis the leaving group starting from a position necessarily "outside" the C1−C2−C3 angle forms the anion in the same region. The majority of internal return should then take place before the ion pair had time to relax to the position of minimum energy and thus should lead to recombination. For the fraction of the ion pairs that achieve a position close to the equilibrium before internal return occurs, the latter reaction is elimination, which is also observed experimentally.[40b,c] These reactions of the ion pairs will be addressed in more detail in a future study.

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