

## Theoretical Studies of Carbocations in Ion Pairs. Part 6: The *tert*-Butyl Cation at Various Interionic Distances<sup>1</sup>

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The structure of the *tert*-butyl cation (**1**) ion-paired with the trihydrofluoroborate anion (**A**), previously shown to be appropriate for such studies, was investigated by ab initio calculations, as a function of the interionic distance in the ion pair ( $d$ ). At short distance ( $d = 2.25$  Å), the lowest energy cation conformation was a slightly distorted  $C_s$  form. At intermediate distances ( $d = 2.60, 2.95, 3.30,$  and  $3.65$  Å), the preferred geometry had a  $C_{3v}$  conformation, and at  $d = 4.0$  Å the cation adopted again a  $C_s$ -type conformation, but the anion was no longer in the space above the carbon skeleton of the cation and it was tilted, interacting strongly with only one of the hydrogen atoms. Finally, at  $d = 4.5$  Å, the anion moved to the side of the cation, also interacting with only one hydrogen atom, whereas the cation adopted an asymmetric geometry, close to the  $C_{3h}$  form preferred by the isolated carbocation. Examination of spectral properties could indicate the average or most probable interionic distance in solution. Thus, the Raman spectrum had been interpreted as indicating a  $C_{3v}$  form of the cation, which suggests an interionic distance in the intermediate range. The insensitivity of cation structure to the nature of the anion for interionic distances beyond recombination range has been established by a comparison of anion **A** with the tetrafluoroborate anion (**B**). Optimization of the cation geometry in the triple ion **A.1.A**, held at the interionic distance found in the crystal, showed that the  $C_s$  form with two hydrogens facing the farthest anion was the most stable, but the  $C_s$  form with two hydrogens facing the nearest anion was almost equal in energy and the two  $C_{3v}$  forms (three hydrogens facing the farthest and the nearest anion, respectively) were only slightly less stable. The preferred geometry of the cation in the triple ion was the same as that found previously in a more complex aggregate, in which the cation and the two anions were allowed to move freely. This result shows that geometry optimizations at fixed interionic distances give reliable structures for carbocations in ion pairs or aggregates. The similar stability of the  $C_s$  and  $C_{3v}$  conformations in the triple ion is in agreement with the identification of two sets of hydrogens, each twisted by  $60^\circ$  against the second set, for two of the methyl groups of the *tert*-butyl cation in the crystal.

### Introduction

In previous work, we have shown that ion pairing alters significantly the structure of carbocations. Thus, the conformation of the 2-propyl cation changes from 1,3-staggered ( $C_2$  symmetry, chiral)<sup>2</sup> to 1,3-eclipsed ( $C_s$  symmetry),<sup>3</sup> because of the electrostatic interaction of the anion with two hydrogen atoms, one in each methyl group, facing the anion. The C–H bonds of these atoms are significantly lengthened, and the corresponding C<sup>+</sup>–C–H bond angles are much reduced from the bond lengths and angles of the other methyl hydrogens.<sup>3</sup> The 1-propyl cation, which is the transition structure for the interconversion of 2-propyl cation and protonated cyclopropane in the gas phase (isolated ions),<sup>2</sup> becomes an energy minimum in the tight ion pairs and the only energy minimum at very short interionic distances.<sup>1b</sup> Likewise, the 3-methyl-2-butyl cation is a transition state for the interconversion of 1-protonated 2,3-dimethylcyclopropane isomers in the gas phase,<sup>4</sup> but it is the only energy minimum in the tight ion pairs.<sup>1a</sup> Indeed, experimental studies had indicated that ionization of 3-methyl-2-butyl tosylate and protonation of 3-methyl 1-butene, both in trifluoroacetic acid solutions, involve the “open” ion rather than the protonated 2,3-dimethylcyclopropane as intermediate. In

those experiments, the outcome of the reactions was determined at the tight ion pair stage.<sup>5</sup> Studies in which primary carbocation intermediates gave a better account of experimental results than the corresponding protonated cyclopropanes were also reported.<sup>6</sup>

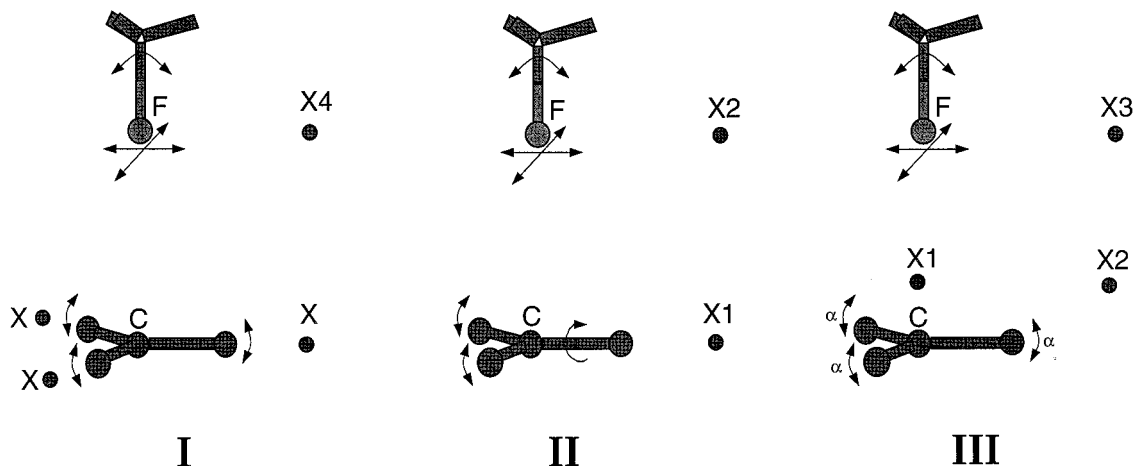
Computations on the *tert*-butyl cation in a five-ion aggregate,  $\text{Li}^+ \text{A}^- \text{Me}_3\text{C}^+ \text{A}^- \text{Li}^+$ , led to a carbocation geometry<sup>7</sup> which had been shown before to predict best the spectral properties determined for the cation in the solid state.<sup>8</sup> (The geometry found stable in the ionic aggregate had been found a transition structure for the isolated cation.<sup>8</sup>) Likewise, inclusion of the 2-propyl cation in an ionic aggregate could predict the values of the principal components of the chemical shift tensor for C-2,<sup>9</sup> previously measured for a solid salt of the cation.<sup>10</sup>

In this paper we report on calculations which showed that the geometry of the *tert*-butyl cation (**1**) in ion pairs changes with the distance between cation and anion, such that it appears that the spectral properties determined for this ion in solution should also change with the “tightness” of the ion pair.

### Methods

The calculations were conducted with the program *Gaussian 94*,<sup>11</sup> as described before.<sup>7</sup> For the anion, we used the trihydrofluoroborate anion ( $\text{H}_3\text{BF}^-$ , **A**),<sup>1,3,7</sup> but we also employed in one calculation the tetrafluoroborate anion ( $\text{BF}_4^-$ , **B**) for

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**Figure 1.** Schematic representation of the control of movement of ions during the optimization of ion pairs. I, four dummy atoms; II, two dummy atoms; III, three dummy atoms. (a) The anion is fixed at the top of C2, (b) the anion is allowed a free plane-parallel movement (straight arrows), (c) the anion is allowed to tilt by the rotation of the F-B bond around F in any direction (curved arrows).

comparison. The geometry optimizations were conducted at the MP2/6-31G\* level. In previous studies in this series, we found that the increase in size of the basis set beyond this level produced negligible changes in the optimized geometries.<sup>3,4</sup> This observation was also tested on some selected cases in this work, by calculations at the MP2 level with the 6-31++G\*, 6-31G\*\*, and 6-31++G\*\* basis sets.

In all cases, the geometry was described in the calculations with the use of dummy atoms.<sup>7</sup> The choice of the latter controlled the movement of the ions.

I. The highest relative mobility of the ions was achieved with the use of four dummy atoms (Figure 1.I). Three of these (X1, X2, X3) were placed in an equilateral triangle, with the central ( $sp^2$ ) carbon, C2, in its middle. The other three carbons were connected to the latter, and their bond angles and dihedral angles were defined from the dummy atoms but were afterward fully optimized. The fourth dummy, X4, was connected to one of the other three with a fixed bond, perpendicular to the X1,X2,X3 plane and of a length,  $d$ , which defined the interionic distance. The angle  $\theta(X3,X4,F)$  was kept at  $90^\circ$ . The system was investigated at three levels of constraint: (a) The anion was held above the  $sp^2$  carbon and perpendicular to the X1,X2,X3 plane by fixing the dihedral angles  $\varphi(C2,X3,X4,F)$  at  $0^\circ$  and  $\varphi(X3,X4,F,B)$  at  $180^\circ$ . (b) The anion was allowed a free plane-parallel movement by optimizing  $\varphi(C2,X3,X4,F)$  with  $\varphi(X3,X4,F,B)$  held at  $180^\circ$ . (c) The anion was also allowed to tilt, by optimizing both  $\varphi(C2,X3,X4,F)$  and  $\varphi(X3,X4,F,B)$ , as well as  $\theta(X4,F,B)$ .

II. For intermediate mobility of ions, two dummy atoms were used (Figure 1.II). The first, X1, was connected to the  $sp^2$  carbon, C2. The second, X2, was connected to X1, and the X1...X2 distance defined the interionic distance,  $d$ , between C2 and the plane containing the fluorine atom of the anion. The fluorine atom was connected to X2. The angles  $\theta(C2,X1,X2)$  and  $\theta(X1,X2,F)$  were held at  $90^\circ$ . At the constraint level (a),  $\theta(X2,F,B)$  was held at  $90^\circ$ ,  $d(X2\cdots F)$  was equal to  $d(X1\cdots C2)$ , and the dihedral angle  $\varphi(X1,X2,F,B)$  was held at  $180^\circ$ . For level (b), the parameters  $d(X2\cdots F)$  and  $\varphi(C2,X1,X2,F)$  were optimized, thus allowing free plane-parallel movement of the anion over the cation, while maintaining the anion with the fluorine atom facing the cation. For level (c), both  $\theta(X2,F,B)$  and  $\varphi(X1,X2,F,B)$  were optimized, allowing the anion to tilt.

III. The lowest relative mobility was achieved with three dummy atoms (Figure 1.III). The first, X1, was connected to C2 at a fixed distance,  $d_1$ , and the other three carbon atoms

were defined such that  $\theta(X1,C2,C1) = \theta(X1,C2,C3) = \theta(X1,C2,C4)$ . The second, X2, was connected to X1 at a fixed, arbitrary distance and had  $\theta(C2,X1,X2) = 90^\circ$ . The third, X3, was connected to X2 at a distance,  $d_2$ , such that  $d_1 + d_2 = d$  (the interionic distance), with  $\theta(X1,X2,X3) = 90^\circ$  and  $\varphi(C2,X1,X2,X3) = 180^\circ$ . X3 was also connected to F, with  $\theta(X2,X3,F) = 90^\circ$ . At the constraint level (a),  $d(X1-X2) = d(X3-F)$ ,  $\theta(X3,F,B) = 90^\circ$ ,  $\varphi(X1,X2,X3,F) = 0^\circ$ , and  $\varphi(X2,X3,F,B) = 180^\circ$ . At the level (b),  $d(X3\cdots F)$  and  $\varphi(X1,X2,X3,F)$  were optimized to allow the plane-parallel movement of the anion over the cation. At the level (c),  $\theta(X3,F,B)$  and  $\varphi(X1,X2,X3,F)$  were also optimized, to allow the anion to tilt as well.

The triple ion,  $H_3BF^- \cdot Me_3C^+ \cdot FBH_3^-$  (**A.1.A**) was generated from the ion pair (**1.A**) with three dummy atoms. The second anion was placed with the fluorine (F') connected to X1 in the direction opposite to the first anion, at a distance  $d_1 + d'$ , where  $d'$  is the interionic distance between the cation and the second anion. The boron was also connected to X1, at a distance collinear to  $d_1 + d'$  and longer than it, which was optimized. Other parameters for the second anion were  $\theta(X2,X1,F') = \theta(X2,X1,B') = 90^\circ$  and  $\varphi(X3,X2,X1,F') = \varphi(X3,X2,X1,B')$ . Only the constraint level (a) was examined, that is, B, F, C2, F', and B' were collinear.

## Results and Discussion

In reactions catalyzed by solid acids, the carbocations, if generated at all, can appear only tightly paired with the anions of the acid sites.<sup>12</sup> In solution, however, the carbocations span the whole range from tightly ion-paired to free, depending upon the properties of the anions and of the solvents. It was, therefore, of interest to determine whether the carbocation structure or conformation changes with the interionic distance. We have now examined this matter for the *tert*-butyl cation (**1**). The model anion used in the ion pairs was trihydrofluoroborate (**A**),<sup>13</sup> the same as in the previous work.<sup>1b,7</sup> As discussed in the Methods section, three levels of constraint of the anion were considered: (a) with the anion frozen above the  $sp^2$  carbon (C2), (b) with the anion allowed a free plane-parallel movement above the cation, and (c) with the anion allowed both to move in plane and to tilt over the cation. There was essentially no difference between cases (a) and (b), because the anion always ended up at the top of C2 after optimization. The level (c) always gave a significantly lower energy, because of secondary electrostatic

interactions between the positive hydrogen atoms in the cation and negative hydrogen atoms in the anions. Nevertheless, in all cases where a comparison was made, the changes in the geometry of the cation optimized at level (c) from the geometry at level (b) were unimportant.

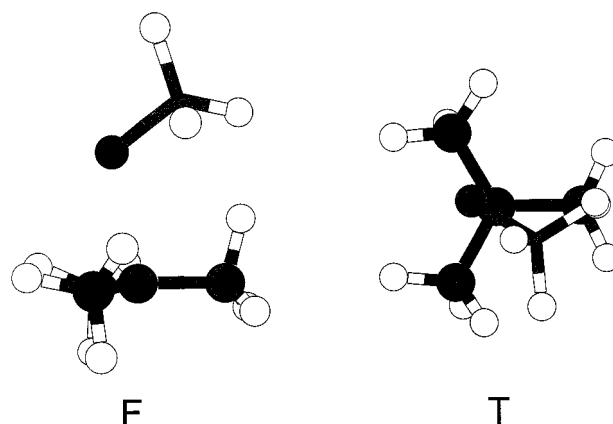
High-level *ab initio* calculations on the isolated *tert*-butyl cation by Sieber et al., conducted with inclusion of electron correlation in the geometry optimization, indicated a form of  $C_{3h}$  symmetry and one of  $C_s$  symmetry equally stable (the former was more stable by 0.14 kcal/mol when zero-point energy corrections were included). The true energy minimum was asymmetric ( $C_1$ ) but close to the  $C_{3h}$  form.<sup>8</sup> The input geometry in our calculations was, therefore, the  $C_{3h}$  conformation with the geometric parameters obtained in the calculation for the isolated ion.<sup>8</sup> It has to be noted that in most of our calculations, the optimized geometries are close to the indicated symmetry group but do not belong rigorously to it. To make the distinction, we refer in those cases to cation *conformation*, rather than cation *symmetry*.

**Short Interionic Distance.** The shortest interionic distances ( $d$ ) which can be examined are determined by the nucleophilicity and basicity of the anion. For the 1-propyl cation and its protonated cyclopropane isomer, anion **A** allowed calculations from  $d = 2.25$  Å up. The calculations on **1.A** reported here also started from  $d = 2.25$  Å.

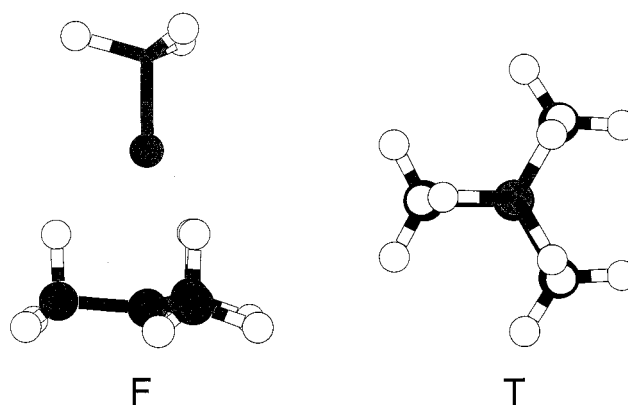
At the highest relative mobility of ions (Mode I, four dummy atoms), the cation adopted the  $C_s$  symmetry. The anion stayed at the top of the  $sp^2$  carbon (C2), even when allowed to move in a plane parallel to the basal plane containing C2 and three dummy atoms (level (b), as defined in the Methods section). One methyl group pointed a hydrogen toward the anion (*proximal hydrogen*, Hp, dihedral angle  $\varphi(\text{F,C2,C1,Hp}) = 0^\circ$ ), and the other two methyl groups pointed one hydrogen each in the opposite direction (*distal hydrogens*, Hd),  $\varphi(\text{F,C2,C3,Hd}) = \varphi(\text{F,C2,C4,Hd}') = 180^\circ$ . The bond angle  $\theta(\text{C3,C2,C4})$ ,  $120.6^\circ$ , was slightly larger than  $\theta(\text{C1,C2,C3})$  and  $\theta(\text{C1,C2,C4})$ , both  $119.4^\circ$ . The bond length  $d(\text{C1-Hp})$ , 1.103 Å, was equal to  $d(\text{C3-Hd})$  and  $d(\text{C4Hd}')$ , 1.102 Å, which indicates that at this short distance the fluorine atom interacts stronger with C2 than with Hp. Nonetheless, the bond angle C2-C1-Hp ( $100.8^\circ$ ) was smaller than the bond angles C2-C3-Hd and C2-C4-Hd' ( $106.0^\circ$ ).

When the anion was allowed to tilt (Mode I.c in the Methods section), it adopted a position in which the angle  $\theta(\text{C2,F,B})$  was reduced to  $111.6^\circ$  and two of its hydrogen atoms (Ha, Hb) interacted with the proximal hydrogen (Hp) at C1. The two interactions were not equally strong, as shown by the unequal distances, 1.771 Å for  $d(\text{Hp}\cdots\text{Ha})$  and 2.502 Å for  $d(\text{Hp}\cdots\text{Hb})$ , because Hb interacted stronger with a hydrogen at C3, at 2.209 Å. As a consequence, the boron atom was not situated above the C1-C2 bond, but it was displaced toward C3, as shown by the dihedral angle  $\varphi(\text{B,F,C2,C1}) = 31.2^\circ$ . The C1-Hp bond was stretched to 1.116 Å. The short Ha $\cdots$ Hp distance and the value of the (Ha,Hp,C1) angle,  $165.5^\circ$ , indicate the existence of a hydrogen bond. This ion pair, **1.A** (2.25 Å), is shown in Figure 2. The multiple interactions between the positive atoms in the cation and negative atoms in the anion disturbed the symmetry, such that the dihedral angle  $\varphi(\text{Hd,C3,C4,Hd}')$  increased to  $11.0^\circ$  from close to zero ( $0.4^\circ$ , C3 and C4 methyl groups eclipsed) in the ion pair with the anion held perpendicular above the cation, but the other changes in geometry of the cation were small.

At the same interionic distance, when the relative mobility of the ions was low (three dummy atoms, Mode III in the



**Figure 2.** Geometry of the ion pair **1.A** at the interionic distance ( $d$ ) of 2.25 Å, optimized at the MP2/6-31G\*\* level with the highest degree of freedom (Mode I.c, four dummy atoms, the anion can move and tilt). **F**: front view. **T**: top view.



**Figure 3.** Geometry of the ion pair **1.A** at the interionic distance ( $d$ ) of 2.60 Å, optimized at the MP2/6-31G\*\* level in the Mode I.b (four dummy atoms, the anion can move but not tilt). **F**, **T** as in Figure 2.

Methods section) and the anion movement was constrained (levels (a) and (b)), the  $C_{3h}$  conformation of the cation (input geometry) was preserved. One methyl group was slightly rotated. Again, the optimized geometry was close to the indicated symmetry group, but did not belong rigorously to it.

Allowing the anion to tilt in the ion pair with the rigid relative orientation (Mode III.c) led essentially to the same structure **1.A** (2.25 Å) as for Mode I.c, indicating that the  $C_s$  conformation is, indeed, the most stable for the *tert*-butyl cation at the shortest interionic distances. Another noteworthy result was that no elimination occurred at the shortest interionic distance, even when the anion was allowed to move and tilt freely.

**Intermediate Interionic Distance.** Geometry optimization at interionic distances  $d$  of 2.60, 2.95, 3.30, and 3.65 Å gave ion pairs with the cation in the  $C_{3v}$  conformation, exemplified in Figure 3 for  $d = 2.60$  Å. The pyramidalization of the cation, with the concavity toward the anion, increased with the distance up to  $d = 3.30$  Å. The bond lengths of the proximal hydrogen atoms were about the same for  $d = 2.95$  and  $3.30$  Å (1.120 Å) and longer than for  $d = 2.60$  Å (1.114 Å).

The propensity of the ion pair toward elimination, forming HF, boron trifluoride, and isobutene, varied unexpectedly with the distance and anion orientation. Thus, at  $d = 2.95$  Å, optimization was possible with full relative mobility of the ions (four dummy atoms) and the anion being allowed to tilt (Mode I.c, in the Methods section). The anion adopted a position similar to that shown in Figure 2 with an even smaller C2 $\cdots$ F-B angle ( $88.1^\circ$ ). Different from the ion pair **1.A** (2.25 Å) in Figure 2,

**TABLE 1: Main Geometrical Parameters of the tert-Butyl Cation in the Ion Pairs 1.A and 1.B, at  $d = 2.60$  Å, and in the Triple Ion A.1.A, from the Geometry Optimization<sup>a</sup>**

geometrical parameter	1.A <sup>b</sup> MP2/6-31G*	1.A <sup>b</sup> MP2/6-31G**	1.A <sup>b</sup> MP2/6-31++G**	1.B <sup>b,c</sup> MP2/6-31G*	A.1.A <sup>d</sup> MP2/6-31G**
$d(\text{C1}-\text{C2})$	1.457	1.456	1.459	1.459	1.452
$d(\text{C2}-\text{C3})$	1.457	1.456	1.459	1.459	1.453
$d(\text{C2}-\text{C4})$	1.457	1.456	1.459	1.459	1.453
$\theta(\text{C1},\text{C2},\text{C3})$	119.41	119.34	119.66	119.51	119.53
$\theta(\text{C1},\text{C2},\text{C4})$	119.41	119.34	119.66	119.51	119.54
$\theta(\text{C3},\text{C2},\text{C4})$	119.41	119.34	119.66	119.63	120.532
$\varphi(\text{C1},\text{C2},\text{C3},\text{C4})$	164.71	163.85	168.34	166.72	172.696
$d(\text{C1}-\text{Hp})^e$	1.114	1.111	1.109	1.112	1.109
$d(\text{C1}-\text{Hd})^f$	1.089	1.085	1.086	1.090	1.084
$\theta(\text{C2},\text{C1},\text{Hp})$	97.80	97.08	99.54	100.39	97.97
$\theta(\text{C2},\text{C1},\text{Hd})$	111.96	113.97	113.49	113.61	113.14
$d(\text{C3}-\text{Hp})^{e,g}$	1.114	1.111	1.109	1.111	1.109
$d(\text{C3}-\text{Hd},\text{i})^{f,g,h}$	1.089	1.085	1.086	1.090	1.083
$d(\text{C3}-\text{Hd},\text{o})^{f,g,h}$	1.089	1.085	1.086	1.090	1.085
$\theta(\text{C2},\text{C3},\text{Hp})^{e,g}$	97.76	97.08	99.54	99.98	98.44
$\theta(\text{C2},\text{C3},\text{Hd},\text{i})^{f,g,h}$	111.96	113.97	113.49	113.72	113.51
$\theta(\text{C2},\text{C3},\text{Hd},\text{o})^{f,g,h}$	111.96	113.97	113.49	113.59	112.60

<sup>a</sup> Distances in Å, bond angles ( $\theta$ ) and dihedral angles ( $\varphi$ ) in degrees. **A**: trihydrofluoroborate, **B**: tetrafluoroborate. <sup>b</sup>  $C_{3v}$  conformation, one hydrogen in each methyl group faces the anion; optimization mode I.b (four dummy atoms, perpendicular anion allowed to move). <sup>c</sup> The anion moved slightly off-center,  $d(\text{F}\cdots\text{C2}) = 2.667$  Å, hence the small differences in  $\text{C}-\text{C}^+-\text{C}$  angles and  $\text{C}-\text{Hp}$  bond lengths. <sup>d</sup>  $C_s$  conformation, one hydrogen at C1 faces the nearest anion, one hydrogen each at C3 and C4 faces the farthest anion; optimization in the mode III.a (three dummy atoms, both anions perpendicular to the cation). <sup>e</sup> Hydrogen facing the fluorine (proximal). <sup>f</sup> Hydrogen away from fluorine (distal). <sup>g</sup> The same values were found for the C4 methyl group. <sup>h</sup> i = inward, o = outward.

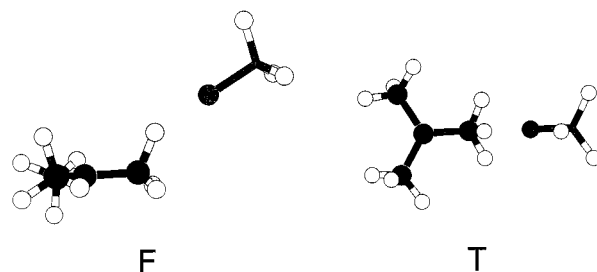
however, the B–F bond was eclipsing the C1–C2 bond, that is,  $\varphi(\text{B},\text{F},\text{C2},\text{C1}) = 0.0^\circ$  and, of course, the cation conformation was  $C_{3v}$ .

Holding the anion perpendicular to the basal plane of the anion at  $d = 2.95$  Å led to elimination when four dummies were employed. Optimization as an ion pair was achieved for the more rigid disposition of ions with three dummy atoms (Mode III.b, in the Methods section) and the  $C_{3v}$  conformation was preserved.

At the distances  $d = 3.30$  and  $3.60$  Å, the elimination was avoided by optimization with perpendicular position of the anion and three dummy atoms (Mode III). Allowing the plane-parallel movement of the anion (Mode III.b) or freezing it (Mode III.a) led to the same ion pair. For  $d = 2.60$  Å, optimization with free movement of the cation relative to the anion (Mode I, four dummy atoms) was achieved, but when the anion was allowed to tilt elimination occurred even for the optimization of the most rigid ion pair of Mode III.c (three dummy atoms).

The effects of the increase in the basis set (to MP2/6-31G\*\*), introduction of diffuse functions (MP2/6-31++G\* and MP2/6-31++G\*\*), and replacement of the anion **A** with the less nucleophilic tetrafluoroborate (**B**) were examined in geometry optimizations at  $d = 2.60$  Å in Mode I.b. The main structural parameters thus obtained are listed in Table 1. It is seen that the differences between these calculation results are quite small. Nonetheless, rigidization of the cation expressed by a slight decrease in the degree of puckering and reduction in the C–Hp bond lengths can be observed.

**Long Interionic Distance.** At the interionic distance of  $4.0$  Å, the anion kept above the center of the cation (Mode III.a and III.b of geometry optimization) still exerts an electrostatic effect strong enough to lengthen the C–Hp bonds to  $1.116$  Å. When full mobility of the anion in the orientation with the fluorine toward the cation (Mode I.a and I.b) is allowed in the optimization, the anion moves out of the region above the carbon atom plane and close to one of the methyl groups, as shown in Figure 4, thus reducing the energy of the ion pair by  $9.8$  kcal/mol (MP2/6-31G\*). The long carbon–hydrogen bond,  $d(\text{C1}-\text{Hp}) = 1.175$  Å and the short  $\text{F}\cdots\text{Hp}$  equilibrium distance,  $1.771$



**Figure 4.** Geometry of the ion pair **1.A** at the interionic distance ( $d$ ) of  $4.00$  Å, optimized at the MP2/6-31G\*\* level in the Mode I.b (four dummy atoms, the anion can move but not tilt). **F**, **T** as in Figure 2.

Å, indicate the formation of a strong hydrogen bond. Because of the reduced level of interaction with the anion, the rest of the molecule adopts a conformation close to that calculated for the isolated 2-propyl cation (methyl groups staggered). As a result, the cation adopts a slightly distorted  $C_s$  conformation (two hydrogens “up”). Allowing the anion to tilt, turning its hydrogen atoms toward the cation, led to elimination in either mode of optimization.

Finally, at distances of  $4.5$  Å and larger, the anion moved entirely to the side of the cation, still interacting with only one hydrogen of the latter. The cation adopted a conformation close to  $C_{3h}$ , reminiscent of the energy minimum of the isolated ion. The optimization, conducted in Mode I.a (four dummy atoms), was repeated at MP2/6-31G\*\* and MP2/6-31++G\* without any significant change in the optimized geometry. Thus, at interionic distances of  $4.5$  Å and beyond, the effect of the anion does not change the preferred geometry of the cation.

**The tert-Butyl Cation in a Triple Ion.** In our calculations, the ions of opposite sign have usually to be held apart in order to avoid interionic reactions (recombination, elimination). In a study which modeled the tert-butyl cation in a crystal for comparison with X-ray diffraction results,<sup>14</sup> a triple ion  $\text{H}_3\text{BF}^-\text{Me}_3\text{C}^+\text{FBH}_3^-$  (**A.1.A**) was placed between two parallel planes in which two lithium cations were allowed to move (“double-decker sandwich”).<sup>7</sup> The two planes contained the triple ion between them in the same way in which electrically charged grids contain ions in the reaction chamber in gas-phase studies.

No interionic reaction (elimination or recombination) occurred, even though the carbocation and the two anions in the central triple ion were allowed to move freely. The distance between the lithium ion planes was varied until the distances between the ions in the central triple ion were about the same as the distances measured in the crystal (2.93 and 3.11 Å).<sup>14</sup> For a perpendicular orientation of the anions relative to the carbon plane of the cation, the most stable geometry had a  $C_s$  conformation with one hydrogen atom (at C1) facing the nearest anion and two hydrogens, at C3 and C4, pointing toward the farthest anion.<sup>7</sup> When the anions and cation were not allowed to tilt relative to each other, a  $C_{3v}$  conformation could also be optimized as a minimum.<sup>7</sup> To examine the effect of the forced separation of ions upon their structure, we optimized in this study the geometry of the triple ion itself with the interionic distances held at 2.95 and 3.10 Å. Starting from the  $C_{3h}$  conformation, the calculation led to the same  $C_s$  conformation with one hydrogen facing the nearest anion. Its main geometrical parameters are also listed in Table 1. The  $C_s$  conformation with two hydrogens facing the nearest anion, also an energy minimum, was only 0.01 kcal/mol higher in energy (MP2/6-31G\*\*), because the interionic distances on the two sides differ very little. In the "double-decker sandwich," only the lower energy form could exist, because the conformer interconversion is achieved by the movement of the ions, which has no barrier, rather than by methyl group rotation, which has a barrier.

Likewise, two  $C_{3v}$  conformations, with three hydrogens facing the farthest and the nearest anion, respectively, were optimized at the fixed interionic distances. They were 0.11 and 0.23 kcal/mol above the lowest-energy  $C_s$  conformation. As discussed in the previous paragraph for the  $C_s$  conformer, the more stable conformer was the only one observed in the five-ion aggregate.<sup>7</sup> Projections of the optimized geometries of the triple ions are not given here, because they are the same as those published for the systems with two extra lithium cations ("double decker sandwich").<sup>7</sup> The similar stability of the  $C_s$  and  $C_{3v}$  conformations is in agreement with the identification of two internally rigid sets of hydrogen atoms, each twisted by 60° against the second set, for two of the methyl groups of the *tert*-butyl cation in the crystal.<sup>14</sup>

The present results, taken together with those published before,<sup>7</sup> showed that optimization of a triple ion with frozen interionic distances gave the same structure for the carbocation as for the aggregate which got optimized to the same interionic distances. It is thus seen that geometry optimizations at fixed interionic distances give reliable structures for carbocations in ion pairs or aggregates.

**Expected Consequences of Ion Pairing on Spectral Properties.** The calculations predict that the spectra determined for the *tert*-butyl cation in solution should change with the distance from the nearest anion. It is most interesting that in one of the early studies of this species, its Raman spectrum in  $\text{FSO}_3\text{H}-\text{SbF}_5-\text{SO}_2$  solution was interpreted as consistent with the  $C_{3v}$  symmetry.<sup>15</sup> This result would indicate that the average or most probable distance between a cation and an anion in that solution was between 2.60 and 4.0 Å. It would be, of course, highly desirable to have the experiments repeated at the current state of the art. As observed in our previous work, the computational duplication of spectra requires large anions (closer to those employed in the experimental determination of the spectra) or large basis sets.<sup>9</sup>

## Conclusions

The comparison of trihydrofluoroborate (**A**) and tetrafluoroborate (**B**) has shown that the cation structure is not sensitive

to the nature of the anion, as long as the interionic distance is beyond the recombination range. The study of triple ions **A.1.A** has shown that optimizations at fixed interionic distances give reliable structures for carbocations in ion pairs and aggregates. This conclusion is especially important for studies of larger carbocations, where the choices in the nature and mobility of anion are limited by computer limitations.

The geometry of the carbocation, in particular the symmetry class closest to the calculated geometry, was found to change with the interionic distance. As a consequence, the spectral properties of persistent carbocations in solution are predicted to be a function of the average or most probable interionic distance. In particular, the Raman spectrum of *tert*-butyl cations was interpreted as corresponding to the conformation which is stable at interionic distances between 2.6 and 4.0 Å.<sup>15</sup> This conclusion is important enough to warrant a redetermination of the old spectra.

The interionic distance also influences the reactions of carbocations in ion pairs. In the case studied here, the front side of the cation is not accessible to attack by nucleophiles for interionic distances below 4 Å. As the interionic distance increases within this range, the cation deviation from planarity increases. The convex side of the latter is away from the anion, which maintains a stable position in the center of the positively charged pocket. Therefore, the attack by a nucleophile at short time after ionization, before the anion moved away, should occur strictly with inversion, unless the anion delivers a molecule of solvent. For a larger interionic distance (greater than 4 Å in the present case), nucleophilic attack occurs equally from both sides, because the anion has migrated to a preferred location at the side of the cation.

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